HANDBOOK
of
METAL
ETCHANTS

Editors

Perrin Walker
William H. Tarn



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PREFACE

This book is a collection of cleaning and etching solutions extracted from the open technical literature from about 1940 to the present. It began when the authors and co-workers became involved with the development of germanium and silicon semiconductor devices as solutions for cleaning, removal, polishing and defect development were needed and, over the years, has expanded to include compound semiconductors, other device materials, and all metals or metallic compounds used in the processing and assembly of devices in their various shapes and physical forms . . . the entire field of inorganic materials and their chemical processing . . . with, here in this single volume, all major metal elements, and the majority of metallic compounds currently involved in our High Technology fields.

The collection includes several solutions as originally formulated by the authors and co-workers as new compounds were being developed, many of which have been published or presented by ourselves or other workers in the chemical processing field.

With the continual influx of new scientists, engineers and technicians into the Metals, Solid State, Electronic or Silicate and Ceramic fields, there is always a "need-to-know" availability of chemical solutions already developed. Even at that, old solutions appear in the literature as "new" development, approximately every 10 to 15 years, mainly due to a lack of time or the nonavailability of a technical library for extensive literature search. This is not to castigate such "new" development, as it often includes a greater understanding of chemical and material reactions utilizing advanced equipment capability that was not originally available.

In any event, many books have been published over the years with regard to chemical processing of materials, often on a particular metal or metallic group . . . but not all-inclusive . . . and more often involved with the material processing with but a short, selected list of chemical solutions and limited discussion of their application. There are exceptions, such as the ASTM E407-70 pamphlet — no longer in print — that has an extensive numbered list of formulations developed for the "metal" industries . . . mainly for irons, steels and copper alloys. The A/B Metals Digest published by Buehler Ltd. is another example, but this too is concerned with the so-called "heavy metal" industries, some natural minerals, and is largely involved with the preparation of metallographic specimens for study . . . not Solid State and Electronic material processing. The ASM Metals Handbook Series of some 12 volumes probably presents one of the most extensive collections of data with regard to metal processing — again — the metal industries with etchant solutions for general material processing and plating.

Many of the worldwide technical journals today are specifically published for Solid State and Electronics, but there is such a vast amount of literature available that it is all but impossible for any one individual to stay abreast of the new data and developments. The format of presentation varies by Journal and again may be more concerned with development other than chemical processing — a newly developed compound often extensively studied for crystallographic structure with little or no mention of chemical solutions.

An understanding of crystallography is essential, yes, but any new material requires eventual development of basically four types of chemical solutions: (i) cleaning; (ii) general removal; (iii) polishing, and (iv) defect development etchants. Fortunately, the vast majority of metals and metallic compounds form in the Isometric (Cubic) System, and a brief introduction to Crystallography is presented in Appendix F.

There are many excellent books on the market that discuss the crystal defect state in detail with particular regard to Solid State materials, but the field of mineralogy (geology "hard-rock") established much of the basic data on natural minerals — Dana & Ford *A Textbook of Mineralogy* — not only includes an extensive section on Crystallography, but describes all known minerals — over 4000 — their crystal structure, refractive index, specific gravity, formula, pyrolitic data (including etchants), natural occurrence, and major industrial

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use. Many artificially grown compounds are found as natural minerals, several are included in this book, where they have been studied and/or grown. Sphalerite, ZnS, as one example — zinc sulfide — as its structure is basic to many compound semiconductors . . . Isometric System, Tetrahedral Class.

Though this is a book of cleaning and etching solutions, crystal structure cannot be overemphasized, as much of chemical processing is directly related to the crystal structure of the materials in both general study and device fabrication. A knowledge of bulk crystal plane directions, as an example, is essential in the structuring of many specific microelectronic devices.

The objective of this book is to present at least one solution for all major metals and metallic compounds in current use and/or under development for immediate, hands-on application, and can be used as a "starting place" for further specific solution development.

Hopefully, those who have an immediate need-to-know will find it of use.

Perrin Walker
William H. Tarn
Los Angeles, California
1990

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THE EDITORS

Perrin Walker is currently retired after 30 years in the Solid State industry as a scientist and engineer, and has over 20 years military service.

He holds a B.A. degree with honors in Geology from the University of Virginia, Charlottesville, Virginia, 1953 with work toward an M.S. degree at UCLA in 1954. He has been a member of Sigma Gamma Epsilon, the Electrochemical Society, and the N.R.A.

With his crystallography and chemistry background, much of his work has been in R & D on semiconductor and quartz crystal surface chemistry and chemical processing of all inorganic Solid State materials. He also has been involved in processing parts and equipment design, and all phases of device design, testing and fabrication, to include sales. He has been the line engineer in charge of half a dozen government device development contracts, supervisor of operations, to include an MIC Laboratory, and Manager of Quartz Crystal R & D.

Mr. Walker holds patents in semiconductor processing, and has presented papers in both the semiconductor and geology fields. He is still involved with studies in both Solid State and Geology, actively pursuing a career as a freelance writer (both technical and non-technical), is a published cartoonist, also with published sketches and drawings of macro- and micro-fossils in geology.

William H. Tarn is recently retired after being employed for 45 years in the research and development areas of a panoply of disciplines. The disciplines each required, at some point in time, the chemical reaction of a surface etchant against an often obstinate and uncooperative metallic surface; hence his interest in chemical etches.

Mr. Tarn worked during World War II under research and development O.S.R.D. contracts and holds a patent for a 'Resilient Mechanical Wheel' that required neither rubber nor etching. The Synthetic Liquid Fuel Program of the Department of the Interior and the infant semiconductor industry were later sites of surface chemistry activities that led to etch use in preparation and sensitization of metallic surfaces for assault by intermediate or terminal chemical agents.

Mr. Tarn holds several patents and has been the co-author of several papers in these fields and on these subjects; he also states emphatically that although he has accidentally skin tested approximately 20% of the etches herein, there are no commercial cosmetic applications for the mixtures and advises great care be used in their application.

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PUBLISHING STATEMENT

Cleaning and etching solutions and general data presented are for information, and direct application in chemical processing by those operators with a basic understanding of chemistry and physics of materials. The solution discussion sections are as applied by the referenced author(s) published articles, and reflects those applications only. With the continual advance in purity of chemicals, materials, and solvents it should be understood that results discussed are relative to the period of time, locale, chemicals and chemicals involved, and that results may vary within the known limits of chemical reactions. Information is accurate and reliable to the best of our knowledge according to known applications and practices, but the authors make no guarantee as to completeness or accuracy and assume no liability in that regard.

NOTE ON SAFETY

Many of the etching solutions discussed in this book represent a safety hazard, not only from the type chemicals involved, but their temperature, type reactions, methods of applications, and so forth.

Cryogenic liquids can be dangerous due to reduced temperature, being inert, or explosive; all cyanides are extremely toxic; fluorine compounds are extremely dangerous as they attack nerve tissue, yet do not show an immediate "burn" reaction like most acids; chlorine gas and silanes are irritants on exposed skin, unbreathable, with attack of mucous membranes. Alkalies are most dangerous when being used hot; and the strong acids give immediate skin burns.

In mixing acids and salts as solutions, the end products of reaction should be known, to include reaction results from the material involved.

Safety procedures are not specifically discussed in this book, but individuals should be sufficiently knowledgeable and instructed prior to handling metals, chemicals, gases and solutions in this regard.

DISCLAIMER

Specific etchant solutions are patented or a part of device patents, which may include chemical processing as part of the disclosure, and other chemical processes or solutions can be classified as Company Proprietary. There are a few such patented solutions — with patent number — included in this etchant assembly but to the best of our knowledge . . . no company proprietary information. What may be classified as company proprietary, per se, for a given operation, is often already in the open literature — there are only certain chemicals and mixtures applicable to a particular metal or metallic compound. This is particularly true in the area of clean/etch sequences and etch sequences, the latter involved with multilayer or composite structures — several such sequences are shown in this text as they have appeared in the open literature. There are cases of "new" etchants or chemical processes developed, which are already in the open literature — sometimes — for several years prior to the "new" development and, in many instances, the same or closely similar solutions are developed simultaneously by different experimenters in generate laboratories and areas of the world, such that it is sometimes difficult to determine priority of development. This disclaimer is to state that there has been no attempt to release any information not already available in the metals and metallic compounds processing areas.

All information herein is as extracted from open literature, and is as originally written by the authors, from the source references cited.

The Editors

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INTRODUCTION

In the development or fabrication of any metal or metallic compound, chemical processing is involved at one or more steps — from the study of a newly developed material — to a final market product. This includes wet chemical etching (WCE) — liquid solutions; dry chemical etching (DCE) — ionized gases; a solid metal, such as copper as a reactive agent; molten fluxes at elevated temperature; molecular gases, such as in hydrogen firing; and electrolytic solutions that include the use of electric current. Plating of metals or compounds is a separate subject, not covered to any extent in this book, though chemical preparation of surfaces and a few plating solutions are presented where they have particular application in Solid State processing.

A major factor in chemical processing involves the physical structure of the material on which it is applied — in many instances, specific solutions have been developed for processing of . . . colloidal, amorphous, crystalline, and single crystal structure. In addition, any one solution can have a number of different applications: general removal, polishing, preferential, structuring, selective . . . development of pinholes in an oxide thin film . . . and temperature alone can alter a solution from a slow cleaning system to polishing or preferential. Water is the primary diluant for solution reactivity control, but both alcohols and solvents are similarly used as well as other acids as buffering agents. Other special additives, such as surfactants and chelating agents for foaming and de-foaming, glycerin or ethylene glycol for viscosity control, and soaps for improved solution surface wetting, may be included in a solution formulation. Gases may be bubbled through a solution: chlorine as an active agent or inert nitrogen for a stirring action only. Solvents alone, such as trichloroethylene, TCE, are used in liquid form or as hot vapor degreasers; acids, such as HF or HCl, also are used as liquids or in hot vapor form.

Surface oxidation can be of major concern in chemical processing as all metals and many metallic compounds always have a passivating native oxide on their surfaces. Such oxides are considered surface contamination, as are oils, greases, dirt, or other organic residues, for they can mask a surface and produce erratic etching results. Further, if such contamination remains on a surface that is subjected to some form of heat treatment during processing, it can diffuse into the material and alter both physical and electrical parameters. HF or other fluorine-containing compounds are the primary oxide removers, but surfaces may be intentionally oxidized as a surface cleaning step (boiling water, HNO_3, H_2O_2); and many etching solutions can leave a trace oxide after use, and are followed by a final HF strip. Needless to say, oxides, nitrides, borides, and carbides are controllably grown on surfaces as final passivating element or as masks against etching, diffusion, metallization, epitaxy growth, and so forth, and may be an active element in a device construction.

The physical properties of a metal or compound are assembled to present factors that can be important to chemical processing, such as melting points, chemical reactivity, crystal structure and so forth. This includes their use as bulk material; thin or thick films; as a mixture, such as alloys; and in multilayer construction, where each individual metal/compound layer may require a specially designed solution that will attack that material but not the others in the assembly. There are several collective sections in Chapter 2 as solutions containing chlorine, fluorine, bromine, chromium, etc., with selected etchants formulas, listed by material from A to Z, brief application and format reference number. These can be used for a quick summary of solution effect where a user is working with multilayer or composite systems.

Chapter 1 discusses in some detail the etchant presentation used in Chapter 2 — all elements and gases, and major compounds start with: (1) Physical Properties; (2) General: associated natural minerals and general industrial use; (3) Technical Application: development and studies, usage and devices, with emphasis on Solid State, and (4) Etching: a brief mention of applicable chemicals. Three formats are used in presenting each numbered

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solution in order to assemble all pertinent information in an easily read manner for consistency of descriptions. The bulk of Chapter 1 is a discussion of the items listed in the Formats: Etch Name, Time, Temperature, Type, Composition, Discussion, Reference, and so forth. All etchants have an assigned number using the chemical formula or an acronym: AL-xxxx, for Aluminum; GAS-xxxx, for Gallium Arsenide, etc. Some natural minerals are included by name, particularly where they are of importance with regard to their artificial counterparts or, like Alpha-Quartz, as a device.

Chapter 2 — Etchant Solution — is the alphabetical list of solutions, and includes some techniques that are not strictly etchants, per se, but special forming or fabricating methods, such as sphere forming or the cutting and use of cylinders, bars, and oriented single crystal cubes, rhomboids, octahedrons, and so forth. Many such forms are used in the study of etch rates on concave and convex surfaces . . . the finite crystal form of a sphere . . . establishing bulk plane directions for controlled etching of channels, via holes, etc. This includes similar oxidation rates on crystallographic planes using such forms. Gases are discussed in some detail — as gas or as cryogenic liquids — with their application in chemical processing, and includes their growth and study as single crystals. There is a section on Mounting Materials, including some organics, such as waxes, resins, and lacquers (photo resists), etc., as they are involved in material process handling, mainly cleaning solutions.

Over 80 of the major elements and gases — over 600 metallic compounds, for a total of approximately 700 items with at least one cleaning or etching solution are presented. Where there is a large number of solutions involved, such as under silicon (400+); gallium arsenide (300+) etc., a "Selection Guide" is included: solution mixture, such as HF:HNO_3 or H_2SO_4:H_2O_2:H_2O, with application — polish, preferential, etc. — and the assigned etchant numbers are shown.

Discussion sections of each Format include the material structure and formula: a-Si:H, GaAs:Cr, (100) (SI), clean/etch sequences used, and other materials to which the solution was applied. The lower case letter following an Etchant Number (AL-0027a) signifies another solution was used on the material in the referenced article. The discussion is "as applied" by the reference article; and it may vary with the period of development and use due to the improvement of material or higher purity chemicals now available.

The objective of this book is to present hands-on applicable solutions from the open literature for all major metals and compounds in a single reference volume to reduce time for an extensive literature search and it includes most of the current high technology materials.

A number of technical journals, both domestic and foreign; books; magazines; industrial technical brochures and pamphlets; and technical conferences have been used in the assembly of this book for the specific data. Much of the referencing done throughout uses the assigned solution number as developed in Chapter 2, as the Formats include the specific, say, journal/volume number/page/year. In most cases, the article title is not included, because only the type material and chemistry of concern is presented. Several of the tables, such as for material hardness, or the Physical Properties lists, are compiled from up to half a dozen sources, to include data developed by the authors, and do not reflect a pure abstract of any one source.

The end-of-book Appendix H is a complete list of materials, their formulas, and Etchant Format letter acronyms used in Chapter 2.

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* Singular or inclusive year dates. Standard abbreviations used.

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Chapter 1

MATERIAL FORMAT SECTION

INTRODUCTION

The cleaning and etching solutions are those that have been developed for the processing and study of artificially grown single crystals. Some natural single crystal minerals are included where they have been studied in conjunction with their artificial counterparts or are representative of the crystallographic structure of materials as a class, such as sphalerite, ZnS and wurtzite, ZnS for binary compounds; chalcopyrite, $CuFeS_2$, for ternary and sylvanite, $3Cu_2S{\cdot}V_2S_5$ for quaternary compounds in addition to spinel, $MgAl_2O_4$; rutile, TiO_2; corundum, Al_2O_3; wolframite, $(Fe,Mn)WO_4$ and others for binary and ternary oxides. There are a hundred or more such compounds that have been presented in the literature with regard to their methods of growth or in study of their crystallographic classification, but do not include cleaning or etching solutions and are, thus, not included.

It should be realized that there are over 4000 natural single crystal minerals that have been studied and classified in the field of mineralogy, to include evaluation for pyrolytic and solubility reactions. This information is in book reference (1) *A Textbook of Mineralogy* and in the section on "Physical Constants of Inorganic Compounds" — book references (3) and (4) *The Handbook of Chemistry and Physics* published by CRC Press, which lists elements and compounds with brief notations as to solubility in water, acids, alkalies, alcohols, or some mixed acids, but no specific solution formulas and application data, and do not include many etch mixtures that have been developed in the metals and solid state technologies. The latter text also includes the name of the natural mineral where it is referenced to a chemical compound, and both texts are excellent references for general solubility information.

In addition to single crystals, many elements and compounds are now being grown and used in other crystallographically classified forms, such as colloidal, amorphous and crystalline. The latter are sometimes referred to as "polycrystalline" and may be as sub-micron, micro-, or macro-crystallites or as a bi-crystal. All of these "forms" may be used separately or in combination as multiple layers of metallic compounds/oxides/nitrides/metals, etc. Such variations are included in this list of cleaning and etching solutions under their primary single crystal element or compound and, in many cases, they require special formulation mixtures for controlled etching and processing.

Another classification is the effect of solutions on the material. This includes some of the following: (i) general removal; (ii) polishing; (iii) preferential; (iv) stain; (v) decoration as metal diffusion to develop defect structures; (vi) plating; (vii) selective, and others.

Where the solution is used for a physical action: (i) step-etch; (ii) thinning; (iii) etch-stop; (iv) pinhole; (v) via hole; (vi) channel, etc., the material itself may be in a specific form, such as a wafer, cylinder, bar, wire or as oriented cubes, octahedrons, tetrahedrons or rhomboids and spheroids. It may be as a single crystal sphere, a bi-crystal or polycrystalline sphere used for etching to finite crystal form, oxidation reactions of spheres are studied or they are used to fabricate a device. Some metal alloys spheres are included where they are of specific importance in fabrication or have been grown as a single crystal, such as brass.

Special sections include borides, carbides, nitrides, and silicides and even a brief section on plastics — lucite, epoxies, and polyimides used in device assembly, mainly for cleaning or removal of such materials.

In some instances, even though the basic etch format is used, there is no etchant shown as it is a growth or forming technique thought worthy of inclusion, such as the forming of spheres. Ice, as an example, is grown and studied using a cryostat microscope stage and

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"etching" is done by varying cryotemperature, and ice spheres are made by spraying water into liquid nitrogen, argon, or oxygen.

Many metals and compounds are used as substrates, which may or may not be involved with a final operating device. Ceramics and dielectrics, such as alumina, beryllia, quartz, and sapphire, are metallized and photo resist patterned in the fabrication of electronic circuits — pressed powder, fused or single crystal substrates — or parts may be used as stand-offs or heat sinks in addition to their electronic applications. Semiconductors, such as gallium arsenide (GaAs) and indium phosphide (InP), are used as substrates for layered thin film construction of heterostructure or heterojunction devices. Many single crystal compounds, such as sodium chloride (NaCl), potassium chlorides (KCl), and magnesium oxide (MgO), are used for thin film metallization studies, with the films deposited, then removed by the float-off technique for study under a transmission electron microscope (TEM). The natural mineral muscovite, one of the micas, is used in a similar manner.

Where the thin film is an absorber and nonreflective for TEM study, graphite coatings with gold thin films are used to fabricate replicas of the surface and can require special chemical removal techniques, such as for float-off.

Where a single crystal wafer is being prepared for processing, it may be cut from an oriented ingot, mechanically lapped and polished, and then cleaned and etched, or it may be cleaved, used as-cleaved or mechanically lapped, etc. In any case, cleaning and etching sequences have been developed for processing. Many such sequences being assembled for specific device line processes are considered company proprietary, but several also have been published in the open literature and are described in the discussion portion of etch formats. Any basic clean/etch sequence may consist of any of the following, alone, in combination, and not necessarily in the order shown: (i) chem/mech lap polish to remove previous cutting/mechanical lap damage; (ii) degreasing; (iii) etching steps; (iv) solvent cleaning steps and a final (v) solvent or acid dip clean.

There also is a degree of cross-referencing involved in the discussion section of etch formats where the solution has been applied to more than one metal or compound in the article referenced. That same etchant and reference will occur under each individual metal or compound with its own, specific etchant number. For example: aqua regia ($3HCl:1HNO_3$) will appear under gold (letter prefix: AU-xxxx); it also will appear under platinum (letter prefix: PT-xxxx); where both metals were under study in the article. This leads to a certain amount of repetition, but each etchant has a distinctive number assigned which is associated with the element or compound. There also is a degree of repitition involved with particular solutions, such as the bromine-methanol, BRM, mixtures. The concentration of bromine varies from about 0.5 to 20% and, regardless of the general acronym BRM, each concentration is a specific solution as applied, and so listed.

Where the same concentration, or etch mixture, appears in more than one author/article, they too have an etch number assigned and immediately follow the primary etch format as an additional reference, and may show another use of the solution.

Repetition also occurs with certain etchants where they are applied for a different purpose. Hydrofluoric acid (HF) is an example, as it may be used for (i) removal; (ii) pinholing; (iii) thinning, etc., such that it will appear as a separately numbered etch solution in each application case.

A few compounds only have been deposited as a thin film, some amorphous, others as a single crystal, still others as polycrystalline films. Several are included whether an etch solution is included or not, because of the tremendous development, application and interest in thin film technology.

There are many aspects of cleaning and etching not mentioned in the above discussion, but we believe the etchant formats are self-explanatory. The following sections describe the methods used to present the materials of Chapter 2: Etchant Section. The introduction sections to each element, metal or compound vary in length according to their light or heavy usage,

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and the three basic formats have been organized to present a consistent approach for presenting data. The format items are described in some detail.

A. INTRODUCTION TO MATERIALS

All of the major elements and compounds are introduced with the following: (i) physical properties, (ii) general description, (iii) technical application, and (iv) etching, general.

(i) Physical properties — The physical properties of the element or compound, and some electronic properties where applicable. This may be extensive or brief depending upon the availability of information found in the literature. Some new compounds show no physical properties, and trinary or quaternary compounds may follow their binary compounds with no individual list of physical properties. Crystal structure is shown by crystal system-class according to standard crystallographic notation. Cleavage (fracture) is shown as many single crystal compounds are being used as-cleaved, or cleaved sections are used in both study and processing.

(ii) General — Occurrence as a natural single crystal mineral or element and associated minerals. If it is not a natural crystal, then artificial compounds; general industrial use to include other applications such as in medicine, food preservation and so forth. The basic gases are discussed and, where they are major constituents of etchants, they also appear under the applicable material in the etch formulation. Some natural single crystals are under their mineral name, such as magnetite, Fe_3O_4 and/or included under their chemical name, such as zinc sulfide, ZnS and sphalerite, ZnS, where the two compounds have been involved in comparative studies.

(iii) Technical application — Primarily as solid state material. If not a semiconductor, the compound application in semiconductor processing, or other use as a material or device in high technology. This includes use as other than a single crystal structure, such as a colloid, amorphous or crystalline form. It should be realized that both semiconductors and metals, as well as other metallic compounds are in use, alone, or in combination in all of their possible physical forms. Other materials have use in semiconductor processing, but also in other applications, such as oxides or ceramics or as dielectric material as capacitors or resistors, or their use as light frequency filters, lenses, lasers, and fiber optics.

(iv) Etching — General solubility in acids, alkalies, alcohols, halogens. As single or mixed acids; ionic gases; molten fluxes, and so forth.

Immediately following the Physical Properties list is the General Section. The "General" section is headed by the material name and is introduced by the name and formula of the material: example: CALCIUM CARBONATE, $CaCO_3$ or CALCITE, $CaCO_3$

Following the (iv) etching section, the formatted etchant section is introduced with the following heading: example: CALCIUM CARBONATE ETCHANTS

B. ETCHANT FORMATS

The three formats used have been designed for consistency of presentation in order to include all pertinent data in a concise, readable and repetitive form. As will be seen, all information is not present for many of the etchants as it may not have been included in the reference article. In many cases, it is easy to assume, say, that a solution was used at room temperature — the normal application of that particular mixture — but unless it was so stated in the referenced article, the temperature (TEMP) is left blank.

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I. Wet chemical etching (WCE) format

(1) Etch Number
(2) ETCH NAME:
(3) TYPE:
(4) COMPOSITION:
(formula)
(8) DISCUSSION:
(9) REF:

(5) TIME:
(6) TEMP:
(7) RATE:

II. Electrolytic etching (EE) format

(1) Etch Number
(2) ETCH NAME:
(3) TYPE:
(4) COMPOSITION:
(formula)
(8) DISCUSSION:
(9) REF:

(5) TIME:
(6) TEMP:
(10) ANODE:
(11) CATHODE:
(12) POWER:
(7) RATE:

III. Dry chemical etching (DCE) format

(1) Etch Number
(2) ETCH NAME:
(3) TYPE:
(4) COMPOSITION:
(formula)
(8) DISCUSSION:
(9) REF:

(5) TIME:
(6) TEMP:
(13) GAS FLOW:
(14) PRESSURE:
(12) POWER:
(7) RATE:

The WDC format is used as the general format, such as for use of molecular gas as against DCE ionized gases. Also includes molten flux etches, special forming and fabrication techniques that may not include a specific etchant.

C. FORMAT ITEM DESCRIPTION

(1) ETCH NUMBER

Every referenced etchant has an assigned number under each element, metal or compound, and consists of three items: (1) capital letter designation of the material; (2) an individual number, and (3) lower case letter where more than one etchant appears for the material in the referenced article.

Up to four capital letters are used and are the chemical symbols for the material, element, compound, etc., where it is a singular element or a binary compound. In some instances, these are "common usage" acronyms, such as GAS for gallium arsenide, (GaAs) as GAS-xxxx. For yttrium iron garnet, $Y_3Fe_2O_{12}$, the acronym YIG-xxxx. For trinary or quaternary compounds, where a chemical formula is in conflict, a special acronym is used, such as for molybdenum selenium sulfide, $MoSeS_2$ (acronym: MOSS-). And there is the special case of carbon, C-; diamond, D-; and a third for natural or artificial graphite, GR-, all three being forms of carbon.

All element or compound numbers start: -0000, e.g., AL-0001; then BE-0009; SI-0274; and so forth. This leaves sufficient numbering space for any currently foreseeable new etchant solutions as they are added to the handbook.

The use of the lower case letter following the number is limited to those references where more than one solution has been used in the article on that particular element, compound, etc. The full reference will appear under the "a" designated solution only; whereas the "b", "c", etc. solutions will be shown as: REF: Ibid.

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Example: CD-0004a .... REF: Doe, J — *J Appl Phys*, 57,112(1985)
CD-0004b .... REF: Ibid.

A complete example of a full format and additional reference is shown following the description of REF.

(2) ETCH NAME

If it is a singular acid, alkali, salt, the full name is used, e.g., hydrochloric acid. It also is shown where the singular acid, alkali, etc. is water diluted, e.g., hydrochloric acid, dilute. It is not shown if dilution is with other than water — alcohols, solvents, etc.

The vast majority of solutions show no name as they are mixtures. On the other hand, where a name is in common usage it is shown and may be a modification of an original formulation. The following is an example of one such solution:

ETCH NAME: Camp #4	The original solution development
ETCH NAME: CP4	Common usage acronym
ETCH NAME: CP4A	CP4 without bromine
ETCH NAME: CP4, modified	CP4 with bromine replaced by iodine, etc.
ETCH NAME: CP4, modified	CP4 with a different bromine content

A similar case is the bromine-methanol (BRM) classification. The acronym is used in the literature without regard to bromine concentration and no attempt has been made to classify these solutions as modifications. As in many instances the referenced article only says: " . . . a BRM solution was used . . . ", which leaves a bit to be desired.

There are some poorly named solutions, such as the "1:1:1", but it is still shown as an ETCH NAME: per article reference. The use of the name "White Etch" is another example, as it has been used to describe HF:HNO_3, and HF-HNO_3:HAc solutions — none of which are white, but transparent, clear and colorless solutions.

The buffered hydrofluoric acid solutions (BHF) are in the same variation category as are the BRM solutions — even HF, dilute has been called BHF, or KF has been used in place of NH_4F, etc. A general standard in use is 1HF:1NH_4F(40%), though the reference may show only " . . . BHF . . . " used. Unless it has been shown in the article, the BHF formulation is not shown under COMPOSITION.

(3) TYPE

Divided into two parts: (1) a "chemical" designation and (2) an "application" designation. The objective of this two-part approach is to show how an acid or solution mixture is used for more than one application as described in the various referenced articles.

Terms used are as brief and concise as possible and the "chemical" descriptive term may not necessarily agree with pure chemistry nomenclature, but all terms are chosen for general repetitive consistency.

Some of the more commonly applied terms are shown below in the two categories:

Chemical	**Application**
Acid	Cleaning, polish
Alkali	Damage removal, polish, jet
Alcohol	Dislocation, preferential
Gas	Isotropic, oxide etch
Halogen	Anisotropic, oxide removal
Ionic gas	Junction, selective
Metal	Macro-etch, sphere

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Chemical	Application
Molten flux	Micro-etch, structure
Salt	Mesa, stain
Solvent	Orientation, step
Electrolytic	Forming, thinning

There are others in both categories.

All electrolytic solutions are chemically designated "electrolytic" and followed by an application term even though common practice would say: "electropolish", as example; whereas many of the electrolytic solutions described have far more than just the polish application.

This is not a plating handbook, but there are some plating solutions shown, primarily where they have been used in developing p-n junctions, as metal contact plating, or are of particular use in Solid State or metal processing.

Three examples of TYPE: designation are shown below:

TYPE: Acid, polish
TYPE: Alkali, cleaning
TYPE: Electrolytic, thinning

(4) COMPOSITION

Divided into two parts: (1) volume/quantity used and (2) chemical formula of constituents.

In many instances, the volume/quantity was not shown in the referenced article and is therefore designated as an "x". Where it is obvious that the volume/quantity such as a single acid, alkali, etc. is not critical, it too is shown as "x":

x .... HF, conc.	or	x .... HNO_3 x .... H_2O	or	x .... 2% Br_2 x .... MeOH

The third example above is very common for the BRM and BHF solutions where the total volume is not critical, provided the percent concentration of bromine, fluorides, etc. is maintained.

Many mixed solutions are shown by volume percentage. This is common to the metals industries and some early solid state articles:

6% .... $HClO_4$
35% .... butyl cellusolve
59% .... MeOH

Where dry chemical compounds are used, such as ferric chloride, $FeCl_3$ or potassium permanganate, $KMNO_4$, they are usually formulated as a water diluted solution, specifically as gram-weight per liter of water: g/l. Both liquid acids or dry chemicals may be mixed by viscosity, using the Baumé scale, °Bé, which should not be confused with the temperature scales "degree" designation, e.g., °F or °C, although it is called "degrees Baumé". Using ferric chloride as an example:

x .... $FeCl_3$ (35°Bé)	or	x .... 20% $FeCl_3$	or	x .... x% $FeCl_3$

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It also may be shown as

112 g .... $FeCl_3$	*or	50 g .... $FeCl_3$
10 ml .... HCl		1000 ml .... H_2O
50 ml .... H_2O		

* as a g/l solution

Liquid acids, solvents, etc. are usually measured and used by milliliter, ml, volume as commercially supplied with water diluted concentrations shown as 70% HNO_3; 30% H_2O_2; 49% HF etc.

The most common method of designating volume/quantity of a solution mixture, where the total volume is neither critical nor required, is to use a numerical ratio of constituents:

1 .... HF	or	3 .... HCl	or	1 .... Br_2
5 .... HNO_3		1 .... HNO_3		10 .... MeOH
12 .... CH_3COOH (HAc)				

Where a mixed acid is used as a "constituent" in a particular formulation, it is shown as:

1 .... *CP4
3 .... HNO_3
6 .... H_2O

*CP4: 30HF:50HNO_3:30HAc:0.6Br_2

Saturated solutions may be shown in two contexts:

50 ml .... HF	or	100 ml .... HCl
20 ml .... NH_4F, sat. sol.		x .... *Br_2

*saturate with bromine

To differentiate between using an acid in concentrated form as against its use in vapor form: ("conc." shown only when referenced.)

x .... HF, conc.	or	x .... HF, vapor

When a specific mixture is described, it is usually in milliliters, ml (liquid) or grams, g (gm still seen) for dry chemicals:

250 ml .... 30% KOH	or	20 g .... KOH	or	10 ml .... HF
		100 ml .... H_2O		30 ml .... HNO_3
				100 ml .... HAc

In some of the older literature, milliliters appear as centiliters, cc, but the two terms are equivalent. Some volumes are shown in cubic centimeters, cm^3, such as 150 cm^3 HCl, which is equivalent to 150 ml HCl. There are some large volume solutions measured in gallons and ounces, etc. The latter more often are in the metals and plating area, rather than Solid State.

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Solutions also may be shown as a Normal or Molar solution:

1 .... 12 *N* HCl or x .... *EDTA 2 *M*
1 .... 17 *N* HAc x .... NH_4OH for pH 3.5
1 .... 1 *N* $K_2Cr_2O_7$

*Ethylene diamine tetraacetic disodium salt

In the second example, the EDTA solution is available as a standard molar mixture and, in this case, a specific acid/base pH value is established using ammonium hydroxide.

Cleaning solvents are used for liquid immersion or (hot) vapor:

x .... TCE or x .... TCE, vapor or x .... TCE, spray

Where metals, or metal salts are used for either developing p-n junctions by plating, or as a defect decoration agent with in-diffusion:

50 g .... $Cu(NO_3)_2$ or x .... Au
100 ml .... H_2O
\+ .... intense light

There are a number of clean/etch sequences that have been developed, many of them are company proprietary to a specific line operation, but several have been published in the open literature and follow a general pattern of any one or more of the following, and not necessarily in the order shown below:

(1) Chem/mech lap to remove damage, such as BRM on a polishing cloth
(2) Degrease in TCE, Freon, etc., as vapor, spray, or liquid (RT/hot)
(3) Alcohol rinse with acetone, methyl or ethyl alcohol
(4) Acid etch — a slow polish and/or cleaning solution
(5) Alkali etch — as an etch or surface conditioner (optional)
(6) Water rinse — DI, Hi-Q, etc., [also after (1) and (4)]
(7) Alcohol rinse [as in (3)]
(8) HCl + water rinse (often 50% HCl)
(9) HF + water rinse (50% HF common)
(10) Nitrogen blow dry — may be He, Ar, air, etc. (RT/warm/hot) or IR lamps, other heaters, or air dry
(11) As an additional process, final cleaning or drying in vacuum, in a furnace with hot gases, etc.

These sequences are shown in the discussion section of formats where they may be a major operation step. Some references may not include any clean/etch steps, but only the primary solutions associated with the material study even though one would normally prepare the surfaces by using one or more of the clean/etch steps shown.

A gas or gas mixture may be used as an etch in either its molecular or ionic form, alone. A molecular gas also may be bubbled through a liquid and act only as a carrying vehicle for the liquid; for stirring action of the solution only; or be an active element in the solution reaction. The molecular gases are shown by their normal diatomic representation; whereas the ionic gases as in the example for argon, below. In some cases, the ionization (+) symbol

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is not present, but it will be apparent that ionic gases are applied, because the dry chemical etching (DCE) format it used. The last example shown below is of this type:

x .... N_2 or x .... Cl_2 or x .... Ar^+ ion or x .... CF_4
x .... 5% O_2

Heat in vacuum, alone, is used for both preferential etching as well as for annealing, e.g., thermal heat treatment. A vacuum system may be back-filled to a partial pressure with gas, but when gases are used, it is usually as an oven or furnace system. Oxygen or O_2/N_2 or CO_2/N_2 for oxidation; N_2 or N_2/Ar for nitridization; H_2 or forming gas (FG) 85% N_2/15% H_2 as a reducing atmosphere, all along with heat. Where heat is the primary operator, it is represented as an etch under composition; as shown below; but if molecular gases are involved in addition to heat, the gas is shown:

x .... heat or x .... N_2, hot

There are special cases where pressure, with or without heat, have been used to initiate defects under various conditions of temperature, or under vacuum using vapor pressure change as the agent:

x ... pressure or x .... vacuum

Another special case is the use of light. It may be white light or referenced to a color and/or specific frequency spectrum, used alone for drying; as a work light, such as etching silver under red light; as a damage induction/reaction vehicle; in conjunction with plating; or to enhance etching:

20 g .... $Cu(NO_2)_3$ or	x .... light or	5 .... HF
100 ml .... H_2O		2 .... HNO_3
+ .... *intense light		+ .... *light
*Mercury lamp		*Sodium (5890 Å) yellow

Where acid-slurries are used for lapping and etching, the acid, solvent carrier, and abrasive are shown. Occasionally, only an abrasive where it is the only agent used for polishing the material:

50 g .... 0.5 μm Al_2O_3 or x .... diamond, powder
5 ml .... HNO_3
50 ml .... ethylene glycol (EG)

Acid-saw systems are under the metal or other material used as the cutting agent (iron wire, cotton thread, tantalum rod, etc.) and may include abrasives to improve slicing and cutting action.

Where two or more solutions are shown under COMPOSITION there are three methods of designation using the lettering or numbering systems as shown in the following three examples:

(1) If two or more solutions are to be mixed together:
(i) 4 .... HF (ii) 10 g .... $AgNO_3$
3 .... HNO_3 100 ml .... H_2O

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mix: 1 part (i):3 parts (ii), when ready to use.

(2) Where two or more solutions are to be used in order:
(A) 1 .... HF (then) (B) x .... MeOH
6 .... H_2O

(3) When two or more solutions are to be used separately:
(1) 1 .... HF (and/or) (2) 1 .... HF
1 .... H_2O 50 .... H_2O

Where water is used as the diluent or rinse it is shown as H_2O, without regard to purity designation, but should be considered as distilled water (DI H_2O) unless otherwise specified:

x .... HF or x .... H_2O, salt or x .... H_2O, tap
x .... H_2O

There are many types of water, but only two are normally used in all industrial processing, as either natural water with only solid matter removed, or as purified water, e.g., DI water. The latter most commonly distilled on-site, and may be double-, even triple-distilled with names such as "Hi-Q". Occasionally, it is known as demineralized water (dm-H_2O). Referenced use is as fresh, potable (drinking) water, not saline, e.g., salt water, except as noted . . . when used as a quenching medium or direct etchant, itself.

Although water is a neutral solvent, it is applied as an etching solution on water-soluble minerals and artificial compounds. See the section on Water for a more extensive discussion, to include "cold etchants" as mixtures that may contain ice, or snow, or be cryogenic liquids.

(5) TIME

Appears only when given in the referenced article. Usually a single time and temperature; occasionally repetitive time steps or two times at two different temperatures, as separate etching levels; sequence etching times and temperatures and so forth. The time can vary from seconds to minutes to hours depending upon the material and application. Some examples are

TIME: 12 sec or TIME: 10 sec, 3 times or TIME: 4 h or
TIME: 2 min or 15 sec
RT 80°C

In metallographic sectioning, etching for micro- or macro-structure, terms such as "dip" or "swab" may be shown under TIME. These are a method of applying a solution, but were used as a time referent in the article. In defect and structure etching, final surface cleaning or tuning device electrical parameters, an initial etch time may be shown and followed by one or more dip periods to obtain optimum results. This is particularly applicable to photo resist metallization patterning on circuit substrates and is shown in the discussion section of the format.

A time may be shown, and no temperature. In such cases, the solution was probably used at room temperature but again, information is included only if it appears in the referenced article.

(6) TEMP

Appears only when shown in the referenced article. In most cases, when a solution is used at other than room temperature the reference includes temperature. Fortunately, most

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etching is done at room temperature even though there may be an increase in temperature during the etching period due to the exothermic nature of the solution or the heating effects of an RF plasma in dry chemical etching.

Temperature can have a major affect on etching results with any given solution. The hydroxides, KOH and NaOH, for example, when used at room temperature as 2—10% concentration liquid solutions, are used for surface cleaning; as 20—50% liquid solutions they are heavy scale removers on many metals; and when used hot to boiling are progressively preferential. When used as a molten flux at elevated temperature (360°C), they are also-preferential. All liquid etch solutions become progressively more surface preferential and slow below room temperature, even though they may be a polishing solution at room temperature, and the reverse is true. Much above 40°C, an exothermic solution becomes too rapid for good polishing control. For this reason, in batch etching semiconductor wafers, a large volume of solution is used — allowing it to cool between etch periods — or etching is done in a cycle-controlled etching bath using water, glycols or Freons chilling piping to dissipate heat.

There are three primary temperature scales in common use:

(1) Centigrade, °C	Also called Celsius. Used in scientific works and as the atmospheric scale in Europe . . . also now in the Americas.
(2) Fahrenheit, °F	Widely used in the metals and plating industries and as the atmospheric scale in the U.S., in addition to Centigrade.
(3) Kelvin, K	Scientific scale based on absolute zero. Absolute, °A, is equivalent. Note that "K" does not use the degree (°) notation, although it still does appear with the degree sign in some publications.

Correspondence between these scales is as follows:

Comparative Temperatures Table

Reaction	°F	°C	°A or K	Correspondence
Boiling	212	100	373	°F = 9 × °C/5 + 32
		50	323	
			20 293	
Room temp		72	22.2 298	°C = (°F − 32) × 5/9;
Freezing	32	0	273	
	−40	−40		
		−200	73	
Zero		−273	0	

Under the temperature heading of the etchant formats, room temperature is shown as RT whenever possible, even though "room temperature" has been shown in articles from 20 to 25°C. It should be noted that many of the electrical measurements in the Physical Properties sections are made at 20 or 25°C.

Verbal terms also are used in describing a temperature, such as cool, warm, hot, or boiling.

The following arbitrary temperature levels have been established for use in this text for consistency:

Cryogenic: −270 to −30°C — Liquified gases, such as LN_2, LHe, LOX, etc. Normally used to chill other liquids, though they can be a direct etchant under special conditions.
Freezing: −30 to 0°C — Certain acids or acid/ice-snow mixtures. Freezing level can produce a slush etch solution with cryogenic liquids for chilling.

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Cold: 0 to +10°C — Some acid mixtures, alone; others housed in a bath of ice water, acetone/ice, methanol/ice, etc.
Cool: 10 to 20°C — Acid mixtures chilled with cold water or other cold solvents, cryogenic liquids, etc.
RT: 22.2°C or 72°F — Standard atmosphere and pressure (760 mmHg), much etching done at room temperature.
Warm: RT to 40°C — Heat with light, gases or electricity (*Note:* "Chrome Etch" is widely used at a controlled 30°C).
Hot: 40 to 80°C — Varies with liquid and mixture, but below boiling point.
Boiling:

Low boil: 80 to 100°C — Slow solution movement; fine, sporadic bubbles.
Medium boil: 100 to 130°C — Convection currents in solution; continual surface movement.
High boil: above 130°C — Severe convection currents in solution; massive bubbles explosive to surface; and violent, erratic surface. Some solutions, even above 130°C, show a roiling or rolling boil without severe, massive bubbling.

Note: Most hot etching is done at low or medium boil.

Vapor: above 100°C — Specific temperature dependent on solvent or gas used.
Vacuum +/− gas: to 1000°C or more; vacuum as low as 10^{-10} Torr.

(7) RATE

Not listed in formats unless it is referenced in the article as the majority of solutions are used without regard to removal rates.

In processing single crystal materials, such as the semiconductors, removal rates relative to the wafer surface as well as bulk crystallographic planes can be a critical factor of the device design and structuring. Because of this, whenever a new single crystal compound is developed, much of the initial studies are involved in establishing the etching of planar, concave, and convex surfaces. Convex surfaces are studied with spheres and hemispheres — the fast etch planes; concave surfaces — slow etch planes — are developed by controlled pit damaging and etching with pit shape and bulk planes controlled by the planar surface orientation, such that a (111) surface develops triangle type pits and a (100), square pits. In both concave and convex etching, the type etchant solution used is an additional variable — hexagonal pits can be etched on (111) surfaces (superimposed negative and positive tetrahedrons); one solution will etch a sphere to finite crystal form as a dodecahedron, (110); another as a cube, (100) and yet, another as an octahedron, (111) or tetrahexahedron, (hk0). All of the above are in addition to defect study — dislocations, slip, stacking faults, twinning — and other structures.

Removal rates on single crystals and materials in general, where only small amounts of material are removed, are commonly measured in angstroms per unit time: 50 Å/sec; 1200 Å/min. In the metals, ceramic, and glass industries — corrosion and similar studies — rate measurement may include a total volume gram-weight loss with time. The etch rate and time for some more chemically inert metals, such as tungsten, titanium, or molybdenum, which have extremely slow attack rates, may be only in mils-per-year (mpy).

Where material removal rates are more substantial, measurements are in millimicrons, mμ; in microns, μm; or in mils (1 mil = .001″), with the time in seconds (sec), minutes (min) or hours (h). Rate is always shown relative to time. Some examples are

10 Å/sec or 20 μm/min or 1.5 mils/h or 4 μ/10 min

The following table shows the correspondence of thickness measurements of some of the more widely used units:

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Thickness Measurement Table

Angstroms (Å)	Micro-inch (μ")	Micron (μ)	Mil (mil)	Inch (")
254	1			
10,000	1			
25,400	100	2.5	0.1	.0001
254,000	1000	25	1	.001

The micro-inch measure is common for metal plating thickness, though not limited to plating, with 100 μ" a relative standard, say, for copper, nickel, or chromium; whereas gold is 25—50 μ" in most commercial applications, but supplied as 150 μ" or 300 μ" as gold plated alumina substrates in Solid State circuit processing. These thickness measurements become important in all material processing, as the rate of removal of a specific metal/compound/multilayer on a substrate is critical. Rate vs. thickness is experimentally established, initially, for controlled patterning of thin films in device circuit fabrication. In etching for line-width and depth, an etch solution will attack vertically and laterally at an equal rate, such that initial rubilith pattern widths calculations must take the lateral etch factor into consideration to prevent subsequent undercutting, lifting, peeling of the thin film, or loss of electrical characteristics. In such fabrication, rates of removal must be known, and are an extremely critical factor in microwave device fabrication.

As already said, removal rates are only shown in the etch formats when listed in the referenced articles as a major item, such as the initial study of a new compound. As a secondary function, it may appear in the discussion section of the format along with other processing data.

(8) DISCUSSION

Varies from a few words to a fairly extensive discussion depending upon the application. Many of the earlier solutions that were, say, used for defect etching, plane attack data, etc. are brief; whereas with more current development involving metallization, multiple layers, selective etching, and so forth, to include clean/etch sequences, the discussion is more extensive. In most instances, the discussion starts with the material formula; single crystal orientation where applicable; or other structure, such as amorphous; the physical specimen used, such as a wafer, blank, etc. and the study or fabrication involved where appropriate — with results, say, a new refractive index, dielectric constant, or the test involved, and so forth. Clean/etch sequences or special processing applications are included. Where the referenced article shows the study of other materials, these are shown by chemical formula for cross-indexing purposes.

Some of the general sections, such as Cleaning (solutions/methods) may be a specific solution application or a general discussion that can include other fields than metals/metallic compounds, such as the use of borax . . . a cleaner, a solder flux, a preservative . . . in industry, in home use, in medicine, and so forth.

The introductory sections — "Etching", as an example, describe the basic etching methods . . . wet chemical etching (WCE), or dry chemical etching (DCE), and molten flux etching (MFE), or electrolytic etching, (EE) . . . without inclusion of a specific component clean or etch solution.

In other cases, the WCE etchant format is used for convenience, but involves a special fabrication procedure, such as the fabrication of spheres by lathe cutting, melt forming, or "race track" grinding. The latter starts by using pre-cut single crystal cubes.

(9) REFERENCES

Standard practice for presentation with accepted abbreviations are used. Author(s) with

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last name, first, then initials — then the journal abbreviation (journal, volume number, page, and year). For books, the full title is given, followed by publisher, year, and page; and magazines with month/year/page.

Where there are more than two authors for the article, we have taken the liberty of showing the primary author followed by "et al.". One horrendous example: a full page of 52 authors, and only a page and a half of text! Several foreign journals often list four to eight authors — again, first author shown only, for sake of brevity, otherwise a drastic increase in total book volume which we feel is unwarranted, but no reflection against the input or status of those other authors of the article!

Some sections have an open reference . . . less than 2% as unknown or unavailable references, while others may be as "N/A" for common usage solutions, such as aqua regia; or in the section "Mounting Materials", and similar sections, where only a general discussion is involved.

A consolidation of reference materials used are shown here in Chapter 1 following this introduction, such as the *Journal of Applied Physics* with only year-inclusive dates. Specific articles are referenced following each etchant format as part of the format: REF: xxxx and, where other authors/articles have used the solution, they immediately follow the primary format as an additional references.

As referenced, the article title is not included in most cases, again, for brevity, and because the chemical solutions are the primary concern in this book; whereas the article may have been on another aspect of material developed and study with only minor description of chemical processing.

One example of a primary reference, followed by an additional reference is

*REF: Belyustin, A V — *Sov Phys-Cryst.* 5,143(1969)
SI-0247: Richards, T L & Crocker, M — *J Electrochem Soc*, 121,14(1956)

*This immediately follows the discussion section of the etchant format.

An example of a complete Chapter 2 text etchant format and additional reference is shown below:

AL-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal/clean
COMPOSITION:
1 .... HCl
2 .... H_2O
DISCUSSION:
Al, as thin films . . . etc.
REF: Doe, J — *J Apply Phys*, 27,142(1976)
AL-0007: John, J K — *J Electrochem Soc*, 112,219(1977)
Al, (100) wafers . . . etc.

TIME: 1 min
TEMP: RT

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ELECTROLYTIC FORMAT

As a method of etching, electrolytic etching is more widely used in the metal industries than in solid state and electronics device fabrication. But if the iron industry says "electro-polish" here, we say "electrolytic, polish", using the word polish as an application term because there are a dozen or more such applications: cleaning, forming, thinning, oxidizing, preferential, to mention only a few.

(10) ANODE

Where anodic etching is used, the anode is understood to be the material involved — gallium arsenide, silicon, manganese, etc., but it is not listed unless actually stated in the referenced article.

In special cases there may be more than one anode, or cathode and where a semiconductor p-n junction is being etched the specimen p- or n-type zone may be the anode.

The "etch" solution, proper, may be either a true etchant or a plating solution — again, primarily in developing p-n junctions — such as using copper or silver to selectively plate-out the p- or n-type side of a junction. It may include intense white light (copper) or be operated in the dark (silver). It should be understood that this book is not a Plating Handbook, the only presentation of plating is with regard to junction delineation, or material plating for contact metallization of electronic devices. There are several electrolytic solutions as anodic etching action formulas used, alone, or in conjunction with cathodic "etching".

According to standard electrolytic operation the anode is the positive (+) terminal.

(11) CATHODE

Although there is occasional reference to "cathodic etching", it is not etching in the sense of removal of material, but de-plating or conversion of a surface.

The cathode may be the same material as the anode in special cases, but it is more often a base metal such as lead, steel, stainless steel, iron, copper, nickel, or platinum that is, effectively, inert to the etch solution involved and does not directly affect the anode material being etched. Both anodes and cathodes may be in several forms, such as a bar, a single wire, a wire mesh, etc.

There is much developmental work in progress in the anodic/cathodic oxidation of surfaces, in particular, silicon in potassium hydroxide, KOH, solutions. It is a combination of oxidizing and de-oxidizing the surface by switching from anode-to-cathode. This operation is included due to its importance in the study of metal and metallic compound surfaces.

The cathode material is shown only if it is given in the referenced article and includes the form: rod, wire, screen or special shape, when described in the article.

According to standard electrolytic operation the cathode is the negative (−) terminal.

(12) POWER

Not shown unless it is given in the referenced article; may be voltage or amperage only, preferably both.

Most semiconductor materials are etched in the milliampere (mA) range; whereas many metals, ceramics and dielectrics such as glasses are etched in the ampere (A) range. In both cases, voltage (V) can range from tenths, say 0.2 V, to several volts — 5 V, 20 V, etc. Standard practice is to show amperage per square centimeter, A/cm^2 of surface area: 0.5 mA/cm^2 and so on. Most power is DC, occasionally AC, or a combination of both.

Unfortunately, many references simply say "anodic etching" was used with no details given, as the article is not concerned with chemical processing of a material as a major factor in the study presented.

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DRY CHEMICAL ETCH FORMAT

Note: Gases used in their molecular form, such as H_2 as a furnace reduction gas or N_2 and Ar as inert atmospheres, are shown under the wet chemical etch format, WFCE. Dry chemical etching (DCE), using the dry format (DF), applies to the use of gases in their ionic form, as obtained using RF, RF magnetron, or DC power. Special applications may include a combination of both RF and DC operation.

(13) GAS FLOW

Usually shown as cc/min, occasionally as SCFM:

10 cc/min or 0.5 SCFM

The gas or gas mixture is shown by chemical/application under TYPE as TYPE: Ionized gas, selective (and others) with the formula(s) under COMPOSITION:

x .... Ar^+ ion or x .... CF_4
x .... O_2 (5%)

In the second example, that ionization is not shown as the dry chemical etching format is self-evident. In addition, the Ar^+ (ionic symbol) is used, rather than Ar only, which is representative of a molecular gas. The additional descriptor of PRESSURE also is distinctively DCE processing, although RF or DC power application is not; both RF and DC power also are used in sputter evaporation of metals, epitaxy growth of materials and plating.

(14) PRESSURE

Usually shown as milliTorr of over-pressure of the gas(es) when referenced to DCE processing, but can be shown in atmosphere, (atm):

0.5 mTorr (mT) or 0.2 Pa (Pascal) or 0.4 atm

Ion gas etching includes ion milling as an operating system, or RF plasma cleaning or etching systems. RF plasma cleaners using N_2 or O_2 as ionic gases are being widely used in Solid State device processing, and specific vacuum systems are designed to handle chloride gas etching of aluminum oxide thin films with $AlCl_3$ or BCl_3 as ionic gases. In all cases, the systems operate with an input gas over- or back-pressure.

Pressure as an individual function/operation without regard to dry chemical etching (DCE) appears in the wet chemical etching (WCE) — classification, with pressure shown either in atmospheres or as pounds per square inch (psi).

Many materials are pressurized in the study of their high pressure crystallographic forms and to establish their transition temperatures. Standard hexagonal ice, for example, under pressure, becomes cubic (isometric system, normal (cubic) class), and there are six high pressure forms of silicon.

In chemical vapor deposition, CVD, material growth, specific pressure designated systems are used: low pressure, as LPCVD; high pressure, as HPCVD, and several others.

The growth of artificial alpha-quartz is done at a minimum of 30,000 psi, and in geology studies of rock magma formation, better than 300,000 atm.

Pressure alone is used as an "etchant" for preferentially developing defects in such materials as ice, alkaline halides (ionic crystals) or single crystal rare gases (vary vapor pressure in the vacuum system).

In dry chemical etching (DCE) a number of methods and terms have been developed with their own acronyms. RF or DC plasma etching, PE, is the most general; reactive ion

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etching, RIE, and several others. These may be shown in the format as an ETCH NAME, as a TYPE: chemical designator; or referred in the DISCUSSION section. Additional anodes and cathodes may be used in conjunction with the RF plasma or additional electric bias is applied to specimens. These are shown in an expanded format — a combination of the electrolytic and dry chemical etching formats.

With reference to the terms isotropic and anisotropic as used in wet chemical etching, WCE, they are polishing or preferential etchants, respectively. Isotropic/polish are solutions that attack crystallographic planes at an equal rate in all crystal plane directions producing planar, flat surfaces; whereas anisotropic/preferential solutions attack crystallographic planes at different rates producing structure.

In dry chemical etching, the terms refer to structuring development without regard to their preferential or nonpreferential crystal plane attack . . . ionic gases can be either isotropic or anisotropic in character. From a pure chemical reaction point of view this variation of terms can be confusing, because of this difference in interpretation between wet or dry etching. In physics, geology, and optics the two terms were originally defined with regard to light propagation through solids, and are basic to crystallography, e.g., the refractive index of materials, etc.

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METHODS OF ETCHING

There have been over 200 terms used in the literature to describe a method of etching, and generally fall into one of the three format categories described in the previous section: wet or dry chemical and electrolytic etching. The use of a molten flux, here, is considered a form of wet chemical etching as the chemical flux is in liquid form, and also is used for growing single crystals, such as garnets and ferrites.

In addition to the acid and base definition using the Sorensen pH scale with water neutral at pH 7; acids with pH below 7; and bases (also called alkalies) above pH 7, there are many other categories. Water itself can be considered an acid-like etching solution; alcohols and solvents, though usually considered as cleaning solvents, can act as an etchant on certain materials; molecular gases can be used in conjunction with acids or used alone, such as in hydrogen firing; vacuum as a "vapor" etchant on certain materials; molecular gases can be used in conjunction with acids or used alone, such as in hydrogen firing; vacuum and vapor pressure in vacuum have been used as etching vehicles; thermal heat treatment, alone, or with gases is used both as a part of material fabrication as well as to etch. The halogens are an etchant category of their own, with the bromine-methyl alcohol (BRM) solutions in wide use.

Some highly specialized methods include the use of pressure, ice, cryogenic fluids, and even abrasives. The latter, for example, are used for surface cleaning. Wire-saw cutting is another area used in conjunction with an acid, with an abrasive slurry or acid-slurry. Many of the specialized methods or techniques are categorized under wet chemical etching (WCE) using the wet format (WF).

The use of etching solutions is still referred to as a magic art rather than a science by many people, particularly when it involves developing a new solution as, though known chemicals are used, results are often obtained by trial and error: varying solution constituents; varying constituent concentrations; temperature variations; different methods of application. Other factors include the material being etched and its structure; chemical reactivity or contamination involved.

With time and usage many solutions have become industrial standards, such as aqua regia ($3HCl:1HNO_3$). When it was first formulated in the Middle Ages in Europe, the alchemists of the period thought it to be the universal etch for all metals and metallic compounds which, as we know today, is far from the case. It was the first solution developed that would etch gold, and also will dissolve metals of the platinum group — platinum, iridium, osmium. All of these metals etch slowly in comparison to gold in aqua regia, even when used hot to boiling. It does etch a few other metals and compounds, can be either a removal/polish or preferential solution and, on still other metals, is a surface cleaning solution only. It is particularly useful for removal of heavy metals contamination on surfaces, e.g., copper, iron, etc. The aqua regia solution varies in constituent concentrations, and may be diluted with water or alcohols.

Other acid mixtures have been developed for one material and a specific result, such as CP4 — initially Camp #4 — developed as a light figure orientation etch for (100) oriented germanium wafers, yet, even on germanium, it can be both a preferential or polishing solution. The original solution was 15 ml HF:30 ml HNO_3:15 ml HAc:0.6 ml Br_2. Since its development it has been used on several semiconductor materials and other metals and compounds. Without bromine it is called CP4A, and is considered a better polishing etch for either germanium or silicon than CP4. Further, as CP4-modified, the bromine has been replaced with I_2, $Cu(NO_2)_3$, $Ag(NO_2)_3$, etc. to improve preferential action for a particular type of defect. And depending upon the material involved, CP4 may be applied as a surface cleaning solution.

Nital and Picral — HNO_3:EOH and $(NO_2)3C_6H_2OH$:EOH, respectively, have long been major solutions on iron, iron alloys and steels, both as polish and preferential etchants. The

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acid concentrations are varied, the ethanol replaced by methanol, and both solutions are now used on other metals, such as the wide range of brass and bronze . . . both major copper alloys since antiquity: bronze (the Bronze Age) around 5000 B.C.; brass in use by the Egyptians, possibly, circa 3000 B.C.

The Sirtl etch (1HF:2CrO_3), developed in the early 1960s, has been a major preferential etchant for dislocation and defect development, initially on silicon, now on many other metals and metallic compounds. Since its inception, a dozen other HF:CrO_3-type solutions have been developed for improved defect enhancement in general or for specific type defects. It is interesting to note that like Sirtl etch, many of these solutions have been named after their developers: Schimmel, Sopori, Wright, etc., to include variations and modifications of their original formulations. These solutions are strictly preferential, as are many of the "iodine" etches — there are several iodine etches that have been developed over the years, all called "iodine etchant" although they are different formulas.

The HF:HNO_3, HF:HNO_3:H_2O or HF:HNO_3:HAc solutions are the original oxidation-reduction etchants developed in the Solid State semiconductor industry for general removal, polishing, and preferential attack on wafers, and are used on most metal and metallic compounds. Heavily diluted with either water or acetic acid (HAc), they act as surface cleaning, staining or passivating solutions. The mixture of HF:HNO_3, high in either acid, act as surface staining solutions.

There are a wide range of mixtures with H_2O_2 replacing HNO_3 as the oxidizing agent . . . the peroxide containing etches . . . with similar uses to those containing HNO_3. Another oxidizer type preferential solution is Kalling's etch (HF:$KMnO_4$) developed in the iron and steel industry, and used on semiconductor wafers and other metals.

Caro's etch (1H_2SO_4:3H_2O_2) is primarily a surface cleaning solution on a wide range of metals and metallic compounds, and there are many modifications of that base formula, to include water dilution. These solutions should be handled with care as they become self-heating upon being activated and, once reaction is initiated, will reach a constant boiling level of about 175°C.

Sulfuric acid, H_2SO_4, alone, is a glass cleaner and conditioner, and has been long used in preparing soda-lime glass plates for metallization as chrome glass masks for photolithography. It also is a general removal and polishing solution on many metals, particularly, as an electrolytic etch in the metal industries. As a mixture of H_2SO_4:$K_2Cr_2O_7$ it has long been known as the "glass cleaner" solution in many laboratories, and it is an extremely powerful oxidizer.

The two major alkalies, KOH and NaOH, have several applications depending upon solution concentration, and/or temperature. A 2—10% mixture, at RT, is used for surface cleaning. At 30—40% (RT to about 40°C, warm), good for general removal. As 20—50% solutions, hot to boiling, they become increasingly preferential. As electrolytic solutions, they are good for general removal, polishing, shaping, surface oxidation or selective structuring. As a molten flux, liquified pellets at 360°C, they are highly preferential and used for dislocation development in silicon and other single crystals. Other molten fluxes, such as carbonate and nitrate mixtures are applied as cleaning or etch solutions in general metals processing. Still other fluxes are used in the growth of single crystals, such as ferrites and garnets, and borax has already been mentioned as a flux for alloying.

The primary oxide or nitride remover is hydrofluoric acid, HF, applied as a concentrated solution; or water, even alcohol or solvent diluted; used from RT to boiling; or as hot vapor. Because of HF's rapid attack of oxides, buffered hydrofluoric acid (BHF) mixtures have been developed to better control removal rates. A fairly standard solution is 1HF:1NH_4F(40%), though there are other fluorine compounds used, such as KF and NaF, or NH_4F.HF.

Concentrated, hot phosphoric acid, H_3PO_4, also is both an oxide and nitride removal solution and, as it attacks silicon dioxide at a slower rate than it does silicon nitride, it can be used as a stop-etch where the nitride is on top, and the reduced attack rate of the oxide

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effectively "stops" the reaction. With the oxide over the nitride, the oxide will act an etch mask for photolithographic patterning of the nitride.

Hydrochloric acid (HCl) concentrated, water diluted, or diluted with alcohols, is used as a general surface cleaner. As a hot vapor in epitaxy systems, it is the primary glass tube and graphite susceptor cleaning method. In final rinse cleaning of semiconductor wafers, say, prior to metallization, a two-step process is often used — dip in 50% HCl and water rinse — then dip in 50% HF, and final water rinse, then N_2 blow dry.

The bromine-methanol (BRM) solutions are being widely used on many different metals and metallic compounds as a chemical/mechanical (chem/mech) removal and polishing solution at RT; for general polishing by immersion; or high concentrations of bromine as preferential solutions. When a wafer is patterned with Apiezon-W (black wax), BRM solutions have been used for selective etching structure. Most polishing is done with solutions of less than 5% Br_2, and preferential etching between 5—20% concentration. In conjunction with black wax patterning, solutions have been applied for thinning of specimens for transmission electron microscopy (TEM) study.

It should be noted that any chemical polish solution can be used for thinning, but a reasonably slow solution that will produce a flat, planar surface is preferred. For thick specimens, a rapid etch may be used for initial thickness reduction, followed by final thinning with a slower more controllable etchant such as BRM. Iodine can replace the bromine in BRM solutions with less evaporation loss, and similar results.

Ammonia, NH_3 and ammonium hydroxide, NH_4OH at standard liquid concentration are the most widely applied neutralizers for acid waste sumps before disposal into sewer systems. They may be the sole constituent of an etch on alkaline halides or as an additive constituent in an etchant mixture. Both liquids can be used to neutralize acid burns on the skin, and solid crystalline ammonia is the medical "smelling salts".

Water, alone, is a neutral solution (pH 7 on the Sorenson Scale), and the major quenching medium following etching. It is considered the universal solvent in chemistry and geology as, with time, it will eventually dissolve all compounds. In material processing, it can act as an etching solution on water soluble compounds, such as the alkaline halides (NaCl, KCl, etc.) and, when so applied, is referred to as an "acid" under TYPE in the formats. Sea water, containing dissolved salts, either natural or artificially compounded, has been used as an etchant for single crystal ice; as a quenching medium in metal processing; and even used to etch single crystal sodium chloride (salt), itself . . . the primary saline compound in ocean water.

The "Chrome Etch" solutions contain cerric ammonium nitrate or sulfate, with or without small amounts of HNO_3, HCl, or H_3PO_4. They are commercially available as premixed solutions, and were developed specifically for the controlled etching of chromium thin films on glass masks in the fabrication of chrome photo masks for photolithographic processing. They are commonly used at 30°C. The masks are made with iron oxide in place of chromium or nickel, today, for improved handling. The solutions used on chrome are quite rapid with about 2000 Å metallization, plus a 400—600 Å anti-reflective (AR) coating and the nitrate is preferred, as it has been shown that the sulfate solutions may leave an unwanted film on the glass plate after etching. Note that these solutions also can be used on nickel.

Though alcohols and solvents are mainly used for surface cleaning, often as a final rinse following water quenching of an acid etch for their water absorbing qualities, they can act as etchants on particular materials — in particular alkaline halide crystals.

The following methods of etching are in alphabetical order without regard to chemicals and/or processes involved, and represent the wide variety of terms used throughout the industrial cleaning and etching of materials.

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METHOD DEFINITIONS

1. ABRASIVE CLEAN

Dry or wet abrasive powders used as a method of cleaning material surfaces. Applied as a dry powder under gas pressure; in a water slurry; acid-slurry; as sandpaper; or in other medium, such as grease, or a resinoid disc cutting blade. Silicon carbide, SiC, is a major compound for general processing, original manufacturing name "carborundum"; garnet powder, as the W-0 to W-16 series, graded by abrasive size/grit, with W-5 (600 grit or 16 μm) a general standard surface finish on materials. Surface machining shown in micro-inches, μ″, (250 Å = 1 μ″) with 60 μ″ a standard finish. Abrasive hardness (Mohs scale of 1 to 10); particle physical size and shape; mesh size in millimeters, microns, or inches — shape as blocky, round, slivers, etc., influence surface finish and cleaning.

---

2. ACID ETCH

The designation pH is the abbreviation used to describe the hydrogen-ion concentration of a solution. On the Sorensen Scale, pH values run from 0 to 14 and can be defined as pH 7 is a neutral solution (water). Below pH 7, solution is acid, and the lower the value the greater the hydrogen-ion concentration. Above pH 7 the solution is basic, and the higher the value, the greater the hydroxyl-ion concentration.

Strong acids that are widely used can be represented by sulfuric acid and nitric acid. Weak acids, and this can be confusing, may contain the OH^- hydroxyl radical, such as glacial acetic acid, CH_3COOH (HAc). Even water, the neutral solution at pH 7, is sometimes called an "acid" where it is used as an etching solution on material like the alkaline halides, such as sodium chloride, NaCl or potassium bromide, KBr and similar compounds and salts that are soluble in water.

Almost all known inorganic solids, whether they are an element, natural mineral or artificially grown material can be etched in either a single acid or acid mixture, and the material solubility is controlled by concentration with dilution — usually by water — and by solution temperature.

Semiconduetors and many metal compounds require mixed acids to produce an oxidation-reduction reaction — HF:HNO_3 solutions as an example — where the nitric acid oxidizes the material and the hydrofluoric acid dissolves the oxide formed. Other acids, such as hydrochloric acid, HCl or sulfuric acid, H_2SO_4, convert the material to a water soluble chloride or sulfide, respectively. And, as is the case of many iodine, I_2, solutions, the material removed forms water insoluble compounds that can be removed later as a sludge for material recovery, e.g., gold.

Most acids are obtained and used in liquid form as a specific concentration in water: sulfuric acid, 95%; hydrogen peroxide, 30%, and so forth. Solution mixing and use for etching is mostly done using the commercial concentration supplied as a physical volume quantity, regardless of absolute acid concentration. An exception is in titration of solutions for determination of constituents, certain percentage evaluations of mixed materials, and similar chemical tests and studies.

As wet chemical etching, acids and acid mixtures can be used in several physical ways: by immersion, jet, spray, hot vapor, etc., as well as for specific results: cleaning, polishing, surface structuring, defect development, or thinning, etc. Such methods and/or techniques form the bulk of this Methods of Etching section.

Acids also are used as a liquid electrolyte (electrolytic etching [EE]), including electric current, and the specimen etched by immersion, jet spraying, with similar specific results as in wet chemical etching (WCE).

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3. ACID SLURRY ETCH

A form of mechanical polish lapping where an acid is mixed with an abrasive. This reduces the amount of work damage introduced by the abrasive into the subsurface of material being lapped or polished and can improve surface finish. The etch solution can be an acid or a base as a chemical mixture, such as SiC:H_2O:Glycerin:10%HF, or Al_2O_3:H_2O:10%KOH.

Acid slurries are of particular interest in polishing materials with a Mohs hardness greater than H = 7, such as glass or ceramic compounds for these materials tend to produce an amorphous, smeared layer during normal abrasive lapping, and such layers show different etching characteristics than that of the material bulk. This can affect subsequent processing as a masking surface film (referred to as orange-peel), or initiate the introduction of pinholes in an oxide, etc. The acid action in an acid-slurry will reduce such effects.

Soft, malleable and ductile metals, such as pure gold, lead, copper and silver, are not recommended for acid-slurry etching as they also tend to smear.

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4. ADHESION ETCH

Etching of thin films to relieve stress and evaluate the film failure, as lifting, peeling, crazing, etc. Etching may include heat treatment to initiate or enhance failure.

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5. AGED ETCH

Has two meanings: (1) any solution mixed and allowed to stand for a specified period of time, or (2) any solution used more than one time may be called an aged or used solution. Aqua regia is an example of an etch requiring an aging time before use. See Stagnant Etch; Used Etch.

---

6. AGITATION ETCH

Any solution used with some form of physical movement. It can be movement of the solution, of the part, or a combination of both, and there are various forms of movement:

1. Solution
   - (i) Rotational stirring — a rod in solution, hand or electrically operated
   - (ii) Magnetic stirring — magnet in solution with an exterior magnetic flux
   - (iii) Ultrasonic motion using transducer
   - (iv) Rocking, as on a shaker table
   - (v) Convection, as with boiling solutions
   - (vi) Hand swirling, a form of rotational stirring
   - (vii) As spray on a rotating part
   - (viii) Gas bubbled through the solution as an agitation mechanism
2. Part
   - (i) Vertical motion
   - (ii) Horizontal motion
   - (iii) Spinning motion
   - (iv) Solution rotation, as in angle etching
   - (v) Rocking motion, or various combinations of any of the above

Solutions that produce heavy evolution of gas bubbles are commonly agitated in some manner to prevent bubbles from adhering to surfaces being etched to prevent the appearance of "footprints".

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7. ALCOHOL ETCH

Alcohols are normally considered cleaning or rinsing solutions rather than etchants, but they will attack certain alcohol soluble materials.

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Three widely used alcohols are ethyl alcohol (ethanol) with the acronym of EOH; methyl alcohol (methanol or wood alcohol) with the acronym of MeOH; and isopropyl alcohol (rubbing alcohol) with acronyms of either ISO or IPA. In addition, acetone (Ace acronym) is included here because of its wide use as a cleaning solution in photolithography, even though it is a ketone, not an alcohol.

All alcohols are poisonous with the exception of ethanol (drinking alcohol) which is supplied commercially as denatured alcohol with 5% MeOH or ethylene glycol added to make it nonpotable. Absolute alcohol is 100% EOH (200 proof), but most ethanol is 95% EOH. 5% H_2O (190 proof). Note that most drinking alcohol is 80 proof (whiskeys, rum, brandy, gin, vodka) with proof-gallon as an initial 50% water content.

In addition to being used as a pure alcohol etch, many etching solutions contain alcohol as a constituent — Nital, HNO_3:EOH, as an example.

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8. ALKALI ETCH

Alkaline solutions are greater than pH 7, are the base or basic chemical solutions according to the Sorenson scale of pH as they contain the hydroxyl-radical, (OH^-). They may be in liquid form, such as ammonium hydroxide, NH_4OH or in solid form as potassium hydroxide, KOH, or sodium hydroxide, NaOH. Where ammonium hydroxide is used already in liquid form, the solid hydroxides must be dissolved in water for a specific percent concentration liquid. As a solution, they can be mixed as a Molar solution concentration, e.g., moles per liter of water and shown as, say, 1 *M* KOH or 0.5 *M* NaOH (one mole of any substance is the total of the molecular weights of the elements in the compound that is equivalent to one gram-molecular weight in one liter of water — (1/l — or 1000 ml). A computation example is

Potassium hydroxide, KOH
K = 39.102 (at wt)
O = 15.999 (at wt)
H = 1.008 (at wt)
Total 56.109 g

This says that approximately 56 g of KOH in 1 liter of water is a 1 Molar (1 *M*) solution. It is the gram-mole of the substance. There are tables available that show concentration as a percent solution, such as 10% KOH (109.2 g KOH), which is roughly equivalent to a 2 *M* solution.

It also may be shown as a Baumé, °Bé, solution by specific gravity, such that 12.2 °Bé is equivalent to a 10% solution with a specific gravity of 1.0918, regardless of the chemical(s) involved. Note the degree (°) sign is used with the Baumé scale, but it is not a temperature scale like Centigrade, °C, or Fahrenheit, °F.

The term "hydroxide" is often used in place of alkali or base, and all are equivalent, having the same meaning. In the etchant section of Chapter 2 as the chemical descriptor word, it is shown as TYPE: Alkali, polish/removal/preferential, etc.

In general, hydroxides are weak etches at room temperature and primarily used for surface cleaning in concentrations of 2 to about 15%; when used hot to boiling, usually in concentrations between 20 to 50%, they are removal etchants and can be surface preferential — developing crystallographic structure.

Alkalies also are used as molten fluxes for preferential etching, such as on silicon; or as growth fluxes for high temperature type single crystals, such as garnets and ferrites.

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9. ALLOY ETCH

Any solution used to clean an alloyed joint or structure, such as water for flux removal. The use of an alloy material acting as the etching agent, such as an AlSi(5%) alloy bead

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forming a pit in a single crystal wafer, then etch removed for study of the convex pit side-slopes and their crystallographic planes.

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10. AIR ETCH

Alternate term for Atmospheric Etch. Actual etching is due to oxygen, salt (chlorine), water moisture, or other contaminants in the air such sulfur, acids . . . smog. See Atmospheric Etch.

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11. ANGLE ETCH

There are two meanings: (1) specimen: the part is lapped at a specified angle and then etched. Used to measure diffusion depths; to develop p-n junctions, or epitaxy layer structure in semiconductor devices; or defects and structure in metal alloys, or (2) containers: the etch container is placed on a rotating spindle, say, at a 45° angle. Specimens are mounted on discs of Teflon or SST with Apiezon-W (black wax), placed face-up on the container bottom, with etching done at rotation speeds of between 130 to 300 rpm. The method used to produce extremely planar wafer surface. Also used to etch-thin material for transmission electron microscopy (TEM) study, and to polish spheres, cylinders or other forms by slow rotation during etching.

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12. ANISOTROPIC ETCH

Another term for Preferential Etch. Any etch that attacks crystallographic planes at different rates. Anisotropy and isotropy are terms related to the physical state of matter and in mineralogy are defined with regard to the propagation of light through solids. Recently, the term has been applied in dry chemical etching (DCE) of selective structures whether the solution used is a preferential/anisotropic or polish/isotropic solution. See Dry Chemical Etch; Selective Etch; Preferential Etch.

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13. ANODIC ETCH

Electrolytic etching with the specimen as the anode for cleaning, removal, polishing, structuring, and may include switching from anode-to-cathode. See Electrolytic Etch; Cathode Etch.

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14. ARGON ETCH

Primary: (1) Argon ion, Ar^+, cleaning or etching of surfaces. Secondary: (2) The etching of single crystal argon.

(1) Argon ion (Ar^+) etching and cleaning of surfaces in vacuum has become a widely used technique in processing immediately prior to metallization or epitaxy growth. RF power levels vary from 50 to 500 KeV and the electron energy can be sufficient to cause subsurface damage.

(2) Argon and other gases have been grown as single crystals in vacuum under pressure and cryogenic conditions. Once grown, preferential etching of the solid ingot has been accomplished by varying vapor pressure in the system. Note that molecular argon is used for parts drying or as an inert processing atmosphere, and may preferentially etch a specimen surface at high temperature.

---

15. ATMOSPHERE ETCH

Air, nominally 24% oxygen and 75% nitrogen with water vapor, contaminating gases or other compounds will attack all known inorganic materials with time — hours, days, years — millions of years, geologically.

In Solid State materials processing, atmospheric etching is not widely used although

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Clean Rooms have controlled atmosphere, temperature, and humidity for optimum device quality control.

The metals industries, on the other hand, are vitally concerned with the atmospheric corrosion of metals, alloys and materials with on-going studies in progress for development of improved stability, reliability and corrosion resistance of all materials to weathering — the most general term applied to effects of atmospheric etching reactions in geology.

There are specific component tests, such as salt spray, gas absorption, and corrosion, that are standard evaluation techniques in both Solid State and many other industries that use air as an active medium or carrying medium for other vapors. See Air Etch; Gas Etch; Dry Etch.

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16. ATOMIZER ETCH

Use of an atomizer to apply a fine mist/spray to etch or clean a surface. Also used to fine-tune electrical parameters on a semiconductor device with exposed junctions. A perfume atomizer has been used with a weak, polish acid mixture to etch, or pressure spray cans containing acetone or other solvents for cleaning pressure with nitrogen gas.

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17. AUTOCLAVE ETCH

A closed metal container capable of handling high pressure. Called autoclaves, they have long been used for steam cleaning of medical tools. The type autoclave application can be by process, material, or study involved, to include temperature and pressure levels:

Low pressure: General cleaning of parts. 2—10 psi.
Medium pressure: Artificial alpha-quartz crystal growth. 30,000—50,000 psi.
High pressure: Compression of single crystal metals and compounds in study of high density structures. 300,000—500,000 psi.
Cryogenic: Artificial growth of single crystal ice at liquid nitrogen (−196°C), or liquid helium (−2 K) temperature. Etch by varying vapor pressure, say, of a vacuum system. 2—5 psi (ice); to 30,000 psi or more for high pressure crystallographic forms of single crystals (cryogenic to elevated temperatures).

Steam oxidation of silicon is being done in low pressure autoclaves for both an oxide thin film or, with HF removal of the steam generated oxide, as a method of cleaning surfaces.

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18. BARREL ETCH

A barrel-like container or bottle for cleaning and etching, used closed and rotated horizontally on roller bars; open-topped and mounted on a rotating spindle similar to an angle etch beaker; or close-topped on a shaker table.

The roller bar method, using ceramic jars and abrasives, has been a long standing way of polishing gem stones, and called tumbling. The same system is used for general cleaning of small parts with dry abrasives with the tumbler unit capable of handling from 2—5 lb of material. Machine shops and plating shops may use cement mixer-sized systems for parts cleaning. See Bottle Etch; Angle Etch.

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19. BASE ETCH

Term used in three ways: (1) Any chemical solution with pH greater than pH 7 is a chemical base, or basic solution as determined by the hydroxyl-radical concentration, OH^- radical. (2) The first etch solution used in a clean/etch sequence or the primary solution in such a sequence. (3) A specific etch mixture with established characteristics against which other solutions are evaluated. This has included modification of the original mixture and comparison of reactivity changes. See Alkali Etch; Basic Etch.

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20. BASIC ETCH

Any solution with pH >7 as established by the hydroxyl-ion concentration. The chemical compound is a base as against an acid. Occasionally refers to a primary solution in an etching sequence or process. See Base Etch; Alkali Etch.

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21. BASKET ETCH

The etching of wafers, dice or other parts in some form of a basket holder that is submerged in an etch solution; passed through an etch solution; held in hot vapor; or held for spraying. The latter two largely for cleaning, as in vapor degreasers. Basket design and material depend upon acid mixtures and/or temperature. Ceramic and platinum for high temperature; Teflon, polyethylene, and other plastics, or glass for nonreactivity (glass not with fluorine-containing solutions). There are many Teflon and polyethylene basket designs for processing Solid State materials; steel basket trays for vapor degreasers; wire mesh baskets, and so forth. Teflon will handle temperatures to 200°C, but some plastics will melt in vapor degreasers where temperature levels can range from 80°C (TCE) to about 120°C (PCE/Perk).

CAUTION: Where heavy etching is done, a basket can mask the material surface causing erratic results. Stir the solution and/or rotate the basket against the solution flow direction. See Agitation Etch: Rotation Etch; Stir Etch; Angle Etch; Batch Etch.

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22. BATCH ETCH

The etching or cleaning of any two or more wafers, specimens or parts in a solution at one time. A large glass or polyethylene beaker or similar container with wafers, or parts held in a basket immersed in the solution is the simplest form of batch etching. High volume production systems may have two containers — one etch, one wash — a trough through which parts are passed, or a centrifuge with immersion, spray etching, water quenching, and air or nitrogen drying sequences. Such systems can be manual or automatic cycling, with wafers or parts in a basket holder or fed from a cassette through a belt-spinner-belt to re-cassette loading. Cassette systems are designed for processing wafers and dielectric substrate circuits though photo resist applications; PCB boards though solder alloy furnaces. Plating is done with multiple parts or hangers, and there is "free etching", where parts are dropped loose in the etch solution.

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23. BEAKER ETCH

Any open-topped container used to hold an etch or cleaning solution. Quartz, Pyrex, polyethylene, or Teflon beakers from 200 to 1000 ml are common. Thick walled beakers (Pyrex) are recommended for high temperature. Beakers are widely used for individual wafer/part or small batch processing of materials, to include plating. Teflon and polyethylene beakers are used if solutions contain fluorine compounds. Metal beakers of steel and platinum or ceramic are used in high temperature etching, and as thimbles, cups or crucibles for molten flux etching or as single crystal growth fluxes.

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24. BLANK ETCH

Any etch solution used on a relatively small flat part, such as a 1 × 1 × .010" ceramic or metal substrate. Also called a flat or coupon. Heavily used in the metals industries for a wide variety of evaluation tests (coupons), or in alpha-quartz frequency crystal processing (blanks). See Coupon Etch.

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25. BOILING BEAD ETCH

Ceramic, glass, or metal beads of various sizes placed in the bottom of an etch beaker

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to introduce and control a bubble/agitation action of a hot to boiling solution. Bead material should be inert against etch attack, and not contribute contamination.

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26. BOMB ETCH

A metal container capable of holding high pressure, and used to hold an etching or cleaning solution/gas. See Autoclave Etch.

---

27. BOTTLE ETCH

Use as a closed bottle for etching. Ink patterned and taped silicon wafers have been etched in this manner with solutions of $HF:HNO_3:HAc$ in 500 ml polyethylene bottles. With the etch solution and wafers loaded, the bottle cap attached, the bottle is then placed horizontally on a shaker table for the etch period.

CAUTION: With repeated use the polyethylene will harden and crack. If the cap is not firmly tightened, it can come loose during etching. With insufficient acid or too many wafers, excessive fumes and pressure are generated and the bottle can rupture explosively. Even with good shaker table agitation wafers tend to overlap, stick together, and produce erratic etching results. See Batch Etch; Barrel Etch.

---

28. BRINE ETCH

Natural or artificial salt water used as an etch solution. Not common; some test evaluation on metals and compounds in corrosion study. Quenching in brine solutions is used in fabricating steel alloys and other metal mixtures to obtain specific structure and other physical characteristics. The salt spray test might be considered as a type of brine etch. In the metals industries coupons are exposed to seacoast salt environments in on-going corrosion tests. See Water Etch; Atmosphere Etch.

---

29. BRUSH ETCH

The use of a brush to apply an etch solution to a material surface. It may be for light cleaning/etching, to developed etched structure, to fine-tune electrical parameters of a device, or to produce a particular surface finish. In the latter case, a wire brush may be used with or without electric current applied, for a "brush" surface finish. See Swab Etch; Matte Etch; Satin Etch.

---

30. BULK ETCH

After mechanical lap and polish of a material surface, the surface is etched to remove the residual subsurface damage down to the undamaged bulk metal. Or use of a heavy etch for general bulk removal, which may be measured by total gram-weight loss of a specimen. Occasionally, with regard to a large volume of etching or cleaning solution. See Rough Etch; Removal Etch.

---

31. CAP ETCH

Special terms applied to Solid State processing and etching single crystals with thin films.

(1) After ion implantation of a semiconductor wafer when a CVD silicon dioxide or nitride coating is then deposited on the implanted surface, it is called a "cap". After an annealing cycle to stabilize the implanted element the cap is etch removed with solutions of BHF, HF, or RF plasma (ionized gas).

(2) In molecular beam epitaxy (MBE), the top thin film layer also is referred to as a cap, as an epitaxy or oxide/nitride material layer. If the latter, a suitable fluorine containing etch is used; whereas, if it is an epitaxy material layer, it may be a selective acid or ionized gas etch.

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(3) Metallized thin films are sometimes referred to as capping layers, such as when being pattern etched by photolithographic processing.
(4) The use of a capped crucible etching container may be referred to as a capped method of etching, as in molten flux growth of single crystals with subsequent etch removal from the flux. See Cover Etch.

---

32. CASCADE ETCH

Though often called etching, more commonly a method of final water quenching and washing following an etch period, with reference to the container structure used: a rectangular trough divided into three or four progressively lower sections, usually fabricated from polyethylene sheet or similar high purity plastic. Commercially available systems are about 6″ wide, each trough section about 8″ long, and progressively more shallow. High purity water (18 MΩ) enters the top section, flowing downward through lower sections. To use a cascade, the part to be quenched and rinsed is placed in the lowest trough first, then moved upward to the final top trough. Repeat rinse steps until the megohm meter remains at 18 MΩ in the upper rinse trough.

---

33. CATHODIC ETCH

Electrolytic etching is normally anodic, but switching from anode to cathode acts as a deplating and removal system, not an actual method of etching. The term has been used relative to studying the growth effects of hydrated oxides on metals, and in sputter etching with ionized gases. See Sputter Etch; Dry Chemical Etch; Anodic Etch; Ion Etch.

---

34. CAUSTIC ETCH

An alkali or hydroxide solution with a pH >7. See Alkali Etch; Hydroxide Etch; Base Etch.

---

35. CENTRIFUGE ETCH

Rapid spinning motion of a part during etching or cleaning. A photo resist spinner has been used for acetone cleaning during photo resist application and etching of semiconductor wafers with the holder platen rotating at about 3500 rpm. There are automatic systems designed to clean, etch and dry wafers through automatic cycles with wafers handled from cassettes.

A specialized system, including directional magnetic flux to produce a negative (−) or positive (+) gravity effect during etching has been used to form pits and via-holes in brass and silicon wafers, and referred to as a centrifuge etching method.

Centrifuge systems are used to mixed glass-frits as a liquified slurry, which are then spun onto surfaces and melt-fired (nominal 600—800°C).

---

36. CHEM/MECH ETCH

Chemical/Mechanical etching is being more and more widely used in single crystal wafer processing to remove residual subsurface damage introduced by previous cutting, lapping, or polishing steps. The bromine:methyl alcohol (BRM) solutions are used to remove damage with a slow polish action.

---

37. CHANNEL ETCH

The etching of a groove into a surface. Used in selective structuring of single crystal devices.

(1) Wafer dicing: Semiconductor wafers are channel etched into individual dice shape and

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then, without demounting from the mounting substrate channels are oxidized or metallized as a wrap-around edge coating of the dice.

(2) Wafer channeling: Surfaces coated with oxide/photo resist with channel pattern etch opened in ⟨110⟩ directions on (100) oriented wafers. Dry chemical etching (DCE) or wet chemical etching (WCE) used to channel etch. Method used to fabricate single channels, grids, saw-tooth gratings and so forth. Also for diffusion depth profiling; to observe change in dislocation density, with depth, or dislocation movement in bulk. The channels can have a curved radius, be "V" shaped, or with vertical or sloped side walls and flat bottom.

(3) Snap-Strate: Etch, sandblast, or saw cut a channel into, but not through, the material. The wafer/substrate can then be handled in processing as a unit and, after final structuring, individual units are "snapped" apart. Substrate commonly Alumina, Al_2O_3.

---

38. CLEAVE ETCH

The etch polishing of a cleaved single crystal wafer surface to remove residual cleavage steps.

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39. CLEANING ETCH

Any solution or gas used to clean a surface with minimum etch removal of the material. See Solvent Etch.

---

40. COLD ETCH

Any solution used between about 2—10°C. Selective preferential etching to observe structure, or fine-tuning electrical parameters. There are "cold etches" using snow in their formulas and chemical mixtures, some as eutectics, that form a specific cold temperature. These are used directly or to chill other etch solutions. See Temperature Etch.

---

41. CONDITIONING ETCH

Any solution used to prepare a surface for subsequent processing. Very common in the plating of metals, such as zincating aluminum before metal deposition.

---

42. CONTAMINATION REMOVAL ETCH

Any solution used to clean a surface of unwanted solid material, such as dirt, oil, or grease; or the removal of ionic radicals, such as F^+, Cl^-, Cr^{++}, etc., remaining on a surface after etching. See Alcohol Etch; Solvent Etch.

---

43. CONTROL ETCH

Any etching for a specified time period or at a particular temperature. RF plasma cleaning done without regard to time, but to a specified temperature stop-point. A solution may be established as a standard control mixture, against which other solutions are evaluated.

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44. COOL ETCH

Any solution used between about 10—20°C. Most often used as a slow cleaning and polishing etch. See Temperature Etch.

---

45. CORROSION ETCH

The attack or alteration of any material surface from the action of a solid, liquid, or gas. All metals and alloys are subjected to atmospheric corrosion evaluation; high temperature gas reaction; or molten metals and chemicals used as an etching medium, in determining the stability of materials under varying conditions.

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46. COUPON ETCH

Etching of a specimen cut as a flat form sheet material. Term common to metal flats used in atmospheric corrosion studies, and other metal tests in the metal industries, but not widely used in Solid State processing. See Blank Etch; Wafer Etch.

---

47. COVER ETCH

As a specialized term where methyl alcohol is over a BRM mixture: MeOH/Br_2:MeOH. The part to be etched is slowly lowered into the BRM solution, etched, then slowly withdrawn through the pure methanol "cover" to quench etching action without exposure to air.

---

48. CRUCIBLE ETCH

The use of graphite, ceramic, or high temperature metals, such as platinum, as a cup to hold an etching solution. Most commonly used in molten flux etching, such as defect development in silicon with KOH pellets at about 360°C; or crystal growing from such fluxes, followed by their etch removal. See Cup Etch.

---

49. CRYOGENIC ETCH

The use of cryogenic liquids as an etching medium, such as liquid chlorine, LCl_2 at −102°C. Also refers to the use of cryogenic liquid as a chilling agent for other acid solutions, such as liquid nitrogen, LN_2. See Temperature Etch.

---

50. CRYSTALLOGRAPHIC ETCH

Any solution that will develop single crystal plane structure by preferential attack. Specific solutions have been developed on most metals and metallic compounds during evaluation development, and include etching spheres (convex), and pits (concave) surfaces. See Finite Form Etch; Dissolutionment Etch; Anisotropic Etch.

---

51. CUP ETCH

Any open container when used to hold an etching solution may be referred to as a cup. Usually a small ceramic, graphite, or high temperature metal (Pt, Mo, Ti, Ta) used as a crucible for either an etch solution or solid molten metal, and may include a cap or cover. See Beaker Etch; Crucible Etch.

---

52. CUTTING ETCH

The use of an etch solution, alone, or a wire soaked in the etch to cut material. See Acid-saw Etch; Acid-slurry Etch.

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53. CYCLIC ETCH

Etching with sequential periods of time. May include water or alcohol quenching between etch cycles, or the removal to air and return to etch without quenching. See Sequence Etch; Step Etch.

---

54. DAMAGE REMOVAL ETCH

Any etch solution used to remove either the surface or subsurface damage present or induced by previous abrasive lapping, etc. It is usually a slow polish type etch, such as bromine:methanol that both remove the damaged zone and polish simultaneously. See Chem/Mech Etch.

---

55. DECORATION ETCH

The use of a metal thin film diffused or alloyed into a single crystal surface to enhance defect structure for observation. Other materials used are fluorescent dyes that may or may not be biased electrically to develop color patterns (liquid crystal, etc.); and, though not an

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etch, carbon or iron powders have been brushed on preferentially etched surfaces to enhance defect observation. See Stain Etch; Heat-tint Etch.

---

56. DEFECT ETCH

A general term denoting the etch development of any bulk or surface anomaly in a material whether or not it is single crystal, colloidal, amorphous or crystalline in structure. Much of the etching study on materials is concerned with the recognition and elimination of a wide range of defects, several of which have developed specific etching names as shown below.

See:			
	Dislocation Etch	Stacking Fault Etch	Slip Etch
	Preferential Etch	Polarity Etch	Crystallographic Etch
	Anisotropic Etch	Thermal Etch	
	Lineation Etch	Vacuum Etch	

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57. DEFINITION ETCH

Term used in two ways: (1) an etch used to develop a particular structure, such as fine-line definition, and (2) a solution developed for a particular purpose — a definitive etch.

---

58. DEGREASING ETCH

Usually a solvent for removal of oils or greases, rather than etch solution, although an etch may be used. Laboratory glass is etch cleaned in a solution of H_2SO_4:$K_2Cr_2O_7$, and soda-lime glass plates used for chrome photo resist masks are scrub cleaned with soap.

---

59. DESCALING ETCH

An etch used to remove heavy contamination from metal surfaces. Term widely used in metal processing, but not in Solid State development where most materials are supplied as nominally clean parts.

---

60. DICING ETCH

Any etch solution used to cut and separate discrete devices or units from a semiconductor or other type material in wafer or thin sheet form. See Channel Etch.

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61. DIP ETCH

The etching or cleaning of a specimen for a very short period of time — the "time" is difficult to define but can be arbitrarily said to be between 1—3 sec. This form of etching has been used for (1) a final surface cleaning step; (2) to develop and optimize a defect or structure; (3) to fine-tune electrical or frequency parameters of a device, etc. It may be a single "dip" or a series of such dips, depending on requirements.

---

62. DISLOCATION ETCH

The preferential etch development of structure in a single crystal material that can be related to crystallographically oriented defects associated with bulk structure or surface defects. Dislocations can be introduced during ingot growth; by heat treatment, alone, or in conjunction with alloying, diffusion, epitaxy, cutting, and lapping; by controlled bending or striking of a surface in defect studies; or inadvertent damaging from process handling, etc. The study of dislocations in single crystals is probably one of the most important areas of developmental work in the Solid State field, because of the major effects defects produce on device parameters. See Defect Etch.

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63. DISSOLUTIONMENT ETCH

In the broadest context the term dissolution or dissolutionment etch refers to any solution that will dissolve a material. In the study of single crystals, it is used with specific reference to the etching of spheres to finite crystal form (FCF) with development of crystal facets (planes) on convex surfaces. Also in determining the general etching for characteristics of all metals and metallic compounds.

---

64. DRIP ETCH

To apply a single, or series of droplets on a surface. Usually applied to a limited area. Iron specimens have been etched in this manner with DI water. See Pinhole Etch; Structure Etch; Selective Etch.

---

65. DROP ETCH

Term has been used in three ways: (1) the free etching or cleaning of a part by physically dropping free into the solution; (2) placing of a drop of solution on a surface to etch and/or plate a semiconductor p-n junction; develop pinholes in oxide/nitride thin films, etc., and (3) dropping of a part down through a column of solution with distance, time, and temperature used to control fabrication, e.g., the shot tower technique used in sphere forming.

---

66. DRY CHEMICAL ETCH (DCE)

The use of an ionized gas for cleaning or etching surfaces. Ar^+ ion cleaning of single crystal wafer surfaces has become a standard technique in processing. Also used for selective etching of structure in device design. Gases used may be inert, like argon; or they may be a reactive species, such as BCl_3. The latter type called reactive ion etching (RIE). DCE is one of the three major etch formats used to describe etching.

---

67. DRY ETCH

Not considered a true form of etching, yet drying can affect the surface or bulk of a specimen. Water removal from a surface can cause crazing, cracking or leave stains. Bulk removal can alter both chemical formula and crystal structure. Heat treatment or annealing and hydrogen firing are two methods. The latter a method of surface cleaning in a reducing atmosphere.

---

68. DRY ICE ETCH

Solid CO_2 used as a direct etching medium. Also used as a mixture with alcohols or acetone for chilling another etch solution, or for removal of water vapor from process gases . . . drying the gas by chilling and freeze-out of the water vapor as ice.

---

69. ELECTROLYTIC ETCH (EE)

The use of electric current applied to any etching or cleaning solution. Many such solutions are shown in the following section for different metals and metallic compounds using the electrolytic etchant (EE) format for presentation of data. The specimen being etched in the anode and a metal (such as Cu, Pb, Fe) as the cathode. Additional anodes and cathodes may be included, there can be anode-cathode switching, or the specimen separately electrically biased. Both liquids and molecular gases are used.

---

70. ELECTRON BEAM ETCH

E-beam or EB vacuum systems are used for metal evaporation from a rotatable copper hearth containing from one to four crucibles. The beam is magnetically bent up and around into the crucible, a 270° beam being a standard, today. The E-beam can be used to etch remove and vaporize metals on a specimen surface at controlled rates by varying power

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input. Also used to anneal a specimen (heat treatment), in addition to being a method of metal evaporation.

---

72. ETCH/CLEAN SEQUENCES

See Clean/Etch Sequences under Composition.

---

73. ETCH-STOP

An etch solution that will attack one material but not another in a multilayer thin film structure. Hot H_3PO_4 will etch remove Si_3N_4 much more rapidly than SiO_2, such that the oxide can work as an etch-stop mechanism. The method is used in structuring devices, and in the removal and thinning of layers for TEM study.

---

74. FAILURE ETCH

Any solution use in the study of device failure, and used to etch develop, surface stain or otherwise expose the causes of failure.

---

75. FATIGUE ETCH

Specific solutions used on metals and their alloys in the study of material failure due to fatigue, such as cracking from bending or crazing from atmospheric corrosion. This is a major test evaluation method of study applied to metals and alloys with specimens prepared by metallographic techniques for observation after the test period. See Metallographic Etch.

---

76. FIGURE ETCH

Any form of defect or structure developed in a surface by etching, regardless of the type etchant, e.g., gas, liquid, solid. Figures also can be formed by temperature, pressure, or direct flame. As a pressure formed figure, called a "percussion figure" on mica, (0001) surfaces developing as a six-rayed star. Star line pattern representative of bulk prism plane directions and used for orienting the micas.

---

77. FINISH ETCH

The final etch used on a material surface. Term primarily used in the metals industries, and can apply generally or to a specific etch or technique developed to produce a particular surface finish. See Matte Etch; Satin Etch.

---

78. FINITE FORM ETCH

Preferential etching of single crystal spheres of any metal or metallic compound to produce a solid with crystallographically oriented exterior planes that are the fast etching planes of a convex surface. Planes developed vary with solution mixture, as cube, (100); octahedron, (111); dodecahedron, (110); or tetrahexahedron, (hk0) as most common forms, e.g., also called finite crystal form etching, and primarily applies to materials that form in the isometric (cubic) system. See Dissolutionment Etch; Sphere Etch.

---

79. FLAME ETCH

Use of a propane torch or similar gas torch to produce etching action on a surface. Has been used to develop surface etch figures on high melting point temperature metals and alloys. Also used for surface cleaning of metals and their alloys during brazing operations.

---

80. FLASH ETCH

Any very rapid etch applied for a short period of time. It can be a liquid solution or an electrical spark. The latter used in spectrographic analysis. See Dip Etch; Electric Spark Etch.

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81. FLAT ETCH

Either to etch a surface to be planar and flat, or etching of a material sheet in the form of a "flat". See Blank Etch; Coupon Etch.

---

82. FLOAT-OFF ETCH

The removal of thin film layers from a surface for microscope study by TEM, SEM, etc. Etch solution attacks the substrate, but not the film. Sodium chloride, NaCl, (100) substrates use water, H_2O; silicon Si, wafers when used as a substrate in this manner, use HF:HNO_3 to dissolve the silicon substrate for film removal. Mica, (0001), MgO, (111) and other materials used as substrates have their own etch mixtures, such as HF for quartz and glass blanks. This is a separated and distinct method . . . the float-off technique . . . as against the lift-off technique used for photo resist and excess metallization removal in device fabrication (with acetone).

---

83. FLOOD ETCH

To rapidly cover a specimen surface with an etching or cleaning solution, usually with reference to washing or quenching acid reaction, rather than etching. An etching container is flooded with water to stop etch action. See Flush Etch.

---

84. FLUSH ETCH

To cover a surface with a moving liquid etch solution. Used as a light surface cleaner, or to produce an etch-washed pattern for a decorative effect. Also refers to water quenching an etch solution by flushing to stop etch action. See Flood Etch; Matte Etch; Satin Etch.

---

85. FLUX ETCH

Use of a molten metal or solid chemical compound for etching. May also refer to the use of a flux, such as borax, in metal alloying and brazing, and solutions used to clean and remove residual borax after joint fabrication. See Molten Flux Etch.

---

86. FORM ETCH

Either etching a material to a specific shape, or etching of a particular shape. Spheres are etched to finite crystal form; rectangular bars are control-thinned as electronic reeds; silicon is via hole pattern etched as an inking mask; many metal shim stocks are electroformed or pattern etched as evaporation masks; tantalum is etch formed as an antenna, etc. See Finite Form Etch; Sphere Etch.

---

87. FORMING ETCH

Preferential, selective, or electrolytic etching of a specimen to a bulk shape, or structuring a surface by etching pits, via holes, channels. Diamond is etched with a saw-tooth structure as a filter element.

---

88. FREE ETCH

The etching of specimens by dropping them loose into a solution without being held in any manner. See Bottle Etch.

---

89. FREEZE ETCH

The use of a solution below 0°C to effect etching action, or, the quenching of a material from an elevated temperature into a liquid bath solution.

---

90. FUME ETCH

Use of hot acid or solvent vapors for etching or cleaning action. Hot HCl/H_2 vapors are used in epitaxy systems for general cleaning of quartz tubes, graphite susceptors and spec-

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imens; hot HF vapors for oxide removal or hot water vapor (steam) for hydrated oxide growth conversion of a surface followed by HF Strip as a surface cleaning step. See Vapor Etch; Vapor Degreasing.

---

91. GAS ETCH

The use of a gas to produce etching action in its molecular form, such as argon, Ar; hydrogen, H_2; nitrogen, N_2, etc. It usually includes heat and/or pressure. Argon, as an example, under pressure and heat in a vacuum system has been shown to preferential etch semiconductor surfaces producing hillocks and pits similar to those observed with wet chemical etching. See Ion Etch; Dry Chemical Etch (both as ionic gases, not molecular).

---

92. GATE ETCH

Specialized term denoting channel etching for the active area of a Schottky Barrier device, such as a field effect transistor (FET). The channels are either wet chemically etched or electron photolithographically etched on the submicron width scale. An active gate metal, either aluminum or gold is then pattern evaporated in the channel, and may be followed with RF plasma final etch forming with ionized gases (aluminum with BCl_3).

---

93. GENERAL ETCH

Any etch solution can be so called when used without other specific definition, such as a general removal etch; and there is an etch solution with the name General Etch.

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94. GRAPHIC ETCH

A repetitive pattern of figures etched onto a surface. Such patterns can be controllably produced for decorative effects or developed in nature — meteorites have a distinctive etched structure called Widmanstatten Figures that appear much like a grossly twinned single crystal ingot; also the Neumann Line structure associated with twin lamellae — several of the quartz-feldspar granites show a fine graphic structure of a clear quartz network enclosing the softer pink or white feldspar. See Matte Etch; Satin Etch.

---

95. GRAVITY ETCH

A highly specialized method of etching where the specimen is subjected to either a positive (+) or negative (−) gravitational force by centrifugal action during preferential etching to form controlled structures. Brass and gallium arsenide have been via hole and pit patterned in this manner. A specimen may be dropped down through an etch solution column for a controlled distance for forming or cleaning.

---

96. GROOVE ETCH

In single crystal wafer structuring of devices, the etching of a channel in surfaces. It may be as a "V" groove, have a bottom curvature of known radius; as a saw-tooth series of ridges; have vertical side walls with a flat bottom, and side walls may be specific crystal planes.

---

97. HALOGEN ETCH

Refers to a chemical class of elements as etching agents: fluorine, chlorine, bromine, and iodine. In Solid State processing, the term is most often applied to the bromine:methyl alcohol (BRM) solutions. Chlorine, as a gas, is bubbled through other etch solutions for added etching action; hot HCl or HF vapors are used as etchants; and iodine can replace bromine in the BRM solutions, and is used in several designated/named "iodine" etches. Low concentration bromine BRM solutions are polish etchants, hot vapors are primarily cleaning agents, and the iodine solutions are mainly preferential.

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98. HEAT ETCH

The use of heat only, to effect an etching or cleaning action. Used under vacuum conditions to flash clean specimen surfaces. Used in air to oxidize a specimen surface. Occasionally referenced as heating of a liquid or gas for etching action. See Thermal Etch; Heat-tint Etch; Hot Etch.

---

99. HEAT-TINT ETCH

Heating of a specimen on a hot plate in air to produce oxide colors. Used in the study of metallographic specimens. A crystalline material varies in color by rate of oxidation of individual crystallite grains according to their crystallographic plane orientation. A single crystal material or alloy can be differentiated by phase structure or internal crystallographic plane directions by similar color variation. In an alloy mixture or similar specimen, different metal or compounds can be determined by their characteristic oxide color when heat tinted for a specific time. Single crystal spheres of metals and compounds have been widely studied by controlled furnace oxidation in the study of oxidation kinetics and growth rates related to internal crystal plane location and orientation. See Heat Etch; Thermal Etch.

---

100. HEAVY ETCH

Any etch solution used to remove a large volume of material. Measurement is done by mils of surface removal, or by total specimen gram-weight loss. See Rough Etch; Removal Etch.

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101. HOT ETCH

Any solution used for etching or cleaning above room temperature as either a liquid or gas, and may be shown in °F, °C, or K. Also shown as warm, hot, or boiling. See Temperature Etch.

---

102. ICE ETCH

Solid ice has been used as an etching medium in the sense of the freeze-out of a hot, liquid metal poured on the ice surface. Mixed with water or alcohol it is used to cool other etch solutions and, along with snow, has been used as a constituent in formulating a series of "cold etches" for specific temperature levels. Also can refer to the etching of single crystal ice specimens grown under cryogenic conditions in cold cryostats. See Water section, Chapter 2 for Cold Etchants.

---

103. IMMERSION ETCH

Complete submersion of a specimen in a liquid etch solution, or in a molten flux solid chemical solute. It is the most common form of etching as wet chemical etching (WCE) or electrolytic etching (EE), which are two of the Etchant Formats used in the next section. (Dry chemical etching (DCE) is the third format.)

---

104. INDUCED DAMAGE ETCH

Preferential etching to develop defects or structure in a surface that has been subjected to some form of damage. Such damage may be a controlled scratch or a point of damage introduce by a diamond-type stylus to develop specific defects, or to initiate the etch forming of a pit, via hole, channel, etc. Also has been used with reference to residual subsurface damage remaining after cutting or mechanical lap and polish. Such damage being removed by chem/mech polishing or straight chemical etching in Solid State device fabrication. See Defect Etch.

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105. INITIAL ETCH

Any solution that is the first in a series, or the first etch applied in a specific material process.

---

106. ION ETCH

A gas in its ionized rather than molecular state used to clean or etch a surface. RF plasma N^+ or O^+ cleaning systems are widely used in Solid State material processing. Argon, as ionic Ar^+, also is widely used in Solid State processing to final clean surfaces under vacuum immediately prior to metallization and compound growth or deposition, and can introduce subsurface damage. Other ionic gases, such as helium (He^+), xenon (Xe^+), etc., are used in material irradiation damage and thin film adhesion studies. Electron irradiation from a TEM microscope or an electron-beam in vacuum system; lasers, for annealing or alternating materials; and nuclear particles have all been used as forms of ion etching. See Argon Etch; Dry Chemical Etch; Irradiation Etch; Particle Etch.

---

107. IRRADIATION ETCH

The use of ionized gases or radiation particles to affect etching action. May also be used to induce damage into surfaces in the broader study of irradiation effects. Note that a single crystal, when irradiated, will revert toward the noncrystalline, amorphous state, and the reverse — an amorphous material will tend toward single crystal or the crystalline state. Such alternations of the immediate subsurface of Solid State materials is of major consideration in device structuring, particularly, when an active diffused junction is in the <1 μm region, as such altered zones can severely affect the electronic functions of devices.

---

108. ISOTROPIC ETCH

Another name for a polish etch solution. The etch attacks all crystal planes at an equal rate, producing a flat, planar surface. The opposite is anisotropic (preferential) etching. The terms anisotropic and isotropic originally applied to the propagation of light through a solid mineral. They also are now used in dry chemical etching (DCE) with regard to shaping a pit, channel or via hole with ionized gases without reference to the polish (isotropic) or preferential (anisotropic) nature of a liquid etch solution.

---

109. JAR ETCH

(Jug). The use of any closed vessel for etching in which parts or specimens are immersed. See Beaker Etch; Bottle Etch.

---

110. JET ETCH

A fine stream of liquid under pressure applied as an etchant, and most often for shaping the exterior of a solid specimen, structuring a material surface, etch cutting a hole through a wafer, etc. May be a single or multiple jet system with or without electric current. There are jet systems combining etch/cut action for slicing or dicing material with high velocity gas, steam, water, or an acid. There also are hot-melt electrical plasma composites deposited on surfaces . . . not etch action, but used in constructing Solid State substrates.

---

111. JUNCTION ETCH

As a semiconductor term, the development of a p-n junction by staining, etching or selective plating. In the heavy metals industry, weld joints can be developed or cleaned by etching or light sandblasting. In the plating and cladding industries, etching to develop interface joints between layers can be done with a jet. See Layer Etch; Stain Etch; Selective Etch; Jet Etch.

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112. KEY ETCH

A primary etch solution within a clean/etch sequence, or any solution applied in a processing step that is considered a fundamental solution. A solution around which other solutions or processing revolve.

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113. KRYPTON ETCH

The use of ionized krypton, Kr^+, as an etch or material damaging agent by irradiation. The use of vapor pressure change to etch single crystal krypton grown under pressure and cryogenic vacuum conditions.

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114. LASER ETCH

Use of electrons propagated by light at a controlled frequency and power level to effect an etching action. Several types of lasers are used to etch channels and other structures for operational Solid State devices; for material cutting, such as preparing circuit substrates; as annealing to increase crystallite size on dendritic crystals, or in conversion of carbon to a diamond-like-compound (DLC). See Electron-Beam Etch; Flash Etch; Irradiation Etch; Ion Etch.

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115. LAYER ETCH

As applied in Solid State processing, the etch development of epitaxy multilayer structures in device fabrication or in material studies. As a more general term, the etch removal of a specific layer of material from a dissimilar material. It may be total removal as in oxide or nitride stripping from a semiconductor surface, or selective removal through a photo resist or similar surface coating to develop patterns for subsequent device fabrication. See Junction Etch.

---

116. LIFT-OFF ETCH

A specific technique developed to remove thin film metallization from a photolithographically prepared wafer surface. Wafers are soaked, sprayed and/or lightly scrubbed with a plastic foam Q-tip in acetone. The acetone dissolves the photo resist layer used for patterning which loosens excess metal by lift-off, and exposes the metallized pattern for further device processing. This is a separate and distinct operation, though similar to the float-off technique. See Float-off Etch.

---

117. LIGHT ETCH

The term has been used in two contexts: (1) as a physical term to differentiate between light-medium-heavy etching; or in the sense of a slow, minimum removal etch, and (2) the use of light alone, or in conjunction with solutions to enhance etching reaction or for selective plating action. White light most widely used, such as a strobe light for semiconductor p-n junction plating with copper. See Electron Beam Etch; Laser Etch.

---

118. LIGHT FIGURE ETCH

The use of preferential etchants to develop surface etch pit and dislocations on the surface of a cut single crystal ingot face or wafer and used to crystallographically orient the surface by reflected light. This is standard practice in the processing of single crystal ingots of all materials. It should be noted that many single crystal ingots can be cleaved into wafers on preferred fracture planes, which does not always require etching to obtained surface figures for light figure orientation (LFO). After etching face-cut silicon ingots in boiling KOH, 5 min, as an example, the ingot is mounted on a ceramic block, then on an x-y-z positioner and a pinhole light is reflected off of the surface back into a black box. The pattern that

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appears at the back of the box is then used to orient the ingot for cutting wafers. Orientation accuracy can be $<^1/_2°$. See Preferential Etch; Light Figure Orientation Etch.

---

119. LIGHT FIGURE ORIENTATION ETCH

The same as item 118. As initially developed in Solid State semiconductor ingot processing, the etching of silicon in hot KOH solutions; germanium in KOH:I_2, or acid solutions, such as CP4. The reflected surface defect pattern are used to orient the ingot for wafer slicing. See Light Figure Etch.

---

120. LINEATION ETCH

In semiconductor development the term was originally applied to distinctly aligned dislocation patterns associated with stress induced during the rotation/pull growth of Czochralski (CZ) single crystal ingots. The patterns are very distinctive on (111) and (100) oriented wafer surfaces: a series of over-lapping dislocations reducing in size from the wafer periphery toward wafer center, and disappearing before reaching the wafer center. On (111) surfaces, as three lines at 120° and associated with the bulk ⟨211⟩ directions; whereas on (100) surfaces, four such lines at 90° and associated with ⟨110⟩ bulk directions. With improved growth control, this form of defect rarely observed today.

Any crystallographically oriented line segment — representative of slip in a single crystal surface — may be termed lineation or slip. Where a series of such line segments are closely parallel — called stacking faults (SFs). This type of defect can be introduced by processing — oxidation, diffusion, epitaxy, ion implantation, and is often associated with oxide and nitride thin films. For these latter, HF:CrO_3 preferential etchants have been tailored for stacking fault study. See Defect Etch.

---

121. LIQUID ETCH

Any wet chemical etch (WCE) solution used to effect etch action. Also the use of a solid chemical molten flux etch, such as KOH pellets at 360°C. See Acid Etch; Alkali Etch; Solution Etch; Molten Etch.

---

122. LONG ETCH

A time period for etching, as against a short or dip time period. Solution is either a slow etch on the material, or a cleaning solution with an extended soak time. This latter is common in metal processing, such as in soak etching or conditioning a surface prior to plating.

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123. LOOSE ETCH

Any solution used where parts are dropped free and not held in any way in the solution during the etch period.

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124. LOW ETCH

Applied with specific reference to the level of a solution above a part being etched, where insufficient covering acid will not block the in-diffusion of atmosphere over the open container. If the solution level is too shallow, it also can cause erratic etching results.

---

125. MACRO ETCH

Defects and structure observable on a surface with the unaided eye after etching. The term is widely used in the metallographic preparation of metals and alloys in the metals industries, and in geologic study of thin sections. It has occasionally been used with reference to preferential etching of semiconductor and other single crystal surfaces. See Preferential Etch; Structure Etch; Anisotropic Etch; Heat-Tint Etch.

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126. MAGNETIC ETCH

Not a real etching method, yet has been used in two ways: (1) magnetic powder has been brushed on wafer surfaces of ferromagnetic materials to develop domain structure, such as barium titanate and ferrites; (2) iron or carbon powder brushed on a preferentially etched wafer surface to accentuate defects and etched patterns. There are magnet-stir hot plates where a Teflon or plastic-coated magnet is dropped into the solution, then solution rotation and heat controlled by the hot plate dials. Barium titanate, being fabricated as an ultrasonic transducer, is electrically (magnetic flux) poled in water to orient domains. See Gravity Etch.

---

127. MATTE ETCH

A surface finish etch used for decorative purposes on metal surfaces, such as copper or nickel. The surface has a low-profile grain-like structure with a dull sheen, and can be as a semi-matte finish. See Satin Etch; Silk Etch.

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128. MEDIUM ETCH

Used in two ways: (1) with regard to time, as a slow, medium, or fast etch, and (2) with regard to solution strength, as weak, medium, or strong.

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129. MELT-AWAY ETCH

The separation of a thin film from a substrate for microscope study by heat liquefying and removal of the substrate. Etch removal of a metal thin film or alloyed pre-form, wire, etc., to observe the pit formed in the material surface by the metal. Semiconductor wafers with alloyed p-n junctions have been etched from the back to observe the buried junction-front in the bulk wafer. Sodium chloride, (100) substrates have been heated to the liquid state in order to remove a thin film for TEM study, rather than the usual use of water to dissolve the substrate/film interface.

---

130. MELT-BACK ETCH

A specialized Solid State term relative to wafer surface etching during epitaxy growth, such as using indium on indium phosphide, InP, or gallium on gallium arsenide, GaAs during liquid phase epitaxy (LPE). The method is used to clean the surfaces to reduce the growth of defects in the epitaxy film.

---

131. MESA ETCH

The etching of a roughly cylindrical column or pylon on a single crystal surface as a p-n junction device structure. In Solid State, as a single mesa, it is the mesa diode. As an array of mesas in the fabrication of SCRs, they are elements for power distribution and control in the electrical operation of the device. Mesas are commonly formed with a slightly preferential etch such that the mesa side slopes have a degree of crystallographic orientation. Using dry chemical etching techniques, the mesa sides can be more cylindrical without crystal facets. See Pylon Etch; Structure Etch.

---

132. METAL ETCH

In the broadest sense, any solution used to etch any metal. More commonly, the use of a liquified metal as an etch medium on high temperature, chemically inert metals, such as molybdenum, tantalum, or titanium. Occasionally refers to the metallizing of a material surface with in-diffusion to decorate defects. See Decoration Etch; Molten Flux Etch.

---

133. METALLOGRAPHIC ETCH

Term primarily used in the preparation of metals and alloys as specimens for defect and structure analysis using preferential etches. Common in the metals industries and in geology,

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and most Solid State companies maintain a metallographic laboratory for material inspection and evaluation of processing. The etch can be macro- or micro-etch as a size definition. See Macro Etch; Micro Etch; Preferential Etch.

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134. METALLURGICAL ETCH

Not common, but any etch applied to a metal or alloy specimen with reference to the field of metallurgy or metallurgical engineering as a science. Also with reference to the use of a metallurgical microscope for material observation.

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135. MICRO ETCH

Any defect, figure, or structure etched on a surface that cannot be easily observed by the unaided eye, and requires a microscope for proper viewing. Both macro- and micro-etch are terms widely used in the study of metallographic specimens in general metal processing, not as often used in Solid State processing. See Metallurgical Etch; Macro Etch.

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136. MILLING ETCH

In Solid State it refers to the use of an ion milling vacuum system where ionized argon (Ar^+) or nitrogen (N^+) is used to etch remove and pattern thin film metallization on circuit substrates or active devices. In general metal processing, it occasionally means the use of a lathe or cutting mill for a combination of cutting, etching, or shaping of a part, and may be as an electrolytic etch with the lathe head as the cathode.

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137. MINIMUM ETCH

An etch used for a short period of time, or one that removes little or no material during the etching period. See Slow Etch.

---

138. MIST ETCH

The use of an etch as a spray of finely divided particles as from an atomizer. The method has been used for final etch cleaning of a surface; to fine-tune and optimize electrical characteristics of an exposed p-n junction semiconductor device; or to develop defects, structure, or figures in a surface for optimum clarity observation. Used in metallographic specimen etching to develop fine structure of crystallites, phases etc. See Vapor Etch.

---

139. MOLAR ETCH

Any solution mixed by its molecular weight. The total of the atomic weights of the compound elements is one molecular gram-weight of the substance as dissolved in one liter of water (1 liter = 1000 ml):

HCl:	H = 1.008 (at wt)	KOH:	K = 39.102 (at wt)
	Cl = 35.453		O = 15.999
			H = 1.000
Total	36.461 g	Total	56.109 g

Using potassium hydroxide, KOH, as an example, approximate solutions would be: (1) 1 *M* KOH = 56 g/l; (2) 2 *M* KOH = 112 g/l; or (3) a 0.5 *M* KOH solution about 28 g/l.

A Molar solution may be used as the etching solution by itself, or be only one constituent of an etch mixture. See Normal Etch.

---

140. MOLTEN FLUX ETCH

Any metal or compound liquidized at or slightly above its melting point without the inclusion of water or other liquid solvent. In Solid State processing, as an example, KOH, NaOH, or a 1KOH:1NaOH (eutectic) mixture are used as dislocation etches in their molten

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state at about 365°C. Other molten fluxes of nitrates and carbonates ($NaNO_3$ or KCO_3, examples) are used in the metal industry for etching, cleaning or structuring of materials. These fluxes also are used for growth of certain compounds, such as single crystal garnets. See Flux Etch; Melt-back Etch.

---

141. NAMED ETCH

Many etch solutions have a number, letter, chemical, individual's name, or a combination of such. Where names have been given to a specific etch solution, it is shown after ETCH NAME in the etchant formats used in Chapter 2. The following is a list of some of the variations in nomenclature that have appeared in the literature:

Name	Example
Chemical name	Single acid/chemical: HCl; H_2SO_4; KOH, etc.
Chemical name + letter	*Iodine A; Tri-iodide etch
Chemical acronym	Mixed solutions: bromine-methanol (BRM), or **buffered hydrofluoric acid (BHF)
Volume ratio	*** 1:1:1
Letter(s)/volume ratio	BK-112; BK-213
Letter(s)/number	CP4; SR2
Individual's name	Billig's etch; Sirtl etch; Wright etch; Dash etch; Makuri's reagent, etc.
Individual's name + number	Ellis #1; Camp #2
Color	White etch****
Individual's name(s), acronym	A/B etch*****; BJ etch
Two component mixture	AB etch*****
Company abbreviation	RCA etch*****
Company abbreviation + number	RCA #1; GE-3
Company + chemical symbol	WAg
Number only	See ASTM 407-70 pamphlet

*There are several "iodine etch" mixtures of varying composition, several developed many years ago for a specific metal or compound, such that the general term "iodine etch" can be any one of several solutions.

**Both the BHF and BRM designations should be considered general terms, not a specific etch solution as there are, literally, several hundred possible compositions, and many different mixtures are shown by the acronym only.

***The use of a numerical volume ratio, alone, is not recommended. From the example show — 1:1:1 — there are many acid mixtures with such a ratio.

A letter designation along with the ratio — BK-112 — is an improvement as it becomes a specific etchant nomenclature, but the user still needs to know the acids involved.

****The use of the name "White etch" is misleading. When $HF:HNO_3$ solutions were first being applied to silicon etching several of them were termed "White etch", even though the solutions are clear and transparent, not white in color.

*****The use of the terms AB or A/B can be confusing. In the former case, it has been used to describe a two-part solution with an "A" portion and a "B" portion used separately; but also has been shown as A-B — with the total quantity of the two solutions mixed together when ready for use, or, a specified ratio of the solutions mixed. And another conflict with the use of an "A" and "B" nomenclature is the A/B etch named after Abrahams and Bioucchi.

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The use of the term "RCA etch" is also questionable, as several hundred etch solutions have been developed at RCA over the years. In this case, the "RCA etch" usually refers to the "A" and "B" solutions developed for cleaning silicon by Kern and Puotinenr. Further, some developers have used only the "A" or "B" portion of those two solutions without letter designation, yet still call out "RCA etch".

---

142. NATIVE OXIDE ETCH

Almost all inorganic metals and compounds become surface passivated by an oxide when exposed to air. Such oxides are called native oxides as they are a normal attribute of the surface and not artificially produced. The removal of this type of oxide can be critical to metal processing, such as preparing aluminum surfaces for plating as well as copper, nickel, iron, and steels. It is of major importance in preparing semiconductor wafers for etching, metallization, diffusion, etc., as such residual oxides can affect device characteristics.

Any etch solution used to remove such oxides is called a native oxide removal etch to differentiate it from a solution used to etch an oxide thin film or material, such as titanium dioxide, TiO_2 or quartz, SiO_2, and called an "oxide etch". It should be realized that a "native" oxide only occurs under natural atmospheric conditions, even though it is called such in Solid State processing where residual surface oxide remains after chemical treatment. See Oxide Etch

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143. NEUTRAL ETCH

A very slow, nonreactive etch, when used as a cleaning solution, or the use of water as a pH 7 neutral wash or quenching solvent.

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144. NITRIDE ETCH

There are several artificially grown nitride compounds, such as silicon nitride, Si_3N_4 and aluminum nitride, AlN. The metal industries use a nitridization process to condition metal surfaces and the Solid State industry is developing and applying both oxide and nitride surface thin films in processes. In either case, any etch solution used to remove or pattern a nitride is called a nitride etch, and many also can be used on oxides.

---

145. NORMAL ETCH

An etch solution mixed on the basis of the total valence of the metallic radical ions in solution. To obtain the number of grams of a compound for a Normal solution: divide one gram-molecular-weight (1 mole) by the total valence number of the element and radical: (See #139 for computation of the gram mole.). Examples of Normal solution computations are

(1) Sodium hydroxide, NaOH:
Na^{+1} = metallic valence of "1"
(OH^{-1} = hydroxyl valence of "1" [ref. only]) and 40 (Na at wt) = 40 g or 1 gram-mole = 40 g

1 Normal (*N*) solution. In this instance, it also happens to be a 1 Molar (*M*) solution.

(2) Sulfuric acid, H_2SO_4
H_2^{+1} = metallic valence of "2"
($SO_4^{-1/2}$ = sulfate valence of "2" [ref. only]) and 98 (total at wt elements) = 49 g or 1 gram-mole = 49 g

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In this case, 49 g/l of water (1000 ml H_2O) of sulfuric acid is a 1 *N* solution. It also happens to be a 0.5 *M* solution.

Note: If a 50 ml *N* solution of a chemical base, such as sodium hydroxide, is mixed with an equal quantity of an acid *N* solution, such as sulfuric acid, the resulting solution will be neutral (pH 7, like water).

Both ammonia, NH_3, and ammonium hydroxide, NH_4OH are the primary chemical base solutions used to neutralize acid sumps before effluent discharge into waste disposal sewer lines.

Many etchants are mixed with both *N* and *M* constituents, even combining acids and bases, but equal quantities of *N* and *M* solutions are not mixed or else a neutral solution will result without etch action.

---

146. OIL ETCH

Petroleum base oils can act as etchants on some metals, even though they are normally only thought of as coolants in metal cutting, and similar processing. For critical materials, such as semiconductor wafers and assembly or test parts, such oil coolants with various additives for rust prevent, foaming, etc. can be severely degraded because of chemical attack, residual films, and other anomalies, such that silicones are used as replacement liquids for petroleum oils.

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147. ORIENTATION ETCH

A preferential solution used to determine the single crystal orientation of a specimen surface by development of surface etch pits. See Light Figure Etch; Optical Orientation Etch; Figure Etch.

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148. OXIDE CLEANING ETCH

A solution developed to clean an oxide surface with minimum or no removal. It can be acid, alkali, or solvent.

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149. OXIDE ETCH

Any solution used to etch a metallic oxide material. See the immediately following terms for special case applications.

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150. OXIDE REMOVAL ETCH

In Solid State processing, often refers to removal of a native oxide on a material surface prior to further processing. It also is used where a deposited oxide thin film (SiO_2, Al_2O_3) is being pattern etched or removed. See Native Oxide Etch.

---

151. OZONE ETCH

Ozone, O_3, is an extremely strong oxidizing agent. In Solid State and some metal processing it is used, by itself, as a surface cleaner. Caution should be exercised as concentrations greater than 1% in air can be hazardous to health. There are ozone producing commercial cleaning systems used in metal processing for material surface cleaning. Similar units are used in movie theaters or other commercial offices and buildings as an air freshener, and for cigarette smoke removal. (Ozone ash trays are on the market for home or office use.)

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152. PARTICULATE ETCH

Any solution used to remove a material matrix and expose embedded particles without affecting the particles. This is common in some ore processing operations where gangue

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material is separated, and in some material studies. The etch may expose the particulate, only, or be used to remove the particles for separate microscope study.

153. PASSIVATION ETCH

The term is used in two ways: (1) a solution developed to remove a passivating thin film from a surface, such as a native oxide, or (2) a solution that will introduce a surface film passivation. An iodine solution has been used on diamonds in the latter case as passivation against etching with H_3PO_4, and an I_2:MeOH rinse applied as an ionic surface contamination removal system on silicon wafers prior to diffusion.

154. PATTERN ETCH

Any etch solution that will develop structure in or on a surface and there are several different applications and methods: (i) to develop defects in surfaces; (ii) to differentiate between elements, structure, or minerals in a mixture material; (iii) to etch through a masking layer, such as photo resist patterned thin film oxides to remove the oxide down to the substrate in the desired pattern; (iv) etching via holes, or (v) circuit pattern etching of substrates. See Photo Resist Etch; Thermal Etch; Defect Etch; Figure Etch; Vacuum Etch; Structure Etch.

155. PHASE ETCH

Common to metal and metal alloy etching of steel in the etch development of alpha-, beta-, or delta-phase structure, and the recognition of martensite, carbide, and similar crystal structures.

156. PHOTO RESIST ETCH

Photo resist lacquers, such as the AZ- series, COP-, or PMMA types used in device and circuit fabrication of semiconductor devices, have their own solutions called developers, and used after UV exposure of the resists in fabricating patterns. The developers are designed for each type of commercial photo resist formulation, many contain hydroxide, such that caution should be observed if the material being processed in particularly vulnerable to attack by alkaline solutions.

Note that in removing photo resists before or after metallization of the specimens or wafers, the most widely used solvent is acetone (a ketone) by soaking, spraying, or light scrubbing of the specimen surfaces.

157. PICKLING ETCH

Term common in metal processing and plating. Metal surfaces are soak-cleaned for conditioning, such as for removal of scale, or other type contamination. See Scale Etch; Conditioning Etch.

158. PINHOLE ETCH

Small, roughly circular defects in a deposited thin film are referred to as "pinholes" and may or may not go completely through the film. Any solution or method used to locate and observe such pinholes is called a pinhole etch. Such pinholes can be created by contamination on a substrate surface, be due to insufficient cohesion within the growing thin film, or from entrapment of particles in the film. Oxide and nitride thin films are particularly prone to pinholing in Solid State processing, and are the subject of much study. The term also is applied to the etching of a controlled pinhole, such as for thickness measurement of the film, diffusion depth profiling, or observation and study of epitaxy layer structures. See Structure Etch; Profile Etch.

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159. PIT ETCH

A preferential etch used to develop dislocations or surface damage pits in single crystal wafers or similar specimens as wet chemical etching (WCE). This includes controlled damage pit development as a device structure. Dry chemical etching (DCE) through a photo resist, metal, or oxide/nitride thin film mask, as well as WCE, also for device fabrication. Note that dislocation pits conform to crystallographic structure and bulk plane directions, such as the sharp triangular pit on a (111) wafer surface, and do not increase in size to any extent with extended etching; whereas a surface damage pit does not conform to crystal planes and directions, expand in size with extended etching with a flat pit bottom that may be heavily terraced, and will disappear when the bulk, undamaged material surface is reached. Undamaged bulk surfaces can be recognized by their usual high reflectivity, and common near-mammillary and near-hexagon structure, particularly recognizable on (111) oriented surfaces. The (100) wafer bulk surface is more block-like in structure, coincident with the square outline dislocation and surface etch pits. See Preferential Etch; Via Hole Etch; Selective Etch.

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160. PLANAR ETCH

A polish etch that produces a very flat, highly reflective surface. Now a major surface finish for three-dimensional layered electronic device and circuit substrate structuring.

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161. PLANE ETCH

Preferential solution used to develop a crystal facet, or plane in a single crystal material. Occasionally with reference to etching a planar surface. See Planar Etch; Crystallographic Etch; Structure Etch.

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162. PLASMA ETCH

The use of ionized gas particles to effect cleaning or etching. Either RF or DC plasmas are used, RF more common in microwave, high frequency electronic device fabrication. See Dry Chemical Etching; RF Plasma Etch.

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163. POLAR ETCH

Any etch used on a polar material, such as the compound semiconductors and, in particular, the (111) oriented surfaces. Gallium arsenide, as an example: the positive (111)Ga [(111)A] surface vs. the negative $(\overline{1}\overline{1}\overline{1})$As[$(\overline{1}\overline{1}\overline{1})$B] surface show different etching phenomena. One surface will etch preferentially with defects; whereas the opposed surface, usually the negative $(\overline{1}\overline{1}\overline{1})$B, will be erratic, and it is difficult to develop an etch solution that will equally polish both surfaces. Note that in compound semiconductors there also may be different electronic characteristics. See Polarity Etch.

---

164. POLARITY ETCH

Any solution used to develop the preferential etching characteristics of polar compounds, such as GaAs, InP, AlSb, or their associated trinary and quaternary forms. See Polar Etch.

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165. POLE ETCH

A specialized term applied to the etching of magnetizable structure in materials such as barium titanate, Ba_2TiO_3, where the magnetic domains are aligned by polarization with electrolytic solutions and a magnetic flux. Garnet memory devices as a computer chip are similarly poled. The term also is applied in the etching of single crystal spheres for finite crystal form, when the solution produces only crystallographic "pole" figures at axial points, rather than developing exterior facets (planes) as a finite crystal solid form.

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166. POLISH ETCH

Any etch solution that attacks a material surface at an equal rate in all crystal plane directions without regard to their orientation. This is the opposite of preferential etching. In all Solid State single crystal etching, and much metal etching, a polished surface is required in the fabrication of devices and parts, such that polish etching is of great importance, and a major criterion in processes. It also is now called isotropic etching. See Isotropic Etch.

---

167. PREFERENTIAL ETCH

Any etch solution that will attack crystallographic planes at different rates, and produce structure as controlled by those planes. It is the opposite of polish etching. Much of the structuring and selective etching of semiconductors wafers and similar materials as devices is done with preferential etching, as well as in crystallographic study of single crystals. Such device processing includes formation of pits, channels, "V" grooves, via holes, saw-tooth structures. This was the only method of selective structuring semiconductor devices (wet chemical etching or electrolytic etching) until the fairly recent advent of dry chemical etching. Preferential etching also is now called anisotropic etching. See Anisotropic Etch.

---

168. PRE-PLATE ETCH

Any acid, alkali, salt, or alcohol solution used to clean or condition a material surface prior to plating. See Pickling Etch; Descaling Etch.

---

169. PRESSURE ETCH

The forming of material, or alteration of a surface by direct pressure, alone, and may include heat or a gas atmosphere when a furnace or vacuum is used. Natural pressure produces etch figures on meteor surfaces during atmospheric entry; six-rayed star percussion figures are formed on (0001) oriented mica sheets by striking; controlled point pressure damaging of single crystal wafer surface is used in forming etched pits or grooves in device structuring. See Autoclave Etch.

---

170. PRIMING ETCH

The term is applied with two meanings: (1) the type preparation of a surface prior to plating, such as a priming etch for conditioning, and (2) the adding of a small piece of the material to be etched to the etching solution prior to use. The latter method is used on highly reactive solutions, such as $1HF{:}3HNO_3$, to obtain an even etch rate from the beginning. See Seeded Etch; Conditioning Etch.

---

171. PROFILE ETCH

The term is used in two ways: (1) selective etching of any form of structure in or on material, and (2) profile etching. The latter includes etching through thin film or metal masks; etching to observe and measure diffusion depths; to study epitaxy layer structures. Many wafers are processed with (100) surface orientation and, for profile study of structures, are cross-sectioned by cleaving in a ⟨110⟩ bulk plane direction. See Angle Etch.

---

172. PYLON ETCH

Any etch used to form vertical, roughly cylindrical structures on a surface. A slightly preferential etch will produce facetted side-wall slopes with WCE; whereas smooth, unfacetted walls can be fabricated by DCE etching. See Mesa Etch.

---

173. QUALITY ETCH

Applied with regard to the purity of acids and chemicals used, such as electronic grade vs. commercial grade liquids or gases.

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174. QUANTITY ETCH

The etching or cleaning of a number of parts at a single time, or the use of a large volume of solution. See Batch Etch; Volume Etch.

---

175. RAPID ETCH

Any fast etching solution as against a slow etch. As an example, the 1HF:3HNO_3 mixture is the most rapid etch solution of this two-component etching system.

---

176. RASTER ETCH

Electron beam (E-beam) etching using high intensity electrons; electron lithography, where a computer is used for beam positioning and exposure of photo resist patterns; and laser etching may be referred to as raster etching or annealing, as has been irradiation with ionic gases or radiation with particles in the sense of using a controlled beam of energized particles, electrons, etc., to effect an etching action. The term relates to the raster tracking element of a computer screen.

---

177. RATE ETCH

Used in two ways: (1) the time period for any solution required to obtain desired results, or (2) the physical reactivity time/rate of specific mixtures. The latter most important when using exothermic solutions. Determining etch rates is a major factor in processing.

---

178. REACTIVE ION ETCH

A form of dry chemical etching (DCE) where one or more of the ionized gases is a reactive gas, such as BCl_3 used in etching aluminum oxide surface films. Common acronym: RIE. This form of etching is increasingly used for selective etch structuring of electronic devices that contain layered epitaxy and metallized structure. Note that there are a number of specifically designed dry ionized gas etching systems with their own special acronyms, though all operate in a similar manner. See Dry Etch; Gas Etch; Dry Chemical Etching (DCE).

---

179. REDOX ETCH

Originally referred to as oxidation-reduction reaction, where one acid is a reducing agent, and the other an oxidizer. HF:HNO_3 solutions are an atypical example, where HF acts as the reducer and HNO_3 the oxidizer. As a REDOX etching system, the term is applied to selective etching with pH control of the solution.

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180. RELIEF ETCH

Etching of any form of structure on a surface. It can be as a raised mesa, pit, channel, or via-hole completely through the material. See Figure Etch; Structure Etch; Selective Etch.

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181. REMOVAL ETCH

Any solution that will dissolve and reduce the thickness or weight of a material. All etches are removal type and many are classified by their etch-rate of removal. See Rough Etch; Heavy Etch.

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182. RF PLASMA ETCH

Another term for dry chemical etching (DCE), and used as a general term for any form of ionized gas etching or cleaning.

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183. ROLLING ETCH

Any solution used with a rolling motion. Single crystal spheres are etch polished in a beaker held at about 45° and hand swirled to produce a slow rolling action of the spheres.

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Occasionally used with reference to a boiling solution that has a rolling or roiling motion. It also has been used with regard to allowing a specimen to roll and tumble down an incline during an etching period, or the etching of an extruded, rolled metal sheet . . . to include etching in or against the rolled direction.

---

184. ROUGH ETCH

Has been applied with two meanings: (1) general reduction in thickness or size without regard to surface finish and measured in mils of depth removed from a surface or by total gram-weight loss of a specimen and (2) a controlled etch to roughen a surface. Glass microscope slides have had one side roughed with HF vapor etching to improve thin film gold adhesion for TEM study of the film growth and structure characteristics, and some metal parts are surface finished with a named roughness, such as a matte or satin finish. See Removal Etch; Matte Etch; Satin Etch.

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185. SAND ETCH

The term has been applied with reference to the use of a dry abrasive to effect removal action with the abrasive under gas pressure (nitrogen) applied by spray or jet. The method also is used to clean, roughen, or condition a surface.

Abrasives are usually considered as lapping and polishing compounds, although fine jets of sand have been used to fabricate screws, to drill holes through material, or form cavities (pits) in a surface. The use of S.S. White Dental Unit was one of the original methods used to dice silicon and germanium wafers, and the units are still used for sand cleaning of surfaces, e.g., bead blasting technique for cleaning metal parts. See Abrasive Etch.

---

186. SATIN ETCH

Specialized term used in the metal industry where an etch solution produces a surface finish that has the appearance of satin cloth. The surface structure contains variable length and width lines, roughly parallel with some cross-hatching, and with the reflective sheen of satin cloth. The method is called satin finishing, and is used as a decorative finish on copper, nickel, brass and other metals. See Matte Etch.

---

187. SATURATION ETCH

A solution containing the maximum amount of a dissolved chemical in water, alcohol or solvent at room temperature and standard pressure. If such a solution is mixed above room temperature, and under pressure, it is called a super-saturated solution. The latter solution is not used to any extent in material processing, but saturated solutions can be used in six contexts:

1. A chemical is mixed as a saturated solution. In the Etchant Section, Chapter 2, such solutions are shown under COMPOSITION as:

   Example: 50 ml .... CrO_3, sat. sol.

2. One constituent of a solution may be "saturated" with a second. This is shown as:

   Example: 100 ml .... MeOH
   x .... *I_2

   * saturate MeOH with I_2

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3. When steam is used for cleaning it may be under pressure, and referred to as "saturated steam".
4. Where a cloth pad is used for chem/mech polishing or damage removal from surfaces, the pad may be "saturated" with the etch solution.
5. Single crystals that are water or solvent soluble are grown from saturated solutions. High purity sodium chloride, NaCl, is artificially grown by evaporation from such solutions, cut as (100) oriented substrates, and used for thin film metal evaporation or epitaxy growth of compounds in material studies.
6. After repeated use of an etchant, removal rate control can be lost due to the solution becoming "saturated" with by-products that no longer allow etch reaction to continue. One mixture constituent can be completely used, leaving the solution "saturated" with a nonreactive constituent. This is common to solutions containing hydrogen peroxide, H_2O_2, where the peroxide rapidly depletes.

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188. SAW (ACID) ETCH

When wafers are cut from an ingot by a wire that is wetted with acid, it is called the acid-saw technique (AST). The wire can be of iron, SST, rayon, plastic thread, etc.

In cutting, lapping, or polishing a surface mechanically there is always a subsurface damaged zone remaining with damage depth determined by abrasive grit size and other factors. Solid State wafers, such as silicon or gallium arsenide, are often chem/mech polished with bromine-methanol (BRM) solutions to remove this damaged zone. This has been referred to as saw damage removal etching.

---

189. SCALE ETCH

Term used in metal processing where slow etch solutions are used to remove surface contamination — oxidation, oils, dirt — that are called "scale". See Descaling Etch; Soak Etch.

---

190. SEEDED ETCH

Any solution to which is added a small piece of the material to be etched. This technique is used with solutions that initially show a rapid rate of attack in the first few seconds, then a more controllable linear rate. A mixture of $1HF:3HNO_3$ is of this type. By initially seeding such a solution, allowing the piece to completely be dissolved, the etchant becomes more controllable for linear controlled removal.

---

191. SEGREGATE ETCH

Any etch used to remove a matrix material to expose a particulate or segregate embedded. This may be as a contaminant included during ingot growth or a new compound due to regrowth, such as is observed in fabricating silicides as blocking layers in Solid State devices. See Particulate Etch.

---

192. SELECTIVE ETCH

Either wet chemical etching (WCE) or dry chemical etching (DCE), where the solution or gas is used to structure a surface, or to remove specific material layers in a heterojunction/heterostructure device. In the latter case, the etch will attack one material layer and not another, and by suitable masking of surfaces with a thin film oxide, photo resist, or metal, then exposing a pattern, pits, channels, via-holes, or other structure can be etched selectively.

---

193. SEQUENCE ETCH

A single solution, or a series of different solutions used in a consecutive order of etching steps. Clean/etch sequences are of this type, and can include vapor degreasing, etch removal

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of subsurface damage, acid etching, alkali etching, with water and/or alcohol rinses following etching, or the rinses as individual steps.

The term also is applied to the etching of different layers of heterostructure devices where different etch mixtures are used again consecutively. See Series Etch; Step Etch; Stop Etch.

---

194. SERIES ETCH

Term has been used in two ways: (1) a single etchant used two or more times in sequence, such as in dip etching or (2) different acids, alkalies, and alcohols used in a sequence. See Sequence Etch; Chem/Mech Etch.

---

195. SHAPING ETCH

Any solution used to etch form a solid material. May be electrolytic etching, and term has been used with reference to electroforming.

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196. SHIM ETCH

Either the etching of shim-stock material, such as thin nickel sheet pattern etching for use as an evaporation mask; or the etch thinning of a material to shim thickness, e.g., at or under about 0.010″.

---

197. SHORT ETCH

Any etch solution used for a brief period of time, as against a long period, such as a soak etch. See Dip Etch.

---

198. SIZING ETCH

In Solid State material processing the term applies to the etch reduction of physical size to a particular dimension, such as in thinning of a specimen for TEM microscope study. In general material processing, there is a gelatinous substance called "size", much like a weak glue which is used as a surface coating with applications similar to those in photolithographic processing with photo resist lacquers.

In paper manufacture, size is added to the pulp to prevent ink from running, and is the more accurate meaning, where tree rosins and alums are added as the sizing compounds.

---

199. SLOSH ETCH

Any etch solution used with either movement of the solution or the part. See Agitation Etch.

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200. SLOW ETCH

The removal rate of a solution as against a rapid or fast rate. Many polish etch solutions are designed to be slow for maximum planarity of surfaces, and for the prevention of erratic surface anomalies that can occur from a too rapid etch. See Soak Etch.

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201. SLUSH ETCH

Etches containing ice or snow as cold solutions.

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202. SNOW ETCH

Some cold etch solution use snow as one constituent to establish a specific temperature. As a group, they are sometimes referred to as the "snow etches". See section on Water, Chapter 2, for "Cold Etchants".

---

203. SOAK ETCH

A slow cleaning or etching solution where the part remains immersed for an extended

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period of time. Common to the metal and plating industries for surface preparation. See Conditioning Etch.

---

204. SOLID ETCH

The term has been used in two ways: (1) the etching of any solid material, or (2) molten flux etching with a liquified solid chemical compound, such as KOH pellets. See Molten Flux Etch.

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205. SOLUTION ETCH

A term used for wet chemical etching (WCE) where the etchant is a liquid; whereas dry chemical etching (DCE) uses ionized gases.

---

206. SOLVENT ETCH

The use of a chemical solvent as a cleaning or etching solution as against an acid, alkali, or alcohol. A few metallic compounds can only be etched in a solvent. Trichloroethylene, TCE; trichloroethane, TCA; and Freons are the primary vapor degreasing solvents used for parts cleaning.

---

207. SPARK ETCH

The use of an electric spark to generate an etching action. As a cutting method, called spark erosion; as a etching method an electrically activated wire loop in alcohol is used to observe pinholes in oxide and nitride thin films by the appearance of bubbles come from the substrate surface as the wire passes over in the alcohol solution. Metal spheres, both single crystal and polycrystalline, have been formed from chips of material by electrical sparking from a copper pot under argon, and spark vaporization of material from a surface is a standard method for spectrographic analysis.

---

208. SPHERE ETCH

The term has been used in two ways: (1) the slow polish etching of a material sphere, or (2) the preferential etching of a single crystal sphere to finite crystal form (FCF). Single crystal spheres have been widely used to establish etch and oxidation rates on convex surfaces in metal and metallic compound development for device structuring applications. See Finite Form Etch.

---

209. SPIN ETCH

Etching of a specimen with the solution and/or part rotating. See Agitation Etch; Photo Resist Etch.

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210. SPUTTER ETCH

A term for RF or DC plasma etching. See RF Plasma Etch.

---

211. SQUIRT ETCH

Any solution used in the form of a liquid jet or spray. Term often applied when a polyethylene bottle know as a "squirt bottle" is used, and there are many designed jet etch systems. See Jet Etch; Mist Etch; Spray Etch.

---

212. STACKING FAULT ETCH

Specialized dislocation term used in single crystal processing. Specific preferential etches have been developed to accentuate this form of defect, which can be common to oxide and nitride thin films. The defect appears as a series of short, parallel slip lines in a translucent to transparent thin section, and are a three-dimensional defect relative to x,y,z crystallographic axes. They occur due to inherent stress factors from the difference between coef-

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ficients of expansion of oxide/nitride thin films and the substrate materials on which they are deposited. The stacking faults can be in both the oxide/nitride or in the immediate substrate surface near the interface between the two compounds (SiO_2/Si interface, as an example). See Defect Etch; Preferential Etch.

---

213. STAGNANT ETCH

The term is applied to an etch mixture that has been allowed to stand before use. The H_2SO_4:H_2O_2 mixtures have been so used, with effective depletion of the hydrogen peroxide. CP4 also has been allowed to sit 24 h before use with the effective vaporization loss of the bromine fraction. Aqua regia (1HCl:3HNO_3) is an example of a solution that requires aging before use, but it is not a stagnant solution. See Aged Etch.

---

214. STAIN ETCH

Any liquid solution or gas, such as air or oxygen, producing a coloration action on a surface with minimum etch removal. HF:HNO_3 solutions, either high in HF on high in HNO_3, will stain a surface rather than etch. Other solutions, such as those containing salts of copper, silver or gold, also will produce stains. Both HF and HNO_3 develop red/blue/yellow color; whereas metal stains are grey to black.

Staining has been used for depth profiling of diffused p-n junctions; in delineating exposed planar junctions; or to observe epitaxy layer structures in cleaved ⟨110⟩ cross-sections, which are stained after cleaving. Spheres have been oxidized in oxide growth rate studies relative to crystal planes, and metallographic samples are heat-tinted by oxidation in air on a hot plate. See Junction Etch; Metallographic Etch.

---

215. STANDARD ETCH

The term has been used in three ways: (1) a solution developed for a particular process becomes a standard for that process; (2) a solution used as a reference in material or chemical analysis, and (3) a solution that has become standard for a particular use, such as CP4 as a polish etch, or Sirtl etch for defects.

---

216. STEAM ETCH

The use of water at its boiling point as a cleaning or etching solution. Steam cleaning under pressure for cleaning buildings, clothing, and small parts in autoclaves. In material processing the steam actively getters and uses a portion of the material surface in forming the oxide, such as a silicon wafer surface atoms being used to form silicon dioxide. See Autoclave Etch.

---

217. STEP ETCH

Any solution used to form an etched step in a material surface. The method is used in device structuring; to measure a layer thickness; to profile diffused junction depths; to trace defects in a material bulk; and may be single or multiple steps. A specimen surface is successively coasted with stripes of Apiezon-W (black wax) or photo resist coated in a similar manner, being etched to a controlled depth between each coating to form the steps. See Junction Etch; Structure Etch; Selective Etch.

---

218. STILL ETCH

A solution used without movement of either the solution or the part being etched. Some very slow polishing etches have been used in this manner.

---

219. STIR ETCH

Any solution used with a rotational motion. Magnetic stirring hot plates; hand swirling;

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a hand or electrically operated stirring rod in solution, etc. In etching wafer surfaces for planarity, rotation speed is controlled so as to prevent flow patterns being developed.

---

220. STOP ETCH

Also called: "Etch-Stop." Any etch solution that will attack one material and not another in a layer-type structure. A fairly recent term as applied to the selective etching of semiconductor heterostructure devices, although the method has been in existence for many, many years in both the metals and semiconductor industries without having a specific name applied to the process, such as the etch removal or pattern etching of an oxide with HF that does not attack the underlying substrate. The solution may not be a complete "stop", as with an Si_3N_4 thin film on SiO_2 etched with H_3PO_4 where the oxide etches at a much slower rate, effectively working as an etch-stop. See Oxide Etch; Selective Etch; Layer Etch.

---

221. STRAIN ETCH

Similar to Stress Etch. Terms often used in combination as stress and strain studies. The bending of a thin material, such as a semiconductor wafer, will develop dislocations due to strain. Such defects have been studied as both a positive (+) or negative (−) strain direction relative to (100), (111)A or $(\overline{111})$B faces, and ⟨110⟩ directions. See Stress Etch.

---

222. STRESS ETCH

A preferential solution used to develop stress figures in a material. Stress may be from normal wear-and-tear; induced by heat treatment; physically induced by tension, compression or torque with or without heat. The latter method used in material studies. See Strain Etch.

---

223. STRONG ETCH

A general term applied to the use of concentrated acids or alkalies, as against a diluted solution, or a solution using weak acids.

---

224. STRUCTURE ETCH

Any solution used to develop physical structure whether it is a defect in the material, a selectively etched pit, mesa, channel or the shaping of a solid. See Defect Etch; Mesa Etch; Dislocation Etch; Sphere Shaping Etch; Channel Etch; Stacking Fault Etch; Selective Etch; Groove Etch.

---

225. SUBTRACTIVE ETCH

Term applies to the selective etching of multiple thin film layers. The removal of one layer without affecting others. See Stop Etch; Selective Etch; RIE Etch.

---

226. SWAB ETCH

Use of cotton or plastic foam type material on a stick. Medical Q-tips are used and, in Solid State processing, the cotton has been replaced with plastic foam to prevent reaction from the glue used to attach the cotton. Used with acetone for cleaning photo resist lacquers from surfaces. In processing metallographic specimens, swab etching is a common term and method of etching surface structure. Some metallographic solutions used on irons, steels, and copper in the Etchant Section, Chapter 2 show TIME as "swab", when shown for "time" in the referenced article.

---

227. SWIRL ETCH

Any solution used with a rotating motion. See Stir Etch; Agitation Etch; Angle Etch.

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228. TEMPERATURE ETCH

Temperature of cleaning or etching solutions vary with solution mixture, application requirements, and may be as a solid, liquid, or gas. May also refer to the use of temperature, alone, as a (heat/thermal) etch agent, under vacuum or furnace conditions. Much WCE etching is done at room temperature, but many solutions are exothermic, thus heating the solution during the etching period. To control such reactions, water or solvent cooling coils surround a water bath holding the etch solution vessel have been designed to limit such temperature rise. And temperature can be a major control factor for particular etch mixtures . . . at room temperature (RT) a $1HF:8HNO_3$ solution is a good polish etch . . . but at 8°C becomes preferential . . . and at 50°C too rapid and erratic for control. See the previous section discussion on TEMP in Etchant Formats for a description of the various levels of temperature as used in this book.

---

229. THERMAL ETCH

Term has been applied as (1) the use of heat in vacuum; (2) the use of heat in furnaces with a gas atmosphere. In the latter case, also called heat treatment (metals), and annealing (Solid State), though both terms have been used in all material processing areas. Pure heat alone can develop etch figures or structures on surfaces. See Heat Etch; Heat-Tint Etch.

---

230. THIMBLE ETCH

Any cup shaped vessel used to hold an etch solution. Specifically referenced to using small, ceramic, high temperature metal (platinum), or graphite crucibles to contain highly reactive, hot chemicals or liquid metals, such as KOH pellets at 360°C for dislocation etching of silicon wafers. See Cup Etch; Beaker Etch.

---

231. THINNING ETCH

Any solution used to reduce thickness of a specimen. Widely used with reference to preparing specimens for transmission electron microscopy (TEM) studies.

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232. TRIM ETCH

Any etch used to reduce thickness, width, or length of a part, specimen, or device by small increments, only. This can include laser trimming, such as in fine-tuning paired diode devices for electrical matching parameters. See Sizing Etch; Thinning Etch.

---

233. TUMBLE ETCH

A closed-end cylinder — called a "tumbler" — has long been used to polish rock and mineral specimens, or for surface cleaning of parts. Dry abrasive, a wet slurry or acid-slurry abrasive is added to specimens, then the tumbler rotated horizontally on a set of parallel bars. Rotation can be with a hand-operated crank but today tumblers are electrically operated. For parts clean/etch cycles, time is in minutes; whereas gem stone polishing is in days. Specimens and parts can be tumble etched in a beaker with the solution being stirred and parts floating free. See Spin Etch; Bottle Etch; Agitation Etch.

---

234. ULTRASONIC ETCH

Any solution used with an ultrasonic generator to develop agitation during an etching or cleaning period. There are small cup to very large basin-type systems. The latter include vapor degreasing systems. The cup types are used for cleaning and etching small parts with an etch beaker seated in a water bath that transmits the vibration frequency to the solution. Most systems are fixed frequency, but variable frequency units are available. A barium titanate, Ba_2TiO_3, transducer is used to translate physical motion of the titanate into electrical frequency, much like piezoelectric quartz crystal radio frequency blanks. See Vapor Degreaser Etch; Vibration Etch.

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235. USED ETCH

Any solution applied for more than one period of time. In high volume processing where several parts are batch etched at one time, large volumes of etch solutions are used to sustain solution action without constituent depletion, and ensure good repetitive, temperature independent etching without having to replenish with fresh solution after each etch period. In metal plating, the plating baths are automatically monitored, and additional solution added when plating rate reduces to a pre-set level. See Cyclic Etch; Aged Etch; Stagnant Etch.

---

236. VACUUM ETCH

The use of pure vacuum to effect etching action by varying the vapor pressure. This method has been used to preferentially etch single crystal gases grown under cryogenic and pressure conditions in vacuum.

---

237. VAPOR DEGREASING ETCH

Vapor degreasing has wide use in cleaning parts with a combination of hot liquid, hot spray, and a hot vapor head in which parts are held. In the large systems, the hot liquid tank may include an ultrasonic transducer. Size ranges from a beaker on a hot plate to large tanks with an overhead crane hoist. Parts are lowered and held in the hot vapor head until they are deemed clean; they are then slowly removed and are found clean and dry. Although trichloroethylene (TCE), dichloroethylene (DCE, Perk), or trichloroethane (TCA) have been used in the past, Freon solvents are being used as replacements due to the carcinogenic nature of chlorinated solvents. See Vapor Etch.

---

238. VAPOR ETCH

Any solution used in vapor form to effect an etching or cleaning action. HNO_3, H_2O, and H_2O_2 are all used to oxidize a surface, then the oxide stripped with HF as one method of surface cleaning. In epitaxy system, hot HCl vapor is used to clean the quartz tube walls, the susceptor carrier and, in some cases, the material surface about to be deposited upon. See Atmosphere Etch; Corrosion Etch; Vapor Degreasing Etch.

---

239. VIA HOLE ETCH

Specialized term in semiconductor processing where a crystallographically orient hole is selectively etched through a wafer. The side walls of the hole are then metallized through from top to bottom surface, often referred to as wrap-around plating for an electrical ground plane. See Selective Etch.

---

240. VIBRATION ETCH

Any form of vibration used in conjunction with an etching or cleaning solution. The two most common systems are an ultrasonic transducer or a shaker table. Vibration alone is a standard assembly test vehicle, and can cause part or assembly failure. Such vibration tests include acceleration/deceleration, and g-force generators with an x,y,z spin component.

---

241. WASH ETCH

Used with reference to the pouring of a solution across a surface. Not widely used for etching, as it tends to cause surface channelling. Standard water quenching of parts after etching is sometimes referred to as "wash" clean, but is not an actual etching method.

---

242. WATER ETCH

Though water is considered neutral, with pH 7, the major liquid used for quenching an etch solution, and for general washing and rinsing, it can act as an acid etch on water soluble compounds. Such compounds can be polished, preferential etched, or selective etched with water only. Sodium chloride, NaCl, is one such compound that is widely used as a (100)

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oriented substrate for thin film metal evaporation and epitaxy growth in morphological studies with thin films removed by the float-off technique for TEM observation.

High purity water, as well as brine and atmospheric moisture, will slowly corrode many metals and alloys. The metal industry uses coupons of new materials in corrosion tests by exposure to salt atmosphere along seacoasts, and study irons and steels by dripping high purity water onto surfaces over extended periods of time.

In the study of ice, it is grown as single crystals and water is used to polish or preferential etch surfaces. See Brine Etch; Atmosphere Etch.

---

243. WEAK ETCH

The use of a highly diluted etch mixture or a singular liquid, such as ammonium hydroxide, NH_4OH and ammonia, NH_3, which are both weak bases.

---

244. WET CHEMICAL ETCHING (WCE)

One of the three major divisions in chemical etching. It is the use of any liquid to effect cleaning or etching action and still the most widely used method of etching. See Liquid Etch.

---

245. WHITE ETCH

The term has been applied to mixtures of $HF:HNO_3$ with or without HAc/H_2O. It is not recommended, as these solutions are clear and transparent, not an opaque white. See Named Etch.

---

246. WORK DAMAGE ETCH

Any polish etch used to remove residual sub-surface damage remaining after cutting and mechanical lap and polish in preparing a wafer or similar specimen. The bromine:methanol (Br_2:MeOH) or BRM solutions are currently used on many metals and metallic compounds for this purpose, as they not only remove such damage, but act as slow polishing solutions.

---

247. X-RAY ETCH

Though X-rays are a photographic technique used in both medicine and material studies, X-rays, as well as other particles, have been used in material surface studies. Fluorite, CaF_2, will show color changes when subjected to X-rays, such that here it is referred to as a method of etching. Radiation or irradiation using ionized gases or atomic particles can produce similar effects in material, as well as cause internal, bulk damage. Again, not a true etching phenomenon, but of major importance in material processing. All space hardware is subjected to radiation evaluation as one high reliability test, and X-ray may be included.

---

248. YELLOW ROOM ETCH

Any solution used in a Yellow Room for the processing of material by photolithographic techniques. Photo resist lacquers are affected by exposure to white light, such that all processing is done under yellow light with humidity controlled at 40% ± 5 RH, and temperature between 70—72°F for optimum results. Too much humidity and photo resist will not harden properly; whereas too low a humidity, the lacquer will harden too rapidly and crack. If the temperature approaches 80°F, the resist also will not cure or harden properly even under controlled oven bake out conditions.

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NAMED ETCHANTS

In the past it used to be fairly common practice to assign a name or number to an etching solution when it was developed, often the developer's name, or a number associated, for example, with the mixture components, a company, and so forth. Some approaches used are discussed in the Methods of Etching section under "Named Etches".

The ASTM E407-70 pamphlet, as originally assembled and published, is a list of solutions developed for the commercial metals industries — copper, iron, steel, aluminum, and their alloys — many with both a name and assigned number, such as Nital (HNO_3:EOH), ASTM #74 — Fry's Reagent, ASTM #79, etc. The pamphlet does not assign solutions for specific metals as does this book, but where the solution has been used in Solid State development and known to be from the pamphlet, it is referenced by ASTM number in addition to our assigned metal-associated number.

The *Buehler Ltd A/B Metals Digest* series is another excellent source. Although each booklet is individualistic, they cover equipment and metal processing mainly with regard to metallographic study of specimens, and include geologic mineral cross-sections to some degree. Several of the booklets include excellent photographs, to include data on the solution used to develop micro- and macro-structure of the specimen shown. Many of their solutions used are from the ASTM pamphlet, but also include solutions developed by the Buehler organization.

The ASM Metals Handbook Series — some ten books — cover all aspects of industrial metal processing, fairly comprehensive from aluminum to zirconium. Volume 2 is, in large part, the etching and cleaning book of the series as applied to large volume commercial processing. Much of general metals processing includes surface preparation solutions, electrolytic etching, thermal heat treatment, and plating solutions. For plating, which is not covered to any extent in this book: Lowenheim, F A — *Modern Electroplating*, sponsored by the Electrochemical Society (John Wiley & Sons, publisher) is an excellent reference.

Many cleaning and etching solutions have been developed in the Solid State area of which semiconductors was an initiating technology in the late 1940s. In some instances solutions have been carried over from the general metals industries, but many others have been formulated with particular regard to single crystal technology and today all of the associated physical structures (colloidal, amorphous, crystalline), as well as associated metals, ceramics, glasses, and other compounds. Again, several solutions have been named by their developer, such as the Camp #1, #2, #3, #4, etc. series. As a common usage acronym, the Camp #4, as an example, is best known as CP4 or CP4A (without bromine). Preferential defect solutions containing chromium salts have largely been named for their developers: Sirtl Etch among the first, then Sopori, Schimmel, Wright, and so forth. And there is the well known WAg etch (Westinghouse Silver etch). Two other solution types bear mention: the bromine:methyl alcohol (BRM), and buffered hydrofluoric acid (BHF) series. Both are in wide current use referred to by their acronyms, but have a wide range of component mixtures. BRM solutions below 5% BR_2 are polish types; above, can be preferential. A more or less standard BHF mixture is 1HF:1NH_4F (40%), but even dilute HF has been referred to as a BHF solution, or a mixture may contain NaF, KF, yet all are still called BHF as a general acronym.

The following list includes most of the named and/or numbered solutions as discussed and applied in the Etchant Section, Chapter 2 accompanied by the assigned Etchant Numbers for referencing purposes.

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Etchant name	Material references
"A" etch	LIF-0010a; NACL-0007e; TA-0003a
A-B or A/B etch	GASB-0014c; GAS-0059; INAS-0005d; INP-0051
A/B, modified	INP-0021d
AB etch (RCA etch)	SIO-0043
Allen's etch	INSB-0001d
Aqua regia	ALAU-0002; WB-0001b; CDSE-0005b; CDTE-0018b; CAW-000b; CUIS-0003; GA-0002; GAS-0056a; GAP-0011; AU-0001; IR-0001; MO-0008a; PMA-0001a; OS-0001b; PD-0001; PT-0001; QTZ-0003; RU-0001; SIO-0052; SIN-0016; TAN-0001; TE-0002; TH-0002; SN-0005b; TIO-0004; TIW-0006; W-0001d; V-0002a; ZNTE-0005b; ZR-0007; ZHPD-0001; ZRRH-0001
Aqua regia, dilute	GAS-0044c; AU-0005; NICR-0003; PD-0002b; PTSB-0001; TE-0008
Aqua regia, modified	GAS-0056b; GAP-0022e; NI-0005
Barber etch	NACL-0007b
BCK-111	INP-0031a
BHF	SI-0020; SI-0021a; SI-0022; SI-0023; SI-0028; SIO-0009; SIO-0011a; SIO-0013; SIO-0071; SIN-0008a; SIN-0009; TIN-0003; SIC-0010e
BHF, modified	SIN-0008b; SIN-0014; SIN-0023
Bichromate finish dip	BRA-0008b; CU-0008c
Billig's etch	GE-0139b
BJ etch	GE-0027
BOE (BHF)	SIO-0017; SIN-0006
BPK-221	INP-0031b
Brilliant etch	CU-0011a
Bright dip	BRA-0008d
Brite dip	AL-0013; CU-0028; CUO-0005
BRM	ALAS-0001; CDTE-0008; CDTE-0017b; CUIS-0001b; GAS-0001a; GAS-0006; GAS-0173b; GAP-0006; GAP-0009; GE-0038; INSB-0028; INSB-0022j; INAS-0002; INP-0001; INP-0006; INP-0009; INP-0062c; FE-0102; FE-0113; FE-0100; MN-0002, SIC-0005b; SI-0001
Bromine etch (for arsenic)	AS-0002b
BSG	SIO-0048
Camp #2 (Superoxol, CP2)	GE-0065a; SI-0165
Camp #3 (CP3)	GE-0065b
Camp #4 (See CP4)	
Camp #8 (See CP8)	
Caro's etch	GAS-0125; SI-0103; SI-0169b
Chrome etch	CR-0006; CRO-0002; CRO-0004; CRO-0005

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Chrome etch, modified	CR-0015; CR-0016
Chrome dislocation etch	SI-0038a
Chrome regia	AU-0017; SI-0019; SIN-0018
Cook's etch	NACL-0007c
Copper etch	SI-0153c; SI-0153d
Copper dislocation etch	SI-0038b
CP4 (Camp #4)	GE-0065c; AU-0016; INSB-0001f; INAS-0009; SI-0173; SIGE-0001; TE-0005; ZNO-0004
CP4, dilute	GE-0201b; INSB-0021
CP4, modified	SB-0001g; SB-0001h; GE-0219; INSB-0006f; LIF-0001a; TE-0003; INAS-0003; INAS-0006d
CP4, variety	INSB-0021; SI-0055
CP4A	GE-0063; INSB-0029; INSB-0022c; FEGE-0002; SI-0102d
CP8	SI-0062
Dash etch	SB-0001a; SI-0046
Dash etch, modified	SB-0001b; SB-0001d; SB-0001e; SB-0001f; SI-0153b; SI-0046a; SI-0154a
DE-100	GE-0047; SIO-0023
Dash copper decoration etch	SI-0154a
E Etch	CDTE-0006a; ZN-0008d
EAg1	CDTE-0006b
EAg2	CDTE-0006c
EDTA	CA-0003b
Erhard's etch	SI-0158
Ellis #1	GE-0150q; GE-0060c
Ellis #5	GE-0150o
Ellis #7	GE-0150r
Etch #1	INSB-0014a
Etch #2	INSB-0014b
Ferric cyanide etch	GE-0150s; GE-0060d
Freeze etch	BE-0004b
Fry's reagent	FE-0112; FESI-0008
Flick's etch	AL-0017
General etch	CU-0011b
Glass cleaner etch	SIN-0015
Gold etch (on silicon)	SI-0064
Glyceregia	SI-0018
H etch	INP-0021c; INP-0051
Healy's junction etch	SI-0069
Hypo	AGCL-0007a
H 100	INSB-0022f
Iodate etch	PBTE-0002a
Iodine etch	AL-0031; GE-0218; GE-0137c; GE-0205; FE-0109; PBTE-0002b; SI-0240; SI-0242a
Iodine A	GE-0185
Jacquet's etch	AL-0048; BRA-0014
Jewitt-Wise etch	NI-0004a
Kalling's etch	ST-0001b; YXM-0001
Keller's etch	AL-0023

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KKI	INP-0062d
Krum etch	AL-0011
Landyren's etch	SI-0102f
Matte dip	BRA-0008c
Moly etch	MO-0015
Murakami's reagent	MO-0005b; TAC-0001; TIC-0005; WC-0001
Nital	AL-0027; AL-0022b; FE-0102; FE-0113; FECV-0001; FENI-0001; ST-0001; ST-0009c; ST-0010b
Nital, variety	FESI-0005b
"0"°C etch	GAS-0030b
Pickling etch	BRA-0008e
P etch	CDTE-0006d; SIO-0001b
P-1	ZN-0008a
P-2	ZN-0008b
P-3	ZN-0008c
PBr	CDTE-0006e
P-ED (EPW)	SI-0116; SI-0119
Peroxide etch (on germanium)	GE-0060f
Picral	FE-0106b; ST-0001c; ST-0001g; ST-0009e; ST-0010b
Pliskin etch	SIO-0021b
RCA etch (A-B)	QTZ-0012; SAP-0004a; SI-0031
RC-1	GAS-0048
Scale dip	BRA-0008a
Schell etch	GAS-0044
Schimmel etch	SI-0037
Schimmel, modified	SI-0038
Secco etch	SI-0036
Secco, modified	SI-0152
Silver etch (for silicon)	SI-0209
Silver glycol etch	SI-0041a
Sirtl etch	SI-0039; SIC-0012a
Sirtl, modified	SI-0153a; SI-0132
Sopori etch	SI-0043
Sopori, modified	SIU-0044
Superoxol (Camp #2)	GAS-0167a; GE-0002; GE-0005; GE-0150i; GE-0202; INSB-0024a; INAS-0006b
Superoxol, modified	INP-0022a; GE-0150j-n
SR4	GE-0124; SI-0172
SSA	GAS-0101
Tri-iodide etch	CD-0005; AU-0007; AU-0021; AUSN-0001; AUGE-0001; AUGA-0001; AUZN-0001
Vilella's etch	ST-0001e
Vogel's etch	SI-0034
"W" etch	LIF-0010b; NACL-0007d
WAg	GE-0150p; GE-0060c
Warekois' reagent	ZNTE-0002a

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White etch	GE-0015b; SI-0056; SI-0057; GE-0190
Wright etch	SI-0045
1:1:1	GAS-0037a; GE-0028; SI-0020
X-1114 etch	GE-0147d
(100) etch	GE-0060e

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Chapter 2

ETCHANT SECTION

Refer to Appendix C (Metals and Metallic Compounds with Reference Acronyms) for the alphabetic list of all materials in this chapter. We have made no attempt to categorize formats or etchants by chemicals or type format — three types: (1) Wet Chemical Etching, (2) Dry Chemical Etching, and (3) Electrolytic Etching as in most instances there is only one to a half-dozen referenced and formated etchants on any particular material.

There are exceptions, such as for aluminum, gallium arsenide, germanium, indium antimonide, and silicon, where the number of specific etchants is extensive (silicon has over 450 referenced items). In this case, a Selection Index has been included following the general introduction which lists chemical formulas, solution applications, and the material format numbers.

Where certain elements such as chlorine, fluorine, sulfur, or phosphorus are widely used in etchant formulations a section titled: "Etchants Containing xxxx" precedes the formats . . . an A—Z selection of etch formulas — material — application — format reference number. This is a quick reference for those interested in associative reactions with regard to multilayer thin film or composite constructions. This includes some special groups, such as aqua regia, the buffered hydrofluoric acid (BHF) solutions, bromine:methanol (BRM) category, or silver and chromium mixtures that are specifically preferential in character.

Some binary and trinary compounds follow their parent element without a general introduction, and a few natural minerals are shown where they have been specifically involved in Solid State development.

The list of solutions is far from complete, but it will give the user at least a starting place for immediate application or further development to included additional data obtainable from the referenced article accompanying each etchant format.

ADHESION

General: Many natural minerals contain thin films of alteration products on their surfaces or grow as incrustations on dissimilar minerals as a surface coating. Magmatic intrusion and percolation of mineralized waters into cracks of solidified rock formations form solid veins and, if introduced into a vug or void, can form fine crystals as an encrustation within the void: "dinosaur eggs" are silica, SiO_2 are concretionary segregates found in compressed sedimentary rocks — they may be a solid multicolored agate — or contain fine single crystals of clear quartz, occasionally tinted as purple amethyst, yellow citron, etc. as an incrustation growth in the hollow concretion.

All encrustations and vein-type deposits are of geologic interest in the study of mineral and rock formation, but are of little concern with regard to adhesion, other than in separation of gangue materials, such as in metal ore processing. Layer adhesion is of importance in making jewelry, as layer separation during fabrication can destroy the item. Moonstones, as one example, are similar in many respects to the "dinosaur eggs" in formation, but are solid colloidal to amorphous in internal structure with a hard white outer coating of magnesium and calcium sulfate with extremely good adhesion. With the coating removed by etching, the moonstone cut and polished, it shows fine light halos due to its noncrystalline structure.

Technical Application: Thin film adhesion is of major concern in all material processing, regardless of the method of deposition: vacuum evaporation, epitaxy growth, electrolytic plating, to include all phases of subsequent processing, temperature effects, in particular.

In Solid State processing most of the metal elements have been deposited, singly, as multilayers of metallization; as metallic compounds, with or without subsequent recrystal-

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lization (silicides); or as oxides, nitrides, carbides, and borides. Many have been studied for adhesion as single crystals and similar structure of thin films. In both adhesion and physical properties studies or interface reactions, the substrate may be removed for thin film microscope study by SEM or TEM.

Only a few direct studies of adhesion are shown here, but many are mentioned in the format discussion sections throughout this chapter under the specific metals and metallic compounds involved.

Etching: Varies with material and type adhesion test involved.

ADHESION ETCHANTS

AD-0001
ETCH NAME: van der Graaf
TYPE: Particle, conditioning
COMPOSITION:
x .... electron

TIME:
TEMP:
POWER: 1013—1019 cm^{-3} or 1—5 MeV cm^{-2}

DISCUSSION:

Au, Pd, and Ag thin films deposited on different substrates in a study of adhesion and the effects of van der Graaf power and ionic species impingement on the metal surfaces. Film thicknesses were 500 Å, and electrons applied were He^+, Cl^+, H^+, and F^+, and used on different metal/substrate combinations. Substrates were Teflon, SiO_2, CaF_2, Al_2O_3. Si, InP, GaAs, W, and ferrite. The silver/silicon samples were processed after van der Graaf treatment as follows: (1) remove silver with HNO_3, (2) rough thin silicon with HF:HNO_3, (3) final thin with CP4A. Adhesion was generally improved by about 30%, with center areas of films being thinner relative to the flux dose level. After electron treament all films passed the standard tape test.

Etch thinning was done in order to observe the metal/substrate interface by microscope examination. (*Note:* CP4A is 3HF:5HNO_3:3HAc.)
REF: Werner, B T et al — *Thin Solid Films*, 104,163(1983)

PHYSICAL PROPERTIES OF AIR, N_2/O_2 + TRACE GASES

Classification	Gas
Atomic numbers	7 & 16
Atomic weight	58 (nominal)
Melting point (°C — solid) >200 atms	−200 (variable)
Boiling point (°C — liquid)	−180 (variable)
Density (g/cm^3) 22°C (dry)	137
Hardness (Mohs — scratch) solid	1—2
Crystal structure (isometric — normal)	(100) cube
Color (gas)	Colorless
(liquid/solid)	Bluish
Cleavage (cubic — solid)	(001)

AIR, N_2/O_2

General: The term atmosphere refers to the gaseous envelop of aeriform fluid that surrounds the earth and commonly called air. It is a mixture of gases not a compound, containing 21% oxygen, 78% nitrogen with trace rare gases in addition to dust particles and water vapor. Dust and water content vary seasonally and with locale, as do other compounds. Volcanic areas release chlorine and sulfur which combine as hydrochloric acid, HCl and

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sulfuric acid, H_2SO_4 or hydrogen sulfide, H_2S; industrial areas release a variety of contaminants, now called "smog", though "smog" has been associated with the cities of man since ancient times, as far back as 4000 B.C. Decaying vegetation releases ammonia, NH_3; swamps produce methane gas, CH_4 — it is "foxfire" seen burning at night — man and the animals release carbon dioxide, CO_2, as they breath and utilize the oxygen in the air; whereas plants use the CO_2 and release oxygen, O_2 . . . a symbiotic ecology. The jungle areas of the Congo River in Africa, and the Amazon River in South America are major sources for oxygen and, with the deforestation of the Amazon basin for farming, there may be a major shift in the O_2/CO_2 cycle in the atmosphere.

Air is clear and does not appear to have weight. The standard measurement is 760 mmHg at 0°C, as measured in a tube about 30" in height and 8 cm in diameter. This weight is approximately 15 pounds per square inch (psi) for a total pressure on the human body of some 18 tons. This is called 1 atmosphere (atm) of pressure, and the amount of pressure reduces with increased height above sea level as the air envelope thins out to the vacuum of space. At standard pressure water boils at 100°C; at 720 mmHg it boils at 98.72°C. At about 17,000 feet on Mount Blanc water boils at 85°C.

At normal temperatures it is a clear gas, but as a liquid (−180°C) or solid (−200°C), it has a pale bluish color tint. The pressure liquefaction and fractionation of air is a major industry for the fabrication of liquid air, L_{air} (−180°C) — liquid oxygen, LOX (−183°C), and liquid nitrogen, LN_2 (−195°C). All of the gases have been grown in solid form, to include single crystal structure for morphological study, e.g., helium excepted.

Water vapor in the air is of critical importance, not only for the seasonal planting and harvesting of crops, but today, the weather patterns of the atmosphere are of vital concern to aircraft traffic control and space vehicle launching. Wind-shear has been responsible for several airplane crashes; the explosion of the Challenger shuttle has been attributed, in part, to freezing temperatures at launch time; and a satellite launch into a rainstorm was destroyed by lightning strikes. Relative humidity (RH) is the measure of water vapor content in the air (100% = maximum saturation). The higher the temperature and humidity the more uncomfortable for human beings, as it reduces the perspiration ability to cool the body. The most comfortable zone is 70—72°F temperature with humidity between 45—60%. Very low humidity, for example, 10% in desert areas, can cause dehydration; in Arctic areas such low humidity, even though the land is covered with ice, can cause severe frostbite and even death from breathing . . . dry, freezing, dehydrated air. Temperature, humidity, and particulate content of air can be critical in industrial processes, such as electronic assemblies and semiconductor device fabrication. The construction of "Clean Rooms" has become a major industry itself, using air conditioning and filtration control for a nominal 70°F, 45% RH, and less than 10% particulate content in the air . . . the particulates measured in micron size. A single piece of dust landing at a critical point of a device structure can destroy the functional capability.

With the beginning development of man's metal culture in the Bronze Age — somewhere around 5000 B.C. — we started using air as an industrial application: smelting of ores and fabrication of bronze. The Iron Age began about 1350 B.C. when the Hittites of Asia Minor developed iron smelting — requiring higher temperatures than bronze, leading to the use of bellows. The Egyptians had already developed kiln firing and soda-lime glass (around 3000 B.C.) initially used as a glaze on pottery, and the same formula is still in use for ordinary glass. Iron tools may have been in use by the Egyptians about this same time.

Sailing ships have been major power bases in the Mediterranean Sea for centuries as trading and ruling civilizations rose and fell (Crete, Egypt, Greece, Phoenicia, Roma). Wooden sailing ship power culminated in the mid-1800s when the British Empire ruled the oceans of the world after Spain, Portugal, Holland, and France. Great Britain was the major sea power after the defeat of the Spanish Armada in 1588 until after World War I, controlling much of the world for over 250 years. Even today, large diesel-powered transport ships

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have had metal sails added to increase speed; fishing fleets still use both sail as well as engines; sport sailing is a worldwide industry. Sailing . . . the world still uses wind power for this purpose.

There is a wide range of air sports: the Chinese developed the flying of kites in ancient times; the French developed hot-air balloons and were racing across Paris in the mid-1800s; Count Zeppelin in Germany invented the first lighter-than-air dirigibles — they were used against England in World War I and culminated as a transport airship with the unfortunate burning of the Hindenburg at Lakehurst, NJ in 1936. A few are still in use today, using helium rather than hydrogen for lift — the Goodyear blimps as an example — and are under consideration again for heavy transport of materials.

Man has always wanted to fly. It goes back to the legend of Icarius with his wax wings during the Cretian dynastic period around 1300 B.C. The Wright brothers are credited with designing and flying the first fixed-wing air machine — the airplane — in the early 1900s, though similar development was being made in Europe in the late 1800s. Small, open-cockpit biplanes and monoplanes were used in World War I — the Americans as the U.S. Army Air Force (did not become a separate branch of the military services until shortly before World War II). These small planes were used for barnstorming around the U.S. in the 1920s and 1930s, the first airmail delivery in the 1930s, and the "clipper ship" flying-boats were crossing the Pacific to the Philippines as early as 1935.

Balloons were used in the American Civil War, and World Wars I and II, mainly for reconnaissance observation, and today weather balloons are an element in weather forecasting. Ballooning as a sport is still in existence, both for height — over 13 miles in 1935 — 15 miles in 1988 — and flown for cross-country distance flying, to include attempts to cross the Atlantic Ocean. The Japanese sent incendiary balloons across the Pacific during World War II into the American northwest — the 555 PIR were used as smoke jumpers — the only black parachute unit at that time. The use of parachutes was first envisioned in Italy in the 1400s, were used for free-fall jumping during the airplane barnstorming days, but the Germans used the first massed airborne parachute troops in the invasion of Holland — 1st German Airborne Division, under the command of General Kurt Student. The largest airborne drop was by the Allies when they jumped into Holland in September of 1945. Elements of the 82nd Airborne Division jumped in Korea, and 101st Airborne Division elements were in Vietnam.

Skydiving has become a civilian sport, as well as being used by the military for small unit drops, and new parachute designs are under continual development.

The development of large aircraft in the 1930s culminated with their use in World War II. The Douglas DC-6 — the military C-47 — is probably one of the best known transport aircraft, and many are still in service today. The B-24 and British Halifax bombers; Germany Messerschmitt . . . British Spitfire . . . American P-51, P-38, P-47, or the Navy Corsairs, as fighter aircraft, and, not the least, the Japanese Zero, to mention only a few. The Germans developed the first jet aircraft toward the end of World War II, and this has led to the present-day military and commercial jet aircraft that have tied much transportation of the world together in hours/days rather than months.

The helicopter bears mention as an aircraft in its own right. This did not become a viable aircraft until the late 1940s, and the first real service (which was military) was in Korea for medical evacuation. By the time of the Vietnam war there were wings of transport and attack helicopters. Have you ever heard of "Puff . . . the Magic Dragon"? It was a helicopter built as a flying gun platform, capable of decimating some 100 square yard of area at a time with a single burst of concentrated fire-power. Military branches of all countries today have both transport and attack helicopters, and there are civilian general transport and construction helicopters, as well as medical-evacuation choppers.

As a source of mechanical power, windmills have been used in Holland for centuries, and several designs were brought to the Americas in the 17th and 18th centuries. Single

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and multiple sets of wind vanes are now in use for production of electricity using wind power as an alternate energy source.

Wind tunnels are used in evaluating air turbulence in aircraft wing and body design, astronauts have used large fans to simulate freefall in space, and air-lift vehicles are under development and evaluation.

Air compressors supply air in many industrial operations, such as for air cylinders or for switches and valves. They supply the air in gas stations for filling tires, and pressurized air for general cleaning in metal workshops, etc. There are now back-pack units and vehicle mounted systems for street cleaning or yard maintenance. Pressurized air is used for materials and devices under pressure testing. **CAUTION:** Air compressors should be well maintained to prevent oil from the compressor pumps leaking into air lines and contaminating parts being cleaned or under test.

Technical Application: Air, both as a gas and as liquid, has many applications in metal and Solid State processing. Liquid air is mainly used for conversion to gaseous, pure air for use as an oxidizing atmosphere or for surface cleaning and drying. Air drying can be simply allowing a part to dry in the room atmosphere at room temperature; on a hot plate; in an air-circulating oven at elevated temperature; or under IR lamps. It can be supplied under pressure in chemical sinks for "blow-off" drying of parts. Where dangerous chemical gases are in use, such as in epitaxy equipment areas, a combination of air-conditioning and exhaust fans are designed to completely evacuate and replace the room volume of air in 1 min in the event of a gas leak. Dry air is supplied in pressurized cylinders alone, or as a gas mixture for special applications (A-1 cylinders at 3600 psi — 9″ diameter, 5 ft high with a two-stage regulator). It also is supplied as wet-air for high purity steam oxidation. In hydrogen belt furnace operation a nitrogen curtain (a series of glass cloth hangers at front and end entrance with nitrogen gas blown down into the curtain zone) are used to prevent air entering the hot furnace, mixing with hydrogen and exploding.

Metallographic samples after polishing are heated in air on a hot plate for "color tinting". The resulting oxidation colors vary with the metal mixtures as the crystallites have different orientations that oxidize at different rates with varying distinctive colors. Where it is a single crystal metal with different phases, the phases can be differentiated by color in a similar manner. When a metal thin film has a preferred deposit orientation there will be a difference in color: Titanium is an example, (1010) surfaces are brilliant reds/blues; whereas (0001) surfaces are tan/yellow-brown. The basal (0001) surface gives good adhesion; the (1010) prism plane tends to peel. Air is supplied by compressors for operation of valves and equipment, or to hoses for heavy duty air cleaning or pressure testing of parts.

As a gas mixture air is not grown as a single crystal, although oxygen, nitrogen, and the rare gases have been grown under vacuum cryogenic and pressure conditions for morphological study.

Etching: N/A

AIR ETCHANTS

AIR-0001
ETCH NAME: Pressure
TYPE: Pressure, preferential
TIME:
TEMP: −196°C
COMPOSITION:

x ... pressure, vapor

DICUSSION:

N_2/O_2 grown as a single crystal in vacuum under pressure and cryogenic conditions is difficult to grow because of the difference in vapor pressure between oxygen and nitrogen.

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Varying vapor pressure under vacuum can develop etch figures and defects on surfaces of the solid.
REF: Schwentner, N et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1971

PHYSICAL PROPERTIES OF ALUMINUM, Al

Classification	Metal
Atomic number	13
Atomic weight	30
Melting point (°C)	660
Boiling point (°C)	2467
Density (g/cm^3)	2.699
Thermal conductance $(cal/sec)(cm^2)(°C/cm)$ 20°C	0.50
Specific heat (cal/g) 25°C	0.215
Latent heat of fusion (cal/g)	94.5
Heat of fusion (k-cal/g-atom)	2.55
Heat of vaporization (k-cal/g-atom)	69.9
Atomic volume (W/D)	10.0
1st ionization energy (K-cal/g-mole)	138
1st ionization potential (eV)	5.98
Electronegativity (Paulings)	1.5
Covalent radius (angstroms)	1.18
Ionic radius (angstroms)	0.51 (Al^{+3})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	22.4 (23.9)
Electrical resistivity (micro-ohms-cm)	2.655
Cross section (barns)	0.215 (0.23)
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.6
Tensile strength (psi)	30,000
Vapor pressure (°C)	1749
Hardness (Mohs — scratch)	2—2.9
(Knoop — kgf/mm^{-2})	100—140
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Silver white
Cleavage (cubic)	(001)

ALUMINUM, Al

General: Aluminum does not occur as a native element, but is found as a constituent in over 200 single crystal minerals. In order, oxygen, silicon, and aluminum are the three most abundant elements in the world, and the oxides SiO_2 and Al_2O_3 are the most inert and stable under normal atmospheric conditions. The mineral bauxite, $Al_2O_3.2H_2O$ — a hydrated aluminum oxide — is the major ore. It is most often found in clay-like deposits called laterites as a mixture with clays and iron oxides, and may contain large amounts of a colloidal form of aluminum oxide. Bauxite's mode of origin is not completely understood, but it is known to form under tropical conditions from the prolonged weathering of aluminum bearing rocks, and as a sedimentary colloidal precipitate which can be associated with volcanic activity. As the mineral corundum it is mostly a constituent in rock forming minerals of the Chlorate Group, but can be an original constituent of igneous rocks and pegmatites. It is not used as an ore of aluminum, but its three varieties are of commercial importance: (1) gem stones: sapphire (blue); ruby (red), and as "Oriental" — topaz (yellow), emerald (green), amethyst (purple); (2) corundum, as a powder for abrasives, and (3) emery, also

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as an admixture with magnetite, Fe_3O_4. When corundum is cut normal to the z-axis and polished encabachon, it may produce a six-rayed star — the star sapphire, with top quality a fine blue-grey.

Pure aluminum metal is second only to gold in malleability, sixth in ductility, and one of the softest of metals (H = 2—3); whereas corundum is second only to diamond in hardness (H = 9 and H = 10, respectively, on the Mohs Scale of hardness). The metal is silver-white in color and, as is highly electropositive, when in contact with other metals, will corrode rapidly. It has about 60% of the electrical carrying capacity of copper, and has been used for high power transmission lines as it is much lighter than copper. It also has been used in finer wire form for house current power and lighting, but the wire tend to oxidize with time, say, over 20 years to the oxide — a nonconductor and industrially considered a high temperature ceramic. The conversion of aluminum to aluminum oxide has a high heat of formation which is strongly exothermic: Al + Fe_2O_3, when heated to form Al_2O_3 + Fe produces 198,000 calories of heat (thermite), and used both for welding and as an explosive. Aluminum foil, when ignited in photoflash bulbs, produces heat equivalent to that of the sun surface (some 8000 K) with intense white light.

By far the greatest use of aluminum is as a construction metal. Physical strength is increased with the addition of small amounts of other metals, such that the majority of "aluminum" materials are in some form of an alloy. As an example, duralumin — containing Cu, Mg, and Mn — after heat treatment has the strength of mild steel and, when duralumin sheets are clad with pure aluminum, becomes even more weather resistant to corrosion. Applications include airplane skins; car and truck bodies; engine blocks; building girders and house siding; window and door frames, including the wire mesh screening; cooking pots and pans; as well as aluminum foil, and hundreds of small products, such as screws, bolts, rods, tweezers, and so forth. Evaporated on glass, it is a low-cost replacement for silver mirrors, and evaporated or sprayed on glass or plastic as an anti-reflective (AR) coating. In sports: baseball bats, water and snow skis, the frame for back-packs, and tennis racket frames. Aluminum paint is either oil-base or plastic-base, e.g., acrylic spray paint. In some plastics it is added as flakes for "glitter" with wide use in jewelry items. Military use includes dropping of thin aluminum foil to confuse radar and heat-seeking missiles; as weapon frames, and as a constituent in both flares and incendiary bombs. In the clothing industry for some everyday wearing apparel but, more importantly, in the construction of fire retardant and chemical protective suiting and space suits. There are medical applications of compounds, such as the hydroxide, $Al(OH)_3$ as a salve. The hydroxide also is used as a mordant for setting dyes in the clothing industry, and as a clarifier in water treatment. Alums — double sulfates of aluminum salts and sodium, potassium or ammonium salts — also have important medical and chemical applications.

In the pottery industry — clays have been in use since earliest times in the Middle East, circa 12,000 B.C. — and, with the Egyptian development of soda-lime glass around 3500 B.C., the pottery industry has become known as the ceramic pottery industry, e.g., the inclusion of glass as a surface glaze. Archaeologists date the rise and changes of ancient civilizations by the designs, and pigments used on glazed pottery. Note that many clays contain alumina, such that the pottery industry includes aluminum compounds, but aluminum metal has only been available in quantity since the discovery of the electrolytic method for processing the ore within the past century.

Technical Application: Pure aluminum metal is a p-type dopant in Solid State processing of silicon, and was used as wire or cut pre-forms, then as an evaporated thin film to fabricate the first silicon diodes and transistors that led to development of the semiconductor industry in the early 1950s. The metal is still used on silicon and other compound semiconductors, although aluminum chloride, $AlCl_3$, is used as a gaseous diffusant source. And today, an AlSi(2—5%) alloy is more widely used as a pre-form than the pure metal as an aluminum alloy device. Aluminum is evaporated as electrical contact pads on many devices, with

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aluminum wire ultrasonically bonded to the pads. Ultrasonic vibration is used to break through the thin native oxide that always grows and stabilizes on aluminum metal surfaces exposed to air.

Aluminum should not be used in direct contact with gold as with time and/or heat the two metals form distinctive purple compounds that are extremely brittle and destroy the electrical integrity of an operating device. The reaction is called "purple plague". Walker (author) first recognized purple plague as a problem during a failure analysis of a high power silicon diode, and L. Bernstein carried on the study with several excellent papers and reports, circa 1960.

Where aluminum and gold are used in a device structure, they are separated by evaporated layers of other metals, such as Pd/Cr for a complete layer structure as Au/Pd/Cr/Al. Such layers are not only a vertical separation, but are horizontally off-step separated, as both gold and aluminum can show slow "creep" characteristics on a device surface under operating load, particularly, at elevated temperature.

The chemical processing of thin film aluminum is a basic problem as, when pure aluminum is exposed to air, it forms a passivating, stable oxide layer on the surface, and the oxide is impervious to most liquid chemical processing solutions for controlled removal and patterning. The aluminum deposits as a microcrystalline layer, crystallite size controlled to some degree by rate and temperature of evaporation, such that the ensuing oxide also is crystalline in structure. Acid attack initiates along these oxide crystallite boundaries, undercutting the "oxide" with a more rapidly attack of the underlying pure aluminum. This can produce the easily recognizable "Swiss cheese" effect, and remaining oxide on a surface will create a high resistance zone if other metals are subsequently over-evaporated, reduce electrical efficiency, and, in many cases, poor metal adhesion with eventual peeling and loss of metal contact. RIE — reactive ion etching — using an RF plasma with gas mixtures, such as BCl_3 or $AlCl_3$, are now in use for improved etch removal of the residual oxide, and most aluminum structures are processed with these gases in current device fabrication.

In quartz crystal radio frequency blank processing the evaporated metal electrodes are usually gold, silver or aluminum. Aluminum is given preference due to its lesser mass loading effect on crystal frequency.

SELECTION GUIDE: Al

(1) Acetone: *Note:* Applies to lift-off of all thin film metallization deposited on photo resist lacquers.
  (i) Lift-off: AL-0088
(2) H_2O: *Note:* Applies to all thin films deposited on soluble substrates.
  (i) Float-off: AL-0095
(3) Br_2:MeOH: (BRM)
  (i) Removal/Polish: AL-0082a
(4) HCl, conc: (Electrolytic)
  (i) Preferential: AL-0060; -0082b ;-0098
(5) HCL:H_2O
  (i) Removal: AL-0003b; -0004
  (ii) Polish: AL-0034
  (iii) Preferential: AL-0005
(6) HCl:$FeCl_3$:H_2O:
  (i) Cutting: AL-0083
  (ii) Preferential: AL-0003
(7) H_2SO_4, conc: (electrolytic)
  (i) Anodizing: AL-0020b
(8) Air: O_2/N_2 w/H_2O (electrolytic)
  (i) Anodizing: AL-0040; -0049; -0050; -0052

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(9) H_2SO_4:H_3PO_4:
  (i) Polish: AL-0041a
(10) H_2SO_4:H_3PO_4:HNO_3:
  (i) Polish: AL-0035; -0097; -0045
(11) H_3PO_4:HAc: (electrolytic)
  (i) Polish: AL-0024; -0087; -0090
(12) H_3PO_4:HNO_3:H_2O:
  (i) Cleaning: AL-0033
  (ii) Removal/Polish: AL-0009; -0033b
(13) H_3PO_4:HNO_3:HAc:H_2O:
  (i) Removal/Polish: AL-0010; -0014; -0084
  (ii) Selective: AL-0031
(14) H_3PO_4:H_2O_2:H_2O:
  (i) Removal/Polish: AL-0011; -0067
(15) H_3PO_4:H_2O:Glycerin:
  (i) Removal/Polish: AL-0007
(16) H_3PO_4:HNO_3:Al-Brite:
  (i) Polish: AL-0013
(17) H_3PO_4:Cr_2O_3:
  (i) Oxidation removal: AL-0002
(18) H_2SO_4:$Na_2Cr_2O_7$:H_2O:
  (i) Cleaning: AL-0032
(19) HF:H_2O:
  (i) Preferential: AL-0023b;
  (ii) Removal: AL-0091
(20) HF:NH_4F:HF: (BHF)
  (i) Cleaning: AL-0030a
(21) HF:HCl:H_2O:
  (i) Preferential: AL-0017; -0020a
(22) HF:HCl:MeOH/EOH: (electrolytic)
  (i) Polish: AL-0025b
(23) HF:HNO_3:HCl:H_2O:
  (i) Cleaning: AL-0081
  (ii) Preferential: AL-0030; -0020a; -0058; -0059a
  (iii) Polish: AL-0030
(24) HF:HNO_3:HCl:Glycerin: (electrolytic)
  (i) Polish: AL-0027
(25) HNO_3:MeOH: (electrolytic)
  (i) Polish: AL-0027
(26) $FeCl_3$:H_2O:
  (i) Removal: AL-0004
(27) $CuCl_3$:H_2O:
  (i) Polish: AL-0022a
(28) $HClO_4$:MeOH: (electrolytic)
  (i) Polish: AL-0037; -0038; -0039a; -0042; -0033; -0035
(29) $HClO_4$:EOH:H_2O:Butyl Cellusolve: (electrolytic)
  (i) Polish: AL-0044
(30) $HClO_4$:HAc: (electrolytic)
  (i) Polish/Removal: AL-0046; -0049; -0048
(31) $HClO_4$:EOH:Glycerin: (electrolytic)
  (i) Thinning: AL-0047; -0091

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(32) $NaOH:H_2O$: (electrolytic)
  (i) Removal/Polish: AL-0064
(33) $NaOH:H_2O$:(Glycerin)
  (i) Removal/Polish: AL-0033a; -0093; -0062; -0077; -0078
(34) $NaOH:HNO_3:H_2O$:
  (i) Cleaning: AL-0030
(35) $NaOH:HNO_3$:MeOH:
  (i) Preferential: AL-0041b; -0045; -0055a
(36) $KOH/NaOH:H_2O$:
  (i) Cleaning: AL-0001; -0061; -0062; -0066
  (ii) Oxidation: AL-0002
  (iii) Removal: AL-0003a; -0062; -0063; -0065
(37) $KOH:H_2O$: (electrolytic)
  (i) Cleaning/Removal: AL-0064
(38) $KOH:K_3Fe(CN)_6:K_2B_4O_7.4H_2O$:
  (i) Removal: Al-0019a; -0084
(39) KI:MeOH:
  (i) Selective: AL-0094
(40) CCl4:
  (i) Removal: AL-0091; -0092
(41) Br_2/HBr:
  (i) Removal: AL-0092

GAS: (molecular)
(1) Air (oxidation): AL-0061; -0049; -0030; -0052
(2) Chlorine, Cl_2 (removal): AL-0092

GAS: (ionic) (DCE)
(1) $BCl_3/AlCl_3$ (selective): AL-0051; -0089($+O_2$)
(2) BBr_3 (removal/polish): AL-0056; -0059b; -0054
(3) $SiCl_4$ (removal): AL-0089 ($+O_2$)
(4) Neon, Ne (preferential): AL-0040

ABRASIVES:
(1) SiC, paper (polish/forming): AL-0076
(2) Al_2O_3, powder (polish): AL-0100

ANODIZING/OXIDATION:
(1) H_2SO_4 (electrolytic): AL-0020b
(2) Air, N_2/O_2 + H_2O: AL-0040; -0049; -0050; -0052; -0030; -0061
(3) Water, H_2O (cleaning): AL-0101
(4) $KOH/NaOH:H_2O$ (cleaning): AL-0002

NAMED/NUMBERED ETCHANTS:
(1) BHF:($HF:NH_4HF.HF$) (cleaning): AL-0030a
(2) BRM: (Br_2:MeOH) (removal/polish): AL-0082a
(3) Flick's Etch ($HF:HCl:H_2O$) (preferential): Al-0027; -0023c
(4) General Etch ($HF:H_2O$) (preferential): Al-0023d
(5) Iodine Etch (I_2:MeOH) (structuring): Al-0031
(6) Jacquet's Etch ($HClO_4$:HAc — electrolytic) (removal): AL-0048
(7) Keller's Etch ($HF:HNO_3:HCl:H_2O$) (preferential): AL-0023a; -0043
(8) Nital (HNO_3:EOH/MeOH) (polish): AL-0022b; -0065a; -0061

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THERMAL

(1) + H_2 or N_2/H_2 (reducing atm) (cleaning/annealing): AL-0102
(2) + O_2 (oxidizing atm) (cleaning/anodizing): See Air or Anodizing
(3) + Vacuum (preferential): AL-0039a-b

ELECTRICITY:

(1) Thin Film (creep): AL-0041

FATIGUE:

(1) See Thermal-vacuum
(2) Pressure: AL-0096

Both pure beryllium and an aluminum/beryllium alloy, AlBe (30%) have been evaporated to further reduce the mass-loading effect.

Aluminum has been evaporated on telescope lenses, then overcoated with a thin layer of silica, SiO_2 for wear resistance. The aluminum used as an absorber and reflector. And such lenses are periodically stripped for recoating.

Aluminum parts are used in package assemblies and, the combination of aluminum and alumina are important as radiation resistant packages. Aluminum foil is used as a grounded wrapping for static sensitive devices, and as a temporary shield in vacuum evaporator bell jars.

Single crystals of pure aluminum, as well as several alloys, have been grown for general morphological study, electrical evaluation and a wide range of defect, corrosion and fatigue failure studies. These studies include the other physical structures of aluminum: colloidal, amorphous and crystalline.

Etching: Soluble in HCl, HNO_3, H_2SO_4, alkalies and acid mixtures. Gas mixtures as an RF Plasma.

ALUMINUM ETCHANTS

AL-0033a
ETCH NAME: Sodium hydroxide — TIME:
TYPE: Alkali, removal — TEMP:
COMPOSITION:
x .... 1 *M* NaOH
DISCUSSION:
Al thin film removal from vacuum evaporation systems. Used for removal of metal build-up from stainless steel, glass, copper, and ceramic surfaces. Can damage titanium and silver surfaces. Another notes that hydroxide cleaning can leave residual contamination on parts unless thoroughly washed. (*Note:* An excellent article on cleaning procedures for vacuum deposition equipment.)
REF: Nichols, D R — *Solid State Technol,* December 1979

AL-0033b
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
20 .... H_3PO_4
2 .... HNO_3
5 .... H_2O

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DISCUSSION:

Al thin film removal from vacuum evaporation systems. Use for removal from steels, glass and ceramics. Do not use on copper parts.

REF: Ibid.

AL-0003

ETCH NAME: Hydrochloric acid — TIME: 2—10 min

TYPE: Acid, removal — TEMP: RT

COMPOSITION:

(1) x .... HCl, conc.

(2) 1 .... HCl
1—10 .... H_2O

DISCUSSION:

Al thin film removal from vacuum evaporation systems. Used to remove multiple layer films of aluminum/nickel/chromium/gold and gold germanium from steel, glass and ceramic — dilute solutions more commonly used, particularly on copper parts. Used to soak and scrub parts with a stainless steel brush. Used with lint-free cloth dampened with solution to wipe base plates and other in-place fixturing after light scrapping to remove heavy build-up. Such surfaces should be well wiped down with a water soaked cloth after acid cleaning and follow with methyl alcohol. Vacuum pump-down after cleaning to at least 10^{-6} Torr before system use.

REF: Walker, P — personal application, 1960—1980

AL-0005: Hurden, M J & Averbach, B L — *Acta Metall*, 9,237(1961)

Al (111) and (100) wafers and ingots. A 50% solution was used to "heavy" etch specimens in a study of dislocation density in deformed aluminum.

AL-0033c

ETCH NAME: Potassium hydroxide — TIME: Variable

TYPE: Alkali, removal — TEMP: RT to 180°F

COMPOSITION:

x .... 8—10% KOH (NaOH)

DISCUSSION:

Al and Al alloys. At room temperature solution is slow and used as a surface cleaning etch. Used hot for heavy removal. RT solutions used for removal of aluminum evaporation onto bell jars and fixtures of vacuum systems — glass, SST, and ceramic material.

REF: Ibid.

Al-0060: Walker, P & Menth, M — personal application, 1981

Al, evaporated film deposits in vacuum systems. Solution used for cleaning systems. Follow with heavy water washing and IR lamp drying. Vacuum bake system before use. Also used sodium hydroxide.

Al-0002: Stirland, D J & Bicknell, R W — *J Electrochem Soc*, 106,481(1959)

Al, specimens used in a study of surface oxidation. A 3% NaOH solution, RT, 3 min used to clean surfaces. After anodizing, a solution of 35 ml H_3PO_4:20 g Cr_2O_3/l used to remove the oxide.

Al-0001: DeSorbo, W — *Phys Rev*, 111,810(1958)

Al, single crystal specimens used in a study of imperfection at low temperature. Used a solution of 15% NaOH, warm as a pickling solution to clean surfaces.

AL-0061: Walker, P — personal application, 1964

Al and AlSi (5%) alloy as spherical pellets used in fabricating Silicon Sphere Alloy Zener diodes. Used a 1% KOH solution to clean wafers with multiple alloyed junctions after fabrication prior to DC leakage evaluation. Contour plots of leakage of devices on wafers used to determine segregation zones in ingots with wafers cut and numbered consecutively for traceability.

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AL-0062: Tarn, W H & Walker, P — personal application, 1976

Al, thin film evaporation on soda-lime glass used for photo resist masks and special lenses. A 30% NaOH solution, warm (40°C) used to remove aluminum and clean the glass.

AL-0063: Menth, M — personal communication, 1982

Al, thin films evaporated on telescope lenses for reflectivity control. A 15—20% NaOH solution at RT or warm used to remove aluminum prior to re-work of old lenses.

Al-0064: Tegart, W J McG — *The Electrolytic and Chemical Polishing of Metals in Research and Industry*, Pergamon Press, London, 1956

Al and Al alloys. Alkali solutions used for etching and cleaning. Includes a discussion of chemical and electrolytic etching as preferred over mechanical lapping of metals in order to preserve bulk characteristics.

AL-0065: ASTE Committee — *Tool Engineers Handbook*, McGraw-Hill, New York, 1949

Al, alloy specimens, and other soft metals such as tin and zinc. Buffer alkali solutions with silicates to reduce etch attack. A 5% NaOH solution plus carbonates, silicates, phosphates, or borates as buffers recommended for general etching.

AL-0066: Campos, R & Walker, P — personal application, 1961—1963

Al alloy piping and parts on 2000 gallon capacity cryogenic trailers. 5—10% NaOH solutions used for corrosion removal cleaning of surfaces with plastic brush scrubbing, and heavy water wash after etching. Final drying with warm nitrogen gas.

AL-0019a
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:

x .... KOH
x .... $K_3Fe(CN)_6$
x .... $K_2B_4O_7.4H_2O$

DISCUSSION:

Al, thin films on semiconductor wafers. Use COP type photo resists to coat surfaces and develop patterns using standard photolithographic techniques. Use solution shown to remove exposed aluminum. COP resists etch more slowly than the aluminum.

REF: Turner, J K — *J Vac Sci Technol*, 15,962(1978)

AL-0010
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:

1520 ml .... H_3PO_4
120 ml .... HAc
50 ml .... HNO_3
300 ml .... H_2O

DISCUSSION:

Al, thin films deposited on GaAs and silicon (100) wafers. Use AZ-type photo resists to coat and open patterns with standard photolithographic techniques. The solution was used to remove aluminum and will attack both wafer and aluminum. After etching, rinse in DI water; MeOH and nitrogen blow dry.

REF: Shipley Sales Brochures, 1975—1980

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AL-0014
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
80 ml .... H_3PO_4
5 ml .... HAc
5 ml .... HNO_3
10 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
Al thin films evaporated as part of a layer metallization structure on Si(100) substrates, as Ni/TiN/Al/Si(100). After photo resist patterning, etch remove Ni and TiN, then use solution shown for removal of aluminum layer.
REF: Ballard, N L et al — *J Electron Mater*, 13,327(1984)

AL-0009
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
80 ml .... H_3PO_4
5 ml .... HNO_3
0—20 ml .... H_2O
TIME:
TEMP: 40°C
RATE: 1500 Å/min
DISCUSSION:
Al specimens. Used as a general removal etch with agitation. (*Note:* Rate shown is a guideline, only as water content varies.)
REF:

AL-0011
ETCH NAME: Krumm etch
TYPE: Acid, removal
COMPOSITION:
8 .... H_3PO_4
1 .... H_2O_2
1 .... H_2O
TIME:
TIME: 35°C
RATE: 100 Å/sec
DISCUSSION:
Al thin films evaporated on GaAs, (100) wafer substrates. Solution used to remove aluminum and in photo resist pattern etching. Solution will also attack gallium arsenide at a more rapid rate than aluminum.
REF: Siracusa, M — personal communication, 1979

AL-0067
ETCH NAME:
TYPE: Aid, removal
COMPOSITION:
2 .... H_3PO_4
1 .... H_2O_3
3 .... H_2O
TIME:
TEMP: RT
DISCUSSION:
Al thin films evaporated on silicon and gallium arsenide, (111) wafers. Solution used as a general removal etch in studies of metal/substrate interfaces.
REF: Topas, B — personal communication, 1970

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AL-0007
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
30 ml .... H_3PO_4
10 ml .... H_2O
50 ml .... glycerin
TIME:
TEMP: 80°C
RATE: 60 Å/sec
DISCUSSION:
Al thin films evaporated on GaAs, (100) substrates used in fabricating GaAs FETs. Solution used to remove the aluminum gates of devices in studying the Al/GaAs interface.
REF: Walker, P — personal development, 1979

AL-0013
ETCH NAME: Brite dip
TYPE: Acid, polish
COMPOSITION:
x .... H_3PO_4
x .... HNO_3
x .... Al-brite
TIME:
TEMP: RT
DISCUSSION:
Al specimens and alloys. Mixtures of these acids are polish type solutions for aluminum. The addition of Al-Brite to the solutions improves the surface polish and gives better etch control.
REF: Bulletin #H681-10M — *Metal Finishing Products*, Heatbath Corp., 1984

AL-0032
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
27 .... H_2SO_4
3 .... $Na_2Cr_2O_7$
70 .... H_2O
TIME: 10 min
TEMP: 150°F
DISCUSSION:
Al alloys as sheet material and as an evaporated thin film on other materials. Solution is the preferred surface cleaning etch in preparing surfaces for plastic film adhesion, giving the best adhesion results. After etching, rinse in cold water, then hot water, and air dry. (*Note:* Solution is a form of the standard glass cleaner mixture.)
REF: Skeist, I — *Epoxy Resins*, Reinhold, New York, 1959, pp 190—192

AL-0024
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
2 .... H_3PO_4
7 .... CH_3CHOOH (HAc)
TIME: 3—5 min
TEMP: RT
ANODE: Al
CATHODE:
POWER: 10, 20, 30 & 40 V
DISCUSSION:
Al specimens used in a study of interfacial structures. Solution used to polish material prior to etch developing structure.
REF: Randall, S T & Bernard, A — *J Appl Phys*, 34,1210(1964)

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AL-0004
ETCH NAME: Ferric chloride
TYPE: Salt, removal
COMPOSITION:
x .... $FeCl_3$
Note: A standard solution is 35° Baumé
TIME:
TEMP: 110°F
DISCUSSION:
Al and Al alloys. A general etch for aluminum and several heavy metals, such as irons and steels. It has been used as a general removal or polishing solution as well as a preferential etch depending upon concentration and method of application. Use at RT, hot to boiling. After etching, wash heavily in water until all traces of the brown colored solution is removed.
REF: Meyer, W M & Brown, S H — *Proc Am Electropl Soc*, 36,163(1949)

AL-0029
ETCH NAME: Boron trichloride
TYPE: Ionized gas, removal
COMPOSITION:
(1) x .... BCl_3
(2) x .... $CHCl_3$
(3) x .... Cl_2/Ar
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
Al thin film evaporations used in semiconductor device fabrication. Gas used for reactive ion etching (RIE) for controlled removal of aluminum after photo resist patterning. Better removal control of Al_2O_3/Al than by wet chemical etching.
REF: Bruce, R H & Malafsky, G P — *J Electrochem Soc*, 130,1369(1983)

AL-0022a
ETCH NAME: Cupric chloride
TYPE: Salt, polish
COMPOSITION:
x .... $CuCl_2$
x .... H_2O
TIME:
TEMP:
DISCUSSION:
Al single crystal specimens. Wafers were polished in this solution prior to X-ray studies of surface and bulk structure.
REF: Walker, C B — *Phys Rev*, 103,547(1956)

AL-0023a
ETCH NAME: Keller's etch
TYPE: Acid, microetch
COMPOSITION:
2 ml .... HF
5 ml .... HNO_3
3 ml .... HCl
190 ml .... H_2O
TIME: Dip
TEMP: RT
ASTM: #3
DISCUSSION:
Al, alloy and cast aluminum specimens. Solution used as a general micro-etch in the study of surface structure.
REF: *A/B Metal Digest*, 21(2),23(1983) — Buehler Ltd
AL-0043: ASTM E407-70
Reference for Keller's Reagent as #3.

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AL-0023b
ETCH NAME: Hydrofluoric acid
TYPE: Acid, macro-etch
TIME: Swab/dip
TEMP: RT
COMPOSITION:
1 ml .... HF
199 ml .... H_2O
DISCUSSION:
Al, low alloy content specimens. Solution used as a macro-etch by swabbing the surface or immersion dipping to develop surface structure.
REF: Ibid.
AL-0021: Tokumaru, Y & Okada, Y — *Jpn J Appl Phys Lett*, 23,123(1984)
Al thin film aluminum deposited on both Si, (100) and GaAs, (100): Cr semi-insulating (SI) wafers. Solution used to remove aluminum after photo resist patterning.

AL-0030
ETCH NAME:
TYPE: Acid, polish, preferential
TIME: (1) 5 sec or (2) 15 sec
TEMP: (1) 0°C (2) 8°C
COMPOSITION:
(1) 4 .... HF
35 .... HNO_3
61 .... HCl
(2) 1 .... solution (1)
100 ml .... H_2O
DISCUSSION:
Al single crystal specimens. Solution (1) used as a polish etch; solution (2) is slightly preferential. Ice/acetone = 8°C, and dry ice/acetone = 0°C used for the two cold temperature applications.
REF: Tucker, G E G & Murphy, P C — *J Inst Met*, 8,235(1953)

AL-0017a-b
ETCH NAME: Flick's etch
TYPE: Acid, macro-etch
TIME: 10—20 sec
TEMP: RT
COMPOSITION:
(1) 10 ml .... HF
5 ml .... HCl
90 ml .... H_2O
(2) x .... HCl, conc.
DISCUSSION:
Al, cast alloys. Etch used for preparation of metallographic specimens as a macro-structure solution. After etching with solution (1) remove black smut that remains by dipping in concentrated hydrochloric acid (2) and rinse in DI water.
REF: *A/B Met Dig*, 21(2),23(1983), Buehler Ltd

AL-0020a
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
3% .... HF
47% .... HNO_3
50% .... HCl
DISCUSSION:
Al specimens. Specimens were anodized and etched in solution shown in a study of dislocation loops and patterns developed in aluminum by oxidation.
REF: Bassett, G A & Edeleanu, C — *Phil Mag*, 5,709(1960)

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AL-0020b
ETCH NAME: Sulfuric acid
TYPE: Electrolytic, anodizing
COMPOSITION:
10% .... H_2SO_4

TIME:
TEMP:
ANODE: Al
CATHODE: Pt
POWER: 15 V

DISCUSSION:
Al specimens. Specimens were anodized and etched in a study of dislocation loops and patterns. Also used 3% NaCl at 1.5 V. A third anodizing solution was 4 ml H_2SO_4:12 g $Na_2H_3PO_4$:100 ml H_2O at 30 V.
REF: Ibid.

AL-0037
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... $HClO_4$
5 .... MeOH

TIME:
TEMP: 0 to −10°C
ANODE: Al
CATHODE:
POWER: 20 V

DISCUSSION:
Al, (100) wafers used in an oxidation study. Both single crystals and tri-crystals used. Polish surfaces in solution shown prior to oxidation.
REF: Doherty, D E & Davis, K S — *J Appl Phys,* 34,619(1963)
AL-0038: Alden, J H & Backofen, W A — *Acta Metall,* 9,352(1961)
Al, (100) wafers used in a study of fatigue crack formation. Solution used prior to stressing specimens as an electropolish using 60 V power.
AL-0039a: Noggles, T S — *J Appl Phys,* 28,913(1957)
Al, (100) wafers used in a study of thermal etch patterning surfaces. Solution used to electropolish surfaces prior to thermal annealing. Polishing done at less than −10°C with power at about 16 A/cm^2.
AL-0042: Alden, J H — *Rev Sci Instr,* 31,897(1960)
Al, single crystal specimens used in a material failure study. Solution used to electropolish specimens at −50°C with solution continually stirred.
AL-0015: Mehdizadeh, P & Block, R J — *J Electrochem Soc,* 119,1090(1972)
Al, single crystal ingots grown by boat method (Bridgman) using a graphite crucible. After cutting for surface orientation, specimens were electropolished in a perchloric acid/alcohol solution prior to studying slip caused by oxidizing surfaces.
AL-0107: McGrath, J T & Waldron, G W J — *Phil Mag,* 9,249(1964)
Al:Mg(1%) ingots and wafers used in a dislocation study. Solution used as an electropolish with EOH replacing MeOH in the formula shown.

AL-0018
ETCH NAME: Iodine etch
TYPE: Halogen, structuring
COMPOSITION:
(1) 10 g .... I_2
100 ml .... MeOH
(2) x .... MeOH

TIME: 3—8 min
TEMP: 70°C
RATE: 1 mil/min

DISCUSSION:
Al thin films and crystalline aluminum sheet. Specimens were anodized, then a channel pattern was cut through the oxide with a diamond scribe. Solution shown was used to etch channels in the aluminum. Rinse in MeOH to remove residual iodine. KMER photo resist

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was also used for pattern definition and oxide removed with H_3PO_4 to expose the aluminum.
REF: Walker, P & Schwartz, B — personal application, 1957

AL-0027
ETCH NAME: Nital, modified
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HNO_3
2 .... EOH
TIME:
TEMP:
ANODE: Al
CATHODE:
POWER:
DISCUSSION:
Al, single crystal specimens used in a study of twin boundaries. Solution used to polish specimens prior to preferential etching.
REF: Aust, K T — *Trans Met Soc AIME*, 221,758(1961)

AL-0022b
ETCH NAME: Nital, modified
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HNO_3
2 .... EOH
TIME:
TEMP:
ANODE: Al
CATHODE:
POWER:
ASTM: #74
DISCUSSION:
Al, single crystal specimens. Solution used to polish surfaces for a lattice vibration X-ray study.
REF: Ibid.
AL-0064a: ASTM E407-70
Reference for ASTM #74. Solution shown as: 1—5 ml HNO_3:100 ml EOH/MeOH.
AL-0108: Grooskreutz, J C & Shaw, G G — *J Appl Phys*, 35,2194(1984)
Al, (100) specimens used in a study of anodic structure on oriented surfaces. Various mixtures of Nital as HNO_3:MeOH were used.

AL-0025a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
2% .... HF
15% .... HNO_3
42% .... HCl
15% .... glycerin
TIME: 7—10 min
TEMP: 0—8°C
ANODE: Al
CATHODE:
POWER:
DISCUSSION:
Al, single crystal specimens. Solution used to electropolish surfaces.
REF: Hone, A & Pearson, E C — *Met Prog*, 53,363(1948)

AL-0006
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... 5% NaOH
x .... 50% HNO_3
TIME:
TEMP:
DISCUSSION:
Al, polycrystalline sheet. Coupons cut from sheet and used in a study of anodization. Clean surfaces with solution shown before oxidizing.
REF: Ibid.

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AL-0031
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
80 ml .... H_3PO_4
5 ml .... HNO_3
5 ml .... HAc
10 ml .... H_2O
DISCUSSION:
Al, thin film evaporation layer used in a diode metallization structure as Ni/TiN/Al on a Si, (100) substrate. After photolithographic processing for diode pattern structure and metal layer evaporation, each metal was selectively removed — aluminum with the solution shown.
REF: Martin, T L et al — *J Electron Mater*, 3,309(1984)

AL-0039b
ETCH NAME: Heat TIME:
TYPE: Thermal, preferential TEMP:
COMPOSITION:
x .... heat
DISCUSSION:
Al, (100) wafers used in a study of surface etch pits developed from concentration of vacancy clusters during vacuum thermal annealing. Surfaces were etch polished prior to thermal anneal. See AL-0039a.
REF: Ibid.
AL-0012: Pierce, J M & Thomas, T L — *Appl Phys Lett*, 39,165(1981)
Al, 0.2 μm thick thin films evaporated on Si, (100) heated substrates (360°C) pre-coated with thin film SiO_2. Evaporated aluminum film was photo resist patterned as conductors and overcoated with p-SiO_2 (BSG). After aluminum wire bonding, current was applied at different temperatures on discrete conductors and electromigration was observed as chains of single crystal aluminum crystallites.

AL-0040
ETCH NAME: Neon TIME:
TYPE: Ionized gas, preferential TEMP:
COMPOSITION: GAS FLOW:
x .... Ne^+ ions PRESSURE:
POWER:
DISCUSSION:
Al, single crystal specimens ion bombarded to develop and observe etch figures on surfaces. Other materials studied were Bi, Cd, Mg, Cu, Sn, and Zn.
REF: Yurasova, V E — *Kristallografiya*, 2,770(1957)

AL-0023c
ETCH NAME: Flick's Etch TIME: 10—20 sec
TYPE: Acid, micro-etch TEMP: RT
COMPOSITION:
(1) 10 ml .... HF (2) x .... HNO_3
5 ml .... HCl
90 ml .... H_2O
DISCUSSION:
Al, specimens and cast alloys. Solution used as a structure etch. Used HNO_3 to remove smudge remaining after etching.
REF: Ibid.

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AL-0023d
ETCH NAME: General
TYPE: Acid, micro-etch
COMPOSITION:
1 ml .... HF
199 ml .... H_2O
TIME: Dip/swab
TEMP: RT
DISCUSSION:
Al, specimens and alloys with low aluminum content. Solution used as a macro-etch by swabbing or dipping specimens.
REF: Ibid.

AL-0025b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
4% .... HF
70% .... HCl
25% .... MeOH/EOH
TIME: 7—10 min
TEMP: 0—8°C
ANODE: Al
CATHODE:
POWER:
DISCUSSION:
Al, single crystal specimens. Solution used to electropolish surfaces in solution shown.
REF: Ibid.

AL-0026
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HNO_3
x .... $NH_4F.HF$
TIME:
TEMP:
DISCUSSION:
Al, polycrystalline sheet. Coupons cut and used in a study of aluminum anodization. Clean surfaces with solution shown before oxidizing.
REF: Sharp, D J et al — *Thin Solid Films*, 111,227(1984)

AL-0034
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, polish
COMPOSITION:
1 .... 30% HCl
3 .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Al, specimens. A general electropolish for aluminum.
REF: Berglund, T & Dearden, W H — *Metallographer's Handbook of Etching*, Pitman & Sons, London, 1931

AL-0035
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
25 ml .... H_2SO_4
70 ml .... H_3PO_4
5 ml .... HNO_3
TIME: $^1/_2$—2 min
TEMP: 85°C

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DISCUSSION:

Al, specimens used in developing polished surfaces. The solution will also polish Al:Cu and Al:Si alloys.

REF: Herengue, J & Segond R — *Rev Met,* 48,262(1951) (in French)

AL-0097: Herengue, J — *Rev Alum,* 30,261(1953)

Al specimens and alloys. A discussion of chemical polishing.

AL-0036

ETCH NAME:

TYPE: Acid, cleaning

COMPOSITION:

95% .... H_3PO_4

5% .... HNO_3

TIME:

TEMP:

DISCUSSION:

Al, high purity slugs cleaned in this solution before being used to grow AlSb. After etch cleaning, rinse with in DI water.

REF: Allred, W P et al — *J Electrochem Soc,* 107,117(1960)

AL-0103

ETCH NAME: Hydrochloric acid

TYPE: Electrolytic, preferential

COMPOSITION:

x .... HCl, conc.

TIME:

TEMP:

ANODE: Al

CATHODE:

POWER:

DISCUSSION:

Al, specimens. Solution will develop etch figures.

REF: Mahl, M & Stranski, L — *Z Phys Chem,* 257,53(1942)

AL-8104

ETCH NAME: Sodium hydroxide, dilute

TYPE: Alkali, polish

COMPOSITION:

2 g .... NaOH

1000 ml .... H_2O

TIME:

TEMP: RT

RATE: 1 μm/h

DISCUSSION:

Al, cold-rolled specimens used in a study of the effect of thickness on dislocations. Solution used with agitation to produce a highly polished surface without any pitting prior to dislocation etching.

REF: Ham, R K & Wright, M G — *Phil Mag,* 9,937(1964)

AL-0105

ETCH NAME:

TYPE: Acid, preferential

COMPOSITION:

1 .... HCl

1 .... H_2O

x .... *$FeCl_3$

TIME:

TEMP:

*Saturate solution with $FeCl_3$

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DISCUSSION:
Al, (100) wafer surfaces preferentially etched in this solution.
REF: Jacquet, P — *Comp Rend*, 201,1473(1935)

AL-0050
ETCH NAME: Sodium hydroxide
TYPE: Electrolytic, removal
COMPOSITION:
x .... 2.5 *M* NaOH

TIME:
TEMP:
ANODE: Al
CATHODE:
POWER:
RATE: 0.005 mg/cm²/h

DISCUSSION:
Al:Ni specimen surface coatings produced by electrodeposition or diffusion of nickel. Solution shown used as a cleaning etch.
REF: Couch, D E & Connor, J H — *J Electrochem Soc*, 107,272(1960)

AL-0051
ETCH NAME: Carbon tetrachloride
TYPE: Solvent, removal
COMPOSITION:
x .... CCl_4

TIME:
TEMP: Boiling

DISCUSSION:
Al, specimens. A study of the reaction of carbon tetrachloride on aluminum. Aluminum reacts rapidly in concentrated CCl_4. A number of additives were used to inhibit the rate.
REF: Minford, J D et al — *J Electrochem Soc*, 106,185(1959)

AL-0058
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
15% .... HF
15% .... HCl
15% .... HNO_3, fuming
25% .... H_2O

TIME:
TEMP:

DISCUSSION:
Al, specimens. Solution used to develop etch figures. (*Note:* "Fuming" concentration and color not specified.)
REF: Tucker, C M — *Met Alloys*, 1,655(1930)

AL-0059a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
10 .... HF
46 .... HCl
15 .... HNO_3
26 .... H_2O

TIME:
TEMP:

DISCUSSION:
Al, specimens. Solution used as a preferential etch on aluminum. (*Note:* Does not specify fuming nitric acid; otherwise similar to AL-0058.)
REF: Barrett, C & Levenson, L H — *Trans Am Inst Min Met*, 137,112(1940) (England)

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AL-0041a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
10 .... H_2SO_4
90 .... H_3PO_4
TIME: 2 min
TEMP: 70°C
DISCUSSION:
Al, (001) wafers used in a study of lithium precipitation along dislocations. After polishing in this solution — coat surfaces with 0.1% Li (usually in oil), heat and bubbles will appear along dislocation lines.
REF: Murray, G T — *J Appl Phys,* 32,1014(1961)

AL-0041b
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
2 ml .... HF
50 ml .... HNO_3
32 ml .... HCl
50 ml .... MeOH
TIME: 10 sec
TEMP: 10°C
DISCUSSION:
Al, (001) wafers. Following treatment show in Al-0041a, develop dislocation density with this solution — lithium created "bubbles" vary but are about equal in number to dislocation pits — all pits were on one side of wafer and showed movement after annealing at 575°C for 9 h.
REF: Ibid.

AL-0045
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
3 .... HF
47 .... HNO_3, fuming
80 .... HCl
TIME: Seconds
TEMP: RT
DISCUSSION:
Al, (100) and other orientations used in a study of thermal etching. After thermal annealing at 460 to 610°C use solution shown as a dislocation etch. (*Note:* Red or yellow fuming, not shown.)
REF: Foss, D & Herbjornsen, O H — *Phil Mag,* 13,945(1966)
AL-0055a; Lacombe, P & Beaujard, L — *Inst Met J,* 132,1(1947—48)
Al, high purity specimens used in a study of etch figures and structure. Solution used at 10°C, $^1/_2$—1 min. If iron or other metal ions are in the HCl, it will affect controlled etching. With addition of water in the solution shown etch figures increase in number but decrease in size with water increase. The HCl produces primarily localized attack and HF uniformally dissolves aluminum.

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AL-0044
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
78 ml .... $HClO_4$
700 ml .... EOH
120 ml .... H_2O
100 ml .... butyl cellusolve
TIME: 2 min
TEMP:
ANODE: Al
CATHODE:
POWER: 25—35 V/cm^2
DISCUSSION:
Al, (1000) specimens used in a study of surface etching effects of 8 KeV Ar^+ ion bombardment. Polish surfaces with solution shown before bombardment. Specimens of zinc and gold also were studied but etched in other solutions.
REF: Cunningham, R L et al — *J Appl Phys*, 31,839(1960)

AL-0016
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
25 ml .... H_2SO_4
70 ml .... H_3PO_4
5 ml .... HNO_3
TIME: 30—120 sec
TEMP: 65°C
DISCUSSION:
Al, and aluminum alloys. Used as a general cleaning and polishing etch. See AL-0035.
REF: Tegart, W J McG — *The Electrolytic & Chemical Etching of Metals*, Pergamon Press, London, 1956

AL-0046
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
12 .... $HClO_4$
88 .... HAc
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Al, (001) wafers and other orientations. Solution used to polish specimens in a study of stress-induced desorption. Also studied molybdenum and magnesium.
REF: Fouerstein, S & John, I W — *J Appl Phys*, 40,3334(1969)

AL-0047
ETCH NAME:
TYPE: Electrolytic, thinning
COMPOSITION:
1 .... $HClO_4$
1 .... glycerol
7 .... EOH
TIME:
TEMP: 0°C (ice)
ANODE:
CATHODE:
POWER:
DISCUSSION:
Al, single crystal wafers. Specimens etch thinned in this solution for a study of electrical resistivity of dislocations.
REF: Rider, J G & Foxon, T B — *Phil Mag*, 13,289(1966)

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AL-0049
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
20 .... $HClO_4$
80 .... HAc

TIME: 1—2 h
TEMP: 20°C
ANODE:
CATHODE:
POWER: 35 V & 500 mA/cm^2

DISCUSSION:
Al, single crystal specimens. Polish surfaces in this solution. Specimens were subjected to various environments in a study of surface etch pit development.
REF: Kasen, M K et al — *Phil Mag*, 13,453(1966)

AL-0048
ETCH NAME: Jacquet's etch
TYPE: Electrolytic, removal
COMPOSITION:
345 ml .... $HClO_4$
655 ml .... HAc

TIME: 30 min
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Al, single crystal specimens cut from an ingot that was slow cooled. Specimens were polished in this solution with a removal of about 30 μm per side. Used in a dislocation density study as related to slow cooling.
REF: Nes, E & Nost, B — *Phil Mag*, 13,855(1966)

AL-0026
ETCH NAME: Air
TYPE: Gas, oxidation
COMPOSITION:
x .... air

TIME: 15—48 h
TEMP: 550°C

DISCUSSION:
Al, single crystal sphere. Sphere electropolished prior to oxidation. No change in 15 h sitting in air; faint patterns after 48 h of oxidation. Developed foggy pole figures at axial points of (100); (110) and least on (111).
REF: Gwathmey, A T et al — *Mater Advisory Comm Aeronaut Tech Notes* #1460(1948)
AL-0050: Bedair, S M et al — *J Appl Phys*, 39,4026(1968)
Al, (100) wafers used in a study of oxidation. Forms an amorphous oxide film below 600°C. Above 600°C film becomes crystalline Al_2O_3.
AL-0052: Bond, H E & Harvey, K B — *J Appl Phys*, 34,440(1963)
Al, specimens. Work was done with synthetic sapphire that was polished on a maple lap with diamond dust in oil. With 1% by weight ZrO_2 in the material, dislocations are seen on the (0001) basal plane. Oxide growth on aluminum can cause subsurface damage and pitting where O_2 moves to the Al_2O_3/Al interface pitting the metallic aluminum.

AL-0053
ETCH NAME: Boron trichloride
TYPE: Gas, selective (RIE)
COMPOSITION:
x .... BCl_3

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Al, thin films deposited on GaAs, (100) wafer substrates. Layered structures were: (1) Al/Ni/SiO_2 or (2) Al/Ni/SiN_x. Surfaces were photo resist processed for patterning to include

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via-holes through the gallium arsenide in fabricating monomicrowave ICs. Both BCl_3 and CF_4:O_2 were used for removal of aluminum. Removal of nickel referred to as a nickel lift-off technique.
REF: Gelsgberger, A E & Claytor, P R — *J Vac Sci Technol*, A(3),863(1985)

AL-0054
ETCH NAME: Boron tribromide
TYPE: Gas, removal (RIE)
COMPOSITION:
x .... BBr_3

TIME:
TEMP:
GAS FLOW: 40 cc
PRESSURE:
POWER: 125 W

DISCUSSION:
Al, and Al_2O_3/AlN thin films. The oxide was formed by anodization of aluminum deposited on SST plates or aluminum evaporated on silicon (100) wafers containing an SiO_2 thin film: Al/SiO_2/Si(100) structure, which was given a 1 min treatment in nitrogen prior to and after BBr_3 etching. RIE ionized gas etching used in studying etch reactions of aluminum oxide, aluminum nitride and aluminum.
REF: Landaner, A & Hess, D W — *J Vac Sci Technol*, A(3),962(1985)
AL-0056: Jacquet, P — *Met Corros*, 18,198(1943)
Al, specimens. A polish etch for aluminum. Use at 22—25 V and 0.8—2.5 A/cm^2 or 3—4 A/cm^2. Agitate during etching to prevent irregularities developing as the degree of polish affects development of etch figures. Should be preferentially etched immediately after cleaning surfaces to prevent growth of aluminum oxide and its masking effects.
AL-0059b: Ibid.
Al, specimens. By raising the current of this solution toward the end of the etch period both aluminum and copper can be etched.

AL-0076
ETCH NAME: Abrasive
TYPE: Abrasive, polish
COMPOSITION:
x .... abrasive, paper

TIME: 30—60 min
TEMP: RT

DISCUSSION:
Al, specimens and alloys. Mechanical polish of specimens for metallographic study. Cement an abrasive cloth in a bowl and use an electromagnet for vibration. (*Note:* This is similar to sphere grinding methods using a cylinder "race track" with nitrogen gas as the movement agent against abrasive paper.)
REF: Krill, F M — *Met Abstr*, 8,641(1958)
AL-0080: Krill, F M — *Met Prog*, 700,81(1956)
Al, specimens and alloys, similar work as in AL-0076.

AL-0077
ETCH NAME:
TYPE: Acid, machining
COMPOSITION:
4 mg .... NaOH
1000 ml .... H_2O
200 ml .... glycerin

TIME:
TEMP:

DISCUSSION:
Al, specimens. A method of chem/mech etching and forming parts. System has an abrasive wheel above an etch tank with wheel working-edge vertical. Specimen is held against the wheel as it is rotated through the etch solution in the tank below. (*Note:* This is

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similar to using a grinding wheel with a liquid coolant.)
REF: Fegredo, D M & Greenough, O B — *J Inst Met*, 87,1(1958—59)
AL-0078: Yamamoto, M & Watanabe, J — *Sci Rep Res Inst Tohoku Univ Ser. A*, 8,230(1956)
Al, specimens. A report on acid saw cutting of materials.

AL-0081
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
2 .... HF
3 .... HNO_3
9 .... HCl
5 .... H_2O
TIME: 15 sec
TEMP: RT
DISCUSSION:
Al material used as the metal source in growing AlGaAsP single crystals. Aluminum was cleaned in the solution shown before melting with GaAs, GaP, and GaAsP material to produce aluminum doped single crystal ingots.
REF: Fujimoto, A — *Jpn J Appl Phys*, 22,109(1984)

AL-0082a
ETCH NAME: BRM
TYPE: Halogen, removal
COMPOSITION:
x .... 10% Br_2
x .... MeOH
TIME:
TEMP: Warm
DISCUSSION:
Al foil with an Al_2O_3 thin film grown in a solution of 40% $NH_4B_5O_8.4H_2O$:60% ethylene glycol at RT. The BRM solution was used to dissolve the foil leaving oxide flakes. The oxide also was stripped from foil with 5% H_3PO_4:3%CrO_3 (ALO-0020). Aluminum foil was used in a study of AC etching.
REF: Dyer, C K & Alwitt, R S — *J Electrochem Soc*, 128,300(1981)

AL-0082b
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, preferential
COMPOSITION:
x .... 1 *M* HCl
TIME:
TEMP: 60°C
ANODE: Al
CATHODE: Carbon w/25 mA/cm^2 + 5 Hz sinusoidal current applied
POWER: rms 700 mA/cm^2
DISCUSSION:
Al, foil used in a study of change with AC etching. The solution produces a high density of cubic pits. After etching, rinse in DI water, then MeOH. Pre-treat foil before electrolytic etching with x%NaOH, 10 min and follow with heavy water rinse.
REF: Ibid.

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AL-0083a-b
ETCH NAME:
TYPE: Acid, cutting
COMPOSITION:
(1) 200 ml .... HCl
50 g .... $FeCl_3$
250 ml .... H_2O
(2) 1 .... HNO_3
1 .... H_2O
TIME: 40 min
TEMP: RT
DISCUSSION:
Al, specimens $^1/_8$" thick. Terylene thread soaked in solution (1) used to cut aluminum, brass, and copper. Solution (2) used to cut tin and zinc. (*Note:* Excellent review of metal growth methods.)
REF: Honeycombe, R W K — *Met Rev*, 4,1(1959)

AL-0019b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) x .... H_3PO_4
x .... HNO_3
x .... HAc
(2) x .... x% KOH
x .... $K_3Fe(CN)_6$
x .... $K_2B_4O_7.4H_2O$
TIME:
TEMP:
DISCUSSION:
Al thin film on (100) silicon wafers. Solutions used for pattern etching aluminum with photolithography. Solution (1) will cause COP type photo resists to lift; solution (2) will not affect the resist.
REF: Reynolds, R — *J Vac Sci Technol*, 15,962(1978)

AL-0089
ETCH NAME: RIE
TYPE: Gas, removal
COMPOSITION:
(1) x .... $SiCl_4$
(2) x .... $SiCl_4/O_2$
(3) x .... $BaCl_3/O_2$
(4) x .... O_2
TIME:
TEMP:
GAS FLOW: 24 SCCM
PRESSURE: 75 mTorr (10 Pa)
ANODE:
CATHODE: −180 V
POWER: 0.26 W/cm²
DISCUSSION:
Al thin films deposited on silicon substrates using tungsten as an evaporation film mask. A study of sputter etching of aluminum thin films. Gas mixtures (2) and (3) with O_2 plasma develop SiO_2 films as does pure O_2 (4). Etch rate of the SiO_2 and W films are approximately equal. $SiCl_4$ etch rate was 700 Å/min for aluminum.
REF: Degenkolb, E O — *J Electrochem Soc*, 129,1150(1982)

AL-0088
ETCH NAME: Acetone
TYPE: Ketone, lift-off
COMPOSITION:
x .... CH_3COCH_3
TIME: Variable
TEMP: RT to warm
DISCUSSION:
Al thin films evaporated on glass substrates for four different thicknesses as step-evaporation through photo resist mask patterns. A study of aluminum structure and reactions.

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Acetone used to lift-off excess aluminum and photo resist after evaporation.
REF: Mizuno, K — *J Phys Soc Jpn*, 4,1434(1984)

AL-0092
ETCH NAME:
TYPE: Gas, removal
COMPOSITION:
(1) x .... Br_2 (2) x .... Cl_2 (3) x .... CCl_4 (4) x .... CBr_4
DISCUSSION:
Al thin films evaporated on quartz substrates in a study of etching aluminum thin films by E-beam sputter in ultra high vacuum (UHV).
REF: Park, S et al — *J Vac Sci Technol*, A(2),790(1985)

TIME:
TEMP:

AL-0087
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
DISCUSSION:
Al as high purity, dislocation free specimens used in a general study of such material. Solution used not shown.
REF: Howe, S & Elbaum, C — *J Appl Phys*, 32,742(1961)
AL-0090: Elbaum, C — *J Appl Phys*, 31,1413(1960)
Reference for electropolish solution used in AL-0087.

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

AL-0091
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
DISCUSSION:
Al specimens chemically etch thinned for study of dislocations by transmission electron microscopy (TEM). Thinning solution not shown.
REF: Robinson, D L — *J Appl Phys*, 29,1635(1958)

TIME:
TEMP:

AL-0093
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... 0.2 *M* NaOH
\+ .... light
DISCUSSION:
Al thin films evaporated on SiO_2, Al_2O_3 and ZrO_2 substrates in a study of surface protection against chemical attack. Also studied silver thin films, TiN, Si:H and PbS. Silver thin films removed with 1 *M* HNO_3 + light.
REF: Martin, P J et al — *J Vac Sci Technol*, A(2),341(1984)

TIME:
TEMP:

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AL-0094
ETCH NAME:
TYPE: Electrolytic, selective
COMPOSITION:
6.4 g .... KI
0.32/l .... MeOH

TIME: 30 sec
TEMP:
ANODE: Al
CATHODE: Al
POWER: 0.3 A/mm^2 & 30 V

DISCUSSION:
Al alloys as sheet, plate and rod used in a study of precipitates in the material (alloys #3003, #5182, #2124, #7475). Prepare surfaces by lap polish using 1 μm diamond paste, then selectively etch to expose precipitates for SEM or TEM observation. In alloy #5182, dispersoids were Mn and Mg_2Si; in #2124, Al_2CoMg; in #7475, Cr.
REF: Hower, J — *Metallography (MEIJAP)*, 15,247(1983)

AL-0095
ETCH NAME: Water
TYPE: Acid, float-off
COMPOSITION:
x .... H_2O

TIME:
TEMP: RT

DISCUSSION:
Al, evaporated on KCl, (100) and (111) cleaved substrates as oriented thin films. Some films were converted to AlN by N^+ ion implantation. Al on (111) KCl was hexagonal wurtzite (fcc) structure; on (100) was cubic (100). Water was used to liquefy the KCl/Al interface for film float-off and study by TEM. (*Note:* AlN is hexagonal system.)
REF: Kimura, K et al — *Jpn J Appl Phys*, 23,1145(1984)

AL-0096
ETCH NAME:
TYPE: Mechanical, deformation
COMPOSITION:
x .... pressure

TIME:
TEMP:

DISCUSSION:
Al specimens used in a study of surface deformation in aluminum due to fatigue.
REF: Grooskreutz, J C & Gosselin, C M — *J Appl Phys*, 31,1127(1960)

AL-0098
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, forming
COMPOSITION:
x .... HCl

TIME:
TEMP: Elevated
ANODE:
CATHODE: Pb
POWER:

DISCUSSION:
Al specimens as Al:Si(20%) alloyed with the following metals: Na, Mg, Zn, Cr, Mn, Cu, Cd, Sn, Pb, Sb, Bi, Fe, Ni, and Co. Specimens were electrolyzed in HCl to form single crystal silicon in the anodic slime. Three silicon crystal structures were obtained: (1) with Na, as (111) and (100) granules; (2) with Mg or Mn, as prismatic crystals (111) and (110): and (3) as plate-like (111) with negative (111) predominate with all other metal additives. A study of the crystal structure of silicon in aluminum-silicon alloys. (*Note:* Pure aluminum alloyed into silicon to form p-n junctions produces an Al:Si mixture containing needle to blade-like silicon elements in a fine grained aluminum matrix.)
REF: Obinata, I & Komatso, N — *Metall Abstr*, 8,94(1958)

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AL-0100a
ETCH NAME: Abrasives
TYPE: Mineral, polish
TIME:
TEMP: RT
COMPOSITION:
x .... Al_2O_3, powder
x .... H_2O
DISCUSSION:

Al, and alloys. Solution for general cleaning and polishing. Alumina, as fine ground powder in a water slurry with or without glycerin: (1) as sub-micron grits, Linde A and B; or (2) as alumina in a colloidal suspension of water. With addition of a 1—5% KOH solution these become an acid slurry, and slurry particles of alumina slowly reduce to a fine paste during use. Linde abrasives used with and without KOH for aluminum parts surface cleaning and polishing. Both colloidal alumina and silica for fine surface polishing. Used on aluminum and aluminum alloy specimens in material studies and in cleaning vacuum parts.
REF: Walker, P & Menth, M — Studies/Vacuum Parts (1981—1985)

AL-0101b
ETCH NAME: Water
TYPE: Acid, oxidation
TIME:
TEMP: Hot to boiling
COMPOSITION:
x .... H_2O
DISCUSSION:

Al specimens. DI water used to form a hydrated oxide on aluminum, then remove with HF or BHF solution for surface cleaning. Used in preparing aluminum slugs prior to use in metal evaporation, and for general parts cleaning of aluminum and aluminum alloys.
REF: Ibid.

ALUMINUM ALLOYS, AlM

General: Aluminum does not form metal alloys in nature and does not occur as a native element, although there are well over 200 single crystal minerals containing aluminum as oxides, silicates, phosphates, and sulfates. There also are mineral hydrates.

As artificial aluminum alloys, in the general formula shown above, M = Au, Ag, Be, Zn, and other metal elements. Pure aluminum is soft, like pure copper and gold, such that it is not used as the pure metal for construction parts. Several alloys have specific names, such as aluminum-silicon #43 (5% Si); magalum, with 10% Mg; and there are "zeppelin" braces, angles and channels containing small percentages of Si, Fe, Sn, Mn, and Zn. Beryllium-aluminum, containing 38% Be is one of the lightest known alloys with a density (lb/in^3) of 0.075 g/cm^3 as compared to pure beryllium, 0.067 g/cm^3, and pure aluminum, 0.98 g/cm^3. Aluminum-bronze is another type of alloy. There are both high temperature aluminum brazing alloys and low temperature solders. It is worth noting that aluminum oxide is very difficult to braze or alloy itself, due to the presence of the inert oxide layer that is always present on surfaces after being exposed to air.

Technical Application: Both pure aluminum and aluminum-silicon(5%) are used as a p-type dopant sources on silicon, and evaporated contact pads are still in use for alloyed silicon diodes and transistor devices, such as the silicon Sphere Alloy Zener process that uses Al:Si(5%) pellets. Silicon SCRs, when fabricated with an aluminum pre-form, use aluminum contact wires. Al:Be(38%) has been used as an evaporated electrode on quartz crystal frequency blanks to reduce mass loading effects. Al_x:Au_y alloys produce "purple plague", as a brittle compound that will eventually break and destroy electrical continuity in devices, although it is used as a purple gold alloy for jewelry.

Aluminum alloy materials are basic construction elements in much Solid State processing equipment — electrical transfer plates; cooling plates; lapping plates; high power feed-thrus

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in vacuum systems; RF shielding; test blocks and many other similar applications. In combination with other metals and ceramics, as package material for discrete devices as well as circuit assemblies for both minimum weight and radiation protection. There are several aluminum alloy semiconductor compounds, such as aluminum arsenide, AlAs; aluminum antimonide, AlSb; and aluminum phosphide, AlP. In addition to compound semiconductors, several other aluminum alloys have been grown as single crystals for general morphological study, such as Al:Au, Al:Ag, Al:Cu, Al:Ni, Al:Zn etc.

Etching: Soluble in HCl, H_2SO_4, alkalies, and mixed acids.

ALUMINUM ALLOYS

ALUMINUM:BERYLLIUM ETCHANTS

ALBE-0001
ETCH NAME: Potassium hydroxide — TIME: 2—3 min
TYPE: Alkali, cleaning — TEMP: 30—40°C (warm)
COMPOSITION:
x .... 30% KOH (NaOH)
DISCUSSION:
Al:Be(38%), as 0.060 diameter polycrystalline wire. Wire was etch cleaned in this solution followed by heavy water washing and drying under an IR heat lamp prior to use as an evaporation source for metal contact electrodes on quartz radio frequency crystals. Evaporation was done with "U" shaped clips of wire hung on tungsten coils and, after evaporation, the system was pumped to the 10^{-7} Torr range for 20—30 min before opening the bell jar to eliminate beryllium vapors. Material was used in evaluating improved frequency stability and levels due to reduced mass loading effects.
REF: Walker, P — personal development, 1969

ALUMINUM:CERIUM ETCHANTS

ALCE-0001
ETCH NAME: Potassium hydroxide — TIME:
TYPE: Alkali, removal — TEMP: Hot
COMPOSITION:
x .... 30% KOH
DISCUSSION:
$CeAl_3$ single crystals grown by arc melting and aging at temperature. Used in a material growth study. Also developed $CeCu_6$ and $LaCu_6$. Growth was as Czochralski (CZ) ingots. Included studies on CeB_6 and $CeCu_2Si_2$. No etch shown. (*Note:* Solution shown is for general aluminum alloy etching.)
REF: Onuki, Y et al — *J Phys Soc Jpn*, 4,1210(1984)

ALUMINUM:COPPER ETCHANTS

ALCU-0001a
ETCH NAME: Sodium hydroxide — TIME: 30 min
TYPE: Alkali, removal — TEMP:
COMPOSITION:
x .... 10% NaOH
DISCUSSION:
Al:Cu, single crystal specimens used in a study of particle dispersion due to hardening. After lap/polish of surfaces, specimens were etched in this solution to remove work damage.

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Keller's reagent also was used as the etch.
REF: Dew-Hughes, D & Robertson, W D — *Acta Metall,* 8,147(1960)

ALCU-0002
ETCH NAME:
TYPE: Acid, macro-polish
COMPOSITION:
5 .... HNO_3
15 .... CH_3COOH (HAc)
80 .... H_3PO_4
TIME:
TEMP: Boiling
DISCUSSION:
Al:Cu, single crystal specimens used in a study of the mechanisms of hardening and aging. The solution will polish surfaces and develop slip lines.
REF: Dew-Hughes, D & Robertson, W D — *Acta Metall,* 8,156(1960)

ALCU-0003
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
25 ml .... H_2SO_4
70 ml .... H_3PO_4
5 ml .... HNO_3
TIME: 30 sec to 2 min
TEMP: 85°C
DISCUSSION:
Al:Cu alloy specimens. Used as a polish etch on Al:Cu; Al:Si, and Al.
REF: Heregue, J & Segond, R — *Rev Metall,* 48,262(1951) (in French)

ALCU-0001b
ETCH NAME: Keller's reagent
TYPE: Acid, removal/polish
COMPOSITION:
2 ml .... HF
3 ml .... HCl
5 ml .... HNO_3
190 ml .... H_2O
TIME:
TEMP:
ASTM: #3
DISCUSSION:
Al:Cu, single crystal specimens used in a study of particulate dispersion in hardening. Solution used to remove work damage after mechanical lap and polish.
REF: Ibid.
ALCU-0004: ASTM E407-70
Reference for ASTM number for Keller's reagent.

ALUMINUM:GOLD ETCHANTS

ALAU-0001
ETCH NAME:
TYPE: Electrolytic, structure
COMPOSITION:
x .... $HClO_4$
x .... EOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Al:Au(2%) specimens. Solution used to develop precipitates in this alloy. Before electrolytic etching, remove native oxide with etch solution shown under ALO-0014 under

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Aluminum Oxide Etchants. Also refers to "Lenore's Solution" referencing Thomas, O — *Transmission Electron-Microscopy of Metals*, John Wiley & Sons, New York, 1962, 161 (*Note:* This alloy is a form of purple gold used in the jewelry trade.)
REF: Von Heimendahl, M — *Acta Metall*, 15,1441(1967)

ALAU-0002
ETCH NAME: Aqua regia, dilute
TYPE: Acid, removal
COMPOSITION:
3 .... HCl
1 .... HNO_3
10 .... H_2O
TIME:
TEMP: RT
DISCUSSION:
Al:Au, alloy reaction product observed on the side-walls of high power silicon diodes that had been aluminum evaporated and gold evaporated on opposed wafer surfaces prior to dicing. Reaction appeared after power burn-in as a failure mode, e.g., "purple plague". Solution was used in a series of short-period etch-steps in the initial studies of these brittle compounds. This was the initial observation of this failure mode.
REF: Walker, P — personal application, 1958
ALAU-0003: Bernstein, L — personal communication, 1958
Al:Au thin films with various single crystal structures or as amorphous reactive films. Additional study of purple plague and effects on device failure. Several articles written on this subject (1959—1962).

ALUMINUM:NICKEL ETCHANTS

ALNI-0001a
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... 2.5 *M* NaOH
TIME:
TEMP:
RATE: 0.005 mg/cm²/h
DISCUSSION:
Al:Ni, alloy thin films deposited by electrodeposition or by nickel diffusion into aluminum. Solution used for general removal.
REF: Cough, D E & Connor, J H — *J Electrochem Soc*, 107,272(1960)

ALNI-0001b
ETCH NAME:
TYPE: Fused salt, removal
COMPOSITION:
400 g .... NaCl
560 g .... KCl
150 g .... Na_3AlF_6 (Cryolite)
TIME:
TEMP: 700—800°C
ANODE: Graphite
CATHODE:
POWER: 2—10 A/cm²
DISCUSSION:
Al:Ni, alloy thin films. A form of molten flux etching and cleaning of high temperature melting point metals and alloys. Cryolite, Na_3AlF_6, is a natural mineral used in processing aluminum ore as a primary reducing flux.
REF: Ibid.

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ALNI-0001c
ETCH NAME:
TYPE: Fused salt, removal
COMPOSITION:
99 g .... $AlCl_3$
200 g .... NaCl
TIME:
TEMP: 160—180°C
ANODE: Carbon or tungsten
CATHODE:
POWER: 1—4 A/cm²
DISCUSSION:
Al:Ni, alloy thin film coatings. Crucible and cover were Pyrex, rather than graphite as in ALNI-0001a. Method used to etch the alloy.
REF: Ibid.

ALNI-0002
ETCH NAME:
TYPE: Acid, defect
COMPOSITION:
x .... 10% $HClO_4$
x .... butyl cellusolve
TIME:
TEMP: 5°C
DISCUSSION:
$AlNi_2$, single crystal specimens used in a study of phase change with recrystallization. Solution used to develop structure.
REF: Calvagrac, Y & Fayard, M — *Acta Metall*, 14,783(1966) (in French)

ALUMINUM:SILICON ETCHANTS

ALSI-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
(1) 1 .... HCl
1 .... H_2O
(2) 1 .... HCl
10 .... H_2O
TIME: 10—30 sec
TEMP: RT
DISCUSSION:
Al:Si(5%), foil pre-form and spherical pellets. Both solutions have been used to clean parts before furnace alloying of silicon (111) wafers in a hydrogen atmosphere or in forming gas (85% N_2/15% H_2). The alloy produces less stress in the silicon than pure aluminum and reduces the formation of dislocations along the alloy front. Solution (2) preferred for light cleaning after alloying.
REF: Walker, P — personal application, 1966

ALSI-0002
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
25 ml .... H_3PO_4
70 ml .... H_2SO_4
5 ml .... HNO_3
TIME: 30 sec to 2 min
TEMP: 85°C
DISCUSSION:
Al:Si specimens. Solution used as a polish etch on Al:Si, Al:Cu, and pure aluminum.
REF: Heregue, J & Segond, R — *Rev Met*, 48,262(1951) (in French)

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ALSI-0003
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
5 .... HCl
10 .... HNO_3
84 .... H_2O
TIME:
TEMP:
DISCUSSION:

Al:Si, as an alloy solid solution. Solution used to study the orientation re-growth of silicon in the aluminum-rich solid. Silicon showed a preferred precipitate (111) and (100) orientation.
REF: Rosenbaum, H S et al — *Acta Metall*, 7,678(1959)

ALSI-0004
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... HF
3 .... HNO_3
50 .... HAc
TIME:
TEMP: RT
DISCUSSION:

Al:Si, alloy re-growth p-n junctions in n-type silicon wafers, 3—10 Ω cm resistivity. After aluminum evaporation and alloying into emitter and collector etched pits, excess aluminum was hand-lap removed to define circular pit areas. The silicon wafer or individual die were etched with the solution shown to remove aluminum and expose the internal alloy front in a study of spiking defects in the bulk silicon caused by aluminum alloying.
REF: Walker, P & Waters, W P — device development, 1957

ALSI-0005
ETCH NAME: Hydrofluoric acid
TYPE: Acid, micro-etch
COMPOSITION:
x .... 0.5% HF
TIME:
TEMP: RT
DISCUSSION:

Al:Si(12%) alloy subjected to different processing modifications. Solution was used to develop the various structure alterations observed.
REF: A/B *Met Dig*, 21(2),19(1983) — Buehler Ltd
ALSI-0007: Hume-Rothery, W — *Inst Met Proc*, 46,239(1931)
Al:Si material. A general study of macro-etching of alloys.

ALSI-0006
ETCH NAME: RF plasma
TYPE: Ionized gas, selective removal
COMPOSITION:
x .... CF_4
x .... O_2
TIME:
TEMP:
GAS FLOW:
PRESSURE: 1.7 Pa (Argon)
POWER: 0.5 W/cm²
RATE: 100 A/min @ 200°C
DISCUSSION:

AlSi, thin film layers as interconnects on silicon devices along with phosphorus doped silicon dioxide [(PSG) phosphorus silica glass]; p-SiN and AlSiCu as multilayer structures.

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RF plasma etching was used in multilevel structuring of these electrical interconnects.
REF: Kotani, H et al — *J Electrochem Soc*, 130,645(1983)

ALSI-0001b
ETCH NAME: Hydrogen
TYPE: Gas, cleaning
COMPOSITION:
x .... H_2
DISCUSSION:
AlSi(5%) spheres .010 diameter used to fabricate Sphere Alloy Zener diodes. The silicon wafers were held in a graphite assembly for furnace alloying, and the spheres were hydrogen fired as a cleaning step immediately before alloying. After alloying, individual diodes in a hexagonal array were measured for leakage current and plotted to determine segregation and defect areas in the silicon wafer. Results used to improve Float Zone (FZ) ingot growth of zener material.
REF: Ibid.

TIME:
TEMP: 500°C

ALSI-0001c
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... HF
10 .... HNO_3
5 .... H_2O
DISCUSSION:
Si, (111) wafers used to alloy Al:Si(5%), .010 diameter spheres as Sphere Alloy Zener diodes. After alloying, prior to testing and dicing, wafers were lightly etched in the solution shown to optimize electrical parameters.
REF: Ibid.

TIME: 2—3 sec
TEMP: RT

ALSI-0001d
ETCH NAME: Forming gas
TYPE: Gas, alloying
COMPOSITION:
x .... 85% N_2
x .... 15% H_2
DISCUSSION:
Al:Si(5%) and "quad-alloy" (Al:Si:Ag:In) flat preforms about 10 mil thick used in assembly of silicon SCRs. Belt furnace used to alloy pre-forms to moly discs prior to alloying SCR wafers. Both forming gas (FG) and pure hydrogen were used with a graphite heater strip to strip/remove remaining metal alloy from moly discs for re-use of discs.
REF: Ibid (1974)

TIME:
TEMP: 800°C

ALUMINUM:SILVER ETCHANTS

ALAG-0001
ETCH NAME:
TYPE: Alkali/acid, removal
COMPOSITION:
(1) x .... 3 *N* NaOH
(2) x .... HNO_3

TIME:
TEMP:

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DISCUSSION:

Al:Ag, as both polycrystalline and single crystal ingots. Wafers were cut and lapped, then etched in solution (1), followed by washing in solution (2). The material was used in a study of precipitates in cold-worked specimens. Both Al:Ag and Al:Zn alloys were studied.
REF: Jan, J P — *J Appl Phys*, 26,1291(1955)

ALUMINUM:ZINC ETCHANTS

ALZN-0001
ETCH NAME:
TYPE: Alkali/acid, removal
COMPOSITION:
(1) x .... 3 *N* NaOH
(2) x .... HNO_3
TIME:
TEMP:
DISCUSSION:

Al:Zn, as both polycrystalline and single crystal ingots. Wafers were cut and lapped, then etched in solution (1), followed by washing in solution (2). The material was used in a study of precipitates in cold-worked specimens. Both Al:Ag and Al:Zn alloys were studied.
REF: Jan, J P — *J Appl Phys*, 26,1291(1955)

ALZN-0002
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
3% .... $HClO_4$
30% .... butoxyethanol
5% .... MeOH
TIME:
TEMP: 30°C
ANODE: Al:Zn
CATHODE:
POWER: 25 V
DISCUSSION:

Al:Zn(10%), alloy sheet. Blanks were punched from sheet and then annealed. A twin-jet system was used to electropolish specimens.
REF: Nicholls, A W & Jones, L P — *J Phys Chem Solids*, 44,696(1983)

ALUMINUM:ZINC:COPPER ETCHANTS

AZC-0001
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:

Al:Zn,Cu, alloy specimens were homogenized by annealing and aging. Cubic shaped spiral etch patterns observed parallel to the cubic axis after thermal annealing. (*Note:* The z-axis direction as ⟨001⟩.)
REF: Bulnov, W N & Shehegolrva, T V — *Fiz Metalloved*, 5,566(1957)

ALUMINUM IRON ETCHANTS

ALFE-0001
ETCH NAME:
TYPE: Solvent, cleaning
COMPOSITION:
80 .... acetone
20 .... toluene
TIME:
TEMP:

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DISCUSSION:

AlFe alloy specimens used for selective oxidation. Degrease specimens in solution shown before oxidizing.

REF: Grace, R E & Seybolt, A U — *J Electrochem Soc,* 106,582(1958)

PHYSICAL PROPERTIES OF ALUMINUM ANTIMONIDE, AlSb

Classification	Antimonide
Atomic numbers	13 & 51
Atomic weight	148.73
Melting point (°C)	600—700
Boiling point (°C)	
Density (g/cm^3)	4.67
Hardness (Mohs — scratch)	3—4
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Silver grey
Cleavage (dodecahedral)	(110)

ALUMINUM ANTIMONIDE, AlSb

General: Does not occur as a natural compound, although there are other metal antimonides of copper, nickel, and silver as mineral species, as well as mixed metal antimonides. There is no application of the compound in the metal industries, at the present time, but some use in the fabrication of glass and silicates.

Technical Application: The material is a III—V compound semiconductor that has been grown by the Horizontal Bridgman (HB), and Czochralski (CZ) methods. Like the arsenide, the antimonide oxidizes readily when exposed to moisture in air. Both materials are processed and held under liquid solvents or in inert gas atmospheres to prevent oxidation. It also has been deposited as a thin film layer by CVD. As a thin film layer element of a device, it has been fabricated as solar cells.

Etching: Mixed acids of HF:HNO_3, HF:H_2O_2, and HCl:HNO_3.

ALUMINUM ANTIMONIDE ETCHANTS

ALSB-0001a

ETCH NAME: TIME:

TYPE: Acid, polish TEMP:

COMPOSITION:

x .... H_2O_2

DISCUSSION:

AlSb as cut wafers. All processing and handling of aluminum antimonide should be under an inert, dry atmosphere such as argon or nitrogen, as this compound is attacked by atmospheric moisture. Mechanical lap and polish with abrasive slurry under oil. Etch polish with the solution shown.

REF: Herczog, A et al — *J Electrochem Soc,* 105,533(1958)

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ALSB-0001b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... CH_3COOH (HAc)
DISCUSSION:
AlSb as cut wafers. Solution used to polish wafers. See additional discussion under ALSB-0001a.
REF: Ibid.

ALSB-0002a
ETCH NAME: TIME: 1 min
TYPE: Acid, polish TEMP: RT
COMPOSITION:
4 .... HCl
4 .... HNO_3
1 .... H-tartaric acid
DISCUSSION:
AlSb wafers. Used as a polish etch in studying copper diffusion in aluminum antimonide. Follow etching with a 2—3 sec dip in 1HCl:1HNO_3 to remove smut residue left on surfaces after etching.
REF: Wieber, R H et al — *J Appl Phys*, 31,600(1960)

ALSB-0003
ETCH NAME: TIME: 5 min
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HNO_3
1 .... HCl
DISCUSSION:
AlSb wafers. Wafers were mechanically lapped with $303^1/_2$ abrasive grit on an iron lap with kerosene as the liquid carrier, before etch polishing with the solution shown. Material used in a study of elastic constants.
REF: Bulef, D I & Menes, M — *J Appl Phys*, 31,46(1960)
ALSB-0002b: Wieber, E H — *J Appl Phys*, 31,608(1960)
AlSb, wafers used in a study of copper diffusion in the material. Solution used at RT, 2—3 sec as a final cleaning/polish etch.

ALSB-0001c
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
AlSb wafers. Various concentrations of HF and HNO_3 are polish solutions for this material. See additional discussion under ALSB-0001a.
REF: Ibid.

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ALSB-0006
ETCH NAME: TIME:
TYPE: Acid, macro-etch TEMP:
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
AlSb wafers. The referenced author describes this as a macro-etch of aluminum antimonide (See Bulef & Menes ALSB-0003). Fibers of Al_3Ta, 1—5 μm in diameter, were observed in the AlSb after etching as Al_3Ta is insoluble in this etch solution. Under high magnification the surface etch pits are similar to those observed in other compound semiconductors.
REF: Gorton, H C — *J Electrochem Soc,* 107,248(1960)

ALSB-0007
ETCH NAME: TIME:
TYPE: Acid, stain TEMP:
COMPOSITION:
10 g .... $FeCl_3$
100 ml .... HCl
1000 ml .... H_2O
DISCUSSION:
AlSb/GaSb wafers from an ingot grown as a solid solution alloy single crystal. Wafers were lapped mechanically under anhydrous benzene. The acid solution shown was used to etch stain surfaces in a structure study.
REF: Miller, J F et al — *J Electrochem Soc,* 107,527(1960)

ALSB-0008a-b
ETCH NAME: TIME: (1) 1 min (2) 2 sec
TYPE: Acid, preferential TEMP: (1) 25°C (RT) (2) 25°C (RT)
COMPOSITION:
(1) 1 .... HF
1 .... H_2O_2
1 .... H_2O
(2) 1 .... HNO_3
1 .... HCl
DISCUSSION:
AlSb, (111) wafers. Solutions used for preferential etching to develop etch pits and other structures in a general study of aluminum antimonide growth structures. Rotation of tetrahedral etch pits show polarity between (111)A and $(\bar{1}\bar{1}\bar{1})$B surfaces of wafers.
REF: Gatos, H C & Lavine, M C — *J Electrochem Soc,* 107,427(1960)

ALSO-0009
ETCH NAME: TIME:
TYPE: Acid, polish/removal TEMP:
COMPOSITION:
1 .... HNO_3
1 .... HCl
DISCUSSION:
AlSb wafers, as grown p-n junction diodes. Etch was used to develop dendritic filaments of Al_3Te_2 (?). Filaments were 1—5 μm long and parallel to the growth direction of the ingot. (See ALSB-0003).
REF: Gorton, H C — *J Electrochem Soc,* 107,248(1960)

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ALSB-0010a-b
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) 95% .... H_3PO_4
5% .... HNO_3

TIME:
TEMP:

(2) 30 .... HF
50 .... HNO_3
30 .... HAc
0.5 .... Br_2

DISCUSSION:
AlSb, ingot material preparation. Both solutions used to remove oxides and for general cleaning. Solution (1) used on aluminum: solution (2) (CP4) on antimony. Both materials rinsed in DI water after etching prior to mixing for ingot growth.
REF: Allred, W P et al — *J Electrochem Soc*, 107,117(1960)

PHYSICAL PROPERTIES OF ALUMINUM ARSENIDE, AlAs

Classification	Arsenide
Atomic numbers	13 & 33
Atomic weight	100.98
Melting point (°C)	800—900
Boiling point (°C)	
Density (g/cm)	
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Grey silver
Cleavage (dodecahedral)	(110)

ALUMINUM ARSENIDE, AlAs

General: Does not occur as a natural compound, although there are four minerals as arsenates of aluminum with iron, manganese, or copper, all of which are hydrated. There are natural mineral arsenides of bismuth, cobalt, copper, iron, nickel, and platinum. There is no use of the compound in the metal industries though as an artificial compound or as the individual elements they are used as additives in the glass industry.

Technical Application: The material is a III—V compound semiconductor, and has been grown by the Horizontal Bridgman (HB), Czochralski (CZ) methods, or from a Molten Flux (MF), to include a mixed GaAs:AlAs crystal. The material is hygroscopic to the degree that it will react with moisture when exposed to air, oxidizing rapidly. The oxide then forms a stable passivating surface film. To prevent oxidation, wafers are processed and held under inert atmospheres, such as nitrogen, argon, or helium.

As a Solid State device, the compound has been fabricated as electroluminescent diodes and solar cells.

Etching: Mixed acids, $HF:HNO_3$, and halogens.

ALUMINUM ARSENIDE ETCHANTS

ALAS-0001
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 0.5% Br_2
x .... MeOH

TIME:
TEMP:

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DISCUSSION:

AlAs, thin films deposited on (100) gallium arsenide substrates. The substrates were polished in the solution shown prior to growth of AlAs. The AlAs surface will oxidize on exposure to air and stabilize within 24 h. AlAs also can be etched in the solution shown. Process and hold under N_2 to prevent oxidation.

REF: Gordon, N L et al — *J Electrochem Soc,* 119,992(1972)

ALAS-0002
ETCH NAME: Air
TYPE: Gas, oxidation
COMPOSITION:
x .... Air
TIME:
TEMP: RT
DISCUSSION:

AlAs,(110) wafers cleaved from an oriented ingot, and as single crystal spheres. Surfaces allowed to stabilize in air. A major study of microcleavage, bonding character, and surface structure in materials of tetrahedral form as aluminum, gallium, indium antimonides, arsenides, and phosphides.

REF: Wolff, G A & Broder, J D — *Acta Crystallogr,* 12,313(1959)

PHYSICAL PROPERTIES OF ALUMINUM NITRIDE, AlN

Classification	Nitride
Atomic numbers	13 & 7
Atomic weight	40.98
Melting point (°C)	2400
Boiling point (°C)	
Density (g/cm³)	3.05
Refractive index (n=)	1.9—2.2
Band gap (eV)	6.3
Coefficient of thermal expansion ($\times 10^{-6}$ cm/cm/°C)	4.2/5.3// or ⊥ c-axis
Hardness (Mohs — scratch)	7+
(Vicker's — kfg/mm²)	3500
Crystal structure (hexagonal — hemimorphic)	$(11\bar{2}0)$ prism
Color (solid)	Yellowish
Cleavage (prismatic — distinct)	$(11\bar{2}0)$

ALUMINUM NITRIDE, AlN

General: Does not occur as a natural compound. There are no metallic nitrides in nature, although there are many nitrates and nitrites of importance. The metal industries have used the nitridization process for years: firing metals above 1000°C in a nitrogen atmosphere to form a surface nitrided skin that acts as a surface hardening agent, and is more stable to corrosion.

Technical Application: The material has been deposited as a thin film by evaporation of aluminum in a nitrogen atmosphere. In Solid State device development, it is under evaluation as a protective surface coating similar to that of silicon dioxide and nitride. It has been grown epitaxially as both a crystalline structure and single crystal by RF sputtering of an aluminum plate in a nitrogen atmosphere. It is both a dielectric and piezoelectric material similar to alpha-quartz, SiO_2 and, as an epitaxy thin film, has been fabricated as a surface acoustic wave device.

Etching: HF; hot H_3PO_4, and hot alkalies.

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ALUMINUM NITRIDE ETCHANTS

ALN-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal/cleaning
COMPOSITION:
(1) x .... HF, conc.
(2) 1 .... HF
1 .... H_2O
(3) 1 .... HF
10 .... H_2O
TIME: Variable
TEMP: RT
DISCUSSION:
AlN, thin films deposited on (111) silicon wafers by RF plasma sputter deposition. Used in a development study of the material. Films were 1000—2000 Å thick as deposited. Films were then photolithographically processed and etch patterned with the solutions shown in a general study of etching and cleaning of this material. This was some of the original work done on AlN thin films deposited by DC sputtering of a silicon target in nitrogen.
REF: Hersch, N & Walker, P — original development, 1966—1967

ALN-0002
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... H_2O
TIME: Variable
TEMP: Boiling
RATE: 170 mils/year
DISCUSSION:
AlN, specimens. The removal rate shown was computed after etching aluminum nitride in this solution. AlN is unaffected by mineral acids.
REF: Taylor, K M & Lenie, C — *J Electrochem Soc*, 107,308(1960)
ALN-0003: Kohn, J A et al — *Am Mineral*, 41,355(1950)
AlN, specimens. Referenced in ALN-0002, above.
ALN-0004: Renner, Von Th. — *Z Anorg Algem Chem*, 298,22(January 1959)
AlN, specimens. Referenced in AlN-0002, above.
ALN-0005: Long, G & Fuster, L M — *J Am Ceram Soc*, 42,53(1959)
AlN, specimens. Referenced in ALN-0002, above.

AlN-0006
ETCH NAME: Phosphoric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP: Hot
DISCUSSION:
AlN, thin films deposited as surface passivation on (100) gallium arsenide substrates as: AlN/SiO_2/GaAs(100). Solution used after photo resist patterning to remove the AlN layer.
REF: Naki, K & Ozeki, M — *J Cryst Growth*, 68,200(1984)
ALN-0008a: Chu, T L & Kelm, R W Jr — *J Electrochem Soc*, 122,995(1975)
AlN, thin film deposits. Solution used as a general etch.
ALN-0013: Pauleau, Y et al — *J Electrochem Soc*, 129,1045(1982)
AlN, thin films grown by CVD in a study of composition, kinetics and growth mechanisms. Growth at 45°C gave a rough surface; growth at 850°C a smooth surface. Etch was used at 65°C and removal rate varies with growth temperature of the deposit.

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ALN-0007
ETCH NAME: Heat — TIME:
TYPE: Thermal, preferential — TEMP:
COMPOSITION:
x .... heat (electron)
DISCUSSION:
AlN, thin films formed after aluminum evaporation on NaCl (100) substrates by implantation of N^+ ions. The thin films were removed from the substrate by water float-off for morphological study with a high power electron microscope (HVEM) which was used as an annealing vehicle in observing physical changes in the thin film. AlN is hexagonal wurtzite in structure; has a Vicker's hardness of 3500 kgf/mm^2; a band gap of 6.3 eV, and a melting point of 2400°C.
REF: Rauschbach, B et al — *Thin Solid Films,* 109,37(1983)

ALN-0008b
ETCH NAME: Sodium hydroxide — TIME:
TYPE: Alkali, removal — TEMP: RT to hot (80°C)
COMPOSITION:
x .... 10—30% NaOH (KOH)
DISCUSSION:
AlN, amorphous thin films deposited on Si and GaAs substrates. Solution used as a general etch. (*Note:* 2—5% concentrations can be used for surface cleaners at RT and as pin-hole development solutions with AlN.)
REF: Ibid.

ALN-0009
ETCH NAME: Water — TIME:
TYPE: Acid, float-off — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
AlN, thin film (100) and (111) oriented were fabricated for TEM study as follows: potassium chloride, KCl, single crystal substrates of (100) and (111) orientation were mechanically polished; polish etched in water, rinsed in acetone, and nitrogen dried. Single crystal aluminum was evaporated: on (100) KCl was (100) single and sphalerite structure (isometric); on (111) KCl was (111) wurtzite structure (hexagonal). The aluminum was ion implanted with nitrogen to form aluminum nitride films. Films were removed for TEM study by milling the substrates with water.
REF: Kimura, K et al — *Jpn J Appl Phys,* 223,1145(1984)
ALN-0015: Ritajima, M et al — *J Electrochem Soc,* 128,1588(1981)
AlN, thin films deposited on molybdenum substrates by RF reactive ion plating (RIP). AlN forms at 100—1200°C; at 750°C MoO_3 is formed. Above 1200°C N_2O_3 develops. Authors say AlN is unstable in water vapor.

ALN-0010
ETCH NAME: Hydrofluoric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... HF, conc.
DISCUSSION:
AlN, thin films deposited on GaAs:Zn doped, (100) wafers used in a study of Zn^+ ion implantation (I^2) with annealing. After implant, wafers were surface coated with either AlN

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or Si_3N_4 as a cap prior to annealing. Both thin films were removed after anneal with the solution shown.

REF: Moser, K et al — *J Appl Phys*, 57,5470(1985)

ALN-0011: Delavignette, P et al — *J Appl Phys*, 32,1098(1961)

AlN, specimens. Electron microscope used for direct observation of dislocations and stacking faults.

ALN-0012: Barrett, N J et al — *J Appl Phys*, 57,5470(1985)

AlN, deposited as a thin film on GaAs ion implanted with zinc in a study of annealing. Both AlN and Si_3N_4 were used as "caps" after ion implant. After annealing cycles, AlN removed with HF.

ALN-0013
ETCH NAME: TIME:
TYPE: Acid, removal TIME:
COMPOSITION:

x .... acids/alkalies/halogens

DISCUSSION:

AlN, single crystals used in an evaluation of cohesive energy features of tetrahedral semiconductors. Etchant solutions vary with the compounds listed below:

AlN	CdTe	BN	Ge
AlAs	BeO	HgSe	Si
AlSb	*CuCl	HgTe	ZnS
AlP	*CuBr	GaP	ZnSe
*AgI	*CuI	GaAs	ZnTe
*$AgGaSe_2$	*$CuGaSe_2$	GaSb	*$ZnSiF_2$
*$AgInSe_2$	$CuInSe_2$	InP	*$ZnSnAs_2$
*$AgGaTe_2$	*$CuGaTe_2$	InAs	*MgS
*$AgInTe_2$	$CuInTe_2$	InSb	*MgSe
CdS	*$CaSiF_2$	Sn, grey	*MgTe

*This reference also listed under these individual compounds to include etchant solutions. Use solutions as shown under the individual compounds.

REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

PHYSICAL PROPERTIES OF ALUMINUM OXIDE, Al_2O_3

Classification	Oxide
Atomic numbers	13 & 8
Atomic weight	102
Melting point (°C)	1725
Boiling point (°C)	2250 (2050)
Softening point (°C)	2050
Density (g/cm^3)	3.9 (*3.955—4.10)
Thermal conductivity (cal/sec/cm/°C) 25°C	0.077
Coefficient of thermal expansion ($\times 10^{-6}$ cm/cm/°C)	6.6
Specific heat (cal/g/°C) 25°C	0.25
Compressive strength (kg/cm^2)	24,000
Compressive strength ($dynes/cm^2 \times 10^{-10}$)	1.2

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Compressive strength (dynes/cm^2 × 10^9 @ 750°C N_2 atm)	1.0
Modulus of rupture (kg/cm^2)	4800
Dielectric constant (1 kHz) 25—500°C	9.87—10.93
Electrical resistance (ohms mm^2/cm) 500°C/1000°C	10^{11} × 10^6
Young's modulus (× 10^6)	55
Flexural strength (psi × 10^3)	50
Impact resistance (Charpy — in/lb)	7
Dielectric strength (volts/mil)	230
Tensile strength (psi × 10^3)	30
Dissociation factor (1 kHz) 25—500°C	0.0007
Loss factor (1 kHz) 25—500°C	0.0076
Refractive index (n=)	1.77 (1.65)
Hardness (Mohs — scratch)	9
(Knoop — kgf/mm^2)	2000 (1370)
(Vicker's — kgf/mm^2)	1650
Crystal structure (hexagonal — rhombohedral) alpha	(10$\bar{1}$1) rhomb
(isometric — normal) beta	(100) cube
Color (solid — powder/sxtl)	White/black/grey/brown/blue
Cleavage (basal-parting only, or cubic)	(0001) or (001)

Note: Artificial alumina, 99.98%, except where noted (*).

ALUMINUM OXIDE, Al_2O_3

General: Occurs in nature as the mineral corundum. Though it is hexagonal system, rhombohedral division, normal class, it often occurs in elongated pseudohexagonal prisms with a laminated structure; also massive, granular with near rectangular parting (pseudo-cleavage) on (0001) and (10$\bar{1}$1). Fracture is uneven to conchoidal (glassy materials). It is next to diamond (H = 10) in hardness, vs. H = 9 for corundum with a high specific gravity (density) G = 3.95—4.10. Color range is blue, red, yellow, brown, and grey. It is opaque, translucent to transparent as sapphire. Refractive index, n = about 1.76, varying with axial measurement direction. There are three major divisions, with subspecies, all of which are important in industry. As single crystals: (1) sapphire (blue); (2) ruby (red); (3) Oriental topaz (yellow); (4) Oriental emerald (green); (5) Oriental amethyst (purple) and (6) star sapphire, with an asterated structure on the (0001) due to cavities parallel to bulk prism planes. Sapphire and ruby are the two precious gemstones. The others are semi-precious gem stones, though star sapphire with fine color (bluish) may be classed as precious.

Industrially, as artificial materials both ruby and sapphire were initially grown as ingots (boules) by the Verneiul process in the late 1800s for gem stones and, the ruby laser, developed in the mid-1950s, was the first commercial laser unit. It is worth nothing that natural and artificial rubies can be differentiated by internal structure observable with a 20× lens. Internal growth lines in natural material are angular; in artificial stones, curved. This is true for any other mineral.

Corundum: (common) the opaque varieties with dull colors of blue, grey, brown, and black. It has been produced artificially with a melting point of 2050°C, as single crystals from several liquid fluxes, such as lead oxide or sodium sulfide. The artificial abrasive alundum is made by heating bauxite (a hydrated alumina ore) in an electric furnace at 5000 to 6000°C. It occurs in four forms, but the alpha-corundum type is the only one stable at high temperatures.

Alumina, Al_2O_3 — corundum — is one of the most inert compounds known, second only to quartz, SiO_2 in nature. It is not acted upon by single acids, though some acid mixtures

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have been developed. When finely powdered and treated with cobalt solutions it gives a beautiful blue color.

In industry it is classified as a high temperature ceramic and is fabricated as pressed powder sheet, rod, tube, and other forms from a mixture of powdered alumina with silica as a binder. For very high purity alumina, 99.6%, the silica is removed by heat treatment. There are a wide variety of alumina-based ceramics containing other metal oxides that have been developed for special applications. Highest purity alumina is white in color, followed by grey to light tan, and there is a black variety containing graphite. It has wide industrial applications as an insulator: telephone lines, furnace liners and tubes, electrical stand-offs, thermocouple beads, and rods. Spheres are used as boiling beads in hot acid solutions. A major application is as a lapping and polishing abrasive.

Emery is a natural mixture of corundum and magnetite or hematite, both iron ores. Usually dark black with gradation of grain size from very fine to coarse and occasionally containing embedded single crystals of corundum. The primary industrial use is an abrasive (Turkish emery, best quality), or common emery (one form as Arkansas stone).

Technical Application: There are several major uses of alumina and alumina-based ceramics in Solid State processing and device fabrication:

1. General parts: As either or both electrical and heat insulators in vacuum systems and electronic test equipment; furnace tubes or bead for insulation on thermocouples in diffusion and epitaxy systems; inert work surfaces or holders for chemical processing or electrical assembly; in etch solutions as boiling beads; and other applications.
2. Lapping compound: From general lapping grits (180 to 350 mesh) to fine powder polishing compounds (0.2 to 0.5 μm) such as Linde A and B used for slurry paste polishing. Used for mechanical lap/polish of all metals and metallic compounds.
3. Cutting/sawing: Discs and blades with embedded alumina grit or melt-fired onto the cutting edge of a blade to improve wear resistance. These have been used to wafer dice semiconductor and dielectric elements.
4. Solid state packages: A major element in package construction for hermetically sealed devices. Combined with aluminum, a radiation hard package. Alumina is usually the body of the package brazed onto a metal base that acts as a an electrical insulator.
5. Thin film: Evaporated or sputtered (CVD or RF plasma) as an amorphous coating on material surfaces as a dielectric insulator or passivation layer — it resists ionizing radiation. Also used, like silicon dioxide, as a chemical etching or diffusion mask in conjunction with photo resist. Also as an active memory element in semiconductor device assemblies. Applied to aluminum surfaces — anodizing — to produce an inert, hard surface for wear protection. Anodization can be in different colors: red, yellow, blue, brown, and black with a variety of applications, such as color coded buttons.
6. Substrates: High purity alumina, >99.6%, as pressed powder blanks (0.005 to 0.050 thick) are metallized, photo resist patterned, and etched as electrical circuits for a wide range of Solid State devices. It should be noted that high purity alumina with a 1—2 μ″ polish finish can be difficult to metallize without peeling of the metallization during subsequent cutting or temperature processing like glass or other highly polished surfaces. As-fired 4 μ″ substrates do not have this problem, but high frequency microwave devices require highly polished surfaces for optimum electrical parameters.
7. Resistors: A wide range of discrete resistors and resistor networks are fabricated as discrete alumina elements or on substrates. As size and thicknesses increase the resistance values increase: 0.005/.014 thick, to about 0.060/0.080 as squares are nominal sizes.
8. Capacitors: Fabrication is similar to that of resistors and both can be special mixture formulations with other elements and oxides to obtain special electrical characteristics.

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9. Amorphous ruby: Ruby parts are fabricated from a liquid melt poured into molybdenum forms to produce flats, rods, wire bonding tips, and other parts. Bond tips are used in wire bonding (gold, silver, and aluminum) of discrete devices and device assemblies. Flats, rods, tubes are used for a variety of applications including filter elements. Ruby spheres are excellent hard, inert, and high-temperature resistant ballbearings.

Regardless of the many and varied forms and applications of alumina, it is still one of the most difficult materials to etch. As will be seen in the following list of etchants where most are cleaning solutions.

Etching: Difficult. Hot HCl and H_3PO_4 and some hot gases. RIE with RF plasma gases.

ALUMINUM OXIDE ETCHANTS

ALO-0001a
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP: RT & 80°C
COMPOSITION:
35 ml .... H_3PO_4
20 g .... CrO_3/l
DISCUSSION:

Al_2O_3, thin films anodized on aluminum surfaces. Anodize 5 min at 20°C and 500 V in 3% boric acid: 0.05% Borax. A study of film structure and Al_2O_3/Al interfaces.
REF: Stirland, D J & Bicknell, R W — *J Electrochem Soc*, 106,481(1959)
ALO-0021: Dyer, C K & Alwitt, R S — *J Electrochem Soc*, 128,300(1981)

Al_2O_3, thin films grown on aluminum foil and used in a study of AC etching of foil. Oxide grown in 40% $NH_4B_5O_8.4H_2O$: ethylene glycol, RT. Solution shown used to strip oxide. BRM solution (ALO-0020b) used to dissolve foil leaving oxide flakes. Solution was: 5% H_3PO_4:3% CrO_3.
ALO-0001b: Ibid.

Al_2O_3, thin films as native oxide on single crystal aluminum ingots and wafers. Solution used to remove oxide.

ALO-0006
ETCH NAME: Water
TIME:
TYPE: Solvent, cleaning
TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:

Al_2O_3 and $Al_2P_xO_y$ thin films deposited on n-type InP, (100) wafer substrates to form MIS diodes in an electrical parameter study. Alumina not etched — used as an insulator between InP and additional surface metallization. Refractive index shown as n = 1.48—1.50. (*Note:* Natural sapphire n = 1.765.)
REF:

ALO-0022
ETCH NAME: Hydrogen
TIME: To 1 h
TYPE: Gas, cleaning
TEMP: 800—1000°C
COMPOSITION:
x .... H_2
DISCUSSION:

Al_2O_3, pressed powder blanks with 2 μ" (polished) and 4 μ" (as fired) surface finish. Blanks used in fabricating microwave electronic circuits with Au/TiW (10% Ti) metallization

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by evaporation sputter and electrolytic gold up-plating. Up-plated parts subjected to 400°C, 1—5 min on a hot plate in air, show blistering of metallization. Hydrogen firing used to clean alumina surfaces prior to initial metallizing. Showed major reduction of blistering, but did not eliminate. The 2 μ″ finish appears to contained entrapped oils from diamond paste polishing. See AU-0024 for additional discussion of this study.
REF: Walker, P & Valardi, N — personal development, 1985

ALO-0004
ETCH NAME: RCA etch (A-B etch) TIME: 15—20 min
TYPE: Acid, cleaning TEMP: 80°C
COMPOSITION:

(1)		(2)	
1—2	NH_4OH	1—2	HCl
1—2	H_2O_2	1—2	H_2O_2
4—6	H_2O	4—6	H_2O

DISCUSSION:
Al_2O_3 pressed powder blanks with 2 μ″ (polished) and 4 μ″ (as-fired) surface finish metallized and photo resist patterned/etched in the fabrication of microelectronic circuits. The solutions, as shown, were originally developed for cleaning of silicon surfaces (Kern & Puotinen). (Walker) used the system for cleaning alumina, quartz, sapphire, and silicon: place parts in a Teflon holder introduced into solution (1); transferred still wet to solution (2); then rinse 2 min in running DI water and N_2 blow dry. Method used in a study of metal adhesion on alumina. Immediately after cleaning in the two solutions, parts were held under MeOH until introduced into vacuum for metallization and were still wet with alcohol, or parts were DI water rinse, 1 min; HF dip, 30 sec; DI water rinse, 30 sec and N_2 blow dry immediately before introduction into vacuum. Both methods gave good adhesion of sputtered metallization.
REF: Kern, W & Puotinen, D A — *RCA Rev*, 69,187(1979)
ALO-0015: Walker, P — personal application, 1980
Al_2O_3 pressed powder blanks used for microelectronic circuit fabrication. Solutions used to clean surface prior to multilayer metallization.

ALO-0005
ETCH NAME: Hydrochloric acid TIME: 2—5 min
TYPE: Acid, cleaning TEMP: RT or 70°C
COMPOSITION:

(1)		(2)	
x	HCl, conc.	1	HCl
		1	H_2O

DISCUSSION:
Al_2O_3 pressed powder substrates, 2 and 4 μ″ surface finish, used in as study of metallization. Etch soak substrates in either solution, rinse in running DI water, 2 min, and N_2 blow dry. This cleaning gave good sputtered metal adhesion. Also used on fused quartz and sapphire, and single crystal sapphire substrates.
REF: Walker, P — personal application, 1980—1985

ALO-0021
ETCH NAME: Hydrochloric acid TIME:
TYPE: Acid, preferential TEMP: Boiling
COMPOSITION:
x .... 6 *N* HCl
DISCUSSION:
Alpha-Al_2O_3 (0001) wafers used in a study of impurity penetration along dislocation lines. It was shown that traces of both NaCl and $Mg(NO_2)_2$ will contaminate the surface,

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penetrate along dislocation lines, and defect structure can be developed with the solution shown.
REF: Tucker, R N & Gibbs, P — *J Appl Phys,* 29,1375(1958)

ALO-0007
ETCH NAME: Steam
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O, steam
TIME: 6+ min
TEMP: 100°C
DISCUSSION:
Al_2O_3 substrate blanks used for fabrication of metallized circuits in semiconductor device applications. Substrates are panel mounted facing two vertical jets. The top jet contains water plus surfactants; the lower jet, pure water. Jets are moved up and down continuously spraying the substrates for about 6 min. Rack mounted parts are then placed in vacuum ovens at greater than 100°C for at least 28 min. Cleaning is done prior to Au/Cu/Cr metallization. Authors say that this will remove both fingerprints and carbon.
REF: Rogelstad, T & Matarese, G — *J Vac Sci Technol,* A3,516(1985)

ALO-0009
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+, ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
Al_2O_3 substrate blanks used for plasma assisted physical vapor deposition (PAPVD). Ceramics, oxides, nitrides, carbides, and sulfides were cleaned by reactive sputtering (RS) prior to metal deposition by PAPVD or by activated reactive evaporation (ARE). Over 25 substrates and metallizations described.
REF: Bunshah, R F & Deshpandey, C C — *J Vac Sci Technol,* A3,553(1985)

ALO-0010
ETCH NAME:
TYPE: Acid, anodizing
COMPOSITION:
x .... 5% NaOH
x .... 50% HNO_3
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Al_2O_3 anodized coating on aluminum sheet. The aluminum sheet was cleaned in the above solution prior to anodization. An HNO_3:NH_4HF solution also used. After etching, rinse in DI H_2O, then EOH.
REF: Sharp, D J — *Thin Solid Films,* 111,337(1985)

ALO-0011
ETCH NAME: Sulfamic acid
TYPE: Acid, cleaning
COMPOSITION:
x .... NH_2SO_3H
TIME:
TEMP:
DISCUSSION:
Al_2O_3, specimens and other ceramics. Solution is a cleaning acid for ceramics. Solutions

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are strongly acidic but with pH values lower than formic, citric, oxalic, and phosphoric acid. Also used for descaling and pickling of metals.
REF: Bulletin 13332-1, Ashland Chemical Co.

ALO-0012
ETCH NAME: Air
TYPE: Gas, cleaning
TIME: 30 min, minimum
TEMP: 200°C
COMPOSITION:
x .... air
DISCUSSION:
Al_2O_3, substrates and parts both metallized and unmetallized material. If materials are stored for prolonged periods of time, their surfaces can become hydrated with water vapors. Where photolithography is to be used, at least an air oven bake-out is recommended before applying AZ-type photo resist lacquers to obtain better adhesion of resist.
REF: Brochure: *AZ 1300 Series Positive Photo Resists for Semiconductors and Microelectronics,* American Hoerchst Corp, 1983
ALO-0013: Walker, P — personal application, 1983
Al_2O_3, pressed powder substrates "as received" and after metallization with RF sputtered TiW:Au, Ti:Au or Cr:Au. Substrates were air oven baked at 150°C for 20 min; 4, 8, and 24 h prior to gold up-plating in a study of blisters and cracking of metallization. TiW:Au showed worst case blistering which was reduced but not eliminated with extended baking time. Alumina substrates shipped and stored in individual polyethylene envelopes have surface oils(?) contamination. A 2 μ" finish surface contains entrapped oil from diamond paste polishing and shows different blister characteristics than the as-fired 4 μ" surface. Evaluation done at 400°C on a hot plate in air. Best results were obtained when as-received blanks were hydrogen fired at 800 to 1000°C prior to metallization.

ALO-0002b
ETCH NAME: Air
TYPE: Gas, cleaning
TIME: 9 min
TEMP: 1470°C
COMPOSITION:
x .... air
DISCUSSION:
Beta-Al_2O_3:Na doped substrates were high temperature fired to clean surfaces.
REF: Ibid.

ALO-0003
ETCH NAME: Argon + air
TYPE: Gas, preferential
TIME:
TEMP: 1500°C
COMPOSITION:
x .... Ar + air
DISCUSSION:
Al_2O_3:Zr(1%) doped single crystal ingots grown by the Verneuil Process. Wafers were cut basal, (0001) and mechanically polished with diamond paste on a maple wood lap with olive oil as the liquid carrier. No dislocations were observed in the ingot material as-grown. After firing in the atmosphere and at temperature shown — surfaces show asterated sixfold symmetry patterns and hexagonal loops. (*Note:* Cylindrical cavities parallel to prism planes produce asterism in natural corundum and polished encabachon become star sapphires.)
REF: Bond, H E et al — *J Appl Phys,* 34,440(1964)

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ALO-0002c
ETCH NAME: Phosphoric acid — TIME: 1 h
TYPE: Acid, removal/cleaning — TEMP: 150°C
COMPOSITION:
x .... H_3PO_4
DISCUSSION:
Beta-Al_2O_3:Na doped substrates were surface cleaned with this solution in addition to air firing.
REF: Ibid.
ALO-0017:
Al_2O_3:MgO($^1/_2$%) and Al_2O_3:TiO(11%) ceramic substrates and parts were cleaned in the solution shown at 200°C.

ALO-0014
ETCH NAME: — TIME: 30 sec
TYPE: Acid, oxide removal — TEMP: 60°C
COMPOSITION:
"A" 35 .... H_3PO_4 "B" x .... H_2O
10 .... HNO_3
Mix: 1 part "A" to 3 parts "B".
DISCUSSION:
Al_2O_3 native oxide films on Al:Au alloys. This solution used to remove native oxide from specimens before preferential etching to observe precipitates in the alloys. See ALAU-0001 under Aluminum Alloys.
REF: Von Heimendahl, M — *Acta Metall,* 15,1441(1967)

ALO-0016
ETCH NAME: Laser — TIME:
TYPE: Photochemical, forming — TEMP:
COMPOSITION:
x .... Excimer laser
DISCUSSION:
Al_2O_3, thin films deposited on silicon, (100) wafers as a $(11\bar{2}0)$ oriented thin film. Solution was CCl_4:($Al_2CH_3O_6$) and an Excimer laser was used to photochemically deposit aluminum oxide as single crystal sapphire from the liquid solution.
REF: Ehrlich, D J & Tsao, J Y — *J Vac Sci Technol,* A(3),904(1985)

ALO-0018
ETCH NAME: — TIME:
TYPE: Oxide, passivation — TEMP:
COMPOSITION:
x .... Al_2O_3
DISCUSSION:
Al_2O_3 thin film deposition on InGaAsP/InP (100) LED devices as an anti-reflective (AR) coating as an improvement over Si_3N_4. Thickness was 1805 Å onto TO-18 type package headers with LEDs previously bonded.
REF: Chin, A K et al — *J Vac Sci Technol,* B(1),72(1983)

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ALO-0019
ETCH NAME: TIME:
TYPE: Electrolytic, preferential TEMP: 0°C
COMPOSITION: ANODE:
x .... H_3PO_4 CATHODE:
x .... EOH POWER: 20 V
DISCUSSION:

Al_2O_3, thin films anodized on (100) oriented single crystal aluminum blanks used in a study of the alumina layer structure. Solution produced ridging on (110), hillocks on (111) and (100). (*Note:* The blanks must have been beta-Al_2O_3.)
REF: Grooskreutz, J C & Shaw, G G — *J Appl Phys*, 35,2194(1964)

ALO-0023
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... H_3PO_4
x .... H_2O
DISCUSSION:

Al_2O_3 thin films DC reactively sputtered on (111) silicon wafers with a poly-Si epitaxy layer. Two sputter conditions used: "A" — developed 10 Ω cm resistivity; "B" — 40 Ω cm (down vs. up sputtering). After Al metallization wafers were photolithographic processed as MOS structures. Prior to metallization, wafers were heat treated with different schedules in He atmosphere (bubble He through LN_2 to remove O_2 contamination). No etch shown. (*Note:* Etch shown is a general solution for removal and cleaning.)
REF: Chen, M-C — *J Electrochem Soc*, 118,591(1971)

ALO-0024
ETCH NAME: TIME:
TYPE: Molten, flux, removal TEMP: 1200 K
COMPOSITION:
x .... $NaSO_4$
x .... Na_2O_2
DISCUSSION:

Alpha-Al_2O_3 powdered material used in a reaction study with development of a phase diagram for Na-Al-S-O with material in flux shown. At 1 atm, Na_2O is a base; SO_3 is the acid component. Other solubility studies included: Cr_2O_3 beta-Al_2O_3, and NiO.
REF: Jose, P D et al — *J Electrochem Soc*, 132,735(1985)
ALO-0025: Liang, W W & Elliot, J F — *J Electrochem Soc*, 125,572(1978)
Al_2O_3 material. Similar work as in ALO-0024.

ALO-0026
ETCH NAME: TIME:
TYPE: Vacuum, cleaning TEMP:
COMPOSITION:
x .... vacuum
DISCUSSION:

Al_2O_3 as single crystal blanks used in a study of ceramic microstructure and metal adhesion to surfaces by smear/rubbing. (0001), $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces studied. Friction coefficient and adhesion was anisotropic vs. load on (0001) and $(11\bar{2}0)$. Blanks were degassed in vacuum due to inherent surface oxygen present. The (0001) is a glide plane; $(11\bar{2}0)$ and other prism planes are slip planes, and can show plastic deformation. Smeared on metals

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evaluated included Cu, Ni, Rh, Co, and Be. Surface attachment to some degree was due to presence of oxygen bonding. Also studied ferrites (FER-0002) and SiC (SIC-0021).
REF: Buckley, D H — *J Vac Sci Technol,* A3(3),762(1985)

PHYSICAL PROPERTIES OF ALUMINUM PHOSPHATE, $AlPO_4$

Classification	Phosphate
Atomic numbers	13, 15, & 8
Atomic weight	121.29
Melting point (°C)	1540
Boiling point (°C)	
Density (g/cm^3)	2.57
Refractive index (n=)	1.54—1.57
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Greyish
Cleavage (rhombohedral)	(1101)

ALUMINUM PHOSPHATE, $AlPO_4$

General: Does not occur as a pure natural compound, but there are some 40 minerals, mostly as hydrous phosphates of aluminum, potassium, or calcium. The mineral eggonite, $AlPO_4.2H_2O$ is representative of the most pure variety, and there are half a dozen minerals of the same hydrated formula. All are of minor occurrence; whereas bauxite, $Al(OH)_3$, is the chief ore of aluminum as a complex admixture with clays occurring in large tropical area laterite deposits.

As a phosphate there is little use in the metal industry, though the sulfates and oxides have applications. Aluminum metal and its alloys is one of the major industrial metals, equal in importance to copper and iron. The phosphide, AlP, is used as a phosphor-aluminum additive in alloys, and has been grown as a single crystal. All natural phosphates are important fertilizers.

Technical Application: No use in Solid State processing at present, though it has been grown as a single crystal, as has AlP, both for general material studies.

Etching: Soluble in acids and alkalies.

ALUMINUM PHOSPHATE ETCHANTS

ALPH-0001
ETCH NAME: TIME:
TYPE: TEMP:
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

$AlPO_4$, single crystals grown by a hydrothermal temperature gradient process from H_3PO_4 in sealed glass ampoules, and used in a material study. No etch shown. (*Note:* Solution shown is a general etch for phosphates.)
REF: Requardt, A & Lehmann, G — *J Phys Chem Solids,* 46,107(1985)

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ALUMINUM PHOSPHIDE ETCHANTS

ALP-0001
ETCH NAME: Water
TYPE: Acid, polish
COMPOSITION:
x .... H_2O
DISCUSSION:
AlP, single crystal wafers. Solution used to remove and etch polish the material.
REF: Reynolds, A J et al — *Acta Metall,* 14,119(1966)

TIME:
TEMP:

PHYSICAL PROPERTIES OF AMALGAM, HgAg

Classification	Metal
Atomic numbers	47 & 80
Atomic weight	388.5 (variable)
Melting point (°C)	960.5 (Ag)
Boiling point (°C)	357 (Hg)
Density (g/cm^3)	13.75—14.1
Hardness (Mohs — scratch)	3—3.5
Crystal structure (isometric — normal)	(110) dodecahedron
Color (solid)	Silver-white
Cleavage (dodecahedral — partial)	(110)

AMALGAM, HgAg

General: Occurs as a native metal compound, and found in both mercury and silver deposits, usually as small grains or fine crystals. Rare. Quantity of constituents varies widely from AgHg, Ag_5Hg_3, $Ag_{36}Hg$. There are several named minerals by percentage of silver and locale: ordinary amalgam, AgHg (26.4% Ag) or Ag_2Hg (35% Ag); arquerite, $Ag_{12}Hg$ (86.6% Ag); kongsbergite, $Ag_{32}Hg$ or $Ag_{16}Hg$ with over 90% silver. Heating on charcoal will volatilize the mercury, leaving a bead of silver. In mineralogy the term "amalgam" is reserved for AgHg compounds, though native gold occurs as an admixture of AuAg — electrum — also called white or argentiferous gold.

Native amalgam has minor use in industry due to scarcity as a distinct compound as it is a minor fraction of the ore bodies mined for their mercury or silver content. Artificial amalgams are formed as mercury combines with most metals: (1) combining with easy with tin, zinc, gold, sodium and (2) using sodium amalgam with metal salts of iron, nickel, cobalt, manganese or platinum, forms the so-called heavy metal amalgams.

There are a number of mercury containing alloys used as low temperature solders, but as amalgams . . . called amalgam even though it is electrum . . . the best known application is in dentistry, where gold and silver are compounded in small quantities in a mortar and pestle as tooth fillings . . . no mercury . . . yet still called an amalgam.

Technical Application: Natural or artificial amalgams have little use in the Solid State industry per se, though there are a number of binary and trinary compound semiconductors as selenides, tellurides and antimonides. Mercury itself is a dopant species and can be pyrolitically diffused from an HgCl source. Pure mercury has been rubbed on metal surfaces to form a temporary amalgams for mounting or as an electrical contact, and there are high intensity mercury light bulbs.

Etching: HNO_3 and aqua regia (AuAg).

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AMALGAM ETCHANTS

HGAG-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
HgAg, natural single crystal. Concentrated acid used to dissolve the mineral for quantitative analysis. Water diluted acid solutions used to clean surfaces. Where pure mercury was applied as a film contact for electrical testing, concentrated acid was used to removal and clean contacts after tests. Mercury films applied to natural metal oxides — hematite, magnetite and siderite (iron oxides) — removed with dilute acid to observe structural effects as developed by the amalgam reaction.
REF: Walker, P — mineralogy studies, 1951—1953
TIME:
TEMP: RT

HGZN-0001
ETCH NAME:
TYPE: Acid, cut
COMPOSITION:
1 .... HNO_3
1 .... H_2O_2
1 .... alcohol
DISCUSSION:
ZnHg specimens acid saw cut with this solution, and used in a study of embrittlement cracking of this compound. After cutting, wash in water. Dry in alcohol, then with ether.
REF: Westwood, A R C — *Phil Mag*, 9,199(1964)
TIME:
TEMP:

PHYSICAL PROPERTIES OF ANTIMONY, Sb

Classification	Semi-metal
Atomic number	51
Atomic weight	121.75
Melting point (°C)	630.5
Boiling point (°C)	1380
Density (g/cm^3)	6.618 (6.691)
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.045
Specific heat (cal/g) 25°C	0.0494
Latent heat of fusion (cal/g)	38.3
Coefficient of linear thermal expansion:	
(micro-inch °C) 20°C	8^{-11}
($\times 10^{-6}$ cm/cm/°C) 20°C	8.5
Electrical resistivity (micro-ohms-cm)	39.1
1st ionization energy (K-cal/g-mole)	199
1st ionization potential (eV)	8.64
Electronegativity (Pauling's)	1.9
Covalent radius (angstroms)	1.40
Ionic radius (angstroms)	0.62 (Sb^{+5})
Cross section (barns)	5.7
Magnetic susceptibility (cgs $\times 10^{-6}$) 18°C	99
Vapor pressure (°C)	1223

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Hardness (Mohs — scratch)	3—3.5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Tin white
Cleavage (basal — perfect)	(0001)

ANTIMONY, Sb

General: Occurs as a native element in veins associated with silver and arsenic ores although the mineral stibnite, Sb_2S_3, which occurs as a primary mineral in quartz and granitic rock is the major ore of antimony. The native antimony has a specific gravity (density) of G = 6.7, is higher than the purified material (G = 6.6) due to trace presence of silver and iron. It is sectile, brittle, and is slightly malleable when heated. It has a metallic luster with a tin-white color and has a perfect (0001) cleavage, which is not common to pure metallic type elements. Surfaces tarnish readily, particularly in the presence of sulfur.

It is not used as a pure metal in heavy industry, although there are several applications as an additive to irons, steels, aluminum, brass, and bronze. The pure metal is used in special low melting point glasses, and as a black coloring pigment in both glass and clay pottery.

It is one of the elements known to ancient man, and both antimony and arsenic compounds have been used in black facial make-up, particularly as eye shadow, but are no longer in use today due to their toxicity though there are several medical applications.

Technical Application: Although antimony it is not as widely used as phosphorus, it is an n-type dopant in silicon.

It also is used to grow several compound semiconductors such as gallium antimonide, GaSb; indium antimonide, InSb; and aluminum antimonide, AlSb.

Antimony is used as a constituent in several medium temperature solders and some high temperature brazing alloys. Both used in Solid State package assemblies.

Antimony has been grown as a single crystal for morphology and defect studies.

Etching: Aqua regia; hot concentrated H_2SO_4, and mixed acids of HF:HNO_3.

ANTIMONY ETCHANTS

SB-0001a

ETCH NAME: Dash etch	TIME: 5—10 min
TYPE: Acid, polish	TEMP: RT
COMPOSITION:	RATE: 1 mil/min

1 .... HF
3 .... HNO_3
12 .... CH_3COOH (HAc)

DISCUSSION:

Sb, (0001) specimens cleaved after freezing in liquid nitrogen, LN_2, or cleaved under LN_2. Specimens were used in a polish etch development and dislocation etch study of antimony. Solution shown produces a good polish with no gas evolution.

REF: Wernick, J H et al — *J Appl Phys*, 29,1013(1958)

SB-0001b

ETCH NAME: Dash etch, modified	TIME: 5—10 min
TYPE: Acid, polish	TEMP: RT

COMPOSITION:

1 .... HF
3 .... HNO_3
12 .... HAc
1 .... Br_2

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DISCUSSION:
Sb,(0001) specimen cleaved in LN_2. Solution shown produces a fair polish with no gas evolution. See SB-0001a for additional discussion.
REF: Ibid.

SB-0001c
ETCH NAME: Dash, etch, modified
TYPE: Acid, polish
TIME: 5—10 min
TEMP: RT
COMPOSITION:
1 .... HF
3 .... HNO_3
6 .... HAc
DISCUSSION:
Sb, (0001) specimen cleaved in LN_2. Solution shown produces a fair polish with no gas evolution. See SB-0001a for further discussion. (*Note:* This solution is a modification of the original Dash, etc.)
REF: Ibid.

SB-0001d
ETCH NAME: Dash etch, modified
TYPE: Acid, polish
TIME: 5—10 min
TEMP: RT
COMPOSITION:
1 .... HF
5 .... HNO_3
12 .... HAc
DISCUSSION:
Sb, (0001) specimen cleaved in LN_2. Produces a fair polish with no gas evolution. See SB-0001a for further discussion.
REF: Ibid.

SB-0001e
ETCH NAME: Dash etch, modified
TYPE: Acid, polish
TIME: 1 min
TEMP: RT
COMPOSITION:
1 .... HF
5 .... HNO_3
6 .... HAc
DISCUSSION:
Sb, (0001) specimens cleaved in LN_2. Produces a very good polish with no gas evolution. See SB-0001a for further discussion.
REF: Ibid.

SB-0001f
ETCH NAME: Dash etch, modified
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
3 .... HF
5 .... HNO_3
12 .... HAc
1 .... Br_2
DISCUSSION:
Sb, (0001) specimen cleaved in LN_2. Produces a rough and uneven surface and etches

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very rapidly with gas evolution. See SB-0001a for further discussion. (*Note:* Compare results with SB-0001b.)
REF: Ibid.

SB-0004
ETCH NAME:
TYPE: Acid, removal/clean
COMPOSITION:
2 .... HF
3 .... HNO_3
5 .... H_2O
TIME:
TEMP:
DISCUSSION:
Sb, (0001) wafers. Cut wafers under glycol thallate with a high speed cutting wheel to prevent chipping. Mechanically lap with 600 grit, then 000 and 0000 aluminum abrasive paper. Use solution shown as a light etch to remove damage and debris. Specimens used in a study of self-diffusion.
REF: Rosolowski, J H et al — *J Appl Phys,* 31,3027(1964)

SB-0005
ETCH NAME: Sulfuric acid
TYPE: Acid, polish
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot
DISCUSSION:
Sb, single crystal wafers of different orientations used in a study of etch pits. Solution can be used to polish surfaces prior to preferential etching.
REF: Hiramatsu, H & Shigeta, J — *J Phys Soc Jpn,* 13,1404(1958)

SB-0001g
ETCH NAME: CP4, modified
TYPE: Acid, polish
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc
1 .... Br_2
TIME: 1—2 sec
TEMP: RT
DISCUSSION:
Sb, (0001) wafers cleaved under LN_2. Solution produces a very good polish with some pitting and gas evolution. See SB-0001a for added discussion. (*Note:* Original CP4 solution contained 0.6 Br_2 and was developed for germanium.)
REF: Ibid.
SB-0002: Allred, W P et al — *J Electrochem Soc,* 107,117(1960)
Sb, high purity slugs etch cleaned in CP4 solution before using to grown single crystal aluminum antimonide, AlSb. After etching rinse in DI water.

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SB-0001h
ETCH NAME: CP4, modified
TYPE: Acid, polish
COMPOSITION:
2 .... HF
5 .... HNO_3
4 .... HAc
1 .... Br_2
TIME: 1—2 sec
TEMP: RT
DISCUSSION:
Sb,(0001) wafers cleaved under LN_2. Solution produces an uneven polish with both pits and gas evolution. See SB-0001a for added discussion.
REF: Ibid.

SB-0003
ETCH NAME:
TYPE: Cleave, defect
COMPOSITION:
x .... cleave
TIME:
TEMP: −195°C
DISCUSSION:
Sb, (0001) wafers cleaved under LN_2, and used as cleaved. Surface will show direction of trigonal axes and may show 60° twinning. Specimens used in a galvanometric properties study at liquid helium temperatures.
REF: Steele, M C — *Phys Rev*, 99,1751(1955)

PHYSICAL PROPERTIES OF ARGON, Ar

Classification	Inert gas
Atomic number	18
Atomic weight	39.948
Melting point (°C)	−189.2
Boiling point (°C)	−185.7
Density (g/cm³) −233°C	1.65
(g/cm³) 0°C $\times 10^{-3}$	1.784
Specific heat (cal/g/°C) 20°C	0.125
Latent heat of fusion (cal/g)	6.7
Thermal conductivity ($\times 10^{-4}$ cal/cm²/cm/°C/sec) 20°C	0.389
1st ionization potential (eV)	15.577
Cross section (barns)	0.63
Vapor pressure (°C)	200.5
Chemical reactivity	None
Hardness (Mohs — scratch)	2—2.5
Crystal structure (isometric — normal)	(100) cube, fcc
Color (gas)	Colorless
(liquid)	Clear
(solid)	Clear/bluish
Cleavage (cubic — solid)	(001)

ARGON, Ar

General: A natural element in air which contains about 0.94%. It is separated by fractionation of liquid air and is about $2^1/_2$ times more soluble in water than nitrogen though it does not combine with any other element as a compound; whereas nitrogen forms nitrides,

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nitrates, and nitrites. It is an inert, colorless gas at standard temperature and pressure (22.2°C and 760 mmHg) and is best recognized by its characteristic spectra lines in the red end of the spectrum. Symbol may be shown as A only, though Ar is standard (Gr: argon = inactive).

In industry it is used for its inert properties in electric light bulbs and fluorescent tubes. Also used as an inert atmosphere for storage and chemical processing of metals and compounds that react to oxygen or water vapor in air, and as an inert furnace atmosphere in metal processing.

Technical Application: Argon is not directly used in fabrication of Solid State device structural components, but it is used as an inert atmosphere in vacuum or furnace systems, such as RF sputter and epitaxy. It also is used as various gas mixture: Ar/H_2 for a reducing atmosphere in these systems; Ar/N_2 for the sputtering of metal nitrides, such as Si_3N_4 or AlN; Ar/O_2 for evaporation or sputter of metal oxides, such as SiO_2 or BeO, and as $Ar/N_2/O_2$ for oxynitrides and, as an RF ionized gas, Ar^+, for surface cleaning prior to metallization of a specimen. It is widely used in this latter process, but can induce subsurface damage depending upon RF power levels.

Chemical processing of some of the compound semiconductors, such as aluminum arsenide and aluminum antimonide, AlAs and AlSb, respectively, which oxidize in air, are handled under argon or nitrogen atmospheres.

Argon has been grown as a single crystal in a vacuum system under cryogenic conditions and pressure for morphological study. It is fabricated as the argon laser.

Etching: As single crystal, vary vacuum vapor pressure.

ARGON ETCHANTS

AR-0001
ETCH NAME: Pressure
TYPE: Pressure, dislocation
COMPOSITION:
x .... pressure, vapor
TIME:
TEMP: 2 K (L_{He})
DISCUSSION:

Ar, single crystal ingots grown in vacuum under cryogen conditions and pressure. Develop structure and defects by varying vacuum pressure. (*Note:* The reference describes methods and techniques for growing single crystal rare gases.)
REF: Schwentner, N — *Rare Gas Solids,* Vol 3, Academic Press, New York, 1960

PHYSICAL PROPERTIES OF ARSENIC, As

Classification	Semi-metal
Atomic number	33
Atomic weight	74.92
Melting point (°C)	817 (28 atm)
Boiling point (°C)	613 (sublimes)
Density (g/cm^3)	5.72
Specific heat (cal/g) 20°C	0.082
Heat of fusion (k-cal/g-atom)	88.5
Heat of sublimation (cal/g)	102
Atomic volume (W/D)	13.1
1st ionization energy (K-cal/g-mole)	231
1st ionization potential (eV)	9.8
Electronegativity (Pauling's)	2.0
Covalent radius (angstroms)	1.20

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Ionic radius (angstroms)	0.46 (As^{+5})
Linear coefficient of expansion ($\times 10^{-6}$) 20°C	4.7
Electrical resistivity (micro ohms-cm) 20°C	33.3 (35)
Magnetic susceptibility (cgs $\times 10^{-6}$) 20°C	5.5
Cross section (barns)	4.5
Vapor pressure (°C)	518
Hardness (Mohs — scratch)	3.5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb (near-cube)
Color (solid)	Tin white
Cleavage (basal — perfect)	(0001)

ARSENIC, As

General: Occurs in nature as the pure element, but not in quantity. Usually found in association with metallic veins of silver, cobalt, and nickel ores and with cinnabar, realgar, and orpiment. The latter two minerals are sulfides, As_2O_3, noted for their brilliant red or yellow color, respectively. It is believed that amorphous arsenic (black) was first recognized by Albertus Magnus in 1250 A.D. It is silver-white like tin when first cleaved, but oxidizes to dull grey and, when sublimed by heating, re-solidifies as both a crystalline and amorphous structure. The pure metal is not considered dangerous, but several compounds are extremely hazardous.

In industry the metallic element is used as an additive for many alloys of iron and steel, and as a hardening agent in bronze. Many compounds are used as insecticides, such as Paris Green and both Adamsite and Lewisite were used as gases in World War I. Black amorphous arsenic was used as a cosmetic eye shadow in ancient times, but is no longer used due to its health hazard. When the metal is ignited in air it burns to the trioxide, which is noted for an intense garlic odor, and is extremely toxic. It also is used in glass fabrication as a coloring agent, and for low melting point glasses.

Technical Application: Arsenic has several important applications in Solid State device fabrication, both as an n-type dopant in silicon and in the growth of several compound semiconductors.

The most important of the compound semiconductors is gallium arsenide, GaAs; common acronym: GAS-. Aluminum arsenide, AlAs, is not widely used, due to its hygroscopic nature; indium arsenide, InAs has similar problems.

In growth of arsenic compounds, such as epitaxy GaAs thin films or, when used as a diffusion dopant, the element is obtained using arseine, AsH_3, to include growth by OMCVD and MBE. It has been used as a low melting point glass in fabrication of silicon radiation detectors as a paint-on coating over exposed planar junctions.

Arsenic has been grown as a single crystal for general morphological and defect studies.

Etching: HNO_3, halogens, alkalies and mixed acids.

ARSENIC ETCHANTS

AS-0001a
ETCH NAME: Sodium hydroxide — TIME:
TYPE: Alkali, removal — TEMP: Hot
COMPOSITION:
x .... 5—20% NaOH
DISCUSSION:
As,(0001) wafers cleaved from a bulk mass. Solution used as a general removal etch. Specimens used in a study of the DeHass-van Alphan effect.
REF: Berlincourt, T G — *Phys Rev*, 99,1716(1955)

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AS-0001b
ETCH NAME: Nitric acid
TYPE: Acid, removal/polish
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP: RT
DISCUSSION:
As, (0001) cleaved specimens. Solution used as a general removal and polishing etch.
REF: Ibid.

AS-0003: Adachi, H & Hartnagel, H L — *J Vac Sci Technol*, 19,427(1961)
As, as a constituent in single crystal GaAs, p-type wafers fabricated as light emitting diodes with Al or Au dot contacts. Arsenic is removed with HNO_3; whereas gallium is removed with alkalies producing a surface enriched with Ga or As, respectively. Light emission was good or improved with basic (alkali) solutions or by annealing at 350°C in N_2 for 5 min. Strong acid treatment reduced or eliminated emission.

AS-0002a
ETCH NAME:
TYPE: Halogen, dislocation
COMPOSITION:
x .... 10% I_2
x .... MeOH
TIME: 10 sec
TEMP: RT
DISCUSSION:
As, (111)(?) specimens cleaved in air at RT. Wafers were polished with 1HCl:2HNO_3:12HAc. Solution shown was used to develop dislocations. Rinse in MeOH to remove residual iodine with a final DI water wash. (*Note:* Arsenic is hexagonal-rhombohedral with perfect basal (0001) cleavage. It is occasionally observed as a near-cubic rhombohedron, such that the (111) cleavage shown is questionable. The probability is that the specimen was near-cubic in appearance.)
REF: Sheity, M N & Tailor, J B — *J Appl Phys*, 39,3717(1968)

AS-0002b
ETCH NAME: Bromine etch
TYPE: Acid, dislocation
COMPOSITION:
1 .... HF
2 .... HNO_3
1 .... HCl
24 .... HAc (CH_3COOH)
1 .... Br_2
TIME: 45 sec
TEMP: RT
DISCUSSION:
As, (111)(?) specimens cleaved in air at RT. Solution used as a dislocation etch. See note under AS-0002a for additional discussion.
REF: Ibid.

AS-0002c
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HCl
2 .... HNO_3
12 .... HAc
TIME: 1—2 min
TEMP: RT

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DISCUSSION:

As, (111)(?) specimens cleaved in air at RT. Solution used as a polish etch prior to dislocation etching. See note under AS-0002a for additional discussion.

REF: Ibid.

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PHYSICAL PROPERTIES OF BARIUM, Ba

Classification	Alkaline metal
Atomic number	56
Atomic weight	137.36
Melting point (°C)	850 (725)
Boiling point (°C)	1640 (1140)
Density (g/cm^3)	3.5
Specific heat (cal/g) 25°C	0.068
Heat of fusion (k-cal/g-atom)	1.83
Heat of vaporization (k-cal/g-atom)	35.7
Atomic volume (W/D)	39
1st ionization energy (K-cal/g-mole)	120
1st ionization potential (eV)	5.21
Electronegativity (Pauling's)	0.9
Covalent radius (angstroms)	1.98
Ionic radius (angstroms)	1.34 (Ba^{+2})
Electrical resistivity (micro-ohms-cm)	50
Work function (eV)	2.48
Cross section (barns)	1.2
Vapor pressure (°C)	1301
Hardness (Mohs — scratch)	8.5—9
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Silver white
Cleavage (cubic)	(001)

BARIUM, Ba

General: Does not occur as a native element. Barite, $BaSO_4$ (heavy spar), is the major ore and, when transparent, resembles calcite, $CaCO_3$ (Iceland spar). Barite can form in a white "barite rose" structure, equated to the term "rosette" used in material processing. The pure metal has had little use in metal processing, but several compounds are of importance: the sulfate is a white pigment called "blanc fixe" used to weight paper; the carbonate is a rat poison; and nitrates are green coloring in pyrotechnics. Other barium salts have medical applications, such as $Ba(OH)_3$ solutions used to evaluate the intestinal tract as it is opaque to X-ray. The hydroxide also is used in the refining of sugar.

Technical Application: The metal has not been used in Solid State processing, although barium fluoride, BaF_2, is used as a substrate, and is under evaluation as a thin film. In electronic processing of materials, barium titanate, Ba_2TiO_3, is the primary transducer element for ultrasonic generators.

Etching: Soluble in water, single acids, and alcohols.

BARIUM ETCHANTS

BA-0001a
ETCH NAME: Ethyl alcohol — TIME:
TYPE: Alcohol, polish — TEMP: RT
COMPOSITION:
x .... EOH
DISCUSSION:
Ba, specimens. A general removal and polish etch for barium.

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REF: Hodgman, C D et al — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 348

BA-0001b
ETCH NAME: Hydrochloric acid
TYPE: Acid, polish
TIME:
TEMP: RT
COMPOSITION:
x .... HCl
DISCUSSION:
Ba, specimens. This and other single acids can be used as general etchants for barium.
REF: Ibid.

PHYSICAL PROPERTIES OF BARIUM FLUORIDE, BaF_2

Classification	Fluoride
Atomic numbers	56 & 9
Atomic weight	175.36
Melting point (°C)	1280
Boiling point (°C)	2137
Density (g/cm^3)	4.83
Ionic radius (angstroms)	1.43
Surface free-energy (ergs cm^{-2}) 273°C	393 [on (111)]
−195°C	280 [on (111)]
Hardness (Mohs — scratch)	2—3
(Knoop — kgf mm^{-2})	82
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
Cleavage (cubic — distinct)	(111)

BARIUM FLUORITE, BaF_2

General: Does not occur in nature as a compound, although there are several metallic fluorides, such as fluorite, CaF_2, and sellaite, MgF_2. As an artificially compounded material there is major industrial use in the manufacture of white enamels, and it is used in medicine as both an antiseptic and as embalming fluid.

Technical Application: Barium fluoride is one of the few single crystals that show (111) cleavage like diamond and fluorite, as most others in the isometric system — normal class show cubic, (001) cleavage. It has been used as a (111) cleaved substrate in the study of metal thin films, with the deposited films removed by float-off technique with HCl for TEM study.

As a deposited thin film, it has been converted to the oxide, BaO, as a more stable surface coating. Bulk single crystals are used for their optical properties as prisms, lenses, or filter elements. As a (100) or (110) deposited thin film on semiconductor wafers, it has been used as an optical coating in device structuring.

Etching: Soluble in water, acids, and NH_4Cl.

BARIUM FLUORIDE ETCHANTS

BAF-0005b
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
TIME:
TEMP:

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COMPOSITION:
x .... H_2SO_4
DISCUSSION:
BaF_2 specimens. This acid will etch barium fluoride very slowly and incompletely.
REF: Ibid.

BAF-0005c
ETCH NAME: Oxygen
TYPE: Ionized gas, conversion
COMPOSITION:
x .... O^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
BaF_2 single crystal specimens. Etching in an RF plasma of oxygen will convert the BaF_2 surface, in part, to BaO which is an even more inert and stable surface thin film than the fluoride.
REF: Ibid.

BAF-0005a
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
(1) x .... HF, conc. (2) x .... x% NH_4F
TIME:
TEMP:
DISCUSSION:
BaF_2 specimens. The material is soluble in both of the fluorine solutions shown. (*Note:* BHF solutions also apply.)
REF: *Encyclopedia of Chemical Technology,* Vol 10, John Wiley & Sons, New York, 1980
BAF-0006: Tu, C W — *J Vac Sci Technol,* B2,24(1984)
BaF_2 thin films. Material was deposited by MBE on indium phosphide (100) and (110) substrates. Films were deposited as single crystal. Also were co-deposited with SrF_2 as $Ba_xSr_{1-x}F_2$ thin films. Other materials studied were SrF_2 and CaF_2.

BAF-0007
ETCH NAME: Water
TYPE: Acid, polish
COMPOSITION:
x .... H_2O
TIME:
TEMP: RT or warm
DISCUSSION:
BaF_2, (111) wafers used as substrates for metal deposition of aluminum, chromium, and silver in a study of the mechanical properties of optical films. Water can be used to lightly clean and polish barium fluoride surfaces.
REF: Pulker, H K — *Thin Solid Films,* 89,191(1982)

BAF-0003
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
"A" 30 .... H_2SO_4 "B" 40 .... HCl "C" 80 .... Aerosol OT
70 .... H_2O 60 .... H_2O 20 .... HAc (CH_3COOH)
TIME: 4 h
TEMP: RT
DISCUSSION:
BaF_2, (111) wafers were cleaved in air at RT. Polish time is related to time required to reduce and remove cleavage steps. The polishing process was as follows:

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1. Glue wafer to a polishing pad.
2. Mount pad on a brass holder with paraffin — heat up slowly to prevent wafer cracking.
3. Saturate the polish pad with water and add 4 drops of solution "A" and 6 drops of solution "B", using an eye dropper.
4. Lap at 132 rpm — adding H_2O:HCl as needed.
5. Demount and clean in solution "C" (Aerosol OT supplier is Fischer Scientific.)

REF: Bis, R F et al — *J Appl Phys*, 47,736(1976)

BAF-0004
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, float-off — TEMP:
COMPOSITION:
x .... HCl (30%)
DISCUSSION:
BaF_2, (111) wafers cleaved in air and used as a substrate for Hot Wall Epitaxy (HWE) growth of PbSnTe. The substrate was held at 250°C during epi growth. The lead tin telluride film was removed by hydrochloric etch undercutting using the float-off technique. Film thicknesses were from 70 to 2500 Å and used in a morphological study of the compound.
REF: Suyman, H C et al — *J Cryst Growth*, 70,393(1984)

BAF-0009
ETCH NAME: Hydrochloric acid, dilute — TIME:
TYPE: Acid, float-off — TEMP:
COMPOSITION:
x .... HCl
x .... H_2O
DISCUSSION:
BaF_2, (111) wafers cleaved in air and used as a substrate for epitaxy growth of InGaSb. Substrate was vapor degreased in TCE, then rinsed in liquid MeOH, and then acetone. After epitaxy the thin film was float-off removed with dilute HCl.
REF: Eltoukhy, A H & Greene, J E — *J Appl Phys*, 50,505(1979)

BAF-0008
ETCH NAME: Nitrogen — TIME:
TYPE: Gas, cleaning — TEMP: RT
COMPOSITION:
x .... N_2
DISCUSSION:
BaF_2, (111) specimens cut and polished as circular lenses. Nitrogen blow off was used to remove any particulate matter from surfaces before evaporation of thin film chromium, aluminum, or gold with no liquid treatment.
REF: Walker, P — personal application, 1976

PHYSICAL PROPERTIES OF BARIUM TITANATE, Ba_2TiO_3

Classification	Oxide
Atomic numbers	56, 22 & 8
Atomic weight	372.57
Melting point (°C)	
Boiling point (°C)	
Density (g/cm^3)	

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Ferroelectric activity (KeV/cm)	2—450
Hardness (Mohs — scratch)	6—7
Crystal structure (orthorhombic) 286 K (RT)	(100) a-pinacoid
(hexagonal — rhombohedral) 193 K	$(10\bar{1}1)$ rhomb
(isometric — normal) 292 K	(100) cube
Color (solid)	Grey-white
Cleavage (cubic)	(001)

BARIUM TITANATE, Ba_2TiO_3

General: Does not occur as a natural compound. There are minerals as mixed titanosilicates containing barium, such as benitoite, $BaTiSi_2O_9$. The primary use of the artificially grown titanate is as the transducer element for ultrasonic generators. Ultrasonics, in conjunction with vapor degreaser systems, are a major method of cleaning for parts, materials, and equipment from a small beaker-sized ultrasonic unit — to large, walk-in vapor degreasing modules.

Technical Application: The Solid State industry is a major user of ultrasonic equipment in chemical processing of materials. Relatively large floor model vapor degreasers are used with ultrasonic generators for material and parts cleaning. Smaller tabletop units are used for vapor or liquid cleaning, and for active bubble stirring etching solutions in processing semiconductor wafers, circuit substrates, and allied materials.

Barium titanate is grown and used as a single crystal, and has been studied for general morphology with specific attention to ferroelectric properties. It also has been studied in its two other pressure/temperature related crystal forms, and it has been fabricated as a hollow polycrystalline sphere for evaluation of the pressure effects on the Curie temperature.

Etching: HCl, and hot H_3PO_4.

BARIUM TITANATE ETCHANTS

BAT-0001
ETCH NAME: Hydrochloric acid — TIME: 4 min or 4 h
TYPE: Acid, preferential — TEMP: RT to 0°C
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

Ba_2TiO_3 (111) and (100) wafers. Solution used at the two times/temperatures shown to develop magnetic domain structures. (*Note:* Photographs are excellent.)
REF: Camerson, D P — *IBM Res Dev*, 1,2(1957)
BAT-0008a: Schlosser, H & Drougard, M E — *J Appl Phys*, 32,1227(1961)

Ba_2TiO_3 specimens used in a study of surface layer structure above the Curie Point. Solution used as a dip etch for final surface cleaning.
BAT-0012: Hooten, J A & Merz, W J — *Phys Rev*, 988,409,(1955)

Ba_2TiO_3 single crystals. Solution used at RT with several minutes soak. Develops domain related pole figures, and shows that the nose end of an ingot etches more rapidly than the tail end. (*Note:* Nose and tail more often called seed end and tail end.)

BAT-0002
ETCH NAME: Phosphoric acid — TIME:
TYPE: Acid, polish — TEMP: 155°C
COMPOSITION:
x .... H_3PO_4
DISCUSSION:

Ba_2TiO_3 (100) wafers used in a study of ferroelectric domains activated from 2 to 450

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KeV/cm. After etching in the solution shown, pole in water. Use 4 *N* NaCl solution for pulse poling — add 0.1% HF to solution to develop 180° domain walls: pulse 5 sec — wait 15 sec — repulse, and repeat as needed. Domain walls will move with each pulse sequence.
REF: Stadler, H L & Zachmanidis, P J — *J Appl Phys*, 34,3255(1963)
BAT-0003: Stadler, H L — *J Appl Phys*, 34,571(1961)

Ba_2TiO_3 (100) wafers used in a study of etch hillock formation. Etch slightly in H_3PO_4 at 150°C — AC pole specimens in water — wash in acetone — wash in aqua regia, RT, 5 sec, and final etch in 1% HF, RT, 30 sec to develop grain boundaries. Then, to develop hillocks: (1) DC pole in water and (2) etch in 1% HF, RT, 30 sec. Hillocks, ad hoc, are negatively charged areas near domain walls. Mounds and pyramids were observed on (100) surfaces, that were aligned in ⟨110⟩ directions. Changes in resistivity were proportional to strain.
BAT-0004: Pearson, G L & Feldman, W J Jr — *Phys Chem Solids*, 9,28(1958)

Reference for method of developing grain boundaries shown in BAT-0003.
BAT-0005: Myerhofer, D — *Phys Rev*, 112,413(1958)

Ba_2TiO_3 (100) wafers prepared as very thin specimens and used in domain studies. Solution was used at 120°C as a thinning and polishing etch. Rinse in DI water, then alcohol.
BAT-0006: Miller, R C — *Phys Rev*, 111,736(1958)

Ba_2TiO_3, (100) wafers. Solution used at 155°C as a thinning and polishing etch, then DC pole in water with a Pt electrode.
BAT-0007: Miller, R C & Savage, A — *Phys Rev*, 112,755(1958)

Ba_2TiO_3, (100) wafers. Solution used at 155°C, 10—20 min, rinse in DI water, then in alcohol before DC poling.
BAT-0008b: Ibid.

Ba_2TiO_3 specimens. Solution used at 140°C, 15 min to 1 h as a polishing and thinning etch. Follow with HCl final cleaning dip: BAT-0008a.
BAT-0009: Last, J T — *Phys Rev*, 105,1740(1957)

Ba_2TiO_3 specimens. Solution used above 130°C (Curie Point of material) to prevent selective domain etching.
BAT-0010: Last, J T — *Rev Sci Instr*, 28,720(1957)

Ba_2TiO_3 specimens. Wafers were mounted on Teflon or silicone tape, mechanically lapped and then etch thinned with solution at 130°C. Removal rate shown as 1 μm/min.

BAT-0011
ETCH NAME: TIME:
TYPE: Cut, forming TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:

Ba_2TiO_3 polycrystalline hemispheres cemented together to form a sphere. The specimen was used in studying the effects of pressure on the Curie temperature.
REF: Jaffe, H et al — *Phys Rev*, 105,57(1957)

BAT-0013
ETCH NAME: TIME:
TYPE: Thermal, transition TEMP:
COMPOSITION:
x .... heat
DISCUSSION:

Ba_2TiO_3 single crystals used in an electrostatic study of ferroelectric phases. Crystal structure change was rhombohedral at 193 K to orthorhombic at 268 K (RT), to cubic at 293 K.

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REF: Smolander, J & Ahtee, M — *J Phys Chem Solids,* 44,1(1983)

PHYSICAL PROPERTIES OF BARIUM TUNGSTATE, $BaWO_4$

Classification	Oxide
Atomic numbers	56, 74 & 8
Atomic weight	385.28
Melting point (°C)	1200 approx.
Boiling point (°C)	
Density (g/cm³)	5.04
Hardness (Mohs — scratch)	4—5
Crystal structure (tetragonal — pyramidal)	(111) pyramid
Color (solid)	Clear to whitish
Cleavage (octahedral)	p(111)

BARIUM TUNGSTATE, $BaWO_4$

General: Does not occur as a natural compound, although there are other minerals as tungstates of copper or lead alone or with molybdenum. Scheelite, $CaWO_4$ is an important tungsten ore, as is wolframite, $(Fe,Mn)WO_4$. There is no use of barium tungstate in industry, and the natural minerals are primarily used as a source of tungsten. They do have some application as coloring agents in glass.

Technical Application: Single crystal barium tungstate as a Solid State material has been evaluated for general morphology and compound characteristics, but has found no use as an electronic device, to date.

Etching: H_3PO_4.

BARIUM TUNGSTATE ETCHANTS

BWO-0001
ETCH NAME: Phosphoric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... H_3PO_4, conc.
DISCUSSION:

$BaWO_4$ single crystal specimens used in a study of Raman frequency shifts and temperature dependence. Material has the scheelite structure: tetragonal system — pyramidal class. Other tungstates studied were $CaWO_4$ and $SrWO_4$.
REF: Degreniere, S et al — *J Phys Chem Solids,* 45,1105(1984)

PHYSICAL PROPERTIES OF BERYLLIUM, Be

Classification	Alkaline metal
Atomic number	4
Atomic weight	9.0122
Melting point (°C)	1283 (1278)
Boiling point (°C)	2970
Density (g/cm³)	1.85
Thermal conductance (cal/sec)(cm²)(°C/cm) 0°C	0.440
Specific heat (cal/g) 0°C	0.41 (0.45 @ 20°C)
Latent heat of fusion (cal/g)	260

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Heat of fusion (cal/g)	260—275
Heat of vaporization (k-cal/g-atom)	73.9
Atomic volume (W/D)	5.0
1st ionization energy (K-cal/g-moles)	215
1st ionization potential (eV)	9.32
Electronegativity (Pauling's)	1.5
Covalent radius (angstroms)	0.90
Ionic radius (angstroms)	0.35 (Be^{+2})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 25°C	11.5
Electrical conductance (micro-ohms^{-1})	0.25
Electrical resistivity ($\times 10^{-6}$ ohms cm) 20°C	4
Electron work function (eV)	3.92
Cross section (barns)	0.009
Hardness (Mohs — scratch)	6—7
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Silver-grey
Cleavage (prismatic, poor)	$(10\bar{1}0)$

BERYLLIUM, Be

General: Does not occur as a free element in nature. There are about 20 beryllium-containing minerals with none as major occurrences, though several are quite widely distributed. The beryllium aluminum silicates are the main sources of ore: beryl, $Be_3Al_2(SiO_3)_6$ is representative as both an ore and as the precious gem stone sapphire, deep blue; aquamarine, pale blue; emerald, bright green, as well as a yellow variety called yellow beryl. The pure metal resembles magnesium in appearance and chemical properties and is one of the few metals that will scratch glass, H = 6.5—7.

It is the lightest of known metals and is finding increasing use in industry, particularly as an alloy with aluminum for lightweight construction, and other metals where it increases fatigue endurance and corrosion resistance. Beryllium compounds have a sweet odor and many are considered hazardous to health, the oxide in particular due to dusting during cutting.

Technical Application: Beryllium metal is not widely used in Solid State processing although it has use as a dopant species in some compound semiconductors. It has been used as the pure metal and as an aluminum alloy for metal electrode deposition on quartz radio frequency crystals to reduce mass loading effects on frequency, although special handling is required due to the toxicity of beryllium and its compounds.

Etching: Soluble in dilute acids and alkalies.

Note: Caution should be observed in handling beryllium and its compounds due to toxicity and health hazard. There are OSHA regulation requirements that must be met for those processing the material.

BERYLLIUM ETCHANTS

BE-0001
ETCH NAME: Potassium hydroxide
TYPE: Alkali, cleaning/removal
COMPOSITION:
x .... *30% KOH or NaOH

TIME: 2—3 min
TEMP: Warm (30—40°C)

*450 g/l.

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DISCUSSION:

Be, as 0.060 diameter wire. Solution was used to etch clean wire prior to material evaporation as electrodes on AT-cut quartz crystal blanks. After etching, heavy water wash, and IR lamp dry. "U" shaped clips of Be wire were hung on tungsten coils and evaporated in a small oil-pump vacuum system with a 6" diameter/high Pyrex bell jar. After metallization, pump system to at least 10^{-6} Torr and hold 20—30 min to remove Be vapors, before opening.

REF: Walker, P — personal development, 1968

BE-0002

ETCH NAME: Hydrochloric acid

TIME:

TYPE: Acid, removal

TEMP:

COMPOSITION:

x .... HCl

DISCUSSION:

Be, as an evaporated thin film used is a study of reactions with silicon and oxygen at different temperatures. Be was deposited on a (111) silicon substrate containing a layer of SiO_2. The silicon substrate was degreased in TCE: then acetone, methanol, and water rinsed. Then dipped in 10% HF and water rinsed immediately prior to CVD deposition of 4000 Å of SiO_2 followed by beryllium metal evaporation. Wafers were annealed at different temperatures in a study of reactions. Above 400°C Be reacts with SiO_2 forming an insoluble residue, possibly BeO, in part.

REF: Moore, J B & McCaldin, J C — *J Electrochem Soc,* 124,625(1977)

BE-0003

ETCH NAME: Phosphoric acid

TIME: 60 sec

TYPE: Acid, preferential

TEMP: 175°C

COMPOSITION:

x .... H_3PO_4, conc.

DISCUSSION:

Be specimens. Solution used as a defect and structure development etch.

REF:

BE-0004a

ETCH NAME:

TIME:

TYPE: Electrolytic, thinning

TEMP:

COMPOSITION:

ANODE:

1% .... HCl

CATHODE:

2% .... HNO_3

POWER:

97% .... ethylene glycol (EG)

DISCUSSION:

Be, thin film deposits thinned with this solution for electron microscope study of dislocations.

REF: Baird, J D et al — *Nature (London),* 182,1660(1958)

BE-0004b

ETCH NAME: Freeze etch

TIME:

TYPE: Ice, preferential

TEMP: −196°C

COMPOSITION:

x .... ice

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DISCUSSION:

Be, thin films deposited on ice under vacuum at −196°C (LN_2) temperature. Produces a "freeze-out" structure of the beryllium.

REF: Ibid.

BE-0005

ETCH NAME: Heat

TYPE: Thermal, forming

TIME:

TEMP:

COMPOSITION:

x .... heat

DISCUSSION:

Be, polycrystalline spheres from 0.1 to 1.5 mm diameter formed by arc melting under an He atmosphere. Fifty percent of smaller sizes were single crystal. Use chips and flakes in a copper pot that was water cooled, striking the material with sporadic bursts of power to splatter form spheres.

REF: Ray, A E & Smith, J F — *Acta Metall,* 11,310(1958)

BE-0006

ETCH NAME:

TYPE: Acid, removal

TIME:

TEMP:

COMPOSITION:

x .... 6 *N* HCl

x .... NH_4OH (1 mg equivalent)

DISCUSSION:

Be, specimens used in a study of neutron-transfer reactions associated with nitrogen bombardment.

REF: Halbert, M L et al — *Phys Rev,* 106,251(1957)

BE-0007

ETCH NAME:

TYPE: Electrolytic, polish

TIME:

TEMP:

ANODE: Be

CATHODE:

POWER: 15 V

COMPOSITION:

4 ml .... HCl

20 ml .... HNO_3

4 ml .... H_2SO_4

200 ml .... ethylene glycol (EG)

DISCUSSION:

Be, single crystal specimens used in a study of micro-strain. Solution shown used to polish ingots before straining.

REF: Lawley, A et al — *Acta Metall,* 14,1339(1966)

BE-0008

ETCH NAME:

TYPE: Electrolytic, removal

TIME:

TEMP:

ANODE: Be

CATHODE:

POWER:

COMPOSITION:

100 ml .... H_3PO_4

30 ml .... EOH

30 ml .... H_2SO_4

30 ml .... glycol

DISCUSSION:

Be, (001), (100), and (110) cut wafers used as substrates for growth of BeO. After cutting, wafers were lapped down with 3-μm diamond grit using a wheel. Solution shown

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was used to polish and remove residual damage prior to oxidation to convert surfaces to BeO. (*Note:* Glycol was probably ethylene glycol.)
REF: Scott, V D — *Acta Crystallogr,* 12,136(1959)
BE-0009: Mott, B W & Haines, H R — *J Inst Met,* 80,628(1951)
Be, specimens. Solution used as a general etchant for beryllium.

BERYLLIUM ALLOYS, BeM_x

General: Beryllium metallic alloys do not occur in nature. There are only nine minerals listed as beryllium minerals, though it appears as a trace element in several others. The most important ore is beryl, an aluminum silicate, and it occurs as an oxide, sulfide, and phosphate.

Industrially the element is used as an alloy with copper, aluminum, iron, etc., to improve wear, corrosion resistance, and reduce alloy weight.

Technical Application: Beryllium copper shim stock is used in Solid State processing for its spring qualities. In vacuum evaporation it is cut into small "fingers" to hold semiconductor wafers and dielectric substrates in position on a flat plate during metallization and, because of its wear characteristics, does not lose it spring capabilities under such heat application. Similar fingers or plate holder designs are used for holding parts during electrical testing, metal plating, and in chemical processing where the material is not attacked by solutions being used.

An aluminum:beryllium mixture (38% Be) has been used as an evaporation alloy on quartz crystal radio frequency blanks to reduce metal mass loading effects for improved frequency stability. Caution should be observed in such operations due to the toxicity of beryllium compounds — there is a distinctive sweet odor.

Etching: Single acids of HCl, H_3PO_4, and alkalies; HCl:HNO_3 mixtures.

BERYLLIUM ALLOYS

BERYLLIUM:COPPER ETCHANTS

BECU-0001
ETCH NAME: Hydrochloric acid, dilute — TIME: 1—2 min
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
1 .... HCl
20 .... H_2O
DISCUSSION:
Be:Cu, strips 0.005 to 0.030 thick. Material cut as finger clips to hold wafers in position by spring action on evaporation holder plates during metallization of parts. Also used as spring contacts to hold specimens in position in test fixtures. After cutting fingers to shape lightly etch clean in the solution shown. Water rinse, methyl alcohol rinse, and air dry or nitrogen blow dry. After use, with excess metal build-up on fingers from evaporation, peel away metal with tweezers and etch clean as needed.
REF: Fahr, F — personal communication, 1978

BECU-0002
ETCH NAME: Acetone — TIME: 1—2 min
TYPE: Ketone, cleaning — TEMP: RT
COMPOSITION:
x .... acetone
DISCUSSION:
Be:Cu, strips 0.003 to 0.040 thick. Material cut and used as either finger clips to hold

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wafers/substrates in place during vacuum metallization or as holding clips on wafer test assembly units. In evaporation, excess metal is peeled away and/or wire brushed, degreased with TCE, then rinsed in acetone and nitrogen blown dry. Test holder fingers degreased and rinsed as required. "U" clips on tungsten coils similarly cleaned prior to use as an evaporation source.
REF: Walker, P — personal application, 1968/1978

ALUMINUM BERYLLIUM ETCHANTS

BEAL-0001
ETCH NAME: Potassium hydroxide
TYPE: Alkali, cleaning
TIME: 2—3 min
TEMP: 30—40°C
COMPOSITION:
x .... 30% KOH (NaOH)
DISCUSSION:
Al:Be(38%), as 0.060 diameter polycrystalline wire. Solution used to clean wire prior to use as an evaporation alloy on quartz crystal radio frequency blanks to reduce mass loading. After etching, wash heavily in DI water and dry under a heat lamp. "U" clips were hung on tungsten coils for evaporation and, after evaporation, system was pumped to 10^{-6} Torr for at least 30 min to cool the system and eliminate beryllium vapors due to toxicity.
REF: Walker, P — personal development, 1969

PHYSICAL PROPERTIES OF BERYLLIUM OXIDE, BeO

Classification	Oxide
Atomic numbers	4 & 8
Atomic weight	25.02
Melting point (°C)	2550
Boiling point (°C)	
Density (g/cm^3)	2.017 (3.025)
Refractive index (n=)	1.733—1.719
Limit of application (°C)	2400
Specific heat (mean) (J/kg °C)	2180
Coefficient of thermal linear expansion ($\times 10^{-6}$ cm/cm/°C) 25—800°C	7.5
Thermal conductivity (W/m °C) 1000 °C	29
Electrical resistivity ($\times 10^{8}$) 600°C	4
($\times 10^{12}$) 2100°C	8
Hardness (Mohs — scratch)	9
Crystal structure (hexagonal — hemimorphic)	$(21\bar{3}3)$ 3rd order pyramid
Color (solid)	White
Cleavage (basal or pedion)	(0001)

BERYLLIUM OXIDE, BeO

General: Occurs as the mineral bromellite, BeO, and noted from only one location in Sweden. Industrially, the oxide is classified as a high temperature refractory ceramic. It is used as pressed powder alone or mixed with alumina as an insulator, for crucibles, furnace linings, and tubing.

Technical Application: Beryllium oxide is a II—VI compound semiconductor, but in Solid State processing its major use has been as a ceramic substrate for circuit fabrication, particularly for high frequency microwave device application. It is fabricated as a pressed

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powder blank (like alumina), and there is ongoing development to reduce grain size for improved frequency circuit assemblies, to include use as a packaging material. It has been grown and studied as a single crystal, and deposited as a thin film, directly, or converted from a nitride to an oxide by thermal oxidation in evaluation as a surface coating similar to silicon dioxide. **CAUTION:** Beryllium and its compounds are toxic and a health hazard.

Etching: H_2SO_4, H_3PO_4, HF, and alkalies.

BERYLLIUM OXIDE ETCHANTS

BEO-0001a
ETCH NAME: Phosphoric acid — TIME: 60 sec
TYPE: Acid, preferential — TEMP: 175°C
COMPOSITION:
x .... H_3PO_4
DISCUSSION:

BeO, (0001) wafer. Wafers cut from a single crystal and lap/polished with diamond paste. The material shows polarity like compound semiconductors. The (0001)A-beryllium surface is very slowly attacked in this solution. The $(000\bar{1})$B-oxide surface is rapidly etched. The solution develops etch pits and possibly dislocation pits on the (0001)A, but the authors says that further work is needed to develop dislocations. A damaged point on the $(000\bar{1})$B surface developed a four-sided, square prism etch pit. Crystals tend to grow as pyramids with a preferred (0001) basal plane.
REF: Austerman, S B — *J Appl Phys*, 34,339(1963)

BEO-0001b
ETCH NAME: Sulfuric acid — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... H_2SO_4, conc.
DISCUSSION:

BeO, (0001) wafers. Solution used as a preferential etch in a similar manner as shown under BEO-0001a for phosphoric acid.
REF: Ibid.

BEO-0003
ETCH NAME: Sulfuric acid, dilute — TIME: 5—10 min
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O
DISCUSSION:

BeO, pressed powder blanks. After cutting to size for use as substrates for device mounting of power diodes, parts were soaked clean in this solution. Follow with heavy DI water washing, MeOH rinse, and dry under IR lamp. Also used for cleaning of package parts in device assembly.
REF: Walker, P — personal application, 1963—1964
BEO-0007: Scott, V D — *Acta Crystallogr*, 12,136(1959)

BeO, thin films grown on single crystal beryllium wafers cut (001); (100) and (110). Material used in a growth and structure study of BeO. A 15% sulfuric acid solution developed fine cracks parallel to ⟨001⟩ directions. Material cleaved along these line directions.

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BEO-0004
ETCH NAME: Potassium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... 10—30% KOH
TIME:
TEMP:
DISCUSSION:
BeO, (0001) wafers and pressed powder substrates. Solution is a general etch for the material.
REF: Grossmann, J & Herman, D S — *J Electrochem Soc,* 116,674(1969)
BEO-0005a: Shehata, M T & Kelly, R — *J Electrochem Soc,* 122,1359(1975)
BeO, (0001) wafers. Solution used as a general etch.

BEO-0006a
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
COMPOSITION:
x .... HCl, conc.
TIME:
TEMP: 120°C
DISCUSSION:
BeO, (0001) wafers and pressed powder substrates. Referred to as a general etch for the material.
REF: Ehman, M F — *J Electrochem Soc,* 121,1240(1974)

BEO-0006b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... H_3PO_4
x .... H_2SO_4
TIME:
TEMP: Boiling
DISCUSSION:
BeO, (0001) wafers and pressed powder substrates. Solution referred to as a general etch for the material.
REF: Ibid.
BEO-0005b: Ibid.
BeO, (0001) wafers. Solution used as a general etch.

BEO-0002
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
1 .... HF
6 .... H_2O
TIME: 10 min or 30—60 min
TEMP: Boiling
DISCUSSION:
BeO, (0001) single crystal wafers used in a study of dislocation development. Solution develops very sharply defined hexagonal pits after 10 min. With extended etching 1st and 2nd order prisms and pyramidal planes are developed.
REF: Vandervoort, A R & Barmors, W L — *J Appl Phys,* 37,4483(1966)

BEO-0008
ETCH NAME:
TYPE: Mechanical, defect
COMPOSITION:
x .... stress
TIME:
TEMP:

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DISCUSSION:

BeO, (0001) single crystals used in a study of dislocation, slip and fracture. An intron hardness tester was used to point damage surfaces at various temperature levels to induce defects. (*Note:* This is a Knoop hardness tester unit using a specially designed diamond wedge tip.)

REF: Bentlo, G G & Miller, K T — *J Appl Phys*, 38,4248(1967)

PHYSICAL PROPERTIES OF BISMUTH, Bi

Classification	Semi-metal
Atomic number	83
Atomic weight	208.98
Melting point (°C)	271.3
Boiling point (°C)	1560
Density (g/cm^3)	9.8
Thermal conductance (cal/sec)(cm^2)(°C/cm) 20°C	0.020
Specific heat (cal/g) 20°C	0.0294
Latent heat of fusion (cal/g)	12.5
Heat of fusion (k-cal/g-atom)	12.5
Heat of vaporization (cal/g)	204.3
Atomic volume (W/D)	21.3
1st ionization energy (K-cal/g-mole)	185
1st ionization potential (eV)	9.0
Electronegativity (Pauling's)	1.9
Covalent radius (angstroms)	1.46
Ionic radius (angstroms)	0.96 (Bi^{+3})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	13.3
Electrical resistivity (micro ohms-cm)	106.8
Vapor pressure (°C)	1271
(mmHg) 1200°C	100
Modulus of elasticity (psi $\times 10^4$)	4.6
Cross section (barns)	0.034
Poisson ratio	0.33
Shear modulus (psi $\times 10^4$)	1.8
Hardness (Mohs — scratch)	2.56
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Grey/reddish-silver
Cleavage (basal — perfect)	(0001)

BISMUTH, Bi

General: Occurs as a native element as a vein mineral commonly associated with lead, silver, nickel, and cobalt ores. There are a number of bismuth-containing minerals, mostly as silver and lead sulfides and arsenides. The most important ore mineral is bismuthinite, Bi_2S_3. Bismuth is a poor conductor of electricity, is diamagnetic, and expands upon solidification in crystalline form. Bismuth will burn in air with a brilliant blue flame with production of heavy, yellow oxide fumes. Although it is hexagonal — rhombohedral it is usually found in reticulated, arborescent masses and as grains. It has perfect (0001) cleavage, is sectile, and very brittle, but when heated is slightly malleable. For many years it was confused with lead and tin as all are silver-white in color, but bismuth has a reddish hue.

Rarely used in industry as the pure metal, but is a constituent in many alloys —

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particularly low melting solders such as those used in sprinkler heads for fire protection. It has special use as a casting form in low temperature fabrication of parts.

Technical Application: Not used in Solid State processing and fabrication of silicon, germanium, and gallium arsenide devices though it is an n-type dopant in some compound semiconductors.

Bismuth is used in growing II—V compound semiconductors such as bismuth selenide, Bi_2Se_3 and bismuth telluride, Bi_2Te_3. It has been grown as a single crystal for structural data and general morphological studies.

Etching: HNO_3, aqua regia; hot H_2SO_4; slowly in HCl, HF, and halogens.

BISMUTH ETCHANTS

BI-0001
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:

Bi, single crystal specimens from ingots grown by the Bridgman technique. Bars cut with a jeweler's saw. (0001) bar ends were mechanically polished. The solution was used as a "sizing" etch to reduce bar dimensions and to etch clean the bars.
REF: Gallo, C F — *J Appl Phys*, 34,144(1963)
BI-0005: Mullins, W W — *Acta Metall*, 4,421(1956)

Bi, single crystal specimens used in a study of induced grain boundary motion by application of magnetic flux. Solution used as a general removal etch.

BI-0002
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, damage removal
TIME: 15—20 min
TEMP: RT
COMPOSITION:
2 .... HF
98 .... H_2O
DISCUSSION:

Bi, (0001) wafers used in a study of slip and failure from applied tension and its orientation dependence. After mechanical lap and polish, solution used to remove residual damage. Up to 0.2 mm damage removed.
REF: Garber, R I et al — *Sov Phys (Solid State)*, 3,832(1960)

BI-0003
ETCH NAME: Tri-iodide, modified
TYPE: Halogen, polish
TIME:
TEMP: RT to hot
COMPOSITION:
x .... KI, sat. sol.
x .... I_2
x .... H_2O
DISCUSSION:

Bi, (0001) wafers cleaved under liquid nitrogen, LN_2, to minimize strain. Etchant used as a KI saturated solution to polish wafers.
REF: Abeles, B & Meiboom, S — *Phys Rev*, 101,544(1956)

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BI-0004a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
35 g .... KI
1 g .... I_2
10 ml .... HCl
200 ml .... H_2O
TIME: 60 sec, 10 cycles
TEMP:
ANODE: Bi
CATHODE:
POWER: 1 A/cm^2
RATE: 0.015"/60 sec
DISCUSSION:
Bi, (0001) wafers cut and sandblasted as $^5/_8$ diameter discs used in a study of anomalous skin effects. Solution used to etch polish to within 1 μm of surface plane planar orientation for strain-free surface. After etching, rinse in 1HCl:1EOH to remove surface film left on material from electrolytic etching. (*Note:* This is an acidified tri-iodide solution; film remaining is residual iodine. See: Gold.)
REF: Smith, G F — *Phys Rev,* 115,1561(1959)

BI-0015a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
3 .... HAc
1 .... H_2O_2
TIME:
TEMP:
DISCUSSION:
Bi, single crystal specimens. Solution used as a general cleaning and polishing etch for bismuth.
REF: Rutherford, R J — *Proc Am Soc Test Mater,* 24,739(1924)

BI-0006a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
6 .... HNO_3
6 .... HAc
1 .... H_2O
TIME: 1—5 min
TEMP: RT
DISCUSSION:
Bi, (0001) wafers used in a study of dislocations. Solution used to polish surfaces prior to preferential etching.
REF: Lovell, L C & Wernick, J H — *J Appl Phys,* 30,234(1959)
BI-0013: Yim, W M & Stofke, E J — *J Appl Phys,* 38,5210(1967)
Bi:BiMn (4%), single crystals. The BiMn segments were as ordered filaments in the hexagonal bismuth matrix. Ingot was a eutectic crystal. Solution used to polish surfaces in a study of crystal morphology.

BI-0006b
ETCH NAME:
TYPE: Halogen, dislocation
COMPOSITION:
x .... 1% I_2
x .... MeOH
TIME: 15 sec
TEMP: RT
DISCUSSION:
Bi, (0001) wafers used in a dislocation study. After polishing in solution shown under BI-0006a, this solution was used to develop dislocations. (*Note:* This mixture is used on

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silicon, germanium, compound semiconductors, and other metals as a polishing, preferential, selective or surface conditioning solution. Reactions are similar to the bromine-methanol (BRM) mixtures.)
REF: Ibid.

BI-0015b
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... HCl
(2) 1 .... HCl
1 .... EOH
TIME:
TEMP:

DISCUSSION:

Bi, single crystal specimens. Both solutions used as general cleaning etches after etching specimens in iodine solutions to remove residual iodine films from surfaces and as a general etch. (*Note:* Residual surface iodine can be removed by washing in methanol.)
REF: Ibid.
RI-0004b: Ibid.

Bi, (0001) wafers used in a study of anomalous skin effects. The 1HCl:1EOH solution was used to clean residual iodine from surfaces after electrolytic etch polishing in a tri-iodide type solution.

BI-0007
ETCH NAME: Nitric acid, dilute
TYPE: Acid, preferential
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:

DISCUSSION:

Bi, specimens used in a study of galvanomagnetic properties in longitudinal magnetic fields. Pits developed by this solution were used to orient the specimens.
REF: Babiskin, J — *Phys Rev,* 107,981(1957)
BI-0008: Connell, R A & Marcus, J A — *Phys Rev,* 107,940(1957)

Bi, single crystal specimens used in studying the low temperature galvanomagnetic effects. Etch clean in the solution shown.
BI-0009: Hurle, D'T J — *Br J Appl Phys,* 11,336(1960)

Bi, (111) wafers. A $1HNO_3$:$1H_2O$ solution used at RT, 30 sec as a light figure orientation etch. Quench with DI water slowly at end of etch period to reduce formation of hydrated oxide.

BI-0010
ETCH NAME: Neon
TYPE: Ionized gas, preferential
COMPOSITION:
x .... Ne^+ ion
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:

Bi, single crystal specimens. Neon ion bombardment used to develop structure and orientation figures. Other metals studied were Al, Cd, Co, Mg, Cu, Sn, and Zn.
REF: Yurasova, V E — *Kristallografiya,* 2,770(1957)

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BI-0012
ETCH NAME:
TYPE: Cleave, defect
TIME:
TEMP: −195°C
COMPOSITION:
x .... cleave
DISCUSSION:
Bi, (0001) wafers cleaved in LN_2 and used "as cleaved" in a study of thermodynamic properties at liquid helium temperatures. Surface defects on cleaved wafers can be used for bulk orientation of the specimens.
REF: Steele, M C & Babiskin, J — *Phys Rev*, 98,359(1955)

BI-0014a
ETCH NAME: Nitric acid
TYPE: Acid, cutting
TIME:
TEMP: RT
COMPOSITION:
x .... HNO_3
DISCUSSION:
Bi and bismuth alloy specimens used in a cyclotron absorption study. Wafers were cut from ingots by acid saw cutting using a linen string saturated in nitric acid. Specimen surfaces mechanically lap polished on 2/0 emery paper with a solution of 2 kerosene:1 MeOH after being cut.
REF: Kalt, J K et al — *Phys Rev*, 114,1396(1959)

BI-0014b
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: 70—100°C
COMPOSITION:
1 .... HCl
2 .... HNO_3
3 .... H_2O
DISCUSSION:
Bi and bismuth alloy specimens etched polished in this solution after acid saw cutting (BI-0014a). Residual film remaining after etching in solution shown removed by a 5 sec dip in concentrated HNO_3 at RT.
REF: Ibid.

BI-0016
ETCH NAME: Nitric acid
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
x .... 20% HNO_3
DISCUSSION:
Bi, specimens. Material used in a study of ultrasonic attenuation of bismuth at low temperatures. Etching showed a polygonized subsurface layer about 10^1 thick is formed during lapping as a fine crystallite zone.
REF: Reneker, D H — *Phys Rev*, 115,303(1959)

BISMUTH ALLOYS, BiM_x

General: Do not occur in nature as bismuth metallic compounds, though there are a number of bismuth minerals, mainly as sulfides and oxides, with or without other metal elements.

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Bismuth metal has a low melting point (27°C) and, as an industrial alloy with other metals, has wide use as a low temperature solder with specific melting temperatures controlled by the amount of additive metal: Wood's Metal (50Bi:25Pb:12.5Sn:12Cd) or Rose Metal (50Bi:40Pb:22.9Sn) as examples.

Technical Application: No direct application in the fabrication of Solid State devices, though used as a low temperature alloy solder. Available from suppliers in rod, wire, or cut pre-forms. Wire may be used as a fuse in package assembly design as part of a protection circuit.

Several bismuth alloys have been grown as single crystals for general morphological and/or defect studies.

Etching: Varies with compound — aqua regia types, cyanides as acid mixtures.

BISMUTH ALLOYS

BISMUTH:ANTIMONY ETCHANTS

BISB-0001
ETCH NAME: TIME:
TYPE: Acid, dislocation TEMP:
COMPOSITION:
7 .... HNO_3
4 .... tartaric acid, sat. sol.
1 .... H_2O
DISCUSSION:

BiSb, single crystals Te doped. Wafers were cleaved (111) under LN_2 from CZ grown ingots with no further treatment prior to dislocation etching. Increasing the Te concentration increases the dislocation content. Sn doped crystals also studied.
REF: Zemskov, V S et al — *J Cryst Growth,* 71,243(1985)

BISMUTH:CADMIUM ETCHANTS

BICD-0001
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... $K_3Fe(CN)_6$
x .... EOH
DISCUSSION:

Bi:Cd, alloy and single crystal specimens. After mechanical polishing, specimens were preferentially etched in the solution shown to develop defect structure.
REF: Savas, M A & Smith, R W — *J Cryst Growth,* 71,66(1985)

BISMUTH:TIN ETCHANTS

BISN-0001
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... $K_3Fe(CN)_6$
x .... EOH
DISCUSSION:

BiSn, alloy and single crystal specimens. After mechanical polishing, specimens were preferentially etched in the solution shown to develop defect structure.
REF: Savas, M A & Smith, R W — *J Cryst Growth,* 71,66(1985)

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BIS-0002
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
95% .... HCl
5% .... HNO_3
DISCUSSION:
BiSb alloys used in a study of the temperature dependence of electrical properties. After polishing with solution shown specimens were annealed.
REF: Jain, A L — *Phys Rev*, 114,1518(1959)

BISMUTH GERMANATE, $Bi_{14}Ge_3O_{12}$

General: Does not occur as a natural compound and has no industrial applications at present.

Technical Application: Both this germanate and the silicate compound are under development for applications similar to those of artificial garnets, such as YAG — yttrium aluminum garnet, $Y_3Al_5O_{12}$, with isometric system, structure as a cube or dodecahedron. With the formula $Bi_{12}GeO_{20}$ the material is called BGO, the silicon counterpart, BSO, and both also are cubic structure, Space Group 123.

Etching: Mixed acids and halogens.

BISMUTH SILICATE ETCHANTS

BSO-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
$Bi_{12}SiO_{20}$ (BSO) single crystal material under development as a compound with similar applications to those of artificial garnets (YIG, YAG etc.). See discussion under Bismuth Germanate (BIGE-0001) for additional information.
REF: Sterudner, R & Zmija, J — *J Phys Chem Solids*, 7,803(1985)

BISMUTH GERMANATE ETCHANTS

BIGE-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
$Bi_{12}GeO_{20}$ (BGO) single crystal material grown by flux method has cubic structure with Space Group 123. With silicon replacing germanium (BSO) the material is of similar structure. This was a material development study for compounds similar to artificial garnets (YIG and YAG). (*Note:* Solution shown is for reference only and can include glacial acetic acid,

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HAc, or water, H_2O. BRM solutions (x% Br_2:MeOH) and iodine solutions (tri-iodide used on gold), etc. also apply.)
REF: Sterudner, R & Zmija, J — *J Phys Chem Solids*, 7,803(1985)

PHYSICAL PROPERTIES OF BISMUTH SELENIDE, Bi_2Se_3

Classification	Selenide
Atomic numbers	83 & 34
Atomic weight	654.9
Melting point (°C)	710
Boiling point (°C)	
Density (g/cm³)	6.25—6.98
Hardness (Mohs — scratch)	2.5—3.5
Crystal structure (orthorhombic — normal)	(010) b-pinacoid
Color (solid)	Bluish grey
Cleavage (pinacoidal — distinct)	b(010)

BISMUTH SELENIDE, Bi_2Se_3

General: Occurs as the mineral guanajuatite (frenzelite, selenobismitite), and selenium may be replaced in part by sulfur. As a mineral specie it is of rare occurrence and has had no application in the metal industries.

Technical Application: Bismuth selenide is a V—VI compound semiconductor, and has been grown as a single crystal in developing etching characteristics and semiconducting properties. It is shown as being used as a basal (0001) cleaved wafer, which would be hexagonal system, though the natural mineral is listed as being orthorhombic system with b-pinacoid b(010) cleavage.

Etching: HCl and aqua regia. Halogens.

BISMUTH SELENIDE ETCHANTS

BISE-0001a
ETCH NAME: Hydrochloric acid, dilute — TIME:
TYPE: Acid, removal/polish — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... H_2O
DISCUSSION:
Bi_2Se_3, (0001) wafers. Solution used to remove lapping damage and polish surfaces.
REF: Faust, J W — *J Electrochem Soc*, 105,252C(1958)

BISE-0001b
ETCH NAME: — TIME:
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
1 .... HCl
2 .... HNO_3
DISCUSSION:
Bi_2Se_3, (0001) wafers. Solution used for general cleaning and polishing of surfaces. (*Note:* Aqua regia, 3HCl:1HNO_3. The solution shown is a modification, and aqua regia-type solutions reactivity can be reduced by diluting with water.)
REF: Ibid.

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BISE-0002
ETCH NAME: Water
TYPE: Electrolytic, oxidizing
COMPOSITION:
x .... H_2O

TIME:
TEMP: Hot
ANODE:
CATHODE:
POWER:

DISCUSSION:
Bi_2Se_3, (0001) cleaved wafers. Materials were anodized in a study of oxidation reactions. Also studied p-type Bi_2Te_3; p-type GaSe, and GaTe.
REF: Moritani, A et al — *J Appl Phys*, 126,1191(1979)

BISE-0003
ETCH TIME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... x% Br_2
x .... MeOH

TIME:
TEMP: RT

DISCUSSION:
Bi_2Se_3 single crystal ingot grown in a study of new semiconducting compounds. Other compounds were Ag_2Se, Li_3Bi, TlSe, Tl_2Se_3, SnSe, $SnSe_2$, In_2Tl_3, $AgInTe_2$, and In_2Te_3. (*Note:* The term BRM for this solution was not in use prior to about 1965.)
REF: Mooser, E & Pearson, W B — *Phys Rev*, 101,492(1956)

PHYSICAL PROPERTIES OF BISMUTH TELLURIDE, Bi_2Te_3

Classification	Telluride
Atomic numbers	83 & 52
Atomic weight	800.83
Melting point (°C)	573
Boiling point (°C)	
Density (g/cm^3)	7.642
Hardness (Mohs — scratch)	1.5—2
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb (bladed)
Color (solid)	Steel grey
Cleavage (basal — perfect)	(0001)

BISMUTH TELLURIDE, Bi_2Se_3

General: In nature the pure mineral is known as tetradymite, free of sulfur, as the normal formula shows trace sulfur with a density of G = 7.2—7.6, as $Bi_2(Te,S)_3$. There are three other similar minerals, all of which occur in association with gold-bearing quartz veins. There is no use in the metal industries, although there is major use of metallic tellurium.

Technical Application: Bismuth telluride is a V—VI compound semiconductor, and has been evaluated for etching characteristics and semiconducting properties, along with both lead and zinc tellurides. It has been fabricated for its optoelectronic characteristics as a laser and electroluminescent diode, both in its single crystal form and as a deposited thin film element.

Etching: Single acids and mixed acids of $HF:HNO_3$, $HFl:HNO_3$.

BITE-0001a
ETCH NAME:
TYPE: Acid, preferential

TIME: 1—2 min
TEMP: RT

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COMPOSITION:
1 .... HCl
2 .... HNO_3
6 .... H_2O
DISCUSSION:
Bi_2Te_3 (0001) wafers. Solution used to develop etch pits on single crystal wafers. Pits were truncated on three alternate sides. Following etching, rinse in water and dry on filter paper. (*Note:* See SI-0092a-b for discussion of truncated hexagonal pit development.)
REF: Toramoto, I & Takayangi, S — *J Appl Phys*, 32,118(1961)

BITE-0001b
ETCH NAME:
TYPE: Acid, preferential
TIME: 1—2 min
TEMP: RT
COMPOSITION:
10 ml .... HNO_3
10 ml .... HCl
40 ml .... H_2O
1 g .... I_2
Note: Mix iodine in HCl and heat to 60°C, then cool to RT before adding other constituents.
DISCUSSION:
Bi_2Te_3, (0001) wafers. This etch will develop triangular etch pits. After etching, rinse specimens in ethyl alcohol. (*Note:* Methyl alcohol could be used as a final rinse as it is a good solvent for residual iodine.)
REF: Ibid.

BITE-0002
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
1 .... HNO_3
1 .... HCl
2 .... H_2O
DISCUSSION:
n-Bi_2Te_3, (0001) wafers. Described as a "removal" etch for n-type bismuth telluride. (*Note:* BT-0001a.)
REF: Drabble, T R et al — *Proc Phys Soc*, 71,568(1958)

BITE-0003
ETCH NAME: Water
TYPE: Acid, oxidation
TIME:
TEMP: Hot
COMPOSITION:
x .... H_2O
ANODE:
CATHODE:
POWER:
DISCUSSION:
p-Bi_2Te_3, (0001) cleaved wafers. Also p-GaSe, p-GaTe and Bi_2Se_3. Materials were anodized in a study of oxidation reactions.
REF: Moritani, A et al — *J Appl Phys*, 126,1191(1979)

BITE-0001c
ETCH NAME: Nitric acid
TYPE: Acid, preferential
TIME: 1—2 min
TEMP: RT

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COMPOSITION:
x .... 30% HNO_3
DISCUSSION:
Bi_2Te_3 (0001) wafers. Used to develop hexagonal etch pits in bismuth telluride specimens. Pits were truncated similar to those obtained in etch BITE-0001a.
REF: Ibid.

BITE-0004
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
1 .... HNO_3
1 .... H_2O
DISCUSSION:
Bi_2Te_3, (0001) wafers used in developing structural-cell data and the coefficients of expansion of this material. After mechanical lap and polish, solution shown was used to remove residual damage, e.g., strained surfaces.
REF: Francombe, M H — *Br J Appl Phys*, 11,415(1960)
BT-0005: Francombe, M H — *Br J Appl Phys*, 9,415(1958)
Bi_2Te_3 (0001) wafers studied and etched as shown under BITE-0004.

PHYSICAL PROPERTIES OF BISMUTH TRIOXIDE, Bi_2O_3 (BISMITE)

Classification	Oxide
Atomic numbers	83 & 8
Atomic weight	466
Melting point (°C)	860
Boiling point (°C)	
Density (g/cm^3)	8.5
Refractive index (n =)	1.81—2.00
Hardness (Mohs — scratch)	2—3
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
(orthorhombic) artificial	(hk0) prism
Color (solid)	Straw yellow
Cleavage (basal)	(0001)

BISMUTH TRIOXIDE, Bi_2O_3

General: The natural mineral bismite, Bi_2O_3, is probably an hydroxide, and only occurs in nature as an earthy coating and small scales. In chemistry it is listed as the hydroxide: $Bi_2O_3.3H_2O$. It has little use in the metal industries, but in medicine is known as pearl white, pearl powder, etc. Bismuth metal has wide use as a low melting point solder constituent.

Technical Application: The compound has had little use in Solid State processing to date, though it is under evaluation as a thin film for its superconducting characteristics. As a mixed compound: $BaPb_{1-x}Bi_xO_3$ (BPB), it is a superconducting oxide used in the development of Boundary Josephson Junction (BJJ) devices.

Etching: Soluble in single acids.

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BISMUTH TRIOXIDE ETCHANTS

BIO-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
COMPOSITION:
x .... HCl, conc.
TIME:
TEMP:
DISCUSSION:
Bi_2O_3, deposited as a thin film in study of superconducting oxides. Solution used as a removal and patterning etchant.
REF: Moriwaki, K et al — *Jpn J Appl Phys*, 23,L115(1984)

BLISTERS

General: Blisters occur in natural rock formations as cavities or vugs, often produced by gas expansion (water vapor or others) during solidification. Such structure is common to AA lava . . . jagged type lava, such as in northern California ... as against Poi-Poi lava — rope-like — as represented by the Mauna Loa volcano in the Hawaiian Islands. Pumice is a solidified froth of silica, SiO_2, as a volcanic extrusion from an acidic magma with a high void density that produces a very lightweight rock used in construction and as a lapping stone. The so-called "dinosaur eggs" are concentinary nodules that can range from pea size to greater than a foot in diameter, fist-size being most common, and are a segregation solidification of silica most often found in sedimentary beds. When completely filled, they produce varicolor agates and, if only partly filled, may contain fine clear or colored single crystals of quartz. Cavities in other rocks may be similar as partly or completely filled by subsequent intrusion of siliceous waters producing vein deposits. In obsidian (natural glass) there may be segregated blebs of calcite, $CaCO_3$ . . . "snowflake obsidian". Clear, single crystal quartz sometimes contains bubbles or voids with some crystal plane structure containing either entrapped gas or liquids, and the gas/liquid is used in determining the age and atmospheric conditions of formation. Incrustations as drusy coatings on rocks and minerals may show blisters or contain voids with similar entrapped gases and liquids, though less common. Basalt, a common volcanic rock, often contains many small cavities filled with silica blebs or other segregated minerals.

Blisters on the surface of metals and metallic compounds are an unwanted phenomenon in metal processing — the slow weathering of iron to iron oxide (rust) — very often forms a blistered surface, such that most construction irons and steels are coated with red-lead to reduce or prevent oxidation. Most metals and compounds are measured for their porosity — the number of voids in the material sometimes intentionally produced for a specific product.

These are all natural forms as blisters or associated blebs, voids that can be involved with blister formation.

Technical Application: There is ongoing study of the formation of blisters and development of voids in solid metals or compounds and thin films as they occur under different processing conditions.

Any irradiation of a surface can produce both surface blisters and internal voids. Ion implantation (I^2); radioactive particle or ionic gas irradiation, etc., such as Ar^+ ion cleaning — all can introduce physical damage within a material that can lead to blisters. If the material has a crystalline grain structure, such as in thin film metal or epitaxy compound layers, there can be grain-boundary in-or-out-diffusion of both liquids and gases creating voids internally or blisters on surfaces.

Much concern involves adhesion of thin films, where they are evaporated, sputtered, epitaxially grown, or plated, as all such process steps may introduce entrapped gases or

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liquids, such that subsequent heat treatment will develop surface blisters with lifting, peeling, and loss of adhesion. And it often is not apparent until material is heat treated above 400 to 500°C . . . blisters can be observed to start as low as 150°C in a thin film metallization heated on a hot plate in air. It should be noted that if the part is heat treated in an air oven, in vacuum, or a furnace — N_2, H_2 or other atmosphere — blisters may not appear, yet will appear when the same part is placed on the hot plate in air. Plating solutions can develop blisters spontaneously when the plating metal concentration becomes low or if gas and liquids are entrapped at the part/plating interface or within the plating metal film . . . again, sometimes not apparent until heat treatment. And the preparation of surfaces prior to any thin film deposition can be extremely critical: 2 μm″ finish alumina substrates are an example . . . they are polished with diamond paste, and paste oil can be entrapped in the fine surface cracks . . . hydrogen firing at 800 to 900°C was found to be the best method of cleaning. Any organic or other contamination on a surface can be a factor causing subsequent blistering.

The interaction of metal elements in processing can introduce stress and strain with the formation of new compounds due to solid-solid diffusion. Silicides are an example of controlled formation of a new compound but, if they fail to operate as a buffer layer and react with other elements, such as with aluminum in a multilayer structure, another crystallite form can develop with expansion causing swelling, stress, and strain within the bulk and eventual blister or void formation. Where a silicon dioxide layer is used as a diffusion mask, as against boron, it can develop a "rosette" crystalline structure in the otherwise amorphous film as a borosilicate glass, and such structures have been referred to as blisters.

With time under operating electrical load or during temperature evaluation of multilayer devices, there also can be solid-solid diffusion. In one example, where cobalt is a metal constituent, it was shown to migrate to wire bond device contacts causing embrittlement and contact failure. Silver, in particular, but also gold and aluminum thin films have been known to "creep" with time and temperature or under electric bias with subsequent device failure, to include swelling, blistering, and contact void formation. The occurrence of "purple plague" as crystal forms of Al_xAu_y has long been known as a device failure mechanism, again, swelling, blistering, embrittlement, and operational failure.
Note: Purple Gold (70Au:21Al) is used in the jewelry trade and as a decorative finish.

BLISTER ETCHANTS

BLIS-0001
ETCH NAME: Water
TYPE: Acid, diffusion
COMPOSITION:
x .... H_2O, liquid/vapor
TIME:
TEMP: RT to hot
DISCUSSION:

GaAs, (100) wafers doped p-type (Ge) and n-type (Si) and used as substrates for sequential sputter of Ti and Pt, then annealed at 450°C, 2 min in an open tube with FG will produce blisters 5—6 μm diameter with pinholes in blister tops. To clean substrates (1) oxidize and strip with HF; (2) boil in chloroform; (3) boil in acetone; (4) boil in MeOH; (5) N_2 dry; (6) swab with $1HCl:1H_2O$; and (7) NH_4OH rinse to remove residual oxide.

Surface treatment had no effect on blister occurrence; no blisters with Ti, only. TiPt film is polycrystalline with grain boundaries and microvoids, and Pt will catalyze H_2 and O_2 in water vapor at elevated temperature . . . nucleating blister-type points in film from water/gas expansion . . . plastic deformation and rupture of blisters can result. As Au/Ti/Pt the film will blister but not rupture due to gold malleability. A solder bonding flux

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of $ZnCl_2$:NH_4Cl:H_2O produces HCl with both corrosion and blisters. Heating above 375—450°C develops blisters and gas-induced delamination of films.
REF: Henein, G — *Thin Solid Films*, 109,155(1983)

BLIS-0002
ETCH NAME: Oxygen
TYPE: Gas, diffusion
COMPOSITION:
x .... Air, H_2, O_2
TIME:
TEMP: Elevated
DISCUSSION:
Au thin films. Gas diffusion into films forms bubbles along grain boundaries with 1.8 eV activation energy with gas entrapped in voids during film growth. Voids unstable below a few hundred angstroms in size, but stabilize by gas filling as bubbloids or poroid bubbles.
REF: Andrew, R & Lloyd, J R — *Thin Solid Films*, 88,125(1982)

BLIS-0003
ETCH NAME: Irradiation
TYPE: Proton, damage
COMPOSITION:
x .... H^+, H_2, H_3
TIME:
TEMP:
DISCUSSION:
Al alloy #6061-Tg sheet. Proton irradiation at 100 and 200 KeV at −196, −100, +100, and +200°C. Large and small blisters, round and elongated appear aligned in the sheet roll direction after irradiation. At 200°C blisters appear only at grain boundaries. By heating 10 min at 300°C blisters appear at grain boundaries and on general surfaces. After scratching a surface, then 100 KeV rad and 20 min at 250°C anneal, blisters appear along cracks — increase in size as circular blisters with added 10 min at 350°C. Proton beam was $48H:32H_2 2OH_3$. Entrapped hydrogen gas with heat expansion was cause of blister occurrence in the solid material surface.
REF: Milack, T et al — *Thin Solid Films*, 88,2805(1982)
BLIS-0004: Daniels, R A & Cooley, F — *Thin Solid Films*, 88,2815(1982)
Similar work to that of Milack, BLIS-0003.

BLIS-0005
ETCH NAME: Air
TYPE: Gas, blister forming
COMPOSITION:
x .... H_2, O_2, air
TIME: 6 min
TEMP: 300°C
DISCUSSION:
Au/TiW thin films on Al film deposited on (111) silicon wafers. At temperature and time shown Au alters from fcc to bcc cubic structure and, when heated in air, becomes silvery in color due to aluminum diffusion into gold. Gold on Al/Si (111) developed round, doughnut spots (collapsed ring blisters?). As Al/TiW/Si with final Au coating on Al at 300°C becomes a silvery colored surface with blisters due to gas grain boundary diffusion (GBD). Nitrided TiW films convert from bcc to fcc. Addition of N_2 improves barrier effect against Al solid-solid diffusion. Some films were TiO_3WO_7.
REF: Nowicki, R S et al — *Thin Solid Films*, 53,195(1978)

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BLIS-0006
ETCH NAME: Helium
TYPE: Ionized gas ion, implantation
COMPOSITION:
x .... He^+, ion

TIME:
TEMP: 900°C
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Nb, (111) blanks He^+ ion implanted at 0.5—1.5 MeV. Blister shapes strongly dependent on temperature. At 900°C developed "crow-foot" blisters with three ⟨112⟩ directional prongs and preferred (211), (112), (121) orientation. At lower temperatures only round dome blisters were observed with size increase as temperature reduced toward RT. Blister density varied with the direction of implant beam. Blisters caused by expansion of implanted He^+.
REF: Das, S K & Kaminsky, M — *J Appl Phys*, 44,2520(1973)

BLIS-0007
ETCH NAME: Oxygen
TYPE: Gas, crystallization
COMPOSITION:
x .... O_2 (air)

TIME:
TEMP: 500—550°C

DISCUSSION:
Al/TiW/PtSi/c-Si substrate metallized structure. With heating all of the following crystallites can occur: Al_2Pt, $Al_{12}W$, WSi_2 and TiWSi. With O_2 present: Al/TiWO. Surfaces developed pinhole blisters due to expansion and stress of Al_2Pt regrowth, formation, etc., as well as from gas grain boundary diffusion action. Al deposited at 250°C + O_2 developed an Al/O/TiW structure.
REF: Canali, C et al — *Thin Solid Films*, 88,9(1982)

BLIS-0008
ETCH NAME: Boron
TYPE: Metal, blister forming
COMPOSITION:
x .... 0.05—0.2% B

TIME:
TEMP: To 800°C

DISCUSSION:
Ni:B thin films deposited as columnar growth structure. Anneal 4 h at 800°C to form Ni_2B, developing angular voids along grain boundaries with brown Ni_2B crystallites growing at grain boundaries. Annealed 4 h and evaluated at 100°C steps from 400 to 800°C in vacuum and showed little change up to 600°C. The bubbles and dislocations appeared at grain boundaries with deep cracks from the surface with 0.2% boron. With CVD growth of Ni:B films, bubbles were very fine.
REF: Skibo, M & Greulich, F A — *Thin Solid Films*, 113,224(1984)

BLIS-0009
ETCH NAME: Kovar
TYPE: Metal, conversion
COMPOSITION:
x .... Fe, Ni, Co

TIME:
TEMP: 200°C

DISCUSSION:
Au/Fe, Au/Ni and Au/Co thin film metallization. Annealed at temperature shown, metals will diffuse into overlay gold. Under oxidizing conditions Fe + SiO_2 will develop Fe_2O_3. The study was for observation of metal diffusion reactions in Kovar used in device package construction. It was seen that solid-solid diffusion into gold can develop surface blisters.
REF: Schwartz, W E et al — *Thin Solid Films*, 114,349(1984)

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BLIS-0010
ETCH NAME: Metal
TYPE: Metal, blister forming
COMPOSITION:
x .... Ga or Sm
TIME:
TEMP: 200°C and above
DISCUSSION:

Au:Ga and Au:Sm thin films deposited onto NaCl, (100) substrates. The Ib group of elements will diffuse rapidly into group IIIa and IVa elements. Au/Ga and Au/Sm act as diffusion couples with diffusion stress differentials causing large blisters — 1.5 mm size as dome blisters with a "T"-shaped crack rupture on top surface of blisters. Blisters tend to align along cleavage steps on the NaCl surfaces. Segregated white spots appear in films as Au_2Ga as grains, other areas were orange in color as pure Au grains. Blister cracks were due to Kirkendall voids and volume change was caused by interdiffusion.
REF: Nakahara, S & Kinsbron, E — *Thin Solid Films,* 113,15(1984)
BLIS-0011; Nakahara, S & McCoy, R J — *Thin Solid Films,* 88,285(1982)

Pd/Sn and $PdSn_2$ using tin and Sn substrates. Similar results observed as described in BLIS-0010.

BLIS-0012
ETCH NAME: Air
TYPE: Gas, blister forming
COMPOSITION:
x .... Air
TIME: 2—5 min
TEMP: To 400°C
DISCUSSION:

Au/TiW thin films sputter deposited on 2 and 4 μm″ finish alumina blanks. As sputter deposited with about 2000 Å Au/500 Å TiW(Ti 10%) no blisters were present at RT but, after 400°C on a hot plate in air, both circular and elongated blisters appeared. Blisters also occurred with size and density variable under the following process conditions: (1) Up-plating gold from a standard gold cyanide bath . . . (2) HCl cleaning rinse, H_2O rinse, then direct to gold up-plate . . . (3) HCl rinse and H_2O rinse, then electroless nickel 500 Å coating, followed directly by gold up-plate . . . (4) no cleaning of sputtered gold surface prior to Au or Au/Ni plating . . . (5) air oven cleaning evaporated gold surfaces at 150°C for 2, 4, 6 and 24 h prior to Au or Au/Ni plate . . . (6) hydrogen firing of alumina at 800°C prior to initial Au/TiW sputter evaporation. Fused quartz blanks similarly processed as a control against the 2 and 4 μm″ alumina blanks. The 2 μm″ alumina showed worst-case blistering with size, shape (round, elongated or combination), and density-variable with surface treatment before gold up-plating. Presence of HCl developed both fine blisters and black liquid extrusion from ruptured blisters, or appeared at grain boundaries, with limited, erratic distribution vs. total blister density. Air oven bake reduced the number of large blisters, but increased the density of small blisters. A thick nickel layer (about 2000 Å) developed large, circular blisters with complete pop-out and silvery discoloration of Au surface. Hydrogen firing of alumina blanks prior to any metal evaporation reduced but did not eliminate all blisters with up-plated Au. Au or Ti, only, did not produce blisters. TiW, only, developed cracks and peeling associated with crack locations in the alumina blank surfaces. With sputtered films, only, and soaked time at 400°C in air on a hot plate, a glassy WO_x dark grey film with some spectrum colors appeared on surface of gold without blistering. The 4 μm″ alumina finish blanks showed a much lesser blister density with larger size than with 2 μm″ finish. The presence of entrapped gas, oils, and liquids, and the solid-solid diffusion of TiW were considered as the causes of blistering. Blisters developed on quartz substrates only when TiW was present, not with other metal combinations. Since these initial

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experiments were performed, it has been shown that slow, step-heating of Au/TiW thin films will prevent solid-solid diffusion of the TiW fractions that cause blistering.
REF: Walker, P & Velardi, N — personal development, 1984—1985

BLIS-0013
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
x .... HF, conc.
DISCUSSION:
a-Si:H thin films deposited on SST substrates, then aluminum evaporated as p-i-n diodes. Blisters, pinholes, and lifting observed due to deposit conditions and/or substrate surface preparation. The film surface roughness affects solar cell efficiency.
REF: Yacobi, B G et al — *J Electron Mater,* 13,843(1984)

BONDING

General: Many natural minerals themselves, as individual components or as mixture components, form solid bonds. Sandstone is an example of such a two-component bonding system where, under pressure, heat and with time, sand grains are compacted and cemented by the intrusion of colloidal iron oxide. The reason that most sandstone is tan to brown in color is due to the presence of the brown iron oxide. The hydrothermal action of hot waters percolating through subsurface rocks can alter a mineral completely to another compound, cause only surface alteration, or deposit a different mineral compound as a firmly attached surface coating. Limonite pseudomorphs after pyrite, where the sulfur in the pyrite is leached away and replaced by oxygen — still retaining the pyrite crystal form as a face striated cube — is an example of complete alternation, called a limonite pseudomorph after pyrite. Moonstones — colloidal to amorphous silica nodules found along seashores — are often surface coated with a very hard coating of calcium/magnesium sulfate or mixed oxide, white in color, and silica is a common drusy surface coating on many rocks and minerals which may be fine crystals, in part. Both air and water can oxidize the surface of a mineral as a metal oxide surface coating. Petrified wood or wood opal are special cases, where siliceous waters have entered the cellular structure of the buried wood forming a hard silica rock — cat's eye or tiger eye semiprecious gem stones are similarly silicified asbestos minerals. Many types of rock are compacted mixtures of different minerals, some acting as the bonding medium, such as mica or hornblende granite or graphic granite. The latter as silica in an open cellular structure which is filled with the softer feldspars, which are white, pink, and grey-blue colors of the feldspars. When polished, they make fine ornamental stones.

In industry, much of metal fabrication involves some form of bonding within the metal or metal mixture. Irons and steels are heat treated to develop specific structural bonding, such as the alpha, beta, and delta phases; formation of marcasite; iron carbide as Fe_3C, etc.

Other metals are bonded together by pressure and heat — called cladding — such as a copper/gold strip. Metal evaporation or plating form thin film coatings intimately bonded to a surface. Coldweld sealing uses direct pressure, only — 5 to 20 tons — to form copper-copper or nickel-nickel bonds by metal cross-diffusion. Like the natural siliceous waters penetrating wood, plastic resins and lacquers are used to impregnate linen cloth to form a hard, insulating board with the plastic/lacquer as the bonding medium. Shatterproof glass is fabricated by bonding two glass plates with a thin sheet of plastic between as a sandwich, or a metal wire grid is embedded in the glass for structural rigidity, sometimes as an electrical heater system for deicing glass panes.

There are many laminated products — pressed wood, as plywood, as one example — again, using resins, etc. as the binding medium. Paper is "loaded" with barium sulfate powder as a binder to increase weight; colloidal silica is used as a filler and binder in many

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applications; in the fabrication of fire brick, both silica and graphite are used as binders. Needless to say, there are many types of glue used to bond similar or different materials together, and Teflon coatings are applied to cooking ware for a nonstick surface.

Technical Application: In Solid State processing probably the most important bonding applications are wire bonding of devices, substrate circuits, and package assemblies. Several of the etchant formats in this section cover such bonding as methods, rather than etching solutions.

Many of the bonding areas described in the General section above apply to Solid State with regard to products used in both equipment operation and device assemblies. The following Etchant Section here includes some bonding techniques as well as cleaning solutions — see the Mounting Materials section for additional information.

Etching: Acids, alkalies, alcohols, solvents, variable with material.

BONDING ETCHANTS

BB-0001
ETCH NAME: Ball bonding
TYPE: Wire, bonding
TIME: Seconds
TEMP: RT to 150°C
COMPOSITION:
x .... Au, Al, Ag, Cu wire
DISCUSSION:

Ball bonding technique. Wire is fed down through a vertical capillary tube with a ball formed by a hydrogen flame cut-off at the tube tip. Lower tube so that the preformed wire ball is in contact with the contact pad to be bonded. With a combination of time and pressure, with or without heat and ultrasonic vibration, a hemispherical bond contact about 3—4× the wire diameter is formed on the contact pad. Wire diameters range from .0007 to about .010. Dead soft .0007 gold wire is common for microelectronic circuitry, and Au:Be(2—5%) used with automatic bonders where a stiffer wire is required. Wire is supplied on spools of 100 to 500 ft. If cleaning is necessary, vapor degrease with TCE or rinse in alcohols with air, oven bake at 125°C. If bond wire fails to stick: (1) RF plasma clean device or substrate with O^+ or N^+ ion plasmas, 5—10 min, and (2) check hardness of the metal pad surface. In the first case, the surface may be contaminated with oils; whereas in the second case, prior processing may have hardened the pad, such that a soft wire bond will not stick. Aluminum pads can have an oxide layer (use ultrasonic in bonding). Gold pads as an Au/AuGe/Ni multilayer metallization, a common contact pad in high frequency microelectronic devices, can be excessively hardened by the annealing step following metallization. If this occurs, the only correction is to add an additional soft gold evaporated layer before the wafer is diced into individual units as, once diced, the entire dice lot will be rejects. Ball bonding is still widely used, but is limited to a pad area larger than the formed ball bond, such that it is of limited use in high frequency microelectronic circuitry where bond pads are under 5 mils square in area. After bonding, spray clean contacts with acetone; rinse in MeOH, EOH, Freons, or other solvents. The capillary tubes used for wire feed have a rounded tip end that should be free of chips and kept clean, e.g., solvent clean as needed, or replace. Bonding tips are of glass, ruby, or titanium and tungsten.

REF: Harman, G G — *Solid State Technol,* 1984, 186

B8-0002
ETCH NAME: Wedge bonding
TYPE: Wire, bonding
TIME: Seconds
TEMP: RT to 150°C
COMPOSITION:
x .... Al, wire

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DISCUSSION:

Wedge bonding technique. A solid wedge-tipped rod of tungsten, titanium, steel, etc. Tip face is flat with slightly curved edges to prevent cutting action during pressure bonding. Place wire end in position on aluminum bonding pad of device, lower wedge in contact, and apply controlled pressure and ultrasonic vibration with or without heating of part. Special application: bonding .010 aluminum wire to aluminum alloy pads of SCRs. Ultrasonic vibration needed to insure breakthrough of native aluminum oxide films for a good metal/metal bond. Prior to using new aluminum wire, heat treat about 30 min at about 450°C in forming gas (FG) for dead-soft condition, as wire-work hardens rapidly during bonding. Rinse in alcohols and air dry as needed after bonding.

REF: Topas, B et al — personal application, 1970—1976

BB-0003

ETCH NAME: Foot bonding

TYPE: Wire, bonding

TIME: Seconds

TEMP: RT to 150°C

COMPOSITION:

x .... Au, wire

DISCUSSION:

Foot bonding technique (sometimes called wedge bonding). Bonding tip is a capillary tube with an upper round shaft for position holding, being cut down to a rectangular tip face — flat face or with convex or concave center — back-end sharp ledge; front-end curved upward. Lower back of tip has extended portion with angled hole for wire to be drawn down and across tip face toward the front, facing the operator. Bond flat about .005 width (.002 special) and .0005 to .0007 length. Bonding is similar to ball bonding without H_2 ball-forming cut-off. Tip material is of tungsten, titanium, ruby, etc. Gold wire, .0007 diameter common; AuBe for automatic bonders, supplied on 100 or 500 ft spools. With time, wire-work hardens on spool and shows excessive breakage.

Bonding is done like ball bonding with the wire brought down in contact with the gold bonding pad of the device, then pressure, with or without ultrasonic vibration (minimum) is applied. The bond formed is elongated — a .0007 wire widening to about .003 (with an initial .002 tip width) with much the appearance of a human foot, hence the method name. Forward bonding most common, where the initial bond is on the device, second bond on a substrate or package pad, but back-bonding can be done . . . the reverse of forward bonding. Some of these food bonders have the capability of "stitch bonding", where a multiple line of bonds is made before final bond-end break off. With the relatively flat foot bond, it is possible to make bonds-on-top-of-bonds . . . "stack bonding". As many as four wires have been so stack bonded with device pad-pad, pad-substrate, pad-package bonds coming from a single contact pad of the device.

REF: Marich, L A et al — personal communication/application, 1980—1986

BB-0004

ETCH NAME: Weld bonding

TYPE: Part, bonding

TIME:

TEMP: Elevated

COMPOSITION:

x .... Cu

DISCUSSION:

Weld bonding technique. Two opposed carbon electrodes or metal tips similar to a soldering iron, and may be a ring-shaped metal electrode. The wire to be bonded is held on bond area, and welding is accomplished from an electric spark from the carbon electrodes, or an electric pulse from a metal tip. The weld is usually as a cup-shaped joint with some weld splatter and metal erosion points of the surface being bonded. The standard welding techniques use a gas torch with a welding rod material fed against the part or parts being

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joined, such as in bead-welding a seam, or spot welding. An electrode spark is also used to vaporize a metal/compound surface for spectrographic analysis of constituent elements. Glass welding uses torches in a similar manner to metal welding, and requires controlled annealing after welding. Where fluxes such as borox are used in welding, clean with water or commercial solvents designed for the particular flux. Alloy brazing is a form of high temperature welding and used with alloys above 800°C. Below 800°C it is called soldering.
REF: Walker, P & Tarn, W H — personal application (all), 1950/1985

BB-0005
ETCH NAME: Alloy bonding
TYPE: Wire, bonding
TIME: Variable
TEMP: RT and 800°C
COMPOSITION:
x .... Au, Al, etc.
DISCUSSION:
Alloy bonding technique. There are hundreds of alloys available with temperatures ranging from about 50 to 800°C (800 to 2500°C for brazing rather than alloying). Two of the more common solders are #62 60Pb/40Sn, (m.p. 180°C), and #63 (m.p. 220°C) Pb/Sn/Ag(5%) . . . the former also called 60/40 solder and the most common general solder. Bonding is done with a solder iron using solid or rosin-core wire, or a solder pre-form and heat. Parts may be pre-tinned for assembly, such as for a PCB, and passed through a furnace or a gas torch, such as propane; acetylene or oxy-hydrogen may be used depending upon temperature required. Occasionally used to solder wire directly to a discrete device, more often used for final attachment of wires internally or externally in package assemblies. Where a resin core solder or flux is applied in alloying, bond area should be solvent or alcohol cleaned after bonding to remove residual flux. *Note:* Remaining flux and some commercial solvents may contain chemicals that will attack assembled components, but good water washing is often sufficient for cleaning.
REF: Tarn, W H & Walker, P — personal application, 1950/1985

BB-0006
ETCH NAME: Epoxy bonding
TYPE: Parts, bonding
TIME: 30—60 min
TEMP: 120—150°C
COMPOSITION:
x .... Ag-epoxy or polyimides
DISCUSSION:
Epoxy paste technique. As an electrical contact both epoxies and polyimides are loaded with fine particles of Ag, Au, Al, Cu, Ni, Pd, Pt, etc. as a paste. Used unloaded for general bonding of parts where electrical continuity is not required. Pastes are applied to the wire/bond pad, the device or wire positioned, then the assembly is oven-cured with time and temperature depending upon the particular compound mixture. Widely used in microelectronic circuit assemblies for testing, but not in final high reliability packaging. Cure schedules range from about 10 to 45 min at 120 to 150°C, and there is ongoing development of higher temperature pastes (>250°C). Epoxy type pastes do not require cleaning after cure. Alloy pastes with fine beads of the alloy in a resin base are similarly used with heat melting, and do require final cleaning. See BB-0005.
REF: Marich, L A & Rodriguez, S — personal communication, 1979

BB-0007
ETCH NAME:
TYPE: Acid, cleaning
TIME: 10—20 sec
TEMP: RT

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COMPOSITION:
1 .... H_2O_2
1 .... HCl
DISCUSSION:
Pb/Sn type solder joints attaching wire leads to discrete silicon diodes. Copper, dumet, aluminum, and silver wires attached vertically by soldering to the device surface. Operation done by hand or with a carbon/metal holding fixture and parts passed through a furnace in an N_2 or forming gas atmosphere. Solution used for light cleaning of formed bonds, following with water rinse, then alcohol rinsing and air dry.
REF: Walker, P — personal application/development, 1950—1970

BB-0008
ETCH NAME: Alcohols/solvents
TYPE: Alcohol, cleaning
TIME: 10—30 sec
TEMP: RT to hot
COMPOSITION:
(1) x .... MeOH, EOH
(2) x .... TCE, TCA, Freons
DISCUSSION:
Pb/Sn solder joints or other metal alloys. Both alcohols and solvents used as general cleaners for wire alloying to parts. Water only is often sufficient for removal of residual solder fluxes — borax a major flux — used at RT or hot. Some solder fluxes contain fluorine compounds, such that particular care should be exercised during cleaning (CaF_2 standard metal flux).
REF: Fahr, F — personal communication, 1957

BB-0009
ETCH NAME: Cladding
TYPE: Pressure, bonding
TIME:
TEMP: RT to molten
COMPOSITION:
x .... pressure
DISCUSSION:
Metals, plastics, cloth, and wood. Dissimilar metal sheets or strips are formed with pressure/heat by passing thin sheets/strips through rollers with sufficient temperature to cause metal-metal migration at the interface to form a bond by pressure extrusion. A similar process is used with plastics or woods using glues or other binders, and called veneer. Plasticizing may include additional adhesives, or applied as impregnation. Linen cloth sheets are plastic impregnated under pressure to form a nonconductive board (PCBs); sawdust, plant and hair fibers, asbestos, glass wool, wood pulp, mica flakes, are all used with various chemical binders, and press-formed as sheet, blocks, or other shapes. Mica and glass wool products are replacing asbestos for insulation. Plasticized veneer, for relatively chemically inert table tops in laboratories, is replacing natural soapstone, or marbles. Glass-to-metal tube as a graded seal is made for fabricating metal-to-glass assemblies; metal wires are glass-beaded for insulated feed-thrus in package fabrication with melt/press insertion. Mylar (red, blue, white) sheets are pressure clad to clear acetate sheet, as rubylith for photolithographic circuit fabrication or, mylar with a sticky back is used to hold a wafer in place for scribe & break wafer dicing.
REF: Siracusa, M et al — personal communication, 1980

BB-0010
ETCH NAME: Coldweld
TYPE: Pressure, bonding
TIME:
TEMP: RT
PRESSURE: 2—20 tons
COMPOSITION:
x .... pressure

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DISCUSSION:

Copper or nickel clad/plated shim steel or pure nickel Solid State packages with a seal lip or rim used for package sealing of both SCR Hockey Puk, and quartz radio frequency packages. A coldweld sealing system is rated for tons of direct pressure, with 5—7 tons as nominal. There is an upper and lower die operated by a hydraulic press and the two dies may be surrounded by individual cylinders that mesh for a vacuum seal pulled to about 10^{-3} Torr, and capable of gas back-fill after pulling vacuum. Bottom and top die are individually designed for each specific package configuration. The package body to be sealed is seated in the lower die, the cover positioned on the package, then the upper die activated to lower and pressure seal. This produces a copper/copper or nickel/nickel metal seal, and eliminates any weld splatter as observed in resistance welded packages. Small quartz crystal and semiconductor TO-5 type packages have been sealed at 2—5 tons pressure; larger silicon SCR Hockey Puk packages at 6—10 tons pressure. Quartz crystals packages have been sealed in a vacuum system at the 10^{-10} Torr level or, sealed after vacuum pull and backfill with He or N_2/He (15%), to reduce mass loading effects using helium as a lightweight atmosphere within the package. Package surfaces to be sealed should be degreased and dry before assembly.

REF: Walker, P — personal application, 1968—1969

BB-0011

ETCH NAME: Resistance weld

TYPE: Electric, weld

COMPOSITION:

x .... power

TIME: Seconds

TEMP: RT

PRESSURE: 10—200 psi

POWER: 1000—1500 V

DISCUSSION:

A standard Raytheon type resistance welder uses a capacitor bank discharge to effect the weld on steel package parts, which may or may not be gold plated. The system contains a copper bottom package holder and top head for pressure and power discharge, and there is the possibility of weld splatter inside the package. These systems are still a major method of sealing Solid State packages. Another system uses a powered roller head somewhat like a glass cutter tool that, as it is rolled across the sealing surface, produces a bead of microspot welds for sealing, and the head and/or package may be heated during weld passes. It has been used on circular packages, but it is now more widely used on steel square and flat paks in Solid State assembly. This operation requires four individual weld passes with 90° rotation after each two parallel weld passes. The weld seal produces a very fine weld-bead with minimum internal package weld splatter.

REF: Walker, P — personal application, 1962—1980

BB-0012

ETCH NAME: Alloy pre-form

TYPE: Metal, sealing

COMPOSITION:

x .... AuGe, AuSn, etc.

TIME:

TEMP: Variable

DISCUSSION:

Pure metals or metal mixtures cut as pre-forms and used for device/part mounting or package sealing. Operation similar to that discussed under BB-0005 (alloy bonding) as a heated bonding mechanism. Shaped In, Cu, Au pre-form flats or wires used as vacuum system crush-seals, with indium also used for sealing cryopumps. Crush-seals do not use heat, and the pre-form is replaced whenever the system seal is opened and requires re-sealing.

REF: Walker, P et al — personal application, 1958—1985

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BB-0013
ETCH NAME: Metal evaporation
TYPE: Metal, cladding
COMPOSITION:
x .... metal
DISCUSSION:

TIME: Variable
TEMP: Variable

Metal evaporation when applied as a surface cladding. Aluminum, copper, carbon, nickel, iron, etc. have all been used as a thin film metallization on a variety of materials: on metals, plastics, mylar, glass, and so forth. Carbon is evaporated on plastic or mylar sheeting and, with a sticky-back, used as a sunscreen on windows; aluminum is evaporated on plastic or rubber toy balloons, as well as weather balloons for its heat dissipation and reflective capability. Aluminum and nickel are replacing silver as mirrors, including telescope lenses, and are also used on clothing. Copper and aluminum flakes or powder are added to plastic acrylic-type spray paints as a "glitter" coating and surface sealer. Glassy metals and nitrides are evaporated for specific colors of the oxides or nitrides: red, blue, green, gold, etc. Electrolytic plating has been used in a similar manner for color, and may include color additives in solution, such as in the anodizing of aluminum: black, red, green, blue, and so forth. Spray coating with metal powders are applied to surfaces as a thin film bonded material for both decorative effects and in fabricating Solid State substrates or active devices, such as a carbon film resistor. Both brass and bronze are used for their yellow color as replacements for gold, as direct spray coatings or mixed with liquid plastics like aluminum and copper.
REF: Walker, P — personal application, 1955—1985 (mirrors)

PHYSICAL PROPERTIES OF BORON, B

Classification	Metal
Atomic number	5
Atomic weight	10.811
Melting point (°C)	2100 (2300)
Boiling point (°C)	2800 (2550) sub.
Density (g/cm^3)	2.34
Specific heat (cal/g) 25°C	0.309
Heat of fusion (k-cal/g-atom)	5.3
Heat of vaporization (k-cal/g-atom)	128
Atomic volume (W/D)	4.6
1st ionization energy (K-cal/g-mole)	191
1st ionization potential (eV)	8.298
Electronegativity (Pauling's)	2.0
Covalent radius (angstroms)	0.82
Ionic radius (angstroms)	0.23 (B^{+3})
Electrical resistivity ($\times 10^{-6}$ ohms cm) 20°C	4
0°C	1.8
Electron work function (eV)	4.5
Hardness (Mohs — scratch)	9.3
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Grey-white
Cleavage (basal — poor)	(0001)

BORON, B

General: Does not occur as a native element, but is widely found as a constituent in several minerals, such as beryl and chrysoberyl, both beryllium aluminates and major pre-

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cious gem stones, both as "Cat's Eye", or yellow and emerald green mock emerald. The borates form a distinctive mineral group as oxygen salts, some 50 individual minerals, borax, $Na_2B_4O_7.10H_2O$, being one of the best known. Boric acid, H_3BO_3 is of common occurrence in hot springs and associated with volcanic areas.

The pure metal has little or no use in industry, though nitrides and borides have application as dielectrics and high temperature ceramics with similar characteristics to those of aluminum oxide. Boric acid has long been used as a mild antiseptic, and borax is a general cleaner and metal alloy flux, as well as a water softener.

Technical Application: In Solid State processing boron has been the major p-type dopant for silicon wafers since their original development for semiconductor devices. Boric acid was first used, then boracine, and then diborane, B_2H_6, as a gas diffusion source. With ion implantation, I^2, B^+ as an ionic species is now used. The diborane also is used for doping silicon dioxide, SiO_2, for use as a p-type doping drive-in source, or as a thin film passivating layer with the acronym of BSG. Boron nitride (BN) also is used as a drive-in source with silicon wafers sandwiched between BN discs. As BCl_3 as an RF plasma, it is a dry chemical etching (DCE) method for etch removal or patterning of aluminum thin films. It is the best method to date for such processing due to the inherent difficulty of controlled etching of aluminum oxide in device fabrication.

Etching: HNO_3, H_2SO_4, molten salts, and metals.

BORON ETCHANTS

B-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
x .... HF, conc.
DISCUSSION:
B, as an amorphous surface layer remaining after ion implantation of boron in silicon (100) and (111) wafers. HF used to remove the glassy layer remaining on surfaces after implant. Also used on phosphorus and arsenic implantation glassy layers. Acronyms: PSG and ASG, respectively.
REF: Prussin, S et al — *J Appl Phys*, 57,181(1985)

B-0002a
ETCH NAME: Heat
TYPE: Thermal, preferential
TIME:
TEMP: 2000°C
COMPOSITION:
x .... heat
DISCUSSION:
B, single crystal ingot. During growth and cooling from 2000°C, heat will produce macroscopic surface structure similar to that observed by chemical etching: hexagonal, spiral, pyramidal pits, and oval plateaus.
REF: Talley, C P — *Nature (London)*, 182,1593(1958)

B-0002b
ETCH NAME: Nitric acid
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
x .... HNO_3, conc.

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DISCUSSION:
B, single crystal ingots. Solution used as a general etch for boron. Sulfuric acid also can be used.
REF: Ibid.

B-0002c
ETCH NAME: Beryllium
TYPE: Metal, removal/preferential
COMPOSITION:
x .... Be
TIME:
TEMP: Molten
DISCUSSION:
B, as boron nitride test blanks. Metallic beryllium, uranium, nickel, and platinum will attack boron. See Boron Nitride.
REF: Ibid.

B-0003
ETCH NAME: RF plasma
TYPE: Ionized gas, growth
COMPOSITION:
x .... BCl_3
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
B, grown as thin films. Describes a method of evaporating the films and use of ion bombardment to vaporize the metal and melt the boron as a thin film surface layer.
REF: Barnes, D et al — *Atomic Energy Res Establ* (Harwell Mem R/M), 125,4(1951)

PHYSICAL PROPERTIES OF BORON CARBIDE, B_4C

Classification	Ceramic
Atomic numbers	5 & 6
Atomic weight	55
Melting point (°C)	2350
Boiling point (°C)	3500
Density (g/cm^3)	2.50
Application limits (°C in air)	540
(°C in inert atm)	2260
Mean specific heat (J/kg °C) 25—1000°C	2090
Coefficient of linear thermal expansion ($\times 10^{-6}$/cm/cm°C) 25—800°C	5.7
Thermal conductivity (w/m °C) 800°C)	17.3
Hardness (Mohs — scratch)	9.3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Black
Cleavage (cubic)	(001)

BORON CARBIDE, B_4C

General: Carbides do not normally occur as natural compounds, but are artificially fabricated using many different metals. There is a single occurrence of a mineral carbide called moissanite, CSi, which has been found as small green hexagonal platelets in meteoric iron at Cañon Diablo, Arizona. Note that artificial silicon carbide is shown as SiC.

Industrially, boron carbide is one of the high temperature refractory ceramics, though

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not as widely used as silicon carbide, but with similar applications as fire brick, furnace tubes, etc. In powder form, it has been used as a lapping abrasive.

Technical Application: Not used in Solid State processing to any extent, to date, other than as a lapping and polishing abrasive. There are possible applications as a pressed powder substrate for circuit fabrication or in package construction.

Etching: Insoluble in acids. Soluble in fused salts.

BORON CARBIDE ETCHANTS

BC-0001
ETCH NAME: Potassium hydroxide
TYPE: Molten flux, removal
TIME:
TEMP: 365°C
COMPOSITION:
x .... KOH, pellets
DISCUSSION:
B_4C, as pressed powder blanks. Material can be etched in fused salts: alkaline hydroxides, and carbonates.
REF: *A Dictionary of Carbide Terms* — Adams Carbide Corp., Kenilworth, NJ

BORIDES, MBx

General: Do not occur in nature as metallic boron compounds, though boron is a constituent element in many minerals as hydrated silicates, phosphates, sulfides, and carbonates. Borax, $Na_2B_4O_7.10H_2O$, is representative of the borate mineral group.

The borides are artificially grown in industry as high temperature ceramics with a Mohs hardness generally greater than H = 8. In the general formula shown: M = Cr, Mo, Nb, U, V, Ta, W, and Zr; and Bx = B, B_2, B_{12}, or as a pentaborate, B_2O_5. The materials are used as crucibles, furnace tubes, and liners, etc. for their refractive capabilities and general chemical inertness. Some are used in powder form as lapping and polishing abrasives; others for their dielectric properties in sheet, rod, or flats that are metallized as capacitors or resistors.

Technical Application: No major use in Solid State device fabrication, although there is possible application as circuit substrates and packaging assemblies. Some borides are under evaluation as thin film surface coatings with applications similar to those of SiO_2 and Al_2O_3, or as discrete Solid State dielectric elements, sputter evaporated as thin films and planar surface capacitors or resistors in circuit fabrication.

Most of the borides shown in the following section have been grown as single crystal specimens for general morphological studies. See Boron Nitride and Boron Carbide.

Etching: Varies with compound — soluble in HNO_3, H_2SO_4, H_2O_2; alkalies or mixed acids; and aqua regia.

Note: The following are the borides listed:

Cerium boride, CeB_6
Chromium boride, Cr_3B_2
Molybdenum boride, Mo_2B_5
Niobium boride, Nb_3B_3
Rare earth borides, $R_3Ni_7B_2$
Silicon boride, SiB_6
Tantalum boride, TaB_2
Titanium boride, TiB_2
Tungsten boride, WB
Uranium boride, UB_2
Vanadium boride, VB_2
Zirconium boride, ZrB_2

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BORIDE ETCHANTS

CERIUM BORIDE ETCHANTS

CEB-0001
ETCH NAME: Heat
TYPE: Thermal, annealing
COMPOSITION:
x .... heat
TIME:
TEMP: Elevated
DISCUSSION:
CeB_6, ingots grown by Czochralski (CZ) method. Also grown were $CeCu_6$, and $LaCu_6$. Both of these compounds are orthorhombic in structure. $CeAl_3$ was grown by arc melting, and annealed 1 week at 900 to 1000°C. Also grew $CeCu_2Si_2$. All materials were used in a general structural study.
REF: Onuki, Y et al — *J Phys Soc Jpn*, 4,1210(1984)

CHROMIUM BORIDE ETCHANTS

CRB-0001a
ETCH NAME: Perchloric acid
TYPE: Acid, removal
COMPOSITION:
x .... $HClO_4$
TIME:
TEMP: Hot
DISCUSSION:
Cr_3B_2 specimens. Solution is a general etch for this boride. Material used in a composition study. Other chromium borides were Cr_2B, Cr_3B_4, and CrB_2O. Compounds will not etch in HF, HCl, HNO_3, or alkalies.
REF: *Ceramics and High Temperature Materials Handbook*, Vol 85, #1, Coltronics Corp., 1982

CRB-0001b
ETCH NAME: Hydrogen peroxide
TYPE: Acid, removal
COMPOSITION:
x .... H_2O_2
TIME:
TEMP:
DISCUSSION:
Cr_3B_2 specimens. This acid is a general etch for all compounds of this material, as well as other peroxide chemical solutions.
REF: Ibid.

CRB-0001c
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot to boiling
DISCUSSION:
Cr_3B_2 specimens. Very slow etch attack with this solution, but the higher the metal content, the greater the attack.
REF: Ibid.

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MOLYBDENUM BORIDE ETCHANTS

MOB-0001a
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
Mo_2B_5 specimens. Solution is a general etch. Also used on Mo_2B; and MoB. Will not etch in HCl. (*Note:* Mixed HF:HNO_3 will etch.)
REF: Ibid. CRB-0001a
TIME:
TEMP:

MOB-0001b
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
Mo_2B_5 specimens. Solution is a general etch.
REF: Ibid. CRB-0001a
TIME:
TEMP: Hot

MOB-0001c
ETCH NAME: Sodium hydroxide
TYPE: Molten flux, removal
COMPOSITION:
x .... NaOH (KOH)
DISCUSSION:
Mo_2B_5 specimens. Solution is a general etch. It may be preferential on single crystal material.
REF: Ibid. CRB-0001a
TIME:
TEMP: 365°C

MOB-0002
ETCH NAME: Acetone
TYPE: Ketone, cleaning
COMPOSITION:
x .... CH_3COCH_3
DISCUSSION:
MoB surface penetration film developed in a study of boriding metals at less than 670°C. Other metals evaluated were Ni, Fe, Co, Ti, Nb, and Hastalloy B. See Nickel Boride for details of cleaning procedure of substrates and borate baths used in process evaluated. See NIB-0002.
REF: Koyama, K et al — *J Electrochem Soc,* 126,147(1978)
TIME:
TEMP:

NIOBIUM BORIDE ETCHANTS

NBB-0001a
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot to boiling

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DISCUSSION:

Nb_3B_3 specimens. Solution is a slow etch on both Nb_3B_3 and NbB. These borides will not etch in: HCl; HNO_3 or aqua regia (1HCl:1HNO_3).

REF: Ibid. CRB-0001a

NBB-0001b

ETCH NAME: Potassium hydroxide — TIME:

TYPE: Molten flux, removal — TEMP: 365°C

COMPOSITION:

x .... KOH (NaOH)

DISCUSSION:

Nb_3B_3 specimens. A general etch for this material. (*Note:* Eutectic mixtures as 1NaOH:1KOH will also etch, and may be slightly preferential on single crystals.)

REF: Ibid. CRB-0001a

NBB-0001c

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... HF

DISCUSSION:

Nb_3B_3 specimens. This is a slow etch on this material.

REF: Ibid. CRB-0001a

NBB-0001d

ETCH NAME: Potassium sulfate — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... K_2SO_4

x .... H_2O

DISCUSSION:

NB_3B_3 specimens. Several sulfates will etch this material. Some carbonates will also act as etchants.

REF: Ibid. CRB-0001a

RARE EARTH BORIDE ETCHANTS

RNIB-0001

ETCH NAME: Nitric acid — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... HNO_3

DISCUSSION:

RNi_6B_2 buttons were grown by arc melting under argon, then each specimen was annealed 2 weeks at 900°C. In the general formula shown, "R" stands for rare earth, though other workers use "RE" as the acronym. Here, R = Nd, Ce, Gd, Eu, and Yb. Material used in a magnetics and structural study.

REF: Felner, I — *J Phys Chem Solids*, 44,43(1983)

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SILICON BORIDE ETCHANTS

SIB-0001
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
DISCUSSION:
SiB_6 specimens fabricated as 0.5 mm diameter spheres. Water used to clean spheres prior to study of the unit cell space group. The material is orthorhombic system. Weissenberg photographs were made on the b- and c-axes.
REF: Adamsky, R F — *Acta Crystallogr*, 11,144(1958)

TIME:
TEMP:

TANTALUM BORIDE ETCHANTS

TAB-0001a
ETCH NAME: Potassium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... x% KOH (NaOH)
x .... H_2O
DISCUSSION:
TaB_2, TaB, and Ta_3B_4 specimens. This material can be etched in various concentrations of these alkalies. These borides do not etch in HCl, HNO_3, or aqua regia ($3HCl:1HNO_3$).
REF: Ibid. CRB-0001a

TIME:
TEMP:

TAB-0001b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... H_2SO_4
DISCUSSION:
TaB_2 and other specimens. Solutions of these acids are slow etchants on this material.
REF: Ibid. CRB-0001a

TIME:
TEMP:

TAB-0001c
ETCH NAME: Sodium peroxide
TYPE: Acid, removal
COMPOSITION:
x .... x% Na_2O_2
x .... H_2O
DISCUSSION:
TaB_2 and other specimens. The solution is a general etch for this material. Bisulfates and carbonates will also act as etchants.
REF: Ibid. CRB-0001a

TIME:
TEMP:

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TITANTIUM BORIDE

TIB-0001
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
DISCUSSION:
TiB_2 and TiC single crystal wafers used in a study of elastic constants. Both materials were either cleaved (001) or diamond saw cut. Lap polish surfaces with diamond paste. Degrease with TCE, rinse in alcohol and water. Authors say that both materials appear to be harder than diamond. No etch shown.
REF: Gilman, J J & Roberts, B W — *J Appl Phys*, 32,1406(1961)
TIME:
TEMP:

TUNGSTEN BORIDE ETCHANTS

WB-0001a
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF
DISCUSSION:
WB_2, W_2B_2, W_2B_5, and Beta-WB specimens. A general etch for these materials. WB will not etch in HCl; hot H_2SO_4 or HNO_3.
REF: Ibid. CRB-0001a
TIME:
TEMP:

WB-0001b
ETCH NAME: Aqua regia
TYPE: Acid, removal
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
WB_2 and other tungsten borides can be etched in aqua regia.
REF: Ibid. CRB-0001a
TIME:
TEMP:

WB-0001c
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... x% NaOH (KOH)
x .... H_2O
DISCUSSION:
WB_2 and other tungsten borides can be etched in various solution concentrations of these alkalies.
REF: Ibid. CRB-0001a
TIME:
TEMP:

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URANIUM BORIDE ETCHANTS

UB-0001a
ETCH NAME: Sodium peroxide
TYPE: Acid, removal
COMPOSITION:
x .... Na_2O_2
x .... H_2O
DISCUSSION:
UB_4, UB_2, and UB_{12} specimens. Difficult to etch controllably as the materials decompose in peroxides.
REF: Ibid. CRB-0001a
TIME:
TEMP:

UB-0001b
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
UB_4, UB_2, and UB_{12} specimens. Difficult to etch controllably as the materials decompose in acids.
REF: Ibid. CRB-0001a
TIME:
TEMP:

UB-0002
ETCH NAME:
TYPE: Cut, forming
COMPOSITION:
x .... electricity
DISCUSSION:
UB, (110) cut single crystal specimens spark cut for fabrication as spheres. Compound has the ThB_4 structure and grows with a preferred (110) orientation. The material is brittle and fractures easily on (001) with cubic cleavage. Density: 3.98 g/cm^3.
REF: Menovsky, A et al — *J Crystal*, 9,70(1984)
TIME:
TEMP:

VANADIUM BORIDE ETCHANTS

VB-0001a
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
VB_2 and VB specimens. A general etch for these materials. Does not etch in HCl, HF, H_2SO_4.
REF: Ibid. CRB-0001a
TIME:
TEMP:

VB-0001b
ETCH NAME: Potassium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... x% KOH (NaOH)
x .... H_2O
TIME:
TEMP:

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DISCUSSION:
VB_2 and VB specimens. This material can be etched in various liquid concentrations of alkalies.
REF: Ibid. CRB-0001a

VB-0001c
ETCH NAME: Potassium nitrate — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... x% KNO_3
x .... H_2O
DISCUSSION:
VB_2 and VB specimens. Solutions of nitrates will etch this material. Also carbonates, bisulfates, and peroxides.
REF: Ibid. CRB-0001a

ZIRCONIUM BORIDE ETCHANTS

ZRB-0001a
ETCH NAME: Potassium hydroxide — TIME:
TYPE: Alkali, removal — TEMP:
COMPOSITION:
x .... KOH (NaOH)
x .... H_2O
DISCUSSION:
ZrB, ZrB_2, Zr_3B_4, and ZrB_{12} specimens can be etched in various concentrations of the alkalies. Will not etch in HCl or HNO_3.
REF: Ibid. CRB-0001a

ZRB-0001b
ETCH NAME: Sodium peroxide — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... Na_2O_2
DISCUSSION:
ZrB and other zirconium borides. Etching is violent with peroxides.
REF: Ibid. CRB-0001a

PHYSICAL PROPERTIES OF BORON NITRIDE, BN

Classification	Nitride
Atomic numbers	5 & 7
Atomic weight	24.8
Melting point (°C)	2730
Boiling point (°C)	2.25
Density (g/cm³)	
Application limit (°C)	650
Specific heat (mean)(J/kg °C) 25—1000°C	1570
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 25—800°C	7.5 // c-axis
Thermal conductivity (W/m °C) 900°C	26

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Electrical resistivity (ohms-cm $\times 10^{13}$) 25°C	1.7 // c-axis
(ohms-cm $\times 10^{10}$) 480°C	2.3 // c-axis
Refractive index (n=)	1.54—1.68
Dielectric constant (e=)	4—8
Energy band gap (eV)	3—10
Lattice constant (angstroms)	3.615
Hardness (Mohs — scratch)	8+
Crystal structure (hexagonal — normal) alpha	(1010) prism
(isometric — normal) beta	(100) cube
Color (solid)	White
Cleavage (dodecahedral)	(110)

BORON NITRIDE, BN

General: Does not occur as a natural compound, although there are several boron-containing minerals: sassolite, $B(OH)_3$, borax, $Na_2B_4O_7.10H_2O$, as examples. Boric acid, H_3BO_3, occurs in hot springs associated with volcanic action.

As a nitride it is an industrial ceramic with a high melting point, used as a crucible under reducing atmosphere conditions (H_2 or FG) for the processing of liquid metals, such as steels, aluminum and aluminum alloys, tin, bismuth, and others. In an oxidizing atmosphere BN converts to B_2O_3 above 650°C.

Technical Application: In Solid State processing pressed powder BN discs have been used as a diffusion source of boron as a p-type dopant in silicon, with silicon wafers sandwiched between the discs (boric acid was the first such dopant, then diborane, B_2H_6 as a gas.)

The nitride has been CVD grown as amorphous thin films, also for boron doping drive-in, or for use as a dielectric, e.g., capacitor circuit element. Under pressure, with elevated temperature, amorphous films have been converted to hexagonal or cubic single crystal structure. The latter was fabricated as a high temperature functioning diode. BN has been converted to B_2O_3 thin films and applied as passivation surface coatings. Also conversion to boron carbide, B_4C by treatment with CCl_4 vapor at elevated temperature.

Etching: Limited solubility in HCl, HF, H_2SO_4, H_2O_2, H_3PO_4.

BORON NITRIDE ETCHANTS

BN-0002a
ETCH NAME: Phosphoric acid
TYPE: Acid, removal/cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
x .... H_3PO_4, conc.
DISCUSSION:

BN, as pressed powder blanks and parts. Solution used as a general cleaning and material removal etch.

REF: Bulletin C-941 eff 6/81(716/731/3221) — The Carborundum Company

BN-0009: Rand, M J & Roberts, J F — *J Electrochem Soc,* 115,423(1968)

BN, as a thin film amorphous coating on silicon, gallium arsenide, and other semiconductors. Solution used hot for removal of BN through photolithographic patterned gold masks; also used SiO_2 and Si_3N_4 as pattern masks.

BN-0010: Kim, C et al — *J Electrochem Soc,* 131,1384(1984)

BN, as thin film amorphous coating deposition by CVD on (100), n-type silicon wafers, then overcoat with Si_3N_4 to prevent out-diffusion of boron. Wafer heated to drive-in boron as p-type dopant. Remove silicon nitride with HF and remaining boron nitride with hot phosphoric acid.

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BN-0002b
ETCH NAME: Sulfuric acid
TYPE: Acid, removal/cleaning
COMPOSITION:
x .... 20% H_2SO_4
TIME: To 1 h
TEMP: RT
RATE: 10.7 mg/cm³
DISCUSSION:
BN, as pressed powder test blanks. Dilute solutions of H_2SO_4 will attack boron nitride; whereas concentrated solution will not.
REF: Ibid.

BN-0002c
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc. (fuming)
TIME: To 1 h
TEMP: RT
RATE: 8.9 mg/cm³
DISCUSSION:
BN, as pressed powder test blanks. "Fuming" nitric acid will attack boron nitride. (*Note:* Standard concentration is "white" fuming 70%; then "yellow" 72%; and "red" 74% fuming. When fuming nitric is shown, it is usually red fuming.)
REF: Ibid.

BN-0002d
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF, conc.
TIME: To 1 h
TEMP: RT
RATE: 17 mg/cm³
DISCUSSION:
BN, as pressed powder test blanks. Solution will attack boron nitride.
REF: Ibid.
BN-0001b: Ibid.
BN, as pressed powder discs for boron drive-in of sandwiched silicon wafers. Soak in HF, rinse heavily in running DI water, and dry under IR lamp. Use HF 5 min, RT, for cleaning BN.

BN-0001a
ETCH NAME: Paper
TYPE: Abrasion, cleaning
COMPOSITION:
x .... filter paper
TIME:
TEMP: RT
DISCUSSION:
BN, as pressed powder discs. Light hand lapping on Whattman #5 filter paper used to clean surfaces, followed with N_2 blow off. Discs used in a metal plating study. Results were poor due to metal failure to adhere to the powdered surface.
REF: Walker, P & Dokko, P — personal application, 1985

BN-0002e
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal/cleaning
COMPOSITION:
x .... 20% NaOH
TIME: To 1 h
TEMP: RT
RATE: 8.9 mg/cm³

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DISCUSSION:

BN, as pressed powder test blanks. Lower concentrations used for cleaning; higher concentrations for more rapid removal.

REF: Ibid.

BN-0002f

ETCH NAME: Lead oxide — TIME:

TYPE: Molten flux, removal — TEMP: Molten

COMPOSITION:

x .... PbO

DISCUSSION:

BN, as pressed powder test blanks. Molten flux metal oxides attack BN with conversion to B_2O_3.

REF: Ibid.

BN-0003

ETCH NAME: Hydrogen peroxide — TIME:

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

x .... H_2O_2

x .... H_2O

DISCUSSION:

BN, as amorphous thin films on silicon. Various concentrations used in etch patterning film through metal masks.

REF: Hirayama, M & Shomo, J — *J Electrochem Soc,* 122,1671(1975)

BN-0004

ETCH NAME: Argon — TIME: 5 h

TYPE: Gas, crystallization — TEMP: 1000°C

COMPOSITION:

x .... Ar

DISCUSSION:

BN, single crystal films. Initially deposited on copper substrates as clear, amorphous coatings. Heat treatment as shown above showed conversion to single crystal hexagonal BN. BN deposited much below 600°C were unstable in moist atmospheres and devitrified; thick films showed spontaneous delamination from the substrate during cooling after deposition. Films deposited at low temperature also swelled and partly dissolved in water, and thick films tended toward white, opaque, rather than clear.

REF: Motojima, S et al — *Thin Solid Films,* 88,269(1982)

BN-0005: Szmidt, J et al — *Thin Solid Films,* 110,7(1983)

BN, single crystal thin films grown by reactive pulse plasma on silicon, (111) and (110) orientated wafers, p- and n-type. Films were called Borazone and consisted mainly of beta-BN.

BN-0006

ETCH NAME: — TIME:

TYPE: Metal, removal — TEMP: Molten

COMPOSITION:

x .... Be, U, Ni, Pt

DISCUSSION:

BN, (100) as cubic boron nitride. Single crystals with grown junctions fabricated under 55 K atm pressure at 1700°C. For n-type, doped with Be; for p-type, doped with Si. Fabricated

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as a diode the BN appears capable of operating up to 530°C and possibly 1300°C. Diamond also shows semiconducting properties, but is more difficult to fabricate. (*Note:* Silicon carbide, Si_3C, has been fabricated as a high temperature diode.)

REF: Mishima, C et al — *Science,* October 1987

BN-0007: Greenberg, J (Ed) — *Sci News,* 132,241(1987)

BN, (100) new development as a diode reported as shown in BN-0006.

BN-0008: Merbarki, M et al — *J Cryst Growth,* 61,636(1983)

BN, (0001) specimens grown as hexagonal single crystal platelets were yellow to colorless. BN has a layer structure like graphite parallel to the c-axis. Growth was with boron in a silicon flux under nitrogen in an induction furnace at 1850°C.

PHYSICAL PROPERTIES OF BORON PHOSPHIDE, BP

Classification	Phosphide
Atomic numbers	5 & 15
Atomic weight	41.79
Melting point (°C)	1300
Boiling point (°C)	
Density (g/cm^3)	
Electrical resistivity (ohms-cm)	0.41 (100)
	5.64 (111)
Carrier concentration (n) ($\times 10^{17}$ cm^{-3})	1.0 (100) 3.07 (111)
Electron mobility (u) ($cm^2/V/sec$)	145 (100) 36.5 (111)
Lattice constant (angstroms $\times 10^{-6}$)	4.539 (100) 4.536 (111)
Hardness (Mohs — scratch)	9+
(Vicker's — kg/mm^2)	3000-4000
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Red-orange
Cleavage (cubic)	(001)

BORON PHOSPHIDE, BP

General: Does not occur as a natural compound, though there are many boron minerals as phosphates, arsenates, carbonates, and sulfates. The borate group, as hydrous salts, such as borax, has major industrial use. BP is not normally used in metal processing, although it can be a phosphorus additive in irons and steels, brass, bronze, etc.

Technical Application: Boron phosphide is a III—V compound semiconductor with the common (111) polarity of such compounds. The individual elements are silicon dopants: boron, p-type; phosphorus, n-type. They have been occasionally used for dual-doping, but this is not recommended as there can be drastic alteration of the material resistivity with subsequent heat processing.

The material has been grown by the Czochralski (CZ) method; and in a molten flux, both methods as single crystals. It also has been deposited as an oriented thin film. It does not oxidize at elevated temperature, and is under evaluation as a high temperature diode, similar to silicon carbide and boron nitride. As a thin film it has been fabricated as a photovoltaic device.

Etching: Alkali electrolytic solutions. Molten flux salts.

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BORON PHOSPHIDE ETCHANTS

BP-0001
ETCH NAME:
TYPE: Molten flux, preferential
COMPOSITION:
3 .... NaOH
1 .... Na_2O_2
TIME:
TEMP: Molten
DISCUSSION:
BP, (100) and (111) grown as single crystal platelets by a flux method using Cu_3P or $Ni_{12}P_5O$ as the flux at high temperature and under high pressure. Remove crystals from flux by etching in mixtures of HF:HNO_3. The (111) crystals are deep red in color; (100) crystals, orange/red. The molten flux etch shown was used to develop dislocations and other structure. The (111) surface is wavy, representative of slight misorientation. Growth temperature was 1300°C with pressure of 18 atm under argon.
REF: Kumashiro, Y et al — *J Cryst Growth*, 70,515(1984)
BP-0002: Kumashiro, Y et al — *J Cryst Growth*, 70,507(1984)
BP, (100) and (111) single crystal thin films grown by CVD on silicon substrates of like orientation. The BP crystal plates were removed from the silicon by etching away the silicon in HF:HNO_3. A form of float-off for film study under TEM.

BP-0003
ETCH NAME: Sodium hydroxide
TYPE: Electrolytic, removal
COMPOSITION:
x .... 10% NaOH
TIME:
TEMP:
ANODE: BP
CATHODE:
POWER: 0.1—10 A/cm²
DISCUSSION:
BP, single crystal wafers. Solution used in a dark room under red light for general removal and polishing — higher concentrations may show some preferential attack. P-type etches more than 100× faster than n-type.
REF: Chu, T L & Chu, S S — *J Electrochem Soc*, 123,259(1976)

PHYSICAL PROPERTIES OF BORON TELLURIDE, B_2Te_3

Classification	Telluride
Atomic numbers	5 & 52
Atomic weight	404.47
Melting point (°C)	~1800
Boiling point (°C)	
Density (g/cm³)	
Hardness (Mohs — scratch)	7—8
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey/black
Cleavage (cubic)	(001)

BORON TELLURIDE, B_2Te_3

General: Does not occur as a natural metallic telluride, although there are several other natural telluride and selenide minerals. Most boron minerals are silicates or phosphides, and there is the natural occurrence of boric acid, $B(OH)_3$, as the single crystal sassolite or

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extracted from the water of hot springs. The telluride has little use in the metals industry other than as a possible compound semiconductor.

Technical Application: Boron telluride is a III—IV compound semiconductor and has been quite widely studied, alone, as an isomorphous series with selenides, and as telluride-selenide-sulfide mixed crystals. There is no major application as Solid State devices at the present time, although it may be used as a thin film material in heterostructural devices.

Etching: Mixed acids of HF:HNO_3:HAc/H_2O; dichromates alone, or as acid mixtures.

BORON TELLURIDE ETCHANTS

BTF-0001
ETCH NAME: Potassium chromate — TIME: 10 min
TYPE: Acid, preferential — TEMP: 95°C
COMPOSITION:
x .... 0.5 *M* $K_2Cr_2O_7$
DISCUSSION:
B_2Te_3, (111) wafers used in a dislocation study. Solution will develop dislocations on the (111)A — boron surface only.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7
BTE-0002: Gatos, H C & Lavine, M C — *Lincoln Lab Tech Rep*, 293, January 1963
B_2Te_3, single crystal material used in a general development study.

PHYSICAL PROPERTIES OF BORON TRIFLUORIDE, BF_3

Classification	Fluoride
Atomic numbers	5 & 9
Atomic weight	67.82
Melting point (°C)	−127
Boiling point (°C)	−101
Density (g/cm³) liquid	2.99
Hardness (Mohs — scratch)	1.5—2
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
(gas)	Colorless
Cleavage (cubic)	(001)

BORON TRIFLUORIDE, BF_3

General: Does not occur as a natural compound, although there are other metallic fluorides, such as fluorite, CaF_2, and cryolite, Na_2AlF_6, both of which have important optical properties and use as fluxes in metal processing. Note that cryolite has a refractive index ($n = 1.33\times$) that is the closest of any mineral to that of water ($n = 1.00$), such that it "disappears" when introduced into water. The trifluoride is not used in the metal industries but, as a fluoride compound, could be used as a flux in soldering similar to fluorite applications.

Technical Application: Boron trifluoride is under study and development in Solid State processing as a thin film with single crystal orientation. It has possible optical characteristics and applications, and is under evaluation for defect structure.

Etching: H_2SO_4: mixed acids of HF:HNO_3.

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BORON TRIFLUORIDE ETCHANTS

BTF-0001
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
BF_3, (100) oriented thin films grown by CVD. Solution used to develop defects in a structure study.
REF: Caine, E J — *J Electron Mater*, 13,341(1984)

BRASS: 70Cu:30Zn

General: Does not occur as a natural alloy, although there are some carbonates and arsenates. The minerals rosasite, $(Cu,Zn)CO_3.(Cu,Zn)OH_3$, and barthite, $3ZnO.CuO.3As_2O_5.H_2O$ are representative of such hydrates.

Brass is of ancient origin, circa 4500 B.C., as some possible artifacts of brass have been found in Egyptian tombs of the Pharaoh dynastic period, but they are rare and were pre-dated by the discovery of bronze, circa 5000 B.C. There are still individual bronzes and brasses today, but far more trinary mixtures of Cu:Zn:Sn (Bronze, Cu:Sn) which are more commonly called brass. There are other brass mixtures containing Pb, Al, Ni, Mn, P, and Fe, in addition to tin, Sn. Brass is more widely used as it is not as brittle as bronze, and is more easily fabricated. A few of the better known brasses are shown below:

Formula	Name
85Cu:15Zn	Red brass
67-72Cu:28-32Zn:xPb:xFe	Cartridge or spring brass
67Cu:33Zn	Yellow brass (ordinary)
61Cu:39Zn	Wire brass

In addition to the above, there are some well-known named brasses, such as muntz metal, pewter, and German silver. All brasses, as well as several other metal alloys, are heat treated for a specific hardness, such as $^1/_4$- or $^1/_2$-hard, as against the dead-soft heat treatment of aluminum or gold wire used in Solid State device bonding. Brass is a fair electrical conductor and has excellent thermal transfer characteristics, such that it is used as a heat sink for mounting devices in electrical testing. It also is quite resistant to atmospheric corrosion, and can be used outside under variable weather conditions. Brasses are available in a wide range of forms — rod, tube, sheet, wire, thin shim stock, bulk material for shaping or cutting — and finely powdered brass is added to plastics and paint as a coloring pigment. It can be drawn or extruded into shaping, such as for cartridge casings, which is not the case of bronze.

Technical Application: Brass is not used in the direct fabrication of Solid State devices, but it is used in package designs, as general heat sinks, or device test blocks. Where critical devices, such as high frequency microelectronic gallium arsenide FETs are being tested under elevated temperature conditions, there can be a problem of out-diffusion of zinc from the brass into the device under test. This can alter or destroy device characteristics. To prevent this from occurring, copper plate the brass surfaces to a sufficient thickness, such that the copper will act as a blocking layer against zinc diffusion, vs. the temperature level being used.

There are many uses of brass parts in material processing. Shim stock has been used as

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a pattern mask for applying ink to a semiconductor wafer that is then etch-patterned, or the patterned shim used as a metal evaporation mask. Rods are used as either holders for probes in testing, or as the probes themselves. Brass platens have been in use for many years for lapping materials — rocks and minerals — as well as many other compounds. An abrasive slurry is added directly to the platen surface, or a felt-type pad is glued to the surface, then the pad saturated with an etch solution; or an abrasive slurry is drip-fed onto the pad with the platen rotated. Examples are the Buehler, Speed-Fam, or Strausbaugh lapping/polishing machines.

Alpha-brass has been grown as single crystals for morphological studies.

Etching: HCl, H_2SO_4, H_3PO_4, HNO_3, aqua regia, and other mixed acids.

BRASS ETCHANTS

BRA-0001a
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:

(1) 16 .... HNO_3
160 .... H_2O

(2) (6) .... KCl
100 .... H_2O

DISCUSSION:

Brass, cartridge, or eyelet. A general two-step etch for cleaning brass. Etch with the dilute nitric acid solution, water rinse; then follow with the salt solution, and water rinse.

REF: Oberg, E & Jones, F D — *Machinery Handbook*, 4th ed, The Industrial Press, New York, 1968

BR-0002a: Walker, P & Campos, R — personal application, 1961

Brass/bronze piping on cryogenic trailers. Used the (2) solution as 6 g KCl:100 ml H_2O for light cleaning of parts.

BRA-0008a
ETCH NAME: Scale dip or fire-off dip TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:

1 .... HNO_3
1 .... H_2O

DISCUSSION:

Brass specimens and parts. As a "scale" dip, the solution is used to remove oxide prior to a brite dip. As a "fire-off" dip, solution is used as a general removal etch for brass, bronze, copper, and copper alloys.

REF: Bulletin #B-11D — The American Brass Co.

BRA-0004: Maddin, R & Asher, W R — *Rev Sci Instr*, 21,881(1957)

Brass specimens. A Saran plastic thread wetted with the solution mixture was used as an acid-saw to cut specimens.

BRA-0005: McGuire, T R — Yale University, Ph.D. dissertation (1949)

Brass, specimen. Acid-saw cutting method reference from BR-0004.

BRA-0001b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:

4 .... HCl
1 .... HNO_3

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DISCUSSION:
Brass specimens, as cartridge or eyelet. A general etch for both brass and bronze. (*Note:* Solution is very close to aqua regia.)
REF: Ibid.
BRA-0002: Ibid.
Brass and bronze cryogenic trailer piping and parts were etch cleaned in this solution.

BRA-0002c
ETCH NAME: Sulfuric acid, dilute TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
1 .... H_2SO_4
10 .... H_2O
DISCUSSION:
Brass and bronze cryogenic trailer piping and parts. Solution used for corrosion removal.
REF: Ibid.

BRA-0008b
ETCH NAME: Bichromate finish dip TIME:
TYPE: Acid, finish TEMP:
COMPOSITION:
12 oz .... H_2SO_4
4 oz .... $NaCr_2O_3$
1 gal .... H_2O
DISCUSSION:
Brass, bronze, and copper parts. Solution used to remove scale (oxide). Produces a semi-matte finish.
REF: Ibid.

BRA-0008c
ETCH NAME: Matte dip TIME:
TYPE: Acid, finish TEMP:
COMPOSITION:
2 .... H_2SO_4
1 .... HNO_3
x .... *ZnO or ZnS

*x = saturate the solution

DISCUSSION:
Brass, bronze, and copper alloys. Solution will produce a matte finish on parts.
REF: Ibid.

BRA-0006
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... NH_4OH
x .... H_2O_2
DISCUSSION:
Brass specimens and parts. Used as a general etch for brass. Solution reaction reduced with the addition of water as a cleaning etch.

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REF: Bergland, T & Deardon, W H — *Metallographer's Handbook of Etching,* Pitman & Sons, London, 1931

BRA-0013a
ETCH NAME: Phosphoric acid
TYPE: Acid, preferential
COMPOSITION:
x .... H_3PO_4
x .... H_2O
TIME:
TEMP: Hot
DISCUSSION:
CuZn(30%) specimens used in a study of striations and slip. Use very dilute solutions for defect development. Solution cannot be used electrolytically as it will polish specimens. A $(NH_4)_2SO_4$:NH_3 solution did not work. Mechanical hand polishing used to reduce damage depth, and slip did not show below a damage depth of about $^1/_4$ mm.
REF: McLeon, D — *J Inst Met,* 95(1947—1948)
BRA-0019: Boswell, F W C & Weinberg, F — *J Appl Phys,* 31,1835(1960)
Alpha-brass specimens. Specimen blanks were lapped down and etch thinned for direction observation of dislocation movement. A 16 mm movie camera with a 2" focal length, 1.6F lens was used to record the results. (*Note:* A similar movie was made while etching silicon wafers in 1957.)

BRA-0013b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... $2NH_4Cl.CuCl_2.H_2O$
x .... KOH (NaOH)
TIME:
TEMP:
DISCUSSION:
CuZn(30%) specimens. Solution will develop striations and slip. See BRA-0013a for further discussion.
REF: Ibid.

BRA-0014
ETCH NAME: Jacquet's etch
TYPE: Electrolytic, polish
COMPOSITION:
345 ml .... $HClO_4$
655 ml .... HAc
TIME:
TEMP:
ANODE: Brass
CATHODE:
POWER:
DISCUSSION:
Brass specimens. Solution used as a general electrolytic etch.
REF: Barrett, C & Levenson, L H — *Trans Am Inst Min Met (England),* 137,112(1940)

BRA-0015
ETCH NAME: Sodium chloride
TYPE: Electrolytic, preferential
COMPOSITION:
x .... 5% NaCl
TIME:
TEMP:
ANODE: Brass
CATHODE:
POWER:
DISCUSSION:
Brass specimens. Solution used to develop etch figures.
REF: Fesch, C H & Whyte, S — *J Inst Met,* 904,10(1913)

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BRA-0007
ETCH NAME: Ferric chloride
TYPE: Acid, removal
COMPOSITION:
x .... 30—35°Bé $FeCl_3$
x .... H_2O
TIME:
TEMP: RT to hot
DISCUSSION:
Brass, bronze, and copper alloy parts. Solution used as a general etch for metals to include irons, steel, and nickel, and may be for surface cleaning only, polishing, or preferential. (*Note:* Ferric chloride solutions are mixed as Normal; percent as shown; or by Baume, °Bé. The latter is a measure of solution viscosity. A common mixture is as 35°Bé.)
REF: N/A

BR-0008d
ETCH NAME: Bright dip
TYPE: Acid, removal
COMPOSITION:
2 gal .... H_2SO_4
1 gal .... HNO_3
$^1/_2$ fl oz .... HCl
1—2 qt .... H_2O
TIME:
TEMP: RT
DISCUSSION:
Brass, bronze, and copper alloys. Surfaces are usually oxide stripped with a scale dip or pickling solution, such as the solution shown, prior to a brite dip.
REF: Ibid.

BRA-0008d
ETCH NAME: Pickling solution
TYPE: Acid, clean
COMPOSITION:
x .... 12—15% H_2SO_4
TIME:
TEMP: RT to hot
DISCUSSION:
Brass, bronze, and copper alloys. Solution used to soak and remove oxide and scale prior to further treatment of material.
REF: Ibid.

BRA-0009
ETCH NAME: Phosphoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... 35% H_3PO_4
TIME:
TEMP:
ANODE: Brass
CATHODE:
POWER:
DISCUSSION:
Brass, as single crystal alpha-brass. Wafers were cut and polished in the solution shown. Specimens were used in a study of slip modes.
REF: Wilsdorf, H & Fourier, J J — *Acta Metall,* 4,271(1956)
BR-0010: Wilsdorf, H — *Z Metallkd,* 45,14(1954)
BRA-0012: Fourie, J T — *Acta Metall,* 8,88(1960)
Alpha-brass as single crystal specimens used in a study of slip during plastic deformation. Power used was 2.67 V.

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BRA-0016
ETCH NAME: TIME:
TYPE: Pressure, preferential TEMP:
COMPOSITION:
x .... deformation
DISCUSSION:
Alpha-brass single crystals deformed in a study of secondary slip. Also studied copper crystals. Secondary slip nucleates at the end of primary slip lines when internal stress fields are high.
REF: Michell, T E & Thornton, P R — *Phil Mag*, 10,314(1964)

BRA-0017
ETCH NAME: TIME: 120 min
TYPE: Acid, cutting TEMP: RT
COMPOSITION:
(1) 200 ml .... HCl
50 g .... $FeCl_3$
250 ml .... H_2O
(2) 1 .... HNO_3
1 .... H_2O
DISCUSSION:
Brass specimens $^3/_{16}$" thick are soaked in solution (1) used to cut brass, aluminum, and copper. Solution (2) used to cut tin and zinc. (*Note:* An excellent review of metal growth methods.)
REF: Honeycombe, R W K — *Met Rev*, 4,1(1959)

BRA-0018
ETCH NAME: Nitric acid TIME:
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
1 .... 45% HNO_3
1 .... H_2O
DISCUSSION:
Alpha-brass [(Cu:Zn) with 29.38% Cu)]. Cut as 12 mm square blanks and plated with copper containing radioactive tracer $^{29}Cu^{64}$ used in a study of the mechanisms of Cu_2O formation. Brass was cleaned: (1) degrease with TCE; (2) clean in solution shown; and (3) air dry. After plating, blanks were water soaked for 15 h to oxide tarnish surfaces. See CUO-0016.
REF: Birley, S S & Tromans, D — *J Electrochem Soc*, 118,636(1971)

PHYSICAL PROPERTIES OF BROMINE, Br_2

Classification	Halogen
Atomic number	35
Atomic weight	159.83
Melting point (°C)	−7.3 (−7.2)
Boiling point (°C)	58.78
Density (g/cm³) 20°C	3.12
(g/cm³) 59°C	2.93
Thermal conductivity ($\times 10^{-4}$ cal/cm²/cm/°C/sec) 0°C	0.091
Latent heat of fusion (cal/g)	16.2
Specific heat (cal/g/°C)	0.107
Solubility (100 ml H_2O) 50°C	52 ml

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1st ionization potential (eV)	11.84
Ionic radius (angstroms)	1.96 (Br^{+1})
Cross section (barns)	6.7
Vapor pressure (°C)	9.3
Crystal structure (orthorhombic—normal)	(100) a-pinacoid
Color (liquid/solid)	Dark red-brown
Cleavage (basal — solid)	(001)

BROMINE, Br

General: Bromine and mercury are the only two elements that are liquid at standard temperature and pressure (22.2°C and 76 mmHg). Mercury is found as a solid, native element in nature, but bromine is not, being primarily extracted from sea water and from the soil of alluvial plains in the form of an alkaline halide. It is a dark red-brown liquid with an offensive odor and a member of the halogen group of elements: fluorine and chlorine are gases; bromine is a liquid; and iodine, a solid. It is more reactive than iodine but less reactive than either chlorine or fluorine, with fluorine being the most reactive element known. All of the halogens form diatomic molecules as F_2, Cl_2, Br_2, and I_2, even though they are occasionally shown in the literature as monatomic, e.g., Br, Cl, etc.

The most important use of bromine is as ethylene dibromide, $C_2H_4Br_2$, which is added to leaded ethyl gasoline to remove by-products of tetraethyl lead. It also is used for medicinal purposes, KBr or NaBr as sedatives; in silver emulsions (AgBr) for photography; and in the manufacture of "tear gas" as bromine-acetone. It is poisonous if ingested and can produce sores on the skin which are difficult to heal. The vapors can be a severe irritant to eyes, nose, and throat.

As a low percentage mixture in methyl alcohol (up to 3%), it is a major polish and removal etch for many metals and metallic compounds, and can be a preferential etchant above 3%, used to about 20% in MeOH. These Br_2:MeOH mixtures have acquired the acronym BRM. The exact bromine concentration that alters from polish to preferential can vary to some degree by method of application, such that it is not accurately defined. BRM etchants are often used on semiconductor wafer surfaces after cutting and prior to final cleaning as a chemical/mechanical (chem/mech) lapping solution to remove residual subsurface damage remaining after cutting and mechanical lap/polish with abrasives. The solutions also are used for general removal, as a jet for thinning, etc. In all cases, when used as an etch solution, bromine can be replaced by iodine with similar results and, as bromine, is so volatile, iodine is often preferred when solutions are to be used above room temperature. Bromine has been mixed with other alcohols or solvents, and shows similar results as with BRM solutions.

It is used as an additive to other etch solutions, such as Camp #4, now known as CP4. The original CP4 contained 0.6 ml Br_2 and, when used without bromine, is called CP4A. There are several CP4 modifications where the Br_2 has been replaced by I_2, $Cu(NO_2)_3$, $AgNO_3$, etc.

Technical Application: Bromine is used in etching solutions as described in the preceding General section. It has been solidified and studied by freezing.

Etching: Soluble in MeOH.

The following is a selected list of BRM solutions as applied to several semiconductor materials, metals and other compounds. Additional solutions are shown under the individual elements/compounds in this Etchant Section:

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Formula	Material	Use	Ref.
0.5% Br_2:MeOH	AlAs, GaAs	Polish	AS-0001
10 ml P Etch:10 ml Br_2 "PBr Etch" (P: 10 ml HCl:10 ml HNO_3:5 ml H_2O)	CdTe	Preferential	CDTE-0006a
0.05% Br_2:MeOH	GaAs	Polish	GAS-0006
1% Br_2:MeOH	GaAs	Polish	GAS-0003a
1.5% Br_2:MeOH	GaAs	Polish/thinning	GAS-0004b
5% Br_2:MeOH	GaAs	Selective	GAS-0009
1% Br_2:EOH	GaAs	Preferential	GAS-0013
2% Br_2:MeOH	GaAs	Oxide removal	GAS-0132
20% Br_2:MeOH	GaP	Polish	GAP-0007
Br_2, conc.	GaP	Preferential	GAP-0010
HBr, conc.	GGG	Preferential	GGG-0001b
250 ml 30% KOH:25 ml Br_2	Gs, Si	Preferential	GE-0012b
30HF:50HNO_3:30HAc:0.6Br_2 "CP4"	Ge, Si, InAs, InSb	Polish/preferential	GE-0065c
1% Br_2:MeOH	CdInTe	Polish/clean	CIT-0001
1% Br_2:MeOH	CdP_2	Selective	CDP-0001
4% Br_2:MeOH	CdSe	Polish (0001)	CDSE-0002
1% Br_2:MeOH:x1MHCl	CdSe	Clean	CDSE-0004
10% Br_2:MeOH	CdTe	Polish	CDTE-0010
2% Br_2:MeOH	CdTe	Polish/removal	CDTE-0009
2% Br_2:Glycol	CdTe	Smut removal (Te)	CDTE-0011
1 1 *M* $FeCl_3$:1 12 *M* HCl:1 1.25 *M* HBr	Cu	Dislocation	CU-0015
6K_2SO_4:1H_2O_2:1H_2O then 1% Br_2:MeOH	$CuInSe_2$	Polish/clean	CUIS-0003
2% Br_2:MeOH	GaSb	Polish (100)	GASB-0004c
1Br_2:10MeOH	GaSb	Preferential	GASB-0008a
5—10% Br_2:MeOH	InAs	Dislocation	INAS-0005
0.5% Br_2:MeOH	InP	Step-etch (100)	INP-0007
9 *N* HBr (48%)	InP	Preferential	INP-0026
5HF:1Br_2	InP	Preferential	INP-0017b
2$H_3PO_4$1Br_2	InP	Preferential	INP-0038
2H_2SO_4:1HBr (47%)	InP	Dislocation	INP-0051
xBr_2:MeOH	Fe	Oxide removal	FE-0100
1HBr:1H_2O + Cr, pcs	SnO_2	Removal (thin film)	SNO-0002
$CBrF_2$, ionized	W	RF plasma	W-0011
xBr_2:MeOH	ZnSe	Polish/removal	ZNSE-0001
xBr_2:CS_2	ZnSe	Polish/removal	ZNSE-0001

BROMINE ETCHANTS

BR-0001
ETCH NAME: Methyl alcohol
TYPE: Alcohol, preferential
TIME:
TEMP: 0°C to RT
COMPOSITION:
x .... CH_3OH (MeOH)
DISCUSSION:
Br_2, specimens solidified by freezing the liquid to 0°C with liquid nitrogen, LN_2. A

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drop of MeOH on the surface was used to develop etch figures and crystalline structure of the solidified mass. Used in a general etching study of bromine vs. iodine as applied on (111) silicon wafers. A piece of solid bromine was placed on wafer surfaces and allowed to liquefy. A similar piece of iodine was used with just sufficient heating to liquefy, and surface artifacts were compared.

REF: Walker, P & Waters, W P — personal application, 1957

BRONZE, Cu:Sn

General: Bronze does not occur in nature as a specific single crystal, although native copper often contains small amounts of iron, silver, bismuth, lead, antimony, and tin. It was probably the natural occurrence of a copper-tin alloy that led to the discovery and development of bronze as pure copper was extensively mined throughout southern Europe and the Near East in ancient times, e.g., 5000 B.C. or earlier. Pure copper is soft and malleable and the two copper carbonate minerals, which are usually associated with copper vein deposits, are easily recognized by their brilliant colors: azurite (deep blue) and malachite (bright green); both are easily reduced to pure copper at temperatures between 200 to 250°C. Those two minerals also have been in use as semi-precious gem stones since ancient times and are still used in jewelry.

Although the use of gold and copper pre-dates the use of bronze, it was the development of bronze that led to the "Bronze Age" and the beginning of man's metal culture. Pure copper is too soft, but bronze can be cast, shaped, and honed to a fine cutting edge far superior to that of flint or bone, as the latter fracture, chip, and sliver easily. Although bronze is brittle in comparison to irons and steels, it is highly resistant to weathering and corrosion. Bronze artifacts have been discovered in archaeological digs, pre-dating the Christian era, and are still usable as weapons or tools with little wear or alteration.

Today there are many types of bronze with specific names, such as aluminum-bronze; manganin; sea water bronze; phosphor-bronze; bearing bronze, and others. With the development of brass, Cu:Zn, which is not brittle like bronze, and the addition of other metal elements in the two mixtures, the terms brass and bronze have become synonymous in many instances as they are mixtures of Cu:Zn:Sn plus other metal constituents.

Bronze still has many industrial uses, such as the sea water bronze for its resistance to salt water and phosphor-bronze which, when used as thin sheet, has excellent spring characteristics. Because of the high copper content, both bronze and brass are excellent electrical and heat conductors — copper telephone wires are an alloy rather than pure copper, and bronze/brass tools are used in working with magnetic materials as they are nonmagnetic and unaffected by the magnetic flux. Cryogenic liquid piping and fittings are made of bronze as the material structure is tough, and unaffected by continual severe changes in temperature, such as from RT down to −196°C (LN_2), and back up to 100°C on a hot day.

Technical Application: Bronze is not used in direct Solid State material fabrication, although phosphor-bronze spring clips are widely used to hold semiconductor wafers in position during metallization in vacuum systems, or as holders in device test fixtures. Bronze/brass parts also are used as heating or cooling blanks; as abrasive lapping platens; as electrical probes; as an electronic assembly packaging material; as electrical pin contacts; inking and evaporation masks; and electrical test blocks.

There is reference to brass having been grown and studied as a single crystal, but we have no similar reference for bronze, although it is probable that it has been so grown and studied.

Etching: HNO_3, H_2SO_4, and acid mixtures.

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BRONZE ETCHANTS

BRO-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
5 .... HCl
100 .... HNO_3
DISCUSSION:
Cu:Sn(30%), standard bronze specimens. Solution is a general etch for bronze. (*Note:* This is a dilute form of aqua regia and can be used on both bronzes and brasses.)
REF: Oberg, E & Jones, F D — *Machinery Handbook*, 4th ed, The Industrial Press, New York, 1951
TIME:
TEMP:

BRO-0002a
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
5 .... HCl
100 .... HNO_3
150 .... H_2O
DISCUSSION:
Bronze and brass cryogenic trailer piping. Solution used as a general surface cleaner for removal of dirt and grease from these parts. After etching, heavy water wash and pat dry with toweling. Where severe corrosion was present, parts were lightly scrubbed in solution with a stainless steel brush.
REF: Campos, R & Walker, P — AF Contract to Clean Cryogenic Trailers, 1961
TIME: Variable
TEMP: RT

BRO-0002b
ETCH NAME: Sulfuric acid
TYPE: Acid, cleaning
COMPOSITION:
1 .... H_2SO_4
10 .... H_2O
DISCUSSION:
Bronze and brass cryogenic trailer piping and parts. Solution used as a corrosion removal etch to include light scrubbing with a stainless steel brush. Water wash after etching and pat dry with toweling.
REF: Ibid.
TIME: 1—10 min
TEMP: RT

BRO-0003
ETCH NAME: Ferric chloride
TYPE: Salt, macroetch
COMPOSITION:
x .... 5% $FeCl_3$
x .... H_2O
DISCUSSION:
Bronze artifact. Solution used as a macro-etch on bronze arrowheads found at the biblical Migdol Fort, dated in the 6th century A.D. The etch developed a dendritic cast structure. (*Note:* Various concentrations of ferric chloride are used in structure development etching of both bronzes and brasses.)
REF: Peiles, J et al — *Sci Am*, 244,61(August 1976)
TIME:
TEMP:

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BRO-0004a
ETCH NAME:
TYPE: Electrolytic, macroetch
COMPOSITION:
1 g .... CrO_3
90 ml .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 1.5—2 VDC
DISCUSSION:
88—96Cu:2.3—10.5Al:xFe:xSn, as aluminum bronze. Solution used to develop structure in this material.
REF: *A/B Met Dig*, 21(22),23(1983) — Buehler Ltd

BRO-0005
ETCH NAME:
TYPE: Salt, anisotropic
COMPOSITION:
x .... *$FeCl_3$

*1.4 g/cm^3

TIME: 15, 30, or 90 min
TEMP: RT

DISCUSSION:
Bronze:Mg, as magnesium bronze. Solution was used in a centrifuge to produce a positive (+) and negative (−) gravity during the etching period. Used to form pits and via-holes in both bronze and gallium arsenide specimen sheets or wafers.
REF: Kuiken, N K & Tilburg, R P — *J Electrochem Soc*, 130,1722(1983)

BRO-0004b
ETCH NAME:
TYPE: Acid, microstructure
COMPOSITION:
x .... NH_4OH
x .... H_2O_2
TIME:
TEMP:
DISCUSSION:
Bronze specimens. Solution used to develop microstructure. Also used on copper.
REF: Ibid.

BRO-0004c
ETCH NAME: Chromic acid
TYPE: Electrolytic, preferential
COMPOSITION:
x .... 1% CrO_3
TIME:
TEMP:
ANODE: Bronze
CATHODE:
POWER:
DISCUSSION:
Red brass specimens. Solution used to develop structure in a cast alloy that was furnace cooled.
REF: Ibid.

BRO-0004d
ETCH NAME: Chromic acid
TYPE: Acid, preferential
COMPOSITION:
1 g .... CrO_3
99 ml .... H_2O
TIME: Swab
TEMP: RT

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DISCUSSION:

Bronze, as aluminum bronze (See BRO-0004a). Solution used as a wet chemical etch (WCE) rather than electrolytic. Apply with a swab wetted in solution to specimen surfaces to develop structure.

REF: Ibid.

BRO-0004e

ETCH NAME: ALN3-1 TIME: Dip

TYPE: Acid, micro-, macroetch TEMP: RT

COMPOSITION:

5 ml .... HNO_3
5 ml .... H_2SO_4
4 g .... CrO_3
1 g .... NH_4Cl
90 ml .... H_2O

DISCUSSION:

Red brass specimens. Solution used to develop microstructure.

REF: Ibid.

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PHYSICAL PROPERTIES OF CADMIUM, Cd

Classification	Transition metal
Atomic number	48
Atomic weight	112.4
Melting point (°C)	320.9
Boiling point (°C)	765
Density (g/cm^3)	8.65
Thermal conductance (cal/sec)(cm^2)(°C/cm) 20°C	0.22
Specific heat (cal/g) 20°C	0.055
Latent heat of vaporization (cal/g)	286.4
Atomic volume (W/D)	13.1
1st ionization energy (K-cal/g-mole)	207
1st ionization potential (eV)	8.99
Electronegativity (Pauling's)	1.7
Covalent radius (angstroms)	1.48
Ionic radius (angstroms)	0.97 (Cd^{+2})
Linear coefficient of thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	29.8
Electrical resistivity (micro-ohms-cm) 20°C	6.83
Electron work function (eV)	4.07
Vapor pressure (mmHg in °C)	611
Cross section (barns)	2450
Hardness (Mohs — scratch)	2
Crystal structure (hexagonal — normal) alpha	($10\bar{1}0$) prism, hcp
(isometric — normal) beta	(100) cube
Color (solid)	White-silver
Cleavage (basal/cubic)	(0001)/(001)

CADMIUM, Cd

General: Does not occur as a native element. There are three cadmium minerals of which only greenockite, CdS, is of importance as an ore, though cadmium occurs as a trace constituent in several minerals. Greenockite does occur as single crystals, but is most common as a drusy coating associated with zinc deposits, e.g., sphalerite, ZnS. It is a by-product of zinc ore refining, volatilizing first and collected as the brown oxide. As the pure metal it is bluish-silver white, very soft, with a relatively low melting point and, like silver, tarnishes in air (presence of sulfur). When heated in air, it burns to the oxide.

It has industrial uses similar to those of zinc and, as a surface plating, is more corrosion resistant than zinc to salt (NaCl) spray, though it is slowly attacked by salts in a natural sea water environment, and several cadmium compounds are toxic. It is widely used in the plating of bolts and screws as, due in part to its softness, it has excellent low friction binding ability. It is a constituent in many low melting point alloys, and used as a bearing alloy for its low coefficient of friction and resistance to fatigue. It is in the standard cells used for EMF measurement, in vehicle batteries with zinc, and as the "cadmium battery" for electronics, such as transistor radios and hearing aids. As the sulfide, CdS, it is a bright yellow pigment for glass, enamel, and paint.

Technical Application: In Solid State processing, it is a p-type dopant in several compound semiconductors. Like indium, it is used alone or as a constituent in low melting solders for device package assemblies, though it is not recommended for space hardware. As the pure metal pre-form, rings or flats, it is used as a metal crush-seal in vacuum equipment, such as in cryo-pumps.

It is a metal element in a number of binary and trinary compound semiconductors such

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as cadmium sulfide, CdS, cadmium selenide, CdSe, and cadmium telluride, CdTe, as well as ZnCdS, CdHgTe, and trinary materials. It also has been grown and studied as a single crystal for general morphology, defects, and superconductivity.

Etching: HCl, HNO_3, mixed acids, and halogens.

CADMIUM ETCHANTS

CD-0001a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
2 .... CH_3COOH (HAc)
2 .... H_2O_2
TIME:
TEMP:
DISCUSSION:

Cd, (111) and (100) single crystal wafers used in a morphological study. Wafers were etch polished in the solution shown.

REF: Gilman, J J & Johnston, W S — *Dislocations in Crystals*, John Wiley & Sons, New York, 1956

CD-0015a: DeCarlo, V J — *Met Abstr* 8,94(1958)

Cd specimens. Development work on polishing of both pure cadmium and zinc.

CD-0015b: DeCarlo, V J & Gilman, J J — *Trans Am Inst Min Met Eng*, 206,511(1956)

Cd specimens. Similar work to that of CD-0015a.

CD-0002
ETCH NAME: Neon
TYPE: Ionized gas, preferential
COMPOSITION:
x .... Ne^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:

Cd, single crystal specimens. Neon ion bombardment used to develop structure and orientation figures. Other metals studied were Al, Bi, Co, Mg, Cu, Sn, and Zn.

REF: Yurasova, V E — *Kristallografiya*, 2,1770(1957)

CD-0003a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
(1) 75 ml .... HNO_3, fuming
25 ml .... H_2O
(2) 10 ml .... HNO_3, fuming
70 ml .... HAc
TIME: 5—10 sec, then 30—60 sec
TEMP: 20°C RT
DISCUSSION:

Cd, specimens. Use etch (1) to polish and follow with (2) as a wash; rinse in DI water and blow dry with nitrogen.

REF: Tegart, W J McG — *The Electrolytic & Chemical Etching of Metals*, Pergamon Press, London, 1956

CD-0007: McAfee, J — *Aust Eng Yearbook*, (1944)

Cd specimens. Solution used to polish cadmium. Author refers to using a dip etching technique.

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CD-0004
ETCH NAME: Silicone
TYPE: Plastic, forming
COMPOSITION:
x .... silicone
TIME:
TEMP: 120°C
DISCUSSION:
Cd spheres from 44 to 1200 μm diameter formed by whipping the molten metal in a warm silicone oil bath. A study of size effects of material on superconductivity.
REF: Hein, R A & Steel, M V — *Phys Rev*, 105,877(1957)

CD-0005
ETCH NAME: Tri-iodide etch
TYPE: Halogen, removal/polish
COMPOSITION:
4 g .... I_2
20 g .... KI
80 ml .... H_2O
20 ml .... MeOH
TIME: Variable
TEMP: 40—80°C
DISCUSSION:
Cd specimens and alloys. Solution used to clean cadmium pellets and slugs prior to use in evaporation, follow with MeOH rinse, DI water rinse, and N_2 blow-dry. Also used to remove cadmium alloys or to clean surfaces after alloying.
REF: Fahr, F — personal communication, 1978

CD-0006
ETCH NAME: Ammonium hydroxide
TYPE: Alkali, cleaning
COMPOSITION:
x .... NH_4OH
TIME: 10—15 min
TEMP: RT
DISCUSSION:
Cd powder used for epitaxy growth of CdSe and $(Cd,Se)1_{-x}Zn_x$. Material was cleaned as follows: (1) soak in solution shown, (2) rinse in DI water, and (3) vacuum dry at 50°C. Once cleaned, the material can be stored for up to 2 weeks without requiring re-cleaning surfaces.
REF: Kim, S U & Parks, M J — *Jpn J Appl Phys*, 223,1070(1984)

CD-0008
ETCH NAME:
TYPE: Mechanical, defect
COMPOSITION:
x .... stress
TIME:
TEMP:
DISCUSSION:
Cd dislocation free single crystals used in a study of non-basal glide of (1011) oriented wafers in the $\langle 12\bar{1}0\rangle$ direction.
REF: Price, P B — *J Appl Phys*, 32,746(1961)
CD-0009: Price, P B — *J Appl Phys*, 32,1750(1961)
Cd, dislocation free single crystals used in a study of non-basal glide $(10\bar{2}2)$ of $(10\bar{2}2)$ oriented wafers in the $\langle 11\bar{2}3\rangle$ direction.
CD-0010: Coleman, R V & Sears, O W — *Acta Metall*, 5,131(1957)
Cd, single crystals. Describes a method of growing crystals.

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CD-0011
ETCH NAME: Hydrochloric acid
TYPE: Acid, thinning
TIME:
TEMP:
COMPOSITION:
x .... HCl
x .... H_2O
DISCUSSION:
Cd specimens used in a study of the de-Hass-Van-Allen effect in cadmium at high magnetic fields. Solution used to reduce thickness of specimens.
REF: Grasse, A D C — *Phil Mag*, 17,847(1964)
CD-0012a: Kratechuil, P & Hemela, J — *Acta Metall*, 14,1757(1966)
Cd single crystal specimens used in a study of dislocations developed in deformed crystals. After annealing to remove oxide, crystals were etch cleaned/polished in HCl at RT, 1 min before preferential etching.

CD-0012b
ETCH NAME:
TYPE: Acid, dislocation
TIME: 5 min
TEMP: RT
COMPOSITION:
160 g .... CrO_3
20 g .... Na_2SO_4
500 ml .... H_2O
DISCUSSION:
Cd single crystals subjected to deformation used in a study of dislocations developed from strain. After etching in solution shown for 5 min, rinse in DI water. Solution used to develop dislocations.
REF: Ibid.

CD-0003b
ETCH NAME: Tri-iodide
TYPE: Halogen, polish
TIME:
TEMP: RT to hot
COMPOSITION:
1 g .... I_2
3 g .... KI
10 ml .... H_2O
DISCUSSION:
Cd, as single crystals and alloy specimens. Solution used for general removal and polishing. After etching, rinse in MeOH. See CD-0005.
REF: Ibid.

CD-0013
ETCH NAME:
TYPE: Mechanical, orientation
TIME:
TEMP: RT
COMPOSITION:
x .... indentation
DISCUSSION:
Cd single crystal wafer used in a study of lattice and grain boundary diffusion. Indent surfaces with a diamond point, and direction of cracks developed can be used to crystallographically orient the material.
REF: Wajda, E S — *Acta Metall*, 3,39(1955)
CD-0014: Lang, L G & Hien, N C — *Phys Rev*, 110,1002(1958)
Cd single crystal wafers cut from ingots by an acid saw technique.

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CD-0015
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
COMPOSITION:
x .... TCE
TIME: 1—2 min
TEMP: Hot
DISCUSSION:
Cd cut pre-forms and alloy wire. Parts were vapor degreased in TCE before use in alloying microelectronic devices and package assemblies. After degreasing, parts were stored in a nitrogen dry box until ready for use.
REF: Marich, L A et al — personal communication, 1983

PHYSICAL PROPERTIES OF CADMIUM ANTIMONIDE, CdSb

Classification	Antimonide
Atomic numbers	48 & 51
Atomic weight	234.17
Melting point (°C)	1000
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Metallic grey
Cleavage (cubic)	(001)

CADMIUM ANTIMONIDE, CdSb

General: Does not occur as a natural metallic compound, although there is native antimony, and half a dozen minerals as arsenides, sulfides, not including several antimonates, etc. The most important mineral is stibnite, Sb_2S_3, as an ore which may contain both gold and silver.

There is no industrial application at present other than being evaluated as a compound semiconductor.

Technical Application: Cadmium antimonide is a II—V compound semiconductor and has been evaluated for characterization of its physical and semiconducting properties.

Etching: HCl, other single acids, mixed acids, or halogens.

CADMIUM ANTIMONIDE ETCHANTS

CDSB-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, polish
COMPOSITION:
x .... HCl, conc.
TIME:
TEMP:
DISCUSSION:
CdSb, (100) wafers used in a study of indium doping acting as a donor impurity. With increase of indium, diamagnetism becomes temperature dependent. Develops two types of holes (In and Sb) as local donor sites with 3 Sb sp-hybrid bonds and mixed conduction.
REF: Pilat, I M — *Phys Rev*, 110,354(1959)

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PHYSICAL PROPERTIES OF CADMIUM ARSENIDE, Cd_3As_2

Classification	Arsenide
Atomic numbers	48 & 33
Atomic weight	486.05
Melting point (°C)	>1000
Boiling point (°C)	
Density (g/cm³)	~6
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube
(hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Greyish
Cleavage (basal)	(0001)

CADMIUM ARSENIDE, Cd_3As_2

General: Does not occur in nature as a metallic compound and, at present has no industrial application other than as a possible semiconductor compound.

Technical Application: Cadmium arsenide is a II—V compound semiconductor and has been evaluated for its physical and semiconducting characteristics alone and as a mixed single crystal of Cd_3As_2:Zn_3As_2.

Etching: HCl, other acids, and mixed acids.

CADMIUM ARSENIDE ETCHANTS

CDAS-0001
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

Cd_3As_2 single crystal specimens and Cd_3As_2:Zn_3As_2 as mixed single crystals used in a study of the anomalous thermal conductivity of these materials. Solution shown will polish both materials.

REF: Spitzer, D P et al — *J Appl Phys*, 37,3795(1966)

PHYSICAL PROPERTIES OF CADMIUM FLUORIDE, CdF_2

Classification	Fluoride
Atomic numbers	48 & 9
Atomic weight	150.4
Melting point (°C)	1100
Boiling point (°C)	1758
Density (g/cm³)	6.64
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal) alpha	(100) cube, bcc
(isometric — tetrahedral) beta	(111) tetrahedron
Color (solid)	White
Cleavage (cubic/octahedral)	(001)/(111)

CADMIUM FLUORIDE, CdF_2

General: Does not occur in nature as a compound due to its solubility in water. The

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alpha form is body-centered cubic (bcc), and the normal room temperature structure; whereas the beta form is the high temperature structure. Atomic structure is similar to fluorite, CaF_2, with a unit cell of eight fluorine atoms surrounding a central Cd or Ca atom (bcc). The main source of cadmium as the pure metal comes from sphalerite, ZnS, as a constituent trace element in the ore (about 0.2%), and there are three minor cadmium minerals: as a sulfide, oxide, and carbonate.

There has been little use as the fluoride in industry to date, but as a sulfide (CdS) it is one of the best and most stable yellow pigments used in paints, and for the coloring of glass. Cadmium metals as an alloy with bismuth are low temperature alloys.

Technical Application: No major use in Solid State processing to date, although it has been grown and studied as a single crystal both for general morphology and, when doped, for its semiconducting properties. As a CVD thin film it has been evaluated as a dielectric, as it has optical properties similar to fluorite, but is less used due to water solubility. Thin films also have been used for cadmium drive-in doping of semiconductor materials.

Etching: Soluble in water and acids.

CADMIUM FLUORIDE ETCHANTS

CDF-0001a
ETCH NAME: Water
TYPE: Acid, polish/removal
TIME:
TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:

CdF_2 specimens. As the material is slightly soluble in cold water, water can be used to polish surfaces. (*Note:* Mix with alcohol to reduce etch rate.)
REF: Hodgman, C D et al — *Handbook of Chemistry and Physics,* 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 356
CDF-0004: Sullivan, P W — *J Vac Sci Technol,* B2,202(1984)

CdF_2 as CVD deposited thin films on GaAs wafers used in a study of dielectric coatings. After photo resist patterning, film was E-beam annealed (EBA). Fluorine desorbs during annealing, and the remaining CdF_x can be removed by water washing. Also studied SrF_2 (SRF-0001).

CDF-0001b
ETCH NAME: Hydrofluoric acid
TYPE: Acid, polish/removal
TIME:
TEMP: RT
COMPOSITION:
(1) x .... HF, conc.
(2) x .... HF
x .... H_2O
(3) x .... HF
x .... MeOH/EOH
DISCUSSION:

CdF_2 specimens. HF solutions can be used to polish surfaces, or for general removal. Solution (3) is best for rate control, as CdF_2 is insoluble in alcohols.
REF: Ibid.

CDF-0003
ETCH NAME: Heat
TYPE: Thermal, annealing
TIME:
TEMP: 600—800°C
COMPOSITION:
x .... heat
DISCUSSION:

CdF_2 single crystal ingots, as both doped and undoped materials. Used in a study of

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expansion coefficients and semiconducting properties. During annealing, if oxygen is present a brownish CdO_x film will form on the ingot surface.
REF: Acuna, L A & Fortiz, M — *J Phys Chem Solids*, 46,401(1985)

CADMIUM INDIUM SELENIDE, $CdIn_2Se_4$

General: Does not occur as a natural compound. See cadmium selenide for additional general discussion.

Technical Application: Cadmium indium selenide is a ternary semiconductor compound with polar characteristics similar to binary compounds. It is a ternary chalcogenide under development and application for its semiconductor capabilities both as a bulk single crystal element as well as an amorphous glassy material. This compound, and other chalcogenides, have been used to fabricate circuits as an alterable amorphous-semiconductor memory element for computer applications.

Etching: Aqua regia and additive mixtures of aqua regia solutions.

CADMIUM INDIUM SELINIDE ETCHANTS

CDISE-0001a
ETCH NAME: Aqua regia, variety — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
4 .... HCl
1 .... HNO_3
DISCUSSION:
$CdIn_2Se_4$ single crystal specimens used to fabricate photoelectrochemical cells from ternary chalcogenides. First, mechanically polish with 0.5 μm alumina. Etch in solution shown; follow with "poly sulfide". (See CDISE-0001b) at RT, seconds, then rinse in 10% KCN.
REF: Tennes, R et al — *J Electrochem Soc*, 129,1506(1982)

CDISE-0001b
ETCH NAME: — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
1 .... *aqua regia
10 .... 2 *M* KOH + S/Na_2S

*3HCl:1HNO_3

DISCUSSION:
$CdIn_2Se_4$ single crystal specimens. Solutions of aqua regia diluted with KOH, S, or Na_2S used as alternate polishing solutions. (See CDISE-0001a)
REF: Ibid.

CDISE-0002
ETCH NAME: — TIME:
TYPE: — TEMP:
COMPOSITION:

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DISCUSSION:

Chalcogenides used as amorphous-semiconductor elements for alterable memory elements in computer applications. (*Note:* Excellent discussion of this subject.)

REF: Adler, D — Amorphous Semiconductor Devices, *Sci Am*, December 1979

CADMIUM INDIUM TELLURIDE, $CdIn_2Te_4$

General: Does not occur in nature as a native compound, although there are a number of selenide and telluride metallic compounds, but not with cadmium. There are no industrial applications, other than as a compound semiconductor.

Technical Application: The material is a II—III—VI trinary compound semiconductor and is under development as a possible laser diode or for photovoltaic devices.

Etching: Soluble in mixed acids of HCl:HNO_3 or HF:HNO_3 types, and halogens.

CADMIUM INDIUM TELLURIDE ETCHANTS

CDITE-0001
ETCH NAME: BRM
TYPE: Halogen, polish
TIME: 10—30 sec
TEMP: RT
COMPOSITION:

x .... 1% Br_2
x .... MeOH

DISCUSSION:

$CdIn_2Te_4$ as cut wafers from both p- and n-type doped polycrystalline ingots. Specimens were used in a study of general morphology. Surfaces were chem/mech polished in solution shown to remove native oxide, lap damage, and contamination. Band gap: 0.88 eV. Dielectric constant: 200. Space group crystal structure: S_4.

REF: Ou, S S et al — *J Appl Phys*, 57,354(1985)

PHYSICAL PROPERTIES OF CADMIUM IODIDE, CdI_2

Classification	Iodide
Atomic numbers	48 & 53
Atomic weight	366.25
Melting point (°C)	388
Boiling point (°C)	713
Density (g/cm³)	5.67
Hardness (Mohs — scratch)	2—3
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Brownish
Cleavage (basal — perfect)	(0001)

CADMIUM IODIDE, CdI_2

General: Does not occur as a natural compound as it is soluble in water. The mineral greenockite, CdS, is the most stable compound and is found in association with sphalerite, ZnS. Cadmium is a minor constituent in the zinc sulfide, and is collected during refining of the ore. Heated in air pure cadmium metal will burn to a brown powder of cadmium oxide, CdO.

There are no industrial applications for the iodide, though the sulfide as "cadmium yellow" is one of the most stable pigments in paints and as a glass coloring agent.

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Technical Application: Cadmium iodide is a II—VIII compound semiconductor and under evaluation. It is a layered structure similar to CdS and ZrS_2 with distinctive basal (0001) cleavage.

It has been grown as a single crystal by zone refining under argon for general study and semiconductor characterization. Processing is done under argon as wafers react to moisture in the air.

Etching: Easily soluble in hot and cold water and most acids.

CADMIUM IODIDE ETCHANTS

CDI-0001
ETCH NAME: Water
TYPE: Acid, polish
COMPOSITION:
x .... H_2O
DISCUSSION:

TIME:
TEMP:

CdI_2, (0001) wafers cleaved from an ingot grown by zone refining under argon. Water can be used to polish surfaces. Material is under general study.
REF: Unnilrishnan, N V et al — *J Phys Chem Solids*, 45,1205(1984)

PHYSICAL PROPERTIES OF CADMIUM OXIDE, CdO

Classification	Oxide
Atomic numbers	48 & 8
Atomic weight	124.41
Melting point (°C)	900 del
Boiling point (°C)	
Density (g/cm^3)	8.192
Hardness (Mohs — scratch)	4—5
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Brown/black
Cleavage (cubic)	(001)

CADMIUM OXIDE, CdO

General: Occurs as a natural compound and called cadmium oxide, CdO. It has been observed as minute octahedrons and as a black, brilliant coating on smithsonite, $ZnCO_3$ (calamine), which contains trace cadmium and indium. Cadmium metal is easily converted to a brown oxide by heating in air to about 350°C. There is no industrial application for the oxide, although cadmium metal is an alloy in steels, and has wide use in low temperature solders.

Technical Application: The oxide has had no use in Solid State processing to date, although there are a number of compound semiconductors containing cadmium as selenides and tellurides. The oxide has been studied for general morphology as a single crystal, but is considered an unwanted compound in processing cadmium-containing compound semiconductors.

Etching: HCl and NH_4OH easily soluble.

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CADMIUM OXIDE ETCHANTS

CDO-0001
ETCH NAME: Ammonium hydroxide
TYPE: Acid, cleaning
COMPOSITION:
x .... NH_4OH
TIME: 5—15 sec
TEMP: RT
DISCUSSION:
CdO as a surface oxide on cadmium pellets used for metal evaporation and epitaxy, or as cadmium alloys used for soldering. Solution used to clean surfaces.
REF: Fahr, F — personal communication, 1978

CD0-0002
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
COMPOSITION:
x .... HCl, conc.
TIME:
TEMP:
DISCUSSION:
CdO native oxide on cadmium used for epitaxy growth of HgCdTe films in a study of chemical etching and oxidation. Remove cadmium oxides with HCl.
REF: Aspenes, D E & Arwin, H — *J Vac Sci Technol,* A(2),1309(1984)

PHYSICAL PROPERTIES OF CADMIUM PHOSPHIDE, CdP_2

Classification	Phosphide
Atomic numbers	48 & 15
Atomic weight	192.37
Melting point (°C)	>1000
Boiling point (°C)	
Density (g/cm³)	4.5
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Grey-black
Cleavage (octahedral)	(111)

CADMIUM PHOSPHIDE, CdP_2

General: Does not occur as a natural mineral, although there are many phosphates with a PO_4^- radical. The artificial compound has been used industrially as an additive in making steels, but has no other major applications.

Technical Application: The compound is under evaluation in Solid State as a surface thin film deposited on single crystal indium phosphide, InP, for possible photo diode applications.

CADMIUM PHOSPHIDE ETCHANTS

CDP-0001
ETCH NAME: BRM
TYPE: Halogen, removal
COMPOSITION:
x .... 1% Br_2
x .... MeOH
TIME:
TEMP: RT

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DISCUSSION:

CdP_2 deposited as a thin film on InP, (100) wafers as a photo diode, and studied for noise generation. Solution shown used to etch-form mesa structures in the thin film.
REF: Susa, N — *Appl Phys Lett,* 39,168(1981)

PHYSICAL PROPERTIES OF CADMIUM SELENIDE, CdSe

Classification	Selenide
Atomic numbers	48 & 34
Atomic weight	191.3
Melting point (°C)	~1000
Boiling point (°C)	
Density (g/cm^3)	~6
Band gap (eV)	1.8
Hardness (Mohs — scratch)	5—6
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Yellowish
Cleavage (basal — distinct)	(0001)

CADMIUM SELENIDE, CdSe

General: Does not occur as a natural mineral although there are several selenium metallic compounds, such as aguilarite, $Ag_2(S,Se)$; berzelianite, Cu_2Se; tiemannite, HgSe. There are no industrial applications other than as a compound semiconductor.

Technical Application: Cadmium selenide is a II—V compound semiconductor with hexagonal structure. It is a polar compound with regard to prism, $(10\bar{1}0)$ faces, and has distinctive basal (0001) cleavage. Most wafer processing is done with the (0001) surface, though second order prism faces, $(11\bar{2}0)$ have been used.

It has been grown as a single crystal ingot by the Horizontal Bridgman (HB), Czochralski (CZ), and Float Zone (FZ) methods. Epitaxy growth on substrates is by Vapor Transport (VT), and Vapor Phase Epitaxy (VPE). Also developed as the trinary compound: $CdS_{1-x}Se_x$.

A variety of devices have been fabricated from both compounds, such as photoconductors, solar cells, piezoelectric devices, photoconductors, and laser diodes. See CdS for other piezoelectric applications.

Etching: Aqua regia and its varieties and in mixed acids with HNO_3. Halogens.

CADMIUM SELENIDE ETCHANTS

CDSE-0001a
ETCH NAME: Aqua regia, variety — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
1 .... HCl
3 .... HNO_3
DISCUSSION:

CdSe, (0001) wafers used in a study of etch pit and structure development of the material. Authors say that both (0001)A and $(000\bar{1})$B surfaces develop similar etch figures and a heavy selenium film remains after etching. The Se film can be removed with H_2SO_4. (*Note:* This is an extensive article on etching of II—IV compound semiconductors.)
REF: Warekois, E P et al — *J Appl Phys,* 33,690(1962)

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CDSE-0002a
ETCH NAME: BRM — TIME: 5 sec
TYPE: Halogen, cleaning — TEMP: RT
COMPOSITION:
x .... 4% Br_2
x .... MeOH
DISCUSSION:
CdSe, (0001), $(10\bar{1}0)$, and $(11\bar{2}0)$ used in a study of surface etching and morphology on the stability of CdSe:S_x photoelectrochemical cells. Dip in BRM solution; rinse in polysulfide solution, then DI H_2O, and repeat BRM dip. This was one of several etch treatments evaluated. This was treatment #1.
REF: Hodes, O & Manassen, J et al — *J Electrochem Soc*, 128,2325(1981)

CDSE-0002b
ETCH NAME: Aqua regia — TIME: 15 sec
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
CdSe, (0001) and other orientations (CDSE-0002a). This is treatment #3: dip in fresh aqua regia; rinse in $S_x^=$, then DI H_2O, and repeat aqua regia.
REF: Ibid.
CDSE-0005b: Gatos, H C & Lavine, M C — *Lincoln Lab Tech Rep*, 293, January 1963.
CdSe, (0001) used in a defect study. Aqua regia developed sharply bevelled pits on the (0001)A surface, but not on $(000\bar{1})$B, cadmium (A) and selenium (B) surfaces, respectively.

CDSE-0002c
ETCH NAME: Chrome regia — TIME: 5 sec
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
6 .... CrO_3
10 .... HCl
4 .... H_2O
DISCUSSION:
CdSe, (0001) and other orientations (CDSE-0002a). This is treatment #2. Dip in solution shown; rinse in $S_x^=$ solution, then rinse in DI H_2O and repeat chrome regia dip. (*Note:* This is one variety of the chrome regia etchants.)
REF: Ibid.

CDSE-0002d
ETCH NAME: — TIME:
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
(1) 3 .... HCl
1 .... HNO_3
(2) 6 .... CrO_3
10 .... HCl
DISCUSSION:
CdSe, (0001) and other orientations (CDSE-0002a). This is treatment #2, as a combination of treatments #3, then #2. Dip in aqua regia; $S_x^=$ solution rinse: water rinse; repeat aqua regia — follow with chrome regia dip; $S_x^=$ rinse; water rinse, and repeat chrome regia.
REF: Ibid.

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CDSE-0002e
ETCH NAME: Photo etch
TYPE: Electrolytic, cleaning
COMPOSITION:
9.7 .... HCl
0.3 .... HNO_3
90 .... H_2O
TIME: 4—5 sec
TEMP: RT
ANODE:
CATHODE:
POWER:
DISCUSSION:
CdSe, (0001) and other orientations (CDSE-0002a). This is treatment #5. Solution shown was used as a photo etch under AMI illumination and was short circuited with a counter carbon electrode. Use aqua regia #3 treatment, then the electrolytic solution shown, rinse in $S_x^=$ solution, and water rinse.
REF: Ibid.

CDSE-0002f
ETCH NAME: Aqua regia, variety
TYPE: Acid, cleaning
COMPOSITION:
97% .... HCl
3% .... HNO_3
TIME: 4—5 sec
TEMP: RT
DISCUSSION:
CdSe as a deposited polycrystalline thin film on a titanium substrate. This is treatment #6 using a reduced activity aqua regia solution to reduce etch rate on the thin polyfilm. Follow treatment #3 procedure (CDSE-0002b) using solution shown above; then the photo etch step shown under CDSE-0002e.
REF: Ibid.

CDSE-0002g
ETCH NAME:
TYPE: Electrolytic, reactive
COMPOSITION:
x .... 1 *M* KOH
x .... Na_2S
x .... S
x .... H_2O
TIME: To 20 h
TEMP: 35°C
ANODE:
CATHODE:
POWER:
DISCUSSION:
CdSe, (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ wafers used to study the overgrowth of CdS from a polysulfide electrolyte and decay of photoelectric current following different surface treatments to include polycrystalline thin film CdSe on titanium substrates. The electrolyte shown was used as the evaluation vehicle, e.g., S will replace Se in CdSe until CdS film stabilizes in thickness and stabilizes the CdSe/CdS interface.
REF: Ibid.

CDSE-0001b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HCl
30 .... HNO_3
10 .... CH_3COOH (HAc)
TIME: 8 sec
TEMP: 40°C
DISCUSSION:
CdSe, (0001) wafers used in a study of etch pit and structure development of II—IV

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compound semiconductors. The (0001) surface developed aligned hexagonal pits in the solution shown; both (0001)Cd and (000$\bar{1}$)Se surfaces were coated with selenium after etching, which can be removed by dipping in H_2SO_4.
REF: Ibid.

CDSE-0003
ETCH NAME: Aqua regia, dilute
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3
12 .... H_2O
DISCUSSION:
CdSe polycrystalline thin films deposited on titanium electrodes. The dilute aqua regia solution shown was used to clean and etch polish surfaces. (See CDSE-0002f).
REF: Tomkiewicz, M et al — *J Electrochem Soc*, 129,2016(1982)

CDSE-0004
ETCH NAME: BRM
TYPE: Halogen, cleaning
TIME:
TEMP: RT
COMPOSITION:
x .... 1% Br_2
x .... MeOH
DISCUSSION:
CdSe,(11$\bar{2}$0), n-type wafers used in a study of photocurrent decay in polysulfide electrolytes for corrosion and stability. Back surfaces of wafers were metallized for ohmic contact with front face exposed in an electrolytic solution. A cotton swab soaked in the solution shown was used to wipe-clean surfaces prior to each measurement in the electrolyte. See CDSE-0002g.
REF: Frese, K & Canfield, D — *J Electrochem Soc*, 132,1649(1985)

CDSE-0005a
ETCH NAME:
TYPE: Acid, preferential
TIME: 8 sec
TEMP: 40°C
COMPOSITION:
0.1 .... HCl
30 .... HNO_3
20 .... 18 *N* H_2SO_4
DISCUSSION:
CdSe, (0001) wafers used in a study of etch pit development. The (0001)A developed hexagonal etch pits; the (000$\bar{1}$)B developed no pits. Both surfaces were coated with selenium films after etching. Rinse in H_2SO_4 to remove residual selenium.
REF: Gatos, H C & Lavine, M C — *Lincoln Lab Tech Rep*, 293, January 1963

CDSE-0001c
ETCH NAME:
TYPE: Acid, preferential
TIME: 8 sec
TEMP: 40°C
COMPOSITION:
1 .... HCl
10 .... CH_3COOH(HAc)
30 .... HNO_3
1 .... 8 *N* H_2SO_4

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DISCUSSION:

CdSe, (0001) wafers used in an etch pit development study on II—IV compound semiconductors. Solution develops hexagonal etch pits on (0001)A, only, not on $(000\bar{1})$B. Remove residual selenium films with dip in H_2SO_4.

REF: Ibid.

CDSE-0006

ETCH NAME:

TIME: 20 sec

TYPE: Acid, removal

TEMP: RT

COMPOSITION:

5 .... HCl

1 .... HNO_3

DISCUSSION:

CdSe, (0001) or $(11\bar{2}0)$ wafers cleaved from Czochralski (CZ) grown ingots. Solution used as a general removal/polish etch. First, mechanically lap with Linde A (0.3 μm) alumina, then etch in solution shown. Also worked with CdS.

REF: Heller, A et al — *J Electrochem Soc,* 124,697(1977)

CDSE-0007

ETCH NAME: Ammonium hydroxide

TIME: (1) 10—15 min (2) Heat

TYPE: Acid, clean

TEMP: RT 300°C

COMPOSITION:

(1) x .... NH_4OH (2) x .... heat

DISCUSSION:

CdSe and $(Cd,Se)_xZn_{1-x}$ single crystal thin films grown in a material study. Prepare metals by (1) cadmium powder: soak clean in solution shown; DI H_2O rinse; dry at 50°C, (2) selenium powder: bake at 300°C, then regrind. Authors caution that improper cleaning can cause detonation.

REF: Kim, S U & Park, M J — *Jpn J Appl Phys,* 23,1070(1984)

CDSE-0008

ETCH NAME: Nitric acid

TIME: (1) Wash (2) 15 min

TYPE: Acid, cleaning

TEMP: RT 400°C

COMPOSITION:

(1) x .... 25% HNO_3 (2) x .... heat

DISCUSSION:

CdSe thin films co-evaporated on Ti (0001) substrates as polycrystalline films. Heat treat in air at 400°C, 15 min, to homogenize films. Clean CdSe surfaces with HNO_3: then in 1 *M* S:5 *M* Na_2S:1 *M* KOH to remove residual selenium.

REF: Haak, R et al — *J Electrochem Soc,* 131,2709(1984)

CDSE-0009a

ETCH NAME: Aqua regia

TIME:

TYPE: Acid, cleaning

TEMP:

COMPOSITION:

(1) 3 .... HCl (2) x .... 10% KCN

1 .... HNO_3

DISCUSSION:

CdSe, thin films electrodeposited on titanium substrates. Solution used was 0.1 *M* $CdSO_4$:0.01 *M* SeO_2:0.5 *M* H_2SO_4 at 6 mA/cm^3 power. CdSe films were etch cleaned in

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aqua regia; cyanide solution (2) used to remove residual Se with DI water rinse. Fabricated as photoelectrochemical solar cells (PECs) with n-type CdSe films.
REF: Silberstein, R P et al — *J Vac Sci Technol*, 19,406(1981)

CDSE-0009b
ETCH NAME: Xenon — TIME:
TYPE: Light, reactive — TEMP:
COMPOSITION:
x .... Xe
DISCUSSION:
CdSe ($10\bar{1}0$) cleaved wafers used in a study of insulated gate FETs and IGFETs with evaporated aluminum. Studied contact potential difference (CPD) and time resolved charge injection (TRCI) at the aluminum interface. Wafers were cleaved in an ultra high vacuum (UHV) at 2×10^{-10} Torr. CdS wafers similarly studied. Flooding surfaces with high intensity xenon light shows potential and injection effects in Al, CdSe and CdS.
REF: Ibid.

CADMIUM SILICON ARSENIDE, $CdSiAs_2$

General: Does not occur as a natural compound; the primary cadmium minerals are mainly sulfides, although there are several arsenates, but none contain cadmium. There is no industrial use, other than as a compound semiconductor.

Technical Application: The material is a II—IV—V compound semiconductor, and has been evaluated for its characteristics as a possible laser, photoconductor, and photo-diode. The material has been grown as a single crystal, and as a thin film layer in heterojunction structures.

Etching: HCl, and mixed acids: HCl:HNO_3 or HF:HNO_3.

CADMIUM SILICON ARSENIDE ETCHANTS

CSA-0001
ETCH NAME: — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
1 .... H_2O
DISCUSSION:
$CdSiAs_2$, (001) and (111) wafers cut from an n-type, indium doped ingot grown by Vapor Transport (VT) in a tin flux. Wafers were etch polished in the solution shown before silver and gold contacts were evaporated.
REF: Avirovic, N et al — *J Cryst Growth*, 67,185(1984)

PHYSICAL PROPERTIES OF CADMIUM SULFIDE, CdS

Classification	Sulfide
Atomic numbers	48 & 16
Atomic weight	144.5
Melting point (°C) 100 atms	1750
Boiling point (°C)	
Density (g/cm³)	4.82 (4.9—5.0)
Refractive index (n=)	2.506—2.529

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Energy band gap (eV)	2.45
Hardness (Mohs — scratch)	3—3.5
Crystal structure (hexagonal — hemimorphic) alpha	m(10$\bar{1}$0) prism
(isometric — tetrahedral) beta	(111) tetrahedron
Color (solid)	Yellow
Cleavage (prismatic — distinct)	a(11$\bar{2}$0)

CADMIUM SULFIDE, CdS

General: There are three natural compounds with greenockite, CdS, the more important, as it is fairly abundant. It is rarely found as crystals, but common as coatings or incrustations on other minerals, primarily zinc compounds, e.g., sphalerite, ZnS (zinc blende).

It is an industrial ore of cadmium, and the natural compound is also used as a yellow pigment in paints. In glass optics there are applications for its piezoelectric properties for filter type devices alone or in conjunction with quartz, SiO_2. (See Cadmium Selenide, CdSe, for similar applications.)

Technical Application: Cadmium sulfide is a II—V compound semiconductor with hexagonal structure. It is a polar compound with regard to prism faces, (10$\bar{1}$0), and has distinctive (0001) cleavage, such that wafer processing is usually done with (0001) basal surfaces. The second order prism face, (11$\bar{2}$0) has been used.

As a piezoelectric material it has been dual-evaporated in alternate orientation layer structure: CdS/SCd/CdS . . . n. As many as 15 thin film layers have been so deposited on alpha-quartz radio frequency blanks for both frequency crystals and electronic filter-type structures.

CdS is grown as a single crystal ingot in both the alpha and beta-CdS form, or epitaxially deposited as an amorphous thin film, a-CdS. It also occurs naturally as an amorphous film. There is a trinary compound as $Zn_{x-1}Cd_xS$.

Although it is relatively soft (H = 3—3.5) it has been fabricated as Solid State devices, such as photoconductors, solar cells, thin film transistors, and laser diodes.

Etching: Easily etched in most acids and NH_4OH.

CADMIUM SULFIDE ETCHANTS

CDS-0001a
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, damage removal — TEMP:
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

CdS, (0001) and (10$\bar{1}$3) wafers. Solution used to remove cutting and lapping damage from surfaces. Material used in a defect study.

REF: Scranton, R A — *J Appl Phys,* 50,842(1979)

CDS-00020: Heller, A et al — *J Electrochem Soc,* 123,697(1977)

CdS, (11$\bar{2}$0) cleaved wafers. Solution used 20 sec at RT to lightly polish clean surfaces as a general etch. First lap polish with Linde A (0.3 μm alumina), then apply solution.

CDS-0017: Richard D et al — *J Vac Sci Technol,* A2(2),132(1984)

CdS thin films doped with O_2 and deposited by spray pyrolysis on glass and sapphire substrates, or substrates pre-coated with SnO_2 or ITO. CdS surfaces were cleaned with HCl after deposition.

CDS-0019a: Chikawa, J & Namayama, T — *J Appl Phys,* 35,2492(1964)

CdS single crystal specimens used in a study of dislocations, structure and growth mechanisms. Specimens were first polished in HCl before thermal etch treatment to develop defect and structure.

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CDS-0005b
ETCH NAME: Hydrochloric acid — TIME: 10 sec
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
x .... 9 *N* HCl
DISCUSSION:
CdS, (100) wafers cut perpendicular and parallel to the single crystal ingot c-axis used in a study of copper diffusion as insulating layers on CdS. Solution was used to polish surface prior to copper evaporation.
REF: Ibid.

CDS-0001b
ETCH NAME: Potassium dichromate — TIME: 10 min
TYPE: Acid, polish/preferential — TEMP: 95°C
COMPOSITION:
x .... 0.5 *M* $K_2Cr_2O_7$
x .... 16 *N* H_2SO_4
DISCUSSION:
CdS, (111) wafers. Solution used to etch polish both CdS and ZnS wafers with similar results. Produces a highly polished surface containing dislocation etch pits on $(\overline{1}\overline{1}\overline{1})$B (sulfur) surface; shallow disc-like structure on the (111)A (cadmium) surface or $(\overline{1}\overline{1}\overline{1})$B (zinc) surface.
REF: Ibid.
CDS-0005a: Simheny, M et al — *J Appl Phys*, 39,152(1968)
CdS, (100) wafers cut perpendicular and parallel to the single crystal c-axis used in a study of copper diffusion as insulating layers in CdS. Solution used as a preferential etch at 90°C for 5—10 min to observe defects induced by copper.

CDS-0011a
ETCH NAME: — TIME: 2 min
TYPE: Acid, preferential — TEMP: RT (25°C)
COMPOSITION:
6 .... HNO_3, fuming
6 .... CH_3COOH (HAc)
1 .... H_2O
DISCUSSION:
CdS, (0001) wafers. The $(000\overline{1})$S surface develops hexagonal etch pits, but only a sulfur film on (0001)Cd. (*Note:* HNO_3, white fuming = 70%; yellow fuming = 72%; red fuming = 74%. This is a major article on etching II—VI compounds.)
REF: Warekois, E P et al — *J Appl Phys*, 33,690(1962)
CDS-0004a: Gatos, H C & Lavine, M C — *Lincoln Lab Tech Rep*, 293, January 1963
CdS, (0001) wafers used in a similar defect etching study. (*Note:* A major article on etching of this compound.)

CDS-0002
ETCH NAME: — TIME: 1—2 min
TYPE: Acid, removal — TIME: RT
COMPOSITION:
1 .... HCl
1 .... CH_3COOH (HAc)
1 .... H_2O
DISCUSSION:
CdS, (0001) wafers used with particular interest on the (0001)A (cadmium) surface.

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Work also done with thin film deposits on alpha-quartz substrates as Ag/CdS/quartz. Mechanically polish CdS wafers, then remove lapping damage with solution shown. (*Note:* The Ag/CdS/quartz assembly is a radio frequency device structure.)
REF: Lubbert, C — *J Appl Phys,* 47,366(1976)

CDS-0011b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
CdS, (0001) wafers. This solution develops conical etch pits on (0001)S surfaces that approach hexagonal form. The (0001)Cd surface is rough and granular.
REF: Ibid.

TIME:
TEMP:

CDS-0003
ETCH NAME: Hydrochloric acid
TYPE: Acid, preferential
COMPOSITION:
x .... HCl vapor
DISCUSSION:
CdS, (0001) wafers used in an etch pit study. Wafers were wetted in water prior to being held in HCl vapor to develop etch pits.
REF: Eland, A J — *Phillips Tech Rev,* 22,266(1960—1961)
CDS-0012: Pisarerko, Zh D & Sheinkman, M K — *Sov Phys (Solid State),* 3838(1960)
CdS, (0001) cleaved wafers used in a study of dislocations. Hold wafers 4—5 cm above 20—30% HCl liquid in the vapors at 100°C for 1—2 min, then wash in DI H_2O. Other etchants evaluated, but this solution gave the best results.
CDS-0013: Reynolds, D C & Czyzak, S J — *J Appl Phys,* 31,95(1960)
CdS, (0001) wafers used in a study of dislocations. Used a boiling solution of HCl with wafers held in hot vapors, and followed with DI H_2O rinse. The (0001)A surface does not develop pits; the $(000\bar{1})$B surface develops pits. Two dislocation density materials evaluated: 10^1 and $10^7/cm^2$.

TIME: 1 min
TEMP: Hot

CDS-0022
ETCH NAME: Perchloroethylene
TYPE: Solvent, cleaning
COMPOSITION:
x .... CCl_2:CCl_3 (PCE, Perk)
DISCUSSION:
CdS, (100) wafers. Mechanical lap and polish and then clean with the following sequence: (1) decrease in PCE, (2) wash in HCl, (3) DI water rinse, and (4) rinse in acetone.
REF: Sherohman, J W — *J Electrochem Soc,* 128,1817(1981)

TIME:
TEMP:

CDS-0006a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... H_2SO_4
x .... 0.3 *M* $KMnO_4$

TIME: 2—3 min
TEMP: RT

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DISCUSSION:

CdS, (100) wafers. Referred to as a new optical quality etch for II—V compounds. Mixture is a dark green color. The permanganate should be added slowly as there is violent reaction with the sulfuric acid. Produces smaller etch pits (?) and a cleaner surface than the "Chromate Etch". (See CDS-0002.) This etch was compared to HCl; H_3PO_4 and dilute HNO_3 which also are etches for II—V compounds. (*Note:* See Silicon Dioxide section for comparative standard glass cleaner solution.)

REF: Rowe, J E & Forma R A — *J Appl Phys*, 39,1917(1968)

CDS-0007a

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, preferential, vapor — TEMP: Hot

COMPOSITION:

x .... HCl, vapors

DISCUSSION:

CdS, (0001) wafers used in a study of defects and dislocations. Wafers were suspended in HCl vapors. The (0001)A surface develops dislocation etch pits; none on $(000\bar{1})$B.

REF: Woods, J — *Br J Appl Phys*, 11,296(1960)

CDS-0008: Reynolds, R C & Green, L C — *J Appl Phys*, 29,559(1958)

This reference cited for use of HCl, vapor.

CDS-0007b

ETCH NAME: — TIME: 10 min

TYPE: Acid, preferential — TEMP: 80°C

COMPOSITION:

5 ml .... H_2SO_4

1250 ml .... H_2O

1 g .... Cr_2O_5

DISCUSSION:

CdS, (0001) and $(10\bar{1}0)$ wafers used in a study of defects and dislocations. Place wafers in solution at RT and bring up to 80°C; rinse in DI water, then in MeOH. Etch pits results were as follows:

(0001)A: Hexagonal pits with variable side lengths. Etch for 30 sec only and pit sides are of equal length.

$(000\bar{1})$B: Conical pits only.

$(10\bar{1}0)$: Triangle pits — one side perpendicular to the c-axis; apex in the $(000\bar{1})$B direction.

$(11\bar{2}0)$: No pits developed.

REF: Ibid.

CDS-0009: Votava, E — *Seitz Naturforsch*, 13a,542(1958)

CdS specimens. Used HCl by immersion, rather than as hot vapor. Results were similar to those obtained in CDS-0007a.

CDS-0010

ETCH NAME: Hydrochloric acid, dilute — TIME:

TYPE: Acid, cleaning — TEMP: RT

COMPOSITION:

x .... HCl

x .... H_2O

DISCUSSION:

CdS, (0001) wafers used to fabricate photojunctions by diffusing copper into insulating

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CdS. Wafer surfaces were rinsed in the solution shown and then in DI water prior to copper diffusion.
REF: Rockemuehl, R R et al — *J Appl Phys*, 32,1324(1961)
CDS-0014: Sullivan, M V & Bracht, W R — *J Electrochem Soc*, 114,295(1967)
CdS, (111) wafers. Solution used as 30HCl:70H_2O as a chem/mech polish for both the (111)Cd and ($\overline{1}\overline{1}\overline{1}$)S surfaces using rotation on a pellon type cloth.

CDS-0015a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
13.7 g .... KCl
0.5 ml .... HCl
100 ml .... H_2O
TIME:
TEMP: RT
DISCUSSION:
CdS, (111) wafers. Solution used as a chem/mech polish at 58 rpm rotation on a pellon-type pad. Used to polish the (111)Cd surface.
REF: Pritchard, A A & Wagener, S — *J Electrochem Soc*, 124,961(1977)

CDS-0015b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
13.3 g .... KCl
16 ml .... HCl
100 ml .... H_2O
TIME:
TEMP: RT
DISCUSSION:
CdS, (111) wafers. Solution used as in CDS-0015a to polish the ($\overline{1}\overline{1}\overline{1}$)S wafer surface.
REF: Ibid.

CDS-0016
ETCH NAME:
TYPE: Acid-slurry, polish
COMPOSITION:
90 ml .... HNO_3
10 g .... $AgCl_3$
1000 ml .... H_2O
300 ml .... silica
TIME:
TEMP: RT
DISCUSSION:
CdS, (0001) wafer. Solution used to chem/mech polish wafers at 240 rpm with pellon-type pad.
REF: Pickhardt, V Y & Smith, D L — *J Electrochem Soc*, 124,961(1977)

CDS-0011c
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... 16 *N* H_2SO_4
x .... 0.5 *N* $K_2Cr_2O_7$
TIME: 5—15 min
TEMP: 95°C

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DISCUSSION:
CdS, $(10\bar{1}0)$ wafers. Solution is a general polish for (111)Cd surfaces, but develops etch pits on the $(\bar{1}\bar{1}\bar{1})$B surfaces.
REF: Ibid.

CDS-0007c
ETCH NAME:
TYPE: Acid, preferential
TIME: 10 min
TEMP: 80°C
COMPOSITION:
1 ml .... H_2SO_4
0.08 g .... Cr_2O_3
100 ml .... H_2O
DISCUSSION:
CdS, $(10\bar{1}0)$ wafers. Solution used as a preferential etch.
REF: Ibid.

CDS-0018
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
2 .... HCl
5 .... EOH
DISCUSSION:
CdS, (0001) wafers used in a study of electrochemical coupling. Solution used to develop pits and defects.
REF: Wilson, R B — *J Appl Phys*, 37,1932(1966)

CDS-0019b
ETCH NAME: Heat
TYPE: Thermal, dislocation
TIME: (1) 2—5 sec
TEMP: (1) RT
COMPOSITION:
(1) x .... HCl, conc. (2) x .... heat
DISCUSSION:
CdS, single crystal specimens used in a study of dislocations, structure and growth mechanisms. Specimens polished in HCl before thermal etching to develop dislocations and structures.
REF: Chikawa, J & Nakayama, T — *J Appl Phys*, 35,2492(1964)

CDS-0021
ETCH NAME:
TYPE: Acid, removal/cleaning
TIME: $^1/_2$ h
TEMP: Boiling
COMPOSITION:
1 .... 5% NaOH
1 .... 10% NaCN
DISCUSSION:
CdS wafers copper plated and diffused used in a study of the dependence of hole ionization energy relative to imperfections and impurity concentration. Solution used to wash and remove excess copper remaining after diffusion; follow with water rinsing until pH paper is neutral.
REF: Bube, R H & Dreeben, P B — *Phys Rev*, 115,1578(1959)

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CDS-0023
ETCH NAME: Xenon
TYPE: Light, reactive
COMPOSITION:
x .... Xe
DISCUSSION:
CdS, (0001) wafers and CdSe ($10\bar{1}0$) cleaved wafer in UHV. Wafers fabricated as insulated gate devices with aluminum gates for IGFETs. High intensity xenon light will affect the activity of aluminum in both materials. See: CDSE-0009a-b.
REF: Sinerstein, R P et al — *J Vac Sci Technol*, 19(3),406(1981)

TIME:
TEMP:

PHYSICAL PROPERTIES OF CADMIUM TELLURIDE, CdTe

Classification	Telluride
Atomic numbers	48 & 52
Atomic weight	240
Melting point (°C)	1041
Boiling point (°C)	
Density (g/cm^3)	6.20
Energy band gap (eV)	1.45
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Black
Cleavage (cubic — distinct)	(001)

CADMIUM TELLURIDE, CdTe

General: Does not occur as a natural compound. There are several tellurides and tellurates with iron and other metals. Cadmium telluride has had little use in industrial metal processing, other than as a compound semiconductor.

Technical Application: Cadmium telluride is a II—V compound semiconductor with the sphalerite, ZnS, structure. It is similar to other polar type compounds with positive (111) water surfaces as (111)Cd, and negative ($\overline{111}$)Te opposed wafer surfaces which show different etching characteristics, such that the material is more often used in the (100) orientation for device processing, though the polarity effects have been widely studied. It has been grown as a single crystal by the Horizontal Bridgman (HB), Czochralski (CZ), and Float Zone (FZ) methods. Also grown as an epitaxy thin film by Vapor Transport (VT), Chemical Vapor Deposition (CVD), and by Vapor Phase Epitaxy (VPE). It is isomorphous with InSb, and further grown as a trinary semiconductor: $Cd_xHg_{1-x}Te$. Devices made from both the binary and trinary compounds include photoconductors, photodiodes, and laser diodes.

Etching: Mixed acids of HF:HNO_3, HCl:HNO_3, and halogens.

CADMIUM TELLURIDE ETCHANTS

CDTE-0006b
ETCH NAME: EAg1 etch
TYPE: Acid, preferential
COMPOSITION:
10 ml .... *E etch
5 mg .... $AgNO_3$

TIME:
TEMP:

*See CDTE-0015b

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DISCUSSION:

CdTe, (100), (111) and (110) wafers. The (110) wafers were cleaved; the (100) and (111) were saw cut. All orientations were mechanically polished with "chrome green" (CrO) as 1—3 μm grit. Several etches developed as polish and preferential solutions for studying CdTe polarity and defects. (*Note:* Cr_2O_3 is the normal green form of chromium oxide.)

REF: Inoue, M et al — *J Appl Phys,* 33,2578(1962)

CDTE-0031: Iwanaga, H J — *J Cryst Growth,* 62,690(1979)

CdTe, (111) and (110) wafers used in a study of pit structures. Solution used at RT, 3 min. The (111)A surface develops triangle pits; $(\bar{1}\bar{1}\bar{1})$B also developed triangle pits, but deeper than on (111)A. Isosceles triangles with pointed bottoms developed on the (110)B, and similar pits with flat bottoms on the (110)A. Etch time 3 min at RT.

CDTE-0006a

ETCH NAME: E etch — TIME:

TYPE: Acid, polish — TEMP: RT

COMPOSITION:

10 ml .... HNO_3

20 ml .... H_2O

4 g .... $K_2Cr_2O_7$

DISCUSSION:

CdTe, (100), (111), and (110) wafers used in development of defect etches and a study of polarity effects on CdTe. This solution is a polishing etch and was used before preferential etchants were applied. See CDTE-0006b-f.

REF: Ibid.

CDTE-0017d: Ibid.

CdTe, (111) wafers. Solution used at RT with agitation and produced a mirror polish. Rate: 4.2 μm/min. See CDTE-0017a.

CDTE-0006c

ETCH NAME: EAg2 etch — TIME:

TYPE: Acid, preferential — TEMP: RT

COMPOSITION:

10 ml .... *E Etch

10 mg .... $AgNO_3$

*See CDTE-0006a

DISCUSSION:

CdTe, (100), (111), and (110) wafers. See CDTE-0006a,b for discussion.

REF: Ibid.

CDTE-0006d

ETCH NAME: P etch — TIME:

TYPE: Acid, polish — TEMP: RT

COMPOSITION:

10 ml .... HCl

10 ml .... HNO_3

5 ml .... H_2O

DISCUSSION:

CdTe, (111), (100) and (110) wafers. Solution used as a polishing etch prior to pref-

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erential etching for defects and polarity effects. See other CDTE-0006 references for additional discussion.
REF: Ibid.
CDTE-0017e: Ibid.

CdTe, (111) wafers. Solution produces pits as used at RT with agitation. Rate: 12.5 μm/min. See CDTE-0017a.

CDTE-0006e
ETCH NAME: PBr etch
TYPE: Halogen, preferential
COMPOSITION:
(1) 10 ml .... P etch
10 mg .... Br_2
(2) 10 ml .... P etch
5 mg .... Br_2
TIME:
TEMP: RT
DISCUSSION:

CdTe, (111), (100), and (110) wafers. Both solutions develop etch pits. They also can be used as p-n junction delineation solutions. See other CDTE-0006 references for further discussion.
REF: Ibid.

CDTE-0006f
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat
TIME:
TEMP: 600°C
DISCUSSION:

CdTe, (111), (100), and (110) wafers used in developing polish and preferential etch solutions and other methods of developing structure. Wafers were placed in vacuum at 5^{-10} mmHg. Thermal etching develops etch structures that can be correlated with chemical liquid etching. See other CDTE-0006 references.
REF: Ibid.

CDTE-0012a
ETCH NAME:
TYPE: Acid, float-off
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:
DISCUSSION:

CdTe, thin films grown on muscovite mica (0001) cleaved substrates. After growth the films were removed from the mica by the float-off technique with the solution shown for TEM study of structure.
REF: Davenere, A et al — *J Cryst Growth*, 70,452(1984)

CDTE-0001a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
3 .... HF
2 .... H_2O_2
1 .... H_2O
TIME: 2 min
TEMP: RT
DISCUSSION:

CdTe, (111) wafers. The (111)Cd surface shows a near-polish with cup-like figures that

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disappear upon further etching. The ($\overline{111}$)Te surface develops triangular etch pits. The Te film that remains after etching can be removed by dipping in HCl.
REF: Warekois, E P et al — *J Appl Phys*, 33,690(1962)
CDTE-0017f: Ibid.

CdTe, (111) wafers. Solution used at RT with agitation. Polished the (111)Cd surface. Rate: 3.4 μm/min. See CDTE-0017a.

CDTE-0001b
ETCH NAME:
TYPE: Acid, polish
TIME: 8—10 min
TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:

CdTe, (111) wafers. Described as a good polish etch for both wafer surfaces, (111)A and ($\overline{111}$)B, and does not develop etch pits. The grey tellurium film remaining after etching can be removed by dipping in HCl.
REF: Ibid.

CDTE-0001c
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
2 .... HF
3 .... HNO_3
1 .... H_2O
DISCUSSION:

CdTe, (111) wafers. Solution will develop triangle etch pits on the ($\overline{111}$)B face but a semi-polish on (111)A.
REF: Ibid.

CDTE-0002
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
(1) x .... H_2SO_4
x .... $K_2Cr_2O_7$
(2) x .... Br_2
x .... MeOH
DISCUSSION:

CdTe, (111) n-type wafers doped with either aluminum or chlorine. Wafers were first mechanically polished, then etch polished in the number (1) solution shown. After etching, rinse in the BRM number (2) solution.
REF: Vazquez-Lopez, C et al — *J Appl Phys*, 50,5390(1979)
CDTE-0017g: Ibid.

CdTe, (111) wafers. Solution mixture was $3gH_2SO_4$:$7gK_2Cr_2O_7$, and was used at RT with agitation. Produced polished surfaces. Rate: 2.3 μm/min. See CDTE-0017a.
CDTE-0024b: Ibid.

CdTe, (111) wafers and other orientations used in a study of anodic oxidation. Etch clean wafers in solution (1) before oxidation.

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CDTE-0004
ETCH NAME:
TYPE: Acid, preferential
TIME: (1) 1 min (2) 30 sec
TEMP: RT RT
COMPOSITION:
(1) 3 .... HF
2 .... H_2O_2
1 .... H_2O
(2) x .... 0.1% Br_2
x .... MeOH
DISCUSSION:
CdTe, (111) wafers and ingots. Solution used to develop defect in both wafers and ingots in a study of twinning. Etch in solution (1) and DI water rinse; follow with solution (2) and DI water rinse. The BRM solution will polish surfaces accentuating the defects developed by the acid solution. See CDTE-0001a.
REF: Vere, A W et al — *J Electron Mater,* 12,551(1983)

CDTE-0005a
ETCH NAME:
TYPE: Acid, isotropic & defect
TIME:
TEMP:
COMPOSITION:
(1) x .... 0.5% Br_2
x .... MeOH
(2) 5 ml .... HNO_3
10 ml .... H_2O
2 g .... $K_2Cr_2O_7$
(3) 42 .... HF
20 .... H_2O_2
29 .... H_2O
DISCUSSION:
CdTe, (111) wafers. Mechanical lap with abrasives on a glass plate in the following order: (1) 240-grit SiC; (2) 600-grit SiC and (3) 0.3 μm alumina. Then use solution (1) to chem/mech polish by dripping solution onto a polishing pad with hand lap or mechanical rotation. Wax coat surfaces with a pattern opened area with the black wax (Apiezon-W) acting as a dike. Use etch solution (2) to chemically etch-mill pits into the bulk CdTe surface. Then use solution (3) as a defect etch to develop dislocations in the previously etched pits. This will develop defects in the material bulk. Remove the dark Te film remaining in pits after defect etching with alcohol. (*Note:* See Silicon, SI0092a-k for similar bulk defect study.)
REF: Weirauch, D F — *J Electrochem Soc,* 132,250(1985)

CDTE-0005b
ETCH NAME:
TYPE: Acid, isotropic defect
TIME: See discussion
TEMP: RT
COMPOSITION:
(1) "A" 5 ml .... HNO_3
10 ml .... H_2O
2 g .... $K_2Cr_2O_7$
"B" x .... H_2O
(2) 42 .... HF
29 .... H_2O_2
29 .... H_2O
DISCUSSION:
CdTe, (111) wafers. Mechanically polish: (1) 5 μm, then (2) 0.3 μm alumina. Plate surface with gold using $AuCl_3$, 15 sec. (*Note:* Standard electrolytic gold plating bath or electroless?). Mix solution (1) as 4 "A":1"B", and etch polish surfaces after first scratching through gold film to induce microcracks in the CdTe. Then polish etch, RT, 2 sec into scratched areas. Use solution (2) as a defect etch, RT, 20 sec. Remove grey Te film in etched areas with solution (1). Cleave wafers on ⟨110⟩ for observation and study of scratched damaged zones in cross-section.
REF: Ibid.

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CDTE-0007
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
3 .... HF
2 .... H_2O_2
1 .... H_2O
DISCUSSION:
CdTe, (111) wafers. Authors say that this solution leaves a high Te content surface film after etching and suggest that high electropositive elements tend to pile-up at the surface for reasons unknown. See CDTE-0001a, where solution was developed and used as a preferential etch.
REF: Reiyi, V T et al — *Thin Solid Films,* 113,157(1984)

CDTE-0008
ETCH NAME: BRM TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
x .... Br_2
x .... MeOH
DISCUSSION:
CdTe, (111) wafers grown by the Horizontal Bridgman (HB) method, and used for epitaxy growth of CdTe on both (111)A and $(\overline{111})$B oriented surfaces. Wafers were mechanically lapped and then polished in a BRM solution prior to epitaxy. Epitaxy growth was by Vapor Transport (VT) using a vertical, three-zone furnace under argon with wafers at the bottom. Epitaxy would grow only on the (111)A surface and showed triangular steps with (110) slopes. *Note:* Argon was used to thermally etch both surfaces while still in the growth system: the (111)A showed terracing; whereas $(\overline{111})$B showed random etching only.
REF: Kuwamoto, H — *J Cryst Growth,* 69,204(1984)

CDTE-0009
ETCH NAME: BRM TIME: 5 min
TYPE: Halogen, removal/polish TEMP: RT
COMPOSITION:
x .... 2% Br_2
x .... MeOH
DISCUSSION:
CdTe, (111) wafers, n-type, high resistivity. Mechanically polish with 0.3 μm alumina, then etch with the solution shown to remove about 20 μm. A Te rich surface film is left. Rinse in MeOH to remove residual bromine, DI water rinse, and N_2 blow dry. Place wafers in vacuum, and hold 8 h at 900°C with 0.5 atm Cd back-pressure to suppress Cd vacancies. Then evaporate indium pads for ohmic contact. See CDTE-0005a and CDTE-0002.
REF: Nozaki, S et al — *J Electron Mater,* 14,137(1985)
CDTE-0021: Sagar, A et al — *J Appl Phys,* 39,5336(1968)
CdTe, (111) wafers. Used a 0.5% Br_2:MeOH solution as a general polishing etch, RT, up to 45 min. Clean Te surface deposits that remain with CS_2.

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CDTE-0010
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 10% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:
CdTe, (111) wafers, p-type. After mechanical lap and polish, degrease in TCE, and rinse in DI water. Use solution shown to etch polish surfaces.
REF: Selim, F A & Kroger, E A — *J Electrochem Soc*, 124,401(1977)

CDTE-0011a
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
(1) x .... x% Br_2
x .... MeOH
(2) 3 .... HF
2 .... H_2O_2
3 .... H_2O
(3) x .... 2% Br_2
x .... glycol
TIME:
TEMP:
DISCUSSION:
CdTe, (111) wafers used as substrates for epitaxy growth of CdTe on both (111)Cd and $(\overline{111})$Te surfaces by LPE (liquid phase epitaxy) — deposited substrate surfaces were rich in Te. In preparing substrates, use solution (1) as a polish etch. After epitaxy, use solution (2) to develop dislocations in the epitaxy layers. Follow with solution (3) to remove black "smut" remaining after dislocation etching by dip cleaning, RT, 5 sec, then MeOH rinse, DI water rise, and N_2 blow dry. Dislocation etch (2) develops star-shaped pits and low angle grain boundaries in the epitaxy layers that show correspondence between the two polar wafer faces.
REF: Astles, M et al — *J Electron Mater*, 13,167(1984)

CDTE-0011b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HCl
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
CdTe, (111) wafers used in an etch reaction study. The (111)Cd surface develops triangular etch pits with a surface background of shallow, triangular etch figures. The $(\overline{111})$Te surface is covered with a Te film in which triangular figures appear to have been etched.
REF: Ibid.

CDTE-0012b
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 1% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:
CdTe, (111) wafers used for epitaxy growth of CdTe/Bi/CdTe (111). Muscovite mica, cleaved (0001), also used as a substrate — blow mica clean with N_2, and apply no liquids.

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Etch polish CdTe substrates in solution shown before epitaxy. Material used in a study of superlattice capability.
REF: Davenere, A et al — *J Cryst Growth,* 70,452(1984)
CDTE-0020: Pessa, M et al — *J Vac Sci Technol,* A2(2),418(1984)

CdTe, (111), p-type wafers used as substrates for epitaxy growth of CdTe thin films. Wafers were chem/mech polished in a BRM solution. Final clean in vacuum with Ar^+ ion bombardment for 10 min at 2.5 KeV power.
CDTE-0021: Bhat, I & Ghandhi, S K — *J Electrochem Soc,* 131,1923(1984)

CdTe, (100) wafers cut 3°-off toward (110), and used for epitaxy growth of HgTe thin films. Clean substrates as follows: (1) degrease with solvents, and (2) etch in 2% Br_2:MeOH to remove 20 μm of surface depth and polish simultaneously.

CDTE-0013
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
3 .... HF
2 .... H_2O_2
2 .... H_2O
TIME:
TEMP: RT
DISCUSSION:

CdTe (111) wafers used as substrates for epitaxy growth of HgCdTe on (111)Cd and ($\overline{111}$)Te surfaces in a study of epitaxy morphology and lattice mismatch. Solution used to etch polish wafers prior to epitaxy. The negative Te surface produced the better lattice match.
REF: Edwall, A D et al — *J Appl Phys,* 55,145(1984)

CDTE-0016a
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal/polish
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME: 2 min
TEMP: 30°C
RATE: 100 μm/min
DISCUSSION:

CdTe, (111) wafers used in a phase equilibria and properties study. Solution used as a general removal and polishing etch. It leaves a layer of Te and Te-oxides on surfaces that can be removed by the solution shown under CDTE-0016b.
REF: Phillips Res Rep, #4,361(1969)

CDTE-0016b
ETCH NAME:
TYPE: Alkali, removal
COMPOSITION:
x .... 10% NaOH
x .... $Na_2S_2O_4$
x .... H_2O
TIME:
TEMP: 60°C
DISCUSSION:

CdTe, (111) wafers used in a properties study. Solution used to remove Te and Te-oxides remaining as surface films on wafers after etch polishing in nitric acid. See CDTE-0016a. Also see Tellurium section for additional etchants.
REF: Ibid.
CDTE-0017h: Ibid.

CdTe, (111) wafers. Solution mixture was: 10% NaOH:x Na_2SO_4, used at RT with agitation. Produced a bright surface. Rate: 1—2 μm/min. See CDTE-0017a.

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CDTE-0017a
ETCH NAME: Sodium hydroxide
TYPE: Alkali, polish
COMPOSITION:
x .... 50% NaOH
TIME:
TEMP: RT
RATE: 1.6 μm/min
DISCUSSION:
CdTe, (111) wafers used in an etching reaction and rate experiment. Solution produced a bright surface. In this work, HCl and H_2SO_4 at RT showed no removal. Agitate solution during etching. Rate determined by weight loss and should be used as a guide.
REF: Gaugash, P & Milnes, A G — *J Electrochem Soc*, 128,924(1981)

CDTE-0017b
ETCH NAME: BRM
TYPE: Halogen, preferential
COMPOSITION:
x .... 0.5% Br_2
10 mg .... $AgNO_3$
x .... MeOH
TIME:
TEMP: RT
RATE: 2.2 μm/min
DISCUSSION:
CdTe, (111) wafers used in an etch reaction and rate experiment. Solution was medium red in color and produced pits on (111) surfaces. Was also used as a p-n junction etch. See CDTE-0017a for further discussion.
REF: Ibid.

CDTE-0017c
ETCH NAME: Nitric acid
TYPE: Acid, burn
COMPOSITION:
x .... HNO_3 conc.
TIME:
TEMP:
RATE: 3.5 μm/min
DISCUSSION:
CdTe, (111) wafers. Solution left a dark precipitate on surface that could be removed easily by light mechanical rubbing. See CDTE-0017a for additional discussion.
REF: Ibid.

CDTE-0017i
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HCl
50 .... HNO_3
18 .... H_2SO_4
10 .... HAc
TIME:
TEMP: RT
RATE: 8 μm/min
DISCUSSION:
CdTe, (111) wafers used in an etch and rate experiment. Solution produced polished surfaces. See CDTE-0017a.
REF: Ibid.

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CDTE-0017j
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
2 .... 45% HF
1 .... HNO_3
1 .... HAc
TIME:
TEMP: RT
RATE: 60 μm/min
DISCUSSION:
CdTe, (111) wafers. Solution used with agitation and produced pits. See CDTE-0017a for additional discussion.
REF: Ibid.

CDTE-0018a
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
1 .... Br_2
20 .... MeOH
TIME:
TEMP:
DISCUSSION:
CdTe, (100) wafers used for fabrication of CdTe:HgTe heterojunctions. Solution used to polish CdTe surfaces. Produces a clean, highly reflective surface.
REF: Almasi, G S & Smith, A C — *J Appl Phys*, 39,233(1968)

CDTE-0018b
ETCH NAME: Aqua regia, dilute
TYPE: Acid, polish
COMPOSITION:
3 .... HCl
1 .... HNO_3
1 .... HAc
TIME:
TEMP:
DISCUSSION:
CdTe, (111) wafers used to growth CdTe:HgTe heterojunctions. Solution may leave a black smudge on surface, but it does not affect device performance.
REF: Ibid.

CDTE-0019
ETCH NAME:
TYPE: Acid, structure
COMPOSITION:
1 .... HF
2 .... H_2O_2
2 .... H_2O
TIME:
TEMP:
DISCUSSION:
CdTe, (111) wafers cut from an ingot grown by the Vertical Bridgman (VB) technique. Specimens were cleaned in the following sequence: 13% Br_2:MeOH, RT, 3 min to etch remove work damage, and DI water rinse. EAg-1 etch (CDTE-0006b) used to develop etch pits on (111)Cd surfaces. Substructure was developed by the solution shown. This structure was cellular due to subgrains from supercooling (?), or from high temperature stress (?) during growth. Slow ingot growth will reduce such structure.
REF: Oda, O et al — *J Cryst Growth*, 71,273(1985)

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CDTE-0022
ETCH NAME: Isopropyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... C_2H_7OH(ISO, IPA)
TIME:
TEMP: RT
DISCUSSION:

CdTe, growth as single crystal ingot by Czochralski (CZ) method is difficult due to twinning and low angle grain boundary development. At less than 50°C, ingot is poly-CdTe. Between 50—150°C good single crystal, but some ⟨122⟩ directional defects. CdTe is isomorphous with InSb. CdTe thin films grown on InSb by MBE showed high perfection of films. Clean surfaces with alcohol as shown. (*Note:* MBE = molecular beam epitaxy.)
REF: Farrow, R F C et al — *Appl Phys Lett*, 39,954(1981)
CDTE-0023: Yellin, N et al — *J Electron Mater*, 14,85(1985)

CdTe ingot growth. Initial poly-CdTe ingot grown by Vertical Unseeded Vapor Growth (VUVG). Place poly-ingot in closed quartz ampoule under excess Te/Cd vapor for Vapor Transport (VT) conversion to single crystal.

CDTE-0024a
ETCH NAME:
TYPE: Electrolytic, oxidation
COMPOSITION:
x .... 1 *N* KOH
x .... MeOH
+ .... light
TIME:
TEMP:
ANODE: CdTe
CATHODE:
POWER: 1 mA/cm²
DISCUSSION:

CdTe, (111) and other orientations. Wafers used in a study of anodic oxidation. After etch cleaning wafers in H_2SO_4:$K_2Cr_2O_7$, evaporate gold on wafer back prior to anodic oxidation, shown above. Then evaporate nickel as for gated FET type devices. Voltage anneal with a potential drop across wafer.
REF: Talasek, R T & Syooaios, A J — *J Electrochem Soc*, 132,887(1985)
CDTE-0024a:

CdTe, (111) wafers, and other orientations, used in a study of anodic oxidation.

CADMIUM MERCURIC TELLURIDE ETCHANTS

CDHT-0001
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HCl
6 .... HNO_3
TIME:
TEMP:
DISCUSSION:

CdTe:HgTe specimens. Solution used as a polish etch on this material. After etching, rinse in 1HCl:1MeOH.
REF: Gatos, H C & Lavine, M C — *Prog Semicond*, 9,1(1965)
CDHT-0002: Agajanian, A H — *Solid State Technol*, 16,73(1973)

$Cd_{1-x}Hg_xTe$ specimens. Reference has additional etch solutions for this compound.
CDHT-0003: Agajanian, A H — *Solid State Technol*, 18,61(1975)

$Cd_{1-x}Hg_xTe$ specimens. Reference for additional etch solutions for this material.
CDHT-0004: Agajanian, A H — *Solid State Technol*, 20,36(1977)

$Cd_{1-x}Hg_xTe$ specimens. Reference for additional etch solutions for this material.

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PHYSICAL PROPERTIES OF CALCIUM, Ca

Classification	Alkaline metal
Atomic number	20
Atomic weight	40.08
Melting point (°C)	845
Boiling point (°C)	1420 (1487)
Density (g/cm^3)	1.55
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.3
Specific heat (cal/g) 25°C	0.149
Latent heat of fusion (cal/g)	52
Heat of vaporization (cal/g)	1000
Atomic volume (W/D)	29.9
1st ionization energy (K-cal/g-mole)	141
1st ionization potential (eV)	6.11
Electron work function (eV)	2.706
Electronegativity (Pauling's)	1.0
Covalent radius (angstroms)	1.74
Ionic radius (angstroms)	0.99 (Ca^{+2})
Linear coefficient of thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	22.3
Electrical conductance (micro-$ohms^{-1}$)	0.218
Electrical resistivity ($\times 10^{-6}$ ohms cm) 0°C	3.91
Modulus of elasticity (psi $\times 10^6$)	3.2—3.8
Tensile strength (psi)	6900
Cross section (barns)	0.43
Vapor pressure (°C)	1207
Hardness (Mohs — scratch)	1.5—2
(Brinnel — kfg/mm^2)	16—18
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Silver-white
Cleavage (cubic)	(001)

CALCIUM, Ca

General: Does not occur as a free element in nature but is widely distributed in carbonate minerals — calcite, $CaCO_3$ and aragonite, $CaCO_3$ as the primary single crystals — in massive form as chalk, limestone, dolomite (containing magnesium and calcium), marl. sea shells. As a calcium sulfate, the minerals gypsum, $CaSO_4.2H_2O$ and the dehydrated anhydrite, $CaSO_4$. The sulfates are known as Plaster of Paris. The name — calcium — is from Latin calx = lime, hence the name for limestone. Both calcium carbonate and calcium hydroxide occur in natural ground waters and produce "hard" water. Calcium oxide, CaO, is "quick-lime" and, as slack lime, $Ca(OH)_2$. Lime as mortar was in use by the Romans in the 1st century A.D. and a wall fresco has been discovered in Asia Minor dated to about 1600 B.C. Fluorite, CaF_2, and the phosphate apatite are of importance.

Calcium is the fifth element in abundance and, in addition to its occurrence in inorganic minerals, is found in leaves, teeth, and bones, such that it is an essential ingredient for mammillary growth. Both calcium and phosphorus are supplied by milk.

Metallic calcium is silver-white in color although it turns yellowish when exposed to air as it reacts with nitrogen. It will burn if heated in air, is electropositive like alkali metals, and is used as a deoxidizer in metal alloys and steel. In its oxide, sulfate, carbonate, and fluoride forms it is used as mortar, cement, plaster, as a flux in glass and metals, in paper making, sugar refining, water purification, and in agriculture to neutralize acid soil. When

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limestone is pressurized and heated, the natural metamorphic process, it becomes marble. Both materials have been used since ancient times for construction, objets d'art, or utensils, such as plates and drinking cups. Alabaster is a pure white form of marble, and there are both marbles and limestones that are color banded. The limestone called onyx is black, and there are many other limestone forms and names.

Both natural calcium, derived from the carbonates, and organic calcium, derived from seashells, are used medicinally in pill form for human consumption. As a dry powder both calcium and magnesium are available in the chemical laboratory and, when mixed as a paste, can be applied to the skin to neutralize acid burns.

Technical Application: Metallic calcium is not used in Solid State processing to any extent, though it may be an element in tungstates, molybdates, and garnets that are artificially fabricated. It has been grown as the nitride, Ca_2N_3.

Etching: Deliquesces in water to the hydroxide. Soluble in acids; slowly soluble in alcohols.

CALCIUM ETCHANTS

CA-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
Ca specimens. Solution used in the general study of the metal. Process and hold under argon to prevent reaction with air (nitrogen).
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1947, 395

CA-0001b
ETCH NAME: Air
TYPE: Gas, reactive
TIME:
TEMP: RT to hot
COMPOSITION:
x .... air
DISCUSSION:
Ca, as pure metal specimens. Reacted in air to develop a yellowish, stable coating of the oxynitride, $Ca_2N_3O_x$. See CAN-0001 for the pure nitride formation.
REF: Ibid.

CA-0001c
ETCH NAME: Water
TYPE: Acid, reactive
TIME:
TEMP: RT to hot
COMPOSITION:
x .... H_2O
DISCUSSION:
Ca metal. Reacted in water to produce the hydroxide, $Ca(OH)_2$, called "slacklime". When "lime" (CaO) is reacted with water, it is called "quicklime". Both limes, mixed with gypsum and clay, are cement.
REF: Ibid.

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CA-0001d
ETCH NAME: Sulfur
TYPE: Metal, reactive
COMPOSITION:
x .... S
DISCUSSION:
Ca metal. Powdered and mixed with sulfur to form anhydrite, then water added to form gypsum as Plaster of Paris, $CaSO_4.nH_2O$. It is still used for plaster body casts; major use is in construction as general plaster, plaster wallboard; for holding small stones in mineral cutting; shaped as objets d'art.
REF: Ibid.

TIME:
TEMP: Hot

PHYSICAL PROPERTIES OF CALCIUM CARBONATE, $CaCO_3$

Classification	Carbonate
Atomic numbers	20, 6 & 8
Atomic weight	100
Melting point (°C)	1339
Boiling point (°C)	898.6
Density (g/cm^3)	1.71
Refractive index (n=)	w = 1.65849; e = 1.48625
Hardness (Mohs — scratch)	3
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Clear/white
Cleavage (rhomb — perfect)	$(10\bar{1}1)$

CALCIUM CARBONATE, $CaCO_3$

General: There are two primary natural minerals — calcite and aragonite — both representative of a group of minerals with the general formula MCO_3. The Calcite Group is hexagonal-rhombohedral in structure with M = Ca, Mg, Fe, Mn, Zn, and Co. The Aragonite Group is orthorhombic in structure with M = Ca, Ba, Sr, and Pb. Within each group the minerals are isomorphous, giving rise to a wide variety of subspecies.

Calcite is the more stable of these two calcium carbonates and is discussed here. Common name: Iceland Spar. It has perfect (1011) rhombic cleavage, though twinning is common and forms a bi-crystal with c(0001) as a common vertical axial plane. When pure, it is transparent and clear, although it may have pale shades of red, green, blue, yellow, etc. As a transparent, flat-faced rhomb, the single crystal acts as a lens, but is more common in compact masses (chalk) or limestone, or as stalactites, stalagmites, and nodular forms, such as are found in caves or around geysers. It is one of the most widely distributed minerals even as a small fraction in volcanic rocks ("snowflake" obsidian — natural glass containing "flowers" of calcite). Common and widespread in sedimentary rocks of varied character — as vein cement — to massive formations of chalk and limestone. Under pressure and heat, metamorphic compaction, it is marble. It is deposited from lime-bearing waters, the carbonates, vs. siliceous-bearing waters that form the silicates. Also found as calc-sinter or travertine around hot springs and as calcareous rock from sea life shells (organic derivation). Formation temperature varies from about 90°C (springs/caves) to 800—900°C (volcanic).

Calcium carbonates have wide industrial use in the manufacture of mortars and cements; as a building and ornamental material; as a flux in metallurgy; as blackboard "chalk" in glass (soda-lime); in fertilizers, animal feed; and in paint as whitewash. For human consumption it is a de-acidifier as aspirin, Maalox and, in paste form, used to neutralize acids burns (also magnesia — the mineral magnesite, $MgCO_3$ — a member of the Calcite Group).

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As a single crystal, due to its high birefringence, it is used as a polarizing prism in microscopes and should be handled carefully to prevent scratch damage.

Technical Application: No current use in Solid State processing and fabrication though it is under evaluation as a cleaved substrate for thin film metal evaporation and semiconductor epitaxy growth morphology studies, similar to the present uses of sodium chlorides, NaCl.

As a constituent in glass — soda-lime — this glass is the primary type used to fabricate photo resist glass masks. As a constituent in alloy fluxes, it is used in some solder applications for device assemblies. Both calcium and magnesium are kept in chemical laboratories for neutralization of acid burns as already mentioned.

Natural single crystals have been extensively studied for their optical characteristics.

Etching: Soluble in HCl with effervescence, other acids, and slightly soluble in water.

CALCIUM CARBONATE ETCHANTS

CAC-0001
ETCH NAME: Hydrochloric acid — TIME: 5—10 sec
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

$CaCO_3$ $(10\bar{1}1)$ cleaved substrates from natural "Iceland Spar". Specimens were used in a study of surface energies of calcite. After cleaving, surfaces were etch polished and rinsed in alcohol. Solution shown used as a rapid polish with effervescence of the material.
REF: Gilman, J J — *J Appl Phys*, 31,2208(1960)

CAC-0002
ETCH NAME: Hydrochloric acid, dilute — TIME: Variable
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
1 .... HCl
10 .... H_2O
DISCUSSION:

$CaCO_3$, as polarizing prisms. Solution used to lap/polish remove scratches from microscope prisms using a felt pad. Also to clean marble surfaces.
REF: Walker, P — personal application, 1952
CAC-0005: Gross, K A — *Phil Mag*, 12,801(1965)

$CaCO_3$, $(10\bar{1}1)$ cleaved wafers used in an energy study of deformed and annealed natural calcite using X-ray techniques. A 10% HCl solution was used to polish surfaces.

CAC-0003a
ETCH NAME: Nitric acid, dilute — TIME: 90 sec
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
1 .... HNO_3
x .... H_2O
DISCUSSION:

$CaCO_3$, r$(10\bar{1}1)$ cleaved wafers and other orientations. A study of dislocations and plastic deformation evaluating a number of acids. Alkalies are too slow at room temperature and mineral acids show an excessive rate of attack with CO_2 evolution. Weak acids with an inert carrying liquid are best. If a dislocation moves away from the original etch pit due to stress,

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the pit becomes flat-bottomed and, with further etching, a sharp-bottomed pit will appear at the new dislocation point. (*Note:* A very fine article with excellent pictures.)
REF: Keith, R E & Gilman, J J — *Acta Metall,* 9,1(1961)

CAC-0003b
ETCH NAME: Formic acid
TYPE: Acid, dislocation
COMPOSITION:
x .... HCOOH (90%)
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.
CAC-0004: Keith, R E & Gliman, J J — *Acta Metall,* 8,1(1960)
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers used in a dislocation pit etch development study. Formic acid gave best results with only one type pit.

TIME: 15 sec
TEMP: RT

CAC-0003b.1
ETCH NAME: Formic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... HCOOH (90%)
1 .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.

TIME: 5 sec
TEMP: RT

CAC-0003b.2
ETCH NAME: Formic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... HCOOH (90%)
10 .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0333a.
REF: Ibid.

TIME: $1^1/_2$ sec
TEMP: RT

CAC-0003b.3
ETCH NAME: Formic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... HCOOH (90%)
1 .... EOH
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.

TIME: 45 sec
TEMP: RT

CAC-0003b.4
ETCH NAME: Formic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... HCOOH (90%)
1 .... glycerin

TIME: 90 sec
TEMP: RT

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DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.

CAC-0003c.1
ETCH NAME: Glacial acetic acid
TYPE: Acid, dislocation
COMPOSITION:
x .... CH_3COOH (HAc)
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.
TIME: 360 sec
TEMP: RT

CAC-0003c.2
ETCH NAME: Acetic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... CH_3COOH (HAc)
1 .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.
TIME: 75 sec
TEMP: RT

CAC-0003c.3
ETCH NAME: Acetic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... CH_3COOH (HAc)
10 .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.
TIME: 30 sec
TEMP: RT

CAC-0003d
ETCH NAME: Propionic acid
TYPE: Acid, cleaning
COMPOSITION:
x .... CH_3CH_2COOH
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. Solution showed no attack in 6 min, but did give some cleaning action. See CAC-0003a.
REF: Ibid.
TIME: 6 min
TEMP: RT

CAC-0003d.1
ETCH NAME: Propionic acid, dilute
TYPE: Acid, dislocation
COMPOSITION:
1 .... CH_3CH_2COOH
1 .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.
TIME: 120 sec
TEMP: RT

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CAC-0003e
ETCH NAME: Lactic acid — TIME: 15 sec
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
x .... $CH_3CHOHCOOH$ (85%)
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. CAC-0003a.
REF: Ibid.

CAC-0003f
ETCH NAME: Maleic acid — TIME: 10 sec
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
x .... HOOCCH:CHCOOH, sat. sol.
x .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. See CAC-0003a.
REF: Ibid.

CAC-0003g
ETCH NAME: Tartaric acid — TIME: 10 sec
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
x .... $HOOC(CHOH)_2COOH$, sat. sol.
x .... H_2O
DISCUSSION:
$CaCO_3$, r(10$\bar{1}$1) cleaved wafers. Developed dislocations with a fresh solution. Used after 2 months, there was no reaction. See CAC-0003a.
REF: Ibid.

CAC-0003h
ETCH NAME: EDTA — TIME:
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
x .... $(HOOC\text{-}CH_2)2NCH_2CH_2$
DISCUSSION:
$CaCO_3$, (10$\bar{1}$1) cleaved wafers. There was no reaction with this solution. Also no pit forming reaction with oxalic acid. See CAC-0003a.
REF: Ibid.
CAC-0014: Keith, R E & Gilman, J J — *Acta Metall*, 8,1(1960)
$CaCO_3$, (10$\bar{1}$1) cleaved wafers used in a dislocation pit etch development study. Formic acid gave best results producing only one type pit.

PHYSICAL PROPERTIES OF CALCIUM FLUORIDE, CaF_2

Classification	Fluoride
Atomic numbers	20 & 9
Atomic weight	76.08
Melting point (°C)	1360
Boiling point (°C)	
Density (g/cm^3)	3.18 (3.01—3.25)

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Refractive index (n =)	1.4339
Hardness (Mohs — scratch)	4
(Knoop — kgf mm^{-2})	163
Ionic radius (angstroms)	1.06
Surface free energy (ergs cm^{-2}) −273°C	543 (111)
−195°C	450 (111)
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Yellow-green/variable
Cleavage (octahedral-distinct)	o(111)

CALCIUM FLUORIDE, CaF_2

General: Occurs as the mineral fluorite, is fairly common, and found as a vein deposit, alone, or with silver, zinc, etc. Like diamond, it is one of the few minerals with distinctive (111) cleavage, even though it is in the normal class of the isometric system, where most materials shown cubic (001) cleavage. It is noted for its wide range of colors that can vary within a crystal, or be banded. Colors can be altered by heat, X-rays, UV light, pressure, etc., and may show blue fluorescence.

It was in use as a solder flux before the discovery of fluorine, and is the major ore for fluorine, used in the making of hydrogen fluoride (HF), e.g., hydrofluoric acid. Fluorite as a powder has major use in making opalescent glass and enamel, such as for cookware. It is used in jewelry making for its colors, even though the mineral is relatively soft.

Technical Application: There is no direct use in Solid State device fabrication, although it is under evaluation as a surface coating for its optical properties. It is used as a microscope prism for its high birefringence, and has applications as a filter element or as lenses. There is still use of the powdered material as a solder flux in package fabrication.

Fluorite has been widely studied as the natural single crystal due to its transparency for observing the physical, electrical, and electronic effects of various treatments, such as X-ray, pressure, etc., already mentioned in the proceeding General section.

Etching: Slow in acids, water — easily in ammonium salts.

CALCIUM FLUORIDE ETCHANTS

CAF-0001
ETCH NAME: Water — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:

CaF_2, (100) thin films deposited on GaAs, (100) substrates. After deposition, wafers were photolithographically processed for an open square pattern, then E-beam annealed. After annealing, water was used to wash away the CaF_2 thin films. Also processed SrF_2 (SRF-0001) with dilute HCl used to wash-away the strontium compound.
REF: Sullivan, P W — *J Vac Sci Technol*, B2,202(1984)
CAF-0004: Tu, C W — *J Vac Sci Technol*, B2,24(1984)

CaF_2, (100) and (110) thin films deposited on InP substrates of similar orientation. Thin films were grown by MBE, including SrF_2, BF_2, and $Ba_xSr_{1-x}F_2$ co-deposited from the two compounds. Water used to wash away CaF_2; dilute HCl for SrF_2; HF for BaF_2 and the mixed compound.

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CAF-0002
ETCH NAME: Sulfamic acid
TYPE: Acid, dislocation
COMPOSITION:
6 g .... H_2NSO_3H
100 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
CaF_2, (111) cleaved wafers used in a dislocation study. Specimens were studied as-cleaved without further surface conditioning prior to preferential etching in the solution shown.
REF: Steijn, R P — *J Appl Phys*, 34,419(1964)

CAF-0003
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... EOH
TIME: 5 min
TEMP: RT
DISCUSSION:
CaF_2, (100) cleaved wafers. Both natural fluorite and artificially grown material were used in an X-ray reflection study. Specimens prepared by immersion in alcohol with light scrubbing on surfaces using a cotton swab during the cleaning period.
REF: Barton, V P — *Acta Crystallogr*, 11,848(1958)
CAF-0008: Walker, P et al — personal application, 1968
CaF_2, natural octahedral, (111) crystals prepared for light irradiation study. Specimens polished on a Buehler metallographic wheel at high rpm with a pellon-type pad soaked with alcohol. Intense light of different frequencies colors used to develop internal defect. Similar light frequency effects evaluated on alpha-quartz radio frequency blanks. Artificial material fabricated as lenses was wash-cleaned in alcohols prior to metallization with Au:Cr thin films.

CAF-0005
ETCH NAME: Nitric acid
TYPE: Acid, preferential
COMPOSITION:
x .... 0.2 *N* HNO_3
TIME:
TEMP:
DISCUSSION:
CaF_2, (111) cleaved wafers used in a study of cleavage and dislocation pits as compared to diamonds. Solution shown developed trigon pits like those on natural diamond faces, but no etch would artificially develop similar pits on diamond. The CaF_2 was difficult to cleave on (111).
REF: Patel, A R et al — *Phil Mag*, 9,951(1964)
CAF-0007: Amelinck, S et al — *Physica*, 23,270(1975)
CaF_2, (111) oriented wafers used in a study of etch pits. Pits can occurs on natural fluorite faces under normal growth conditions, and can appear on both natural and artificially grown material cleaved surfaces without etching.

CAF-0006a
ETCH NAME: Ammonia
TYPE: Base, polish
COMPOSITION:
x .... NH_3
TIME: Seconds
TEMP: RT

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DISCUSSION:

CaF_2 as natural fluorite crystals as octahedron, (111) solid forms. Solution used to clean and polish (111) faces of bulk crystals. As (111) cleaved sections, solution used to polish thin specimens for microscope study.

REF: Walker, P — mineralogy study, 1952

CAF-0006b

ETCH NAME: Ammonium hydroxide — TIME: Seconds

TYPE: Base, cleaning — TEMP: RT

COMPOSITION:

x .... NH_4OH

DISCUSSION:

CaF_2 specimens as artificially grown and cut lenses. Specimen surfaces were lightly polish cleaned by hand lap on a hard felt surface saturated with the solution prior to vacuum metallization with Au/Cr thin films. Water wash and nitrogen blow dry after cleaning.

REF: Walker, P — personal application, 1975

CAF-0009

ETCH NAME: Sulfuric acid — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

x .... H_2SO_4, conc.

DISCUSSION:

CaF_2, (111) wafers cleaved from natural fluorite crystals. Solution developed triangular etch pits with 1:1 correspondence between the opposed positive and negative (111) faces of wafers.

REF: Pandya, N S & Pandya, J K — *Curr Sci*, 27,437(1958)

CALCIUM SILICON FLUORIDE ETCHANTS

CASF-0001

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... HF

x .... HNO_3

DISCUSSION:

$CaSiF_2$ single crystals were used in evaluating cohesive energy features of tetrahedral semiconductors. Forty materials were studied.

REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

CALCIUM TIN FLUORIDE ETCHANTS

CATF-0001

ETCH NAME: Ammonium hydroxide — TIME:

TYPE: Base, removal/cleaning — TEMP:

COMPOSITION:

x .... NH_4OH

DISCUSSION:

$CaSnF_2$ deposited as a thin film in forming a semiconductor-dielectric-semiconductor

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(SIS) structure. Compound referred to as a spinel, deposited as a Ge/$CaSnF_2$ multifilm structure on silicon (111) substrates.
REF: Tu, G W et al — *J Vac Sci Technol*, B2,212(1984)

PHYSICAL PROPERTIES OF CALCIUM MOLYBDATE, $CaMoO_4$

Classification	Oxide
Atomic numbers	20, 42, & 8
Atomic weight	200
Melting point (°C)	1200
Boiling point (°C)	
Density (g/cm^3)	4.35
Refractive index (n=)	1.974—1.984
Hardness (Mohs — scratch)	3—3.5
Crystal structure (tetragonal — normal)	(111) pyramid
Color (solid)	Yellowish
Cleavage (basal)	(001)

CALCIUM MOLYBDATE, $CaMoO_4$

General: Does not occur as a pure compound, but the mineral powellite, $Ca(W,Mo)O_4$ is found as a mixed element compound with about 10% $CaWO_4$. The pure molybdate has been referred to as powellite in the literature.

The pure compound can be made by roasting molybdenite, MoS_2 with coke and lime, the material then used in making other molybdenum compounds. The pure metal is used in fabricating high speed steels, and other compounds in the dyeing of silk or other fabrics.

Technical Application: Both natural and artificial single crystals have been studied for general morphology; electronic and electrical properties; and crystallographic structure changes with pressure and temperature.

Etching: Soluble in acids.

CALCIUM MOLYBDATE ETCHANTS

CAMO-0001
ETCH NAME: Pressure — TIME:
TYPE: Pressure, alternation — TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:
$CaMoO_4$ as single crystals were studied in a high pressure chemistry test of molybdnates and tungstates at about 56 Pa pressure. Other materials evaluated were $CaWO_4$, $PbWO_4$, and $CdMoO_4$. No etch shown, but H_3PO_4 is a general removal solution on tungstates.
REF: Hazen, R M et al — *J Phys Chem Solids*, 46,253(1985)

PHYSICAL PROPERTIES OF CALCIUM NITRIDE, Ca_2N_3

Classification	Nitride
Atomic numbers	20 & 7
Atomic weight	148.26
Melting point (°C)	900
Boiling point (°C)	

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Density (g/cm³)	2.63
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — normal) alpha	(100) cube
(tetragonal — normal) beta	(110) prism
Color (solid)	Brown/black
Cleavage (cubic/basal)	(001)

CALCIUM NITRIDE, Ca_2N_3

General: Does not occur as a natural compound even though there are over 250 calcium minerals as fluorides, sulfides, carbonates, silicates, etc. (Nitrogen alone does not form pure nitride compounds.)

The nitride has no application in industry at present, though several calcium compounds are of importance, such as calcite, $CaCO_3$.

Technical Application: Not used in Solid State processing at present, though it has been grown as a single crystal thin film on calcium substrates in material evaluation. There are possible applications as a dielectric for its optical properties, or as a surface protective coating similar to those of other nitride compounds.

Etching: Soluble in dilute acids.

CALCIUM NITRIDE ETCHANTS

CAN-0001
ETCH NAME: Nitric acid — TIME:
TYPE; Acid, removal — TEMP: RT
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:

Ca_2N_3 thin films deposited on calcium substrates in a study of the use of high purity nitrogen to reduce contamination. Deposited at 600°C, nitride is tetragonal — at 675°C is cubic structure. Also worked with magnesium nitride (MGN-0001), and references work done with lithium nitride (LIN-0001). If O_2 or air is present during deposition in the N_2 atmosphere, white spots of CaO or MgO appear in the otherwise black nitride films.
REF: Aubry, J & Streiff, R — *J Electrochem Soc,* 118,650(1971)

PHYSICAL PROPERTIES OF CALCIUM TUNGSTATE, $CaWO_4$

Classification	Tungstate
Atomic numbers	20, 74, & 8
Atomic weight	289.92
Melting point (°C)	>1200
Boiling point (°C)	
Density (g/cm³)	6.06 (5.9—6.1) R
Refractive index (n=)	1.918—1.934
Crystal structure (tetragonal — pyramidal)	(111) pyramid
Color (solid)	Yellow/brownish
Cleavage (pyramidal — distinct)	p(111)

CALCIUM TUNGSTATE, $CaWO_4$

General: Occurs in nature as the mineral scheelite, $CaWO_4$, which is a major ore of tungsten. The mineral forms under pneumatolytic or hydrothermal conditions in pegamatites,

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or as ore veins in association with granites. It is commonly yellow to brown in color, and fluoresces a bright yellow-white under a black light. Fused with salt of phosphorus it melts to a glass at about 1200°C with a fine blue color.

Industrially it is a major ore of tungsten, and the black light is used during grinding to insure complete segregation of the gangue material. Also used as a fine blue pigment in glass and enamels.

Technical Application: No application in Solid State processing at this time, though it has been grown and studied as a single crystal for defects and general morphology, to include possibly frequency applications.

Etching: Hot H_3PO_4, and mixed acids.

CALCIUM TUNGSTATE ETCHANTS

CAW-0001a
ETCH NAME: Phosphoric acid
TYPE: Acid, removal
TIME:
TEMP: 250°C
COMPOSITION:
x .... H_3PO_4
DISCUSSION:
$CaWO_4$, (001) wafers. Ingots were grown with (100) orientation and wafers were cut as (001) basal orientation. Solution used to remove work damage after mechanical lap and polish.
REF: Lockayne, B — *Phil Mag*, 10,911(1964)

CAW-0001b
ETCH NAME: Aqua regia
TYPE: Acid, preferential
TIME:
TEMP: 55°C
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
$CaWO_4$, (001) wafers used in a study of deformation and slip. Solution used to develop slip patterns and dislocation etch pits.
REF: Ibid.
CAW-0002: Lockayne, B — *Br J Appl Phys*, 16,423(1965)
$CaWO_4$, (001) wafers. Ingots were grown with (100) orientation, and and cut (001) basal as free of low-angle grain boundaries. After mechanical lap, solution used to etch polish and develop dislocation distributions.

CAW-0003a
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: 200°C
RATE: 0.009—0.06 μm/sec
COMPOSITION:
3 .... H_3PO_4
1 .... CrO_3, sat. sol.
DISCUSSION:
$CaWO_4$, (100) wafers. Solution used to etch polish specimens in a study of dislocations.
REF: Ibid.

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CAW-0003b
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
1 .... HF
2 .... CrO_3, sat. sol.
TIME: 2—25 min
TEMP: RT
RATE: .003 μm/sec
DISCUSSION:
$CaWO_4$, (001) wafers. Solution used to develop dislocation pits and pits showed a 1:1 correspondence from positive to negative wafer surfaces.
REF: Ibid.

CAW-0004
ETCH NAME: Phosphoric acid
TYPE: Acid, polish
COMPOSITION:
x .... H_3PO_4, conc.
TIME:
TEMP: Hot
DISCUSSION:
$CaWO_4$, single crystal specimens used in a study of Raman frequency shifts and temperature dependence. Other tungstates studied: $SrWO_4$ and $BaWO_4$.
REF: Degreniers, S et al — *J Phys Chem Solids*, 45,1105(1984)

CAW-0005a
ETCH NAME: Phosphoric acid
TYPE: Acid, polish
COMPOSITION:
x .... H_3PO_4
TIME: 15 min
TEMP: 300°C
DISCUSSION:
$CaWO_4$, single crystal specimens used in a study of plastic deformation. Solution used to remove residual lap damage and polish, though it can be rough if etching is over 15 min. Use a Pt basket to hold specimens, place in acid at RT, then bring up to 300°C boiling point — reduce to 150°C before removal to boiling water quench. If quenched above 150°C, specimen surface cracks.
REF: Arbel, A & Stokes, R J — *J Appl Phys*, 36,1460(1965)

CAW-0005b
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
1 .... H_3PO_4
1 .... NH_4Cl, sat. sol.
2 .... H_2O
TIME: 15—20 min
TEMP: 100°C
DISCUSSION:
$CaWO_4$, single crystal specimens used in a study of plastic deformation. Solution used to develop defects after material stressing. Place specimen in solution at RT, raise to 100°C for etching period, then quench directly into water at RT.
REF: Ibid.

CAW-0006
ETCH NAME:
TYPE: Pressure, alteration
COMPOSITION:
x .... pressure
TIME:
TEMP:

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DISCUSSION:

$CaWO_4$ single crystals used in a high pressure chemistry test of materials above 56 Pa pressure. Both tungstates and molybdates were studied: $PbWO_4$, $CaWO_4$, $PbMO_4$, and $CdMo_4$. $CaWO_4$ noted as the mineral scheelite.

REF: Hazen, R M et al — *J Phys Chem Solids*, 46,253(1985)

PHYSICAL PROPERTIES OF CALIFORNIUM, Cf

Classification	Actinide
Atomic number	98
Atomic weight	251
Melting point (°C)	
Boiling point (°C)	
Density (g/cm^3)	
Ionic radius (angstroms)	0.98 (Cf^{+3})
Half-life (years)	800
Cross section (barns)	3000
Electrochemical equivalents (g/amp-h)	3.1
Valence electron potential (eV)	44.1
Hardness (Mohs — scratch)	3—4
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey
(gas)	Green
Cleavage (cubic)	(001)

CALIFORNIUM, Cf

General: A naturally occurring gas as one of the radioactive decay series. No use in industry at the present time.

Technical Application: No use in Solid State processing to date. It has been studied in solid form.

Etching: Soluble in HCl.

CALIFORNIUM ETCHANTS

CF-0001

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

Cf specimens. Solution used to dissolve the material in a study of the properties of the isotope $^{2}Fm_{52}$ (fermium).

REF: Friedman, A M et al — *Phys Rev*, 101,1472(1956)

CARBIDES, M_xC

General: There is only one known occurrence of a carbide mineral in nature — the mineral moissanite, CSi, found as small green hexagonal platelet in the meteoric iron from Cañon Diablo, Arizona — though the material was originally produced as artificial carborundum, SiC.

Both carbides and borides are part of the ceramic industry of today, though the ancient pottery industry is still referred to as "ceramic pottery" where silicate glaze (SiO_2) with or

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without mineral additives for color as enamels have been in use since about 3500 B.C. when the Egyptians first developed soda-lime glass. There are many industrial applications for the high temperature ceramics, such as for furnace lining fire-bricks, crucibles, and, when mixed with carbon, for radiation resistant materials used in atomic nuclear equipment construction. Ceramics also have been called "Cermets". See General discussion under Ceramics, this chapter, for further discussion.

Technical Application: Several carbides are used as a ceramic in Solid State processing as circuit substrates, in package construction, or as electrical stand-off insulators. As an active discrete device, they are designed as resistors and capacitors, or may be co-deposited as a planar type dielectric in a substrate circuit.

Silicon carbide, SiC, when boron doped, is a semiconductor capable of operating as a diode above 500°C. Boron nitride and diamond also show semiconducting characteristics at elevated temperatures.

The individual carbides are not listed, here, as several are of sufficient importance as both ceramics and dielectrics that they are under their own listed sections following their parent metals. See the Material Index for numbers. Borides are as a collective listed heading. Also see aluminum oxide, Al_2O_3; silicon dioxide, SiO_2; and boron nitride, BN. Many of these compounds are used as ceramics or as dielectrics.

Etching: Difficult. See separate compounds for solutions.

PHYSICAL PROPERTIES OF CARBON, C

Classification	Ceramic
Atomic number	6
Atomic weight	12.01
Melting point (°C)	3727 (3550)
Boiling point (°C)	4830 (4827)
Density (g/cm^3)	2.26 (2.09—2.23)
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.057
Specific heat (cal/g) 25°C	0.165
Heat of vaporization (k-cal/g-atom)	171.7
Atomic volume (W/D)	5.3
1st ionization energy (K-cal/g-mole)	260
1st ionization potential (eV)	11.264
Electronegativity (Pauling's)	2.5
Covalent radius (angstroms)	0.77
Ionic radius (angstroms)	0.16 (C^{+4})
Coefficient of thermal linear expansion ($\times 10^{-6}$ cm/cm/°C) 20°C ($K^{-1} \times 10^{-6}$)	0.6—4.3
	3.0
Electron work function (eV)	4.82
Cross section (barns)	0.0034
Vapor pressure (°C)	4373
Electricity resistivity ($\times 10^{-6}$ ohms cm) 0°C	1375
Bond dissociation energy (kJ mol-1)	606
Cohesive energy (kJ mol-1)	713
Tensile strength (kgf cm-2 $\times 10^{-4}$)	7.7
Thermal endurance coefficient [F(cmK min$^{-1/2}$ $\times 10^{-4}$)]	2.04
Relative F match	52

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Hardness (Mohs — scratch) carbon (hard)	6—7
graphite, natural	1—2
(Vicker's — kgf mm_2) — carbon (vitreous)	2200—2859
(Scleroscope — pressure strike)	10—100
(Shore-ball bounce) — carbon (vitreous)	120—150
Crystal structure (hexagonal — rhombohedral)	(0001) plates 6-sided
Color (solid/powder)	Coal black
Cleavage (basal — perfect)	(0001)

CARBON, C

General: Occurs in nature as the mineral graphite, C, (plumbago, black lead). Industrially called carbon, the high pressure form is diamond. Carbon can be recognized by its extreme softness, greasy feeling, black color and metallic luster. The two terms are interchangeable — graphite or carbon. It is the "lead" in pencils as it was first thought to be a form of lead (Pb). It is in the hexagonal system crystallographically like micas with the prominent basal (0001) cleavage known as micaceous cleavage, which is more apparent in graphite than in artificially grown carbons. The monolayer hexagonal planes contain the atomic "benzene ring" structure with strong binding energy within the monolayer, but weak binding energy between monolayers. In natural graphite these benzene-type carbon rings are vertically aligned directly above each other from layer to layer; whereas in carbon the rings are offset between alternate monolayers. Because of this structure variation many types of carbon materials can be artificially fabricated, often constructed to improve the binding energy between monolayers. In fabrication at 500°C, grain spacing is 10—20 Å, whereas at 2500—3000°C, 70—1000 Å spacing. Further, with controlled granular structure, the material can be cut parallel or perpendicular to grain orientations, thus producing different characteristics.

In addition to being mined as natural graphite, carbon is obtained from petroleum, natural asphalt and tar; from coal — anthracite (hard), and bituminous (soft); from natural gases, such as methane; and from the burning of vegetation. When partially fired to remove water vapor and gaseous impurities, but below the ignition point, it is called "coke", hardwoods similarly processed as charcoal. The charcoal burners of ancient times were a race among themselves, processing hardwood trees as a coke-type fuel for the metals and glass industries, as well as for cooking fires throughout Europe, the Middle East, and Asia. Cooking was being done prior to 1350 B.C. (Iron Age) for the smelting of bronze and today coke is a primary fuel in the fabrication and processing of steels. As lampblack, a near-liquid by-product of oil, or as finely divided carbon powder down to colloidal structure, it is a black pigment for glass, enamels, cement, etc. It also is still the black "lead" in pencils, the term "lead" being a misnomer, as it is graphite or carbon, not lead.

In addition to its use as a fuel or additive to metal products, carbon parts have many industrial uses for its high temperature, and both electrical and heat transfer capabilities. It is extremely inert to chemical attack and, coupled with its high temperature capability, is used as a crucible for processing liquid metals, such as in semiconductor ingot growth pots, as a metal evaporation crucible, or as crucibles in heavy metal processing. For its heat transfer capabilities and as a bulk item, it is used as graphite susceptor plates, alone, or SiC coated in epitaxy systems; as heater strips for alloying parts, or disassembly and recovering of rejected parts; as furnace linings and heater rods or furnace tubes, and as boats, flats, etc., as holding vehicles for parts in alloy furnaces.

As a wire it was one of the first light bulb filaments — is still so used in special applications — or wires can be embedded in glass or plastics as a heater grid, and are used as automotive ignition wires for spark plugs. As a pair of rods, it is used for spark gap welding or vaporizing a metal surface for spectrographic analysis of elements. Also as rods, due to its low neutron cross-section, carbons are the damping rods in atomic piles in nuclear energy plants. As powder, in addition to being a pigment, it is used as a dry lubricant like

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molybdenum sulfides and, sprayed on glass or plastic, acts as a sunscreen. As a powdered mixture in alcohol (Aqua Dag is one commercial product) it is used as a spray or paint-on vehicle on metal surfaces as the replication technique: after drying, the carbon thin film can be removed for microscope study or, coated with thin film gold for reflectivity, for a scanning electron microscope (SEM) study. The dry powder has been brushed on preferentially etched surfaces to enhance defects for microscope examination, as has magnetite and barium titanate. The latter include magnetization of the particles in surface studies of barium titanate, or magnetic nickels, irons, etc.

Although this book is concerned with inorganic materials, carbon is a major element in organic chemistry — C, H, O, N — the four elements of our carbon-base life forms . . . humans, animals, and vegetation. There are thousands of chemicals, solvents, and gases containing these elements involved in both organic chemistry and medicine.

Technical Application: Although carbon alone is not used to any extent in Solid State device fabrication at present, it is under development as a thin film colloid (c-C) or amorphous (a-C) deposited structure, as grown by CVD methods using a variety of sources for the carbon, such as carbon tetrachloride, CCl_4, benzene, C_6H_6, and other such compounds. Deposition is between 400 to 600°C and, with subsequent temperature annealing, the carbon films are being converted to a crystalline diamond-like carbon (DLC) film; also referred to by the acronym i-C. Additional laser anneal has been used to increase the size of crystallites and, eventually, it is hoped to achieve a complete single crystal diamond structure. As diamond it is the hardest of known substances and is chemically inert, it has tremendous applications as a thin film surface coating, in addition to the diamond semiconducting characteristics.

Carbon thin films also are deposited on silicon, Si, wafers for the fabrication of thin film silicon carbide, SiC. See Silicon Carbide section for additional discussion. There are carbon composite materials in use or under development in both the industrial and Solid State areas as parts and device structures. See sections on carbides, graphite, and diamond.

Etching: Acid resistant to most chemicals under normal conditions. Dissolves in boiling HNO_3, KOH, H_2SO_4, H_3PO_4, and in molten fluxes of alkalies and metals.

CARBON ETCHANTS

C-0001a
ETCH NAME: Potassium hydroxide
TYPE: Molten flux, removal
TIME:
TEMP: 350°C
COMPOSITION:
x .... KOH (NaOH)
DISCUSSION:
C, as bulk graphite or thin film deposit. Molten flux of alkalies will attack carbon and graphite, and may be slightly preferential.
REF: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices,* Reinhold, New York, 1967

C-0001b
ETCH NAME: Potassium hydroxide
TYPE: Alkali, removal
TIME:
TEMP: Boiling
COMPOSITION:
x .... 50% KOH (NaOH)
DISCUSSION:
C, as bulk graphite or thin film deposit. Hot, concentrated solutions of alkalies will dissolve graphite and carbon.
REF: Ibid.

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C-0001c
ETCH NAME: Nitric acid
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
C, as bulk graphite or thin film deposit. Nitric acid will dissolve graphite or carbon forming mellitic acid, hydrocyanic acid or $CO_2 + N_2O$, depending upon etching conditions.
REF: Ibid.
C-0002a: Bulletin CD-101-5M-SC-282, Stackpole Corp., 1982
C, as graphite or carbon specimens. Nitric acid will dissolve material and produce mellitic acid, hydrocyanic acid with both CO_2 and NO.

C-0001d
ETCH NAME:
TYPE: Acid, reduction
TIME:
TEMP:
COMPOSITION:
20 ml .... HNO_3
40 ml .... H_2SO_4
20 g .... $KClO_4$
DISCUSSION:
C, as bulk graphite or thin film deposit. This solution volume will dissolve one gram of carbon forming graphitic acid.
REF: Ibid.

C-0002b
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
TIME:
TEMP: Boiling
COMPOSITION:
x ... H_2SO_4, conc.
DISCUSSION:
C, as both carbon and graphite parts. Solution will form mellitic acid or benzene pentacarboxylic acid with CO_2 and SO_2.
REF: Ibid.
C-0006a: Halbert, M L et al — *Phys Rev,* 106,251(1957)
C, specimens used in a study of neutron-transfer reactions by nitrogen ion bombardment. Carbon was etched in "fuming" sulfuric acid. (*Note:* Only reference to sulfuric acid as "fuming".)

C-0003
ETCH NAME: Phosphoric acid
TYPE: Acid, polish
TIME:
TEMP: 240°C
composition:
x .... H_3PO_4, conc.
DISCUSSION:
C, as natural graphite, cleaved as (0001) basal specimens and studied for magnetic domains. Mechanical polish with carborundum paste (SiC), then with 8 μm diamond paste. Use silica crucible to hold specimens during etching to reduce thickness. Solution also used to etch thin and to pinhole specimens for electron microscope (EM) study. (*Note:* Material was called "plumbite", which is a common name for graphite, e.g., plumbago.)
REF: Grundy, P J — *Br J Appl Phys,* 16,409(1965)

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C-0004
ETCH NAME: Argon
TYPE: Ionized gas, preferential
COMPOSITION:
x .... Ar^+ ions

TIME: 15 min
TEMP:
GAS: Argon
PRESSURE:
POWER:

DISCUSSION:
C, (0001) cleaved pyrolytic graphite specimens. Argon ionic bombardment produces conical etch pits.
REF: Tarpinian, A & Gaza, G E — *J Appl Phys*, 31,1657(1960)

C-0005
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O

TIME:
TEMP: RT

DISCUSSION:
C, as thin films deposits on Si, SiO_2, Al, Al_2O_3, KBr, NaCl, ZnMn, GaAs and InP. Deposition was by RF Plasma using butane, C_4H_{10}, with the glow discharge from ultra-pure carbon electrodes. Growth rate: 8—360 Å/min. Film was transparent and amorphous in structure. Water used to wash and clean surfaces to observe hydrophobic/hydrophilic reaction. Film referred to as a diamond-like carbon (DLC) film.
REF: Zelez, J — *RCA Rev*, 43,665(1982)

C-0006b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... H_3PO_4
x .... CrO_3
x .... NaCN

TIME:
TEMP:

DISCUSSION:
C specimens. Solution described as a general etch for carbon. Other chromates can be used, and NaCN added for an equivalent 1 ml of NH_4.
REF: Ibid.

C-0007a
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
50 ml .... HF
150 ml .... HNO_3
100 ml .... CH_3COOH (HAc)

TIME: 1—3 min
TEMP: RT

DISCUSSION:
C, as epitaxy reactor plates and susceptors, or for Silox system deposition of SiO_2 thin films. Graphite susceptors used in metallic compound growth, such as silicon on silicon, gallium arsenide, indium antimonide, etc. They may be plain graphite or coated with silicon carbide. The solution shown is used to etch clean plate surfaces to remove silicon and/or silica growth. Heavily water wash after acid cleaning and wipe dry with toweling; then vacuum oven bake at 130°C and 10^{-3} Torr pressure overnight. **CAUTION:** Where phos-

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phorus gases have been used as a dopant during silicon growth, it can ignite under liquid during cleaning.
REF: Walker, P et al — personal application, 1970—1975

C-0007b
ETCH NAME: Hydrogen/chlorine
TYPE: Gas, cleaning
COMPOSITION:
(1) x .... H_2 (2) x .... HCl, vapor
TIME: 1—3 min
TEMP: 1100°C
DISCUSSION:

C, as epitaxy reactor susceptor plates for Si/Si(111) epitaxy growth. Susceptors with or without SiC coating. The hot hydrogen in reactor system used to clean graphite surfaces prior to introduction of HCl vapors for additional cleaning.
REF: Ibid.
C-0007c: Ibid.

C, as furnace alloy boats and disc parts. Lightly lap parts on Whattman filter paper to clean, then fire through belt furnace in forming gas (85% N_2:15% H_2) at 450°C prior to using newly fabricated parts, or after cleaning old boats and discs. Firing can be done in a hydrogen humpback furnace.

C-0008
ETCH NAME: Carbonization
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP: Elevated
DISCUSSION:

C, as a wood product by charring. Hard woods are partly burned to remove volatiles, the resultant material called charcoal. When natural coal is so processed, it is called "coke". Charcoal has been a fuel for glass and metal fabrication since ancient times, and also is used as a cooking fuel. Coke is widely used in metal processing industries today, as a primary fuel such as for steel manufacture.

In the fractionation of petroleum, the pure carbon fraction is called lampblack and used as a black pigment. Metal surfaces are carbonized with hot CO_2 treatment for hardening and when carbon is added to iron it becomes steel. The carbonization process has been a fundamental step in the manufacture of irons and steels since early times. Two notable steels are Damascus and Toledo steel, both were widely used during the Middle Ages in Europe.

In Solid State processing of epoxies and polyimides used for electrical contact, one method of removal is to heat to the char-point with subsequent scrape-off. Carbon thin films are deposited and, with either heat treatment or laser annealing, converted to diamond-like carbon (DLC). Carbon in an alcohol solution is painted onto material surfaces, hardened by evaporation removal of the alcohol carrier, the resultant film used for surface replication. Molasses has been used as an etching solution constituent on quartz frequency crystal blanks, but can leave carbon flakes on surfaces after vacuum metallization. Carbon powder has been brushed onto material surfaces to enhance surface defects and structure for microscope study.

There are several major products uses for carbon, such as electrical ignition wires; damping rods in atomic reactors; as an additive to high temperature ceramics for both electrical and high temperature capabilities; as powder sprayed on plastic sheeting for sun-screen applications; as a heater strip or rod; as a black pigment in paint, glass, cement.
REF: N/A

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PHYSICAL PROPERTIES OF CARBON DIOXIDE, CO_2

Classification	Gas
Atomic numbers	6 & 8
Atomic weight	44.01
Melting point (°C) 5.2 atms	−56.6
Boiling point (°C) solid	−78.5
Density (g/cm^3) solid −79°C	1.56
(g/l) liquid, −37°C	1.101
(g/l) liquid, 0°C	1.97
Refractive index (n=)	1.38—1.46
Solubility (100 ml H_2O) RT	1.45 g
(100 ml H_2O) 0°C	1.79 g
Hardness (Mohs — scratch) solid	1.5—2
Crystal structure (isometric — normal) solid	(100) cube
Color (gas)	Colorless
(crystalline solid)	White
Cleavage (cubic)	(001)

CARBON DIOXIDE, CO_2

General: Occurs in nature as a fraction of air, in waters, and in the soil. In certain areas it can be associated as a gas from subsurface magmas and volcanoes, or be released into the atmosphere from earth fissures. It is a by-product of combustion; comes from decaying matter; and is the gas resulting from fermentation, such as beers and wines. Animal life breathes air, extracts the oxygen, and release carbon dioxide; whereas vegetation uses carbon dioxide, releasing oxygen back into the atmosphere . . . a symbiotic life cycle.

The decomposition of certain carbonate minerals or reduction of their metallic ores can release the gas. Like nitrogen, it will not support combustion — it is a by-product of combustion — and can be lethal when oxygen is not present. Skin contact should not be made with dry ice as it can cause burn-like blisters.

As a commercially prepared food product, it is dissolved in water as soda water, seltzer water, or carbonated water. In addition to the natural fermentation of beers and wines . . . the British "bubbly" is champagne . . . it is added to soft drinks for effervescence as a carbonated beverage.

Industrially, as solid dry ice (−79°C) it is used as a temporary refrigerant, such as for transportation of epoxy and polyamide pastes that are shipped frozen for extended shelf-life. Where used in large volumes, it usually is transported as a cryogenic liquid at around −37°C. In chemical processing, dry ice has been used as a freezing mixture in acetone (−100 to −80°C) for the removal of water vapor from other gases, or as a chilling medium in etching, as a hardening agent, or as an oxidizer.

Technical Application: Not used directly in Solid State device design, though it is occasionally used as a drying gas or cleaning agent at room temperature like nitrogen, argon, and helium, but at elevated temperatures can be reactive as an oxidizer or carbonizer. CO_2 has been bubbled through etching solutions for stirring action only or as an active element for oxidation and etch action. The gas also has been used as a hot furnace gas as an oxidizing agent, usually in combination with air and/or oxygen, or as a mixed gas with the carbon fraction forming carbides, specifically silicon carbide on silicon surfaces.

As dry ice in laboratories, it is used as a temporary refrigerant for the storage of such materials as gallium, bromine, epoxy, and polyamide formulations.

Dry ice is one of the few compounds that sublimes directly from the solid to the gaseous state without passing through a liquid state, though it can be liquefied under pressure as a

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cryogenic gas. It has been studied as a crystalline mass of dry ice and grown as a single crystal for morphological studies.

Etching: Solid sublimes without melting.

CARBON DIOXIDE ETCHANTS

COD-0001
ETCH NAME: Liquid nitrogen
TYPE: Cryogenic gas, forming
TIME:
TEMP: Freezing (−196°C)
COMPOSITION:
x .... LN_2
DISCUSSION:

CO_2, grown as a single crystal using a cold temperature cryostat in order to measure the refractive index. Index varies with wavelength, and is between n = 1.38 and 1.46.
REF: Tempelmeyer, K E et al — *J Appl Phys*, 39,2968(1968)

COD-0002
ETCH NAME: Methyl alcohol
TYPE: Alcohol, chilling
TIME:
TEMP:
COMPOSITION:
(1) x .... MeOH (2) x .... acetone
DISCUSSION:

CO_2, as solid "dry ice". Used as a mixture of chunks in methanol or acetone it is a "cold solution" used for removal of water vapor in gases. It has been used for drying of argon from pressurized A-1 cylinders where argon was used to backfill sealed quartz tubes containing silicon wafers for closed tube gallium diffusion in fabrication SCRs. Both liquids shown above can act as structure etchants on solid CO_2.
REF: Walker, P & Orwin, H — personal application, 1974

COD-0003
ETCH NAME: Carbon dioxide
TYPE: Gas, oxidation
TIME:
TEMP:
COMPOSITION:
x .... O_2
x .... CO_2
DISCUSSION:

CO_2 is used as a furnace gas mixture to oxidize chromium metal to chromium trioxide in a study of Cr_2O_3.
REF: Torkington, R S & Vaughn, J G — *J Vac Sci Technol*, A(3),795(1985)

CERAMICS

General: The term is still applied to the pottery industry which has been in existence for some 10,000 years, and it includes many natural minerals, such as corundum, Al_2O_3, and quartz, SiO_2, as two crystal varieties; and as a group, both the feldspar and clay minerals. Aluminum silicates as orthoclase or microcline, $KAlSi_3O_8$, and albite, $NaAlSi_3O_8$ are found in some 60% of all rocks and, with weathering, break down forming clay minerals: kaolinite, $Al_2H_2(SiO_4)_2$, as an admixture with sand, iron, and other metal oxides is common clay — from the feldspars. Kaolin is a high purity form of kaolinite which, when heated, burns to a white enamel and is used for fine "bone" china, pottery, and porcelain.

Fuller's Earth is a form of clay that absorbs water, as does montmorillonite. Bentonite is a colloidal clay that will swell in water, and is used as a packing around piping in oil

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fields, and as a filler for rubber products or binder in manufacturing of lead pencils, e.g., carbon powder.

In making pottery, finely powdered clays will form a wet plastic mass that can be shaped, then hardened by heating to remove the water content. The wet mass is called slip. For general clay products, such as pottery, porcelain, brick or tile, and tile piping, it is kiln fired at 1400°C. First firing is a porous product called bisque; prior to second firing the surfaces are coated with a feldspar silicate paste to make the clay water tight (a glaze); prior to third firing, as for enamels, coat or paint with metallic oxides for color — hematite, Fe_2O_3, as red ocher; cobalt for blue; chromium trioxide for green, etc.

Hard porcelain uses a high silicate content clay, is fired at above 1600°C without further treatment, and it forms porous pottery ware, such as terra cotta, bricks, crockery, etc. This type of clay, when fired at a lower temperature along with red ocher (hematite) is standard brick fabrication and, if NaCl (halite, common salt) is added, produces a glaze. Refractory ceramics, such as fire-brick, contain both magnesium and chromium oxides for high temperature stability. It was the application of silicates and glass as a surface glaze on clay pottery (Egyptians with development of soda-lime glass, circa 3500 B.C.) that produced the name: ceramic pottery.

The production of high quality refractory ceramics has become separated from the ancient and original pottery field in modern times as the ceramics industry, which includes both general products such as fire-brick and tile, as well as high purity alumina or beryllia substrate used in Solid State circuit fabrication.

Many composite ceramics are now manufactured with variety of metal oxides, some of which include carbon or graphite. As an example, most alumina substrates are pure Al_2O_3, as a white ceramic, but there is a black alumina containing carbon which can be electrically active rather than an insulator.

Alumina is supplied as pressed powder blanks; as amorphous, fused alumina, called fused sapphire; or as single crystal sapphire. The sapphires are clear and transparent, and can only be differentiated from similar quartz blanks by material hardness . . . H = 7 (quartz) . . . H = 9 (sapphire). Both sapphire and quartz single crystal blanks used as substrates are usually oriented as basal (0001) surfaces.

Transparent, slightly yellow/brown tinted garnet (YIG, YAG, etc.) blanks are available in (001) or (110) orientation, cubic, or dodecahedral, respectively. Red fused alumina — ruby — is manufactured by pouring a liquid melt into high temperature resistant metal forms such as molybdenum. A variety of products are so fabricated, such as tubes, rods, flats (substrates) wire bonding tips, or further processed as high temperature ball-bearings (ruby spheres).

Although the glass industry is a separate entity . . . the clay, pottery, silicate, glass, and ceramic industries are inter-related . . . and glass is not normally considered a ceramic, but the Solid State industry used both silica and quartz blanks as substrate. Clear, fused amorphous silica, or oriented single crystal quartz. The latter, as alpha-quartz; processed as radio frequency crystals from both natural quartz and artificial boules. In glass applications as such substrates, the material is often grouped with and called a ceramic or dielectric.

The ferrites are another group of materials that are distinct, but can be classified as ceramic type materials with regard to some applications in Solid State processing. They are supplied as flats or blanks like other substrates as mixtures of iron, carbon, and other metal additives. They are coal black in color with highly polished surfaces, and specifically formulated for fabrication of microelectronic circuit resistors at different frequencies. All of these substrates, including the ferrites, are metallized, then photolithographically patterned as circuits or discrete devices.

Technical Application: All of the ceramic material mentioned above have wide use and application in Solid State circuit fabrication, in addition to their normal applications as furnace fire-brick; furnace tubes and liners; insulated stand-offs in both vacuum systems and

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test fixtures, or in device packages; as tubes or beads for high temperature thermocouples, or crucibles; as chemical solution boiling beads; the pressed powder alumina as a tool sharpener; as the cutting tool, itself; or as lapping abrasives, to mention only a few such uses.

In device fabrication the ceramics are primarily insulators — for mounting of discrete devices, after metallizing and circuit patterning of the substrate. Several also are used as discrete devices, such as the ferrites as resistors, or glass and ceramics as dielectrics, and for filter elements.

Only those ceramics referred to as cermets are shown here. The others are listed under their individually named sections.

Etching: See individual ceramics, borides, glass, etc. Etch solutions vary with type material, and all are generally difficult to etch.

CERMET ETCHANTS

CMT-0001a
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
1 .... HF
5 .... HNO_3
60 .... H_3PO_4
DISCUSSION:
Cr:SiO (30%) as a deposited thin film surface coating. Solution used for both surface cleaning and material removal. Over 30% SiO limits the etch rate. (*Note:* There is a wide variety of cermet materials.)
REF: Miassel, L I & Glang, R — *Handbook of Thin Film Technology*, McGraw-Hill, New York, 1970.

CMT-0001b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: 50—60°C
COMPOSITION:
20 g .... $K_2Fe(CN)_6$
10 g .... NaOH
100 ml .... H_2O
DISCUSSION:
Cr:SiO (30%) as a deposited thin film coating. Solution used for both surface cleaning and removal of the material.
REF: Ibid.

CERAMIC ETCHANTS

CERM-0001
ETCH NAME: TIME:
TYPE: Metal, contacts TEMP:
COMPOSITION:
x .... $PdCl_2$
x .... H_2O
x .... $SnCl_2$
DISCUSSION:
Ceramics. Dipping parts in a stannous palladium chloride solution prior to electroless

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nickel plating produces a light Pd coating that aids in the gripping power of nickel. Nickel plating evaluated at 95°C with a 0.001 mm thick deposit.

REF: Turner, D R & Sauer, H A — *J Electrochem Soc,* 107,250(1960)
CERM-0002: Pearlstein, F — *Met Finish,* 53,59(1955)

Reference cited in CERM-0001 for palladium solution.

PHYSICAL PROPERTIES OF CERIUM, Ce

Classification	Lanthanide
Atomic number	58
Atomic weight	140.13
Melting point (°C)	795
Boiling point (°C)	3468
Density (g/cm^3)	6.67 (6.90)
Thermal conductance $(cal/sec)(cm^2)(°C/cm)$	0.026
Specific heat (cal/g) 25°C	0.042
Heat of fusion (k-cal/g-atom)	1.2
Latent heat of fusion (cal/g)	8.5
Heat of vaporization (k-cal/g-mole)	95
Atomic volume (W/D)	21.0
1st ionization energy (K-cal/g-mole)	159
1st ionization potential (eV)	6.54
Electronegativity (Pauling's)	1.1
Covalent radius (angstroms)	1.65
Ionic radius (angstroms)	1.07 (Ce^{+3})
Electrical conductance ($micro\text{-}ohms^{-1}$)	0.013
Electrical resistivity (10^{-6} ohms cm) 20°C	75
Poisson's ratio	0.248
Young's modulus ($\times 10^6$)	6.3
Tensile strength (psi)	15.000
Yield strength (psi)	13.200
Magnetic susceptibility (10^{-6} emu/mole)	2.430
Electron work function (eV)	2.84
Cross section (barns)	0.7
Hardness (Mohs — scratch)	1—2
(Vickers — kgf/mm^2)	24
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Steel-grey met.
Cleavage (cubic)	(001)

CERIUM, Ce

General: Does not occur as a native element though there are over 50 minerals containing cerium. These include fluorides, oxides, carbonates, phosphates, niobates, and tantalates. As a group, there is the Cerium Group of metals, which also are members of the Rare Earths.

One major use of cerium metal in industry is as an alloy with iron producing "flints" . . . the cerium producing sparks for cigarette and gas lighters, gas ignition sparkers, etc. As cerium oxide it is used to make incandescent gas mantles, producing an intense white light with only slow disintegration of the material.

Technical Application: Though not used to any extent in Solid State processing to date,

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it has possible application as a doping element in compound semiconductors or as an element in manmade garnets.

Etching: Soluble in dilute acids.

CERIUM ETCHANTS

CE-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:
Ce specimens. Material can be etched in dilute acids.
REF: Hodgman, C D et al — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 364

CE-0002: Walker, P — Mineral study, 1954

Ce as an element fraction in the mineral monazite, $(Ce,La,Di)PO_4$. H_2SO_4, HCl and HNO_3 used in a separation evaluation of constituents of the single crystal elements of the material.

PHYSICAL PROPERTIES OF CERIUM DIOXIDE, CeO_2

Classification	Oxide
Atomic numbers	58 & 8
Atomic weight	172.13
Melting point (°C)	1950
Boiling point (°C)	
Density (g/cm^3)	7.3
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — normal)	(100) cube
Color (solid)	White/yellow
Cleavage (cubic)	(001)

CERIUM DIOXIDE, CeO_2

General: Does not occur in nature as an oxide though there are some 50 cerium containing minerals of the Rare Earth group, and there is the allied Cerium Group of metal elements.

The oxide can be fabricated as a thread, then woven into a cloth-like material used as a gas mantle that produces an intense white light at incandescent heat, and is still used for lanterns, such as the Coleman lantern using white gasoline as the gas source.

Technical Application: Not used in Solid State processing at present, but may have application as a thin film protective coating on semiconductors similar to that of other oxides and nitrides, or as a high temperature dielectric/ceramic material.

Etching: H_2SO_4, HNO_3.

CERIUM OXIDE ETCHANTS

CEO-0001
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP:

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DISCUSSION:

CeO_2 or Ce_2O_3 specimens. Both materials can be dissolved in this solution.

REF: Hodgman, C D et al — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 368

PHYSICAL PROPERTIES OF CESIUM, Cs

Classification	Alkali metal
Atomic number	55
Atomic weight	132.9
Melting point (°C)	28.61
Boiling point (°C)	690
Density (g/cm^3) 18°C/20°C	1.892/1.873
Thermal conductance (cal/sec)(cm^2)(°C/cm) liquid	0.0440
Specific heat (cal/g) 20°C	0.052 (0.048)
Heat of fusion (cal/g)	3.913
Latent heat of fusion (cal/g)	3.766
Heat of vaporization (cal/g)	146
Atomic volume (W/D)	70
1st ionization energy (K-cal/g-mole)	90
1st ionization potential (eV)	3.89
Electronegativity (Pauling's)	0.7
Covalent radius (angstroms)	2.35
Ionic radius (angstroms)	1.67 (Ce^{+1})
Electron work function (eV)	1.89
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.10
Coefficient of thermal linear expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	97
Electrical resistivity (ohms cm $\times 10^{-6}$) 0°C	20
Cross section (barns)	30
Vapor pressure (°C)	509
Hardness (Mohs — scratch)	4—5
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Silver-white
(gas)	Blue (spectra)
Cleavage (cubic — perfect)	(001)

CESIUM, Cs

General: Does not occur as a native element. A primary ore is the mica lepidolite, and the rare pollucite mineral. It also is extracted from certain mineral springs as a halogen. It is an alkaline metal with characteristics similar to potassium, and has a high affinity for oxygen. Due to the latter, it is used as an oxygen "getter" in radio tubes and photo-electric cells, and could be used in ion-pump vacuum systems as a replacement for titanium as a getter. It is used as a catalyst in hydrogenation of certain organic compounds in chemical processing.

Technical Application: There has been no use of the pure element in Solid State processing, to date, though it has been used as an additive to special garnets, ferrites, etc. It is under evaluation as a nitride, CsN, for both a surface coating and for optical characteristics.

Etching: Water and acids.

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CESIUM ETCHANTS

CS-0001
ETCH NAME: Water
TYPE: Acid, removal
COMPOSITION:
x .... H_2O
TIME:
TEMP: RT to hot
DISCUSSION:
Cs metal specimens. Like many of the rare earth elements, the material reacts with water with a recognizable hissing sound, converting to the hydroxide with release of hydrogen, such that it is used to hydrogenate other compounds and materials, particularly in organic chemistry.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1948, 422

PHYSICAL PROPERTIES OF CESIUM BROMIDE, CsBr

Classification	Bromide
Atomic number	55 & 35
Atomic weight	213
Melting point (°C)	636
Boiling point (°C)	1300
Density (g/cm^3)	4.44 (4.5)
Refractive index (n =)	1.6984
Wavelength limits (micron)	0.2—40
Young's modulus (psi $\times 10^6$)	2,3
Coefficient of linear thermal expansion ($\times 10^{-6}$/cm/cm/°C)	48
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Clear
Cleavage (cubic — perfect)	(001)

CESIUM BROMIDE, CsBr

General: Does not occur as a solid natural compound, though cesium metal is extracted from hot springs as a bromide or iodide in solution.

Not used in industry as a compound in metal processing, but does have some medical applications.

Technical Application: Not used in Solid State processing though it can be used as a bromine-type etchant solution on semiconductors and other metallic compounds.

It has been evaluated as a single crystal for general morphology, and for defect studies. The material has been used for its optical and filter element properties of infrared transmission even though it is hygroscopic.

Etching: Soluble in cold water and acids.

CESIUM BROMIDE ETCHANTS

CEBR-0001
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, polish
COMPOSITION:
x .... EOH
TIME:
TEMP: RT

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DISCUSSION:

CeBr, (100) specimens. Material is hygroscopic and soft. Polish surfaces with alcohols. Used for infra-red transmission.

REF:

CEBR-0002

ETCH NAME: TIME:

TYPE: Metal, decoration TEMP: Hot

COMPOSITION:

(1) x .... $HAuBr_4$ (2) x .... Au (3) x .... Ag

DISCUSSION:

CeBr, (001) specimens. Used in a study of dislocation development by metal decoration. Coat surfaces with solution (1) or evaporate metals shown in (2) and (3). Heat treat and anneal for metal decoration drive-in. "Colloidal" gold will diffuse into CeBr and deposit at dislocation sites.

REF: Amelinck, S — *Phil Mag*, 3,307(1958)

CEBR-0003

ETCH NAME: TIME:

TYPE: Alcohol, polish TEMP: RT

COMPOSITION:

25 .... MeOH

1 .... H_2O

DISCUSSION:

CsBr, (001) wafers used to measure the elastic constants using ultrasonic resonance. Mechanically rough lap with A/O 302 grit; polish lap with $303^1/_2$ grit; then Linde A; and then sapphire dust on cloth. Use kerosene as the carrier liquid for mechanical lap/polish. Etch polish in solution shown and rinse in isopropyl alcohol (IPA), then rinse in carbon tetrachloride, CCl_4. See Cesium Iodide.

REF: Bulef, D I & Menes, M — *J Appl Phys*, 31,1010(1960)

PHYSICAL PROPERTIES OF CESIUM CHLORIDE, CeCl

Classification	Chloride
Atomic numbers	58 & 17
Atomic weight	168.37
Melting point (°C)	645
Boiling point (°C)	1290
Density (g/cm^3)	3.97
Refractive index (n =)	1.6418
Hardness (Mohs — scratch)	1.5—2.5
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
Cleavage (cubic)	(001)

CESIUM CHLORIDE, CsCl

General: Does not occur as a natural solid compound though cesium metal is extracted from hot springs and ocean water. The latter may be as a CsCl saline solution.

There is no use of the compound in industrial metal processing, but it may have some medical applications.

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Technical Application: No use in Solid State processing to date, though it can be used as an etching solution on metals and compounds as a chloride.

It has been grown as a single crystal by solution evaporation and by molten flux growth for properties study.

Etching: Soluble in water and alcohols.

CESIUM CHLORIDE ETCHANTS

CSCL-0001
ETCH NAME: Water
TYPE: Acid, removal
COMPOSITION:
x .... H_2O

TIME:
TEMP: RT

DISCUSSION:

CsCl grown as single crystal by solution evaporation, and from a molten flux. Also as $CsCl:Na_2CO_3$(10%) crystals. Water can be used to remove and polish specimen surfaces. Materials used in a growth methods and properties study.

REF: Avakian, P & Smakula, A — *J Appl Phys*, 31,1720(1960)

PHYSICAL PROPERTIES OF CESIUM DIOXIDE, Cs_2O

Classification	Oxide
Atomic numbers	55 & 8
Atomic weight	281.82
Melting point (°C)	300 del.
Boiling point (°C)	
Density (g/cm^3)	4.30
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Red-orange
Cleavage (cubic)	(001)

CESIUM DIOXIDE, Cs_2O

General: Does not occur as a natural compound as it is soluble in water though it may occur as a surface temporary coating on other cesium minerals under very dry conditions.

As cesium metal has a high affinity for oxygen like titanium, it is used as an oxygen "getter" in vacuum tubes, and could be used in ion pump vacuum systems.

Technical Application: No use in Solid State processing to date, though the hydroxide, CsOH, has been used in etching formulations.

This mono-oxide, Cs_2O, has been grown and studied as a single crystal from molten fluxes. Specimens were (111) cleaved with difficulty, as the ⟨100⟩/⟨110⟩ planes direction or (001) basal plane are the more normal cleavage planes in the isometric system — normal (cubic) class.

Etching: Soluble in water and alcohols.

CESIUM DIOXIDE ETCHANTS

CSO-0001
ETCH NAME: Sodium hydroxide
TYPE: Alkali, cleaning
COMPOSITION:
x .... 1 *N* NaOH

TIME:
TEMP:

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DISCUSSION:

Cs_2O, (111) wafers cleaved with difficulty from molten flux grown single crystals (lithium ditungstate flux), and used in a compound study. Solution used to clean surfaces after cleaving.

REF: Finch, C B & Clerk, G W — *J Appl Phys*, 37,3910(1966)

CESIUM PLATINIDE ETCHANTS

CEPT-0001

ETCH NAME: Kalling's etch

TYPE: Acid, polish

TIME: 10—60 sec

TEMP: RT

COMPOSITION:

100 ml .... HCl

5 g .... $CuCl_3$

100 ml .... EOH

DISCUSSION:

CePt specimens arc melted in fabrication, and used in a study of metallic compounds. Solution used as a general removal and polishing etchant. Other compounds evaluated: $CeSi_2$, Ho_2O_{17}, Ho_2Fe_{17}, $Ho_2Co_{14}Fe_3$, UCe_2, UPt_3, UNi_2, UCo_2, V_3Si, V_3Ge, Zr_2Nl_7, $MoSi_2$, $TiSi_2$. Crystals grown by the modified Bridgman method were $Y_2(CoM)_{17}$ where M = Al, Fe, Cu, and Ni.

REF: Slepowronsky, M et al — *J Cryst Growth*, 65,293(1983)

PHYSICAL PROPERTIES OF CESIUM IODIDE, CsI

Classification	Iodide
Atomic numbers	55 & 53
Atomic weight	259.83
Melting point (°C)	621
Boiling point (°C)	1280
Density (g/cm^3)	4.52
Refractive index (n =)	1.7876
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Clear
Cleavage (cubic)	(001)

CESIUM IODIDE, CsI

General: Does not occur as a natural compound, but may be found as a liquid fraction in hot springs and ground water like bromide and chloride.

Not used in industrial metal processing, but can have medical applications.

Technical Application: Not used in Solid State processing, though it can be used as an etchant on metals and compounds.

It has been grown and studied for physical properties as a single crystal.

Etching: Soluble in water and alcohols.

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CESIUM IODIDE ETCHANTS

CSI-0001
ETCH NAME:
TYPE: Alcohol, polish/removal
COMPOSITION:
25 .... MeOH
1 .... H_2O
DISCUSSION:

CsI, (100) oriented single crystal wafers used to measure elastic constants with ultrasonic resonance frequencies. Mechanical rough lap with A/O 303 abrasive, then polish lap with A/O $302^1/_2$, both as slurries on an iron lap platen. Mechanically fine polish with Linde A alumina (iron lap), then with diamond dust on a cloth, all using kerosene as the liquid carrier. For final chemical polish, use solution shown, rinse in isopropyl alcohol (IPA), then carbon tetrachloride, CCl_4. Preparation method can be used on bromides and chlorides.
REF: Bulef, D I & Menes, M — *J Appl Phys*, 31,1010(1960)

TIME:
TEMP: RT to warm

PHYSICAL PROPERTIES OF CHLORINE, Cl^2

Classification	Halogen
Atomic number	17
Atomic weight	35.45
Melting point (°C)	−102 (−100.98)
Boiling point (°C)	−33.7 (−34.6)
Density (g/cm³) −33.6°C	1.57
(g/l — liquid) 0°C	3.214
Thermal conductivity ($\times 10^{-4}$ cal/cm²/cm/°C sec) 20°C	0.182
Latent heat of fusion (cal/g)	21.6
Specific heat (cal/g/°C) 20°C	0.116
Solubility (100 ml H_2O) 20°C	215 ml
1st ionization potential (eV)	13.01
Ionic radius (angstroms)	1.81
Cross section (barns)	33
Vapor pressure (°C)	−71.7
Refractive index (n=) gas	−.000768
Critical temperature (C.T. °C)	140
Critical pressure (C.P. atms)	83.9
Crystal structure (tetragonal — normal)	(110) prism
Color (solid)	Yellow-greenish
Cleavage (basal)	(001)

PHYSICAL PROPERTIES OF CHLORINE HYDRATE, $Cl_2.6H_2O$

Classification	Hydrate
Atomic numbers	17, 1, & 8
Atomic weight	170.01
Melting point (°C)	9.6, del.
Boiling point (°C)	
Density (g/cm³)	1.23
Formation temperature (°C in water)	0

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Hardness (Mohs — scratch) solid	1.5—2.5
Crystal structure (hexagonal — rhombohedral)	r(10$\bar{1}$1) rhomb
Color (solid)	Light yellow
Cleavage (rhombic)	(10$\bar{1}$1)

CHLORINE CONTAINING ETCHANTS

Chlorine is a greenish-yellow gas at standard temperature and pressure (22.2°C and 760 mmHg) very similar to that of fluorine. Chlorine has a disagreeable odor and, if breathed, is excessively irritating to the membranes of the eyes, nose, and throat. In contact with moisture in air it produces heavy white fumes of hydrogen chloride, HCl, which also is a severe irritant and can cause suffocation, even death. Fluorine and chlorine are the gaseous elements of the halogen group, which include bromine (liquid) and iodine (solid) with reducing atomic weight and reactivity in the order shown. As chlorine can be liquefied at 0°C under 6 atm of pressure, it was one of the first gases to be liquefied as a cryogenic gas. If chlorine is introduce into water containing ice, and is chilled, it will solidify as the greenish-yellow hydrate, $Cl_2.8H_2O$.

In the metal industries all metals and alloys are subjected to corrosion studies by other elements and compounds, which include the effect of chlorine at various temperatures and, as chlorine will combine with most elements, it is of major concern in developing acid resistant alloys. In semiconductor processing, silicon has been etch polished or thinned by bubbling chlorine through water under intense light. Both germanium and silicon have been etched electrolytically at 300°C with a jet of gaseous chlorine.

Chlorine forms a number of useful acids and compounds in addition to several dangerous gases: hydrogen chlorine, HCl (hydrochloric acid or muriatic acid). As a solution in water, it was discovered by Glauber (circa 1648) from the interaction of sodium chloride, NaCl (common salt) and sulfuric acid, H_2SO_4. Priestley (1772) collected gaseous hydrogen chloride and named it "marine-acid air" because it was produced from salt, and it is now called muriatic acid.

Both hydrochloric and sulfuric acids occur in nature associated with volcanic activity — the volcano releases chlorine and sulfur as gas — which combine with hydrogen and salt in the air or, if submerged in the ocean, from the salt water. Hydrochloric acid is used as a general solvent of materials; in the preparation of chlorides and chlorine; in the cloth dyeing industry; in medicine as a disinfectant; and plays a major role in human digestion . . . 0.2 to 0.4% HCl in gastric juices.

The use of gas in warfare during World War I led to the outlawing of the use of gas in war by the Geneva Convention, which has been accepted by most humane nations of the world. Gas has been used in warfare since ancient times and, unfortunately, is still being used to some extent. The Japanese attempted gas warfare against the Chinese, on a small scale, during World War II — fortunately, the winds were blowing in the wrong direction, or changed direction, and the Japanese got the worst of it.

Anthrax, a virulent cattle disease, was evaluated during World War II by the British — it not only kills mammilary life but as a bacteria permeates the ground and remains lethal for years. Recently it was reported the Russians used gas in Afghanistan, and Iran has accused Iraq of gas warfare.

Some of the gases developed and used during World War I are described below, mainly as they can be a by-product of metal and metallic compound processing when chlorine and its compounds are used, and some knowledge of their danger should be considered:

- Cl_2 — Chlorine. A 1 part chlorine to 10,000 parts of air concentration causes severe breathing difficulty which will incapacitate a man within about 5 min. The Germans used chlorine for the first time on April 22, 1915. The gas is wind-borne, about 2.5 times heavier than air, and is carried as a ground hugging cloud across the surface.

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One possible reason for the Axis powers not using gas in Europe during World War II could be due to the fact that, though variable by locale and season, the prevailing winds coming off the North Sea and English Channel blow inland — across Germany.

- Chlorine gas is used as a jet etch, as a furnace gas in metal corrosion study, and is bubbled through other solutions as part of an etching system. HCl and $HClO_4$ are acid etches, alone, or in combination with other acids. HCl, from pressurized cylinders, and di-, tri-, and chlorosilanes from liquid sources are used in silicon epitaxy growth, and both can produce heavy chlorine vapors if released to the atmosphere.
- Chlorinated water, Cl_2:H_2O, as well as HCl and $HClO_4$, are used as disinfectants in water. Chlorinated lime, $CaOCl_2$, is a bleaching agent in the wood and textile industries. Chloramine, NH_4Cl, will destroy bacteria, and is used in sewage disposal. Chloral, CCl_3CHO, is a medical hypnotic, Chloroform, $CHCl_3$, is a medical anesthetic alone or with dissolved iodine, I_2, as a solution; and also has been used as a metal surface cleaner. Carbon tetrachloride, CCl_4, has been used in dry cleaning, and is still used in "pyrene" type fire extinguishers, or as a metal cleaning solvent. Many of the chlorinated solvents, such as trichloroethylene, TCE, are being replaced due to their carcinogenic nature. Ethylene chloride, C_2H_5Cl, is a medical anesthetic like chloroform, and occasionally has been used as a cleaning and drying solvent for metals.
- $COCl_3$ — Phosgene. Primarily a respiratory irritant, and more poisonous than chlorine. It also was a war gas during World War I. Caution should be observed in mixing etch solutions with hydrochloric acid and other chlorine compounds, as certain mixtures can produce phosgene. Phosphene, PH_3, as a gas, is used as an n-type dopant in silicon device fabrication, and should not be confused with phosgene, though it too is dangerous if breathed.
- $(C_3CCH_4Cl)_2S$ — Mustard gas. Severe skin burns; attacks lungs, larynx, and bronchial tubes. Probably the best known of the World War I gases as so many soldiers were affected. Hitler, for example, was severely gassed near the end of World War I; in fact, he was in hospital at the end of the war, and had gastritis problems for the rest of his life, possibly one of the contributing causes to his final physical degeneration . . . the treatments he was given over the years also contributed.
- CCl:NO_3 — Nitrochloroform, or chloropicrin. Induces coughing, vomiting, and unconsciousness. The compound sodium hypochlorite, NaClO, as a 0.5% solution is used to reduce the effects of gangrene, which was referred to as trench foot in both World War I and World War II, and has been a major cause of death or loss of limbs associated with wars since ancient time. Secondary effects of all of these war gases are asthma, weakened heart, and gastritis.

Mention also should be made of "tear gas" — a lachrymator — which is a slight inhalation irritant, and mainly affects the eyes and tear glands. There are several concentration mixtures of bromine-acetone which comprise the family of tear gases. They are not permanently debilitating and are widely used throughout the world for crowd or mob dispersal. Interestingly enough, tear gas has an astringent, slightly pleasing odor and, in light concentrations, many individuals can withstand the "tearing" effect for several minutes, although the eyes become irritated and inflamed. Many mixtures of bromine-methyl alcohol (BRMs) are used as etchants for metals and metallic compounds, but do not produce the tear gas effect unless acetone is used with the mixtures. Bromine itself is poisonous and can be a severe irritant. Methyl alcohol is wood alcohol, also poisonous if ingested.

Other than acids and gases, chlorine forms a number of important compounds. Sodium chloride, the mineral halite, NaCl, and potassium chloride, the mineral sylvite, KCl, both occur in sea water and as sublimation products around hot springs and volcanoes. Ammonium chloride, the mineral salt ammoniac (chloramine) NH_4Cl, used in sewage disposal, also is found as a sublimate around volcanic fumaroles. Halite is common salt and essential to the

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human diet. Sylvite, bitter in taste, which is not retained by the body as is common salt, is commercially called "sea salt", and used as a dietary replacement for true salt. In Solid State materials study, both NaCl and KCl are used as single crystal wafers, and cut as (100) oriented substrates for thin film evaporation of metals and epitaxy growth of compounds. The deposited thin films are removed by water as the float-off technique for study by transmission electron microscopy (TEM). In addition, both of these salt chlorides are used in etch solutions, as molten fluxes, or in solder fluxes.

The following is a selected list of chlorine-containing etchants. Aqua regia solutions are shown in a separate list. See the Etchant Section under individual materials for additional solutions.

Formula	Material	Use	Ref.
HCl, conc.	Al	Removal	AL-0003b
1HCl:1—20H_2O	Al	Heavy removal	AL-0003b
4HF:35HNO_3:61HCl	Al	Polish	AL-0030
4HF:35HNO_3:61HCl:100H_2O	Al	Preferential	AL-0030
1$HClO_4$:5MeOH	Al	Electropolish	AL-0017
×$HClO_4$: ×EOH	AlAu(2%)	Electrolytic, defect	ALAU-0001
1HCl:1H_2O	AlSi(5%)	Cleaning	ALSI-0001
4HCl:4HNO_3:1 H-Tartaric acid	AlSb	Polish	ALSB-0002a
1HCl:1HNO_3	AlSb	Macroetch	ALSB-0006
35 ml $HClO_4$:20 mg CrO_3/l	Al_2O_3	Oxide removal	ALO-0001b
×6 *N* HCl	Al_2O_3	Preferential	ALO-0016
1HCl:2HNO_3:12HAc	As	Polish	AS-0003c
HCl, conc.	Ba	Polish/Removal	BA-0001b
HCl, conc.	Ba_2TiO_3	Structuring	BAT-0001
HCl, conc.	Be	Removal	BE-0002
10 ml HCl:1gI_2:200 ml H_2O	Bi	Electropolish	BI-0004
HCl, conc.	Bi_2O_3	Removal	BIO-0001
1HCl:2HNO_3:6H_2O	Bi_2Te_3	Preferential	BITE-0001a
3HCl:1HNO_3 "Aqua Regia"	WB_2	Removal	WB-0001a
4HCl:1HNO_3	Brass Bronze	Removal	BR-0001b
HCl, conc.	Cd_3As_2	Polish	CDAS-0001
1HCl:1HNO_3	CdSe	Preferential	CDSE-0001a
3HCl:1HNO_3:10H_2O	CdSe	Polish	CDSE-0003
1HCl:30HNO_3:30HAc	CdSe	Preferential	CDSE-0001b
HCl, conc.	CdS	Damage removal	CDS-0001a
1HCl:1HNO_3	CdS	Preferential	CDS-0011b
HCl, vapor	CdS	Preferential	CDS-0001
10 ml HCl:10 ml HNO_3:5 ml H_2O "P Etch"	CdTe	Polish	CDTE-0006d
10 ml P Etch:10 mg Br_2 "PBr Etch"	CdTe	Preferential	CDTE-0006e
HCl, conc.	Ca	Removal/polish	CA-0001
HCl, conc.	$CaCO_3$	Polish	CAO-0001
3HCl:1HNO_3 "Aqua Regia"	$CaWO_4$	Preferential	CAW-0001b
HCl, conc.	Cf	Removal	CF-0001
3HCl:1H_2O_2	Cr	Removal	CR-0003
1HCl:2$FeCl_3$(35° Bé)	Cr	Removal/polish	CR-0010
500 ml HCl:500 ml EOH	Co	Electropolish	CO-0001

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Formula	Material	Use	Ref.
1HCl:3$FeCl_3$, sat. sol.	Cu	Polish	CU-0025
1HCl:1H_2O:1$FeCl_3$ sat. sol.	Cu	Preferential	CU-0013b
10 ml HCl:1000 ml HNO_3	Cu_2O	Removal	CUO-0014b
HCl, conc.	Ga	Cleaning	GA-0002
HCl, conc.	GaSb	Removal	GASB-0001a
1 ml HCl:1 ml H_2O_2:2 ml H_2O	GaSb	Preferential	GASB-0008b
HCl, vapor	GaAs	Cleaning	GAS-0028
1HCl:1HNO_3:8glycerin	GaAs	Polish	GAS-0050
2HCl:1HNO_3:2H_2O	GaAs	Preferential	GAS-0057
1HCl:2HNO_3	GaP	Polish	GAP-0002
HCl, conc.	GaP	Removal	GAP-0014
3HCl:1HNO_3 "Aqua Regia"	GaP	Selective	GAP-0011
1HCl:1$HClO_4$:6HNO_3	GaP	Cleaning	GAP-0017
13 *N* HCl	Ge	Preferential	GE-0132a
×% KCl	Ge	Electrolytic, defect	GE-0133a
×% NaCl	Ge	Electrolytic, shaping	GE-0129e
7HCl:1HNO_3: + glycerin	Ge	Removal/polish	GE-0173
2HCl:1HNO_3	GeAs	Removal/polish	GEAS-0001b
3HCl:1HNO_3 "Aqua Regia"	Au	Removal	AU-0001
HCl, conc.	In	Removal	IN-0003
1HCl:2$NaClO_3$:3H_2O	InSb	Polish	INSB-0001e
2HCl:1HNO_3	InSb	Removal	INSB-0002d
×HCl:x0.2 *N* $FeCl_3$ "Etch #1"	InSb	Preferential	INSB-0014a
1 *M* HCl	InAs	Removal	INAS-0001b
HCl, conc.	InP	Removal	INP-0020a
6HCl:1HNO_3:6H_2O	InP	Polish	INP-0021a
40HCl:80HNO_3:1Br_2	InP	Preferential	INP-0021b
3HCl:1H_3PO_4	InP	Selective	INP-0035
3HCl:1HNO_3 "Aqua Regia"	Ir	Removal	IR-0001
45HCl:5HNO_3:40MeOH	Fe	Preferential	FE-0103b
$HClO_4$:HAc	Fe	Electrolytic, thin	FE-0104
1HCl:1H_2SO_4:1H_2O	Fe	Cleaning	FE-0108
x$HClO_4$:xHAc	Fe:Si	Electrolytic, form	FESI-0007
20HCl:20HNO_3:60MeOH	Fe:Be	Electrolytic, thin	FEBE-0001
1HCl:3 Thiourea	PbS	Dislocation	PBS-0001
HCl, conc.	$PbZrO_3$	Polish	PBZO-0001a
xHCl:xH_2O	Mg	Acid saw cutting	MG-0001
1HCl:5H_2O	Fe_3O_4	Preferential	FE-3001
HCl, conc.	MnO_2	Removal	MNO-0002
HCl, conc.	Mo	Cleaning	MO-0013b
×HCl:xHNO_3	Mo	Removal	MO-0001g
3HCl:1HNO_3 "Aqua Regia"	Mo	Polish	MO-0008a
1HCl:1HNO_3	HgSe	Preferential	HGSE-0001b
1HCl:50HNO_3:10HAc: 20 10 *N* H_2SO_4	HgSe	Polish	HGSE-0001a
1HCl:6HNO_3:1H_2O	HgTe	Polish	HGTE-0001a
1HCl:1HNO_3	HgTe	Preferential	HGTE-0001b
1HCl:1HNO_3:1H_2O	HgCdTe	Stain, defects	HGCT-0001
10HCl:33HNO_3:67H_2O	Ni	Clean	NI-0004b
3HCl:1HNO_3 "Aqua Regia"	Ni:Cr	Removal	NICR-0003

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Formula	Material	Use	Ref.
45HCl:5HNO_3:50MeOH	Ni:Cr	Preferential	NICR-0004a
×HCl:×H_2O	Nb	Cleaning	NB-0004a
3HCl:1HNO_3 "Aqua Regia"	Os	Removal	OS-0001b
3HCl:1HNO_3 "Aqua Regia"	Pd	Cleaning	PD-0001
3HCl:1HNO_3 "Aqua Regia"	Pt	Removal	PT-0001
1HCl:1HNO_3	$PtSb_2$	Preferential	PTSB-0001a
1HCl:1HNO_3:1H_2O	$PtSb_2$	Removal	PTSB-0002
3HCl:1HNO_3 "Aqua Regia"	SiO_2(Qtz)	Cleaning	QTZ-0003
3HCl:1HNO_3 "Aqua Regia"	Ru	Removal	RU-0001
HCl, conc.	Sc	Polish	SC-0001a
×HCl:×HNO_3	Sc	Removal	SC-0001c
1HCl:3HNO_3	Si	Defect	SI-0171
×KF:×KCl:2H_2O	Si	Electropolish	SI-0186a
HCl, conc.	Si	Cleaning	SI-0017
40HF:37HCl	SiO_2	Cleaning	SIO-0038b
3HCl:1HNO_3 "Aqua Regia"	SiO_2	Cleaning	SIO-0051
3HCl:1HNO_3 "Aqua Regia"	Si_3N_3	Cleaning	SIN-0016
500 ml HCl:100 ml 10% CrO_3	Si_3N_4	Cleaning/pin-holing	SIN-0018
HCl, conc.	AgCl	Cleaning	AGCL-0003
NaCl, sat. sol.	NaCl	Polish, (100)	NACL-0002b
70HCl:30H_2O	NaCl	Polish, (100)	NACL-0005
1HCl:50HAc:1H_2O: 1$FeCl_3$ sat. sol.	NaCl	Preferential, (100)	NACL-0007a
1HCl:1H_2O	Steel	Preferential	ST-0001a
5 ml HCl:1 g picric acid: 100 ml EOH	Steel	Preferential	ST-0001e
1HCl:2HNO_3	Steel	Cleaning/removal	ST-0007b
4HCl:1HNO_3	Steel	Removal	ST-0007a
1HCl:1OH_2O	SrF_2	Removal	SRF-0001
3HCl:1HNO_3 "Aqua Regia"	TaN	Polish	TAN-0001
1HCl:1CrO_3:3H_2O	Te	Preferential	TE-0001c
3HCl:1HNO_3 "Aqua Regia"	Te	Polish	TE-0002
HCl, conc.	Tl	Removal, slow	TL-0004
3HCl:1HNO_3 "Aqua Regia"	Th	Polish	TH-0002
100 ml HCl:10NH_4NO_3: 500H_2O:×$CuSO_4$	Sn	Defect, (100)	SN-0002a
×5%HCl:×IPA	Sn	Removal	SN-0001a
3HCl:1HNO_3 "Aqua Regia"	Sn	Preferential, (100)	SN-0005b
20$HClO_4$:70HAc	Sn	Electropolish	SN-0007
1HCl:5H_2O	SnO_2	Electrolytic, removal	SNO-0001b
x20% HCl	Ti	Cleaning	Ti-0001a
HCl, conc.	Ti	Removal	TI-0004c
3HCl:1HNO_3 "Aqua Regia"	TiO_2	Cleaning	TiO-0004
3HCl:1HNO_3 "Aqua Regia"	W	Removal	W-0001d
×$HClO_4$:xH_3PO_4	W	Polish	W-0018b
3HCl:1HNO_3 "Aqua Regia"	V	Removal	V-0002a
1HCl:1H_2O	Zn	Removal	ZN-0001a
1HCl:1HNO_3	ZnS	Preferential	ZNS-0002c
3HCl:1HNO_3 "Aqua Regia"	ZnTe	Preferential	ZNTE-0005b

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Formula	Material	Use	Ref.
$3HCl:4HNO_3$	ZnTe	Polish	ZNTE-0002c
$3HCl:1HNO_3$ "Aqua Regia"	Zr	Removal	ZR-0007
$1HClO_4:9HAc$	ZrO	Electropolish	ZRO-0002

AQUA REGIA

This solution was originally developed in the Middle Ages of Europe as $3HCl:1HNO_3$ and, at the time, was thought to be a universal etchant for all materials. It was the first solution capable of dissolving gold, in addition to the Platinum Group metals: Pt, Os, Rh, Re. Of course, since those time it has been found not to be the ultimate etchant, but is in use today on a number of metals and metallic compounds . . . as the 3:1 mixture . . . with other constituent variations, to include water dilution and other chemical additives — applied for cleaning, general removal, polishing, or preferential depending upon the material.

In addition, there are two other "regia" termed formulations: (1) chrome regia, with CrO_3 replacing the HNO_3, and (2) glyceregia, where aqua regia is diluted with glycerin. *Note:* Any solution containing nitric acid and glycerin should be handled with extreme care . . . it is the precursor of nitroglycerin. **CAUTION:** HNO_3:MeOH, red fuming, was one of the first rocket fuels, and can be explosive. These two regia etchants are shown at the end of the following list of aqua regia and its varieties.

Although aqua regia has been shown in the previous "Chlorine Containing . . . " list, it is felt that it would be useful to present the following list covering both aqua regia and its variations, as applied to a number of metals and metallic compounds. The use of aqua regia and its variations is not limited to the materials as shown. An example: if $AgCdTe_2$ can be etched, so could $AgTe_2$ . . . though we have no reference available for the latter.

Note that a polish etchant can be a general removal etchant; whereas, a removal etchant is not necessarily a polish etchant. Also, both types, can be used for pattern etching of thin films and/or structure etching through a mask, e.g., pits, channels, etc. The preferential etchants can be for general defect development or for a specific type dislocation, such as stacking faults. Where aqua regia is used for surface passivation, it can be either chlorination or oxidation, and these factors apply to other etchant solutions.

Aqua regia and variations

Formula	Material	Use	Ref.
$3HCl:11HNO_3:10H_2O$	Al_xAu_y	Step-etch "purple plague"	AIAU-0002
$5HCl:1OHNO_3:84H_2O$	Al:Si	Preferential	ALSI-0003
$4HCl:3HNO_3$	AlSb	Preferential/polish	ALSB-0002a
$1HCl:1HNO_3$	AlSb	Polish/macro-etch	ALSB-0003/ 0006
$1HCl:2HNO_3:3H_2O$	Bi	Polish	BI-0014b
$20HCl:1NHO_3$	BiSb	Polish	BISB-0002
$1HCl:2HNO_3$	Bi_2Se_3	Polish	BISE-0001a
$1HCl:12HNO_3$	Bi_2Te_3	Removal	BITE-0002
$1HCl:2HNO_3:6H_2O$	Bi_2Te_3	Preferential	BITE-0001a
$5HCl:1000HNO_3$	Bronze	Removal	BRO-0001
$4HCl:1HNO_3$	Brass	Removal	BRA-0001b
$4HCl:1HNO_3$	$CdInSe_2$	Polish	CDISE-0001a
$1HCl:1HNO_3$	CdSe	Preferential	CDSF-0001a

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Formula	Material	Use	Ref.
$3HCl:1HNO_3$	CdSe	Cleaning	CDSE-0002b
$3HCl:1HNO_3$	CdSe	Preferential	CDSE-0005b
$3HCl:1HNO_3:12H_2O$	CdSe	Polish	CDSE-0003
$5HCl:1HNO_3$	CdSe	Removal	CDSE-0006
$1HCl:1HNO_3$	CdS	Preferential	CDS-0001b
$2HCl:2HNO_3:1H_2O$	CdTe	Polish	CDTE-0006d
$1HCl:1HNO_3$	CdTe	Preferential	CDTE-0011b
$3HCl:1HNO_3$:1HAc	CdTe	Polish	CDTE-0018b
$1HCl:6HNO_3$	CdTe:HgTe	Polish	CDHT-0001
$3HCl:1HNO_3$	$CaWO_4$	Preferential	CAW-0001b
$3HCl:1HNO_3$	$CaWO_4$	Polish	CAW-0002
$10HCl:1000HNO_3$	Cu_2O	Removal	CUO-0019
$3HCl:1HNO_3$	$CuGaSe_2$	Polish	CGSE-0001
$3HCl:1HNO_3$	$CuInSe_2$	Polish/stain	CISE-0001
$1HCl:1HNO_3:1H_2O$	$CuInSe_2$	Polish	CISE-0002
$1HCl:1HNO_3$	$CuGaTe_2$	Removal	CGTE-0001
$1Hcl:1HNO_3:2H_2O$	$CuInTe_2$	Thinning	CUIT-0001b
$3HCl:1HNO_3$	Apatite	Preferential	FAP-0001a
$3HCl:1HNO_3$	Ga	Preferential	GA-0002
$1HCl:2HNO_3:2H_2O$	GaAs	Polish	GAS-0052
$3HCl:3HNO_3:2H_2O$	GaAs	Polish	GAS-0044d
$3HCl:1HNO_3$	GaAs	Polish	GAS-0056a
$2HCl:1HNO_3:2H_2O$	GaAs	Preferential	GAS-0057
$5HCl:1HNO_3$	GaAs	Polish/junction	GAS-0056c
$2HCl:3HNO_3$:2HF	GaAs	Polish	GAS-0005a
$1HCl:2HNO_3:1H_2O$	GaAs	Removal	GAS-0140d
$1HCl:1HNO_3:2H_2O$	GaAs	Preferential	GAS-0167c
$1—2HCl:1HNO_3$	GaSb	Removal	GASB-0001c
$30HCl:1HNO_3$	GaSb	Surface passivation	GASB-0007b
$1HCl:2HNO_3:1H_2O$	GaP	Polish	GAP-0002
$2HCl:1HNO_3:2H_2O$	GaP	Polish	GAP-0008
$3HCl:1HNO_3$	GaP	Selective	GAP-0011
$3HCl:1HNO_3$	GaP	Cleaning	GAP-0012
$1HC1:6HNO_3:1HClO_4$	GaP	Cleaning	GAP-0017
$3HCl:1HNO_3$	GaP	Preferential	GAP-0022b
$1HCl:1HNO_3$ + Ag/Fe	GaP	Dislocation	GAP-0022e
$7HCl:1HNO_3$: + Gly	Ge	Removal/polish	GE-01773
$3HCl:1HNO_3$	GeSn	Removal	GESN-0001
$2HCl:1HNO_3$	GeAs	Removal, slow	GEAS-0001b
$2HCl:1HNO_3$	Glass:PdNiP	Clean/removal	PDNP-0001
$3HCl:1HNO_3$	Au	Removal/pattern	AU-0001a
$3HCl:1HNO_3:20—50H_2O$	Au	Cleaning	AU-0003b
$3HCl:1HNO_3:xH_2O$	Au:Cs	Removal	AUCS-0001
$1—5HCl:1HNO_3:4—6H_2O$	InSb	Polish/preferential	INSB-0001b,d
$2HCl:5HNO_3$:4HAc	InSb	Polish	INSB-0001c
$2HCl:2HNO_3:3H_2O/25H_2O$	InSb	Polish	INSB-0004
$1—2HCl:1HNO_3$	InP	Removal	INP-0020b
$6HCl:1HNO_3:6H_2O$	InP	Polish	INP-0021a
$40HCl:80HNO_3:1Br_2$	InP	Preferential	INP-0021b
$1—2$ HCl:$1—2HNO_3$	InP	Selective	INP-0062g

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Formula	Material	Use	Ref.
1HCl:3/1.5/2/2.5 HNO_3	InP	Selective/step-etch	INP-0064a,k
1HCl:1HNO_3	InP	Polish	INP-0070
3HCl:1HNO_3	Ir/IrV	Removal/patterning	IR-0001
45HCl:5HNO_3:50H_2O	Fe	Preferential	FE-0003b
10HCl:1HF:5HNO_3	Fe	Dislocation	FE-0011
1HCl:1HNO_3:2H_2O	Fe	Electropolish	FE-0030
1HCl:1HNO_3:3MeOH	Fe:Be	Electro-clean	FFBE-0001
1HCl:1HNO_3	MgTe	Removal	MGTE-0001
1HCl:50HNO_3:10HAc:20 10 *N* H_2SO_4	HgSe	Polish	HGSE-0001a
11HCl:1HNO_3	HgSe	Preferential	HGSE-0001b
6HC1:2HNO_3:3H_2O	HgSe	Preferential	HGSE-0001c
1HCl:1HNO_3:1H_2O	HgTe	Polish	HGTE-0001a
1HCl:1HNO_3	HgTe	Preferential	HGTE-0001b
1HCl:1HNO_3:1H_2O	HgCdTe	Defect/strain	HGCT-0001
2HCl:1HNO_3:3H_2O	HgCdTe	Preferential	HGCT-0002a
xHCl:xHNO_3	Mo	Removal	MO-0001g
3HCl:1HNO_3	Mo	Polish	MO-0008a
1HCl:1HNO_3	Mo	Cleaning	MO-0010
xHCl:xHNO_3:xH_2O/MeOH/EOH	Mo	Removal	MO-0022b
1HCl:2HNO_3	$Fe_2Mo_3O_8$	Removal	FEMO-0001
3HCl:1HNO_3:5H_2O	MoS_2	Removal	MO-0004
4HCl:1HNO_3	Ni	Removal	NI-0005
10HCl:33HNO_3:67H_2O	Ni	Cleaning	NI-0004b
3HCl:1HNO_3	Permalloy	Polish	PMA-0001a
1HCl:1HNO_3:3H_2O	Nichrome	Removal/cleaning	NICR-0006
3HCl:1HNO_3	Nichrome	Removal	NICR-0003
45HCl:5HNO_3:50MeOH	Nichrome	Preferential	NICR-0004a
4HCl:1HNO_3	$RENi_2$	Removal	REN-0001
1HCl:3HNO_3	Os	Removal/cleaning	OS-0001b
3HCl:1$HNO_3$3H_2O	Pd	Removal/cleaning	PD-0001
3HCl:1HNO_3	PdAg	Removal/cleaning	PDAG-0001
3HCl:1HNO_3	PdAu	Removal/cleaning	PDAU-0001
3HCl:1HNO_3:xH_2O	Pd:H	Cleaning	PDH-0001
3HCl:1HNO_3	Pt	Removal/cleaning	PT-0001
3HCl:1HNO_3:xH_2O	Pt:Pd	Preferential/removal	PTPD-0001
3HCl:1HNO_3:xH_2O	Pt:Au	Preferential/removal	PTAU-0001
3HCl:1HNO_3	Pt:Rh	Cleaning	PTRH-0001
3HCl:1HNO_3:xH_2O	PtH	Cleaning	PTH-0001
1HCl:1HNO_3:xH_2O	$PtSb_2$	Preferential	PTSB-0001a-b
3HCl:1HNO_3	SiO_2 (Qtz)	Cleaning	QTZ-0003
3HCl:1HNO_3	Rh	Cleaning	RH-0001
3HCl:1HNO_3	Ru	Removal	RU-0001
xHCl:xHNO_3	Sc	Removal	SC-0001c
3HCl:1HNO_3	$TiWSi_2$	Removal	TWSI-0001
1HCl:1HNO_3	Si	Cleaning	SI-0108a
3HCl:1HNO_3	Si	Cleaning	SI-0108c
3HCl:1HNO_3	SiO_2	Cleaning	SIO-0052
3HCl:1HNO_3	Si_3N_4	Cleaning	SIN-0007
1HCl:1HNO_3:1H_2O	Ag	Removal	AG-0007

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Formula	Material	Use	Ref.
$1HCl:3HNO_3:6H_2O$	Pb:Sn:Ag	Removal/cleaning	AGPS-0001b
$1HCl:1HNO_3$:	$AgSbTe_2$	Polish	SAT-0001
$2K_2S_2O_7$, sat. sol.	$AgFeTe_2$	Polish	SIT-0001
15 ml HCl:10 ml HNO_3: 10 ml HAc:5 ml glycerin	Steel, 300	Electrolytic	ST-0001i
$4HCl:1HNO_3$	Steel	Removal (hi-speed)	ST-0007a
$1HCl:2HNO_3$	Steel, hard	Removal/cleaning	ST-0007b
$3HCl:1HNO_3$	TaN	Polish	TAN-0001
$3HCl:1HNO_3$	Te	Removal/polish	TE-0002
$3HCl:1HNO_3:1H_2O$	Te	Polish	TE-0008
$3HCl:1HNO_3$	Th	Polish	TH-0002
$3HCl:1HNO_3$	Sn	Preferential	SN-0005b
$11HCl:1HNO_3$: $20K_2Cr_2O_7$, sat. sol.	SnTe	Polish	SNTE-0001
$3HCl:1HNO_3$	TiO_2	Cleaning	TIO-0004a
$3HCl:1HNO_3$	TiW	Removal	TIW-0006
$3HCl:1HNO_3$	W	Removal	W-0001d
$3HCl:1HNO_3$	V	Removal	V-0002a
$1HCl:1HNO_3$	ZnS	Preferential	ZNS-0002b
$3HCl:1HNO_3$	ZnTe	Preferential	ZNTE-0005b
$3HCl:4HNO_3$	ZnTe	Polish	ZNTE-0002c
$3HCl:1HNO_3$	Zr	Removal	ZR-0007
$3HCl:1HNO_3$	Zr_2Pd	Polish/removal	ZRPD-0001
$3HCl:1HNO_3$	Zr_3Rh	Polish/removal	ZPRH-0001
	Chrome regia		
$3HCl:1CrO_3$ (10—20%)	Au	Preferential	AU-0017
$5HCl:1CrO_3$(10%)	Si	Preferential	SI-0019
$5HCl:1CrO_3$(10%)	Si_3N_3	Preferential	SIN-0002e
$0.5HCl$:5 $gCrO_3$:50 ml H_2O	Ag	Polish	AG-0012b
$0.01HCl$:5 $gCrO_3$:25 ml H_2O	Ag	Preferential	AG-0012c
$1HCl:1CrO_3:3H_2O$	Ta	Preferential	TA-0001c
$1HCl:1CrO_3:1H_2O$	Ta	Polish/acid saw cut	TA-0002a-b
$1HCl:1CrO_3:3H_2O$	Te	Acid saw cut	TE-0012a
$1HCl:1CrO_3:3H_2O$	Te	Polish	TE-0001c
3000 ml 6 *N* HCl:20 g Cr, metal	SnO_2	Removal	SNO-0005
	Glyceregia		
20—50 ml HCl:10 ml HNO_3: 30 ml glycerin	Steel	Macro-etch/cleaning	ST-0018
$7HCl:1HNO_3$:x glycerin	Ge	Polish/removal	GE-0173
$1HCl:1HNO_3$:8 glycerin	GaAs	Preferential	GAS-0050
$1HCl:1HNO_3$:4 glycerin	PbAg PbSn:PbTi	Preferential	PBAG-0001

CHLORINE, Cl_2

General: Chlorine gas is too active to remain in the free state although it can be a temporary product of volcanic eruptions which immediately converts to hydrochloric acid,

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HCl. Sulfur also is a volcanic by-product, converting to sulfuric acid, H_2SO_4. These two gases are the primary corrosive acid producers in the atmosphere whether from volcanic action or as industrial pollutants. Acid rain is one result, another is smog. Note that smog has been in existence since ancient times.

Chlorine combines to form many metallic compounds as natural minerals, such as cerargyrite, AgCl (horn silver). Probably the best known and one of the most widely used compounds is halite, NaCl (sodium chloride) as common salt, and "sea salt", the mineral sylvite, KCl. The latter used as a dietary replacement for common salt. Man has extracted salt from oceans since ancient times by evaporating sea water in shallow basins — the method is still used — though both salt and sulfur are mined in quantity, today, from salt domes or similar sulfur domes, and from tremendous salt beds buried in the earth from the evaporation of ancient shallow seas that go back in age for millions of years.

Sodium chloride, as halite, is one of the most important — and abundant — minerals in the world. It is a major material in the chemical industry, used as a concentrated brine in metal processing, as well as being separated for the sodium metal content and gaseous chlorine. Chlorine is a greenish-yellow gas with a disagreeable smell, and is extremely irritating to membranes of the nose, eyes, and throat. Dispersed in the air as a cloud, usually as HCl, as a heavy white vapor, it is easily recognized by its astringent action. It can liquefy at 0°C under only 6 atm of pressure, and was one of the first gases to be liquefied. With added water and cooled with ice, it will form a highly unstable greenish-yellow crystalline hydrate.

The gas will combine to form compounds with most elements, other than oxygen, nitrogen, or carbon, and there are many industrial uses for both metallic sodium and gaseous chlorine; the latter in the production of hydrochloric acid.

The gas, usually in combination with water, as a mixture of hydrochloric and hypochlorous acids yields oxygen in a highly active state. Hypochlorous acid, HClO is bleach. When used as a disinfectant, the released oxygen kills bacteria. Perchloric acid, $HClO_4$, is a powerful oxidizing agent, used as a replacement for nitric acid, HNO_3, in etch solutions. It is not an oxidizer in dilute solution and its perchlorate salts are the mostly stable salts of the oxy-acids of chlorine.

Technical Application: Pure chlorine gas has been used under pressure as an electrolytic jet etch, or bubbled through an etch solution as part of the reaction process in Solid State device fabrication.

The acids of chlorine, as mentioned in the General section above, and shown in the preceding list of A—Z materials with formulas of chlorine containing etchants have wide usage in metal and metallic compound processing as liquid acids.

In addition, using the chlorine as a cleaning gas, hydrochloric acid is used in epitaxy systems, and several other chloride compounds have been in use as doping element carriers in semiconductor diffusion for several years. Phosphorus oxy-chloride, $POCl_3$ (pockle) for n-type phosphorus; boron trichloride, BCl_3, as a gas, for p-type boron, or as dry chemical etching (DCE) in the selective etching of thin film aluminum for patterning structure.

The following list of chlorine etchants includes growth as a single crystal for morphological studies.

Etching: N/A

CHLORINE ETCHANTS

CL-0001
ETCH NAME: Pressure
TYPE: Pressure, preferential
COMPOSITION:
x .... pressure

TIME:
TEMP:

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DISCUSSION:

Cl_2 grown as a single crystal in vacuum and under cryogenic temperature and pressure conditions. Preferentially etch crystal surfaces by varying vapor pressure of the vacuum.
REF: Schwentner, N et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1970

CL-0002b
ETCH NAME: Chlorine
TYPE: Gas, etching
COMPOSITION:
x .... Cl_2
x .... acid solutions
TIME:
TEMP: RT to hot
DISCUSSION:

Cl_2, as gas bubbled through an acid solution has been used to create both a stirring and/or etching action.
REF: Ibid.

CL-0002a
ETCH NAME: Hydrochloric acid
TYPE: Gas, cleaning
COMPOSITION:
x .... HCl, vapor
TIME: 1—5 min
TEMP: 800—1200°C
DISCUSSION:

HCl, as hot vapor with dissociation of H_2 and Cl_2 with the acid chlorine vapor used for general cleaning action in epitaxy systems. This includes cleaning of the quartz tube, graphite susceptor plate, and materials to be epitaxially deposited, such as silicon (111) wafer substrates for Si, Ge, GaAs thin film growth in device fabrication.
REF: Walker, P et al — personal application, 1970—1985

CL-0003
ETCH NAME: Chlorine
TYPE: Electrolytic, gas jet
COMPOSITION:
x .... Cl_2
x .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Cl_2 gas used as a jet under pressure for electrolytic forming of etched holes in germanium wafers. See Germanium section for reference.
REF:

CL-0004
ETCH NAME: Chlorine water
TYPE: Acid, disinfectant
COMPOSITION:
x .... Cl_2 (HCl)
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:

Cl_2, as gas dissolved in water . . . chlorinated water, chlorine-water. Used as a general disinfectant in water, for cleaning metal surfaces, and in drinking water to kill bacteria. Pure gas can be used, but more often HCl or a dry chemical chlorine compound, such as a hypochlorate, is used. As a very dilute solution of HCl it is used in medicine for human consumption as an acidifier.
REF: Roe, J H — *Principles of Chemistry*, 7th ed, C V Mosby, St Louis, MO, 1950

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PHYSICAL PROPERTIES OF CHROMIUM, Cr

Classification	Transition metal
Atomic number	24
Atomic weight	52
Melting point (°C)	1875 (1890)
Boiling point (°C)	2582
Density (g/cm^3)	7.2
Thermal conductance ($cal/sec)(cm^2)(°C/cm$)	0.16
Specific heat (cal/g) 25°C	0.11
Latent heat of fusion (cal/g)	21.6
Heat of fusion (k-cal/g-atom)	3.3
Heat of vaporization (k-cal/g-atom)	76.635
Atomic volume (W/D)	7.23
1st ionization energy (K-cal/g-mole)	156
1st ionization potential (eV)	6.76
Electronegativity (Pauling's)	1.6
Covalent radius (angstroms)	1.18
Ionic radius (angstroms)	0.63 (Cr^{+3})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	6.2
Electrical resistivity (micro-ohms-cm)	12.9
Magnetic susceptibility (emu $\times 10^{-6}$)	3.6
Electron work function (eV)	4.37
Cross section (barns)	3.1
Vapor pressure (°C)	2139
Hardness (Mohs — scratch)	9
(Knoop — 100 g load)	700—1200
(Knoop) — $kgf\ mm^{-2}$)	940
Crystal structure (isometric — normal)	(100) cube bcc
Color (solid)	Steel grey/silvery
Cleavage (cubic — poor)	(001)

CHROMIUM CONTAINING ETCHANTS

Several chromium compounds are used as the oxidizing agent in a number of etch solutions. Two widely used are chromium trioxide, CrO_3 and potassium dichromate, $K_2Cr_2O_7$, both used alone or as an additive to other acids. In another instance, metallic chromium is added to solutions. Such solutions have been used on a wide range of metals and metal compounds in addition to oxides and nitrides as surface cleaners to remove contamination, for polishing, thinning, and as preferential or dislocation etchants.

It should be noted that the chromic and chromous ions — Cr^{++} and Cr^{+++} are extremely tenacious and difficult to remove from surfaces even with prolonged and heavy water washing. This is particularly true in cleaning quartz and glassware with the standard "glass cleaner" solution of H_2SO_4:$K_2Cr_2O_7$. It has been shown that quartz diffusion tubes etched in the glass cleaner still contained traces of chromium ions even after 3 days of heavy water washing. This is due to chromium's affinity for oxygen forming Cr_2O_3 and other Cr-complexed surfaces. A final rinse of glassware in a "chrome etch" solution containing either ceric ammonium nitrate or sulfate at 30—40°C is recommended where subsequent diffusion can contaminate parts with chromium which, in turn, can degrade the eventual electrical characteristics of a device.

There are nearly 100 etch solutions shown in this Etchant Section that contain chromium, about half being preferential/dislocation types and the other half polish/removal, all used

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for thinning or structuring. As has been mentioned previously, many etchants are named after their developer and this is particularly true for the dislocation etchants containing chromium that have been initially formulated for silicon. Sirtl's etch, circa 1962, was one of the first and, over the years, several modifications of the Sirtl etch have been introduced for specific enhancement of particular types of dislocations and defects. Such named chromium containing, preferential etchants are Secco, Schimmel, Wright, Erhard's, and others.

The "chrome etch", available commercially mixed, was formulated for controlled removal of chromium and chromium oxide, initially, for the processing of chrome glass masks (CGMs) used in photolithography, and is not included in the following "Chromium Containing Etchants". Chrome regia has already been listed under the "Chlorine Containing Etchants".

The following is a selected list of some of the more prominent etchants containing chromium as applied to metals and compounds. Additional solutions are shown under their individual materials.

Formula	Material	Use	Ref.
$27H_2SO_4$:$70H_2O$;$3Na_2Cr_2O_7$, sat. sol.	Al	Cleaning	AL-0032
35 ml H_3PO_4:20 g CrO_3/l	Al_2O_3	Oxide removal	AL-0001a
0.5 *M* $K_2Cr_2O_7$	B_2Te_3	Preferential	BTE-0001
12 oz H_2SO_4:4 oz$Na_2Cr_2O_7$:1 gal H_2O	Brass	Matte finish/clean	BRA-0008b
5 ml H_2SO_4:1 gCr_2O_5:1250 ml H_2O	CdS	Preferential	CDS-0007b
10 ml HNO_3:10 ml H_2O:4 g $K_2Cr_2O_7$	E Etch CdTe	Polish	CDTE-0006a
10 ml E etch:5 mg $AgNO_3$	CdTe	Dislocation	CDTE-0006b
$3H_3PO_4$:1CrO_3, sat. sol.	$CaWO_4$	Polish	CAW-0003a
xH_3PO_4:xCrO_3:xNaCN	Cu	Removal (dissolves)	C-0006b
$6H_2SO_4$:12CrO_2:82H_2O	Cu	Cleaning	CU-0017
12 oz H_2SO_4:4 oz $Na_2Cr_2O_7$:1 gal H_2O	Cu	Oxide removal/matte	CU-0027b
1 12 *N* HCl:1 17 *N* HAc:1 1 *N* $K_2Cr_2O_7$	GaAs	Polish	GAS-0041
1 ml HF:2 ml H_2O:1 g CrO_3:8 mg $AgNO_3$	A/B GaAs	Dislocation	GAS-0059
0.5 *M* $Cr_2(SO_4)_3$:2 mg Ag	Ge	Electrolytic	GE-0040
1HNO_3:20$K_2Cr_2O_7$, sat. sol.	GeTe	Polish	GETE-0001
1000 ml H_2SO_4:100 g $K_2Cr_2O_7$, sat. sol.	Au	Electropolish	AU-0009
1HCl:1CrO_3:3H_2O	Te	Preferential	TE-0001c
xHAc:xCrO_3:xH_2O	Fe/Ni	Electropolish	FE-0012b
1HF:2CrO_3(33%) Sirtl etch	Si	Preferential	SI-0039
2HF:1 0.75 *M* CrO_3:1.5H_2O Schimmel	Si	Preferential	SI-0017
2HF:1 1.15 *M* $K_2Cr_2O_7$ Secco	Si	Preferential	SI-0036
1HF:1CrO_3(%?) Erhard's	Si	Preferential	SI-0158
60HF:30CrO_3(1 g/l):30HNO_3: 60HAc:60H_2O:0.2 g $Cu(NO_3)_2$ Wright	Si	Preferential	SI-0045
1HF;1CrO_3(38%) Syer	Si	Preferential	SI-0132
1% $Na_2Cr_2O_7$	Si	Cleaning	SI-0066b
xH_2SO_4:x$K_2Cr_2O_7$, sat. sol.	Ta	Cleaning	TA-0003a

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Formula	Material	Use	Ref.
$1HNO_3$:11HCl:$20K_2Cr_2O_7$, sat. sol.	SnTe	Polish	SNTE-0001
1 g Cr:20 ml HBr:20 ml H_2O	SnO_2	Removal	SNO-0001a
300 ml HAc:30 ml H_2O:25 g CrO_3	U	Electropolish	U-0002a
$xHNO_3$:$xCrO_3$:xAl_2O_3 powder	U	Lap and polish	U-0002e
67 ml H_2SO_4:310 ml H_3PO_4:120 ml H_2O: 78 g CeO_3	UC	Polish	UC-0001
16 g CrO_3:5 g $NaSO_4$:15 g H_2O	Zn	Polish	ZN-0008c
160 g CrO_3:500 ml H_2O	Zn	Preferential	ZN-0009
$40H_2SO_4$:$60K_2Cr_2O_7$, sat. sol.	ZnSe	Cleaning	ZNSE-0001b
16 *N* H_2SO_4:5 *M* $K_2Cr_2O_7$, sat. sol.	ZnS	Preferential	ZNS-0001a
0.5 *M* $K_2Cr_2O_7$	ZnS	Dislocation	ZNS-0002
1000 ml H_2SO_4:300 ml $K_2Cr_2O_7$, sat. sol.	SiO_2, Qtz	Cleaning	SI-
Glass cleaner	Si_3N_4		

CHROMIUM, Cr

General: Does not occur as a native element. There are some eight minerals containing chromium, several lead chromates, but the primary ore is the mineral chromite, $FeCr_2O_4$. The formula is variable as iron can be replaced with magnesium, and chromium with aluminum. As the pure chromium, it is one of the hardest known metals (H = 9), and is extremely stable under normal atmospheric conditions.

In the metals industry chromium ore is reduced as an iron alloy called ferrochromium (like ferromanganese and ferrosilicon) and, this alloy added to iron, produces stainless steel (SST), and other special steels. It is a hardening agent in both iron and other metal alloys.

The metal can be easily plated electrolytically and is best known as chrome plate. It forms a hard thin film coating that can be highly polished, and has long been used on vehicles — bumpers, trim, and engine parts. Large, vertical RF plasma sputter systems have been used for chrome plating of razor blades. Such a system has a vertical, central rod of chromium and, for a single sputter cycle, thousands of blades are racked around the inner barrel facing the rod which can be 4 ft long and an inch or more in diameter. Many small parts and tools are chrome plated electrolytically or by RF sputter for general surface protection or wear resistance.

Chromium salts, such as the potassium and sodium chromates are highly colored and extremely active oxidizers. Used as reducing agents to produce chromium hydroxide, $Cr(OH)_3$, they are "chrome tannage" as used in the treatment of leather goods, chiefly gloves of calf skin as glazed kid. Because of their brilliant yellow color, some salts are called "chrome yellow" and used as a paint pigment, and in some special glasses, ceramics, and enamels.

Potassium dichromate mixed with sulfuric acid produces a deep yellow/red solution that turns coal black with usage. It has long been referred to as the "glass cleaner" solution, and used to clean laboratory glassware. Caution should be observed in handling as it is an extremely active oxidizing solution, to include human skin. Sulfuric acid can react violently with water, particularly when hot — always slowly add sulfuric to water; not water to sulfuric.

Technical Application: Metallic chromium has several important uses in Solid State and semiconductor processing. It is a dopant element in some compound semiconductors, but a primary use is in thin film, multilayer metallization as the initial evaporation metal on a highly polished surface where gold, platinum, and palladium are used as the top metal. The precious metals do not adhere well to polished surfaces as they are extremely inert to oxidation; on the other hand, chromium has a high affinity for oxygen, also alloys readily

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with most other metals and compounds, such that it is an excellent tie-down metal as a thin film. Chromium evaporates from the solid phase, not becoming liquid, but going directly to the gas phase — it sublimes — and redeposits as a crystalline structure. Because of this rough crystalline surface, like a lapped rough surface, other metals adhere well. As a multilayer, Au/Cr has long been a general standard for metallization pads and there are others, such as Pd/Cr, Pt/Cr or Au/Pd/Cr, Au/Pt/Cr, etc.

In chrome evaporation, either a tungsten rod plated with chrome is used as a one-shot, throw-away source or chunk chrome pieces/powder in a tungsten boat is the source. In either case, after use, with subsequent exposure to air (oxygen), the surface will oxidize to green chromium trioxide, Cr_2O_3, such that, if the source is to be re-used, it requires heavy out-gassing to remove the oxide before further metallization. If not sufficiently out-gassed, the initial evaporated layer will be a thin film of resistive, glassy trioxide.

For photolithographic patterning, soda-lime glass blanks are chromium evaporated (approximately 2000 Å thick) — the chrome photo resist mask. They commonly have an anti-reflective (AR) coating — oxygen introduced into the evaporation bell jar to form an oxide layer about 400 Å thick (tan color) after chromium has been evaporated, and before opening the bell jar. Such AR coatings have been deposited up to brilliant first order blue or carmine red. These chrome glass masks with or without AR coating have been used as mirrors in a variety of processing applications. One interesting application for a chrome glass plate without AR coating is for a permanent fingerprint identification system. Skin oils act as a mask and activator on chrome, and very clear fingerprints can be developed by light etching in a ceramic ammonium nitrate/sulfate solution. This was developed by these authors and, though not used at present, is a viable approach for better definition than inking.

High purity ingots of chromium using a Vapor Transport (VT) growth method with an iodine atmosphere gas carrier are supplied commercially as a mass of solid chromium crystallites, not a single crystal. Some of the larger, individual crystals, which are single crystal units have been chipped out for morphological study of the metal.

Etching: Easily in HCl or dilute HNO_3, or H_2SO_4. "Chrome Etch" is ceric ammonium nitrate or sulfate.

CHROMIUM ETCHANTS

CR-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

Cr, thin film deposits as a plated surface coating. Solution used to develop cracks in a study of brittle chromium surfaces. CrH will crack subsurface bulk Cr, and cracks propagate by corrosion and stress.

REF: Smith, W H — *Acta Metall,* 103,51(1956)

CR-0002a Walker, P — personal application, 1960—1980

Cr, evaporation film build-up on vacuum glass and metal bell jars or internal fixtures. Remove parts, soak in solution, and scrub with a SST brush. Black smut remaining can be removed with water and wiping with toweling. Can be used on steels, glass, ceramic, and copper parts.

CR-0017a: Nichols, D R — *Solid State Technol,* December 1979

Cr, evaporation deposits in vacuum systems. Solution used for cleaning of bell jars and fixtures. (*Note:* This is an excellent article on the maintenance and cleaning of metal vacuum evaporator systems.)

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CR-0002b
ETCH NAME: Hydrochloric acid, dilute
TIME:
TYPE: Acid, removal
TEMP: RT
COMPOSITION:
1 .... HCl
1—20 .... H_2O
DISCUSSION:
Cr, evaporation deposits in vacuum systems and crystalline chrome pieces. Dilute solutions 1:1 to 1:5 used to clean vacuum base plates and bell jars without removal from the system. Soak heavy toweling with solution and soak/scrub surfaces. In chrome glass mask fabrication "dusting" from chromium particles can be a major cause of film pin-holing and, with eight to ten evaporation runs per day, fixturing may require cleaning on a daily basis.
After breaking down large chunks of high purity chromium for use as an evaporation source, pieces were soaked in the more dilute solutions, DI water washed, and dried under an IR lamp.
REF: Ibid.

CR-0003
ETCH NAME:
TIME:
TYPE: Acid, removal
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... H_2O_2
DISCUSSION:
Cr specimens. Referred to as a general etch for chromium.
REFS: *Metals Catalogue, MRC* (1984)

CR-0017b
ETCH NAME:
TIME:
TYPE: Acid, cleaning
TEMP: RT
COMPOSITION:
1 .... HCl
1 .... glycerin
DISCUSSION:
Cr, as evaporated deposits in vacuum systems. Solution used to remove chrome deposits from stainless steel, glass, ceramic, and copper parts. Do not use on iron.
REF: Ibid.

CR-0017c
ETCH NAME:
TIME:
TYPE: Acid, cleaning
TEMP: RT
COMPOSITION:
5 g .... $KMnO_4$
7.5 g .... NaOH
30 ml .... H_2O
DISCUSSION:
Cr as evaporation deposits in vacuum systems. Solution used to remove chrome deposits from steel, glass and ceramic. Do not use on aluminum.
REF: Ibid.

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CR-0005
ETCH NAME:
TYPE: Acid, patterning
TIME:
TEMP: Warm
COMPOSITION:
453.6 g .... $2NH_4NO_3.Ce(NO_3)_3.4H_2O$
125 ml .... H_3PO_4
2500 ml .... H_2O
DISCUSSION:

Cr, thin film deposits on glass substrates. Solution used for patterning chrome glass masks as photo resist masks. (*Note:* This is one form of the "Chrome Etch" using ceric ammonium nitrate. Nitric acid can replace the phosphoric.)
REF: Angle, D L et al — *Semiconductor Int*, April 1981, 179—196

CR-0006
ETCH NAME: Chrome etch
TYPE: Acid, patterning
TIME: Variable
TEMP: RT or 30°C
RATE: 22 Å/sec
COMPOSITION:
1 g .... $2NH_4NO_3.Ce(NO_3)_3.4H_2O$
10 ml .... HNO_3
100 ml .... H_2O
DISCUSSION:

Cr, thin film evaporation on soda-lime glass used in fabricating photo resist chrome glass masks. Chrome thickness 2000—2500 Å with or without a Cr_2O_3 anti-reflective (AR) coating 400 Å thick (light tan color). Without nitric acid, rate was 40 Å/second. Solution as shown was used as a patterning etch with intense white light (halogen) flooding the surface. Pattern edges etch sharply vertical. Small, half-moon structures along etched edges, termed "mouse-nips", are defect structures that appear to be related to the chrome/glass interface — possibly glass surface defects or due to initial growth nucleation of Cr metal/Cr_2O_3 anomalies.

Solution diluted to 500 ml and used at room temperature without intense light showed a rate of 1—3 Å/sec. Solution used as a slow step-etch in studying the internal structure of the chromium deposits and the chrome/glass interface. Random black spots were observed on the glass surface after chrome removal which could be removed with nitric acid, e.g., probably either CrO or CrO_2, both of which form black oxides. Low spots in the polished glass surfaces can contain an amorphous silica smear from surface polishing? Work compared to commercial "Chrome Etch" (KTI).
REF: Walker, P & Tarn, W — personal development, Optifilm Co., 1974—1975

CR-0007
ETCH NAME: Chrome etch
TYPE: Acid, patterning
TIME: Variable
TEMP: 28°C
COMPOSITION:
1 g .... $2NH_4SO_4.Ce(SO_4)_2.2H_2O$
5 ml .... HNO_3
25 ml .... H_2O
DISCUSSION:

Cr, thin film evaporations on glass substrates used for chrome glass mask fabrication for photo resist applications.
REF: Bulletin 1116B, Rev-HPD/VB/TM/83/1K, MRC Corp., 1975
CR-0004: Trost, E — personal communication, 1974

Cr, thin film evaporation on soda-lime glass used for chrome mask fabrication. Prefers

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ceric ammonium nitrate rather than the sulfate, as the sulfate can leave a scum on glass surfaces.

CR-0015
ETCH NAME: Chrome etch, variation
TYPE: Acid, removal
TIME: 1—2 min
TEMP: RT
COMPOSITION:
12 g .... 2 *N* $H_4NO_3.Cd(NO_3)_3.4H_2O$
60 ml .... H_2O
DISCUSSION:
Au:Cr, thin films deposited by E-beam evaporation on alumina substrates used in a pattern etching study of fine line microelectronic circuit definition. Standard photo resist techniques used with 1350J lacquer. After patterning, gold was removed with tri-iodide etch solution and the chromium with commercial "chrome etch" solution (KTI) to develop the circuit. Chromium also removed with the solution shown for comparative purposes. Both solutions were satisfactory for one mil line definition with the solution shown etching more rapidly. This solution also used for general stripping of chromium from substrates, follow with nitric acid, RT, 1—2 min, DI water rinse 1—2 min, MeOH rinse, and nitrogen blow dry.
REF: Walker, P — personal application, 1983

CR-0010
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
2 .... *$FeCl_3$
1 .... HCl
*30—35°Bé
DISCUSSION:
Cr specimens. Described as a general etch for chromium.
REF:

CR-0001c
ETCH NAME:
TYPE: Electrolytic, polish
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
COMPOSITION:
64% .... H_3PO_4
15% .... H_2SO_4
21% .... H_2O
DISCUSSION:
Cr, thin film deposits as a plated surface coating. Solution used to polish specimens before etching with HCl in a study of cracks in brittle chromium surfaces.
REF: Ibid.

CR-0018
ETCH NAME: Oxygen
TYPE: Gas, oxidation
TIME:
TEMP:
COMPOSITION:
(1) x .... O_2 (2) x .... CO_2

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DISCUSSION:

Cr, thin films evaporated on glass microscope slides used in a study of chromium adhesion and oxidation. Scratch test used a steel stylus with a 0.125 radius to produce parallel scratches cutting vertically into the underlying glass with different gram-weight loads. Cuts observed under transmitted light. Oxidation was done in vacuum under varied back pressure and included treatment with H_2, Ar and methane in addition to O_2 and CO_2 to form Cr_2O_3. It was noted that adhesion tenacity increased with time. See SIO-0040 for preparation of glass substrates. (*Note:* Improved adhesion with time has been observed on both soda-lime glass and alumina substrates.)

REF: Torkington, R S & Vaughn, J G — *J Vac Sci Technol,* A(3)795(1985)

CR-0019

ETCH NAME: RF plasma

TYPE: Ionized gas, removal

COMPOSITION:

68 .... He

30 .... Cl_2

20 .... O_2

TIME: 15 min

TEMP:

GAS FLOW:

PRESSURE: 0.5 Torr

POWER: 100 W

RATES: See discussion

DISCUSSION:

Cr, thin films used as a mask along with PMMA photo resist for photolithographic patterning. Pre-bake PMMA at 150°C, 30 min, and develop in 1 MIBK:3 IPA at 22—23°C, 150 sec for a 3000 Å PMMA layer. Etch rates were: (1) 35 Å/min for PMMA; (2) 110 Å/min for Cr.

REF: Sewell, H — *J Vac Sci Technol,* 15,920(1978)

CR-0008

ETCH NAME: Kodak EB-5

TYPE: Acid, patterning

COMPOSITION:

x .... NaOH

x .... $K_3Fe(CN)_6$

TIME: 1—3 min

TEMP: RT

DISCUSSION:

Cr, thin films evaporated on glass as photo masks or on silicon wafers coated with SiO_2. Used in an evaluation of different epoxy polymers as E-beam (EB) photo resists. Solution shown used to etch pattern deposited chromium — polybutadiene as photo resist coating showed 300× higher sensitivity to EB than KTFR. Develop coating with cyclohexanon at 180°C.

REF: Hirai, T et al — *J Electrochem Soc,* 118,669(1971)

CR-0016

ETCH NAME: Chrome etch, variety

TYPE: Acid, patterning

COMPOSITION:

164 g .... $Ce(NH_4)_2(NO_3)_6$

42 ml .... $HClO_4$

1000 ml .... H_2O

TIME:

TEMP:

DISCUSSION:

Cr, evaporated thin films. Solution used to remove chromium films evaporated on glass masks. Metallization was Cr/As_2S_3/Glass, with the arsenic trisulfide used to improve photo resist pattern definition. After pattern etching chromium with the solution shown, pattern etch remove As_2S_3 with 5% NaOH. (*Note:* See discussion under CR-0006).

REF: Mednikarov, B — *Solid State Technol,* 1984, 177

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CHROMIUM ALLOYS, Cr_xM_y

General: Does not occur in nature as metallic alloy compound. There are about a dozen chromium minerals of which chromite, $FeO.Cr_2O_3$ and crocoite, $PbCrO_4$, are the chief chromium ores.

Industrially, chromium with nickel forms high temperature brazing alloys (soldering below, and brazing above 800°C). There are a wide range of such mixtures as nichromes for specific temperature applications, and are discussed in more detail under Nickel Alloys. Chromel A is 80% Ni:20% Cr, used in steel brazing, and the same mixture has other names. As paired wires — chromel-alumel — it is a widely used thermocouple in the medium temperature range with power/temperature data tables available. There are several iron/nickel/chromium alloys as trinary mixtures in addition to other chromium:metal binary systems.

Technical Application: Other than as general brazing alloys in Solid State processing — mainly for package construction — nichrome is sputter evaporated as a contact pad and, as a thin film with photolithographic patterning, used as an etching mask, e.g., silicon via hole and pit etching with KOH solutions.

Only one chromium alloy is shown here, others are under Nickel and Iron Alloy sections. All alloys have been the subject of study as both mixtures and/or in single crystal form.

Etching: Varies with alloy mixture, but mainly as mixed acids of the oxidation/reduction types ($HF:HNO_3$, etc.).

CHROMIUM ALLOYS

CHROMIUM TITANIUM ETCHANTS

CRTI-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... glycerin
DISCUSSION:
Cr:Ti, alloy specimen. Solution is a general etch for chromium, titanium and their alloys.
REF: Berglund, T & Deardon, W H — *Metallographer's Handbook of Etching*, Pitman & Sons, London, 1931

PHYSICAL PROPERTIES OF CHROMIUM TRIOXIDE, Cr_2O_3

Classification	Metal oxide
Atomic numbers	24 & 16
Atomic weight	152.03
Melting point (°C)	1990
Boiling point (°C)	
Density (g/cm^3)	5.21
Hardness (Mohs — scratch)	8—9
(Knoop — $kgf\ mm^{-2}$)	~2000
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Green
Cleavage (basal — perfect)	(0001)

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CHROMIUM TRIOXIDE, Cr_2O_3

General: Does not occur as a natural compound. The most important ore of chromium is the mineral chromite, $FeO.Cr_2O_3$.

Chromium trioxide is a glass-like material and used industrially for its green color as a paint or glass coloring pigment. (*Note:* Iron imparts a light greenish tinge to glass.) Potassium chromate, $K_2Cr_2O_7$, crystals added to sulfuric acid, H_2SO_4, is the standard "glass cleaner" solution.

Technical Application: Not used in the fabrication of Solid State devices at the present time. It has possible application as a thin film surface protectant to include optical properties for anti-reflection. It is used on chrome glass masks as an anti-reflective (AR) coating.

In powder form it is a lapping and polishing abrasive called "chrome green" and, as an additive to etch solutions, is mainly preferential. There are other chromium oxides: CrO (black); CrO_2 (brown/black); CrO_3 (red); and Cr_2O_3 (bright green). The latter most often recognized as a reaction coating on chromium metal used as an evaporation source in metallization of devices.

Note that CrO_2 thin films have been used as magneto-optics memory devices.

Single crystals of chromium trioxide have been grown and studied for general morphology and defect structure.

Etching: Insoluble in water, acids, alkalies and alcohols soluble in the "chrome etch" formulations containing ceric ammonium nitrate or sulfate. Soluble in fused alkalies. CrO_2 soluble in HNO_3.

CHROMIUM TRIOXIDE ETCHANTS

CRO-0001
ETCH NAME: Chrome etch
TYPE: Acid, removal
TIME:
TEMP: RT to 30°C
COMPOSITION:
1 g .... 2 *N* $H_4SO_4.Ce(SO_4)_2.2H_2O$
5 ml .... HNO_3
25 ml .... H_2O
DISCUSSION:
Cr_2O_3 as amorphous thin films grown on chromium metallized glass masks. The solution will etch both the trioxide and the chromium.
REF: Bulletin 1116B, Rev-HPD/VB/TM/883/1K, MRC Corp 1975

CRO-0002
ETCH NAME: Chrome etch
TYPE: Acid, removal
TIME:
TEMP: 30°C
COMPOSITION:
1 g .... 2 *N* $H_4NO_3.Ce(NO_3)_3.4H_2O$
10 ml .... HNO_3
100 ml .... H_2O
DISCUSSION:
Cr_2O_3 as amorphous thin films grown on chromium metallized glass masks. The solution will etch both the trioxide and chromium.
REF: Walker, P & Tarn, W H — personal development and application, 1976
CRO-0003: Troost, E — personal communication (1976)
Cr_2O_3, amorphous thin films grown on chromium metallized glass masks. Recommends the use of the nitrate rather than the sulfate as the sulfate compound can leave a residual film on the glass.

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CRO-0004
ETCH NAME: Chrome etch
TYPE: Acid, removal
TIME:
TEMP: Warm
COMPOSITION:
453.6 g .... 2 *N* $H_4NO_3.Ce(NO_3)_3.4H_2O$
125 ml .... H_3PO_4
2500 ml .... H_2O
DISCUSSION:
Cr_2O_3 amorphous thin films and thin film chromium deposited on glass substrates. Solution is a general etch for both trioxide and metal.
REF: Smith, R K — *J Appl Phys,* 34,1442(1964)

CRO-0005
ETCH NAME: Chrome etch
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
164 g .... $Ce(NH_4)_2(NO_3)_6$
42 ml .... $HClO_4$
1000 ml .... H_2O
DISCUSSION:
Cr_2O_3 as a thin film contamination on evaporated chromium. Solution used as a cleaning and removal etch.
REF: Mednikarov, B — *Solid State Technol,* 1984, 177

CRO-0006a
ETCH NAME: Sodium hydroxide
TYPE: Molten flux, dislocation
TIME: 5—7 min
TEMP: 550°C
COMPOSITION:
x .... NaOH, pellets
DISCUSSION:
Cr_2O_3, (0001) wafers both cut and cleaved from single crystal boules. Cut wafers were mechanically polished on a wooden lap with diamond paste. Wafers with $(10\bar{1}1)$ orientation were prismatically $[(10\bar{1}0)]$ cleaved in air at RT, and used as-cleaved. After etching in the fused alkali, leach away hydroxide with water to recover specimens. Then wash specimens in hot HCl to clean surfaces, then wash in DI water and dry in air. On basal (0001) surfaces, etch pits were triangular with edges parallel to $(11\bar{2}0)$. On $(10\bar{1}1)$ pits were five sided structures. Dislocations were normal to (0001), random and along grain boundaries. Density measured to be $5 \times 10^5/cm^2$. Potassium hydroxide, KOH, gave less distinct structures.
REF: Brower, W S & Farabaugh, E N — *J Appl Phys,* 36,1489(1965)

CRO-0006b
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
TIME:
TEMP: Hot
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
Cr_2O_3, (0001) and $(10\bar{1}1)$ wafers. Solution used to clean surfaces after preferential etching. After cleaning, wash in DI water and air dry. See CRO-0006a for additional discussion.
REF: Ibid.

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CRO-0007
ETCH NAME: Chrome etch
TYPE: Acid, removal
COMPOSITION:
x .... Chrome etch
DISCUSSION:
P_2Cr_5 as a thin film deposited by E-beam evaporation (EBE) and evaluated for photovoltaic effect. (*Note:* See CRO-0001 for chrome etch solution referenced.)
REF: Toda, K & Crita, M — *J Appl Phys,* 57,5325(1985)

TIME:
TEMP:

CRO-0008
ETCH NAME: Chromium trioxide
TYPE: Material, growth
COMPOSITION:
x .... Cr_2O_x
DISCUSSION:
Cr_2O_3 (111), grown as a single crystal from pressed chromium powder pellets. Furnace was an aluminum tube with a boat pre-coated with Cr_2O_x, then processed at temperature and pressure shown in a CO/O_2(2%) atmosphere. The O_2 partial pressure affected material density. At RT large grains were n-type; at high temperature grains converted to p-type. (*Note:* Cr_2O_3 is hexagonal, not isometric (cubic). (111) should be $(10\bar{1}0)$ prism?)
REF: Young, R W A et al — *J Electrochem Soc,* 132,884(1985)
CR-0009: Torkington, R S & Vaughn, J G — *J Vac Sci Technol,* A(3),795(1985)
Cr_2O_3 thin films grown by oxidizing chromium metal specimens in an O_2 or CO_2 atmosphere. (*Note:* When the metal is used as an evaporation metallization source, it commonly oxidizes after evaporation with a green trioxide coating.)

TIME:
TEMP: 1770 K
PRESSURE: 4×10^{13} atm

CLEANING, GENERAL

General: There are many aspects to the cleaning of surfaces as related to material processing or part and equipment maintenance. Selection of the particular solvent, acid, or alcohol to use is dependent upon the metals, metallic compounds, and other materials involved, and may be a combination of solutions and steps in what are called clean/etch sequences . . . using liquids, hot vapors, ionic gases, molecular gases, and molten fluxes. Cleaning may include pressure, such as in steam cleaning, or as steam drying.

Water alone is considered the universal solvent and, as it is neutral with a pH 7 on the Sorenson Scale, it is the general washing and final rinse solution used after any acid or alkali cleaning step, often followed by an alcohol rinse to remove residual surface water, then with drying in air, nitrogen, argon, or helium. Where heavy dirt and oil contamination are present on parts, they are water washed, to include scrubbing with a soap or detergent solution with or without chelating and sequestering agents. In the processing of critical parts, such as missile and space hardware, both Ivory and Castille soaps are considered as two of the highest purity compounds for detergent cleaning solutions, and Joy liquid soap has been used in cleaning of semiconductor wafers and electronic hardware for the same reason. Ionic and nonionic agents, or a wetting agent such as Glyptal may be added to such detergent solutions, and wetting agents have been added to acid etch solutions, as well, for a cleaning assist action. Laboratory glassware and quartzware are cleaned in either soap solutions or acid solutions, followed by heavy water washing and drying. And in the processing of soda-lime glass blanks as photo resist masks, one step in the cleaning process includes soap solution scrubbing. All soaps and detergents are cleaners or degreasers for removal of dirt, grease, or oil, and used on all materials, not just metals and metallic compounds.

Most small parts as used in the electronics and Solid State industries are free of heavy contamination, such as dirt, and only require light degreasing prior to any chemical treatment.

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Such parts are delivered in clean containers, which may be as plastic bags sealed under nitrogen, plastic envelopes, and boxes, or may be coated with a removable plastic coating, such as lathe cutting or drilling tools; diamond saw blades, or lucite sheeting with a sticky-back paper covering. In some cases, there may be oils, greases and organics from these wrappings and carriers introduced on such surfaces, even though they are relatively clean.

The first step in cleaning such parts, and this applies in particular to semiconductor wafers and their associated metals and assembly parts, is to degrease, liquid or vapor, with solvents. Vapor degreasers have been developed for this purpose from a large glass beaker of boiling TCE to cabinet sized units with boiling liquid, hot vapor, spray heads, with or without ultrasonic vibration, and may include overhead chain hoists to handle heavy single or multiple parts in a basket. Parts are placed in a stainless steel basket — lowered into the boiling solvent for heavy cleaning, or just into the hot vapor head above the hot solvent for general and fine cleaning. The basket is then slowly removed from the vapor head with automatic drying of the hot part. If streaking is observed on surfaces, return parts to the hot vapor as often as needed until clean. The solvent is in a closed, recirculating system, and the working, hot chamber is separated from the return spill-over chamber by a wall with continual spill-over feed of cleaned solvent to the working chamber section. The hot working chamber is surrounded with water cooling coils near the top, hot rising vapors cool and collect on the stainless steel side walls as droplets and return to the chamber bottom — with minimum drag-loss of the solvent to the atmosphere when parts are removed slowly. Both trichloroethylene (TCE) and perchloroethylene (PCE — Perk) are being replaced with either trichloroethane (TCA) or Freons as the solvents due to the carcinogenic nature of chlorinated solvents. Freons are being more widely used as they are inert and leave no residue on surfaces, such as possible Cl^+ ions from TCE and Perk.

Acid and alkali solutions may be as wet chemical etching (WCE) or as electrolytic etching (EE) for liquid solutions, or vapors; or as dry chemical etching (DCE) for ionic gases as RF plasmas. These may be as surface cleaning only, or include minimum polish removal. BRM solutions (Br_2:MeOH) are coming into wide use as bromine (also iodine) clean etch, and polish almost all metals and metallic compounds. Such BRM solutions may be used prior to degreasing or after degreasing as either a chem/mech lap and polish to remove subsurface damage from previous cutting or lapping steps, or as a free-etch for general surface cleaning and polishing. Both acids and alkalies may be used to oxidize a surface as a cleaning step, such as boiling water, nitric acid or hydrogen peroxide, then followed by stripping the oxide with HF. Electrolytic oxidation with KOH or H_2SO_4 and other oxidizing solutions are used in a similar manner, or used to permanently anodize a surface.

Clean/etch sequences follow the general order: etch damage removal; degrease; solution etch clean; alcohol rinse; final acid dip etch clean. There are a number of such sequences described in the Discussion section of Etchant Formats, and can involve any one or all of the steps just mentioned.

Much processing equipment and facility equipment require on-going maintenance cleaning — water lines in particular — and such items as boilers and DI water stills. Hard water and the electrolytic reaction between dissimilar metals cause compounds, such as calcium and magnesium sulfates, or aluminum hydroxide gel to deposit out in piping, and in boilers as scale. High purity water, such as DI water, is an excellent medium for algae growth, such that the water can become contaminated with both flakes of scale from piping as well as skeletons of algae. Improper pipe assembly from weld joints can contribute both particulate matter and unwanted oil-type contamination from fluxes used, and the piping, itself, can slowly disintegrate, introduce particles. Stainless steel piping used in nuclear reactors is internally etch polished to remove proturberances to prevent such particulates occurring.

If not properly maintained, air compressors can introduce oil into air lines, and all equipment is prone to collection of dust and oils from the atmosphere; insulation on high

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power electric lines are spray washed, particularly, in arid areas to remove dust and dirt build-up and prevent arcing: RF generators and their associated lines and insulation, such as used in epitaxy systems, require cleaning even in a clean room environment, also to prevent arcing. Pressurized cans of Freon are used for light cleaning in addition to other solvent or water washing. Water piping is flushed with hydrogen peroxide or potassium permanganate solutions, followed by heavy water flushing, and boilers and stills are etch cleaned with acid solutions . . . HCl, citric acid, etc.

This Cleaning section includes general references for parts and equipment cleaning, and plant maintenance or water systems. Specific applications on metals and metallic compounds will be found under the individually numbered etchants as part of the Discussion section of their formats.

In addition to metal processing technology there are several general methods for cleaning of materials, or approaches used in cleaning parts and surfaces in the home, in small businesses, and similar areas not classified, strictly, as an industrial operation. Several of these are not actual etchants, but a material or method applied in a particular area of work, on specific materials, and so forth. It should be realized that the modern home uses many chemicals on a daily basis, such that some discussion of these items is felt worth mentioning.

Note that several of the items have no reference listed due to the commonality of usage. For those desiring further information, consult any chemical text book, see the information brochure supplied with a product, or contact the manufacturer as they often have pamphlets and brochures available on their specific products.

CLE-0001
ETCH NAME: Citric acid TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... $(COOH)CH_2C(OH)(COOH)CH_2COOH$
DISCUSSION:

Organic acids used for cleaning of power plant equipment. A comparison of formic and citric acids for cleaning water systems.

REF: Loucks, C M et al — *Am Soc Mech Eng Meet,* New York, November—December 1958

CLE-0002: Data Sheet #585 — Chas. Pfizer & Co., Inc. (1958)

Analytical methods of Citrosolv process for determination of dissolved Fe^{++} and Fe^{+++} or copper assay after equipment cleaning.

CLE-0003: Alfano, S — *Electric World,* 5 February 1962

The use of ammoniated citric acid for removal of boiler oxides.

CLE-0004: Data Sheet #557 — Chas. Pfizer & Co., Inc. (1958)

Chemical cleaning of equipment with citric and ammoniated citric acid solutions.

CLE-0005
ETCH NAME: TIME:
TYPE: Sequestrant, cleaning TEMP:
COMPOSITION:
x .... acids/alkalies
+ .... sequestrants
DISCUSSION:

The use of sequestering and chelating agents added to solutions used for the cleaning of water systems.

REF: Loucks, C M — *Power,* December 1961

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CLE-0006
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... acid(s)
DISCUSSION:

A general presentation of the chemistry and cleaning of boilers and heat exchangers in plant maintenance.

REF: Loucks, C M — *Chem Eng*, 5 March 1962

CLE-0007: Data Sheet #593 — Chas. Pfizer & Co., Inc. (1958)

Use of alkaline solutions by immersion or electrolytic etch removal of scale, and for paint stripping.

CLE-0008: Alfano, S & Bell, W E — Int Water Conf, October 1961, Pittsburgh, PA.

Removal of magnetite and copper from boiler surfaces by chemical etching.

CLE-0009
ETCH NAME: Water TIME: Variable
TYPE: Acid, cleaning TEMP: RT to boiling
COMPOSITION:
x .... H_2O
DISCUSSION:

H_2O. Water is the universal solvent, neither an acid nor a base, being neutral with pH 7 on the Sorenson Scale. It is used to quench and stop etching action by soaking; by a dip rinsing; by holding a part in running water in a beaker, or running water as a cascade system; or as a spray. Commercial on industrial water is so called, and used for general cleaning; deionized (DI) water is deionized by boiling and collecting the resulting steam for high purity cleaning requirements. Water can be used chilled; at room temperature (RT); or warm, hot to boiling. The latter is used as boiling water immersion or steam or oxidize a surface. The hydrated oxide may then strip with HF as a cleaning step. It also is used as a cleaning, removal, or polishing solution on soluble compounds, such as the halides.

Water vapor — As a fine mist (fog) for light surface cleaning applied by spraying. Several metallic compounds, such as AlAs as hygroscopic, absorbing water moisture in the atmosphere, and alkaline chemical compounds (KOH, NaOH) deliquesce and liquefy with exposure to air. Pure iron and several iron alloys will oxidize to iron oxides (brown "rust") under normal atmosphere conditions, the brown discoloration observed on "tin" cans, cast iron cooking utensils. Construction girders are coated with red lead to minimize such oxidation.

Steam — Hot water vapor under pressure is used as a cleaning vehicle, as well as a power source for electricity generation or mechanical operation, even as a cutting medium on metals and alloys. Dry cleaning uses steam for pressing, there are steam irons, steam tables in restaurants, building walls, vehicle engines are spray steam cleaned, medical instruments are steam cleaned using an autoclave, these are only a few examples of the use of steam as a cleaning agent.

Water treatment — Natural ground waters contain minerals and organic contamination, as well as industrial wastes, such that water treatment is a major industry, itself. Water can be hard, (arid areas); soft (mountain areas); acidic, with HCl in volcanic areas; acidic with tannic acid in swamps; there are hot sulfur spring and ground waters; and saline water along seacoasts.

Industrial or commercial water . . . filtered to remove solid matter . . . so called "water with the rocks removed" is standard tap water. It still contains dissolved minerals, and is aerated to oxygenize for drinking water, potable water, as against saline nonpotable water. It is the general cooling or wash water in industry, business, and the home.

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Such water may be additionally treated to remove calcium and magnesium sulfates (hard water), with further chemical additives for soft water. Most soaps alone, or detergents, are water softeners to some degree, with or without specific additives in their formulas.

High purity water is distilled by boiling, the resulting steam collected in a separate container (still distillation). In Solid State processing this is referred to as DI water, may be double-, even triple-distilled, and include ion exchange beds containing resins to remove both positive and negative ionic contamination. Although distilled water is potable, it lacks the dissolved mineral content of natural water essential to animal life, and tastes "flat". This DI water is used in car batteries and steam irons, as well as for critical cleaning of electronic parts. And it may be just demineralized, not distilled, sometimes shown as dmH_2O, as against DIH_2O.

The greatest water usage cycle starts with (1) agriculture (greatest volume of use); (2) industrial, which may be prior to, or following agricultural use; and (3) human and animal consumption.

The treatment of waste water is of major concern throughout the industrialize world. All major cities have water waste disposal and treatment plants where both aerobic and anaerobic bacteria are used to clarify the water — it is actually sufficiently clean for use as drinking water — although, if it is not discarded as run-off water, it is usually limited for use in agriculture . . . beginning the usage cycle all over again.

REF: Eisenberg, D & Kadsmann, W — *The Structure and Properties of Water*, Oxford University Press, New York, 1969

CLE-0010a
ETCH NAME: Kerosene
TYPE: Hydrocarbon, cleaning
TIME: Variable
TEMP: RT
COMPOSITION:
x .... C_{10}—C_{16}
DISCUSSION:

Kerosene and gasoline are hydrocarbon derivatives obtained by the fractionation of crude oil, and both are used for cleaning of metals, or as fuels. Petroleum ether, C_4—C_7, also is a solvent with a lower boiling range, e.g., 35—80°C vs. 175—300°C and 40—225°C for kerosene and gasoline, respectively. They are still used as general degreasing solvents at room temperature to warm but, due to flammability, are being replaced by other nonflammable and nonexplosive solvents, such as the Freons.

One clean/etch sequence used for iron is (1) etch with $NaCO_3$; (2) rinse in kerosene/benzene, and (3) wash in alcohol.

REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1947, 652

CLE-0035: Measor, J C & Afzulpurkar, K K — *Phil Mag*, 10,817(1964)

Fe, specimens used in a study of oxidation rates, for clean/etch sequence shown for iron under CLE-0010.

CLE-0023
ETCH NAME: Air
TYPE: Gas, cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
x .... N_2/O_2(24%)
DISCUSSION:

Natural atmospheric air or air in pressurized cylinders, as dry air, is used for both drying and surface cleaning to remove light contamination, such as dust, and there are the household and heavy duty industrial vacuum cleaners for floors, rugs, and furniture. Industrial clean rooms filter in-coming air, and may include electrostatic generators to remove particulate

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dust content where critical parts are being fabricated. Such rooms are closely monitored for a particulate count, in some cases, to less than 10 ppm. Air-conditioning units can include water spray to control humidity, as well as electrostatic elements. Air compressors supply pressurized air for cleaning, in addition to their use for mechanical or electrical operations.
REF: N/A

CLE-00024
ETCH NAME: Cryogenics
TYPE: Liquid gas, cleaning
TIME:
TEMP: −100°C or below
COMPOSITION:
x .... LN_2, and others
DISCUSSION:
LN_2 or other subzero gases or chemical liquids have been used to soak or spray clean surfaces of materials. Pressurized cans of Freon are used to spray clean electronic parts, as both a gas or cold liquid, and such cold sprays are used on specimens surfaces during microscopic examination for both their chilling action and cleaning function. See the section on Water for additional information as "Cold Etchants".
REF: N/A

CLE-0010b
ETCH NAME: Benzene
TYPE: Aromatic, cleaning
TIME:
TEMP: RT to warm
COMPOSITION:
x .... C_6H_6
DISCUSSION:
C_6H_6. Benzene is a coal derivative, as are its homologs, toluene (methyl benzene) and xylene (dimethyl benzene) with general formula C_nH_{n-6}. All are used as general cleaning solvents, alone, or in a clean/etch sequence. In some instances, they are the specific solvent applied to a metallic compound due to the material reactivity with water or other quenching and cleaning solvents. Some benzene compounds are used as hardening agents for photo resist lacquers in photolithographic processing, such as for gallium arsenide devices. These are called the "aromatic compounds" due to their sweet smell. They are relatively heavy liquids and, after use, parts are usually rinsed in alcohol to remove the residual solvents. See CLE-0010.
REF: Ibid.

CLE-0010c
ETCH NAME: Alcohol
TYPE: Alcohol, cleaning
TIME: Variable
TEMP: RT to hot vapor
COMPOSITION:
x .... MeOH, EOH, ISO, etc.
DISCUSSION:
Alcohols are used alone, as a general cleaning solvent; as one or more steps in clean/etch sequences; or as the final rinse after etching and water quenching. Some compounds that are reactive to water are directly quenched in alcohol or the alcohol used as the etchant. Under normal cleaning conditions after acid etching, first water quench, then follow with alcohol rinse, with or without nitrogen blow drying, or simple air drying. Note that solutions containing nitric acid should not be directly quenched with methyl alcohol . . . the combination of red fuming nitric and methanol was one of the first rocket fuels.

Alcohols are derived from different sources and three of the more widely used in industry are methyl, ethyl, and isopropyl. Methyl alcohol (methanol) with the acronym of MeOH, is wood alcohol, as it was initially distilled from wood pulp. Ethyl alcohol (ethanol) with

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acronym EOH, is grain alcohol, though it can be extracted from other vegetation by reduction of starch. It is the nonpoisonous, drinking alcohol; whereas the other alcohols discussed here are poisonous. Isopropyl alcohol with acronyms ISO or IPA is rubbing alcohol.

Industry ethanol contains 5% methanol or ethylene glycol to make it poisonous and nonpotable, although 95% (5% water) pure ethanol is sometimes used. Absolute alcohol is 100%, classified as 200 proof-gallon as drinking alcohol, and used in medicine.

All alcohols will absorb water, such that they are used to remove residual water remaining on a surface following water quench/rinse after etching, with MeOH being more widely used. They also evaporate rapidly, producing a chilling effect. When alcohol is used as a spray, this effect has been used to cool a specimen surface during microscope study. Hot vapors can be used for degreasing or final cleaning like Freons, TCE, TCA, etc., but alcohols are more commonly used as liquids with nitrogen blow-off for drying. Both MeOH and EOH are used as part of etch formulations for either solution viscosity control or cleaning action. Nital (HNO_3:EOH) is a widely used cleaning/polishing/preferential etch on irons and steels, as one example. Many cleaning solutions, as well as shaving lotions and perfumes contain alcohol.

REF: Ibid.

CLE-0015

ETCH NAME: Acids — TIME:

TYPE: Acid, cleaning — TEMP: RT to hot vapor

COMPOSITION:

x .... acid or acid mixtures

DISCUSSION:

Acids and acid mixtures are used for both etching and cleaning, with specific mixtures depending on the material being processed. Weak acids, such as acetic acid (3—5% in vinegar) or an iodine solution are both cleaners and medical antiseptics. Strong acids, such as H_2SO_4 or HCl, even concentrated, are cleaners for the more chemically inert metals, or they are used in dilute form on other metals and metallic compounds.

REF: N/A

CLE-0016

ETCH NAME: Halogens — TIME:

TYPE: Halogen, cleaning — TEMP: RT to boiling or gas

COMPOSITION:

x .... I_2, Br_2, Cl_2, F_2

DISCUSSION:

The halogen group of four elements includes fluorine, the most reactive element known, and the only halogen not used on human tissue as a cleaner or disinfectant. Fluorine, as hydrofluoric acid, HF, is the primary reducing acid for removal of metal oxides . . . glass (SiO_2) is etch polished in liquid HF, and frosted in the vapors. Bromine, Br_2, is poisonous, can cause goiter, so it is not used on humans, but is a widely used cleaning and etching solution when mixed with methanol — Br_2:MeOH — the BRM solutions, and bromine mixed with acetone is "tear gas". Pure choline gas is occasionally used as a cleaning and etching agent, and several of the chlorine compounds are discussed under the Chlorine section. Iodine, as a mixture with potassium iodide, KI, and ethanol is tincture of iodine, and a major medical disinfectant. The I_2:KI:H_2O solutions in metal processing are the tri-iodide etchants for gold, and other metallic compounds. Similar solutions are general disinfectants for plastics, glass in the laboratory, or in the medical facility.

REF: N/A

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CLE-0010d
ETCH NAME: Acetone
TYPE: Ketone, cleaning
COMPOSITION:
x .... $(CH_3)_2CO$
TIME:
TEMP: RT to hot
DISCUSSION:

Acetone has a high affinity for water absorption, such that it is used as a final rinse after etching and water quenching to remove residual water from surfaces. It is used, alone, as the only solvent rinse or in conjunction with alcohols. As a solvent, acetone is the primary agent for dissolving photo resist lacquers, used from a pressurized can as a spray to clean specimen surfaces prior to photo resist application, to clean equipment (spinners, etc.) used in application, and as a soak/spray after photo resist patterning and thin film metallization . . . the lift-off technique.

As a mixture with ice it is used as both a chilling solution for other etch mixtures, and as a drying agent for removal of water vapor from other gases, such as pressurized argon. As a direct spray, it also is used for its chilling action, and has been used on specimen study under a microscope to reduce heat distortion, or reduce electron impingement damage effects using a transmission electron microscope (TEM).

Where acetone is used in a Yellow Room in photolithographic processing, temperature and humidity are controlled, nominally 72°F and 40% RH. This control is not only critical for photo resist lacquers, but in the use of acetone. If humidity is much above 50% RH, an acetone spray will absorb water vapor from the air and deposit droplets on the specimen surface being cleaned . . . contaminating the surface . . . not cleaning it. See the section on Water for "Cold Etchants".
REF: Ibid.

CLE-0014
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
COMPOSITION:
x .... TCE, Perk, TCA
TIME: Variable
TEMP: RT to hot vapor
DISCUSSION:

TCE is one of the chlorinated solvents, all of which are carcinogenic to some degree and, though they are still used for general cleaning and degreasing, are being replaced with Freons and other more inert solvents. Vapor degreasers are used with hot liquid, vapor or spray in cleaning all metals, metallic compounds, and general parts. See the Discussion sections of individual materials for the use of these solvents in specific processing.
REF: N/A

CLE-0017
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions
TIME: 1—10 min
TEMP: RT
ANODE: Material
CATHODE: Pb, Pt, C etc.
GAS PRESSURE: cc/minute as milliTorr (mT)
POWER: KeV range
DISCUSSION:

Argon as ionized gas. Ar^+ ions, are developed by an RF plasma under vacuum, which may be DC power or as RF magnetron (ring magnet on material target being used as the depositing metal(s) to control plasma). These are RF sputter vacuum systems. A basic production type system consists of (1) four target holders above a rotatable specimen holding

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platen; (2) standard vacuum hardware; (3) RF and/or DC controls; (4) a horizontal feeding input/exit section. This latter capable of being brought up-to-air; whereas the working vacuum chamber is held under at least a 10^{-6} Torr vacuum. Three target locations can be used for multilayer deposition of different metals/alloys, the fourth location for argon ion cleaning prior to metal deposition. Power levels vary with materials used, but a nominal range is from 100—150 KeV with a 0.5 mT argon over-pressure (back pressure).

Irradiation: Although argon has been the main ionized gas used for cleaning, all of the inert gases, some reactive gases, and nuclear particles have all been used in bulk and thin film material studies. The latter, thin films, studied both for adhesion and structure alteration; bulk materials and thin films for induced damage, compound regrowth, gas entrapment, bubble or blister formation, and so forth. All such ionic gases and particles can introduce sub-surface damage into a specimen, even Ar^+ ions when being used for surface cleaning, such that power levels vs. material being cleaned can be critical.

Other ionized gases and irradiation studies are shown under the individual metals and metallic compounds.

REF: Farnsworth, H E et al — *J Appl Phys*, 29,1150(1958)

CLE-0018

ETCH NAME: Hydrogen/oxygen

TYPE: Gas, cleaning

TIME:

TEMP: 600—100°C, nominal

COMPOSITION

x .... H_2, O_2, etc.

DISCUSSION:

H_2 in its molecular state, as against ionized H^+, is the reducing atmosphere for removal of oxides from metal surfaces, referred to as hydrogen firing. It also is used for surface cleaning of high temperature metals and alloys, or ceramics and dielectrics, such as alumina and beryllia substrates prior to metallization as microelectronic circuits. Both hydrogen and forming gas (FG) (85% N_2:15% H_2), as a nonflammable mixture, are used in Solid State and metal processing of solder assemblies to prevent oxidation of parts and subsequent adhesion failure. Heat treatment of metals and alloys is usually done in an inert atmosphere, such as nitrogen or argon, but it can be done with hydrogen for specific hydrogen embrittlement of the surface. Note that platinum and palladium as powders — platinum black or palladium black — will absorb large volumes of hydrogen, and are used for such purpose as hydrogen storage systems.

Oxygen: Pure O_2; O_2/Ar, O_2/N_2, or O_2/CO_2 are used to grow metal oxides under hot gas furnace conditions, and may include water vapor as in growing SiO_2 thin films on silicon. Such oxides are "hard" oxides, as compared to the hydrated forms grown from boiling water, HNO_3, or H_2O_2, and from electrolytic KOH solutions. Where the hard oxides are used as etch masks and for surface passivation, the hydrated oxides are often used as a surface cleaning step . . . deposited, then stripped with HF or BHF.

As an oxy-hydrogen torch, the gas mixture is one of the most widely used methods of brazing metals or working glass, other than acetylene or propane torch. As a hot flame, such torches can be used for brazing, annealing, or surface cleaning in the assembly of parts, although the cleaning function is of only minor concern.

REF: N/A

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CLE-0019
ETCH NAME: Dry chemical etching
TYPE: RF plasma, etch/clean
COMPOSITION:
x .... CF_4
x .... O_2 (5%)

TIME: Variable
TEMP: RT
ANODE: Material
CATHODE: Variable by material
GAS PRESSURE: cc/min in milliTorr (mT)
POWER: KeV range

DISCUSSION:

The mixture shown is a generally application gas mixture for many metals and metallic compounds in both the etching and cleaning of surfaces. There are a number of other singular gases or mixtures designed for specific materials, and all gases are used in their ionic species form as against molecular (CLE-0018), as an RF plasma. Where the gas is reactive, such as BCl_3, the system is called Reactive Ion Etching, RIE, and there are several other specialized systems with their own acronyms.

Dry chemical etching (DCE) is one of the major divisions of etching as used in this text, and is more often applied for selective structuring of Solid State devices than as a cleaning method.

REF: Bollinger, D et al — *Solid State Technol,* March 1984, 117

CLE-0020
ETCH NAME: Indium
TYPE: Metal, cleaning
COMPOSITION:
x .... In

TIME: Variable
TEMP: Molten

DISCUSSION:

In, as a molten metal is used as a surface cleaner and light material remover in liquid phase epitaxy (LPE). It is specifically used with indium phosphide, InP, wafers during the growth of additional thin film InP. In LPE systems the wafer substrates are attached to a graphite plate that is wiped horizontally across the surface of the molten metal to effect epitaxy thin film growth. In order to reduce defects being introduced into the growing film from the substrate, the initial operation uses what is called the melt-back technique, where the substrate surface is cleaned with the molten metal before controlled growth is initiated. Further melt-back may be done on the growing thin film during growth, also to improve the quality of the film. Similar LPE melt-back is done with other materials, such as gallium melt-back is used in growing gallium arsenide thin films on gallium arsenide substrates.

Molten Flux: High melting temperature and chemically inert metals, such as titanium, molybdenum, tantalum, and tungsten are surface cleaned or etched in molten metals. The flux can be a metal or mixture of chemical compounds, applied to any material, often as a preferential etch in addition to cleaning. Such fluxes also are used in the growth of single crystals, such as garnets and ferrites. See CLE-0029 — Hone: CLE-0022 — Abrasion.

REF: N/A

CLE-0021
ETCH NAME:
TYPE: Methods, cleaning
COMPOSITION:
x .... solvents/acids/alkalies

TIME:
TEMP:

DISCUSSION:

Methods of surface cleaning described for (1) solvent liquids/vapors; (2) acids — HCl; H_2O_2; HNO_3; HAc, alone or as mixtures; (3) alkalies — both hydroxides and/or carbonates;

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(4) heat treatment — vacuum, wet or dry atmospheres of N_2, H_2, O_2 or air; (5) aqueous oxidation — H_2O_2 and H_2O_2:NH_4OH, and (6) ultrasonic — detergents, solvents, acids, or alkalies. Also electrolytic solutions, and the use of abrasives included.
REF: *Bell Tel Tech Pub*, 3143(1958)

CLE-0022
ETCH NAME: Abrasion
TYPE: Abrasive, cleaning
COMPOSITION:
x .... abrasive grit/paper etc.
TIME:
TEMP: RT
DISCUSSION:

Abrasive lapping of a surface for general cleaning. Sand for scouring; sandpapers, such as SiC or emery; smooth paper or rough filter paper only; colloidal liquid suspensions of SiO_2 or Al_2O_3. Applicable to use on several materials, other than those usually thought of as abrasives, such as metals, glass, woods, and even some plastics.

Pads of steel, copper, and plastic with or without detergents are used to remove heavy contamination on industrial equipment and parts, as well as in general cleaners of pots and pans in a household. Hand brushes of steel, brass, plastic, or copper are used in a similar manner. Grinding wheels and arbor brushes; bead-blast cleaning with sand under pressure; steel, glass and plastic beads rotating to clean surfaces as in removing old paint from small parts.

Abrasives are most often used in slurry form. In Solid State material processing a mixture of W-5 garnet (15 μm grit) in water and glycerin is widely used for lapping wafers with final water washing. Finely powdered white alumina (Linde A and Linde B) and diamond grits of less than 1 μm size are used for final surface polishing and cleaning.
REF: N/A

CLE-0025
ETCH NAME: Borax
TYPE: Borate, cleaning
COMPOSITION:
x .... $Na_2B_4O_7.10H_2O$
x .... H_2O
TEMP:
TEMP: RT to hot
DISCUSSION:

Borax, as the natural mineral, has been in use for over 3000 years with several uses: for washing and cleaning of cloths and dishes; as an antiseptic and preservative; as a solvent for metallic oxides in soldering and brazing; as a general flux in alloying metals. In washing it is a water softener for hard water. The Arabs and Egyptians were using both borax and niter (sodium carbonate) solutions in mummification, and as a flux for gold soldering, as far back as 4500 B.C. during the Egyptian Dynastic Period. "20 Mule Team Borax" was mined from the California Death Valley area beginning in the late 1800s.

In metal processing, to include Solid State materials, borax has been used for surface cleaning, and as a constituent in some cleaning and etching solutions with other acid components.
REF: Dana, E & Ford, W E — *A Textbook of Mineralogy*, John Wiley & Sons, New York, 1950, 743

CLE-0027
ETCH NAME: Broom
TYPE: Broom, cleaning
COMPOSITION:
x .... straw, wood, plastic, etc.
TIME:
TEMP: RT

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DISCUSSION:

Brooms and mops have been in use since most ancient times for general removal of litter on floors, tables, walls, etc. The first brooms were wood twigs, rushes, or leather strips tied together on a wooden handle with plaited grass or leather as a tying rope. Large palm leaves are still in use in the Pacific area, as are tree leaves in Africa and southern Asia.

The use of straw and feathers also is of ancient origin, both still in use today as the standard household short- or long-handle brooms for floors and tables or a feather duster. Horse hair brooms have a long history of use and today plastic brooms of many sizes and shapes are standard in both industry and household use, to include large push brooms. The latter may be of cloth, with or without oil for additional dust collection or for polishing action, such as heavy-duty floor polishers to include waxing, or vehicle driven street sweepers with their circular, rotating brushes.

The standard mop is similar to a broom, but is an assembly of fairly thick ($^1/_8$" diameter) cloth strings or strips that can be used as a dry oil, or wet mop. The latter is used with a mop bucket to hold water and a roller squeezer, and the bucket may be on wheels. There are squeegee type mops with foam plastic inserts for throw-away and replacement when the plastic becomes too stiff and loses absorbency.

Common terms are dusting, mopping, scrubbing, and brushing. The soft camel's hair brushes have special application in painting and cosmetics, and there is a special static removal brush used on engineering vellum, or in static sensitive areas. The brush body contains a replaceable strip of radioactive polonium, Po, behind the camel's hair brush section (about 2" wide) with a handle. Continual rubbing across a paper or plastic/wood surface or cloth, even a metal surface can build up a static charge of electricity . . . it can make paper lift and curl when the hand approaches . . . and an electric spark discharge can occur. This is a common occurrence in households during cold or dry weather, when an individual walks across a rug — building up a static charge — then reaches for a door handle . . . zap . . . a static discharge. The static brush, when wiped across a surface, will remove the static charge. There are other, larger static eliminators available that blow cold or hot air across the polonium strip to remove the charges and there are smaller "spike charge" units electrically activated to eliminate static. Most houses have static arresters (against lightning), metal wire and rods buried in the soil, e.g., grounding. Static electricity is used to collect dust in some homes and many businesses as part of the air-conditioning or heating duct systems. See CLE-0033 for use of ozone, O_3, for elimination of smoke, CLE-0028 for use of a brush.

The legendary Witch's Broom is most often depicted with wooden twigs as the broom section, and there is a plant called Witch's Broom, the tassels sometimes used as a dusting broom. The tail of a fox is called a brush, and has been used as such, as have been other animal furs.

N/A

CLE-0028

ETCH NAME: Brush TIME:

TYPE: Brush, cleaning TEMP: RT

COMPOSITION:

x .... bristles (pig), plastic, etc.

DISCUSSION:

Brush is another name for broom (CLE-0027) but is discussed here separately due to some more specific applications than just general cleaning as associated with brooms and mops. As a hand brush, notably for personal grooming, pig's bristles have been in use since ancient times, today, plastic fibers and other fiber-like materials are more prevalent.

Most well known as a brush and comb set for personal use, the comb is made of —

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originally — wood or tortoise shell — now, also of plastic, metal, etc. With metal bristles, one type of brush is known as a Curry Comb used for grooming horses; another, with a wooden handle and steel bristles, as a heavy duty scrubbing brush on metal parts — removal of scale (oxidation and other contamination products), old paint, thin film metal plating, extraneous thin film metal build-up on parts due to metal evaporation. Smaller steel or brass bristle brushes are used for general scouring of pots and pans in cooking, or to "brush pattern" a softer surface of metal, plastic, leather, wood for decorative purposes. Plastic fiber brushes in a wood or plastic housing are similarly used for scrubbing. Scouring pads — fine metal or plastic mesh — with or without soap detergent in the pad, are general scrubbing brushes.

A fox's tail is called a brush, used as an item of apparel, or used as a dusting brush like a feather duster. Other forms of special brushes are part of manicure sets, such as the finger-like chamois skin brush used for polishing nails, and small eye brushes for make-up shadowing. The whisk broom is a hand-sized "broom" of straw for general surface cleaning, notably used for removing lint from clothing by "whisking". There is a special dusting brush — a wooden handle/holder about $^1/_2$" wide — the brush portion about 2" in depth — total length about 1 ft . . . originally designed for use on a drafting table to remove dust and detritus from erasers, pencils, etc. used in drawing, also now used as a general table duster. There are long metal bristled brushes with the bristles set in a slightly mobile rubber/plastic base, used for grooming and carding the fur of cats and dogs, or as a carding comb used for separating flax fibers. Also the horse curry comb already mentioned under CLE-0027.

REF: N/A

CLE-0029

ETCH NAME: Hone — TIME:

TYPE: Stone, cleaning — TEMP: RT

COMPOSITION:

x .... rock, metal, etc.

DISCUSSION:

Hones are used for cleaning and sharpening, and may be used dry, water wetted, or impregnated with oil. Arkansas stone is a hard, fine grained and dense aluminum oxide rock long used for sharpening metal knives . . . by "honing". Natural emery is a mixture of aluminum oxide and magnetite, magnetic iron ore — Al_2O_3 and Fe_3O_4, respectively, and similar to Arkansas stone in use. Turkish emery is considered of highest quality, and both types of stones are also referred to as whetstones. And today, artificial silicon carbide, SiC, known commercially as carborundum, also is used as a hone. All of these rock type materials have a Mohs hardness rating of H = 9/9+, second only to diamond and capable of cleaning, cutting, or polishing all other materials. There also are artificially hardened or fabricated metals, metal alloys, carbides, and borides. The carbides may be as shaped parts for use with a drill press or hand drill, and used for cutting, shaping, or cleaning of other materials.

In some countries the itinerant knife grinder still comes around with his foot-powered grinding wheel; straight razors are sharpened with a combination of a leather strop and stone hone; and a meat carving knife set includes a serrated metal tong for sharpening. Hand and electric hones use a series of hard steel discs across which the knife edge is drawn for sharpening.

The term "stoning" is sometimes applied to the use of rocks as a cleaning or surface conditioning agent, such as wood being stoned to develop a grain finish structure.

REF: N/A

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CLE-0010e
ETCH NAME: Ether
TYPE: Ether, cleaning
COMPOSITION:
x .... $C_2H_5OC_2H_5$
DISCUSSION:
TIME:
TEMP: RT to warm

Ether (ethyl ether) is made by treating ethyl alcohol with sulfuric acid to produce a colorless, volatile liquid with a pleasing odor. It has long been used as a general anesthetic, but has been largely replaced by other less inflammable and explosive chemical compounds as ether will ignite and burn in air. It is an excellent solvent for fats, gums, and resins, and may be a constituent in some household cleaning solvents, though ammonia, NH_3, is more widely used (Windex).

Ether is used in many chemical processes, and is a fuel additive in high performance racing cars. It is occasionally used in Solid State chemical processing as a cleaning and dry solvent similar to alcohols or nitrogen gas.
REF: Ibid.

CLE-00031
ETCH NAME: Rubber
TYPE: Organic, cleaner
COMPOSITION:
x .... rubbers
DISCUSSION:
TIME:
TEMP: RT

Rubber from the South American rubber tree was imported to England in the early 1800s as Indian rubber as it was found to erase pencil marks from paper by rubbing. It is still so used, to include "gum rubber" as 1″ squares, 2″ long yellowish bars of a soft rubber widely used in engineering drafting. Other than as a paper pencil mark remover, there are many rubber products, today, from vulcanized vehicle tires to plastic rubber products. In industry two artificial rubbers are Buta-A and Viton used as gasket seals in vacuum equipment, and there are others such as Buna-N, isoprene, neoprene, etc.

British gum is dextrin, $C_6H_{10}O_5$, as a by-product in the reduction of starch for its sugar content, when mixed with water is called mucilage (glue). Animal glues are from hooves and horns; acrylics from plastics; white paste glue from flour and water . . . none of which are cleaners . . . but can be dissolved with some of the alcohols and other fluid cleaners described here. Methyl ethyl ketone, MEK, is one such solvent.
REF: N/A

CLE-0032
ETCH NAME: Sand
TYPE: Rock, cleaner
COMPOSITION:
x .... SiO_2, grains
DISCUSSION:
TIME:
TEMP: RT

Sand as water-washed, roughly rounded grains of silicon dioxide, SiO_2. When mixed as a water slurry, sand has been used since ancient times to scour and clean cooking utensils. Under pressure, using dry air or nitrogen as the carrier gases, it is called sandblasting or bead blasting, as it may be artificially fabricated "beads" of glass. In either case, pressurized sand particles are used in many areas and industries to clean material surfaces from removing grime from rock building faces to paint removal from parts; to general cleaning or roughening a metal surface; or to develop grain structure in woods with both cleaning and polishing action. S.S. White Dental units were initially developed with a rubber tube and small exit nozzle using finely powdered sand under pressure to clean teeth. They have been adapted

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for general industrial use as a method of cleaning, cutting, or shaping of parts. One example of such use is in the fabrication of screws, as these mobile nozzles are one of the few methods capable of cutting a re-entrant angle, or to form a circular hollow within a solid material, etc. They also are used in the fabrication of jewelry and in the pattern frosting of glass, rather than using hydrofluoric acid, HF, which is particularly dangerous. These S.S. White units were initially used in the early days of the semiconductor field for both dicing wafers and as general surface cleaners and, more recently, for angle shaping exposed p-n junctions around the wafer edge.

There are many other natural rocks that, when powdered, are used as cleaning, removal, or polishing abrasives. Selection depends on the Mohs hardness, abrasive size, and particle shape, e.g., sand has a rounded shape — quartz forms sharp slivers with faster cutting action — as colloidal silica, the submicron-sized spherical particles produce a fine polish. All silicas have a Mohs hardness of H = 7, but it is the particle shape that controls the cutting, polishing, or cleaning action.

Corundum, Al_2O_3 (H = 9) has sharp, flat grains; garnets (H = 5) have blunt grains that break down in size during use, giving finer and finer cleaning and polishing action; limestone, $CaCO_3$, (H = 4—5) has soft grains; diamond, (H = 10), the hardest material, has angular grains and gives fine polishing action, and is most commonly used in an oil paste. Artificial borides and carbides or cubic boron nitride, B_4N, and silicon carbide, SiC, with a hardness of H = 9+, can have a blocky grain structure with rapid cutting action.

Lava soap contains a high percentage of silica grains that were originally obtained from pumice, a froth-like, physically light rock extrusion from volcanic magmas. Pumice is used as a whetstone for cleaning other materials, as well as a lightweight building stone.
REF: N/A

CLE-0010f
ETCH NAME: Ozone
TYPE: Gas, cleaning
TIME:
TEMP: RT to warm
COMPOSITION:
x .... O_3
DISCUSSION:

O_3, as ozone, occurs naturally in the atmosphere in small quantity. Fluctuation of the ozone-oxygen level in the high altitudes over the Antarctic are of concern, as ozone acts as a screen against ultraviolet light rays from the sun. It can be stable for years at very cold temperatures, months at room temperature, but decomposes rapidly above 100°C; almost instantaneously and explosively at 300°C. Ozone can be formed from normal O_2 by passing air through an electric discharge, e.g., the pungent odor associated with lightning storms. The rapid quenching of flames from a burning wood fire produces some ozone, and it is part of some chemical processes; 1 ppm in air can be injurious to health.

Ozone is an extremely powerful oxidizer, and electrically powered ozone generators are used in buildings such as theaters, restaurants, etc. as air fresheners. There are small cigarette ash tray units available that will dissipate the smoke from a burning cigarette. Larger units, with air being blown through an electric discharge, are used to clean metal surfaces in industry: the part is held in the ozonized air for a few seconds to clean.
REF: Ibid.

CLE-0034
ETCH NAME: Soap
TYPE: Organic, cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
x .... $3C_{17}H_{35}COO$

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DISCUSSION:

Soap is made by treating fats and oils with sodium or potassium hydroxide. Sodium soaps are hard, while potassium soaps are soft. Other oils may be added, such as lanolin (from sheep) in Dove soap. Other oils are used, such as palm oil (Palmolive soap) — or scented with chemicals and natural herbals — sandlewood, lemon, Attar of Roses, are all used. Two of the highest purity soaps are Ivory and Castille soap, both recommended for the cleaning of critical parts, such as missiles and space hardware. Lava soap contains a high percentage of powder pumice (volcanic silica froth rock), specifically designed for removal of heavy grease, oil, and grime; anyone who has been in the U.S. military is familiar with the semisoft, yellow blocks of lye soap, with a high sodium hydroxide content for improved chemical cutting action. Both KOH and NaOH may be referred to as "lye", and sodium hydroxide as "caustic soda". In water solution, alone, they have a soapy feeling and, in high concentration, can cause blisters and burns on the skin, though they are not quite as dangerous as acids. The hydroxides are chemical bases, and when mixed as Normal solutions will neutralize a Normal acid solution.

There are many liquid soaps that grade into skin creams with added palm, lanolin, or coconut oils. Both liquid and dry powdered soaps used for dishes and clothes washing are called detergent soaps, and contain chelating or sequestering agents that improve wetting action, control sudsing action for foaming or de-foaming. Pure oils alone have long been used to clense skin. The ancient Greeks rubbed themselves with olive oil, then scraped it off with a stigil. Today there are many oils and creams as sunscreen lotions, and Chapstick is a thickened petroleum jelly similar to Vasoline. The latter may be mentholated. Egyptian records dating back to 4000 B.C. list hundreds of formulas as their priesthood were the original chemists and medical practitioners in the Mediterranean area.

REF: Ibid.

CLE-0036

ETCH NAME: Vacuum TIME:

TYPE: Vacuum, cleaning TEMP: RT

COMPOSITION:

x .... vacuum

DISCUSSION:

Vacuum is created by the removal of air and other gases from a container. A mechanical vacuum pump (oil pump — roughing pump) is constructed with internal moving vanes and chambers that physically pull air from a closed glass or metal chamber through an attached hose to create a vacuum in the chamber. They are nominally rated for a 10^{-3} Torr vacuum level (1 μm), and are used as the initial pump in industrial vacuum systems. These mechanical pumps are called roughing pumps, and there are similar cryo-pumps, chilled with LN_2, that operate the LHe without oil.

Vacuum systems as used in Solid State and metal processing range from small R & D type units to large production systems, but all operate in a similar manner. Once the initial pumpdown is completed with a roughing pump, the system is switched over to a high vacuum pump — hot oil; cryo-pump with helium and charcoal getter; turbo-pump; ion pump — with the cryo-pumps currently most prominent as oil-free systems. There are large, walk-in vacuum chambers, such as those used in testing satellites; and belt systems, where a continuous roll of material, such as mylar, can be fed through and metallized. Vacuum work is most often done on the 10^{-5} to 10^{-6} Torr, but modern systems are capable of levels to 10^{-10} and 10^{-11} Torr. Note that space vacuum is considered to be on the order of 10^{-18} Torr. There are RF/DC sputter systems; ion milling systems; and RF dry chemical etching systems, using ionized gases. The two latter systems are used for structuring material surfaces and multilayer thin films.

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Any vacuum system can be used with vacuum, alone, as a drying and cleaning agent, or in can include heat in inorganic material processing. And organic material, such as foodstuffs, are now vacuum packed, the operation combining a drying action with vacuum sealing the product in a plastic bag. This may be as vacuum freezing, but quick-freezing vegetables is a different process as moisture is retained.

Other vacuum systems include the household vacuum cleaner, and there are units capable of either vacuum or air blowing by including a reversing switch. Large industrial systems may be for cleaning floors, vacuum removal of water and, where oil spills in the ocean occur, for vacuum removal of oil. Vehicle mounted systems are used in street cleaning with a combination of vacuum and air blowing, and rotating brushes.
REF: N/A

CLE-0037
ETCH NAME: Oil
TYPE: Oil, cleaning
COMPOSITION:
x .... oil
TIME:
TEMP: RT to warm
DISCUSSION:

Oil used as a cleaning solution. Mineral oil from petroleum or coal; animal oil, such as lanolin from sheep; or vegetable oils, such as olive, peanut, linseed, safflower, or cottonseed oil. Olive oil has been used in the Middle East and Mediterranean are as a body cleansing oil since at least 3000 B.C. — rub oil into the body, then scrape excess away with a wooden or bone stigil. Oil also is worked into leather to make it pliant, as well as for cleaning action: saddle soap is a soft, high oil content soap used alone for cleaning, or following by waxing. Linseed oil is rubbed into wood to bring out grain structure, as well as for cleaning and polishing. Cottonseed oil is used in large quantities for the making of soaps. Oil mops are made of cloth pads saturated with oil, used for cleaning and polishing floors, and oiled hand clothes on furniture, table tops, etc. The oil aids in dust and dirt removal, and leaves a thin protective surface coating to prevent drying out. Light oils, such as 3-in-1 oil, are used to both remove dust and dirt from parts as well as a lubricant; there are various grades and thickness of car engine oils, some with chemical detergents added to improve cleaning action. There are plastic compounds that grade from a thin oil, to grease consistency, to solids, all of which have been used as cleaners in addition to their properties such as lubricants.

Oils can be homogenized or thickened to cream consistency, such as cold cream used as a facial cleanser . . . lanolin and coconut oil widely used as the base ingredient in such facial creams . . . suntan lotions are similar from a light oil to cream consistency with additional sunscreen additives. There is a new product containing small spheres of artificial sponge in a suntan lotion cream, the sponges helping to retain body oils and perspiration. Natural sponges have long been used, soaked in water or oil for cleaning . . . called "sponging", and, today there are plastic sponges used in a similar manner.

Thickened oils also become greases: grease-paints in various colors for facial decoration . . . used in religious ceremonies since earliest times, the American Indian "war paint", today the circus clown . . . removal is often with cold cream. Cosmoline is a heavy grease used to coat weapons and other metal parts for long-term storage to prevent rusting, and soft iron lapping platens are coated with a light oil or glycerin also as a rust preventative.

Spermiceti — whale oil — is actually a wax-like substance obtained from the head of the sperm whale. Its primary use, again, since ancient times, has been for illumination . . . an oil lamp. The spermiceti flame was used to establish the International Candle-Power unit as a light intensity measurement.

Some nut oils are used in cosmetics. Coconut oil has been mentioned, but almond oil is widely used; peanut oil most often used in cooking. Oil from citrus fruits — orange,

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lemon, lime, tangerine — for food flavoring, in air fresheners, facial creams, soaps . . . the colored rinds called "zests" as food additives. Many flowers produce oils, such as violets and roses. The latter as Attar of Roses, both used as air fresheners, in soaps, etc. Aromatic wood oils: Oil of Cedar was in use in biblical days in Asia Minor from the Cedars of Lebanon, and Sandlewood pre-dates even the use of cedar, circa 3000 B.C. Both used as air fresheners . . . sandlewood as incense . . . cedar for both fine odor and as a preservative against insect pests for storage of clothing . . . the cedar chest.

Waxes are another category derived from oils. Paraffin is from petroleum; beeswax from the honeybee honeycomb; carnauba wax from the conifer tree of the same name; castor oil from the castor bean; beechnut oil from the beechnut tree; myrtl oil from the bush myrtl; neat's foot oil from cow hooves. All of these natural oils can be used in wax formulations. And there are many artificially derived chemicals as oils or waxes, such as banana oil. Such oils are mixed with waxes, such as beeswax:paraffin for polishing and cleaning, as wax produces a more long-lasting, often water repellant surface finish than oil alone.
REF: N/A

CLE-0038
ETCH NAME:
TYPE: Alkali, cleaning
COMPOSITION:
x .... 2—10% KOH/NaOH
TIME:
TEMP: RT to boiling
DISCUSSION:

Hydroxide solutions of low concentration are general metal cleaners and, in electroplating, may be used as a pickling bath or for surface conditioning. Other base chemicals (>pH 7, Sorenson Scale) may be used with the hydroxides or by themselves, such as carbonates and borates. After alkali cleaning, wash parts thoroughly until the soapy feeling of surfaces is removed. Higher solution concentrations, particularly when used hot to boiling, can be preferential etchants on metals, and will produce severe skin burns.

Some household cleaners, such as Drano, contain hydroxide and should not be handled with bare hands.
REF: N/A

CLE-0039
ETCH NAME:
TYPE: Electrolytic, cleaning
COMPOSITION:
x .... x% KOH
or x .... acids
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Hydroxides are used as surface oxidizing solutions with deplating by anode/cathode reversal, or the oxide is stripped with HF as a method of surface cleaning. Acids such as HCl and H_2SO_4 also may be used as electrolytic surface cleaners, or used as wet chemical etching (WCE) cleaners without electric current. HNO_3 and H_2O_2 will be oxidizing like the alkalies.
REF: N/A

CLE-0040
ETCH NAME: Ammonia
TYPE: Base, cleaning
COMPOSITION:
x .... NH_3/NH_4OH
TIME:
TEMP: RT

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DISCUSSION:

Both ammonia and ammonium hydroxide are general surface cleaners, and also used to neutralize acids. Chemical acid sinks are drained into an acid sump, which is then neutralized with ammonia before effluent release into a city sewer system. Note that alcohols are disposed of separately, not down an acid drain, as alcohol/acid mixtures can be toxic or explosive, and alcohols will kill bacterial action used in water waste disposal operations.

Crystalline ammonia is the medicinal "smelling salts". The tarnish observed on silver, often due in part to the presence of sulfur compounds in the air, is easily removed with ammoniated compounds supplied as a paste or saturated cloth. There are similar compounds for brass, bronze, and copper, such as "Brasso".

REF: N/A

CLE-0041

ETCH NAME: Zeolite

TIME:

TYPE: Mineral, cleaning

TEMP: RT

COMPOSITION:

x .... $(Ca,Na_2)O.Al_2O_3.9SiO_2{:}6H_2O$

DISCUSSION:

There are some 30 zeolite minerals as natural hydrated silicates, the formula shown is for the mineral mordenite which is typical as a calcium, sodium, or aluminum silicate. They are used in granular form as drying compounds. Commercial Dri-Rite is dyed light blue in color and, as it absorbs moisture from the air, it turns light pink. Oven baked above 125°C to remove collected water, granules return to the blue color, and material can be re-used. Place a small amount in the bottom of a glass desiccator jar, cover and seal with a vacuum grease, and material will remain dry without oxidizing. Hygroscopic compounds, such as AlAs, are held in desiccators. In food processing, desiccator drying, to include heat and a light vacuum to draw off liquids is one preparation method, and zeolites are used in shipping packages or cartons as a drying compound against possible breaking or spills.

REF: N/A

CLE-0042

ETCH NAME: Hydrofluoric acid

TIME: Variable

TYPE: Acid, cleaning

TEMP: RT to hot

COMPOSITION:

x .... HF

DISCUSSION:

Hf is the primary reducing and oxide removal acid used in Solid State material processing. It is used alone, as a concentrated etchant, water or alcohol diluted, or mixed with other fluorine compounds, as buffered hydrofluoric acid (BHF) solutions. It will remove the "native oxide" that automatically forms on metal surfaces as a passivating layer when exposed to atmosphere, and has long been used in the etch patterning of glass — immerse to polish — vapors for frosting. It is considered a cleaning solution for stripping of thin film oxides only, otherwise it is the reducing acid in oxidation/reduction solution mixture, with HNO_3, H_2O_2 as the oxidizers. Caution should be used in handling any fluorine containing acid or compound due to health hazard.

REF: N/A

CLE-0043

ETCH NAME: Heat

TIME:

TYPE: Thermal, cleaning

TEMP: >22.2°C

COMPOSITION:

x .... heat

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DISCUSSION:

Thermal heat treatment of metals and metallic compounds used as a cleaning or drying agent, alone, under vacuum conditions, or with inert gas atmospheres under furnace conditions. Pure heat also is used in fabricating metal alloys (irons, steels, coppers, aluminums, etc.) for specific structure, and characteristics such as material strength, ductility, hardness, and so forth. With temperature as the main factor, may act as a preferential structure and defect etchant. With reactive atmospheres, in addition to cleaning action, to passivate or condition surfaces by nitridization, oxidation, sulfurization, halogenation, etc. Drying with heat includes the use of white light or IR lamps, such as for drying automotive paints or general parts after water washing or acid treatment.

Clothing is dried and cleaned by hanging in sunlight; salt is collected by evaporation of sea water; foodstuffs are dried either in the sun or by hanging in a cool, dry storage area. These are all methods of cleaning and drying with the use of some form of heat.

REF: N/A

PHYSICAL PROPERTIES OF COBALT, Co

Classification	Transition metal
Atomic number	27
Atomic weight	58.93
Melting point (°C)	1495
Boiling point (°C)	2900
Density (g/cm^3)	8.92 (8.71)
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.1652
Specific heat (cal/g) 25°C	0.1056
Latent heat of fusion (cal/g)	58.14 (62)
Heat of vaporization (cal/g)	1500
Atomic volume (W/D)	6.7
1st ionization energy (k-cal/g-mole)	181
1st ionization potential (eV)	7.86
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.16
Ionic radius (angstroms)	0.72 (Co^{+2})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	12.5
Electrical resistivity (ohms-cm)	6.24
Curie temperature (°C)	1121
Poisson ratio	0.32
Young's modulus (psi $\times 10^6$)	30.6
Tensile strength (psi $\times 10^3$) — annealed	37.0
Compressibility ($cm^2/kg \times 10^{-6}$)	0.50
Electron work function (eV)	4.18
Cross section (barns)	37
Hardness (Mohs — scratch)	8+
(Brinell — kgf/mm)	125
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Grey-reddish
(gas/pigment)	Cobalt blue
Cleavage (prismatic)	$(10\bar{1}0)$

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COBALT, Co

General: Does not occur as a native element. There are some 20 cobalt minerals, the most important being sulfides and arsenides. Cobaltite, CoAsS and smaltite, $CoAs_3$.$NiAs_3$, are ores, though no cobalt minerals occur in large quantity. They are associated with nickel, iron and copper deposits commonly as metasomatic contact deposits. Both metallic nickel and cobalt can show slight, natural magnetism, but magnetite, Fe_3O_4, is black magnetic iron as primary magnetic natural mineral. Irons and steels can be artificially magnetized, but are not magnetic under normal processing conditions.

Primary industrial use of cobalt is as an alloy with iron in the production of steels, including stainless steel, SST. Stellite, an alloy of cobalt, chromium, and tungsten is used for lathe tools and, as it will hold a sharp edge at red heat, is used for medical knives, scalpels, etc. It is a constituent in many of the iron magnets. Cobalt produces a deep blue color, "cobalt blue", used as a pigment in paints and glass. The salts of cobalt are highly colored, particularly pink or blue. Solution saturated paper will turn from pink to blue with the approach of wet weather and, as a writing fluid, is "invisible ink" — *pale pink, changing* to blue when heated.

As the isotope cobalt-60, ^{60}Co, it has a radioactive half-life of about 5.75 years, and is used in nuclear studies and testing. **CAUTION**: Some alloys containing cobalt, when subjected to radiation, can become radioactive with conversion of the cobalt fraction to ^{60}Co.

Cobalt, nickel, and chromium can all be easily electroplated as hard thin film surface coatings, though nickel and chromium are more widely used due to quantity availability.

Technical Application: The metal is used as an n-type dopant in some compound semiconductors, and is under evaluation as a silicide: CoSi, Co_2Si and $CoSi_2$, for use as a blocking layer in heterostructures. As already mentioned, cobalt-60, ^{60}Co, is used in radiation testing of Solid State devices, usually by converting lead, Pb, pellets — for alpha particle radiation — with a 24-h half-life.

It has been grown as a single crystal for general morphological and defect studies, and also has been deposited as an epitaxy thin film, e.g., primarily in the development of silicides.

One interesting study: brush iron powder on a cobalt surface, and the iron will align itself according to the magnetic domains in the cobalt specimen.

Etching: Easily etched in acids, most commonly as electrolytic solutions: HCl, H_3PO_4, and mixed acids.

COBALT ETCHANTS

CO-0001
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
500 ml .... HCl
500 ml .... EOH
TIME: 2—3 min
TEMP: RT
ANODE: Co
CATHODE: SS
POWER: 2 V
DISCUSSION:

Co, (0001) wafers and with other orientations used in a study of growth habits. After etching, wash in boiling DI water, then rinse in alcohol and dry with hot air.
REF: Cliffe, D R & Farr, J P G — *J Electrochem Soc,* 111,299(1964)

CO-0002
ETCH NAME: Iron
TYPE: Metal, preferential
COMPOSITION:
x .... Fe, powder
TIME:
TEMP: RT

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DISCUSSION:

Co, (0001) wafers and other orientations used in a structure study. As cobalt is slightly magnetic, by brushing iron powder across specimen surfaces, the iron will align itself developing magnetic zones/domains.

REF: Hall, E O — *Acta Metall,* 6,110(1958)

CO-0003

ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
23 .... $HClO_4$
77 .... HAc

TIME:
TEMP: 5°C
ANODE:
CATHODE:
POWER:

DISCUSSION:

Co, (0001) wafers used to study stacking faults developed by nuclear magnetic resonance. Study was done with an electron microscope (EM). Solution used to polish and etch-thin specimens for microscope study.

REF: Morgan, J T — *Phil Mag,* 9,607(1964)

CO-0004

ETCH NAME: Neon
TYPE: *Ionized* gas, preferential
COMPOSITION:
x .... Ne^+ ion

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:

Co specimens. Ne^+ ion bombardment used in a study of etch figures obtained on metals by irradiation treatment. Other metals evaluated were Al, Bi, Cd, Mg, Cu, Sn, and Zn.

REF: Yurasova, V E — *Kristallografiya,* 2,770(1957)

CO-0005

ETCH NAME: Phosphoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

Co spheres 5/16″ in diameter polished in the solution shown prior to oxidation experiments. Oxidation was done in air at 400 and 450°C. As cobalt has a structure transition point at 420°C, as expected, the oxidation patterns differentiated between the two structures: below 420°C, hexagonal, hcp, and above, cubic, fcc, oxidation figures were observed.

REF: Kehrer, V J & Leidheiser, H — *J Chem Phys,* 21,570(1953)

PHYSICAL PROPERTIES OF COBALT OXIDE, CoO

Classification	Oxide
Atomic numbers	27 & 8
Atomic weight	74.9
Melting point (°C)	1935
Boiling point (°C)	
Density (g/cm^3)	6.47
Hardness (Mohs — scratch)	6—7

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Crystal structure (isometric — normal)	(100) cube
Color (solid)	Green/brown
(pigment)	Cobalt blue
Cleavage (cubic)	(001)

COBALT OXIDE, CoO

General: Does not occur as a natural compound, although there are over 15 cobalt minerals. The most important ores are as sulfides and arsenates. The oxide has no major use as a compound in metal processing, but cobalt is an important additive in the making of steels. The oxide does have application as a coloring agent (cobalt blue) in the glass and ceramics industries, and is used as a hydrogenation catalyst. There are four cobalt oxides, the monoxide being used as the referent here.

Technical Application: The oxides are not used in Solid State processing, but the monoxide has been grown and studied as a single crystal.

Etching: HF and acid mixtures.

COBALT OXIDE ETCHANTS

COO-0001
ETCH NAME: Hydrofluoric acid — TIME: 5 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
x .... HF
DISCUSSION:
CoO, (100) wafers. Cut and mechanically lap polish with diamond paste. Solution will develop dislocations and sub-boundaries.
REF: Nehring, V W et al — *J Am Ceram Soc,* 14,328(1952)

COO-0002
ETCH NAME: Heat — TIME:
TYPE: Thermal, preferential — TEMP: 1000 K
COMPOSITION:
x .... Heat
DISCUSSION:
CoO, (100) wafers cleaved and strain annealed for use in a study of magnetic susceptibility for both CoO and NiO. Note that temperature is shown in degrees Kelvin. Pure heat used to develop defects and domain structures.
REF: Singer, J R — *Phys Rev,* 104,929(1956)

COO-0003
ETCH NAME: Oxygen — TIME:
TYPE: Gas oxidation — TEMP:
COMPOSITION:
x .... O_2
DISCUSSION:
CoO, (100) wafers used in a study of oxidation to Co_3O_4. Prepare specimens by (1) abrading surface with 800-grit SiC; (2) polishing with 0.5 diamond grit in kerosene, and (3) washing in acetone with ultrasonic agitation prior to oxidizing. Process used in a study of oxidation mechanisms.
REF: Przybylski, K & Smeltzer, W W — *J Electrochem Soc,* 128,896(1981)

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PHYSICAL PROPERTIES OF COBALT SULFIDE, Co_3S_4

Classification	Sulfide
Atomic numbers	27 & 16
Atomic weight	305.06
Melting point (°C)	>1200
Boiling point (°C)	
Density (g/cm³)	4.85 (4.8—5)
Hardness: (Mohs — scratch)	5.5
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Steel grey/reddish
Cleavage (octahedral)	(111)

COBALT SULFIDE, Co_3S_4

General: Occurs as the mineral linnaerite, Co_3S_4, often associated with iron and copper ore deposits, and may be an admixture with these as sulfides. Fairly widely distributed as an ore of cobalt with structure analogous to the spinel group. No direct industrial use other than as an ore of cobalt.

Technical Application: Not used in Solid State processing at present, though it is a spinel-type mineral and may have similar applications as an operating device. The reference shown is for Co_9S_8, and there are other cobalt sulfides, such as jaipurite, CoS as a natural mineral mono-sulfide.

Etching: Soluble in acids.

COBALT SULFIDE ETCHANTS

COS-0001
ETCH NAME: Sulfurous acid — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... H_2SO_3, conc.
DISCUSSION:
Co_9S_8, fabricated as a single crystal sphere 0.28 mm in diameter, used in a study of crystal structure. The solution shown was used to develop defects and structure.
REF: Geller, S — *Acta Metall,* 15,1195(1962)

PHYSICAL PROPERTIES OF COLEMANITE, $Ca_2B_6O_{11}.5H_2O$

Classification	Borate
Atomic numbers	25, 5, 8, 2
Atomic weight	396.4
Melting point (°C)	~1200
Boiling point (°C)	
Density (g/cm³)	2.42
Hardness (Mohs — scratch)	4—4.5
Crystal structure (monoclinic — normal)	(110) prism
Color (solid)	Clear/whitish
Cleavage (b-pinacoidal)	(010)

COLEMANITE, $Ca_2B_6O_{11}.5H_2O$

General: Occurs as a natural mineral associated with borax, and was first discovered in Death Valley, California. It is mined along with borax and has similar medical and industrial

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applications as a soldering and welding flux; as a washing and cleaning detergent; and as an antiseptic or preservative.

Technical Application: There has been no use in Solid State processing to date, although it has been evaluated for ferroelectric and pyroelectric properties, as both the natural and synthetic crystal.

Etching: Hot HCl.

COLEMANITE ETCHANTS

COL-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP: Hot
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
$Ca_2B_6O_{11}.5H_2O$, (010) cleaved wafers. Both the natural and artificial compound were studied for ferroelectric and pyroelectric properties. The material cleaves easily on (010), and is soluble in HCl.
REF: Wieler, H H et al — *J Appl Phys,* 33,1720(1962)

PHYSICAL PROPERTIES OF COLUMBIUM, Cb
(See NIOBIUM, Nb)

COLUMBIUM, Cb

General: Does not occur as a native metal element. It is considered to be a rare element which commonly is found in pegmatites as the mineral series columbite-tantalite. It is quite widely distributed and varies from nearly pure columbite to pure tantalite depending upon locale. When first discovered it was called columbium but, today, is called niobium.

In industry it has been used as the pure metal and as an alloy constituent *in steels* for its high temperature, hardness, and chemically inert characteristics. Items shown here are for references published as columbium. See section on Niobium for physical properties and additional solutions and applications.

Technical Application: The metal, as niobium, has some specific device development applications in Solid State device fabrication as the Josephson Junction device, Nb_2Sn_3.

Etching: Hot H_2SO_4, HF and mixed acids.

COLUMBIUM ETCHANTS

CB-0001
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
2 .... HF
4 .... H_2SO_4
2 .... HNO_3
2 .... HF
DISCUSSION:
Cb, single crystal specimens used in a study of anodic oxidation. Solution used to clean and polish surfaces prior to oxidation. Anodic solution used for oxidation was: 0.1% H_3PO_4 at 5.5 mA/cm^2.
REF: Bakish, R — *J Electrochem Soc,* 107,653(1960)

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CB-0002a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
90 ml .... H_2SO_4
10 ml .... HF
DISCUSSION:
TIME:
TEMP: RT
ANODE:
CATHODE:
POWER: 0.1 A/cm^2

Cb, single crystal specimens used in a study of grain boundaries and etch pits. Solution used to clean and polish surfaces prior to preferential etching. Use mild agitation during etching. Solution also used on tantalum.
REF: Micheal, A B & Huegel, F J — *Acta Metall,* 5,339(1957)

CB-0002b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
10 ml .... HF
10 ml .... H_2SO_4
10 ml .... H_2O
x drops .... H_2O_2
DISCUSSION:
TIME:
TEMP: RT

Cb, single crystal specimens used in a study of grain boundaries and etch pits. Solution used by immersion with agitation to develop sub-boundaries and etch pits. Etch pit density increased with time and pits reduced in size.
REF: Ibid.

CB-0003
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
10 .... HF
90 .... H_2O_4
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

Ta:Cb. single crystal alloys. Five crystals grown with increasing amounts of columbium: 20, 30, 40, 60, and 80%. Material used in a study of alloy strength. Solution used to clean and polish specimens.
REF: Peters, B C & Hendrickson, A A — *Acta Metall,* 14,1121(1966)

PHYSICAL PROPERTIES OF COPPER, Cu

Classification	Transition metal
Atomic number	29
Atomic weight	63.57
Melting point (°C)	1083
Boiling point (°C)	2595
Density (g/cm^3)	8.94 (8.8—8.9)
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.94
Specific heat (cal/g) 20°C	0.0918
Latent heat of fusion (cal/g)	48.9 (50.6)
Heat of vaporization (k-cal/g-atom)	72.8
Atomic volume (W/D)	7.1

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1st ionization energy (k-cal/g-atom)	178.
1st ionization potential (eV)	7.723
Electronegativity (Pauling's)	1.9
Covalent radius (angstroms)	1.17
Ionic radius (angstroms)	0.96 (Cu^{+1})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	16.42
Electrical conductance (micro ohm^{-1})	0.593
Electrical resistivity ($\times 10^{-6}$ ohms cm) 20°C	1.673
Electron work function (eV)	4.47
Cross section (barns)	3.8
Vapor pressure (°C)	2207
Tensile strength (psi) annealed	30,000
Hardness (Mohs — scratch)	2.5—3
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Copper-red
(flame)	Emerald green (oxide)
Cleavage (parting, only)	None

COPPER, Cu

General: Occurs as a native element, usually of secondary origin and found in many localities but seldom in commercial quantities. It is found in beds and veins associated with copper compounds, such as malachite, green copper ore, and azurite, blue copper ore, both being hydrated carbonates of copper. The iron pyrites containing copper and sulfur, and the mineral cuprite, Cu_2O, all occur in copper veins. The symbol, Cu, is from the Latin cuprum, which comes from the Greek cyprium (Cyprian bronze) as, in ancient times, the island of Cyprus was noted for its copper mines. It is thought that copper was the first metal employed by man, after gold, as both occur in fair quantity in the free state of southern Europe and the Mediterranean area. The two sulfides chalcopyrite, $CuFeS_2$ and chalcocite, Cu_2S represent about 75% of the copper ore mined in the world.

Pure copper is ductile and malleable, like gold, and an excellent conductor of heat and electricity as are both gold and silver, all first used as body ornaments, plates, and other utensils.

Bronze, Cu:Sn, was the first metal alloy used by man, leading him out of the Stone Age into the Bronze Age about 5000 B.C. Brass, Cu:Zn, is not as brittle as bronze, and artifacts are said to have been discovered in Egyptian tombs, circa 4000 B.C. but, with the discovery of tin in Great Britain — the Tin Isles of ancient Rome — bronze was the major metal alloy until the discovery of iron smelting by the Hittites of Asia Minor around 1350 B.C. Today there are a large number of alloy mixtures of both bronze and brass.

About one third of the copper mined in the world is used for electrical wiring as an alloy to improve hardness. It is fabricated as rods, tubing, sheet, and as bulk material for a wide number of products. As sheeting, it is used in building construction, such as a roof covering or as rain gutters which, with time and exposure to the atmosphere, can turn green — verdigris — a copper sulfate. It also is available as high purity copper (OFHC copper) used in electronics and Solid State processing. Copper is easily electroplated, and many products are so plated. Gold, silver, and copper are known as the "coinage" metals, although nickel is now a lower cost replacement for silver.

Technical Application: In Solid State processing copper is used as an n-type dopant in some compound semiconductors. As a thin film metallization along with other metals, such as gold, used in device construction as a contact pad on semiconductor devices as well as for circuits on substrate dielectrics. It is as multilayer mixture such as Au/Cu; Au/Cu/Ni; Au/Cu/Cr; or as Cu/Au may be a series of alternating layers of the two thin films. Used in

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a similar manner on metals, such as aluminum, iron, steel, nickel, and molybdenum fabricated as test parts and package elements.

Thin film deposits can be by standard vacuum evaporation, E-beam evaporation, RF sputter from a solid target or by electrolytic plating. The latter method is used in plating PC boards (PCBs) and some of the metal parts used in test and package assembly.

Solid copper parts, as copper alloys or OFHC copper, to include wire or strap contacts, or copper pins are used for both their electrical and heat dissipation characteristics. As a clad material, such as copper/nickel coldweld or resistance weld packages, the copper is the seal metal.

Single crystal copper has been grown, as have several copper alloys, all studies for their general physical characteristics, and trinary compound semiconductors containing copper are under study: $CuInSe_2$; $CuInS_2$; and $CuInTe_2$, as examples.

Etching: Soluble in HNO_3, hot H_2SO_4, slowly in HCl and NH_4OH. $FeCl_3$, mixed acids, and ionized gases.

COPPER ETCHANTS

CU-0001
ETCH NAME: Sodium hydroxide
TYPE: Alkali, cleaning
COMPOSITION:
(1) x .... x% NaOH
(2) 2 .... H_2SO_4
1 .... HNO_3
TIME:
TEMP:
DISCUSSION:

Cu, wire and coupons. Solutions used to clean copper wire prior to plating. First, clean in solution (1), and DI water wash; follow with (2) acid mixture, and DI water rinse. In plating, initially deposit copper to 0.001" before nickel plating.
REF: Bailey, G C & Ehitich, A C — *J Appl Phys*, 50,453(1979)

CU-0002
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
TIME: 1 min
TEMP: RT
DISCUSSION:

Cu, single crystal ingots cut as cylinder shaped specimens. Nitric acid was used to remove cutting work damage from surfaces.
REF: Reshon, D D Jr — *J Appl Phys*, 35,1262(1964)

CU-0003a
ETCH NAME: Nitric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HNO_3
20 .... H_2O
TIME: 1—10 min
TEMP: RT
DISCUSSION:

Cu piping. Solution used for cleaning piping on 2000 gallon LN_2 and LOX transport trailers. Included steel, brass, and bronze parts. Parts were soaked to remove general contamination, heavily water washed and blown dry with nitrogen. Where parts were stored or prepared for shipment they were sealed with warm nitrogen filled plastic bags.
REF: Walker, P & Campos, R — personal application, 1962

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CU-0003b
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HCl
10 .... H_2O
TIME: 1—10 min
TEMP: RT
DISCUSSION:
Cu piping on cryogenic transport tailers. Solution used for general cleaning of steel, bronze, and brass parts. See discussion under CU-0003a.
REF: Ibid.

CU-0008a
ETCH NAME: Nitric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HNO_3
1 .... H_2O
TIME:
TEMP:
DISCUSSION:
Cu and Cu alloys. Solution used to remove copper oxide from parts prior to etch polishing with a Copper Brite Dip solution (CU-0028).
REF: Bulletin B-11D, The American Brass Co.

CU-0004a
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HCl
1 .... H_2O
TIME:
TEMP:
DISCUSSION:
Cu and Cu alloys. Pure copper was annealed and cold drawn. Specimens were used in a study of low temperature transport properties. Solution used to clean specimens.
REF: Powell, R L et al — *Phys Rev,* 115,314 (1959)

CU-0010
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:
DISCUSSION:
Cu single crystal specimens used in irradiation effect studies. Solution was used as a general removal etch.
REF: Vook, R & Wert, C — *Phys Rev,* 109,1529(1958)
CU-0009a: Hurdon, M J & Averbach, B L — *Acta Metall,* 9,237(1961)
Cu single crystal specimens. Solution referred to as a "heavy etch" for copper and used to clean surface prior to studying dislocation density in deformed specimens. Ferric chloride was used to develop dislocations and other structures after deformation.
CU-0089: Magnuson, G D & Carlston, C E — *J Appl Phys,* 34,3267(1963)
Cu single crystal wafers used in an argon bombardment damage study. A weak solution was used to remove lap damage prior 10 KeV Ar^+ ion sputter.

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CU-0011a
ETCH NAME: Brilliant etch
TYPE: Acid, macro-etch
TIME: Dip
TEMP: RT
COMPOSITION:
50 ml .... HNO_3
0.5 ml .... $AgNO_3$
50 ml .... H_2O
DISCUSSION:
Cu and Cu alloys. Solution used to develop macro-structures on metallographic specimens.
REF: A/B Metals Digest, 21 #2,23(1983) — Buehler Ltd

CU-0012
ETCH NAME: Silica
TYPE: Mineral, cleaning
TIME: Variable
TEMP: RT
COMPOSITION:
x .... SiO_2, sand
x .... H_2O
DISCUSSION:
Cu parts as sheet, pans and piping. For general removal of heavy contamination, such as oxidation and dirt from copper and copper alloy surfaces. Method shown has been used for hand scouring of parts. As a dry abrasive using nitrogen for a pressure jet, used for surface cleaning and removal of other metal plating on copper parts, such as from power electrodes in vacuum systems. Also used on other metal parts (steels, stainless steel, nickel) of vacuum systems to produce a rough surface for better adhesion of evaporating metals and reduction of chromium dusting during evaporation on glass photo resist masks.
REF: Tarn, W H — personal communication, 1975

CU-0013a
ETCH NAME: Ferric chloride
TYPE: Salt, removal/preferential
TIME:
TEMP:
COMPOSITION:
x .... $FeCl_3$, sat. sol.
DISCUSSION:
Cu single crystal spheres used in a study of surface plane development. Parts were first cleaned in dilute nitric acid before etching in this solution.
REF: Economou, N A & Trivich, D — *Electrochem Acta,* 3,292(1961)
CU-0009b: Ibid.
Cu single crystal specimens. A ferric chloride solution was used to develop dislocations and other structure after specimens were subjected to deformation.

CU-0014
ETCH NAME: Ferric chloride, dilute
TYPE: Salt, removal/preferential
TIME:
TEMP: Hot
COMPOSITION:
ASTM #100
(1) 300 g .... $FeCl_3$
1000 ml .... H_2O
(2) 90 g .... $FeCl_3$
200 ml .... H_2O
DISCUSSION:
Cu and Cu alloy parts. Both solutions used as general removal etchants on copper parts.
REF: Mackliet, C A — *Phys Rev,* 109,1964(1958)
CU-0009c: Ibid.

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Cu single crystal specimens used in a study of dislocation density after specimen deformation. A dilute ferric chloride solution was used to develop dislocations and other structures. Also studied aluminum single crystals to include X-ray study for bulk deformation observations.

CU-0080a: ASTM E407-70

Cu, specimens. Standard ASTM #100 solution is 10 g $FeCl_3$:90 ml H_2O.

CU-0015
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
1 .... 1 *M* $FeCl_3.H_2O$
1 .... 1 *M* HCl
1 .... 0.25 *M* HBr
TIME:
TEMP:
DISCUSSION:

Cu single crystal wafers of various orientations. Solution used to *etch dislo*cations and structures in single crystal copper surfaces prior to irradiation studies. No change observed in dislocations after irradiation, but initial background terrace structure changed to a finely pitted surface. Required several annealing periods, with etching after each anneal, to remove surface pits.

REF: Young, F W Jr — *J Appl Phys,* 33,749(1962)

CU-0003c
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
6 .... H_2SO_4
12 .... CrO_3
82 .... H_2O
TIME:
TEMP:
DISCUSSION:

Cu cryogenic trailer piping, including brass, bronze and stainless steels. Solution used as a "Brite Copper" dip. See Cu-0028 for other similar solutions.

REF: Ibid.

CU-0043
ETCH NAME:
TYPE: Acid, clean/condition
COMPOSITION:
5 .... $FeCl_3$ (40%)
10 .... HNO_3
82 .... H_2O
TIME: 5—10 min
TEMP: RT
DISCUSSION:

Cu and Cu alloys as sheet or foil were cleaned in this solution prior to being plastic laminated. Metal surface cleanliness is essential to obtain a good plastic/metal adhesion seal. This solution gave the best adhesion results. Several types of plastic sheet were evaluated and also were applied to aluminum.

REF: Skeist, I — *Epoxy Resins,* Reinhold, New York, 1950, 190

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CU-0018
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... H_2SO_4
x .... $Cu(NO_2)_3$
DISCUSSION:
Cu single crystal wafers of different orientations and spheres. Various solution concentrations were evaluated as the pH of solutions affect characteristics of different crystal planes.
REF: Gwathmey, A T et al — *Electrochem Soc Meet, WDC*, 12—16 May, 1957

CU-0019a
ETCH NAME: Copper sulfate, dilute TIME:
TYPE: Salt, preferential TEMP:
COMPOSITION:
x .... $CuSO_4$
x .... H_2O
DISCUSSION:
Cu OFHC copper specimens. Solution used to develop structure caused by fatigue cracking.
REF: Bendler, H A — *Acta Metall*, 8,402(1960)

CU-0020
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... $CuSO_4$
x .... H_2SO_3
DISCUSSION:
Cu single crystal wafers of different orientations and spheres were etched in various concentrations of this solution in a study of crystallographic face orientation.
REF: Gwathmey, A T & Benton, A F — *J Chem Phys*, 8,431(1940)

CU-0011b
ETCH NAME: General etch TIME: Swab
TYPE: Acid, micro-etch TEMP: RT
COMPOSITION:
50 ml .... NH_4OH
50 ml .... H_2O_2
DISCUSSION:
Cu and Cu alloy specimens. Metallographic specimen surfaces are lightly scrubbed with a swab soaked in the solution shown to develop microstructure in material studies.
REF: A/B Metals Digest, 21 12,23(1983) — Buehler Ltd

CU-0022a
ETCH NAME: Nitric acid, dilute TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:
Cu single crystal specimens as spark-cut rods 6.5 cm long. Degrease, thermally anneal,

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then electropolish in phosphoric acid. After subjecting samples to strain, chemically polish in the solution shown. This solution produces a high polish on (111) surfaces and, although it does attack other crystal planes, the (111) is well defined. After polishing specimens they were preferentially etched to develop dislocations and structures caused by strain.
REF: Basinski, Z S & Basinski, S J — *Phil Mag*, 9,51(1964)
CU-0023: Magnuson, G D et al — *J Appl Phys*, 32,369(1961)

Cu single crystal spheres with a (110) orientation cut flats. Solution used to polish spheres prior to Hg^+ ion bombardment studies. During bombardment approximately 20 μm of material was removed and redeposited on the surfaces in hillock form.

CU-0024a
ETCH NAME: TIME: 30 sec
TYPE: Acid, dislocation TEMP: RT
COMPOSITION:

(A) 1 .... Br_2	(B) 45 .... HCl
30 .... HAc	250 .... H_2O

DISCUSSION:

Cu, (111), within 2—3° orientation. Mix the two solutions together when ready to use. Solution will develop triangular surface etch pits that increase in size linearly with etch time. (*Note:* Surface damage etch pits increase in size; but dislocation etch pits normally do not.)
REF: Livingston, J D — *J Appl Phys*, 3,1071(1960)

CU-0025
ETCH NAME: TIME: 5—10 min
TYPE: Acid, dislocation TEMP: RT
COMPOSITION:

20 ml	.... HCl
1 ml	.... HAc
4 g	.... $FeCl_3.6H_2O$
8 drops	.... Br_2
150 ml	.... H_2O

DISCUSSION:

Cu single crystal wafers of various orientations. Specimens were point damaged using a sapphire stylus and then deformed by high temperature annealing prior to etching in the solution shown to develop dislocations and stress structures.
REF: Bailey, J M & Gwathmey, A T — *J Appl Phys*, 31,215(1960)

CU-0026
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:

75 ml	.... $FeCl_3$, sat. sol.
25 ml	.... HCl

DISCUSSION:

Cu, (100) wafers. Solution has been used as both a polish etch, as well as a preferential type etch to develop internal (010) plane directions in a (100) surface.
REF: Burns, J — *Phys Rev*, 119,102(1960)
CU-0010b: Ibid.

Cu single crystal wafers. Solution used as a polish etch.

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CU-0008b
ETCH NAME: Sulfuric acid, dilute
TYPE: Acid, oxide removal
COMPOSITION:
x .... H_2SO_4 (12—15%)
TIME:
TEMP:
DISCUSSION:
Cu and Cu alloys. Solution used as a pickling solution for the removal of scale and oxides from copper surfaces.
REF: Ibid.

CU-0008c
ETCH NAME: Dichromate finish dip
TYPE: Acid, polish
COMPOSITION:
12 oz .... H_2SO_4
4 oz .... $NaCrO_4$
1 gal .... H_2O
TIME:
TEMP:
DISCUSSION:
Cu and Cu alloys. Solution will remove heavy oxides and leave a matte type surface finish.
REF: Ibid.

CU-0027
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) 1 .... HNO_3
20 .... H_2O_2
(2) 40 .... NH_3
10 .... H_2O_2
TIME:
TEMP:
DISCUSSION:
Cu and Cu alloys. Both solutions shown as general removal/polish etchants for copper.
REF: Berglund, T & Dearden, WH — *Metallographer's Handbook of Etching*, Pitman & Sons, London, 1931

CU-0005a
ETCH NAME: Phosphoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP: 70—178°C
ANODE:
CATHODE:
POWER:
DISCUSSION:
Cu single crystal spheres used in a study of oxidation reactions. Electropolish in solution shown; chemical clean in $xHNO_3$:EOH; and H^+ ion clean in vacuum prior to oxidation.
REF: Young, F W Jr et al — *Acta Metall*, 4,145(1956)
CU-0006: Young, F W Jr — *J Appl Phys*, 32,192(1961)
Cu single crystal waters and spheres used in a wide range study of the effect of different etch solutions on development of dislocation etch pits.
CU-0007: Young, F W Jr — *Bull Am Phys Soc*, 5,190(1960)
Cu single crystal wafers and spheres used in a study of dislocation variation in structure as related to (111), (110) and (100) surface planes. Spheres contained oriented flats.

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CU-0028
ETCH NAME: Copper Brite dip
TYPE: Acid, polish
COMPOSITION:

TIME: Seconds
TEMP: RT

(1)	(2)	(3)	(4)	(5)	(6)	(7)
3 .... H_2SO_4	3	7	5	600 ml	2 gal	250 ml
1 .... HNO_3	1	7	3	250 ml	1 gal	125 ml
0 .... HCl	0	0	5	20 ml	$^1/_2$ fl oz	4 ml
1 .... H_2O	10	1	2	130 ml	1—2 qt	250 ml

DISCUSSION:

Cu specimens and parts. The following cleaning procedure is recommended: (1) Degrease: (i) hot TCE — DI H_2O rinse — MeOH rinse — N_2 blow dry, then (2) NH_4OH dip at RT to remove native oxide — DI H_2O rinse — MeOH rinse, and N_2 blow dry. All of the solutions are extremely rapid — dip in solution — immediate water quench and rinse. Produces a highly reflective, polished surface that may not be planar due to rapidity of attack. Not recommended where critical dimensional tolerances are required. Solution (1) used to clean copper vacuum system parts and copper electrical test holders for microelectronic devices. Also to clean copper plated PC boards (PCBs).

REF: (1) Fahr, F — personal communication, 1979

CU-0029a: (2) Walker, P & Fahr, F — personal application, 1979—1980

Cu, OFHC copper parts used as microelectronic device test carriers. Solution used to remove residual "burn" marks from machine cutting. Solution was too rapid and erratic to maintain critical dimensions. Hydrogen firing at 300 to 400°C was more satisfactory. Parts cleaned prior to Au/Ni plating.

CU-0030: (3) Westinghouse Data Sheet (date, number unknown) Cu specimens and parts. Solution applied for general polishing.

CU-0031: (4) *ASTM Metals Handbook #2*, 8th ed, 1974 Cu specimens and parts. Solution applied as a general polishing etch.

CU-0032: (5) Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices*, Reinhold, New York, 1967 Cu specimens parts. Applied as a general polishing solution.

CU-0008e: (6) Bulletin B-11D, the American Brass Company (no date) Cu specimens and parts. Described as a general polishing solution for copper and copper alloys.

CU-0087: (7) Chen, H Y — *J Electrochem Soc*, 118,681(1971)

Cu, OFHC copper discs used as cathodes for electrolytic plating of gold from gel electrolytes. Degrease copper parts with TCE, then acetone and Brite Dip 10 sec, RT. Two cellulose compounds used for gelling in both acidic and cyanide gold solutions. 0.5 μm thick deposits evaluated. Deposit rates of gold were (1) at 0.15 mA/in^2, 2 μm/h, and (2) at 0.15 mA/in^2, 0.6 μm/h. Electrographic porocity meter and pore printing used to evaluate deposits — pore print at 8 V and 800 lb/in^2 pressure.

CU-0029b: Ibid.

Cu, OFHC copper parts, after Au/Ni plating (Au 2000 Å:Ni 500 Å). Solution (1) used at 8°C (ice/acetone) to evaluate completeness of metallization and/or pinholing, grain structure, and grain boundary diffusion of liquids.

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CU-0008d
ETCH NAME: Matte dip
TYPE: Acid, finishing
COMPOSITION:
2 .... H_2SO_4
1 .... HNO_3
x .... *ZnO or ZnS

TIME:
TEMP:

*Saturate the solution

DISCUSSION:
Cu and Cu alloy parts. For decorative purposes the solution will produce a matte type surface finish with dull reflectivity and beaded structure.
REF: Ibid.

CU-0032
ETCH NAME: Ammonium persulfate
TYPE: Salt, cleaning
COMPOSITION:
x .... 2—5% $(NH_4)_2S_2O_8$

TIME: 15 min
TEMP: RT

DISCUSSION:
Cu, (111) single crystal blanks and other orientations. Solution used to clean surfaces prior to oxidation experiments (Cu_2O).
REF: Baur, J P et al — *Acta Metall,* 103,273(1956)
CU-0019c: Ibid.
Cu, OFHC copper single crystal specimens used in a study of the formation of fatigue cracks using an electron microscope (EM) for observation. An ammonium sulfate solution was used to develop cracks.

CU-0024b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
60 .... H_3PO_4
40 .... H_2O

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Cu, (111) wafers used in a study of etch pits associated with dislocations. Solution shown was used to electropolish specimens before preferential etching.
REF: Livingston, J D — *J Appl Phys,* 31,1071(1960)

CU-0024c
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
45 .... HCl
30 .... HAc
250 .... H_2O
1 .... Br_2

TIME: 30 sec
TEMP: RT

DISCUSSION:
Cu, (111) wafers. Solution used to develop etch pits associated with dislocations. Mix the Br_2 + HAc, first; then add to the HCl:H_2O. Pits observed contained flat bottoms and

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varied from small to large in size as sharply defined triangles. Solution referred to as a modification of a Lovell & Wernick etch.
REF: Ibid.

CU-0069
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:
DISCUSSION:

Cu single crystal specimens used in a study of recovery in electron irradiated copper. Dilute nitric acid was used to clean and wash surfaces.
REF: Corbett J W et al — *Phys Rev,* 114,1452(1959)
CU-0019b0: Bendler, H A — *Acta Metall,* 8,402(1960)

Cu single crystals of OFHC copper used in an electron microscope study of fatigue cracks and their formation. A dilute nitric acid solution was used as a crack selective etchant. Also used ammonium persulfate solutions.

CU-0061a
ETCH NAME: Nitric acid
TYPE: Electrolytic, thin/polish
COMPOSITION:
x .... HNO_3 (33%)
TIME:
TEMP: −20°C or less
ANODE: Cu
CATHODE:
POWER:

DISCUSSION:

Cu foil. Solution used was a double-jet to polish and thin copper for TEM study. Copper specimens were also electroless nickel plated; palladium and platinum immersion plated; and evaporated with gold in a study of thin films and deposition reactions. Final coating of all metals with electroless nickel also was done as part of a thin film adhesion study. Nickel plates more rapidly on Pd than unplated Cu.
REF: Flis, J & DuOette, J — *J Electrochem Soc,* 131,254(1984)

CU-0022b
ETCH NAME: Phosphoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

Cu single crystal specimens. First, spark-cut as rods, then etch polish in the solution shown prior to thermal annealing to reduce dislocation content.
REF: Ibid.
CU-0074a Inman, M C & Barr, L W — *Acta Metall,* 8,112(1960)

Cu single crystals were cut as cylinders and electropolished in the solution shown in a study of antimony diffusion into copper.
CU0024d: Ibid.

Cu, (111) wafers cut within 2—3° of plane. Wafers used in a dislocation study. First, etch polish in solution shown before dislocation etching (CU-0024a).

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CU-0061b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HNO_3
x .... MeOH
TIME:
TEMP: 0°C
ANODE: Cu
CATHODE:
POWER: 6 V
DISCUSSION:
Cu, foil. See discussion under CU-0061a. Solution used to electropolish copper before various plating sequences in a study of nickel adhesion.
REF: Ibid.

CU-0062a
ETCH NAME: Toluene
TYPE: Ester, cleaning
COMPOSITION:
x .... $C_6H_5CH_3$
TIME:
TEMP:
DISCUSSION:
Cu specimens. Solution used in a study of surface cleaning. Toluene is excellent for removal of fatty acids, such as palmitic, stearic and oleic acids from copper and gold surfaces. Authors say that less than one monolayer of contamination remains. Fatty acids were ^{51}C isotope tagged.
REF: Fatzer, G D et al — *Int J Appl Radiat Isot,* 10,167(1961)

CU-0063
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... EOH
TIME:
TEMP:
DISCUSSION:
Cu, blanks as plated substrates used for a metallization, stress and failure study. First, ultrasonically clean in EOH, then Ar^+ ion sputter clean in vacuum prior to CVD deposition of Ni, Ti and Al_2O_3 with copper substrates at 200°C, and increased to 350°C. Metallizations were (1) Al_2O_3/Cu; (2) Al_2O_3/Ti/Cu, and (3) Al_2O_3/Ti/Ni/Cu. Tensile strain up to 10% was observed. After metallization, temperature cycle increased to 600°C. Alumina showed parallel cracks after deposition and was amorphous, a-Al_2O_3, below 400—450°C. Without a metal interface between alumina and copper, alumina peels from copper.
REF: Jarvinen R et al — *Thin Solid Films,* 114,311(1984)
CU-0064: Walker, P & Velardi, N — personal application, 1985
Cu, OFHC copper parts. After gold plating of parts and DI water washing, final rinse with acetone, then either methanol or ethanol and nitrogen blow dry. Used for final cleaning and drying of parts.

CU-0065a
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
COMPOSITION:
x .... TCE
TIME: Minutes
TEMP: 75—80°C
DISCUSSION:
Cu, OFHC parts, semiconductor packages, and other metals and compounds. TCE is a general degreasing solvent used as a liquid, hot or cold, with or without ultrasonic agitation, as a spray or hot vapor. The latter as vapor degreasers. Vapor degreaser systems can be from a beaker on a hot plate to large tanks with overhead cranes for handling large parts,

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and operate with a combination of hot liquid (in an ultrasonic tank), hot vapor head above working tank, and a mobile spray nozzle. Where the part is cleaned in a vapor degreaser, the part will dry as it is slowly pulled from the hot vapor head. Where used as a hot or cold liquid, DI water wash after degreasing, then rinse in acetone, then MeOH or EOH, and nitrogen blow dry. TCE is considered carcinogenic and is being replaced by 1-1-1 trichloroethane, TCA. TCE also has been used for gross leak testing of hermetically sealed packages.
REF: Walker, P — personal application, 1970—1985

CU-0065b
ETCH NAME: Freon TA
TYPE: Solvent, cleaning
TIME: Minutes
TEMP: 75 to 85°C
COMPOSITION:
x .... Freon TA
DISCUSSION:
Cu, OFHC copper parts, semiconductors and other metals or compounds. Solution used in a similar manner as that described for TCE (CU-0065a). There are several Freon mixtures with various alcohol additives to include aziotropes, such as Freon TF, Freon TM, etc. Freon is a Dupont registered trade name, and other manufacturers have similar solutions with their own trade names, such as the Genusolves (Allied Chemical), etc. Freons evaporate completely, leaving no residual or contamination from the solvent on cleaned surfaces, such that they are of major use in the cleaning of semiconductor and assembly parts. Freons are also used as special mixtures for gross leak testing of hermetically sealed packages as, if there is a leak, the solution completely evaporates; whereas TCE and similar solvents so used can leave a residue within the package.
REF: Ibid.

CU-0033
ETCH NAME:
TYPE: Acid, polish/clean
TIME: 3—10 min
TEMP: RT
COMPOSITION:
20 g .... $2NH_4NO_3.Ce(NO_3)_3.4H_2O$
10 ml .... HNO_3
150 ml .... H_2O
DISCUSSION:
Cu, wire and OFHC copper parts. This solution is similar to commercial "chrome etch" formulations and was developed for use on chromium evaporated on soda-lime glass as photo resist masks, but it can be used on both nickel as well as copper thin films and parts. The solution is a very slow polishing and cleaning etch for copper and useful where part dimensions are critical. By varying the nitric acid content, removal rates can be closely controlled on the angstroms/minute level.
REF: Walker, P — personal development and application, 1975

CU-0067
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
1 .... HNO_3
10 .... H_2O

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DISCUSSION:

Cu, bicrystals used in a study of grain boundary diffusion. Specimens wet cut and lapped with 600-grit alumina and then etched in the solution shown to develop grain boundary structure.

REF: Austin, A E & Richard, N A — *J Appl Phys,* 32,1462(1961)

CU-0034

ETCH NAME: Nitric acid
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... HNO_3

TIME: 1—10 min
TEMP: RT

(2) 1 .... HNO_3
25 .... H_2O

DISCUSSION:

Copper polycrystalline parts. Solutions used in cleaning cryogenic piping and parts of 200 gallon LN_2 transport trailers. Also used as a general cleaner for copper and copper alloys.

REF: Campo, F & Walker, P — cryogenic parts cleaning, 1962

CU-0035

ETCH NAME: Potassium cyanide
TYPE: Acid, removal
COMPOSITION:
x .... 20% KCN

TIME:
TEMP:

DISCUSSION:

Cu, copper thin films. Solution used to remove copper from Ge, Si, and GaAs surfaces.

REF: Valardi, N — personal communication, 1984

CU-0036a

ETCH NAME: Nitric acid, dilute
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
1 .... H_2O

TIME: 5 min
TEMP: RT

DISCUSSION:

Cu single crystal specimens used in a study of plastic flow at 90 and 170°C. Solution used as a polishing etch.

REF: Conrad, H — *Acta Metall,* 6,338(1958)

CU-0036b

ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HNO_3
2 .... MeOH

TIME: 45 min
TEMP: −10 to 0°C
ANODE:
CATHODE:
POWER:

DISCUSSION:

Cu single crystal specimens. After etching rinse in (1) tap water, (2) DI water, (3) acetone rinse, and (4) air dry.

REF: Ibid.

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CU-0037
ETCH NAME:
TYPE: Acid, sizing
COMPOSITION:
x .... 30% HNO_3
TIME:
TEMP:
DISCUSSION:
Cu single crystal specimens used in a study of surface effects on plastic properties. Solution used to etch specimens to required dimensions. (*Note:* This use of the term "sizing" reflects a physical action, not the use of chemicals as size in reducing ink running in paper.)
REF: Rosi, F D — *Acta Metall,* 5,349(1957)

CU-0038a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Cu single crystal spheres used in a study of oxidation on smooth convex surfaces. Spheres were polished after cutting with the solution shown, then etched to remove oxide before controlled oxidation.
REF: Harris, W W et al — *Acta Metall,* 5,574(1957)

CU-0038b
ETCH NAME:
TYPE: Electrolytic, oxide removal
COMPOSITION:
x .... KCl, sat. sol.
TIME: 5—10 min
TEMP:
ANODE:
CATHODE:
POWER: 30—50 mA/cm^3 & 5—10 V
DISCUSSION:
Cu single crystal spheres. Solution used to remove native oxide left after electropolishing in phosphoric acid before controlled oxidation.
REF: Ibid.
CU-0039: Evans, U R & Stockdale, J — *J Chem Soc,* 2,651(1929)
Reference for etchants shown in CU-0038a and CU-0038b.
CU-0040: Phelps, R T et al — *Ind Eng Chem Anal Ed,* 181,391(1948)
Cu specimens. Used solution to remove native oxide from parts.
CU-0041a: Greenfield, I G & Wildorf, H G F — *J Appl Phys,* 32,827(1961)
Cu specimens. Used solution to clean copper surfaces of residual oxide.

CU-0041a
ETCH NAME: Phosphoric acid, dilute
TYPE: Electrolytic, polish
COMPOSITION:
1 .... H_3PO_4
1 .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Cu single crystal specimens used in a study of the effects of neutron irradiation on plastic deformation. Solution used to polish specimens before irradiation.
REF: Greenfield, I & Wilsdorf, H G F — *J Appl Phys,* 32,827(1961)

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CU-0024e
ETCH NAME: Phosphoric acid, dilute
TYPE: Electrolytic, polish
COMPOSITION:
60 .... H_3PO_4
40 .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Cu, (111) wafers used in an etch pit and dislocation study. Solution used to polish surfaces prior to preferential etching (See CU-0024a).
REF: Ibid.
CU-0044: Moser, R T & Whitmore, J — *J Phys Chem Solids,* 31,115(1960)
Cu single crystal hemispheres grown or machined from a rod. Specimens were thermally etched at high temperature in vacuum to develop facets, spirals, and etch pits. Solution shown used to polish specimens prior to thermal treatment.

CU-0042
ETCH NAME: Neon
TYPE: Ionized gas, preferential
COMPOSITION:
x .... Ne^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
Cu single crystal specimens. Neon ion bombardment used to develop structure and orientation figures. Other metals studied were Al, Bi, Cd, Co, Mg, Sn, and Zn.
REF: Yurasova, V E — *Kristallografiya,* 2,770(1957)

CU-0024g
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
45 .... HCl
30 .... HAc
250 .... H_2O
1 .... Br_2
TIME: 30 sec
TEMP: RT
DISCUSSION:
Cu, (111) single crystal wafers within 2—3° of orientation. Solution develops triangular etch pits and pits increase in size, linearly, with etch time. (See CU-0043a.)
REF: Ibid.

CU-0045
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... H_3PO_4
1 .... HNO_3
1 .... HAc
TIME:
TEMP: 70°C
DISCUSSION:
Cu single crystal specimens. Etch polish in the solution shown. Specimens used in a study of ductile fracture.
REF: Saimoto, S et al — *Phil Mag,* 12,319(1965)
CU-0046: Ebeling, R & Ashby, M F — *Phil Mag,* 13,437(1966)

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Cu single crystal specimens. Etch polished as shown above. Specimens used in a study of dispersion hardening.

CU-0047
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
33 ml .... H_3PO_4
33 ml .... HNO_3
33 ml .... HAc
TIME: 1—2 min
TEMP: 60—70°C
DISCUSSION:

Cu specimens used in an etching study. The solution will remove copper and copper oxide, and is particularly good for oxide removal.
REF: de Jong, J J — *Metalen*, 9,2,(1954) (in Dutch)
CU-0073: Tegart, WJ McG — *The Electrolytic and Chemical Etching of Metals*, Pergamon Press, England, 1956

Cu specimens. Solution described as a polish etch for copper, and a removal etch for Cu_2O oxide.

CU-0048
ETCH NAME:
TYPE: Acid, oxidation
COMPOSITION:
x .... $CuSO_4$
+ .... O_2
TIME:
TEMP:
DISCUSSION:

Cu single crystal sphere ground to shape and electropolished with (111), (100), (110), (311) and (210) flats lapped and polished. Mixture shown was used to oxidize surfaces in a study of growth spirals in Cu_2O.
REF: Miller, G T & Lawless, K R — *J Appl Phys*, 29,863(1958)

CU-0011c
ETCH NAME: ALN3-1
TYPE: Acid, macro-, micro-etch
COMPOSITION:
5 ml .... HNO_3
5 ml .... H_2SO_4
4 g .... CrO_3
1 g .... NH_4Cl
90 ml .... H_2O
TIME: Dip
TEMP: RT
DISCUSSION:

Cu specimens and copper alloys. Solution is both a macro- or micro-etch depending upon type alloy and used in a material structure study.
REF: Ibid.

CU-0011d
ETCH NAME: Geard #1
TYPE: Acid, preferential
COMPOSITION:
5 ml .... HCl
20 g .... $FeCl_3$
100 ml .... H_2O
TIME: Swab
TEMP: RT

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DISCUSSION:
Cu, specimens and copper alloys. A general micro- or macro-etch on most alloys of copper. Apply by swabbing the surface.
REF: Ibid.

CU-0069
ETCH NAME: Smog
TYPE: Gas, corrosion
COMPOSITION:
x .... Air (+ SO_2, H_2S, O_3, HCl, Cl_2, vapor)
x .... H_2O, vapor (as RH)
TIME:
TEMP:
DISCUSSION:
Cu specimens used in a study of atmospheric corrosion using an artificially developed smog with variable water vapor as humidity factor. Also studied silver with same smog atmosphere, but in dry air.
REF: Rice, D W et al — *J Electrochem Soc,* 128,275(1981)

CU-0050b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HNO_3
x .... EOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Cu single crystal spheres. Solution used as a polish etch. See CU-0050a for discussion.
REF: Ibid.

CU-0051
ETCH NAME:
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:
Cu single crystal spheres formed by asymmetric cooling of copper on a tungsten ribbon in high vacuum. Used in an oxidation study of tungsten carbide growth on a copper sphere.
REF: Menael-Kopp, C — *Z Naturforsch,* 122,1003(1957)

CU-0060
ETCH NAME: Ammonium peroxydisulfate
TYPE: Salt, polish
COMPOSITION:
x .... x% $(NH_4)_2S_2O_8$
+ .... $HgCl_2/PdCl_2$
TIME: Variable
TEMP: 45°C
DISCUSSION:
Cu specimens used in a study of the effects of the solution shown. The addition of metal salts will increase the removal rate. (*Note:* Solution also called ammonium persulfate.)
REF: Schlabach, T D & Diggery, B A — *Electrochem Technol,* 2,118(1964)

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CU-0061
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
600 ml .... H_3PO_4
12.9—19 g .... CuO
400 ml .... H_2O
TIME:15—40 h
TEMP:
ANODE: Cu specimen
CATHODE: Cu sheet
POWER: 1.0—1.1 V
RATE: 0.01—0.2 μm/min
DISCUSSION:

Cu specimens. First, dip specimens in HNO_3, rinse in water and while still wet introduce into solution shown above. Hold specimen surface in a horizontal position during etching. After etching, with potential still applied, rinse in H_3PO_4, 30 sec. With 12.5 g CuO and high purity copper specimens gave the best results. There were some parallel ripples on surfaces less than 100 Å in height.
REF: Powers, R W — *Electrochem Technol,* 2,274(1964)

CU-0068
ETCH NAME: Chlorine
TYPE: Gas, removal
COMPOSITION:
x .... Cl_2, vapor
TIME:
TEMP: See discussion
DISCUSSION:

Cu, (100) single crystal wafers cut within 3° of orientation, with some twinning observed, were used in a study of the surface reactions with chlorine gas. Three general reactions were observed at different temperature levels: (1) less than 150°C, CuCl growth; (2) 150—580°C, Cu_3Cl_3, as a gas, and (3) above 650°C, CuCl as gas.
REF: Winters, H F — *J Vac Sci Technol,* A(3),786(1985)

CU-0013b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HCl
1 .... H_2O
x .... *$FeCl_3$
TIME:
TEMP:

*Saturate the solution.

DISCUSSION:

Cu, single crystal sphere 1 cm diameter. After polishing with nitric acid and then ferric chloride, the solution shown was used to preferentially etch. Developed (001) pole figures.
REF: Ibid.

CU-0052
ETCH NAME: Copper sulfate
TYPE: Acid, oxidation
COMPOSITION:
x .... 50 g/l $CuSO_4.5H_2O$ pH: 3.8
TIME: Variable
TEMP: RT
DISCUSSION:

Cu, single crystal spheres $^5/_8$ and $^3/_4$" diameter with (100), (110), (111), (012), and (311) flats. Solution used to oxidize surfaces in a study of epitaxy relationships of Cu_2O. In 5 min a general orientation pattern will form; 24—60 h oxide will show pitting; 5 sec to 90

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h and Cu_2O crystals form. After oxidizing spheres in the solution, wash in DI water and blow dry with nitrogen.
REF: Lawless, K R & Miller, G T Jr — *Acta Crystallogr,* 12,594(1959)

CU-0053
ETCH NAME: TIME:
TYPE: Thermal, forming TEMP:
COMPOSITION:
x .... heat
DISCUSSION:
Cu, single crystal spheres formed by melting the tip of single crystal wire. Wire was 1—2 mm diameter; spheres, 2—3 mm diameter. Other materials used were Ag and Au.
REF: Rose, D K & Gerisder, H — *J Electrochem Soc,* 110,350(1963)
CU-0086: Young, F W & Gwathmey, A T — *J Appl Phys,* 31,225(1960)
Cu, single crystal specimens. Heating in ultra high vacuum (UHV) develops facets and spiral etch pits.

CU-0071b
ETCH NAME: Water TIME:
TYPE; Acid, float-off TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
Cu, thin films evaporated on NaCl, (100) substrates in a general study of thin film defects by TEM. After film deposition, copper was removed by dissolving the NaCl surface with water using the float-off technique. Copper thin films deposited on mica, (0001) substrates were removed with 10% HF. A study of copper structure.
REF: Ibid.

CU-0071a
ETCH NAME: TIME:
TYPE: Deformation, defect TEMP:
COMPOSITION:
x .... stress
DISCUSSION:
Cu, single crystals used in a study of secondary slip caused by stress deformation. Secondary slip nucleates at the end of primary slip lines when the internal stress fields are high. Also studied single crystal alpha-brass.
REF: Mitchell, T E & Thornton, P R — *Phil Mag,* 10,314(1964)

CU-0062b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... *$K_2Cr_2O_7$

*100 g/l

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DISCUSSION:

Cu, single crystals used in a cleaning study. The solution shown was radiotracer tagged with ^{35}S and ^{51}Cr isotopes and used as a surface cleaning etch.

REF: Fatzer, O D et al — *Int J Appl Radiat & Isot,* 10,167(1961)

CU-0062c

ETCH NAME:

TYPE: Electrolytic, polish

COMPOSITION:

x .... x% CrO_3

TIME: 2 min

TEMP: 120°C

ANODE: Cu

CATHODE:

POWER:

DISCUSSION:

Cu specimens. See discussion under CU-0062a and CU-0062b.

REF: Ibid.

CU-0085

ETCH NAME:

TYPE: Acid, cutting

COMPOSITION:

(1) 200 ml .... HCl
50 g .... $FeCl_3$
250 ml .... H_2O

(2) 1 .... HNO_3
1 .... H_2O

TIME: 60 min

TEMP: RT

DISCUSSION:

Cu specimens $^1/_8$" thick. Terylene thread soaked in solution (1) used to cut copper, aluminum and brass. Solution (2) used for tin and zinc. (*Note:* Excellent review of metal growth methods.)

REF: Honeycombe, R W K — *Metall Rev,* 4,1(1959)

CU-0087

ETCH NAME: Argon

TYPE: Ionized gas, cleaning

COMPOSITION:

x .... Ar^+ ions

TIME:

TEMP:

GAS FLOW:

PRESSURE:

POWER:

DISCUSSION:

Cu, (111) wafers used as substrates for thin film deposition of copper by condensation of metallic vapor which can produce twinning. Substrates were Ar^+ ion bombardment cleaned prior to copper deposition. Epitaxy growth of copper evaporated at an angle as a function showed that the greater the angle, the greater the increase of twinning observed. (*Note:* Growth of silica at an angle will produce a columnar growth structure rather than normal amorphous thin films.)

REF: Lafourcado, L et al — *C R Acad Sci (Paris),* 249,230(1959)

CU-0088: Yurasova, V E — *Zh Tekh Fiz,* 28,1966(1958)

Cu, single crystal specimens. Cathode positive sputtering as ion bombardment used in a study of surface micro-relief and erosion. Etch pits observed in Cu and Zn and slip traces on deformed Zn.

COPPER ALLOYS

General: Copper occurs as a native element as well as in a number of single crystal metallic compounds: horsfordite, Cu_6Sb; mohawkite, Cu_3As; rickardite, Cu_4Te_3; barzelianite, Cu_2Se. The two major copper sulfides are chalcocite, Cu_2S and covellite, CuS. The copper iron sulfides: bornite, $CuFeS_4$ and chalcopyrite, $CuFeS_2$. The latter mineral structure is a

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base for the artificial ternary chalcogenides. Possible the two most well known copper minerals, due to their brilliant colors, are the copper carbonates: malachite (green) and azurite (blue), both being primary copper ores as well as semi-precious gem stones. Cuprite, Cu_2O, is the major oxide of copper, also an ore as are all the copper alloy compounds mentioned. They occur in vein deposits alone, or are associated with iron.

There are many artificial alloys of copper, the two most well known being bronze, Cu:Sn and brass, Cu:Zn. Mixtures of Cu:Sn:Zn are used for bell metal and gun metal, and there are special mixtures such as phosphor-bronze; silicon bronze; manganese bronze. There are similar alloys of brass: cartridge brass, wire brass, aluminum brass, etc., and mixtures of Cu:W are some of the alloys referred to as heavy metal. As pure copper is soft, ductile and malleable it is usually used in some form of alloy for strengthening purposes, although OFHC copper, the highest purity form of copper, has application for its low electrical resistance and heat dissipation characteristics.

Technical Application: There are many uses for pure copper and copper alloys in Solid State material processing as evaporated contact pads in device fabrication, as package assembly parts and, of major importance today, as PCBs (laminated plastic linen boards, copper plated) used to hold electronic circuit assemblies for computers and similar products. Such boards are capable of being inserted and removed in a variety of equipment, and are widely used in the miniaturization of operating functions.

OFHC copper and brass are both used as test blocks for mounting semiconductor devices. Heavy metal, Cu:W alloys, are used as physical weights for belt furnace alloying of parts; phosphor-bronze, Cu:Sn:P, sheet is cut and used as holding spring clips for both metal evaporation of wafers on a flat plate, or devices on a test plate, as is Cu:Be. There are epoxy and polyimide pastes containing copper powder as one constituent for use as electrical contact materials, e.g., "loaded" epoxies.

Several binary and trinary copper alloys have been grown and studied as single crystals for general morphology and structure. There are also trinary and quarternary sulfide and selenide compound semiconductors containing copper.

Etching: Soluble in HNO_3, H_3PO_4, and mixed acids, variable with type alloy.

COPPER ALLOY ETCHANTS

COPPER:ANTIMONY ETCHANTS

CUSB-0001
ETCH NAME: Nital — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... HNO_3
x .... EOH/MeOH (H_2O)
DISCUSSION:

Cu_2Sb, and $SbAu_2Sb$ specimens. Structure could be observed on material without etching. Solution shown was used to accentuate defects and structure.
REF: Savas, M A & Smith, R W — *J Cryst Growth,* 71,66(1985)

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COPPER:BERYLLIUM ETCHANTS

CUBE-0001
ETCH NAME: TIME:
TYPE: Acid, structure TEMP:
COMPOSITION:
100 ml .... H_2O_2
35 ml .... 20% KOH
125 ml .... H_2O
DISCUSSION:
Cu:Be:Ni alloy specimens. Specimens used in a study of the effects of pressure on age hardening. Solution used to develop defect and structure.
REF: Phillips, V A — *Acta Metall,* 9,216(1961)

CUBE-0002
ETCH NAME: Nitric acid, dilute TIME:
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
100 ml .... HNO_3
100 ml .... H_2O
DISCUSSION:
Cu:Be, spring shim stock, 0.010—0.015" thick, cut and used as spring clips to hold semiconductor wafers on SST plates during metallization. After cutting and shaping, clips were degreased in hot TCE vapors, rinsed in MeOH, and N_2 blown dry. Solution shown used to lightly etch clean clips before use: (1) etch; (2) DI water rinse; (3) MeOH rinse; and (4) N_2 blow dry. Same method used to clean clips after metal depositing with a combination of physical scrap/removal of loose metallization build-up, and etch cleaning.
REF: Fahr, F & Walker, P — personal application, 1980

COPPER:CERIUM ETCHANTS

CUCE-0001
ETCH NAME: Ferric chloride TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... 25% $FeCl_3$
DISCUSSION:
$CeCu_6$, grown as a single crystal ingot by the Czochralski (CZ) method. Material is orthorhombic in structure and was used in a material growth study. Also developed $LaCu_6$ CZ grown ingots, and $CeAl_3$ by arc melting and aging at temperature. CeB_6 and $CeCu_2Si_2$ are also grown as single crystals. No etchant shown. (*Note:* Ferric chloride solutions are general etchants for copper and copper alloys or compounds.)
REF: Onuki, Y et al — *J Phys Soc Jpn,* 4,1210(1984)

COPPER:GALLIUM ETCHANTS

CUGA-0001a
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... $FeCl_3$
x .... EOH

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DISCUSSION:

Cu:Ga alloy specimens used in a study of transformation due to strain. Specimens were subjected to strain at elevated temperatures, quenched directly into an ice/brine solution, or a 10% NaOH solution. Solution shown used to develop defects and structure. Also studied Cu:Zn and Cu:Ga:Ge alloys.

REF: Massaski, T B — *Acta Metall,* 6,243(1958)

CUGA-0001b

ETCH NAME: Ammonium hydroxide — TIME:

TYPE: Base, preferential — TEMP:

COMPOSITION:

x .... NH_4OH

x .... H_2O

DISCUSSION:

Cu:Ga alloy specimens. Solution used to develop defects and structure. See CUGA-0001a for additional discussion.

REF: Ibid.

COPPER:GERMANIUM ETCHANTS

CUGE-0001

ETCH NAME: Phosphoric acid — TIME:

TYPE: Electrolytic, polish — TEMP:

COMPOSITION: — ANODE:

x ... H_3PO_4 — CATHODE;

POWER:

DISCUSSION:

Cu:Ge alloys of varying compositions grown and used in a study of optical absorption at 4.2 K. Solution was erratic for germanium concentration alloys above 7% Ge, as the material will not polish. Other alloys were studied.

REF: Rayne, J A — *Phys Rev,* 121,456(1961)

COPPER:GOLD ETCHANTS

CUAU-0001

ETCH NAME: — TIME:

TYPE: Electrolytic, polish — TEMP:

COMPOSITION: — ANODE:

x .... HAc — CATHODE:

x .... CrO_3 — POWER:

DISCUSSION:

Cu_3Au single crystal specimens used in a study of long range order from strain hardening. Solution used to polish specimens prior to straining.

REF: Davis, R G & Steloff, N S — *Phil Mag,* 12,297(1965)

CUAU-0002

ETCH NAME: Phosphoric acid — TIME:

TYPE: Electrolytic, polish — TEMP:

COMPOSITION: — ANODE:

x .... H_3PO_4 — CATHODE:

POWER:

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DISCUSSION:

Cu_3Au single crystal specimens used in a study of ordering strength and dislocations in superlattice materials. Solution used to polish specimens. The material Ni_3Mn also was studied.

REF: Markoikowski, M J & Miller, D S — *Phil Mag*, 6,871(1961)

COPPER:LANTHANUM ETCHANTS

CULA-0001

ETCH NAME: Ferric chloride — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... 25% $FeCl_3$

DISCUSSION:

$LaCu_6$ grown as single crystal ingots by the Czochralski (CZ) method. See discussion under Copper:Cerium (CECU-0001) for further discussion.

REF: Onuki, Y et al — *J Phys Soc Jpn*, 4,1210(1984)

COPPER:NICKEL ETCHANTS

CUNI-0001

ETCH NAME: Nitric acid — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

x .... HNO_3

DISCUSSION:

CuNi single crystal specimens fabricated as spheres. Solution will develop pole figures at (100), (110), and (111) plane locations, and is not actually preferential as a finite crystal form etchant.

REF: Schmunk, R E & Smith, C S — *Acta Metall*, 8,396(1960)

COPPER PALLADIUM ETCHANTS

CUPD-0001

ETCH NAME: Nitric acid — TIME:

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

1 .... HNO_3

1 .... H_2O

DISCUSSION:

Cu:Pd thin films co-evaporated on Pyrex blanks in a material study. Quartz was evaluated as a substrate material, but it will form SiPd. Solution used to etch remove or etch pattern thin film after annealing cycles.

REF: van Langeveld, A D — *Thin Solid Films*, 109,179(1983)

COPPER:ZINC ETCHANTS

CUZN-0001

ETCH NAME: — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

x .... $FeCl_3$

x .... EOH

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DISCUSSION:
Cu:Zn alloy specimens used in a study of transformations due to strain. Solution used to develop defects and structure. See CUGA-0001a for additional discussion.
REF: Massaski, T B — *Acta Metall,* 6,243(1958)

PHYSICAL PROPERTIES OF COPPER BROMIDE, $CuBr_2$

Classification	Bromide
Atomic numbers	29 & 35
Atomic weight	223.4
Melting point (°C)	498
Boiling point (°C)	
Density (g/cm³)	3.0×
Hardness (Mohs — scratch)	2—3
Crystal structure (monoclinic-normal)	(100) a-pinacoid
Color (solid)	Black
Cleavage (basal)	(001)

COPPER BROMIDE, $CuBr_2$

General: Does not occur as a natural compound due to high solubility in water, but can occur in solution and be extracted from ocean waters and some hot springs like other bromides, chlorides and some iodides. There is no major industrial use.

Technical Application: Copper bromide has been studied in association with some 40 other compounds for semiconductor characteristics and, even though water soluble, may have useful optical characteristics like some other bromides.

Etching: Water and alcohols.

COPPER BROMIDE ETCHANTS

CUBR-0001
ETCH NAME: Ethyl alcohol — TIME:
TYPE: Alcohol, removal — TEMP: RT
COMPOSITION:
x .... EOH (MeOH)
DISCUSSION:
CuBr single crystals used in an evaluation of cohesive energy features of tetrahedral semiconductor materials. Solution shown was used as a general polish and removal etchant on surfaces. Some 40 materials were studied.
REF: Aresti, A et al — *J Phys Chem Solids* 45,361(1984)

PHYSICAL PROPERTIES OF COPPER CHLORIDE, $CuCl_2$

Classification	Chloride
Atomic numbers	29 & 17
Atomic weight	134.48
Melting point (°C)	498
Boiling point (°C)	993
Density (g/cm³)	3.045
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Yellow
Cleavage (cubic)	(001)

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COPPER CHLORIDE, $CuCl_2$

General: Does not occur in natural as a solid compound due to water solubility, but can be extracted from ocean and ground waters in solution, particularly in areas associated with copper mining. May occur as a mixed component in arid areas with potassium chloride, carbonates, and sulfates. There is no major use in industry, other than as a copper source in electrolytic copper plating or as a component in etch solutions.

Technical Application: In Solid State processing it has been used as a copper doping source in some compound semiconductors and, as in the general metal industries, for electrolytic copper plating. The chloride also has been used as a constituent in some preferential etchants, and for copper plate-out from solution with subsequent heat treatment drive-in for defect decoration with copper. It has been studied along with other halides for semiconducting properties, and can have applications as an optical filter.

Etching: Water and alcohols.

COPPER CHLORIDE ETCHANTS

CUCL-0001
ETCH NAME: Ethyl alcohol — TIME:
TYPE: Alcohol, removal — TEMP: RT
COMPOSITION:
x .... EOH (MeOH)
DISCUSSION:

CuCl as single crystals were used in an evaluation of cohesive energy features of tetrahedral semiconductors. Alcohols were used for general removal and polishing of surfaces. Forty materials were studied.
REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

PHYSICAL PROPERTIES OF COPPER IODIDE, CuI

Classification	Iodide
Atomic numbers	29 & 53
Atomic weight	190.4
Melting point (°C)	605
Boiling point (°C)	1200
Density (g/cm^3)	5.62
Refractive index (n =)	2.346
Hardness (Mohs — scratch)	2.5
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Brown
Cleavage (dodecahedral)	(110)

COPPER IODIDE, CuI

General: Occurs in nature as the mineral marshite, CuI, as a minor compound associated with copper deposits. There is little use of the natural mineral in the metal industry due to scarcity, but the artificial compound has both chemical and medical applications.

Technical Application: There is no use in Solid State device fabrication, to date, other than occasional use as a constituent in etching solutions. The compound has been characterized for semiconducting properties, and has possible application in optics as a filter element.

Etching: KI, KCN, and NH_4OH

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COPPER IODIDE ETCHANTS

CUI-0001
ETCH NAME: Potassium iodide
TYPE: Halogen, removal
COMPOSITION:
x .... KI
x .... H_2O (EOH)
TIME:
TEMP: RT
DISCUSSION:
CuI grown as single crystals in an evaluation of cohesive energy features of tetrahedral semiconductors. Solution shown used as a general removal and surface polishing etch. Forty materials were evaluated.
REF: Aresti, A et al — *J Phys Chem Solids* 45,361(1984)

PHYSICAL PROPERTIES OF COPPER OXIDE, Cu_2O

Classification	Oxide
Atomic numbers	29 & 8
Atomic weight	143.14
Melting point (°C)	1235
Boiling point (°C)	1800
Density (g/cm^3)	5.85—6.15
Refractive index (n =)	2.849
Hardness (Mohs — scratch)	3.5—4
Crystal structure (isometric — plagiohedral)	(111) octahedron
Color (solid)	Black (CuO)
(solid)	Copper-red (Cu_2O)
(flame)	Emerald green
Cleavage (cubic — interrupted)	(001)

COPPER OXIDE, Cu_2O

General: As the natural mineral cuprite, Cu_2O (red copper ore), it is a primary ore of copper, and also occurs as the monoxide: tenorite, CuO. The latter, as black incrustations whereas cuprite is brilliant conchineal-red. Both colors appear on pure copper parts with exposure to air, but the green "verdigris" is copper sulfate from sulfur in the atmosphere. Other than industrial ores of copper, both forms are important as coloring agents in paints and glass, and the mineral is used for its flame color in pyrotechnics.

Technical Application: Though not used in general Solid State material processing, both the polycrystalline and single crystal forms are used to fabricated discrete rectifiers, similar to selenium rectifiers. Cu_2O has been grown by oxidation of OFHC copper surfaces and, on alpha-brass, by copper plating and water soak-tarnishing as a copper hydrated thin film. Both methods used in material studies. Most of the listed references here are for removal of "native oxide" films in copper material processing.

Etching: HCl (CuO). HNO_3, NH_4OH, and acid mixtures (Cu_2O).

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COPPER OXIDE ETCHANTS

CUO-0001
ETCH NAME: Ethylenediamine TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
x .... 1% ethylenediamine
DISCUSSION:
Cu_2O, as a native oxide thin film on surfaces. This amino acid will remove the oxide but will not etch the pure copper metal.
REF: Stiegler, J O & Noggles, T S — *J Appl Phys*, 31,1827(1960)

CUO-0002
ETCH NAME: Nitric acid, dilute TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:
Cu_2O as a native oxide on copper surfaces. Dilute solutions are used to remove native oxides and etch polish copper surfaces. Cleaned specimens were control oxidized at 1030 to 1095°C for 3—4 h and then annealed for 40 to 150 h. Large area single crystals (10 to 40 mils) were formed with size increasing as annealing time was increased.
REF: Toth, R S et al — *J Appl Phys*, 31,1117(1960)
CUO-0003: Bulletin B-11D, The American Brass Co.
Cu, and Cu alloys. Used a 1:1 mixture for removal of native oxide and to etch polish copper surfaces.
CUO-0004: Walker, P & Campos, R — personal application, 1961—1962
Cu alloys as cryogenic trailer piping. Used a 1:20 solution for removal of surface contamination. Solution applied by soaking and scrubbing with an SST brush. Heavy DI water wash after etch cleaning and wipe dry with lint-free toweling.

CUO-0005
ETCH NAME: Copper Brite dip TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
3—7 .... H_2SO_4
1—7 .... HNO_3
0—5 .... HCl
1—10 .... H_2O
DISCUSSION:
Cu, and Cu alloys. There are several specific mixtures of this "Brite Dip" which is sometimes referred to as a "scale" removal etch. Used to remove oil/grease contamination or copper oxide, and as surface polish etches for copper. Solutions are extremely reactive, producing a bright copper surface. They should not be used on parts requiring close dimensional control as etching proceeds by pinholing and undercutting of the surface contamination, such that surface planarity and tolerances cannot be maintained. See CU-0028 for other specific mixtures.
REF: Walker, P & Fahr, F — personal application, 1978—1983

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CUO-0006a
ETCH NAME: Ammonium hydroxide
TYPE: Hydroxide, oxide removal
COMPOSITION:
x .... NH_4OH
TIME:
TEMP: RT to hot
DISCUSSION:

Cu_2O, native oxide. Solution will remove both Cu_2O and CuO oxides and slowly etch copper.

REF: Hodgman, C D et al — *Handbook of Chemistry and Physics,* Chemical Rubber Co., Cleveland, OH, 1943, 380

CUO-0007: Walker, P — personal application, 1980—1985

OFHC copper parts used in test assemblies of microelectronic devices. Surfaces were cleaned by soaking parts in solution shown, then wash in DI water, and final rinse with MeOH, and N_2 blow dry.

CUO-0017: Horn, F N — *J Appl Phys* 32,900(1961)

CuO single crystals doped with iron and grown by the Czochralski (CZ) method in a study of ferrites. Other ferrites grown and studied were Fe_3O_4, and iron doped ZnO, Ga_2O_3, and MnO.

CUO-0008
ETCH NAME: Phosphoric acid
TYPE: Acid, polish
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP: 130°C
RATE: 1 μm/min
DISCUSSION:

Cu_2O, material use as rectifiers in a study of etching effects on device operating parameters. Etching will reduce the forward current while a lapped surface will increase current.

REF: Makovskii, F A & Usachev, B P — *Zh Tekh Fiz,* 27,2786(1957)

CUO-0009
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
33 ml .... H_3PO_4
33 ml .... HNO_3
33 ml .... HAc
TIME: 1—2 min
TEMP: 60—70°C
DISCUSSION:

Cu_2O, as a native oxide on copper specimens. Solution will etch both copper oxide and copper, but is particularly good for removal of oxides.

REF: de Jong, J J — *Metalen,* 9,2(1954) (in Dutch)

CUO-0015: Tegart, W J McG — *The Electrolytic and Chemical Etching of Metals,* Pergamon Press, England, 1956

Cu_2O, native oxide on copper surfaces. Solution can be used to etch both copper and copper oxides and is very good for oxide removal.

CUO-0010
ETCH NAME: Ammonium sulfate
TYPE: Acid, cleaning
COMPOSITION:
x .... 2—5%$(NH_4)_2SO_4$
TIME: 15 min
TEMP: RT

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DISCUSSION:

Cu_2O as thin films grown on OFHC copper by oxidation. Clean copper with solution shown before oxidation. After etching, wash in DI water.

REF: Baur, J P et al — *Acta Metall,* 103,273(1956)

CUO-0011

ETCH NAME: Oxygen

TYPE: Gas, preferential

TIME: 10 min

TEMP: 250°C

PRESSURE: 10 mmHg

COMPOSITION:

x .... O_2

DISCUSSION:

Cu, single crystal sphere. Used in a study of oxidation rates as related to crystallographic faces and plane zones.

REF: Gwathmey, A T et al — *J Chem Phys,* 8,431(1940)

CUO-0012: Gwathmey, A T et al — *J Phys Chem,* 46,969(1942)

Cu, single crystal spheres with cut and oriented flats. Oxidation rate varies with crystallographic faces in the following decreasing order: (100)<(210)<(111)<(110)<(311). Thickness variation can be as much as fivefold. Rate varies with orientation, temperature, and oxygen pressure.

CUO-0013

ETCH NAME: Oxygen

TYPE: Gas, preferential

TIME: Variable

TEMP: Variable

COMPOSITION:

x .... O_2

DISCUSSION:

Cu, single crystal spheres. A comprehensive article of oxidation of materials — thickness, epitaxy orientation, rates. Other materials were Ni, Fe, Nb, Co, Al, Cr, Ge, Ag, Mg, Pd, Zn, Cd, Be, Pb, Sb, Ta, Mn, Fe-Ni, brass, and U. Included cleaved or cut wafer surfaces of some of the materials.

REF: Gwathmey, A T & Lawless, K R — Gatos, H C Ed — *The Surface Chemistry of Metals and Semiconductors,* John Wiley & Sons, New York, 1960, 483

CUO-0014a

ETCH NAME:

TYPE: Acid, removal

TIME:

TEMP: RT

COMPOSITION:

300 ml .... H_2SO_4

400 ml .... HNO_3

5 ml .... HCl

295 ml .... H_2O

DISCUSSION:

Cu specimens. Described as a copper oxide removal etch. (*Note:* See CU-0028, Copper Brite Dip solutions. This is a variation of the CU-0032 solution.)

REF: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices,* Reinhold, New York, 1967

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CUO-0014b
ETCH NAME: TIME: 2—3 sec
TYPE: Acid, removal TEMP: RT
COMPOSITION:
1000 ml .... HNO_3
10 ml .... HCl
DISCUSSION:
Cu specimens. Described as a copper oxide removal etch.
REF: Ibid.

CUO-0006b
ETCH NAME: Ammonium chloride TIME:
TYPE: Salt, removal TEMP: RT
COMPOSITION:
x .... x% NH_4Cl
DISCUSSION:
Cu_2O specimens, or as a native oxide on copper. Described as a copper oxide removal etchant.
REF: Ibid.

CUO-0016
ETCH NAME: Water TIME: 15 h
TYPE: Acid, oxidation TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:
Cu_2O thin films plated from solution onto alpha-brass, Cu:Zn with 29.38% Cu. Plating solution was: 0.04 *M* $CuSO_4$:1.57 $(NH_4)_2SO_4$ for pH 7 balanced with NH_4OH, and containing tracer $^2O^{64}Cu$. After plating, 12 mm blanks were soaked in water for 15 h to oxide tarnish, then DI water washed, and sealed in polyethylene bags for radiation count. A study of the mechanisms fo Cu_2O formation.
REF: Birley, S S & Tromans, D — *J Electrochem Soc,* 118,636(1971)

PHYSICAL PROPERTIES OF COPPER PHOSPHIDE, Cu_3P

Classification	Phosphide
Atomic numbers	29 & 15
Atomic weight	221.73
Melting point (°C)	~1200
Boiling point (°C)	
Density (g/cm^3)	6.4—6.8
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey/black
Cleavage (cubic)	(001)

COPPER PHOSPHIDE, Cu_3P

General: Does not occur in nature as a pure metallic phosphide, although the mineral libethenite, $Cu_2(OH)PO_4$, and tsumebite, $Pb,Cu(PO_4)_x$ are minor phosphate minerals. Artificial copper phosphide is fabricated in industry as phosphor-bronze, and used for its spring qualities.

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Technical Application: As phosphor-bronze the material is widely used in Solid State processing as spring clips for holding semiconductor wafers or parts during vacuum metallization, and as general holding clips during device testing.

The material has been grown as a single crystal with germanium doping for evaluation as a compound semiconductor.

Etching: Soluble in HNO_3 and mixed acids ($HF:HNO_3$).

COPPER GERMANIUM PHOSPHIDE ETCHANTS

CUGP-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... HF
x .... HNO_3
x .... H_2O
DISCUSSION:

$CuGe_2P_3$ single crystal ingots grown by the Horizontal Bridgman (HB) method as a p-type semiconductor. Specimens were cut as parallelapipeds (001), (110)/(110), and mechanically polished in a material properties evaluation. (*Note:* Solution shown can be used to etch clean phosphor-bronze.)

REF: McDonald, J E — *J Phys Chem Solids,* 8,951(1985)

PHYSICAL PROPERTIES OF COPPER SELENIDE, Cu_2Se

Classification	Selenide
Atomic numbers	29 & 34
Atomic weight	206.10
Melting point (°C)	>1200
Boiling point (°C)	
Density (g/cm^3)	6.71
Hardness (Mohs — scratch)	3—4
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Silver-white
Cleavage (cubic)	(001)

COPPER SELENIDE, Cu_2Se

General: Occurs in nature as the mineral berzelianite, Cu_2Se and klockmannite, CuSe. The variety umangite, $CuSe.Cu_2Se$ is dark cherry-red in color, and there are other trinary or quaternary constituent copper selenides, such as crookesite, containing thallium and silver.

The main industrial use of these minerals is as minor ores of copper and selenium.

Technical Application: Trinary copper selenides are under evaluation as tetrahedral compound semiconductors in Solid State, but not used as devices at the present time. The following two copper selenides are trinary compounds.

Etching: Soluble in mixed acids.

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COPPER GALLIUM SELENIDE ETCHANTS

CGSE-0001
ETCH NAME: Aqua regia, variety — TIME:
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
$CuGaSe_2$ single crystal evaluated for cohesive energy features of tetrahedral semiconductors. Forty materials were studied. (*Note:* See copper indium selenide for addition solutions.)
REF: Aresti, A et al — *J Phys Chem Solids,* 45,361(1984)

COPPER INDIUM SELENIDE ETCHANTS

CISE-0001
ETCH NAME: — TIME: 2 min
TYPE: Acid, polish/stain — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
$CuInSe_2$ single crystal specimens. Crystalline ingot grown by Horizontal Bridgman (HB) process, then large single crystal grains were cut out and mechanically lapped with 0.3 μm alumina. After indium diffusion, the solution shown was used to acid stain the p-n junction after angle lapping.
REF: Shih, T et al — *J Appl Phys,* 66,420(1984)
CISE-0002b: Ibid.
$CuInSe_2$ singe crystal wafers. Annealed under Se vapor to produce a p-type layer as a p-n junction. Solution used as a junction stain.
CISE-0005: Ciszek, T F — *J Electron Mater,* 14,451(1985)
$CuInSe_2$ ingots grown by LEC or the Bridgman/Stockberger process with slow directional solidification for large grains. Material is p- or n-type depending on the charge. Preferred crystal growth habit is (112) tetragonal.

CISE-0002a
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, junction — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
$CuInSe_2$ wafers annealed under Se to produce a p-type layer as a p-n junction. Solution used as a junction stain.
REF: Tell, B et al — *J Appl Phys,* 48,2477(1977)

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CISE-0003
ETCH NAME: TIME:
TYPE: Acid/halogen, cleaning TEMP:
COMPOSITION:
(1) 6 .... H_2SO_4 (2) x .... 1% Br_2
1 .... H_2O_2 x .... MeOH
1 .... H_2O
DISCUSSION:

$CuInSe_2$ p-type wafers. Grown from a melt by directional freezing with a preferred (112) tetragonal orientation. Specimens were cleaned and polished sequentially in these two acid solutions to remove carbon and oxygen contamination.
REF: von Bardeleben, H J — *J Appl Phys*, 66,320(1984)
CISE-0004: von Bardeleben, H J — *J Appl Phys*, 66,586(1984)

PHYSICAL PROPERTIES COPPER SULFIDE, CuS

Classification	Sulfide
Atomic numbers	29 & 16
Atomic weight	159.29
Melting point (°C)	103
Boiling point (°C)	220 del.
Density (g/cm^3)	4.6
Refractive index (n =)	1.45 (Na)
Hardness (Mohs—scratch)	1.5—2
Crystal structure (hexagonal—normal)	(1010) prism
Color (solid)	Indigo blue
Cleavage (basal)	(0001)

COPPER SULFIDE, CuS

General: Occurs as the mineral covellite, CuS in association with other copper vein ores. It is of secondary in origin and, occasionally, as a volcanic sublimate. Industrial use is as a minor copper ore in association with the other vein ores.

Technical Application: No direct use in Solid State processing, but has been artificially grown as a single crystal. Both the natural and artificial materials have been studied for general morphological data.

Etching: Soluble in HNO_3, HCl, H_2SO_4, and KCN.

COPPER SULFIDE ETCHANTS

CUS-0001
ETCH NAME: Nitric acid TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
1 .... HNO_3
10 .... H_2O
DISCUSSION:

CuS specimens as the natural mineral covellite. Solution used as a slow removal etch of the purplish tarnish on surfaces in a general study of the copper minerals.
REF: Walker, P — mineral study, 1953

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COPPER GALLIUM SULFIDE ETCHANTS

CUGS-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
DISCUSSION:
TIME:
TEMP:

$CuGaS_2$ single crystals grown at less than 630°C in quartz ampoules with tin as a metal solvent. Clean copper with HCl. Clean quartz ampoule with boiling HCl and rinse in EOH. SnS platelets nucleate on the tin during compound grown and have a metallic luster. The $CuGaS_2$ crystals are transparent with red color. A Ga_4SnS_{7-8} crystal was transparent and colorless. A $CuGaSn_2$ crystal was orange in color. $CuGa_3S_5$ is cubic and $CuGa_5S_8$ is sphalerite structure isometric system, tetrahedral class. (*Note:* Reference to "cubic" is the isometric system, normal class commonly call the cubic system.)
REF: Tsubaki, K & Sugiyama, K — *J Electron Mater,* 12,43(1983)

PHYSICAL PROPERTIES OF COPPER DISULFIDE, Cu_2S

Classification	Sulfide
Atomic numbers	29 & 16
Atomic weight	159.20
Melting point (°C)	1100
Boiling point (°C)	
Density (g/cm^3)	5.5—5.8
Hardness (Mohs— scratch)	2.5—3
Crystal structure (orthorhombic — normal)	(110) a-pinacoid
(isometric — normal) >91°C	(100) cube
Color (solid)	Lead grey
Cleavage (pinacoidal — indistinct)	(110)
(octahedral — poor)	(111)

COPPER SULFIDE, Cu_2S

General: Occurs in nature as the mineral chalcocite, Cu_2S and is found as a vein deposit along with other copper ore minerals. It is mined for both the copper and sulfur content.

Other than as copper ores in industry, the chemical $CuSO_4$ "Blue Vitrol" has important use in agriculture as an algicide, and additional use in chemical processing.

Technical Application: Copper sulfide, Cu_2S, doped with indium is a trinary compound semiconductor, and under evaluation for general properties and device applications.

The pure sulfides as both CuS and Cu_2S, natural and artificial minerals, have been studied for general morphology. The $CuInS_2$ trinary material in the following section is in the crystallographic tetragonal system, and under evaluation as a trinary compound semiconductor.

Etching: Soluble in single acids, and mixed acids.

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COPPER INDIUM SULFIDE ETCHANTS

CIS-0001a
ETCH NAME: Nitric acid
TYPE: Acid, dislocation
COMPOSITION:
x .... HNO_3
TIME: 3—4 min
TEMP: RT
DISCUSSION:
$CuInS_2$, (112) wafers. Grown as small single crystals with preferred (112) surface orientation. Nitric acid was used to develop dislocations on the (112)B sulfur surface, as material is a polar compound. A sulfur film is left on the surface after etching. (*Note:* Remove sulfur with sulfur disulfide, CS_2.)
REF: Thiel, F A — *J Electrochem Soc,* 129,1570(1982)

CIS-0001b
ETCH NAME: BRM
TYPE: Halogen, dislocation
COMPOSITION:
x .... 2% Br_2
x .... MeOH
TIME: 10—15 sec
TEMP: RT
DISCUSSION:
$CuInS_2$, (112) wafers. Solution used to develop dislocations on the (112)A positive CuIn polar surface.
REF: Ibid.

CIS-0001c
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME: 45 min
TEMP: RT
DISCUSSION:
$CuInS_2$ (112) wafers. Solution used to develop dislocations on the (112)A positive CuIn polar surface.
REF: Ibid.

CIS-0002
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HCl
1 .... HNO_3
1 .... H_2O
TIME: 10 sec
TEMP: RT
DISCUSSION:
$CuInS_2$ wafer. Crystals are tetragonal system. Mechanically polish wafers with diamond grit, then etch polish with the mixture shown, and rinse in water.
REF: Barradas, R T et al — *J Phys & Chem Solids,* 45,1185(1984)

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CIS-0003
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
1 .... HNO_3
3 .... HCl
DISCUSSION:
$CuInS_2$ wafers. Ingots grown by travelling heater method (THM) using starter powdered material with an indium flux in a sealed quartz ampoule. Cut wafers were mechanically polished with 0.06 μm alumina. Then degreased in TCE, rinsed in acetone, then MeOH, and etch polish with aqua regia.
REF: Hsu, J et al — *J Cryst Growth* 70,427(1984)

CIS-0004a
ETCH NAME: Nitric acid, dilute — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
1 .... HNO_3
3 .... H_2O
DISCUSSION:
$CuInS_2$, n-type wafers. Etch polish in this solution.
REF: Russak, M & Creter, C — *J Electrochem Soc,* 132,1741(1985)

CIS-0004b
ETCH NAME: — TIME:
TYPE: Acid, photo-etch polish — TEMP:
COMPOSITION:
x .... HCl
x .... HNO_3
x .... H_2O
DISCUSSION:
$CuInS_2$ n-type wafers. Solution used with intense white light to photo-etch polish surfaces.
REF: Ibid.
CIS-0005: Tenne, R P & Hodges, P — *Appl Phys Lett* 37,428(1980)
$CuInS_2$ wafers. Used solution as a polishing etch.
CIS-0006: Takeuchi, S et al — *J Phys & Chem Solids* 8,887(1985)
$CuIn_5S_8$, (111) oriented single crystal ingots grown by a Growth Freeze method. Material was n-type, and growth was (111) preferential. Wafers were cut and mechanically lapped and polished in a study of semiconducting properties.

COPPER PHOSPHO-SULFIDE, Cu_6PS_5:I/Cl/Br

General: Does not occur as a natural compound, although there are several copper sulfide minerals containing iron, bismuth, arsenic, and antimony, but not phosphorus. The structure has been referred to as the silver sulfo-germanate, argyodite, $4Ag_2S.GeS_2$ — isometric with octahedral, (111) habit, and Spinel Law twinning, e.g., 180° rotation on o(111) as bi-crystal or multiple twin lamellae. Sphalerite, ZnS, shows similar twinning lamellae, but is isometric system, tetrahedral class, not normal (cubic) class.

There is no industrial use of the compound to date, although copper sulfide minerals are important ores for both elements. There are many copper phosphate compounds in chemistry.

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Technical Application: The compound has been grown by Vapor Transport (VT) from vapor/liquid/solid (VLS) materials with halogen doping: Cl_2, Br_2, and I_2. As undoped Cu_3PS_4, crystals are transparent yellow; doped with iodine, Cu_6PS_5:I, were transparent red crystals. Electrically the material is a conductor, and has been studied for general morphology.

Etching: soluble in HNO_3 and NH_4OH.

COPPER PHOSPHO-SULFIDE ETCHANTS

CPS-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:

Cu_6PS_5:I, single crystal platelets grown by Vapor Transport (VT) with a CuI liquid flux. Crystals are transparent, red in color, forming in the isometric system, normal (cubic) class, as high temperature 43m space group. Nitric acid was used as a general etching solution.
REF: Tributsch, H & Betz, G — *J Electrochem Soc*, 131,640(1984)

CPS-0002
ETCH NAME: Ammonium hydroxide — TIME:
TYPE: Base, removal — TEMP:
COMPOSITION:
x .... NH_4OH
DISCUSSION:

Cu_6PS_5:halogens. Halogens: Cl_2, Br_2, I_2. Crystal grown by Vapor Transport (VT) between 870—900°C and above 970°C. A vapor/liquid/solid (VLS) flux was used: $PSCl_3$ (liquid); Co_2S (black powder). Cu_3PS_4 was grown as yellow, transparent crystals. Materials were conductors, and structure was referred to the natural mineral argyodite, $4Ag_2S.GeS_2$. Solution shown can be used as a removal etchant. With the flux shown, crystals of Cu_6PS_5:Cl also were grown.
REF: Fiechter, S et al — *J Cryst Growth*, 61,275(1983)

PHYSICAL PROPERTIES OF COPPER TELLURIDE, Cu_4Te_3

Classification	Telluride
Atomic numbers	29 & 43
Atomic weight	551.28
Melting point (°C)	1000
Boiling point (°C)	
Density (g/cm^3)	7.4
Hardness (Mohs — scratch)	3.5
Crystal structure (isometric — tetrahedral)	(112) tetrahedron
Color (solid)	Purple/black
Cleavage (tetrahedral)	(112)

COPPER TELLURIDE, Cu_4Te_3

General: Occurs as the natural mineral rickardite, Cu_4Te_3, and weissite, Cu_5Te_3. Both minerals occur in massive form associated with pyrite and tellurium ores in minor quantity. There is no industrial use other than as minor ores of tellurium and copper.

Technical Application: Copper telluride doped with either gallium or indium has been

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evaluated as a possible compound semiconductor of the I—VII type. Grown as a single crystal these trinary compounds show a distinctive (112) growth habit.

Etching: Variations of aqua regia.

COPPER TELLURIDE ETCHANTS

CUTE-0001
ETCH NAME: Aqua regia, variety — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
Cu_4Te_3 specimens as the natural mineral rickardite. Solution used as a surface cleaning and light removal etchant in a material study.
REF: Walker, P — mineralogy study, 1953

COPPER GALLIUM TELLURIDE ETCHANTS

CGTE-0001
ETCH NAME: Aqua regia, variety — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HCl
x .... HNO_3
DISCUSSION:
$CuGaTe_2$, single crystals used in an evaluation of cohesive energy features of tetrahedral semiconductors. Forty materials were studied.
REF: Aresti, A et al — *J Phys & Chem Solids,* 45,361(1984)

COPPER INDIUM TELLURIDE, $CuInTe_2$

General: Does not occur as a natural metallic compound, though there are other binary and trinary telluride minerals. There is no application of the compound in the metal industries.

Technical Application: Copper indium telluride has been grown as a ternary compound semiconductor, and is under development and study for its semiconducting characteristics.

Etching: Soluble in mixed acids of $HCl:HNO_3$ with or without water.

COPPER INDIUM TELLURIDE ETCHANTS

CUIT-0001a
ETCH NAME: Hydrofluoric acid, dilute — TIME:
TYPE: Acid, float-off — TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O
DISCUSSION:
$CuInTe_2$, thin films. The thin films were deposited on glass substrates by CVD. Films were removed from the glass by undercut etching of the glass — the float-off technique for removal of films from substrates and study under a transmission electron microscope (TEM).
REF: Kazmnerski, L L — *J Vac Sci Technol,* 14,769(1977)

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CUIT-0001b
ETCH NAME: Aqua regia, variety
TYPE: Acid, thinning
COMPOSITION:
1 .... HCl
1 .... HNO_3
2 .... H_2O
TIME:
TEMP: RT
RATE: 1000 Å/min
DISCUSSION:
$CuInTe_2$, thin films. Thin films were deposited on glass by CVD. Before removal from the glass, films were etch thinned in the solution shown. After float-off (CUIT-0001a) specimens were studied morphologically using an electron microscope (EM).
REF: Ibid.

CUIT-0002
ETCH NAME: Aqua regia, variety
TYPE: Acid, removal
COMPOSITION:
x .... HCl
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
$CuInTe_2$, single crystals used in an evaluation of cohesive energy features of tetrahedral semiconductors. Forty materials were studied.
REF: Aresti, A et al — *J Phys & Chem Solids*, 45,361(1984)

PHYSICAL PROPERTIES OF CORUNDUM, Al_2O_3

Classification	Oxide
Atomic numbers	13 & 8
Atomic weight	101.94
Melting point (°C)	2050
Boiling point (°C)	2250
Density (g/cm^3)	3.95—4.10
Refractive index (n =)	1.75—1.76
Hardness (Mohs — scratch)	9
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Grey/black
Cleavage (basal)	(0001)

CORUNDUM, Al_2O_3

General: The natural mineral is widely distributed and associated with chlorate type rocks, as well as limestone and dolomite. The two latter in massive amounts, such as in the chalk cliffs of Dover, England. As emery, $Al_2O_3.Fe_3O_4$, it is a major abrasive. Clear, color tinted varieties are gem stones: ruby (red); sapphire (blue), etc. It is still used as a lapping and polishing abrasive. See Aluminum Oxide, Al_2O_3, for additional discussion.

Technical Application: The natural mineral has little application in Solid State processing other than as a polishing abrasive, but the artificially pressed powder or single crystal (sapphire) blanks have major use as circuit substrates, and other high temperature ceramic applications. Also there are amorphous ruby parts artificially fabricated. See Aluminum Oxide for an expanded discussion.

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Natural corundum has been studied for many years, and was first grown as an artificial single crystal in the late 1800s by the Verneiul process for artificial rubies and sapphires.

Etching: Single acids, mixed acids, and molten fluxes.

CORUNDUM ETCHANTS

COR-0001
ETCH NAME: Metal — TIME:
TYPE: Metal, removal — TEMP:
COMPOSITION:
x .... Si
DISCUSSION:
Al_2O_3, (0001) natural corundum discs. Metallic silicon vacuum evaporated on corundum will etch the material.
REF: Reynolds, F H & Elliot, A B M — *Phil Mag*, 13,1073(1966)

COR-0002
ETCH NAME: Potassium bisulfate — TIME:
TYPE: Molten flux, removal — TEMP: 590°C
COMPOSITION:
x .... K_2SO_4, pellets
DISCUSSION:
Al_2O_3, as natural corundum. Material will dissolve in potassium bisulfate when used as a molten flux. Has been used in the metallographic study of single crystal compounds.
REF: Dana, E S & Ford, W E — *A Textbook of Mineralogy*, 4th ed, John Wiley & Sons, New York, 1950, 482

COR-0003
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid cleaning — TEMP: Hot
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
Al_2O_3, natural single crystals cut and polished en cabachon on the z-axis (0001) basal plane as star sapphires. Wash in HCl after polishing, then in H_2O for general cleaning.
REF: Walker, P — mineralogy development, 1953

PHYSICAL PROPERTIES OF CRONSTEDITE, $4FeO.2Fe_2O_3.3SiO_2.4H_2O$

Classification	Silicate
Atomic numbers	26, 14, 1, 8
Atomic weight	859
Melting point (°C)	>1000
Boiling point (°C)	
Density (g/cm^3)	3.34—3.45
Refractive index (n=)	1.80
Hardness (Mohs — scratch)	3.5
Crystal structure (monoclinic — normal)	(hk0) prism
Color (solid)	Black/brownish
Cleavage (basal — perfect)	(001)

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CRONSTEDITE, $4FeO.2Fe_2O_3.3SiO_2.4H_2O$

General: Occurs as a minor natural mineral in association with other iron ores in England and Brazil. No use in industry other than as a minor ore of iron.

Technical Application: The natural mineral has been studied in Solid State for general morphology and defects. In thin section, transmitted light is brilliant emerald-green, and the material may have application as light frequency lenses and filters.

Etching: H_2SO_4, HF.

CRONSTEDITE ETCHANTS

CRON-0001
ETCH NAME: Hydrofluoric acid, dilute — TIME:
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
x .... HF
x .... H_2O
DISCUSSION:
$4FeO.2Fe_2O_3.2SiO_2.4H_2O$, (001) cleaved wafers used in a general material study. Solution used to develop dislocations on the cleaved surfaces. Authors say their specimens were brittle, although natural material is shown to be elastic in thin section. They also referred to chronstedite as a kaolin-type mineral, e.g., kaolinite, $Al_2O_3.2SiO_2.2H_2O$.
REF: Steadman, R & Pugh, J D — *Phil Mag*, 12,969(1965)

PHYSICAL PROPERTIES OF CRISTOBALITE, SiO_2

Classification	Oxide
Atomic numbers	14 & 8
Atomic weight	~60
Melting point (°C)	>1200
Boiling point (°C)	
Density (g/cm³)	2.27
Refractive index (n =)	1.486
Hardness (Mohs — scratch)	7
Crystal structure (tetragonal — normal) alpha	(110) prism
(isometric — normal) beta	(111) octahedron
Color (solid)	White
Cleavage (cubic — poor)	(001)

CRISTOBALITE, SiO_2

General: A naturally occurring high temperature form of silica and considered as a polymer of quartz. Occurs in small white octahedrons, often twinning according to the Spinel Law. The alpha to beta forms have a transition temperature range between 195 to 275°C with initial formation temperature >1200°C. The alpha-cristobalite is tetragonal; whereas beta-cristobalite is isometric.

There is no industrial use of this form of silica as a natural product due to scarcity. See silicon dioxide, SiO_2 for major discussion.

Technical Application: There is no use of cristobalite in Solid State processing, although silicon dioxide, SiO_2, as a thin film, or its various mixtures and forms as glass (silica) have major applications.

Artificially grown cristobalite has been observed as minute crystals in quartz epitaxy

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tubes as a by-product of oxidizing other metals and metallic compounds. Both natural and artificial crystals have been studied.

Etching: HF, KF, NH_4F

CRISTOBALITE ETCHANTS

CRIS-0001
ETCH NAME: Heat
TYPE: Thermal, conversion
COMPOSITION:
x .... heat
TIME:
TEMP: 195—275°C
DISCUSSION:

SiO_2, as alpha-cristobalite carried through inversion point to beta-cristobalite on a hot-stage microscope using polarized light for observation. Authors say that transformation time was less than 0.1 sec.

REF: Krisement, O & Tromel, G — *Z Naturforsch,* 14a(7),685(1959)

CRIS-0002
ETCH NAME: Hydrofluoric acid
TYPE: Acid, preferential
COMPOSITION:
(1) x .... HF, conc.
(2) x .... HF, vapor (hot)
TIME: Minutes
TEMP: RT
DISCUSSION:

SiO_2, as natural single crystal alpha-cristobalite and beta-cristobalite used in a general study of natural SiO_2 compounds. Solutions used to polish and preferential etch specimens in a structure study.

REF: Walker, P — mineralogy study, 1952—1953

CRIS-0003
ETCH NAME:
TYPE: Thermal oxidation
COMPOSITION:
x .... air
TIME:
TEMP:
DISCUSSION:

Si, (100) wafers cut from Czochralski (CZ) ingots used in a study of re-dissolution of precipitated oxide. Material oxidized at 1000°C for 256 days. Precipitated dislocation complexes (PDCs) appeared as plate-like structures on (100) surfaces parallel to ⟨110⟩ directions. Precipitates were cristobalite. (*Note:* Crystallites of cristobalite have been observed in quartz furnace tubes as a by-product after silicon oxidation at elevated temperatures.)

REF: Shimura, F — *J Appl Phys Lett,* 39,987(1981)

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PHYSICAL PROPERTIES OF DEUTERIUM, D

Classification	Heavy hydrogen (^3H)
Atomic number	H_2 isotope
Atomic weight (protium)	1.07825
*(deuterium)	2.00147 (D_2)
(tritium)	2.01605
Melting point (°C)	−252.7 (101.42)*
Boiling point (°C)	−2254.3 (3.82)*
Density (g/cm^3)	1.11 (D_2O)*
Hardness (Mohs — scratch) solid	1—2
Crystal structure (isometric — normal)	(100) cube
Color gas/liquid	Colorless
(solid)	White
Cleavage (cubic — solid)	(001)

DEUTERIUM, D

General: Occurs in nature in all substances containing hydrogen in a ratio of about 5000:1 as normal (light) hydrogen H_2 to heavy hydrogen, ^3H or D. The latter is called deuterium and, as a transmutation particle — a deuteron. By repeated electrolysis of water, using nickel-iron electrodes, the light hydrogen off-gases and deuterium is concentrated about sixfold in the residue. This was the original source of "heavy water", D_2O, initially thought to be essential in the design of an atomic bomb. High concentrations of deuterium also can be obtained from metal processing areas where electrolytic cleaning tanks containing sodium or potassium hydroxide have been in operation for years as collected in a sludge concentrate.

Deuteron particles are used in cyclotrons and particle accelerators for bombardment producing protons, alpha particles or neutrons. In medicine, heavy water, D_2O, has been used as a tracer compound in the study of water elimination by the human body. It was shown that deuterium appeared in perspiration within hours of ingestion, but required about 30 days for complete elimination in urine.

Technical Application: Deuterium is not used in general processing and fabrication in Solid State, though it has been used in chemical processing as a tracer element. Many metals and metallic compounds are now being hydrogenated for special purpose applications as thin films or in the development of hydrogen storage batteries — a-Si:H. a-Ge:H, a-SiN:H using normal light hydrogen.

Deuterium and the other isotopes of hydrogen shown under the Physical Properties section have applications in atomic physics, radiation chemistry, and in irradiation studies. Several of their compounds are shown here in this section on deuterium, such as TiD_2, ScD_2, and $ErTi_2$:D_2.

Etching: See parent metal element for applicable chemicals.

DEUTERIDE ETCHANTS

TID-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
TiD_2 as thin films. Molybdenum blanks were used as substrates for metallization with

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titanium and scandium. The materials were furnace treated with heavy hydrogen, ^3H, to form deuterides, $ErTi_2$ was also deuterided.
REF: Adachi, T et al — *J Vac Sci Technol,* 19(1),119(1981)

SCD-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
ScD_2 as thin films. See TID-0001 for discussion.
REF: Ibid.

TIME:
TEMP:

DEU-0001
ETCH NAME: Deutron
TYPE: Particle, transmutation
COMPOSITION:
x .... deutrons
DISCUSSION:
Deutron particles used in cyclotrons to produce protons, alpha particles, and neutrons. Used in the study of transmutation of elements and materials.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry,* 3rd ed, D Van Nostrand, New York, 1947, 77 & 300

TEMP:

TRIT-0001
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... H_2SO_4
1 .... HCl
1 .... H_2O
DISCUSSION:
SST tubing used in atomic reactors for handling tritium — a heavy isotope of hydrogen. Internal bore of tubing etch cleaned in this type of solution to remove burrs and draw marks for a highly polished internal surface to prevent spontaneous ignition of tritium during flow passage. After etching, rinse heavily with water, then with MeOH, and use the heat of a torch flame to heat and dry tube lengths. See FE-0024 for general tube cleaning.
REF: Mills, T — personal communication, 1972

TIME:
TEMP: RT

PHYSICAL PROPERTIES OF DIAMOND, C

Classification	Nonmetal (carbon)
Atomic number	6 (carbon/graphite)
Atomic weight	12 (carbon/graphite)
Melting point (°C)	1900 (to carbon)
Boiling point (°C)	2000 (to CO_2 — in air)
Density (g/cm^3)	3.516—3.525
Refractive index (n =)	2.4195 (1.3—1.4)
Dielectric constant (e =)	5.68—5.70
Absorption constant (cm^{-1}):	

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Wavelength (microns) — 0.405	0.12 (type II xtls)
(microns) — 0.226	14.8 (type II xtls)
Absorption band (microns — 0.4 eV)	4.8
Volume expansion ($\times 10^{-6}$) 28—105°C	4.36
Hole mobility (eV)	45
Activation energy (eV)	5+
Electron mobility (cm $sec^{-1}/V\ cm^{-1}$)	800
Carrier lifetime ($\times 10^{-9}$ sec)	9
Energy gap (eV)	7 (5.6)
Lattice constant (angstroms)	3.567
Hardness (Mohs — scratch)	10
Crystal structure (isometric — normal)	(111) octahedron
Color (solid)	Colorless (+ pastel hues)
Cleavage (octahedral — perfect)	(111)

DIAMOND, C

General: Occurs as a native element as the high pressure form of carbon or graphite. Diamond crystal structure is the atypical octahedron, o(111), which is called the "diamond" form. Both of the elemental semiconductors, silicon and germanium, are called "diamond" crystallographic structure. The elements sulfur, carbon, and selenium are physically and chemically related to the transition class of metals, such as carbon, manganese, molybdenum, etc. Diamond and fluorite, CaF_2, both have (111) cleavage, rather than cubic (100) as is common to the isometric — normal class. Because of its high refractive index, producing high birefringence, it is the most prized gem stone in the world and is found as transparent stones in various colors, with the clear, blue-white being "top-water"; yellow most common; but also green, orange, brown, and black (high carbon content, and called "bort"), and many diamonds have carbon flecks internally. Diamonds are found in "blue ground" pipes in Africa; one occurrence in the U.S.; in stream gravel in Brazil, Southeast Asia, India, and the northern mid-continental U.S. The DeBeers syndicate controls diamond production and sales throughout the world.

Diamonds have been grown artificially using a high pressure trigon system. At high temperature, in oxygen, diamond will burn to CO_2; in vacuum at 1900°C it will convert to graphite. "Industrial diamonds" are those diamonds that do not meet gem-grade quality, and are primarily used as finely powdered lapping and polishing abrasives either in an oil paste, in a solvent slurry, embedded in metal, rubber, or plastics, and as a "diamond" blade for cutting. It is the hardest known element or compound and is used in determining hardness of minerals and other materials in the Mohs hardness scale of 1—10, with diamond H = 10. Using the Mohs-Wooddell scale: Diamond H = 42.5, which is the more accurate. Some of the artificial carbides and borides approach diamond in hardness (H = 9+), and the Knoop hardness scale (kfg/mm^2) using the pressure of a shaped diamond stylus gives an even more accurate measure of hardness.

Technical Application: Oriented single crystal diamonds are used as mounting substrates in semiconductor device assembly as both heat sinks and active elements in the assembly structure.

Diamond abrasive in an oil paste is still a major lapping and polishing medium for all metals and metallic compounds. As diamond grit impregnated metal or resinoid blades, saw blades have been in use for cutting rocks and minerals since the 1800s, and are the primary method of cutting Solid State ingots as wafers, and the dicing of wafers as discrete devices, as well as the cutting of ceramics as circuit or dielectric substrates. As diamond embedded blocks and other shapes in rubber, metals, plastics, etc., used for general lapping, honing, polishing, and similar applications. As a single crystal material it is fabricated for optoelectric device applications, and is under study for various reactions, such as irradiation-produced

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color centers, similar to those observed in NaCl; for its brilliant phosphorescence with applied electrical discharge under vacuum; and reactions in a similar manner in ultraviolet light.

Doped with boron, it is an n-type semiconductor, capable of operating as a diode above 500°C like both SiC and BN. And carbon thin films are being deposited, then converted by annealing to a diamond-like-carbon (DLC) structure with possible applications as both an electrically active thin film or surface passivator. Such DLC structure also is referred to as an i-C structure. In this book there are three sections: (1) Carbon, C-; (2) Diamond, D-; and Graphite, GR-, as the basic types of this material.

Etching: Insoluble in acids and alkalies. Soluble by dry chemical etching (DCE); and in molten fluxes.

DIAMOND ETCHANTS

D-0001
ETCH NAME:
TYPE: Ionized gas, removal
COMPOSITION:
x .... Xe^+
x .... NO_2, fumes
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:

D, (111) wafers used to fabricate photoelectric devices. Degrease and clean surfaces with water and alcohol prior to photo resist patterning. Gases shown used to etch a grating structure in the diamond surface by ion beam assisted etching (IBAE), which is a form of reactive ion etching (RIE).
REF: Efemow, N N et al — *J Vac Sci Technol,* B3,416(1985)

D-0002
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HF, conc.
TIME: xx h
TEMP: Hot
DISCUSSION:

D, (111) wafers used in irradiation damage studies. HF used to clean surfaces prior to irradiation, follow with through washing in water after etching.
REF: Primak, W et al — *Phys Rev,* 103,1184(1956)

D-0003
ETCH NAME: Boron
TYPE: Metal, implantation
COMPOSITION:
x .... B
TIME:
TEMP:
DISCUSSION:

D, (111) wafers cut 6°-off toward (110) used in a study of diamond semiconducting properties. Boron was ion implanted for a 5×10^{15} concentration at 200 KeV for maximum amorphous implantation (I^2) structure.
REF: Maby, F W et al — *J Appl Phys Lett,* 39,157(1981)

D-0004
ETCH NAME:
TYPE: Electron, crystallization
COMPOSITION:
x .... laser
TIME:
TEMP:

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DISCUSSION:

D, crystallized from thin film carbon deposits by laser annealing. The resulting crystallization is called diamond-like-carbon (DLC) structure and shown to be high in hydrogen. Tensile cracking was observed with greatest stress at crystallite edges. Compressive stress causes inward bulging of the crystallites.

REF: Nir, D — *Thin Solid Films*, 112,41(1984)

D-0005

ETCH NAME: Tungsten — TIME:

TYPE: Metal, preferential — TEMP: 1200—1500°C

COMPOSITION:

x .... W

DISCUSSION:

D, (111) platelets used in a study of plasticity. Tungsten metal used to etch diamond surfaces at elevated temperature.

REF: Evans, T & Wild, R K — *Phil Mag*, 12,479(1965)

D-0006

ETCH NAME: Oxygen (air) — TIME:

TYPE: Gas, preferential — TEMP: 1000°C, nominal

COMPOSITION:

x .... O_2, moist air

DISCUSSION:

D, (100), (111), and (110) oriented wafers used in a defect development study. Heating in moist air will develop structure, but will not develop structure in O_2/H_2O or O_2/N_2 pure atmospheres. Below 1000°C trigon pits show a positive (+) orientation; above 1000°C a negative (−) orientation. Above 1000°C pits tend to be more hexagonal to rounded in shape rather than sharply triangular. Pits observed on all orientations below 1000°C, but not on (100) above that temperature.

REF: Evans, P R & Sauter, T — *Contemp Phys*, 2,217(1961)

D-0007

ETCH NAME: Abrasion — TIME:

TYPE: Abrasive, hardness — TEMP:

COMPOSITION:

x .... SiC

DISCUSSION:

D, (111) specimens used in a study of the relative hardness of crystallographic directions in the (111) surface. There are eight (111) octahedral exterior surface planes; four bulk (100) cubic planes at 45°; and two dodecahedral planes at 90° in each (111) surface. Author says all planes are resistant to abrasion. (*Note:* Hardness differences can be observed using the geologic Sclerometer test — draw a diamond stylus across a single crystal oriented surface in a known bulk plane direction under a specified load to determine directional bulk plane hardness. This is a standard geological mineral test.)

REF: Wilks, E M — *Phil Mag*, 6,701(1961)

D-0010

ETCH NAME: Soap — TIME: 5 min, nominal

TYPE: Detergent, cleaning — TEMP: Hot

COMPOSITION:

x .... Joy soap

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DISCUSSION:

D, (111) oriented small parts used as stand-offs in device assembly. Units as squares or rectangles, and others with an angled surface section. Prior to metallization by evaporation or plating (Au/Cr or Au/Ni, respectively) as thin films, parts were degreased in hot TCE vapors, then scrubbed and soaked in a soap solution, then followed by heavy DI water washing, and N_2 blow dry. Some parts were photo resist patterned after cleaning, and used as both active and passive device structures.

REF: Fahr, F & Walker, P — personal application, 1980/1984

D-0008

ETCH NAME: Methane TIME:

TYPE: Gas, growth TEMP:

COMPOSITION:

x .... CH_4

DISCUSSION:

i-C, initially deposited as carbon from methane on glass predeposited with thin films of either gold or aluminum. Deposition of carbon was by RF plasma and films were annealed to develop a diamond-like-carbon (DLC) structure, which is also called the i-C structure. The carbon films were then evaporated with additional metals and patterns developed by standard photolithography to produce MIM (metal-insulator-metal) device test structures for evaluation of dielectric properties of the i-C films.

REF: Lamb, J D & Woolam, J A — *J Appl Phys,* 57,5420(1985)

D-0009: Szmidt, J et al — *Thin Solid Films,* 110,7(1983)

D, thin films deposited by reactive pulse plasma of graphite onto silicon, (111) and (110) substrates. Used in a comparative study of diamond and boron nitride as surface coating dielectrics.

D-0011

ETCH NAME: TIME:

TYPE: Thermal, preferential TEMP:

COMPOSITION:

x .... heat

DISCUSSION:

D, (111) single crystal specimens. A study of the etching of trigon pits on diamond surfaces.

REF: Patel, A R & Patel, S M — *Br J Appl Phys,* 1,1445(1968)

D-0012: Mitchell, E W J — *J Phys Chem Solids,* 8,444(1959)

D, specimen. A review of work done on diamonds.

D-0013

ETCH NAME: TIME:

TYPE: Pressure, fabrication TEMP:

COMPOSITION:

x .... pressure

DISCUSSION:

D, fabricated as artificial diamond. A Pressure Trigon system consisting of three large pressure cylinders at 60° aimed at a central point capable of pressures in excess of 100,000 psi. Place a small carbon sample at the center point on a holding base and apply pressure to structurally condense the carbon to form a diamond.

REF: *Sci Am,* (May 1978)

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D-0014
ETCH NAME: TIME:
TYPE: Electroless, plating TEMP:
COMPOSITION:
x .... nickel
DISCUSSION:
D, as polycrystalline 4 μm sized particles embedded in nickel. Material fabricated by the Shock Sinter Method (SSM). Plated specimen discs used in a study of possible catalytic face orientation reaction of diamonds during electroless nickel plating with a phosphate type bath.
REF: Feldstein, N & Lancsek, T S — *J Electrochem Soc*, 131,3026(1985)
D-0015: Cowan, et al — U.S. Patent 3,401,019
Reference for Shock Sinter Method of fabricating polycrystalline diamonds.

D-0016
ETCH NAME: Iodine TIME:
TYPE: Halogen, passivation TEMP: Elevated
COMPOSITION:
x .... I_2
x .... H_2O/MeOH
DISCUSSION:
D, as single crystal elements. Iodine washed onto surfaces as a surface passivation with some adsorption. This acts to reduce chemical attack by acids, specifically, H_3PO_4.
REF:

DIELECTRICS, M_xO or M_xN

General: Many of the natural oxide or silicate minerals can be considered as dielectric compounds, and several of these natural minerals or their artificial counterparts are so used. Quartz, SiO_2, and corundum, Al_2O_3 are representative of natural oxide dielectrics; zircon, $ZrSiO_4$, as a silicate; sellaite, MgF_2, as a fluoride dielectric, as well as the natural halides. The mineral rutile, TiO_2, usually as transparent, clear artificial titanium dioxide, is a major dielectric compound used in fabricating microelectronic circuits, as well as being used as the artificial gem stone "titania".

In the general metal industries, the majority of the natural minerals are used as ores for their metal content, rather than as dielectrics, though several are used as surface coatings for passivation, corrosion resistance, etc. All of the nitrides are artificial, and the nitridization of metal surfaces with hot nitrogen gas furnace treatment has long been used for hardening and corrosion resistance of surfaces and metal nitrides show dielectric properties just as do the oxides and silicates.

Technical Application: All of the minerals mentioned, nitrides and artificial compounds specifically designed for dielectric levels are used in Solid State device processing. They may be as discrete resistors or capacitors or as thin film coatings fabricated as planar surface elements on a device or on a circuit substrate.

As the majority of dielectric materials also have electrical and light frequency characteristics, they are used as filter elements, as well as capacitors or resistors, and there are ferrite materials used as resistors in microelectronic fabrication that are specifically designed for microwave frequency levels.

All of the dielectric materials may be fabricated as pressed powder blanks (crystalline), as deposited amorphous thin films, as single crystal films, or as hydrogenated thin films, such as colloidal c-SiN:H, etc. TiO_2, as an example, is supplied as a pressed powder blank or an oriented single crystal blank — parallel or normal to the c-axis, each with different dielectric constant values.

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The dielectric materials are not listed here but appear following their parent metals, such as aluminum oxide, after aluminum, etc.

Etching: See individual compounds.

PHYSICAL PROPERTIES OF DYSPROSIUM, Dy

Classification	Lanthanide
Atomic number	66
Atomic weight	162.50
Melting point (°C)	1407
Boiling point (°C)	2600
Density (g/cm^3)	8.54
Thermal conductance $(cal/sec)(cm^2)(°C/cm)$	0.024
Specific heat (cal/g) 25°C	0.041
Latent heat of fusion (cal/g)	25.2
Heat of vaporization (k-cal/g-atom)	67
Atomic volume (W/D)	19.0
1st ionization energy (k-cal/g-mole)	157
1st ionization potential (eV)	6.8
Covalent radius (angstroms)	1.56
Ionic radius (angstroms)	0.92 (Dy^{+3})
Electrical resistivity (micro ohms-cm) 298 K	92.6
Compressibility ($cm^2/kg \times 10^{-6}$)	2.55
Magnetic moment (Bohr magnetons)	10.64
Tensile strength (psi)	35,700
Yield strength (psi)	32,600
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	99,800
Transformation temperature (°C)	1384
Coefficient of linear thermal expansion ($\times 10^{-6}$/cm/cm/°C) 25°C	8.6
Cross section (barns)	940
Hardness (Mohs — scratch)	3—4
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Grey
Cleavage (basal)	(0001)

DYSPROSIUM: Dy

General: Does not occur as a native element. It is a member of the rare earth yttrium group in the lanthanide series, and is mainly found in pegmatites in minerals such as gadolinite and fergusonite with other rare earths. The metal salts are noted for their brilliant yellow color, but there is little use of the metal in industry due to scarcity.

Technical Application: There has been no use of the metal in Solid State processing, to date, though it has been grown as a single crystal for general morphological study. Spheres have been used to evaluate magnetic properties, and material defects by etching.

Etching: Mixed acids with HNO_3 + HAc/HCl/HF/H_2O_2.

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DYSPROSIUM ETCHANTS

DY-0001
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
4 .... HNO_3
6 .... HAc
DISCUSSION:
Dy, as single crystal spheres used in a study of magnetic properties. Solution shown used to develop defects and grain structure.
REF: Behrendt, D R et al — *Phys, Rev,* 109,1544(1958)
DY-0002: Bond, W L — *Rev Sci Instr,* 22,344(1951)
Reference for method of making single crystal spheres.
DY-0003: Bond, W L — *Rev Sci Instr,* 25,410(1954)
Dy, specimens. Reference for crystal structure of the material, and other physical data.

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ELECTRIDE, $C_xH_yO_zM$

General: A new class of crystalline materials called "Electrides" has been developed from original development of alkalides. It is a cross between a metal and semiconductor fabricated from an organic solvent molecule of cylindrical or rope-like structure enclosing an alkali cation in a cavity. Initial development required fabrication below −20°C, but a new solvent has produced stable compounds up to 45°C. The compounds are highly reactive and can spontaneously disintegrate, but single crystals of several millimeters in size have been grown by special vacuum evaporation and drying techniques.

The compounds have shown optical, opto-electric (including infrared), and magnetic properties similar to those of Solid State semiconductors and, with further stability development, may well lead to a new class of semiconductor compounds. Some work with other organic semiconductors also is included.

Technical Application: None at present.

Etching: N/A at present.

ELECTRIDE ETCHANTS

ETD-0001
ETCH NAME: TIME:
TYPE: TEMP:
COMPOSITION:
DISCUSSION:

Electride, $C_xH_yO_zM$, where M = Li, Na, P, K, Rb, Ce, the alkali metals. An alkali anion, such as potassium is enclosed in the cavity of a cylindrical or rope-like solvent molecule structure, and shows possible semiconducting type properties. These compounds are a cross between metals and semiconductors. Vary in color from black to dark blue.
REF: Dye, J L — *Sci Am*, (Sept 1987), 66

ORG-0002
ETCH NAME: TIME:
TYPE: Pressure, forming TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:

$C_{14}H_{10}$, as single crystal anthracene were grown and evaluated as an organic semiconductor. The material contains three benzene rings, and can be a derivative from both petroleum and coal.
REF: Matte, H & Pick, H — *Z Physik*, 134,566(1953)

ORG-0003
ETCH NAME: TIME:
TYPE: Pressure, forming TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:

$C_{10}H_3$ as single crystal naphthalene were grown and evaluated as an organic semiconductor. The material contains two benzene rings, and can be a derivative of petroleum and coal.
REF: Pick, H & Wissman, W — *Z Physik*, 6,959(1955)

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ORG-0001
ETCH NAME: TIME:
TYPE: Pressure, forming TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:
Atomatic substances, such as derivatives from petroleum and coal fabricated as single crystals, are predicted to have semiconducting properties.
REF: Many, A et al — *J Chem Phys,* 23,1733L(1955)

EPOXY & POLYIMIDE

General: All plastics, epoxies, and polyimides are artificial compounds formed by the polymerization of simple hydrocarbons and their derivatives. Epoxies are liquid paste formulations as a singular compound that is self-hardening at room temperature or as an "A" and "B" component, proportionally mixed when ready for use, and both types oven cured. The epoxy compounds, alone, are nonconductive sealing compounds used for mounting parts on substrates or for sealing packages. As a loaded-epoxy — metal powder additives — they are conductive pastes used in the electronic and Solid State industries for the assembly of devices and parts. Silver epoxy, Ag-epoxy, has high electrical conductivity and is widely used, although gold, aluminum and copper are also available. As all epoxies can slowly self-harden at room temperature, they are often refrigerated with only the quantity to be used for a specific assembly mixed at room temperature when ready to be used.

Some mixtures have a working life of 4 to 8 h, once mixed, while others may set in 5—10 sec. Both epoxies and polyimides are air oven cured between 100—150°C for 20 to 50 min. Some polyimides cure up to 200°C, and 250—300°C capability is under development.

Storage-life is from 6 months to 1 or 2 years, even 3 years at room temperature, and some epoxies have still been useful after 3 years. Both epoxy and polyimide can be refrigerated at +40°C, and some are kept frozen from 0 to −40°C. They are often shipped from the supplier in dry ice (solid CO_2 at −78°C). Refrigerating extends working-life and shelf-life, even though they are still listed for 6 months to 1 year usability.

There is no physical contact danger with most epoxies and polyimides, but there can be some processing problems. If overcured, particles may flake. Where silicon diodes were mounted under nitrogen in a glass package, with time, silver epoxy dried and flaked causing device contact failure, such that the use of epoxies and polyimides are not recommended for high reliability type assemblies. Where silver epoxy is used and the mounting substrate then put through an oxygen RF plasma cleaner system, the epoxy will turn coal-black on the surface . . . a surface silver oxide is formed. It is usually insufficient to affect electrical contact integrity on test samples, but such discoloration often is not acceptable for a finished product. The black oxide can be removed by rinsing assemblies in ammonium hydroxide.

Technical Application: Both unloaded and loaded epoxies and polyimides are used in Solid State devices assemblies for electrical testing. Discrete semiconductor devices, resistors, capacitors, etc. are mounted on circuit substrates with a small dot of epoxy, or for package sealing, to include a pressure extruded package.

Where there is an epoxy mounted device failure under test, the device and epoxy can be removed and replaced by heat-charring the epoxy (heat to about 200°C), then scraping away the device/epoxy without affecting other components of the circuit. There is equipment available for this purpose . . . it consists of a hot stage, a jet of hot nitrogen, and a metal tong for scraping. For complete removal and cleaning of a circuit substrate, acid etching can be used.

Etching: Mixed acids or heat.

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EPOXY ETCHANTS

GOLD EPOXY

EPAU-0001a
ETCH NAME:
TYPE: Acid, removal
TIME: 1—3 min
TEMP: RT
COMPOSITION:
30 ml .... HNO_3
10 ml .... HCl
100 ml .... H_2O
DISCUSSION:
Au, spherulitic particles in an epoxy matrix as a contact paste, such as Epo-Tech #81. Used as an electrical contact in device assembly. Where parts are unaffected or for general removal, the etchant shown has been used for removal and cleaning. Water content was variable, depending upon desired soak time.
REF: Walker, P — personal development/application, 1981

EPAU-0001b
ETCH NAME: Heat
TYPE: Thermal, removal
TIME:
TEMP: 300—400°C
COMPOSITION:
x .... heat
DISCUSSION:
Au, pellets in an epoxy matrix used as an electrical contact paste, such as Epo-Tech #81. Heat part until epoxy carbonizes (chars) and then scrape surface to remove remaining char. See Carbon section for specific etchants.
REF: Ibid.

SILVER EPOXY

EPAG-0001a
ETCH NAME:
TYPE: Acid, removal
TIME: 1—3 min
TEMP: RT
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
Ag, pellets in an epoxy matrix used as an electrical contact paste, such as Ablestik #519. Widely used in assembly of semiconductor devices for electrical test evaluation and in package assembly. Solution used to etch remove silver epoxy.
REF: Walker, P — personal development/application, 1980

EPAG-0001b
ETCH NAME: Heat
TYPE: Thermal, removal
TIME:
TEMP: 300—400°C
COMPOSITION:
x .... heat
DISCUSSION:
Ag, pellets in an epoxy matrix used as an electrical contact paste in device and parts

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assembly for test evaluation or in a final packaging of units. Heat part until epoxy carbonizes, then scrape surface for removal.
REF: Ibid.

ALUMINUM EPOXY

EPAL-0001
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot
DISCUSSION:

Al, pellets in an epoxy matrix or boron doped. Used with n-type silicon solar cells. Can be used as a contact paste on aluminum where #62 solder is used (180°C m.p.). Ti doped epoxy used for p-type silicon. (*Note:* Solution is a general removal solution for plastics.)
REF: Brochure: Electroscience Lab, NJ, 1983

PHYSICAL PROPERTIES OF ERBIUM, Er

Classification	Lanthanide
Atomic number	68
Atomic weight	167.28
Melting point (°C)	1497
Boiling point (°C)	2900
Density (g/cm^3)	9.05
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.023
Specific heat (cal/g) 25°C	0.040
Heat of fusion (k-cal/g-atom)	4.1
Latent heat of fusion (cal/g/°C)	24.5
Heat of vaporization (k-cal/g-atom)	67
Atomic volume (W/D)	18.1
Covalent radius (angstroms)	1.57
Ionic radius (angstroms)	0.89 (Er^{+3})
Electrical resistivity (micro ohms-cm) 298 K	86.0 (107) (10^7)
Coefficient of thermal linear expansion ($\times 10^{-6}$ cm/cm/°C) 25°C	9.2
Compressibility ($cm^2kg \times 10^{-6}$)	2.39
Cross section (barns)	166
Magnetic moment (Bohr magnetons)	9.5
Tensile strength (psi)	42,400
Yield strength (psi)	38,700
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	44,100
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Dark grey
Cleavage (basal)	(0001)

ERBIUM, Er

General: Does not occur as a native element. It is a member of the rare earth yttrium group in the lanthanide series (elements 63—71). Most rare earths are found in acidic pegmatite dikes: the mineral gadolinite, for the yttrium group; monazite, for the cerium group; or allinite, for both groups, e.g., cerium group includes elements 57—63. All of the rare earth elements are considered quite active metals similar to alkalines: they burn in air

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to their oxides; the oxides dissolve in water to hydroxides with hydrogen evolution; and their salts are brilliantly colored, often yellow. As erbium is one of the rarer rare earths, it has found little use in industry.

Technical Application: There has been only minor use in Solid State processing, to date. It has been grown as a single crystal in a general study of the growth of rare earth elements with thermal etching used to develop defects and structure. It also has been deposited by RF (magnetron) sputter and CVD as a thin film on silicon with conversion to a silicide: ErSi, Er_2Si, and $ErSi_2$ for evaluation as a blocking layer in device construction. As an additive element, it has been used in the growth of artificial garnets with possible device applications.

Etching: Mixed acids HF:HNO_3; HF:H_2O_2, etc. Thermal heat treatment.

ERBIUM ETCHANTS

ER-0001
ETCH NAME: Heat — TIME:
TYPE: Thermal, preferential — TEMP:
COMPOSITION:
x .... heat
DISCUSSION:
Er, single crystal specimens. A growth method study of rare earth elements. After crystal growth, annealing developed defects, low angle grain boundaries, and other structure. Additional metals studied were dysprosium, gadolinium, holmium, thulium, terbium, and yttrium.
REF: Nigh, H E — *J Appl Phys,* 34,3323(1963)

ER-0002
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
Er, as an evaporated thin film with Si on (110) GaAs wafers Si doped n-type used in a study of ion beam etching. See ERSI-0001 for heat formation of the silicide, under Silicides. Also GAS-0247.
REF: Wu, C S et al — *J Electrochem Soc,* 132,918(1985)

ERBIUM DIHYDRIDE ETCHANTS

ERH-0001
ETCH NAME: — TIME:
TYPE: Acid, Float-off — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
ErH_2 and ErH_3 formed by epitaxy growth after evaporation of erbium on NaCl substrates. In hydrogen at 298 K (RT) material was poly-ErH_2; at 488 K using different NaCl substrate surface orientations: (1) ErH_2 (100) on (100) NaCl; (2) ErH_3 (100) on (100), (110) and (111) NaCl. Heating the dihydride in H_2 will convert from the isometric-normal (cubic) (100) fcc thin film orientation to hexagonal-normal (0001) hcp ErH_3 structure (trihydride). Presence of H_2 in NaCl surfaces influences dihydride growth. The (100) NaCl substrates were cleaved;

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whereas the (110) and (111) substrates were cut and polished. Both substrate polishing before Er metallization and float-off of the hydride compounds for TEM study can be done with water.
REF: Rahman Khan, M S — *Thin Solid Films,* 113,207(1984)

ETCHING

General: Etching is the dissolutionment or dissolving of any material by any medium: liquid, gas or solid. In chemistry, water (H_2O) is considered the universal solvent as it will dissolve all natural minerals with time to the state of a water soluble salt.

Salt itself can be an etching solution and, as brine (salt water), a major solvent of water soluble compounds as reflected by the ocean waters of the world. Subsurface ground waters can contain elements, such as sulfur, iron, or silica (siliceous water) and, as such hot waters percolate up through rock fissures and strata, they become mineral formers.

In nature, not only are all minerals formed from solution, but are often altered after forming by the action of gases and liquids. As atmospheric action, this process is called weathering in geology or oxidation in chemistry and material processing. As oxidation, iron to iron oxides (rust); as sulfurization, the green verdigris (copper sulfate) that appears on copper. Corrosion is another term applied to atmospheric weathering, particularly in metal and alloy evaluations, which are subjected to seacoast environments (salt air) as well as being submerged in salt water. They also are furnace evaluated under various hot gas conditions, all for corrosion effects and chemical stability. Smog has been in existence for centuries wherever man has built a city or established an industry, such as smoke from hibachi cooking fires in Japan, peat smoke in the British Isles, or exhaust smoke from the smelting of metal ores . . . most open-hearth operations are no longer in existence due to such pollution.

Needless to say, the controlled cleaning and etching of materials is the subject of this book. Acids, alkalies, alcohols, solvents, solid metals, or compounds are all involved, and certain names have been established as references for different applications. Wet chemical etching (WCE), for the use of liquid chemicals; dry chemical etching (DCE), for the use of ionized gases; electrolytic etching (EE), where electric current is included; or molten flux etching (MFE), using liquified metals or chemical compounds at elevated temperature, are the four main divisions. There are other primary etching methods, and many subcategories beyond these four, such as the difference between a molecular and ionized gas, the use of pressure, only, or the use of vacuum, etc. This section has been assembled where the referenced articles are general in nature, or the reference may be shown as "N/A" due to common usage.

Technical Application: See specific metals and metallic compounds by individual names for additional detailed solutions and their applications.

Etching: Generalized. See individual elements and compounds for specific solutions.

ETCHING ETCHANTS

DIRECT PRESSURE ETCHING (DPE)

PRE-0001
ETCH NAME: Pressure
TYPE: Pressure, forming
TIME:
TEMP: RT to molten
COMPOSITION:
x .... pressure
DISCUSSION:
Direct pressure can be an etching agent, though more often as a forming vehicle. In furnace reduction of metal ores, the hot, liquid metal is extracted at atmospheric pressure,

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and poured as a raw ingot called pigs in the metal industry. Subsequent alloys and parts are re-melted as mixtures, and can be poured into forms for rough shape with final lathe grinding/cutting to shape. Such molds often include pressure as part of the shaping technique. Some oxides, such as ruby, are directly hot formed from a melt in pressurized molds as rods, sheet, etc. Pressure extrusion — metal through diamond hole-dies (wire) — through heated rollers (metal/glass sheet) — into a form (plastic packages, lamp shades, etc.). This may include vacuum forming such as heating a plastic sheet, then pulling a light vacuum to draw the material to a desired shape (TV modules, tote boxes, etc.). It may be as direct pressure molding, such as in the compaction of powders (medical pills, metal or plastic parts), and can include heat to melt the material during forming. Extrusion molding is used to form a plastic compound around a device or assembly as a package.

Pressure figures on certain compounds, such as the micas, are obtained by striking the surface. On micas this produces a six-rayed percussion figure on an (0001) basal plane surface. Meteoric iron surfaces have classified structure developed by a combination of heat and pressure during passage through the atmosphere.

Single crystals are subjected to increasingly high pressure in Solid State study of high pressure crystallographic structures — silicon has at least six such crystallographic structures — irons and steels have alpha, beta and delta phase structures — ice is normally hexagonal system, but has a high pressure transition form that is isometric (cubic) system, and many other metals and compounds, both natural and artificial, have similar transition pressures/temperatures with an alteration of the atomic lattice to that of another crystal system. In geology and physics, pressures on the order of 300,000 atm are used on rocks in the study of magma formation. In Solid State, liquified sodium chloride, NaCl, has been pressurized between two glass plates in a material study, and many ferrite compounds are similarly pressure studied. Carbon has been converted to diamond by direct pressure only.
REF: See individual metals and compounds for specific applications.

DRY CHEMICAL ETCHING (DCE)

DCE-0001
ETCH NAME: RF plasma
TYPE: Ionized gas, cleaning/defect
COMPOSITION:
x .... CF_4
x .... O_2 (5%)

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:

Gas, ionized. As singular or mixed gases applied by an RF or DC plasma to effect etching action for cleaning, general preferential etching or surface structuring. The mixture shown has general usage, and there are several others with specific design applications.

Argon, as Ar^+ ion cleaning, is a fairly standard practice before sputter metallization, alloy, or metallic compound deposition. Most vacuum sputter systems have one to four target locations with one location used for argon ion cleaning. Specimens are placed on a rotating platen below the targets, Ar^+ ion cleaned, then the platen rotated beneath sputter targets for metal or compound deposition. These systems may include a magnet on targets, and are then called RF magnetron sputter systems.

Where a gas is reactive, such as Cl^+ or BCl_3, the method is called reactive ion etching (RIE), and there are other acronyms for similar specialized systems. The mixture shown can be classified in this category.

RF plasma cleaning systems using N^+ or O^+ ions are widely used in Solid State material

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processing, such as for surface cleaning of semiconductor wafers, or their substrate circuit assemblies. This form of cleaning removes organic contamination from surfaces, and has been used for etch removal of germanium thin films.

Ion milling also uses an RF plasma of argon. In this case, the vacuum system has a tillable and/or rotatable copper plate on which a substrate is waxed down with a low vapor pressure wax, such as Apiezon M, and a controlled jet of ionized argon used to etch pattern the thin film metallization for a circuit substrate, or similar pattern etch a device structure on a wafer. Ion bombardment is a general term for similar action, as is irradiation. The latter referring to both gas ions (H^+, He^+, Xe^+, Ne^+, N^+, O^+, etc.) and ionized particles: protons, neutrons, deutrons, electrons, etc. All such etching is done under vacuum conditions, though electron irradiation can be done with an electron microscope (EM), or transmission electron microscope (TEM).

An allied operation is ion implantation, I^2, where ionized gases are implanted into a semiconductor wafer to form p-n junctions, or p^+ and n^+ layers, such as in forming semi-insulated structures (SI). Both gallium arsenide, as GaAs:Cr, (100) (SI), and indium phosphide, InP:Fe (100) (SI) wafers, as examples.

All ionized gases can produce sub-surface damage in materials or thin films and, as irradiation, many metals and metallic compounds have been studied for such effects. This includes effects on thin film adhesion, amorphatization, and high reliability radiation testing with Van der Graaf or Triga facilities. Dry chemical etching (DCE) is strictly the use of ionized gases, not gases used in their molecular state. The latter are included here in this text as a subsection of wet chemical etching (WCE).

REF: Bierlein, T K & Mastel, B — *Rev Sci Instrum*, 30,832(1959)

REF: See individual metals/compounds for specific applications.

ELECTROLYTIC ETCHING, EE

EE-0001

ETCH NAME: Electrolytic etching
TYPE: Electrolytic, polish
COMPOSITION:
(1) x .... acids/salts
(2) x .... alkalies
(3) x .... alcohol

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

Electrolytic etching. Any liquid solution used with an electric current applied between the positive (+) anode and negative (−) cathode to effect anodic etching action where the part being processed is the anode. Although cathodic etching is referred to in the literature, as such, it is a deplating or film removal type action, not true etching of a bulk part. Switching from anode-to-cathode is done in some etching sequences, as in growing a hydrated oxide on a metal surface such as silicon. The power applied varies with the type material, and metals usually are in the milliampere range; whereas with oxides, nitrides, and silicates, effectively, the insulator materials require amperage levels of current. In electrolytic etching, both an ampere and voltage level are used and should be shown, although very often only the amperes are shown. Many industrial metals and alloys are best electrolytically etched, but most of the Solid State semiconductor type materials use wet chemical etching. Electrolytic etching may include the use of molecular gas bubbled through a solution, often used as a jet etch system.

Metal plating from solution is another method of using electrical current applied to a liquid mixture containing a metal salt, such as gold, nickel, copper or chromium sulfides, chlorides, cyanides, etc. This is not a plating book, per se, such that only a few plating

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systems are shown where they are widely used in processing Solid State materials. Electrolytic gold from cyanide baths with electroless nickel under plating, Au/Ni thin films, used in both device and substrate circuit fabrication; or Au, Ag and Cu plating of p-n device junctions, as two examples. (*Note:* All electrolytic solutions in this book appear in the etchant format shown, above. The first "chemical" descriptor term of TYPE is always "Electrolytic", followed by an "Application" term, as shown above. This approach has been used due to the number of electrolytic applications involved, even though standard practice would say: electropolish, electroplating, etc.)
REF: N/A
EE-0002: Niggins, J K — *J Electrochem Soc,* 106,999(1959)

Electrolytic etching in a study of anodic dissolution of metals and electropolishing.
EE-0003: Rowland, P R — *Nature* 171,931(1963)

A study of the mechanisms of electropolishing.
EE-0004: Lowenheim, F A — *Modern Electroplating,* 3rd ed, John Wiley & Sons, New York, 1974, 52

The electroplating of metals. Includes specific cleaning chemicals and procedures for preparation of materials for plating, as well as plating formulas and processes.
REF: See individual metals/compounds where solutions are listed in this Electrolytic Format.

GAS ETCHING (GE)

GE-0001
ETCH NAME: Hydrogen
TYPE: Gas, removal/growth
TIME:
TEMP: 500—1500°C
COMPOSITION:

x .... H_2

DISCUSSION:

Gas or gas mixtures used in their molecular state to effect a cleaning or etching action. Hydrogen firing (reducing atmosphere) — also called furnace firing — is used to remove surface oxides or scale; in the alloy of assembly of parts, to prevent oxidation; and with pressure included, to hydrogenate materials (Si:H, SiC:H, etc.). Forming gas (FG) 85% N_2:15% H_2 is used in a similar manner, but is nonflammable or explosive.

Inert gases (N_2, Ar, He, etc.) are used as furnace gases in general processing and, at elevated temperature, some are used for their reactive qualities, such as nitrogen for surface nitridization, or oxygen to grow an oxide thin film . . . combined, these two gases will form oxynitrides. In the open atmosphere, at RT to hot, inert gases — N_2, most commonly — but also Ar or He are used as pressure jet blow-off drying systems, or parts are dried in air, with and without heating (IR lamps, hot plates, etc.). Flame torches are another use of gases, with acetylene; oxyhydrogen; and propylene among the leaders. Such torches are used for soldering, brazing, drying, or cleaning of parts and assemblies. Other gases are used as hot vapors from acids, such as chlorine from hydrochloric acid, or oxygen from water, nitric acid and hydrogen peroxide. Chlorine to clean surfaces, oxygen to either oxidize or as a surface cleaning step with the oxide removed with hydrofluoric acid.

In any case, this is the use of gases in their molecular state, not as dry chemical etching (DCE) with the gas in its ionized state.
REF: See individual materials, general formats.

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MOLTEN FLUX ETCHING (MFE)

MFE-0001
ETCH NAME: Molten flux etching
TYPE: Salt, preferential
TIME: Variable
TEMP: Elevated
COMPOSITION:
x .... KOH, NaCl, Fe etc.
DISCUSSION:

Molten flux etching is the use of a salt (NaCl); a metal (Fe, Cu, etc.); an alkali (KOH, NaOH, etc.) from their solid state, liquified at their melting point temperature to effect removal, polishing or development of defects. They can be mixtures: KOH:NaOH (eutectic), or NaCl:$NaCO_3$, etc. High temperature, chemically inert metals, such as titanium or molybdenum, are so etched for both cleaning and polishing of surfaces. On single crystals, such as silicon, molten flux alkalies are used for defect development. Molten metals may be the primary etching mediums on certain other metals, or be diffused into another to decorate and enhance dislocations, defects, and structure.

Molten fluxes also are used for single crystal growth of materials, such as garnets and ferrites.

The general wet chemical etching (WCE) etchant format is used to present molten fluxes, as well as metals, by name, when used as an etching medium or method of decorating defects.

Note that tin and zinc are plated from molten fluxes, as tin plating or galvanized zinc. The part is dipped into the molten metal, then withdrawn with a thin coated surface.
REF: See individual materials for specific applications.

THERMAL ETCHING (THE)

THE-0001
ETCH NAME: Thermal etching
TYPE: Thermal, removal/defect
TIME:
TEMP: Elevated
COMPOSITION:
x .... heat
DISCUSSION:

Thermal etching of metals and compounds is the use of pure heat as an etching medium. The reference shown below as a study of the influence on surface energy of metals. But thermal etching also is used to develop etch figures on any metal surface or, if a single crystal, to develop dislocations, defects, and structure. Pure thermal etching is done under vacuum conditions; otherwise a gas is included, such as in furnace heat treatment and annealing. The use of heat only can be for surface cleaning and drying and, where a specimen is heated on a hot plate in air, it is called heat-tinting . . . oxide colors used to differentiate sample structure in metallographic study of metals subjected to various test conditions of strain, fatigue, etc.
REF: Moore, A J — *Acta Metall*, 6,293(1958)
REF: See individual metals/compounds shown as heat and thermal etching in the wet chemical etching format.

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VACUUM ETCHING (VE)

VE-0001
ETCH NAME:
TYPE: Vacuum, preferential

COMPOSITION:
x .... vacuum

TIME:
TEMP: Cryogenic to elevated
VACUUM: 10^{-4} to 10^{-10} Torr

DISCUSSION:

Vacuum, used as a preferential etching vehicle, and often includes a temperature level. As thermal heat treatment, ingots, wafers, or parts are subjected to elevated temperatures up to some 2000°C under vacuum; gases are grown as single crystals under pressure cryogenic conditions in vacuum, and the changes in vapor pressure of the system used to preferentially etch structure. It has been observed that some metals, under an ultra high vacuum (UHV), have shown surface etching effects as pits or hillocks. Vacuum also is used as a drying medium in metal processing, as well as in food processing.

REF: See individual materials, general formats.

WET CHEMICAL ETCHING (WCE)

WDC-0001
ETCH NAME: Wet chemical etching
TYPE: Chemical, removal/defect
COMPOSITION:
x .... chemicals, solvents, alcohols

TIME: Variable
TEMP: Cold, RT to hot

DISCUSSION:

Wet chemical etching is the use of liquids for etching, cleaning, or development of structure, as acids, bases, alcohols or solvents. This is the primary method of processing all metals and metallic compounds, and may include gases, such as bubble chlorine through an etch; or intense light, as in plating out from an etch solution to accentuate multilayer structure or p-n junctions in semiconductor devices.

The majority of solutions shown in this book are WCE with the format as shown above. The format also is used for all chemical processing not covered by DCE; EE; or the other methods discussed in this section.

REF: See individual solutions under the specific materials.

PHYSICAL PROPERTIES OF EUROPIUM, Eu

Classification	Lanthanide
Atomic number	63
Atomic weight	152
Melting point (°C)	826
Boiling point (°C)	1439
Density (g/cm^3)	5.26
Specific heat (cal/g) 25°C	0.0395
Heat of fusion (k-cal/g-atom)	2.2
Latent heat of fusion (cal/g)	16.5
Heat of vaporization (k-cal/g-atom)	42
Atomic volume (W/D)	28.9
1st ionization energy (K-cal/g-mole)	131

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1st ionization potential (eV)	5.67
Covalent radius (angstroms)	1.85
Ionic radius (angstroms)	0.98 (Eu^{+3})
Electrical resistivity (micro-cm) 298 K	91.0
Compressibility ($cm^2/kg \times 10^{-6}$)	8.29
Neutron cross section (barns)	4600
Magnetic moment (Bohr magnetons)	7.12
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	33,100
Coefficient of thermal linear expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	26
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Steel-grey
Cleavage (cubic)	(000)

EUROPIUM, Eu

General: Although it occurs in nature it is extremely rare, as a member of the Rare Earth group of elements, and usually assigned to the yttrium sub-group even when found with cerium sub-group elements. Gadolinite, $Be_2FeY_2Si_2O_{10}$, is variable in formula, and with a high cerium oxide content called cergadolinite. As "gadolinite earths" the variety is high in yttrium sub-group elements. Often occurs in pegmatites with other rare earth bearing minerals. Monazite, $(Ce,La,Di)PO_4$ is similarly variable in rare earth content, and there are some commercial deposits as monazite sands. Monazite often contains a high percentage of thorium oxide, ThO_2, mined chiefly for that compound in India.

All rare earths are considered quite active metals, similar to calcium: they burn in air to their oxides: the oxides dissolve in water with a hissing sound, like quicklime; and hydroxides are alkaline. Europium has little use in industry due to scarcity.

Technical Application: No major use in Solid State processing at present, though there is a europium containing artificially grown garnet which may have use as an optical device, filter element, etc.

Europium has been grown as a single crystal and studied for its physical properties, to include paramagnetic behavior.

Etching: Air conversion to oxide.

EUROPIUM ETCHANTS

EU-0001
ETCH NAME: Argon — TIME:
TYPE: Gas, storage — TEMP: RT
COMPOSITION:
x .... Ar
DISCUSSION:
Eu specimens. Samples processed under argon. Fresh surfaces prepared by cutting with a knife, then wrapped in tantalum foil and stored in a silica capsule under argon to maintain a bright surface. Specimens used in a study of paramagnetic behavior.
REF: Colvin, R V et al — *Phys Rev,* 122,14(1961).

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PHYSICAL PROPERTIES OF EUROPIUM OXIDE, Eu_2O_3

Classification	Rare earth
Atomic numbers	63 & 8
Atomic weight	352
Melting point (°C)	
Boiling point (°C)	
Density (g/cm³)	7.42
Hardness (Mohs — scratch)	4—5
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Pale rose
Cleavage (cubic)	(001)

EUROPIUM OXIDE, Eu_2O_3

General: Does not occur as a natural compound by itself, though it may be an oxide, in part, as extracted from the mineral gadolinite (see Europium for further discussion).

Technical Application: Not used in Solid State processing at present, though europium metal is one constituent in some artificial garnets. The oxide is obtained by burning the metal in air, and the oxide is hygroscopic. The oxide is pale rose in color and called europia.

Etching: Soluble in water.

EUROPIUM OXIDE ETCHANTS

EUO-0001
ETCH NAME: Water — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
Eu_2O_3 specimens. Material will dissolve in water with a hissing sound like quicklime, and resulting hydroxide is alkaline.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry,* 3rd ed, D Van Nostrand, New York, 1941, 423

EUROPIUM SULFIDE ETCHANTS

EUS-0001
ETCH NAME: — TIME:
TYPE: — TEMP:
COMPOSITION:
DISCUSSION:
EuS, single crystal spheres fabricated for general morphological study. No etch shown. Europium is a rare earth element, and both the element and its compounds are highly reactive. As this is a sulfur compound, it can probably be etched in CS_2 like sulfur.
REF: Franzblau, M L et al — *J Appl Phys,* 38,4462(1967)

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FERRIC OXIDE, Fe_2O_3

General: Occurs in nature as the iron mineral hematite, Fe_2O_3 — common name red iron ore, and is a major ore of iron. It is found in rocks of all ages and in several forms, from single crystals resplendent black in color to massive earthy "red ocher"; in botryoidal shape as "kidney ore"; as "oolitic hematite", originating as a probable colloidal precipitate from iron bearing ocean waters around a central sand-grain core, forming much like a pearl in an oyster.

Although it is not magnetic, it may appear to be so when it is an admixture of hematite and magnetite, Fe_3O_4 — magnetic black iron ore. Both occur with the mineral corundum, Al_2O_3 as emery, Al_2O_3:Fe_2O_3/Fe_3O_4. Hematite can be distinguished by its cherry-red streak, infusibility in a bunsen burner flame, and can be reduced to a grey magnetic powder with soda in an RF flame.

Industrially it is a major ore of iron. As powder, it is a red paint pigment, and a coloring agent in glass, ceramics and enamels. Also as a powder, it is "red rouge", used both in cosmetics and as a lapping and polishing abrasive with a Mohs hardness of about H = 6. It can be fabricated artificially by treating ferric chloride with steam at high temperature; or by the action of air and hydrochloric acid on iron; and formed from several molten fluxes.

Technical Application: As ferric oxide (iron sesquioxide) it has no direct application in Solid State device fabrication. It is used as a lapping abrasive, as a thin film in the fabrication of photo resist masks; and as an optical filter. As MFe_3O_4, it is fabricated as microwave and memory devices; as $M_3Fe_5O_{12}$ (garnet) for bubble memory devices, microwave filters, and surface wave devices and as $PbFe_{12}O_{19}$. As already mentioned, also as thin film, semitransparent photo resist mask.

Etching: Slowly in HCl.

See Hematite, Fe_2O_3

FERRIC OXIDE ETCHANTS

FEO-1000
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP: Warm
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

Fe_2O, thin film deposited on soda-lime glass as a photo resist mask. Film patterned by photolithography and etched in hydrochloric acid in fabricating photo masks for semiconductor processing. More widely used than chromium as it is harder, less prone to physical handling damage, and more stable.

REF: Lipman, R — personal communication, 1983

FERRITE, FeM_xM_y

General: The word is from Latin: ferrum, hence the symbol for iron, Fe, and the word "iron" is Anglo-Saxon. Native iron does occur, occasionally in large ore bodies, but more often as small grains in other rocks of basic origin. Iron occurs with two valences: Ferric, Fe^{+++} and Ferrous, Fe^{++}, and magnetic iron (extracted from magnetite, Fe_3O_4) contains iron of both valences, such that it is called ferrosoferric iron.

In iron processing the term ferrite refers to soft iron with less than 0.04% carbon, also called wrought iron . . . the original form of iron first smelted by the Hittites in Asia Minor (Turkey) around 1350 B.C. and is still used for decorative purposes. In metallographic specimens it can be recognized as a constituent by its soft dove-grey color.

Ferrite also refers to a group of metallic compounds as a class of materials . . . even metal oxides containing iron have been called ferrites. In effect, any material containing

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iron may be referred to as a ferritic compound, ferrous or ferric, depending upon iron valence. All ferrite compounds are of interest for their ferromagnetic, ferro-electric, or ferro-optic capabilities with several developed as operational devices in Solid State.

Technical Application: In Solid State development of semiconductor device assemblies, a class of ferrites has been designed as resistor materials with particular metal additives, such as zinc, manganese, etc., for specific power and/or frequency levels associated with the microelectronic circuitry. They are supplied as square blanks — dark black, highly polished surfaces in thickness ranges of 0.0005 to 0.025, and 1 × 1″ square or larger. The blanks are metallized by plating (Au/Ni) or evaporated/sputtered (Au/Cr and other combinations), then cut to the required size as a discrete resistor element. Metallization of ferrite of this type can be difficult for, like other highly polished surfaces, metal adhesion can be a problem. Roughing the face by abrasion (400-grit SiC) can be used when possible (not for high frequency), or lightly oxidizing — 10 min at 200°C on a hot plate in air — will aid in the thin film metal adhesion.

Most ferrites used as resistor elements are crystalline, pressed powder blanks; others have been grown as single crystals, such as iron carbide, Fe_3C. See Iron Alloys, Iron, and Steel sections for additional discussion and etchant solutions.

Etching: Nital, Picral, and mixed acids.

FERRITE ETCHANTS

HCFE-0001
ETCH NAME: Kalling's etch
TYPE: Acid, polish
TIME: 10—60 sec
TEMP: RT
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH
DISCUSSION:

$Ho_2Co_{14}Fe_3$ specimens arc melt fabricated, and used in a study of metallic compounds. Solution used as a general removal and polishing etchant. Also studied Ho_2Fe_{17}. See Cesium Platinide for other materials studied.
REF: Slepowronsky, M et al — *J Cryst Growth,* 65,293(1983)

MAGT-0004
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
x .... HCl, conc.
DISCUSSION:

Fe_3O_4, specimens from ingots grown by the Czochralski (CZ) method. A study of single crystal iron ferrites grown by this method. Other iron doped materials were ZnO, Ga_2O_3, CuO, and MnO.
REF: Horn, F N — *J Appl Phys* 32,900(1961)
FER-0001a: Walker, P — mineral study, 1950—1964

Fe_3O_4 natural single crystal specimens used in a study of iron oxides. Solution used concentrated, and as $1HCl:1H_2O$ for surface cleaning. Also studied other natural iron specimens of hematite, Fe_2O_3, limonite, $2Fe_2O_3.3H_2O$ and goethite, $Fe_2O_3.H_2O$ [FeO(OH)].

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FER-0001b
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
TIME:
TEMP: 85°C
COMPOSITION:
x .... TCE, vapor
DISCUSSION:
Fe:Mn:Zn, pressed powder blanks used as resistor material for microelectronic circuits. Blanks were highly polished 1 × 1 × .015/.025″ size. After vapor degreasing in TCE, bake out in air oven at 150°C for 30 min prior to metallizing with Au/Ni plating or Au/Cr evaporation.
REF: Walker, P et al — personal application, 1980—1985
FER-0002: Buckley, D H — *J Vac Sci Technol*, A3(3),762(1985)
Fe:Mn:Zn and Fe:Ni:Zn ferrites used in a study of ceramic microstructure and adhesion of thin films. The iron absorbs O_2 even in vacuum or under argon. The study applied sliding contacts across the metal thin film surfaces. The metal film remains in place, and bonding was assisted by the presence of O_2. Cu, Ni, Rh, Co, and Be were rubbed across surfaces in this evaluation.

FER-0003
ETCH NAME:
TYPE: Thermal, defect
TIME:
TEMP: Elevated
COMPOSITION:
x .... heat
DISCUSSION:
Ferrite specimens as crystalline material used in a study to determine directions of magnetization in polycrystalline ferrites. Thermal etching was better than chemical etching to develop well defined grain boundaries with the remainder of the surfaces relatively smooth. To thermal etch: first, mechanically polish surface, then hold in furnace for 10 min at the same temperature and atmosphere used for annealing/sintering.
REF: Callaby, D R — *Phys Rev*, S31.375S(1961)

FER-0004
ETCH NAME:
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... EOH
DISCUSSION:
$MFeM_2$, material grown in evaluating new semiconducting type compounds as ferrites. M = Ag, Cu, and M_2 = S, Se, Te. Solution shown can be used for general cleaning.
REF: Zhuze, U P et al — *Zh Tekh Fiz*, 28,233(1958)

MAGT-0005
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP: (1) Boiling
(2) Molten
COMPOSITION:
(1) x .... HCl, conc.
(2) x .... $NaSO_4$, fused
DISCUSSION:
Fe_3O_4 single crystal material grown in a "skull melter" with RF generator. This was an isomorphic ingot series from Fe_3O_4 to $FeTiO_3$ (natural mineral is ilmenite). The titano-

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magnetites are grown by oxygen control (fugacity, fO_2). During growth, O_2 concentration was buffered with CO_2/CO. With addition of tin or tin foil to either solution shown above, and containing dissolved ferritic material, a brown-violet to fine blue or violet color is observed in solution depending on the amount of titanium present. (*Note:* This color reaction in solutions containing Ti has been a primary method used in determinative pyrolytic mineralogy of ilmenite for many years.)
REF: Aragon, R et al — *J Cryst Growth,* 61,221(1983)

COFE-0001
ETCH NAME: Nital — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3
x .... EOH
DISCUSSION:
CoFeO, (100) wafers cut from ingots grown by the Verneuil arc-image furnace method. After cutting and mechanically polishing, re-anneal at 1200°C several days in air for ferrite material $CoO_4(Co_{1-c}Fe_c)O$.
REF: Hoshino, K & Peterson, R L — *J Phys Chem Solids,* 46,229(1985)

RFE-0001
ETCH NAME: Nital — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3
x .... EOH
DISCUSSION:
RFe_2, as rare earth ferrites. R = Sm, Gd, Tb, Dy, Ho, and Er. Materials were fabricated in an arc melt furnace under argon. Then ingots were annealed 200 h in sealed quartz ampoules.
REF: Klimker, H et al — *J Phys Chem Solids,* 46,157(1985)

PHYSICAL PROPERTIES OF FLUORAPATITE, $(CaF)Ca_4(PO_4)_3$

Classification	Phosphate
Atomic numbers	20, 9, 15, & 8
Atomic weight	480
Melting point (°C)	1200
Boiling point (°C)	
Density (g/cm³)	3.17—3.23
Refractive index (n=)	1.630—1.648
Hardness (Mohs — scratch)	5
Crystal structure (hexagonal — tripyramidal)	$(21\bar{3}0)$ prism, 3rd order
Color (solid)	Colorless to colored
Cleavage (basal — imperfect)	(0001)

FLUORAPATITE, $(CaF)Ca_4(PO_4)_3$

General: As the natural mineral "apatite", there are two major subspecies: fluor- and chloroapatite, with the former more common, and there are a number of additional varieties of differing constituent composition among, the two subspecies. It is quite widely distributed, often occurring in iron and tin mines. It has a variety of colors — blue, yellow, green, pink,

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brown and white. The fine transparent varieties have been used as gem stones, even though the mineral is relatively soft for this purpose. Along with other phosphate rocks and minerals, the apatites have primary use as industrial fertilizers.

Technical Application: Apatite-type single crystals have been grown and doped for use as long-pulse CW laser devices, both as a phosphate, and as a silicate oxy-apatite (no phosphate), but otherwise similar in crystal structure. The fluorapatite, rather than chloro-apatite, is the base material, and doping elements are rare earths. The silicate types are being developed as improved Q-switch lasers.

Etching: Aqua regia; fluorine salts, and molten fluxes.

FLUORAPATITE ETCHANTS

FAP-0001a
ETCH NAME: Aqua regia
TYPE: Acid, preferential
TIME: 1—3 min
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

$Ca_5(PO_4)_3F$:Nd as artificially grown single crystals doped with neodymium, and used as long pulse CW lasers. In this study a series of silicate oxy-apatites were grown as possible materials for improved Q-switch lasers. General formula of these compounds: $MeLn_4(SiO_4)_3O$ with Me = Mg, Ca, and Ln = Y, La, Gd. $SrLa_4(SiO_4)_3O$ and $CaLa_4(SiO_4)_3O$ discussed in detail. Crystals were melt grown in an iridium boat under argon, and some IrO flakes were observed on the single crystal wafers. Polish wafers in molten eutectic flux: NaF:KF at 350°C prior to preferential etching with aqua regia. Aqua regia develops pits at dislocation sites. (*Note:* Formula for natural fluorapatite is $(CaF)Ca_4(PO_4)_3$, and as chloroapatite is $(CaCl)Ca_4(PO_4)_3$).
REF: Hopkins, R H et al — *J Electrochem Soc*, 118,637(1971)

FAP-0001b
ETCH NAME:
TYPE: Molten flux, polish
TIME:
TEMP: 350°C
COMPOSITION:
1 .... NaF
1 .... KF
DISCUSSION:

$Ca_5(PO_4)_3F$ and silicate oxy-apatites. Single crystal specimen wafers were polished in the eutectic molten flux shown prior to dislocation etching with aqua regia. See FAP-0001a for further discussion.
REF: Ibid.

PHYSICAL PROPERTIES OF FLUORINE, F_2

Classification	Halogen
Atomic number	9
Atomic weight	38 (F2)
Melting point (°C)	−233
Boiling point (°C)	−187

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Density (g/cm^3 — solid) −187°C	1.108
(g/l — liquid) 18°C	1.69
Thermal conductance ($\times 10^{-4}$ $cal/cm^2/cm/°C/sec$) 20°C	0.579
Specific heat (cal/g/°C) 20°C	0.18
Latent heat of fusion (cal/g)	10.1
1st ionization potential (eV)	17.42
Ionic radius (angstroms)	1.33 (F)
Cross section (barns)	0.010
Vapor pressure (°C)	202.7
Refractive index (n =)	1.000195
Hardness (Mohs — scratch) solid	1—2
Crystal structure (isometric — normal) solid	(100) cube
Color (solid)	Yellow-green
(liquid)	Yellow-green
(gas)	Pale yellow
Cleavage (cubic — solid)	(0001)

FLUORINE CONTAINING ETCHANTS

Fluorine is a pale greenish yellow gas at standard temperature and pressure (22.2°C and 760 mmHg) that can be condensed as a pale-yellow liquid with a boiling point of −187°C. It is the most reactive element known and a member of the halogen group of elements which includes chlorine, bromine, and iodine, in order of reactivity. Chlorine, too, is a gas; bromine a liquid; and iodine a solid. Fluorine does not occur as a free element in nature although traces of hydrogen fluoride are occasionally found in association with volcanic activity. The best known fluorine mineral is fluorite, CaF_2, which has been used as a flux material in metallurgy as "fluorspar" even before the discovery of fluorine and its establishment as a separate element in 1886 by Moissan. Prior to its discovery, fluorspar was known to contain calcium and some other element that reacted much like chlorine. Because of its high reactivity with elements such as sulfur, phosphorus, carbon, silicon, and boron — it will catch fire in fluorine, although most metals, with the exception of gold and platinum, will burn in the presence of the gas.

Of all of the compounds of fluorine, the best known is probably hydrogen fluoride, HF — better known as hydrofluoric acid. It is the primary etch for glass, with silicon tetrafluoride, SiF_4, as a gaseous by-product. Glass is etched by either immersion in the liquid (a smooth surface) or by vapor (a rough surface). The latter is widely used for pattern etching of glass objects — drinking glassware, plates, and objets d'art. Microscope slides have been vapor etched to roughen the surface for improved adhesion of thin film metal deposits where, after deposition, the metal film is removed by the float-off technique, e.g., immersion in HF. Gold thin films have been prepared in this manner for morphological and defect study under high power magnification.

In processing semiconductor wafers, silicon dioxide, SiO_2, and silicon nitride, Si_3N_4 are deposited as thin films — 1000 to 3000 Å thick — and used as masks against subsequent pattern etching, diffusion or epitaxy growth. The oxide/nitride surfaces are photolithographically processed with patterns developed by UV exposure of a photo resist coating. The underlying oxide or nitride then removed by etching with hydrofluoric acid or a mixture of $HF:NH_4F$ to expose the semiconductor surface for diffusion, etching, epitaxy etc. The $HF:NH_4F$ solutions are called buffered hydrofluoric acid (BHF) etchants. The ammonium fluoride, NH_4F, is commonly used as a 40% concentration and added to concentrated HF, although it is sometimes added as a saturated solution (sat. sol.). This NH_4F saturated solution in HF is a primary etchant for frequency tuning of quartz crystal blanks used for radiofrequency devices. As the concentration of NH_4F varies by individual preference or application, the acronym BHF should be considered a general classification term, not a specific etch mixture. Such solutions also have been referred to as buffered oxide etch

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(BOE), though BHF is more common. The mixture ratio of HF to NH_4F varies from 1HF:1NH_4F(40%) to 1HF:100NH_4F, sat. sol., and may include dilution with water, and the ammonium fluoride may be replaced with ammonium bifluoride, $NH_4F.HF$.

Other fluoride compounds are used as etching and cleaning solutions on both semiconductors and other metals and compounds such as sodium and potassium fluoride, NaF and KF, respectively. These halide-type compounds may be used as solutions for wet chemical or electrolytic etching or as molten flux etching.

Of all the HF acid mixtures, solutions of HF:HNO_3; HF:HNO_3:H_2O or HF:HNO_3:HAc — oxidation-reduction systems — are the most widely used etch solutions for a wide range of material processing where they have no, or limited, solubility in single acids. Understandably, there are hundreds of possible ratio combinations with such mixtures and every laboratory, establishes their own particular mixtures as required for a specific process step. Much development and study has been done and is still being done, on these solutions and many of the mixtures referenced in this Etchant Section are of this type. Generally speaking, all of these solutions are polishing-type etchants within certain limits: when high in HF or HNO_3 they are self-limiting where excessive reduction or oxidation produces a passivation reaction. Such solutions are used surface "stain" etch as they produce recognizable color patterns. The HF type stain is difficult to remove as it is, in effect, a fluorine-burn; whereas the HNO_3 stain is an oxide and easily removed with HF. The most rapid mixture is 1HF:3HNO_3, and either water, H_2O or glacial acetic acid, CH_3COOH (HAc or GLA) is used as an inhibitor or rate control agent. Although glycerin is sometimes added to these solutions as a viscosity control agent, it is not recommended as nitric acid and glycerin are the precursor mix for nitroglycerin. If viscosity control is required, ethylene glycol, CH_2OHCH_2OH, is recommended. The excessive addition of water or acetic acid to HF:HNO_3 mixtures can severely alter polishing action to the point where controlled etch reaction is highly erratic and results are poor. Most of the solutions are used at room temperature, due to their relatively high reactivity and exothermic nature and, for batch etching of semiconductor wafers, etching is often done in a controlled temperature bath.

These solutions, as well as most other etchants, become progressively preferential as temperature is reduced toward 0°C, regardless of their polishing capability at room temperature. Several mixtures are used at 8°C, chilled with a mixture of ice in acetone; others chilled with liquid nitrogen for use at 0°C. Such cold etchants are used for surface cleaning, or as slow preferential etchants for structure, electrical tuning of a p-n junction device, etc.

Other widely used HF mixtures are the HF:H_2O_2:H_2O solutions where the nitric acid has been replaced as the oxidizer by hydrogen peroxide, H_2O_2. Hydrogen peroxide is supplied commercially as a 30% solution and, chemically, is called "superoxol". This should not be confused with the etchant that also is called superoxol (Camp #2): 1HF:1H_2O_2:4H_2O (GE-0065a). In addition, there is an etch solution called "Peroxide Etch": 1 mlHF:1 mlH_2O_2:1HAc (see GE-0060f), which should not be confused with the concentrated or dilute pure H_2O_2.

The hydrofluoric/hydrogen peroxide etchants are polishing solutions on most semiconductor and other materials, and used in a similar manner to those hydrofluoric/nitric acids. As H_2O_2 it is an extremely violent and reactive oxidizer, in comparison to others, it has a tendency to dissociate rapidly once in solution with heavy oxygen bubble evolution, particularly when used above room temperature. Because of this, such mixtures can become rapidly depleted in the peroxide, such that the peroxide may be added only when ready for solution use, and use is stopped when complete dissociation in reached. There are always exceptions . . . some solutions are mixed, allowed to sit and "age", then used as a "stagnant" solution.

Potassium permanganate, $KMnO_4$, and chromium trioxide, CrO_3, or other chromium compounds, such as sodium dichromate, $Na_2Cr_2O_7$, etc., are oxidizers and, *when mixed* with HF, are used as defect/dislocation etchants on many semiconductor materials. Several

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$HF:CrO_3$ solutions have been developed, and are discussed in the preceding section on Chromium Containing Etchants. $HF:I_2$ and $HF:Br_2$ with varying halogen concentrations are used as defect/dislocation etchants and discussed in sections similar to that for chromium.

CP4 (Camp #4) etch: $30HF:50HNO_3:30HAc:0.6Br_2$ was originally developed as a defect and light orientation figure (LOF) etch for (100) germanium ingots and wafers, and used at room temperature. It also is a polishing solution, and has been used on a number of other semiconductor, metals, and compounds as a removal, polish, thinning, cleaning or step-etch at room temperature, below room temperature, hot to boiling. Without bromine, it is called CP4A and, as CP4, modified, the bromine has been replaced with I_2, $Cu(NO_2)_3$, $AgNO_3$, etc.

The following list of HF-type etches is presented to show the wide variety of metals and compounds to which such solutions are applied. Many additional solutions are shown under their appropriate etchant section headings.

Formula	Material	Use	Ref.
HF, conc.	Al	Removal	AL-0021
$xHF:xH_2O$	Al	Metallographic macro-etch	AL-0016
$30HF:47HNO_3:50HCl$	Al	Preferential	AL-0020a
$xHF:H_2O$	AlN	Removal & cleaning	ALN-0002
$xHF:xHNO_3:xHAc$	AlSb	Polish	ALSB-0001b
$xHF:xH_2O_2$	AlSb	Polish	ALSB-0001a
$30HF:50HNO_3:30HAc:0.6Br_2$	AlSb	Oxide removal & cleaning	ALSB-0010
HF, conc.	B	Removal	B-0001
HF, conc.	BaF_2	Removal	BAF-0005
$1HF:3HNO_3$	BF_3	Dislocation	BF-0001
$xHF:xH_2O$	Bi	Damage, removal	BI-0002
15 ml HF:15 ml HNO_3:45 ml HCl: 25 ml H_2O	Au	Preferential	AU-0011
$1HF:20CrO_3$, sat. sol.	$CaWO_4$	Dislocation	CAW-0003b
HF, conc.	CdF_2	Polish	CDF-0001b
$1HF:3HNO_3:3H_2O$	$CdSiAs_2$	Polish	CSA-0001
$1HF:1HNO_3$	CdTe	Polish	CDTE-0001e
$2HF:3HNO_3:1H_2O$	CdTe	Preferential	CDTE-0001b
$3HF:2H_2O_2:1H_2O$	CdTe	Preferential	CDTE-0001f
HF, conc.	CoO	Preferential	COO-0001
HF, conc.	D (diamond)	Cleaning	D-0002
$1HF:4HNO_3:5H_2O$	Fe_2C	Thinning	FEC-0001
HF, conc.	GaAs	Selective/removal	GAS-0024
HF, vapor	GaAs	Cleaning	GAS-0129
$1HF:9H_2O$	GaAs	Cleaning	GAS-0112
$2HF:3HNO_3:2HCl$	GaAs	Polish	GAS-0145a
$1HF:1HNO_3:1HAc$	GaAs	Cleaning	GAS-0037a
$1HF:3H_2O_2$	GaAs	Preferential	GAS-0049
$1HF:1H_2O_2:50H_2O$	GaAs	Selective/step-etch	GAS-0051a
$5HF:1H_2O_2:1H_2O$	GaAs	Polish	GAS-0053b
$1HF:1H_2O_2:4H_2O$ "superoxol"	GaAs	Preferential	GAS-0167a
$1HF:1HNO_3$	GaAs	Cleaning	GAS-0047a
$1HF:3HNO_3:2H_2O$	GaAs	Polish, rapid	GAS-0006d

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Formula	Material	Use	Ref.
1 ml HF:2 ml H_2O:6 mg $AgNO_3$: "A/B" 1 g CrO_3	GaAs	Preferential	GAS-0059
1HF:5HNO_3:10HAc	GaSb	Polish	GASB-0002
1HF:1HNO_3	GaSb	Polish	GASB-0001e
1HF:1HNO_3	GaP	Polish	GAP-0001
HF, conc.	Ge	Fracture: HF vs. air medium	GE-0064
1HF:8H_2O	Ge	Preferential	GE-0150e
xHF:xHNO_3:xHCl:xH_2O_2	Ge	Preferential	GE-0170
1HF-3HNO_3:12HAc "Dash Etch"	Ge	Preferential	GE-0065a
1HF:3HNO_3:8HAc	Ge	Polish/thinning	GE-0171
1HF:1H_2O_2:4H_2O "superoxol"	Ge	Preferential	GE-0002
30HF:50HNO_3:30HAc:0.6Br_2 CP4	Ge	Preferential polish	GE-0065c
15 ml HF:30 ml HNO_3:33 ml HAc:80 mg I_2	Ge	Preferential	GE-0185
1HF:1HNO_3	Ge	p-n junction etch	GE-0033
4HF:7HNO_3:2H_2O	Ge	Polish cleaning	GE-0036
HF, conc.	GeN	Removal	GEN-0002
1HF:10H_2O	GeN	Removal	GEN-0002
1HF:1HNO_3	GeAs	Removal	GEAS-0001a
10 ml HF:45 ml HNO_3:45 ml H_2O	Hf	Cleaning	HF-0001
1HF:1H_2O_2:20H_2O	Hf	Removal	HF-0002
1HF:1H_2O_2:4H_2O "superoxol"	InAs	Preferential	INAS-0006a
74HF:75HNO_3:15HAc:0.6Br_2	InAs	Preferential	INAS-0006d
1 ml HF:2 ml H_2O:8 mg $AgNO_3$: 1 gCrO_3 A/B Etch	InAs	Preferential	INAS-0005d
HF, conc.	InSb	Oxide removal	INSB-0027
10HF:25HNO_3:20HAc	InSb	Polish	INSB-0001a
1HF:5H_2O_2:xH_2O	InSb	Polish	INSB-0009
1HF:1H_2O_2:4H_2O "superoxol"	InSb	Preferential	INSB-0024a
30HF:50HNO_3:30HAc:0.6Br_2 CP4	InSb	Polish	INSB-0001f
1HF:1HNO_3	InSb	Removal	INSB-0002e
1HF:1HNO_3:6H_2O	InSb	Preferential	INSB-0005a
1HF:1H_2O_2:2H_2O	InSb	Dislocation	INSB-0025c
8HF:100H_2O	InP	Native oxide removal	INP-0045a
1 ml HF:2 ml H_2O:8 mg $AgNO_3$: 1 g CrO_3	InP	Preferential	INP-0051
1HF:10HBr	InP	Preferential	INP-0027
5HF:1MeOH	InP	Dislocation	INP-0037a
5HF:1Br_2	InP	Dislocation	INP-0037b
100 ml HF:100 ml HNO_3:160 ml HAc: 2 ml Br_2	LiF	Dislocation	LIF-0001e
1HF:2HNO_3	$LiTaO_3$	Preferential	LITA-0002
1HF:2HNO_3	$LiNbO_3$	Preferential	LINB-0002
xHF:xH_2O	MgO	Preferential	MGO-0010
xHF:xH_2O_2	Mo	Removal	MO-0001a
xHF:xHNO_3	Mo	Removal	MO-0001f
xHF:xMnO_4	Mo	Removal	MO-0001c
3.5 ml HF:96 ml H_2SO_4:0.5 ml HNO_3:xCrO_3	Mo	Polish	MO-0008c

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Formula	Material	Use	Ref.
HF, conc.	NB	Cleaning	NB-0004b
HF, conc.	Nb	Electropolish	NB-0007
1HF:4HNO_3	Nb	Polish	NB-0002
HF, conc.	$NbAl^y$	Removal	NBAL-0001
1HF:1HNO_3:10HAc	Nb_3Se	Cleaning	NBSE-0001
HF, conc.	Nb_3B_3	Removal	NBB-0001c
HF, vapor	Ni	Removal	NI-0004b
1HF:1H_2O_2	$PtSb_2$	Preferential	PTSB-0001e
1HF:1HNO_3:1H_2O	$PtSb_2$	Preferential	PTSB-0001c
3HF:5HNO_3:3HAc	$PtSb_2$	Preferential	PTSB-0001f
8HF-2HNO_3	Re	Preferential	RE-0001
1HF:3HNO_3:12HAc "Dash Etch"	Sb	Polish	SB-0001a
1HF:2HNO_3:24HAc:1Br_2	Sb	Dislocation	SB-0003b
HF, conc. + intense light	Si	Junction stain	SI-0188a
HF, conc.	Si	Oxide removal	SI-0002a
HF, vapor	Si	Cleaning	SI-0009
1HF:10H_2O	Si	Cleaning	SI-0004
1HF:3HNO_3:12HAc "Dash Etch"	Si	Preferential	SI-0044
1HF:5HNO_3:1HAc	Si	Thinning	SI-0074
1HF;5HNO_3:1HAc	Si	Polish	SI-0076
1HF:3HNO_3:1HAc	Si	Dislocation	SI-0075
10HF:50HNO_3:30HAc:0.6Br_2 CP4	Si	Polish/preferential	SI-0173
2HF:15HNO_3:5HAc	Si	Structure forming	SI-0173a
1HF:3HNO_3	Si	Polish	SI-0046b
1HF:1HNO_3:50H_2O	Si	Removal/polish	SI-0073
xHF:xMeOH	Si	Cleaning	SI-0016
1HF:1.5 *M* CrO_3:1H_2O	Si	Defect	SI-0030
2HF:0.15 *M* $K_2Cr_2O_7$ "Secco"	Si	Preferential/dislocation	SI-0036
2HF:1 0.75 *M* CrO_3:1.5H_2O "Shimmel"	Si	Preferential/dislocation	SI-0017
1HF:3CrO_3 (33%) "Sirtl"	Si	Preferential/dislocation	SI-0039
50 ml HF:50 ml HNO_3:100 mg $KMnO_4$	Si	Polish	SI-0125
4HF:2$Cu(NO_3)_2$	Si	Junction stain	SI-0188b
xHF:xI_2	Si	Preferential	SI-0159
10 ml HF:2 mg I_2:20 ml MeOH	Si	Preferential	SI-0204
1HF:9NH_4F(40%) "BHF"	Si	Cleaning/slow polish	SI-0021a
5 mlHF:20 mgNH_4F:200 mlH_2O "BHF"	Si	Oxide/nitride removal	SI-0026
30 mlHF:8.4 gNaF/l	Si	Electropolish, jet	SI-0174b
xHF:xH_2O	SiC	Cleaning	SIC-0001
HF, conc.	SiC	Cleaning	SIC-0004
2HF:3HNO_3	SiC	Removal	SIC-0008
2HF:1CrO_3 (33%) "Sirtl"	SiC	Polish	SIC-0012a
1HF:xKF, sat. sol.	SiC	Electrolytic, microstructure	SIC-0013b
1HF:1H_2O	SiO_2(Qtz)	Polish removal	QTZ-0001
1HF:3HNO_3	SiO_2(Qtz)	Cleaning, quartzware	QTZ-0010

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Formula	Material	Use	Ref.
1HF:1HNO_3	SiO_2(Qtz)	Thinning, alpha-quartz	QTZ-0006
1HF:20HNO_3:20EG	SiO_2(Qtz)	Tuning, alpha-quartz	QTZ-0007
50 ml HF:50 g NH_4F.HF:100 ml H_2O: 50 ml Gly	SiO_2(Qtz)	Polish, alpha-quartz	QTZ-0011
HF, conc.	SiO_2	Patterning/pinholing	SIO-0004
HF, vapor	SiO_2	Removal/roughening	SiO-0006
1HF:100H_2O	SiO_2	Cleaning/oxide removal	SIO-0007
1HF:2HNO_3:60H_2O "P Etch"	SiO_2	Removal	SIO-0011a
1HF:100NH_4F, sat. sol. "BHF"	SiO_2	Removal	SIO-0009
1HF:6NH4F (40%) "BHF"	SiO_2	Removal	SIO-0011b
1HF:10NH_4F:15H_2O "BHF"	SiO_2	Step-etch	SIO-0014
200 ml HF:9 g CrO_3:100 ml H_2O	SiO_2	Dislocation	SIO-0021a
xHF:xNH_4F:xH_2O "BOE"	SiO_2	Removal	SIO-0006
HF, vapor	Si_3N_4	Removal	SIN-0002a
HF, conc.	Si_3N_4	Removal/pinholing	SIN-0002c
15HF:10H_3PO_4:60EOH	Si_3N_4	Preferential	SIN-0007
1HF:1H_2O	Ta	Cleaning	TA-0008
2HF:5HNO_3:3HAc "CP4A"	Ta	Acid saw cut/polish	TA-0003
3HF:5HNO_3:1HAc	Ta	Electropolish	TA-0002d
1HF:2HNO_3:1H_2O	Ta	Removal	TA-0001
1HF:1NH_4F (20%)	Ta	Preferential	TA-0004b
2HF:2HNO_3:5H_2SO_4	Ta	Preferential	TA-0004b
1.5HF:2HNO_3:5H_2SO_4	Ta	Polish	TA-0009
1HF:20H_2O	$TaSi_2$	Cleaning	TASI-0001
x%NH_4F	ThO_2	Preferential	THO-0002
1HF:4HNO_3:5H_2O	Ti	Removal	TI-0006
10 ml HF:90 ml H_2O	Ti	Removal	TI-0011a
3HF:16H_3PO_4:1H_2O	Ti	Polish	TI-0010
xHF:xHCl:xH_2O	Ti	Removal	TI-0003
1HF:1MeOH	Ti	Electropolish	TI-0013
1HF:1HNO_3:6H_2O	TiC	Electrolytic, preferential	TIC-0002
xHF:xHNO_3:xHAc	TiC	Electropolish	TIC-0003
10 ml HF:45 ml HNO_3:45 ml H_2O_2	TiN	Cleaning	TIN-0004
13HF:452 g NH_4F:625 mH_2O	TiN	Removal	TIN-0003
1HF:24NH_4F:5H_2O	TiO_2	Removal	TIO-0005
1HF:1HNO_3:10H_2O	V	Electrolytic, preferential	V-0001
HF, conc.	V	Removal	V-0002c
1HF:1H_2O_2:4H_2O "superoxol"	V_3Si	Polish	VSI-0001a
15HF:4H_2O	V_3Si	Dislocation	VSI-0001c
15 ml HF:100 ml HNO_3	V_3Si	Cleaning	VSI-0002
HF, conc.	W	Removal	W-0003b
1HF:1H_2O_2	W	Removal	W-0003b
xHF:xHNO_3:xH_2O	W	Polish	W-0002b
3HF:2HNO_3:1HAc	W	Cleaning	W-0002d
xHF:xHNO_3	W	Polish	W-0018d
HF, conc.	WB_2	Removal	WB-0001a

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Formula	Material	Use	Ref.
$1HF:1HNO_3$	ZnS	Polish	ZNS-0001b
$3HF:2H_2O_2:1H_2O$ "Warekois"	ZnS	Preferential	ZNS-0002a
$1HF:1HNO_3$	$ZnSiP_2$	Polish	ZSP-0001
$3HF:2H_2O_2:1H_2O$ "Warekois"	ZnTe	Preferential	ZNTE-0002
$4HF:30HNO_3$. then xH_2SO_4	Zr	Removal	ZR-0003
$1HF:4HNO_3:2H_2O$	Zr	Electropolish	ZR-0004b
50 ml HF:50 ml HNO_3:50 ml H_2O	Zr	Removal	ZR-0009
8 ml HF:50 ml HNO_3:50 ml H_2O	Zr	Preferential, macroetch	ZR-0008
$xHF:xNH_4F$	Zr	Polish	ZR-0009
10 ml HF:45 ml HNO_3:45 ml H_2O_2	ZrN	Cleaning	ZRN-0001
HF, conc.	ZrO	Removal	ZRO-0001b

ETCH NAME: BUFFERED HYDROFLUORIC ACID (BHF)

General: Glass is both a naturally occurring mineral, as obsidian, as well as a manmade product since the Egyptians first developed soda-lime glass around 3500 B.C., and the same formula is still in use today. Glass has been in use as a pottery glaze (ceramic pottery) since those ancient times, and the present glass industry is now a major industry of its own within the original silicate industries, which include clay and ceramics also, today, as separate industries.

In Solid State, the semiconductor industry, in particular, has been using silicon dioxide, SiO_2 (glass, silica), in device fabrication since about 1950. The common term is "oxide", still used with reference to silicon dioxide, only, although several other metallic oxides are now in use in a similar manner, such as Al_2O_3, TiO_2, etc. This now also includes nitrides, such as silicon nitride, Si_3N_4, and oxynitrides as oxides and nitrides form isomorphous series.

Such oxides and nitrides are deposited as thin films in many types of device fabrication as a final surface passivation, or in processing as a mask against etching, metallization, or irradiation damage; and, when doped with boron, phosphorus, or arsenic, as a drive-in diffusion dopant source. Such doped oxides have acquired their own acronyms such as BSG, PSG, ASG, and PBSG.

Hydrofluoric acid (HF) has long been the primary solution for etching glass. When any glass is immersed in the liquid, it will be etch polished; whereas if it is held in the hot vapors, the surface will be rough or frosted. HF is supplied commercially in a standard 49% solution. Always in polyethylene bottles, as it attacks glass, and most processing laboratories use it from 5-gallon bottles. For general removal of thin film oxides and nitrides, both concentrated and water diluted hydrofluoric acid are used, but are too rapid for patterning or controlled removal, as most thin films are only on the order of 1500 to 3000 Å thick. In pattern etching of any thin film, whether an oxide, nitride, or metal, all acid solutions will etch down vertically through the film, as well as horizontally at an equal rate. This must be compensated for in fabricating fine-line patterns to prevent destructive undercutting of the metal structure.

As HF is too rapid for such fine control, buffered hydrofluoric acid solutions have been developed with the general acronym of BHF which is applied to many HF + fluorine compound mixtures. Such mixtures also have been referred to as a buffered oxide etch (BOE), but BHF is more commonly applied.

Because of mixture variations the "BHF" term should be accepted with caution, unless the specific formulation is shown, as even $HF:H_2O$ solutions have been referred to as BHF solutions. The most widely used fluorine compound used to buffer is ammonium fluoride, NH_4F as $HF:NH_4F$ (40%), but others are used (KF, NaF), only, or in addition to NH_4F. Also, the ammonium bifluoride ($NH_4F.HF$) compound has been used.

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The use of BHF solutions is not limited to silicon dioxide, or silicon nitride, as they are applicable to any glassy metal compound. The following list covers several applications on other metals and metallic compounds. See the individual etchant sections for further usage.

Formula	Material	Use	Ref.
$xHF:xH_2O$	Al	Removal	AL-0021
1 ml HF:199 ml H_2O	Al	Macro-etch	AL-0016
$1HF:1H_2O$ or $1HF:10H_2O$	AlN	Cleaning/removal	ALN-0001
HF, conc. or x% NH_4F	BaF_2	Removal	BAF-0005
$2HF:98H_2O$	Bi	Damage removal	BI-0002
$xHF:xH_2O$	CdF_2	Polish	CDF-0001b
$1HF:9H_2O$	GaAs	Cleaning	GAS-0112
10^{-6} 0.1 *N* KF	Ge	Electrolytic polish	GE-0046
$1HF:10H_2O$	GeN	Removal	GEN-0002
5HF:1MeOH	InP	Dislocation	INP-0037a
$2HF:10H_2O$	InP	Native oxide removal	INP-0045a
$xHF:xH_2O$	MgO	Preferential	MGO-0003
$1HF:1H_2O$	SiO_2 (Qtz)	Removal	QTZ-0001
$1HF:10H_2O$	Si	Cleaning	SI-0004
$1HF:16H_2O$	Si	Native oxide removal	SI-0132a
xHF:xMeOH	Si	Cleaning	SI-0016
$1HF(40\%):1NH_4F(40\%)$ BHF	Si	Native oxide removal	SI-0020
$1HF:9NH_4F(40\%)$ BHF	Si	Native oxide removal	SI-0022
	SiO_2	Controlled removal	
	Si_3N_4	Controlled removal	
$2HF:13NH_4F$ BHF	Si	Native oxide removal	SI-0023
5 ml HF:20 g:NH_4F:300 ml H_2O BHF	Si	Native oxide removal	SI-0026
	Si_3N_4	Controlled removal	
$xHF:xNH_4F:xH_2O$ BHF	Si	Native oxide removal	SI-0028
	SiO_2	Controlled removal	
	Si_3N_4	Controlled removal	
30 ml HF:8,4 g NaF/l	Si	Electrolytic jet polish	SI-0174b
xHF:xEOH (MeOH or glycols)	Si	Electrolytic polish	SI-0041c
2 ml HF:4.3 g NaF:96 ml H_2O	Si	Native oxide removal	SI-0211
108 ml HF:350 g NH_4F:1000 ml H_2O	Si	Controlled removal	SI-0211
50 ml HF:50 g NH_4F.HF:100 ml H_2O:	Si	Native oxide removal	SI-0220
50 ml Gly	SiO_2	Controlled removal	
	Si_3N_4	Controlled removal	
	$Si_3(ON)x$	Controlled removal	
$xHF:xH_2O$	SiC	Cleaning	SIC-0001
xBHF	SiC	Removal	SIC-0005a
xHF:xKF, sat. sol. BHF	SiC	Electrolytic stain	SIC-0013b
$1HF:20H_2O$	SiO	Controlled removal	SIO-0003
$1HF:100NH_4F$, sat. sol. BHF	SiO_2	Controlled removal	SIO-0009
	Si_2N_4	Controlled removal	
$1HF:6\ NH_4F(40\%)$ BHF	SiO_2	Controlled removal	SIO-00011

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Formula	Material	Use	Ref.
	BSG	As above	
	PSG	As above	
	BPSG	As above	
53HF:37HCl	SiO_2	Cleaning, Corning #7720	SIO-0038b
xHF:xNH_4F:xH_2O BOE	Si_3N_4	Removal	SIN-0006
15 ml HF:200 ml NH_4.HF, sat. sol.	Si_3N_4	Controlled removal	SIN-0014
	$Si_3O_xN_y$	As above	
	SiO_2	As above	
50 ml HF:50 g NH_4F:HF:100 ml H_2O:	Si_3N_4	Controlled removal study	SIN-0008b
10 ml Gly	$Si_3O_xN_y$	As above	
1HF:1NH_4F(20%)	Ta	Preferential	TA-0004b
1HF:1H_2O	Ta	Cleaning	TA-0008
20 gNH_4F:100 ml H_2O	Ta	Polish	TA-0003h
x x%NH_4F	ThO_2	Preferential	THO-0002
1HF:1H_2O	Ti	Cleaning	TI-0002
1HF:1MeOH	Ti	Electrolytic polish	TI-0013
2HF:25NH_4F:5H_2O	TiO_2	Controlled removal	TIO-0006
134 ml HF:452 g NH_4F:625 ml H_2O	TiN	Controlled removal	TIN-0003
	TiO_2	As above	
1HF:1H_2O	W	Removal	W-0003b
xHF:xNH_4F	Zr	Polish	ZR-0009

FLUORINE, F_2

General: May occur as a free element in nature associated with volcanic eruptions, but will immediately combine with other elements such as hydrogen or sulfur to form more stable compounds.

In industry it is used as a corrosive gas in the study of metals and alloys for stability against chemical attack, as are chlorine and other mixed gases under various temperature conditions. Both drinking water and toothpastes are fluorinated as a medical specific against tooth decay.

Technical Application: The free gas is rarely used in Solid State processing, although it can be bubbled through a liquid etchant as an additional etching assist element to include stirring action. It has been grown as a single crystal under pressure and cryogenic conditions in vacuum for morphological study.

Etching: Vapor pressure under cryogenic conditions in vacuum.

FLUORINE ETCHANTS

F-0001
ETCH NAME: TIME:
TYPE: Pressure, preferential TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:
F_2, as a gas can be grown as a single crystal under pressure and cryogenic conditions in a vacuum system. Vary vapor pressure to preferentially etch in ingot.
REF: Schwentner, N et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1960

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FRESONITE, $Ba_2Si_2TiO_8$

General: This mineral was found as a minor occurrence near Fresno, California in the U.S. sometime after 1950. There is no use in industry, other than as a very minor ore of titanium.

Technical Application: The material has been studied in Solid State development as a possible piezoelectric material similar to alpha-quartz.

Etching: Mixed acids of HF:HNO_3

FRESONITE ETCHANTS

FRE-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

$Ba_2Si_2TiO_2$ single crystal material. Crystals are space group 4 mm^2. Various concentrations of the acid mixture shown are recommended from work done on $(Ag,Ti)_xSiO_4$. The crystals have piezoelectric properties similar to those of alpha-quartz.

REF: Richards, R L et al — *J Appl Phys*, 49,6025(1978)

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PHYSICAL PROPERTIES OF GADOLINIUM, Gd

Classification	Lanthanide
Atomic number	64
Atomic weight	157.25
Melting point (°C)	1312
Boiling point (°C)	3000
Density (g/cm^3)	7.89
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.021
Specific heat (cal/g) 25°C	0.071
Heat of fusion (k-cal/g-atom)	3.70
Latent heat of fusion (cal/g)	23.5
Heat of vaporization (k-cal/g-atom)	72
Atomic volume (W/D)	19.9
1st ionization energy (K-cal/g-mole)	142
1st ionization potential (eV)	6.16
Electronegativity (Pauling's)	1.1
Covalent radius (angstroms)	1.81
Ionic radius (angstroms)	0.62 (Gd^{+3})
Electrical resistivity (micro ohms-cm) 25°C	131 (134)
Compressibility ($cm^3/kg \times 10^{-6}$)	2.56
Cross section (barns)	46,000
Magnetic moment (Bohr magnetons)	7.95
Tensile strength (psi)	27,800
Yield strength (psi)	25,100
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	356,000
Transformation temperature (°C)	1260
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	4
Hardness (Mohs — scratch)	4
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Grey
Cleavage (basal)	(0001)

GADOLINIUM, Gd

General: Does not occur as a native element. It is one of the Rare Earths and classified in the yttrium sub-group. The primary mineral is gadolinite, $BeOFeY_2Si_2O_{10}$, which is variable in formula, and contains small quantities of many of the rare earth elements: Ce, La, Gd, Cs, etc. Also found in cerium earth minerals of which there are over 50 as silicates and phosphates. Monazite, $(Ce,La,Di)PO_4$, being a major phosphate commercially mined from monazite sands.

No major use in industrial metal processing due to limited quantities, occasionally used as a doping element in irons and steels; in solder alloys; and the rare earth oxides are used as coloring agents in glass and enamel.

Technical Application: No major use in Solid State processing to date. It has been used as a constituent in some artificial garnets.

Gadolinium has been grown as a single crystal in a study of growth methods, defects, and structure, along with other rare earth elements.

Etching: Acids. Air conversion to oxide.

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GADOLINIUM ETCHANTS

GD-0001
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat
DISCUSSION:
Gd, single crystal specimens. Describes a method of growing Rare Earth elements as single crystals. Thermal annealing was done to develop defects, low angle grain boundaries, and structure. Other elements grown were dysprosium, holmium, terbium, erbium, thulium, and yttrium.
REF: Nigh, H E — *J Appl Phys*, 34,3323(1963)

TIME:
TEMP: 800—1000°C

GADOLINIUM NITRIDE ETCHANTS

GDN-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
GdN_{12} specimens formed from alloy arc melted buttons. Wrap in tantalum sheet and anneal 3—9 weeks at 600—900°C and 2×10^{-7} Torr vacuum. Forms in the Cubic Laves structure. A study of Rare Earth (RE) nitrides. Other nitrides formed were La, Nd, Sm, Tb, Dy, Ho, Er, Y, Pr, and Ce. The SmN_{12} was formed in a silica capsule under 0.5 atm argon to prevent Sm evaporation. Nitrides were used in a thermal expansion study.
REF: Ibarra, M R et al — *J Phys Chem Solids*, 45,789(1984)

TIME:
TEMP:

GADOLINIUM TERBIUM IRON ETCHANTS

CDTF-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
1 .... HNO_3
1 .... H_2O
DISCUSSION:
GdTbFe thin films co-sputtered on inch square glass plates with 10—20 rpm holder rotation during metallization, and films were amorphous structure. See Iron for other etchants. (*Note:* A similar rotation method is used for evaporation of chromium for chrome glass masks used in photolithographic processing.)
REF: Taki, J — *J Appl Phys*, 55,2799(1984)

TIME:
TEMP:

PHYSICAL PROPERTIES OF GALLIUM, Ga

Classification	Metal
Atomic number	31
Atomic weight	69.72
Melting point (°C)	29.78
Boiling point (°C)	2403

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Density (g/cm^3)	5.907
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.08
Specific heat (cal/g) 25°C	0.088
Heat of fusion (cal/g)	19.18
Heat of vaporization (cal/g)	950—1020
Atomic volume (W/D)	11.8
1st ionization energy (K-cal/g-mole)	138
1st ionization potential (eV)	6.00
Electronegativity (Pauling's)	1.6
Covalent radius (angstroms)	1.26
Ionic radius (angstroms)	0.62 (Ga^{+3})
Vapor pressure (760 mmHg °C)	2400 (1784)
Cubic coefficient of expansion ($\times 10^{-5}$) 20°C	5.4
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	18
Electrical resistivity (micro-ohms-cm) 0°C	53.4
Electron work function (eV)	3.96
Cross section (barns)	3.0
Hardness (Mohs — scratch)	1.5—2.5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Grey/black
Cleavage (rhombic — poor)	$(10\bar{1}1)$

GALLIUM, Ga

General: Does not occur as a native element. It is a rare element found as a trace constituent in sphalerite, ZnS, other sulfides, and almost always in bauxite, essentially $Al_2O_3 \cdot 2H_2O$, as an admixture with clays. It is part of the aluminum family of elements — Al, Ga, In, Tl — as the reaction of its salts resembles those of aluminum. Besides mercury, cesium, and rubidium, gallium is the only metal that can be liquefied at or near room temperature (Ga m.p. = 29.78°C vs. RT = 22.2°C). Because of this low melting point, high purity gallium used in the Solid State and electronic fields is usually stored under refrigeration.

A primary industrial use is as a low temperature solder, as pure gallium or alloyed with lead, zinc, silver, etc. As it is liquid from near room temperature to 1600°C, it is used as the liquid filler in high temperature thermometers.

Technical Application: Both gallium and indium were two of the first p-type dopants used in the initial development of germanium as a semiconductor, and gallium is a major constituent in several compound semiconductors, such as gallium antimonide, GaSb; gallium phosphide, GaP and gallium arsenide, GaAs. Silicon has been the major semiconductor material since the mid-1950s, but gallium arsenide devices have become increasingly important since about the mid-1960s when they first appeared as a viable product.

Pure gallium and its alloys are used in Solid State and electronics as solders in fabricating assemblies, as have been indium solders. Both gallium and indium are used as paste smear contacts on molybdenum discs to mount and hold wafers during molecular beam epitaxy (MBE) or as a general holder of specimens for microscope study.

References here do not include single crystal gallium, though it can be so grown under vacuum cryogenic conditions like gases.

Etching: Soluble in acids, alkalies, and mixed acids. Clean with alcohols.

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GALLIUM ETCHANTS

GA-0001b
ETCH NAME: Methyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
*x .... MeOH

TIME:
TEMP: 0 to 8°C

* Chill with LN_2

DISCUSSION:
Ga as solid material. Because of the low melting point of gallium, it is usually stored at cold temperature in a refrigerator in sealed ampoules so it will not adsorb contaminating gases. In the liquid state it readily adsorbs oxygen. In order to desorb oxygen from gallium, place the gallium in methyl alcohol chilled with liquid nitrogen, LN_2, at or below the temperatures shown.
REF: Ibid.

GA-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl, conc.

TIME:
TEMP:

DISCUSSION:
Ga as solid material. Concentrated hydrochloric acid was used to clean gallium before mixing with zinc. The Ga/Zn mixture was used as a molten flux in LPE growth of zinc selenide, ZnSe.
REF: Fujitz, S et al — *J Appl Phys,* 50,1079(1979)

GA-0002
ETCH NAME: Aqua regia
TYPE: Acid, preferential
COMPOSITION:
3 .... HCl
1 .... HNO_3

TIME: 3 min
TEMP: 10°C

DISCUSSION:
Ga specimens were used in a study of superconducting transition. Samples were hot wire cut and etched in the solution shown to develop grain boundaries. Zinc hemispheres also studied.
REF: Cochran, J F & Mapother, D E — *Phys Rev,* 121,1688(1961)

GA-0003
ETCH NAME: Potassium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... x% KOH (NaOH)

TIME:
TEMP:

DISCUSSION:
Ga, as a constituent in single crystal GaAs p-type wafers fabricated as light emitting diodes with Al or Au dot contact pads. Where As is removed with HNO_3; Ga is removed with alkalies. Diodes studied for the effects of chemical surface treatment and annealing on

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light emission. Strong acids reduce or eliminate emission; basic solutions are good and 350°C in N_2, 5 min increases efficiency. Alkalies also remove $Ga(OH)_3$ and Ga_2O_3.
REF: Adachi, R & Hartnagel, H L — *J Vac Sci Technol,* 19(3),427(1961)

PHYSICAL PROPERTIES OF GALLIUM ANTIMONIDE, GaSb

Classification	Antimonide
Atomic numbers	31 & 51
Atomic weight	191.5
Melting point (°C)	712
Boiling point (°C)	
Density (g/cm^3)	5.60
Lattice constant (angstroms)	6.09
Energy gap (eV)	0.74
Refractive index (n =)	3.34
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Silver-grey
Cleavage (dodecahedral)	(110)

GALLIUM ANTIMONIDE, GaSb

General: Does not occur as a natural compound, though antimony does occur as a native element in minor quantities, and forms many minerals such as allemontite, $SbAs_2$, and stibnite, Sb_2S_3. The latter is of greater importance as an ore, and there are several other antimonates. There is no industrial use of the compound.

Technical Application: Gallium antimonide is a III—V compound semiconductor with the sphalerite, ZnS structure. It is a (111) surface polar compound with (111)Ga and ($\overline{111}$)Sb surfaces showing different etching characteristics, such that it is usually processed as a (100) oriented wafer like similar polar compounds. Single crystal ingots have been grown by the Horizontal Bridgman (HB); Czochralski (CZ); and the Float Zone (FZ) methods. Thin film epitaxy growth has been by Vapor Transport (VT) and Chemical Vapor Deposition (CVD). It also has been grown as a trinary compound with arsenic, aluminum or indium. Both the binary and trinary materials as wafers or thin films have been fabricated as diodes, transistors, laser diodes, or electroluminescent diodes and photo cathodes.

Etching: Water, HCl, HNO_3, halogens and mixed acids of HF:HNO_3, HCl:HNO_3.

GALLIUM ANTIMONIDE ETCHANTS

GASB-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP: Hot (80°C)
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
GaSB, (111) and (100) wafers used in a development etch study. When used hot, solution will attack gallium antimonide with moderate to vigorous reaction.
REF: Robbins, H & Schwartz, B — *J Electrochem Soc,* 107,108(1960)

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GASB-0001b
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
(1) x .... HNO_3, conc.
(2) 2 .... HNO_3
1 .... H_2O
TIME:
TEMP: RT
DISCUSSION:
GaSb, (111) and (100) wafers used in a development etch study. There are three commercial concentrations of nitric acid: standard, 70%, sometimes called "white" fuming; 72%, "yellow" fuming; and 74%, "red" fuming. All three concentrations were evaluated in addition to the dilute solution shown. In all cases, solutions showed moderate to vigorous reaction.
REF: Ibid.

GASB-0005
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
9 .... HNO_3
TIME: 1—5 min
TEMP: RT
DISCUSSION:
GaSb, (100) undoped wafers used in a study of surface oxidation. Surfaces were etch polished in this solution before oxidation. Oxidation was in air at 300 and 400°C for 1 or 2 h for a Ga_2O_3/GaSb structure. Little or no Sb appears in the oxide but does build up at the Ga_2O_3/GaSb interface.
REF: Harmon, L S et al — *Jpn J Appl Phys,* 23,1534(1985)
GASB-0009a: Fuller, C S & Allison, H W — *J Electrochem Soc,* 109,880(1962)
GaSb, (111) wafers. Solution described as a general polish etch.

GASB-0001c
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) 2 .... HCl
(2) 1 .... HCl
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
GaSb, (111), and (100) wafers. Etch reaction is shown to be moderate to vigorous with both formulations. Used in a development study of etchants for GaSb.
REF: Ibid.

GASB-0000d
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... H_2O_2 (30%)
1 .... NaOH (20%)
TIME:
TEMP: Hot
DISCUSSION:
GaSb, (111) and (100) wafers. A moderate etch reaction. Used in a development study of etchants for GaSb.
REF: Ibid.

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GASB-0002
ETCH NAME: TIME: 20 sec
TYPE: Acid, polish TEMP: RT
COMPOSITION:
(1) 1 .... HF (2) Rinse: HCl, hot (3) HOLD: under HCl
5 .... HNO_3
10 .... HAc
DISCUSSION:
GaSb, (111) and (100) wafers used as substrates for epitaxy growth of AlGaSb thin films. Substrates were mechanically polished with 0.25 μm diamond paste before polish etching. Wafers were placed in the epitaxy vacuum system still wet with HCl, and the acid was allowed to boil off in an H_2 atmosphere with heat at 300°C for several hours of *in situ* cleaning prior to deposition of AlGaSb.
REF: Nenow, D et al — *J Cryst Growth* 3,489(1984)
GASB-0003: Wada T et al — *J Cryst Growth,* 3,439(1984)
GaSb, (111), and (100) wafers. Used this solution formulation as a general polishing etch.

GASB-0004a
ETCH NAME: Water TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
GaSb, (100) undoped wafers used as substrates for MBE growth of GaSb/GaSb. A study of substrate surface preparation with different etching mixtures. Substrates were first lapped with SiC powder on a pad, then with 0.3 μm alumina. Water polishing of surface was used to remove lap/polish damage remaining before polish etching.
REF: Kodama, M et al — *J Electrochem Soc,* 132,659(1985)

GASB-0004b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
2 .... HF
18 .... HNO_3
40 .... CH_3COOH (HAc)
DISCUSSION:
GaSb, (100) undoped wafers used as substrates for MBE growth of GaSb/GaSb. See GASB-0004a. The base etch shown above was followed by: (1) hot HCl, 10 min; (2) 2% Br_2:MeOH, RT, 1 min; (3) $1HNO_3$:30HCl, at 5°C, 1 min. After etching, the wafers were annealed in an MBE vacuum system using REED at 20 KeV prior to epitaxy growth GaSb/GaSb. Prior to etching, after water polish substrates were degreased in TCE, then acetone, then MeOH. After etching, rinse in MeOH and spin dry.

GASB-0004c
ETCH TIME: BRM TIME: 2 min
TYPE: Acid, polish TEMP: RT
COMPOSITION:
x .... 2% Br_2
x .... MeOH

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DISCUSSION:

GaSb, (100) undoped wafers used as substrates. See both GASB-0004a and GASB-0004b, above, for details. Used to etch polish substrate surfaces.

REF: Ibid.

GASB-0009b: Ibid.

GaSb, (111) wafers. Solutions between 1—20% Br_2 used as general chem/mech polish etchants.

GASB-0006a

ETCH NAME: BRM — TIME: 20 sec + 10 sec

TYPE: Halogen, polish — TEMP: RT

COMPOSITION:

x .... 0.05% Br_2

x .... MeOH

DISCUSSION:

p-GaSb, (111) wafers used in a surface cleaning study, as follows: use lens paper saturated with solution as a lapping pad — lap for 20 sec — then dilute with MeOH — then continue lapping for 10 sec. Rinse in the solution shown and rinse in water. Authors state that percentage of bromine is not critical. (*Note:* With the bromine concentration shown, percentage would not be critical.) This surface study also included Si, Ge, GaP, GaAs, InP, InAs and InSb.

REF: Aspenes, D E & Studna, A A — *J Vac Sci Technol,* 20,488(1982)

GASB-0001e

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP: Hot

COMPOSITION:

1 .... HF

1 .... HNO_3

DISCUSSION:

GaSb, (111) and (100) wafers. Solution gives moderate to vigorous reaction.

REF: Ibid.

GASB-0007a

ETCH NAME: — TIME:

TYPE: Acid, passivating — TEMP: RT

COMPOSITION:

x .... HCl

DISCUSSION:

GaSb, (100), both undoped and Te-doped wafers used in a cleaning study before MBE thin film deposition. Spin-on HCl at 3500 rpm to passivate surfaces after acid etching.

REF: Kodama, M et al — *Jpn J Appl Phys,* 23,1657(1984)

GASB-0007b

ETCH NAME: — TIME: 1 min

TYPE: Acid, removal — TEMP: 5°C

COMPOSITION:

1 .... HNO_3

30 .... HCl

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DISCUSSION:
GaSb, (100), undoped and Te-doped wafers used in a cleaning study before MBE thin film deposition. This etch removed O_2 contamination from surfaces. Passivate surfaces with HCl (GASB-0007a).
REF: Ibid.

GASB-0007c
ETCH NAME:
TYPE: Acid, polish
TIME: 40 sec
TEMP: RT
COMPOSITION:
2 .... HF
18 .... HNO_3
40 .... HAc
DISCUSSION:
GaSb, (100) un-doped and Te-doped wafers used in a cleaning study before MBE thin film deposition. This solution leaves a high O_2 content on surface. Follow with $1HNO_3$:30HCl (GASB-0007b), which reduces O_2 content and leaves a highly reflective surface. Passivate surface with HCl (GASB-0007a).
REF: Ibid.

GASB-0008a
ETCH NAME: BRM
TYPE: Halogen, preferential
TIME: 20 sec
TEMP:
COMPOSITION:
1 .... Br_2
10 .... MeOH
DISCUSSION:
GaSb, (111) wafers. This solution of bromine-methanol (BRM) developed shallow etch pits on the (111)A surface.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970, 7

GASB-0008b
ETCH NAME:
TYPE: Acid, preferential
TIME: 1 min
TEMP:
COMPOSITION:
1 ml .... HCl
1 ml .... H_2O_2
2 ml .... H_2O
DISCUSSION:
GaSb, (111) wafers. The solution develops etch figures.
REF: Ibid.

GASB-0010
ETCH NAME:
TYPE: Acid, polish/preferential
TIME: 15 sec
TEMP: RT
COMPOSITION:
1 .... HF
2 .... HNO_3
1 .... HAc

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DISCUSSION:
GaSb, (111) wafers and other orientations. Solution used as a rapid polish etch and will develop etch pits.
REF: Gatos, H C & Lavine, M C — *J Electrochem Soc*, 107,427(1960)

GASB-0011
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... H_2O
DISCUSSION:
GaSb, (111) wafers. Solution used to polish $(\overline{111})$Sb faces.
REF: Faust, J W & Sager, A — *J Appl Phys*, 31,331(1960)

GASB-0012
ETCH NAME:
TYPE: Acid, selective
TIME:
TEMP: 50°C
RATE: 10 Å/sec
COMPOSITION:
1 .... H_2O_2
10 .... citric acid (50%)
[$(COOH)CH_2C(OH)(COOH)CH_2COOH$]
DISCUSSION:
GaSb, (100), p-type wafers with surfaces patterned by photolithography. Solution used to selectively etch pits in the material surface and also can be used to form mesas and other etched structures.
REF: Otsubo, M et al — *J Electrochem Soc*, 123,676(1976)

GASB-0013
ETCH NAME:
TYPE: Acid, selective
TIME:
TEMP:
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc
DISCUSSION:
GaSb, (111) wafers used as substrates for growth of heterojunctions as: GaIn/GaInSb/GaSb(111). After MBE growth wafers were cleaved ⟨110⟩ and the solution used to develop deposited layer structure.
REF: Mroczkowski, K S et al — *J Electrochem Soc*, 117,750(1968)

GASB-0014a
ETCH NAME:
TYPE: Acid, polish
TIME: 1 min
TEMP: RT
COMPOSITION:
1 .... HF
19 .... HNO_3
30 .... CH_3COOH (HAc)
DISCUSSION:
GaSb, (100) wafers within 0.2° of the crystal plane used as substrates for LPE growth of AlGaSb. Growth habit is sensitive to orientation. Substrates were cleaned as follows: (1)

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degrease with organic solvents; (2) etch in solution shown; (3) quench in 18 MΩ DI water and (4) MeOH wash. Under vacuum, prior to epitaxy growth: (1) bake at 700°C up to 24 h; (2) heat clean at 550°C, 1 h; (3) melt-back, 10—15 sec, at 10°C above growth temperature, with a 1—2 h soak prior to melt back with gallium. The etch solution leaves an oxide on the substrate surface and exposure to air will oxidize surfaces. Surfaces were studied by AES profiling in vacuum at 6×10^{-9} Torr. Sputter etching with argon was done at 1 kV under 5×10^{-5} Torr vacuum. In profiling, substrates were: (1) cleaved ⟨110⟩; (2) etched in solution shown and DI water rinsed; (3) then thermal cycled 1 h, at 400°C; (4) 1 h, at 550°C; and (5) Ga melt-back at 400°C. (*Note:* Excellent article on growth temperatures and morphology of AlGaSb surfaces.)
REF: Takeda, Y et al — *J Electron Mater*, 13,855(1984)

GASB-0014b
ETCH NAME: Hydrochloric acid — TIME: x min
TYPE: Acid, oxide removal — TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
GaSb, (100) wafers used as substrates for LPE growth of AlGaSb. Solution used to remove oxide from previous etching or exposure to air. Soak wafers in HCl, then blow off acid with nitrogen — or — HCl soak, then MeOH rinse and nitrogen blow dry. Both methods are effective for removing oxides. See GASB-0014a.
REF: Ibid.

GASB-0014c
ETCH NAME: A-B etch, dilute — TIME:
TYPE: Acid, stain — TEMP: RT
COMPOSITION:
1 .... A-B Etch
10 .... H_2O
DISCUSSION:
GaSb, (100) wafers Te-doped and used as substrates for LPE growth of AlGaSb. After epitaxy deposition, wafers were cleaved ⟨110⟩ and stained in the solution shown to develop AlGaSb/GaSb interface and defect structures in the thin film layer. (*Note:* The A-B solution shown is the Abrahams and Buiocchi preferential etch normally shown as A/B. The A-B designation is sometimes used for the Kern and Puotinen — RCA etch.)
REF: Ibid.
GASB-0017: Abrahams M S & Buiocchi, C J — *J Appl Phys*, 36,2855(1965)
Reference for A-B Etch shown in GASB-0014c (See GAS-0059). Solution mixture is 1 ml HF:2 ml H_2O:1 g CrO_3:8 g $AgNO_3$.

GASB-0015a
ETCH NAME: — TIME: 1 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
1 .... HF
9 .... HNO_3
20 .... HAc

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DISCUSSION:

GaSb, (111) wafers used in a study of growth striations. Mechanically polish surfaces before structure development with solution shown. See GASB-0015b for (211) wafer orientation use.

REF: Tohno, S-I & Katsui, A — *J Electrochem Soc*, 128,1614(1981)

GASB-0015b

ETCH NAME:

TYPE: Acid, preferential

TIME: 1—2 min

TEMP: RT

COMPOSITION:

1 .... $KMnO_4$

0.05 .... HF

20 .... HAc

DISCUSSION:

GaSb, (211) wafer orientation. Solution used to develop growth striations.

REF: Ibid.

GASB-0016

ETCH NAME:

TYPE: Acid, preferential

TIME:

TEMP:

COMPOSITION:

(A) 40 ml .... HF
3 g .... $AgNO_3$

(B) 4 g .... Cu_2O_3
40 ml .... H_2O

(C) 1 .... A
1 .... B
40 .... H_2O

DISCUSSION:

GaSb, (100) wafers cleaved and used as substrates for epitaxy growth of GaAlSb. Mix solution "C" when ready for use as a preferential etchant on the epitaxy layer. Intrinsic GaSb material is p-type; Te dopant for n-type.

REF: Merbarki, P et al — *J Cryst Growth*, 61,636(1983)

PHYSICAL PROPERTIES OF GALLIUM ARSENIDE, GaAs

Classification	Arsenide
Atomic numbers	31 & 33
Atomic weight	145
Melting point (°C)	1260 (1230)
Boiling point (°C)	
Density (g/cm^3)	5.37
Thermal conductance (W/cm/°C) 300°F	0.46
Coefficient of linear thermal expansion [L/L T(°C^{-1}) × 10^{-6}]	5.6
Specific heat (J/g/°C)	0.35
Lattice constant (angstroms)	5.654 (5.63)
Dielectric constant (e =)	10.9
Vapor pressure (°C) 1050°C	1
Refractive index (n =)	3.53
Formation temperature (°C)	600—800
Energy band gap (eV)	1.35
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube, fcc

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Color (solid)	Grey-silver
Cleavage (cubic)	(001)

GALLIUM ARSENIDE, GaAs

General: Does not occur as a natural compound, although there are several other metallic arsenides of iron, copper, cobalt, nickel and platinum whose minerals may contain sulfur as well as arsenic. The only industrial application of gallium arsenide is as a compound semiconductor.

Technical Application: Gallium arsenide is a III—V compound semiconductor with the sphalerite, ZnS structure, even though it is referred to as cubic, fcc. It is a (111) surface polar compound with (111)Ga and ($\overline{1}\overline{1}\overline{1}$)As showing different etching characteristics, such that it is usually wafer processed in (100) orientation as are other such polar compounds.

Germanium and silicon — the two elemental semiconductors — were first developed in the late 1940s, and gallium arsenide was one of the first compound semiconductors developed in the mid-1950s. It was initially grown by the Horizontal Bridgman (HB) method. It is still so grown, but much larger wafers (now up to 8″ diameter) are available as Czochralski (CZ) ingots.

As an epitaxy thin film it is grown by horizontal or vertical CVD, to include OMCVD, or by MBE.

Development of gallium arsenide has been much slower than that of silicon, which is still the major semiconductor that developed the present electronic industry as it is known today. The compound semiconductors, as a group, are more brittle than either germanium or silicon, more problematical in handling and, though gallium arsenide has better high frequency characteristics than the elemental semiconductors, the control of doping to obtain operational devices was an initial problem factor, as was temperature control . . . both gallium and arsenic can vaporize from the solid compound during processing . . . and, in addition, there was far more emphasis on silicon technology up through the late 1960s.

With development of the Schottky Barrier type devices, gallium arsenide has been fabricated as a field effect transistor (FET) with a gate, source, and drain configuration — the base wafer semi-insulating (SI) — doped with chromium, and the active gold or aluminum gate at the compound/metal interface. The material for such devices are shown here as GaAs:Cr, (100 (SI) wafers.

Devices are now fabricated as low noise or power FETS: the LN-FET or P-FET, respectively. This technology has been extended to other compound semiconductors, such as an InP:Fe, (100) (SI) wafer. And today, with the development of molecular beam epitaxy (MBE), multilayered structures are under device development as the heterojunction or heterostructure devices, which include different epitaxy layered elements or compounds, plus oxides, nitrides, metals grown on substrates of GaAs, etc. Some of the devices fabricated are FETs, Gunn and IMPATT diodes, thyristors, rectifiers, and GaAs:Al trinary compounds are being developed as solar cells with up to 30% efficiency, as compared to silicon with only about 18%. Other trinary compounds with phosphorus and indium are under evaluation.

Gallium arsenide is grown in single crystal ingot form and used, directly, as a device; deposited as a single crystal or polycrystalline thin film; or used as a substrate for other epitaxy growth in device fabrication. This latter use, as a chromium-doped semi-insulating substrate, is probably the most widely used wafer form for current device processing, although there is much on-going development of the trinary AlGaAs material for an improved solar cell.

Etching: Mixed acids HF:HNO_3 + HCl or H_2O_2. Alkali + halogen; halogens, molten fluxes. Gases as DCE and thermal etching.

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SELECTION GUIDE: GaAs

(1) Br_2:MeOH (BRM)
- (i) Oxide Removal: GAS-0132
- (ii) Polish: GAS-0001a; -0184a; -0005a; -0012a; -0013a; -0004a; -0200; -0006; -0007a; -0011; -0202; -0010
- (iii) Preferential: GAS-0002; -0173b
- (iv) Selective: GAS-0009
- (v) Thinning: GAS-0004a; -0008

(2) Br_2:EOH
- (i) Polish: GAS-0015
- (ii) Preferential: GAS-0013

(3) I_2:MeOH
- (i) Polish: GAS-0015

(4) $NH_4OH:H_2O_2$
- (i) Polish: GAS-0007c; -0006b
- (ii) Selective: GAS-0018; -0023; -0025
- (iii) Staining: GAS-0022

(5) $NH_4OH:H_2O_2:H_2O$
- (i) Oxidation: GAS-0181
- (ii) Polish: GAS-0007c; -0006b
- (iii) Removal: GAS-0001b
- (iv) Step-etch: GAS-0022
- (v) Junction: GAS-0021

(6) HCl, conc.
- (i) Cleaning: GAS-0028; -0207; -0029; -0018b; -0118; -0199
- (ii) Preferential: GAS-0192
- (iii) Oxide Removal: GAS-0114
- (iv) Removal: GAS-0182b; -0140

(7) HCl, vapor
- (i) Oxide Removal: GAS-0074

(8) $HCl:H_2O$
- (i) Cleaning: GAS-0004a; -0117
- (ii) Removal: GAS-0001c; -0030

(9) HCl:EOH
- (i) Oxide removal: GAS-0001d

(10) $HCl:FeCl_3$
- (i) Preferential: GAS-0174

(11) $HCl:HNO_3$
- (i) Dislocation: GAS-0186; -0189
- (ii) Junction: GAS-0056b
- (iii) Polish: GAS-0056a; -0179
- (iv) Removal: GAS-0190; -0140c; -0197

(12) $HCl:HNO_3:H_2O$
- (i) Preferential: GAS-0167c; -0052; 0044c; -0144a
- (ii) Polish: GAS-0057; -0148; -0176; -0178
- (iii) Junction: GAS-0056a

(13) $HCl:HNO_3$:Glycerin
- (i) Polish: GAS-0050; -0006e; -0051

(14) $HCl:H_2O_2:H_2O$
- (i) Polish: GAS-0104; -0141
- (ii) Removal: GAS-0186
- (iii) Structure: GAS-0060

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(15) H_2O & H_2O:O_2
  (i) Oxidation: GAS-0001e; -0181
(16) NaOCl (Clorox)
  (i) Polish: GAS-0012b; -0113; -0114; -0184; -0195a
  (ii) Preferential: GAS-0173a
(17) HCl:HAc:$K_2Cr_2O_7$
  (i) Polish: GAS-0041
(18) HF, conc.
  (i) Oxide removal: GAS-0191
  (ii) Selective: GAS-0024
(19) HF, vapor
  (i) Cleaning: GAS-0129
(20) HF:H_2O
  (i) Cleaning: GAS-0112
(21) HF:HNO_3
  (i) Cleaning: GAS-0047b
  (ii) Removal: GAS-0140d
(22) HF:HNO_3:H_2O
  (i) Cleaning: GAS-0047a
  (ii) Polish: GAS-0044c; -0006d; -0046; -0045b; -0146b; -0147; -0211a
  (iii) Preferential: GAS-0146d; -0146e; -0177
  (iv) Staining: GAS-0211a
(23) HF:HCl:HNO_3
  (i) Polish: GAS-0055; -0145a
(24) HF:HNO_3:HAc
  (i) Cleaning: GAS-0038b
(25) HF:HNO_3:$AgNO_3$: + H_2O
  (i) Preferential: GAS-0146c; -0048; -0119b
(26) HF:H_2O_2
  (i) Preferential: GAS-0049; -0053a; -0144d
(27) HF:H_2O_2:H_2O
  (i) Junction: GAS-0212b
  (ii) Polish: GAS-0053b
  (iii) Preferential: GAS-0045d; -0044f; -0168; -0144e-f; -0157; -0167a; -0146f; -0144b
  (iv) Structure: GAS-0054; -0160
(28) HF:H_2O_2:H_2SO_4
  (i) Polish: GAS-0088
  (ii) Thinning: GAS-0088
(29) HF:CrO_2:H_2O
  (i) Dislocation: GAS-0192
(30) HNO_3, conc.
  (i) Oxidation: GAS-0139
  (ii) Removal: GAS-0140b
  (iii) Staining: GAS-0042
(31) HNO_3:H_2O
  (i) Junction: GAS-0180
  (ii) Polish: GAS-0145b
  (iii) Preferential: GAS-0043; -0044b; -0183b; -0044a; -0045a; -0120; -0146a
  (iv) Removal: GAS-0140b
(32) HNO_3:Tartaric acid
  (i) Preferential: GAS-0167b

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(33) HNO_3:H_2O:$AgNO_3$
  (i) Preferential: GAS-0045c
(34) H_3PO_4:HNO_3
  (i) Polish: GAS-0110a
(35) H_3PO_4:H_2O_2:H_2O
  (i) Selective: GAS-0108a
  (ii) Removal: GAS-0105; -0106
  (iii) Thinning: GAS-0108b
  (iv) Via-hole: GAS-0109
(36) H_3PO_4:H_2O_2:MeOH
  (i) Polish: GAS-0110b
  (ii) Selective: GAS-0096b
(37) H_3PO_4:H_2O_2:H_2SO_4
  (i) Dislocation: GAS-0004d; -0110c
(38) Vacuum
  (i) Cleaning: GAS-0156
(39) Argon, Ar
  (i) Cleaning: GAS-0184
  (ii) Thinning: GAS-0186b
(40) H_2SO_4:H_2O: + O_2
  (i) Cleaning: GAS-0149
  (ii) Oxidation: GAS-0181
  (iii) Polish: GAS-0187b
(41) H_2SO_4:Polypropaline glycol
  (i) Dislocation: GAS-0121
(42) H_2SO_4:H_2O_2
  (i) Cleaning: GAS-0150; -0194
  (ii) Removal: GAS-0150
(43) H_2SO_4:H_2O_2:H_2O
  (i) Cleaning: GAS-0066; -0069; -0074; -0131; -0198; -0191a; -0195b; -0200; -0077; -0088; -0081; -0082; -0083; -0084; -0085; -0086; -0087; -0091; -0098; -0099; -0100; -0102; -0103; -0125; -0128; -0151; -0152; -0153; -0154; -0155; -0165; -0170; -0171; -0172; -0182a
  (ii) Oxide removal: GAS-0114
  (iii) Junction: GAS-0099; -0169; -0193b
  (iv) Polish: GAS-0062; -0063; -0065; -0069; -0070; -0073; -0075; -0130; -0056b; -0077; -0007h; -0079; -0089; -0091; -0101; -0182a; -0158; -0159; -0160; -0212a
  (v) Preferential: GAS-0064; -0116; -0164
  (vi) Removal: GAS-0068; -0070; -0126; -0212c
  (vii) Selective: GAS-0063a,b-m; -0006g; -0072; -0076; -0078
  (viii) Step-etch: GAS-0067; -0089; -0090
  (ix) Thinning: GAS-0090
(44) I_2:KI:H_2O
  (i) Selective: GAS-0061e-f
(45) Quinone:Hydroquinone
  (i) Selective: GAS-0060
(46) $Ce(SO_4)_2$:$Ce(NO_3)_3$ + H_2O
  (i) Selective: GAS-0061b
(47) $K_3Fe(CN)_6$:$K_4Fe(CN)_6$ + H_2O
  (i) Selective: GAS-0061c-d

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(48) A/B Etch
  (i) Dislocation: GAS-0059; -0130; -0119a; -0181
(49) $KOH:H_2O$
  (i) Junction: GAS-0210; -0212d
(50) NaOH/KOH, molten flux
  (i) Preferential: GAS-0032; -0033; -0034; -0035; -0157; -0163b; -0119b; -0122; -0123; -0124; -0127; -0162; -0163
(51) NaOH:KOH, molten flux
  (i) Preferential: GAS-0036
(52) KOH:NaOH:Gly/EG
  (i) Preferential: GAS-0036
(53) $KOH:H_2O + O_2$
  (i) Oxidation: GAS-0181
(54) $KOH:K_2Fe(CN)_6:H_2O$
  (i) Polish: GAS-0040
  (ii) Preferential: GAS-0019
  (iii) Staining: GAS-0037; -0038b
(55) $NaOH:H_2O_2 + H_2O$
  (i) Junction: GAS-0187
  (ii) Polish: GAS-0175; -0115
  (iii) Preferential: GAS-0031; -0183a; -0185; -0187; -0142; -0167d; -0173c
  (iv) Selective: GAS-0188a
  (v) Removal: GAS-0143
(56) $MeOH:Cl_2$
  (i) Polish: GAS-0187a

GALLIUM ARSENIDE ETCHANTS

GAS-0001a
ETCH NAME: BRM
TYPE: Halogen, polish
TIME:
TEMP: RT
COMPOSITION:
  x .... x% Br_2
  x .... MeOH
DISCUSSION:

GaAs:Cr, (100) (SI) wafers prepared as substrates for epitaxy growth of GaAs. The following cleaning procedure was used: (1) etch polish in solution shown; (2) damage removal/polish in $H_2SO_4:H_2O_2:H_2O$; (3) boil in DI H_2O to develop oxide; (4) remove oxide with $HCl:H_2O$; (5) repeat boiling water and (6) remove oxide with HCl:EOH. (*Note:* Bromine concentration not shown.)

REF: Lewis, B F et al — *J Phys Chem,* 45,419(1984)

GAS-0184a: Bhat, R — *J Electron Mater,* 14,433(1985)

GaAs:Cr, (100) (SI) wafers oriented 6°-off (100) toward (111)A, also (111), and (110) wafers. Wafers used as substrates for OMCVD epitaxy growth of both GaAs and AlGaAs layers. Prepare substrates by (1) chem/mech polish in solution shown to remove lap damage; (2) degrease, and (3) etch clean in $5H_2SO_4:1H_2O_2:1H_2O$.

GAS-0005: Davis, G A et al — *J Cryst Growth,* 69,141(1984)

GaAs, (100) wafers cut 2°-off toward (110), used as substrates for epitaxy growth of GaAs layers. After mixing BRM solution, allow it to sit 10 min before use. Clean substrates as follows: (1) chem/mech polish with solution shown; (2) degrease in boiling TCE, and rinse with MeOH, then (3) etch clean in $10H_2SO_4:1H_2O_2$. Immediately before loading in vacuum, rinse in DI H_2O. (*Note:* Allowing the BRM solution to sit 10 min before use

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produces a "stagnant" solution as some of the bromine will gas-off while diffusing into the methanol. It has been shown by other authors that bromine diffusion in methanol is complete in about 10 min.)

GAS-0012a: Palmateer, S C & Eastman, L F — *J Vac Sci Technol,* B2,188(1984)

GaAs:Cr, (100) (SI) wafers cut from ingots grown by Bridgman method and by HPLEC or LPLEC. After cutting, wafers were chem/mech polished in the solution shown, annealed 24 h in H_2, then re-polished in the solution shown or in Clorox. Wafers were then polished in $5H_2SO_4$:$1H_2O_2$:$1H_2O$ just before loading in an MBE vacuum system for epitaxy growth of GaAs.

GAS-0214: Inarey, S & MacLaurin, B — *J Vac Sci Technol,* A2(2),358(1985)

GaAs, (100), n-type wafers used as substrates for Ge growth and Au metallizing. Clean GaAs: (1) chem/mech polish with BRM solution; (2) MeOH rinse; (3) HCl dip: (4) DI H_2O rinse; and (5) in vacuum MBE system Ar^+ ion sputter clean prior to Ge growth.

GAS-0237: Kolodziejski, L A et al — *J Vac Sci Technol,* B3(2),714(1985)

GaAs, (111) wafers used as substrates for MBE deposition of CdTe and CdMnTe thin films as dilute, magnetic semiconductor superlattices. BRM solutions can be used as removal and polishing etchants for these compounds. There was a 14% mismatch lattice of CdMnTe/GaAs.

GAS-0238: Qadri, S B et al — *J Vac Sci Technol,* B3(2),718,(1985)

GaAs, (110) wafers used as substrates for MBE deposition of Fe thin films for a structural study of films by X-ray. Films were (110) oriented with a 1.34% lattice mismatch. BRM solutions can be used as removal and polishing etchants for these materials.

GAS-0002
ETCH NAME: BRM
TYPE: Halogen, preferential
COMPOSITION:
x .... 1% Br_2
x .... MeOH
DISCUSSION:

TIME:
TEMP:

GaAs, (111)A wafer surfaces etched in the solution shown by immersion. Surface etch pits will have (322) pit side slopes if the bromine concentration is greater than 1%. The plane slope angle was measured as 10° from (111)A surface.

REF: Kozi, L A & Rode, L A — *J Electrochem Soc,* 122,1511(1975)

GAS-0003a
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 1% Br_2
x .... MeOH
DISCUSSION:

TIME:
TEMP: RT
RATE: 1 μm/min on (110)

GaAs, (110), (111), (100) wafers used in a general etch rate study. Etch ratio shown as: 6:5:4.6:1 for (110):($\overline{111}$)As:(100):(111)Ga. Solution used as an immersion etch to establish etch rates. (*Note:* (111)Ga = (111)A and ($\overline{111}$)As = ($\overline{111}$)B in general crystallographic notation of polar compounds.)

REF: Ghandhi, S K — *VLSI Fabrication Procedures,* John Wiley & Sons, New York, 1983

GAS-0004a: Budutt, R et al — *J Electrochem Soc,* 128,1573(1981)

GaAs, (100), n-type wafers used as substrates for growth of GaAs layers by LPE. Substrates were prepared as follows: (1) Syntron system used to chem/mech polish with solution shown; (2) degrease; (3) etch clean in 1HCl:$2H_2O$ and DI water rinse. After LPE growth of (GaAl)As, substrate wafer was thinned with 1.5% Br_2:MeOH for microscope

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study of the epitaxy layer. Other wafers were cleaved ⟨110⟩ and defect etched in H_3PO_4:H_2SO_4:H_2O_2, RT, 1—2 min. Defects are similar to stacking faults.
GAS-0200: Cochran, L & Gomez, A — personal communication, 1979

GaAs:Cr, (100) (SI) wafers used in the fabrication of GaAs FET devices. Wafer back-weighted with steel discs and chem/mech polished on a shaker table using the solution shown.

GAS-0006a
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 0.05% Br_2
x .... MeOH
TIME: 20 sec + 10 sec
TEMP: RT
DISCUSSION:

GaAs, (100), n-type wafers used in a surface cleaning study. Cleaning was done as follows: (1) chem/mech hand lap on lens paper soaked with solution shown and, after 20 sec dilute with MeOH, and continue lapping an additional 10 sec; (2) rinse in NH_4OH:H_2O (AMH solution); (3) rinse in BRM solution shown, and (4) final DI water rinse. Method also used on: Si, Ge, GaP, GaSb, InP, InAs, and InSb.
REF: Aspenes, D E & Studa, A A — *J Vac Sci Technol,* 20,488(1982)

GAS-0004b
ETCH NAME: BRM
TYPE: Halogen, thinning
COMPOSITION:
x .... 1.5% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:

GaAs, (100) wafer substrates used for (GaAl)As epitaxy growth by LPE. After epitaxy the GaAs substrate was etch thinned and removed leaving the (GaAl)As thin film free for TEM study. Stacking faults (SFs) start near the substrate/epitaxy interface. Micro-cracks were observed in the thin sections and attributed to probable tensile stress release.
REF: Ibid.

GAS-0007a
ETCH NAME: BRM
TYPE: Halogen, isotropic
COMPOSITION:
x .... 1—3% Br_2
x .... MeOH
TIME:
TEMP: RT
RATE: See discussion
DISCUSSION:

GaAs, (111), (100), and (110) wafers used in a general etch rate study of various concentrations of bromine-methanol solutions. 1—2% Br_2 concentrations are preferential on both (111)A and (111) faces. For a 1% Br_2 concentration, etch rate increased as: (110)>(111)B>(100)>(111)A with (110) being most rapid. (*Note:* This is an excellent review article of GaAs etching.)
REF: Kern, W — *RCA Rev,* 39,278(1978)
GAS-0011: Christon, A et al — *Semiconductor International,* May 1979, 59

GaAs, (100) and InP, (100) wafers used in the characterization of defects by ASLEEP, SEM, and scanning AES. A 1% Br_2 solution was used at RT, 1—5 min for polishing.

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Depending upon application, bromine content can vary from 0.1 to 5% with good polishing results.

GAS-0202: Walker, P — personal application, 1980

GaAs:Cr, (100) (SI) wafers used in fabricating GaAs LN-FET devices. A 2% Br_2 solution was used as a spray cleaning etch after metallization pattern evaporation. After etching, rinse in MeOH and N_2 blow dry.

GAS-0010: Tuck, E — *J Mater Sci*, 10,321(1976)

GaAs, (100) and GaP, (100) wafers used in a general polish etch study of both materials. A $1Br_2$:9MeOH mixture gave an approximate $^1/_4$ μm/min removal rate. Described as only one of several bromine concentrations evaluated.

GAS-0008
ETCH NAME; BRM
TYPE: Halogen, thinning
COMPOSITION:
x .... 5% Br_2
x .... MeOH
TIME:
TEMP:
DISCUSSION:

GaAs, (100), and InP, (100) wafers used for evaporation of gold thin films. After annealing of metallized wafers, they were black wax patterned and the GaAs and InP substrates were etch thinned in the solution shown for TEM study of line defects at the substrate/gold interfaces and in the gold thin film.

REF: Nakahara, S et al — *J Electrochem Soc*, 131,1917(1984)

GAS-0009
ETCH NAME:
TYPE: Halogen, selective
COMPOSITION:
x .... 5% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:

GaAs, (100), (111) and (110) wafers. Controlled pits were etched into wafer surfaces selectively through photo resist patterned SiO_2 masks. Etch rates for the different plane surfaces were shown to be similar to rates described by Kern (GAS-0007a).

REF: Tarui, Y et al — *J Electrochem Soc*, 118,118(1971)

GAS-0013
ETCH NAME: BRE
TYPE: Halogen, preferential
COMPOSITION:
x .... 1% Br_2
x .... EOH
TIME:
TEMP: RT
RATE: See discussion
DISCUSSION:

GaAs, (100), (111) and (110) wafers used in a general study of etch rates and surface reactions. The solution is preferential on all orientations and etch rates are similar to those described by Kern (GAS-0007a) for BRM solutions. This says that bromine solutions with either methanol (BRM) or ethanol (BRE) show equivalent rates and reactions.

REF:

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GAS-0014
ETCH NAME: BRE
TYPE: Halogen, polish
COMPOSITION:
x .... 2% Br_2
x .... EOH
TIME:
TEMP: RT
RATE: 8 μm/min
DISCUSSION:

GaAs, (111) wafers. Specimen surfaces were polish etched with a jet of the solution shown with specimens rotating, as on a photo resist spinner. Authors say this is nonpreferential on (111) orientations.
REF:
GAS-0260: Bertrand, P A — *J Electrochem Soc,* 132,923(1985)

GaAs:Zn, (100) wafers, p-type, used in a study of photochemical oxidation. Solution shown used 10 sec at RT, with MeOH rinse to remove native oxide; following with EOH rinse and HCl, RT, 15 min and DI H_2O rinse. Hold specimens in a glove box in air at RT for several months to develop a native oxide.

GAS-0003b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
20 .... NH_4OH
7 .... H_2O_2
973 .... H_2O
TIME:
TEMP:
DISCUSSION:

GaAs, (100), (111) and (110) wafers used in a general etch rate study. Etch rates are much slower with this solution than those obtained with bromine-methanol. See GAS-0003a.
REF: Ibid.

GAS-0001c
ETCH NAME: Hydrochloric acid
TYPE: Acid, oxide removal
COMPOSITION:
(1) 1 .... HCl
1 .... H_2O_2
1 .... H_2O
(2) 1 .... HCl
1 .... H_2O
TIME:
TEMP:
DISCUSSION:

GaAs:Cr, (100) (SI) wafers used as substrates for epitaxy growth of GaAs layers. As part of the substrate cleaning process, wafers were boiled in DI water and then stripped with the solution shown or with 1HCl:1EOH.
REF: Ibid.
GAS-0030a: Siracusa, M — personal communication, 1978

GaAs:Cr, (100) (SI) wafers used in fabricating FET devices. Solution used as a dip cleaning step with DI water rinse prior to wafer metallization. The HCl is followed with a dip in 1HF:1H_2O and DI water rinse, immediately before placing in the vacuum system. N_2 blow dry, in both cases. (*Note:* Many authors refer to using this 50% mixture for cleaning purposes.)
GAS-0247: Wu, C S et al — *J Electrochem Soc,* 132,918(1985)

GaAs:Si, (100) n-type wafers used as substrates for metallization with Er and Si in a study of ion beam etching. Clean substrates: (1) in acetone; (2) in isopropanol (*ISO*); (3) wash in solution (1), and (4) rinse in DI H_2O prior to metal evaporation.

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GAS-0004c
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
1 .... HCl
2 .... H_2O
TIME:
TEMP:
DISCUSSION:
GaAs, (100) n-type wafers used as substrates for LPE growth of GaAlAs layers. Solution used as part of substrate cleaning process following degreasing. See GAS-0004a for additional discussion.
REF: Ibid.

GAS-0007c
ETCH NAME:
TYPE: Acid, isotropic
COMPOSITION:
x .... NH_4OH
x .... H_2O_2
TIME:
TEMP:
DISCUSSION:
GaAs, (100) wafers, and other orientations. Solution used as a general polish etch similar to BRM solutions.
REF: Ibid.

GAS-0015
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
$^1/_4$ g .... I_2
250 ml .... MeOH
TIME:
TEMP: RT
DISCUSSION:
GaAs:Cr, (100) (SI) wafers. The amount of iodine can be varied. The mixture as shown was used as a surface polish and cleaning solution similar to BRM solutions prior to metal evaporation. Wafers were used in the fabrication of Low Noise GAS-FETs. Also used as a final dip-rinse of GaAs and silicon, (111) wafers prior to diffusion, and for cleaning alumina, quartz, and sapphire circuit substrates prior to metallization. In both cases, remaining iodine on the surfaces was used to complex remaining ionic contamination from prior etching and cleaning steps to obtain a molecularly clean surface for improved diffusion depth control, and/or better metal adhesion.
REF: Walker, P — personal development, 1965/1980

GAS-0016
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
3 .... *CP4
1 .... MeOH
1 .... H_2O
TIME:
TEMP:
*CP4: 2HF:5HNO_3:2HAc: 1% Br_2
DISCUSSION:
GaAs wafers. A general polish etch for gallium arsenide wafers. After mixing the solution it should be allowed to age before use. (*Note:* This is a form of "stagnant" etching.)
REF: TI Rep

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GAS-0182a
ETCH NAME: TIME:
TYPE: Acid, junction TEMP:
COMPOSITION:
1 .... HF
5 .... HNO_3
DISCUSSION:
GaAs, (100) wafers doped with germanium under arsenic pressure and used in a study of the effect of arsenic during doping. Solution used as a p-n junction staining and development etch.
REF: McCaldin, J O & Harada, K — *J Appl Phys,* 31,2065(1960)

GAS-0018a
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
(1) 1 .... NH_4OH (2) x .... HCl, conc. (3) x .... Ar^+ ions
20 .... H_2O_2
DISCUSSION:
GaAs, (100), n-type, wafers used as substrates for LPE growth of Double Heterostructures (DHs) as follows: n-GaAs cap/InGaAsP/InGaP/GaAs substrate. Solution (1) was used to selectively remove the substrate of DH fabricated diodes that had failed life test, and also remove the n-GaAs cap. The InGaAsP layer was selectively removed with concentrated HCl, and the n-InGaP layer was argon ion sputter removed.
REF: Veda, O et al — *J Appl Phys,* 57,1523(1985)

GAS-0019
ETCH NAME: Ammonium hydroxide TIME:
TYPE: Acid, junction stain TEMP:
COMPOSITION:
1 .... NH_4OH
5 .... H_2O
DISCUSSION:
GaAs, (100) Zn-doped, p-type wafers used as substrates for MBE growth of GaAlAs layers which were alternately doped with Ge, then Mg (both p-type dopants). Wafers were cleaved ⟨110⟩ and stained with the solution shown to develop both diffused junctions as well as layer structure.
REF: Schwartz, B et al — *J Electrochem Soc,* 131,1703(1984)
GAS-0020: Schwartz, B et al — *J Electrochem Soc,* 131,1674(1984)
GaAs wafers. Similar work as in GAS-0019.
GAS-0006b: Ibid.
GaAs, (100), n-type wafers used in a cleaning study. After BRM etching, an NH_4OH:H_2O solution was used as a rinse and called the AMH solution.

GAS-0030b
ETCH NAME: 0°C etch TIME:
TYPE: Acid, cleaning TEMP: 0°C
COMPOSITION:
100 ml .... NH_4OH
1000 ml .... H_2O

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DISCUSSION:

GaAs:Cr, (100) (SI) wafers used in the fabrication of GaAs FET devices. This solution is widely used both to clean the GaAs surfaces as well as to clean evaporated aluminum patterns on wafers, and the ammonium hydroxide concentration may vary from 10 to 200 ml. The solution can be chilled with either LN_2 or dry ice, CO_2.

REF: Siracusa, M — personal communication, 1978

GAS-0021

ETCH NAME:

TIME:

TYPE: Acid, junction

TEMP:

COMPOSITION:

RATE: 0.16 μm/min

3 .... NH_4OH

1 .... H_2O_2

150 .... H_2O

DISCUSSION:

GaAs, (100) wafers zinc diffused. Solution used to develop the p-n diffused junction. Wafers were cleaved, ⟨110⟩ to expose junction prior to etching.

REF: Jett-Field, R & Ghandhi, S R — *J Electrochem Soc,* 129,1566(1982)

GAS-0022

ETCH NAME:

TIME:

TYPE: Acid, step-etch

TEMP:

COMPOSITION:

3 .... NH_4OH

1 .... H_2O_2

1 .... H_2O

DISCUSSION:

GaAs:CR, (100) wafers within $^1/_2°$ of plane, and un-doped wafers used as substrates for MOCVD epitaxy of GaAs/GaAs(100). Epitaxy GaAs was doped with Sn. The solution shown was used for step-etching the epitaxy layer during C-V profiling.

REF: Parsons, J A & Krajenbrink, F G — *J Cryst Growth,* 68,60(1984)

GAS-0006c

ETCH NAME:

TIME:

TYPE: Acid, isotropic

TEMP:

COMPOSITION:

1 .... NH_4OH

700 .... H_2O_2

DISCUSSION:

GaAs, (100) wafers and other orientations. Solution has been applied as a general polishing etch using a saturated pellon pad with rotation.

REF: Ibid.

GAS-0023

ETCH NAME:

TIME:

TYPE: Acid, selective

TEMP:

COMPOSITION:

x .... H_2O_2

x .... NH_4OH for pH 7

DISCUSSION:

GaAs, (100) substrates with epitaxy layer growth of GaAlAs. This solution was used

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to selectively remove the GaAs substrate for thin section study of the general morphology and structure of GaAlAs.
REF: Logan, R A & Reinhart, F K — *J Appl Phys,* 44,4172(1973)

GAS-0024
ETCH NAME: Hydrofluoric acid
TYPE: Acid, selective
COMPOSITION:
x .... HF
DISCUSSION:
GaAs, ($\overline{111}$)B and (100) both n-type and un-doped wafers used as substrates for epitaxy growth of Be doped GaAlAs, p-type. The GaAlAs layers were selectively removed from the GaAs substrates with hydrofluoric acid.
REF: Masu, K et al — *J Electrochem Soc,* 129,1623(1982).

TIME:
TEMP:

GAS-0025
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
x .... NH_4OH
x .... H_2O_2
DISCUSSION:
GaAs, (100) Si-doped wafers used as substrates for LPE growth of GaAlAs layers. This solution was used to selectively remove the GaAs substrate. The author refers the etch to Ralogan & Reinhart — *J Appl Phys,* 44,4127(1973).
REF: Swaninathan, V et al — *J Electrochem Soc,* 129,1563(1982)

TIME:
TEMP:

GAS-0026
ETCH NAME:
TYPE: Electrolytic, oxidation
COMPOSITION:
x .... *EDTA, 2 *M*
x .... NH_4OH

TIME:
TEMP:
ANODE: GaAs
CATHODE: Pt foil
POWER: To 1000 VDC

*Ethylene diamine tetraacetic disodium salt

DISCUSSION:
GaAs, (100) and GaAs, (111) wafers. Both materials were anodically oxidized in a study of oxidation defects. Mixtures of Br:MeOH also were used to develop defects.
REF: Elliot, C R & Regnault, J C — *J Electrochem Soc,* 127,1557(1980)

GAS-0077
ETCH NAME: Hydrochloric acid, vapor
TYPE: Acid, oxide removal
COMPOSITION:
x .... HCl, vapor
DISCUSSION:
GaAs, (100) wafers used as substrates for LPE growth of epitaxy GaAs layers. After epitaxy, wafers were capped with Si_3N_4 or PSG mask layers, which were photo resist patterned for selective beryllium ion implantation. Prior to oxide/nitride capping, wafers were cleaned by: (1) degreasing in boiling solvents; (2) soaking in hot water to form an oxide and (3) removing the oxide with hot HCl vapors. After oxide/nitride coating and

TIME:
TEMP: Hot

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patterning, HCl vapor used to final clean GaAs exposed surfaces prior to Be implant. Be goes to Ga sites and SiO_2 getters Be.
REF: Campbell, P M & Ballga, D J — *J Electrochem Soc,* 123,186(1985)

GAS-0028a
ETCH NAME: Hydrochloric acid, vapor
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl, vapor
TIME:
TEMP: Hot
DISCUSSION:

GaAs, (100), Si-doped wafers used in a study of oxide and nitride coatings on GaAs surfaces. Hot HCl vapors used to clean substrates prior to CVD deposition of SiO_2 or RF plasma deposition of SiN_x. Patterned photo resist openings were fabricated and oxides or nitrides were removed with either: (1) BHF ($5NH_4F$:1HF) or (2) RIE, using CF_4 gas. The GaAs acts as an etch-stop against both BHF or CF_4.
REF: Blaauw, C et al — *J Electron Mater,* 13,251(1984)
GAS-0207: Zelinsky, T — personal communication, 1978

GaAs:Cr, (100) (SI) wafers used as substrates for CVD and MOCVD growth of GaAs. With wafers in the vacuum system, hot HCl vapors are used to final clean surfaces prior to epitaxy deposition. (*Note:* This is a standard method for cleaning of CVD and Epitaxy systems. The substrates, quartz tube system, and graphite susceptors are all etch cleaned with the temperature ranges from 600 to 1250°C depending upon materials.

GAS-0029
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning/selective
COMPOSITION:
x .... HCl, conc.
TIME:
TEMP: Boiling
DISCUSSION:

GaAs, (100) wafers used for epitaxy growth of InGaAs. Substrates were cleaned before epitaxy by: (1) degreasing in TCE; (2) rinsing in acetone; (3) rinsing in methanol, and (4) etching clean in HCl with final DI water rinse.
REF: Penna, T C et al — *J Cryst Growth,* 67,27(1984)
GAS-0018b: Ibid.

GaAs, (100) wafers used for epitaxy growth of a Double Heterostructure (DH) device. The InGaAsP layer was selectively removed with boiling HCl.

GAS-0182b
ETCH NAME: Hydrochloric acid
TYPE: Acid, oxide removal
COMPOSITION:
x .... HCl, conc.
TIME: 10 min
TEMP: 30°C
DISCUSSION:

GaAs, (100) and (111) wafers. Solution used in a cleaning sequence as the final step prior to ZnS epitaxy deposition. See GAS-0182a for additional discussion.
REF: Ibid.

GAS-0140a-b
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
COMPOSITION:
(1) x .... HCl, conc.
(2) 2 .... HCl
1 .... H_2O
TIME:
TEMP: RT

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DISCUSSION:

GaAs, (111) wafers and dice used in an etch development experiment. Both solutions will attack this orientation slowly at RT.

REF: Robbins, H & Schwartz, B — development work, 1960

GAS-0008

ETCH NAME: Hydrochloric acid — TIME: 30—60 sec

TYPE: Acid, preferential — TEMP: RT

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

GaAs, (111) and (100) wafers. Wafers were cleaved ⟨110⟩ and etched in the solution shown to develop triangle etch pits to establish (011) or ($0\bar{1}1$) bulk plane directions. If point of triangle in down, away from the upper (100) or (111)A surface, the bulk plane is (011); whereas, if the point is 180° rotated bulk plane is ($0\bar{1}1$). The ($0\bar{1}1$) is preferred for selective channel and pit structuring.

REF: Pennington, P & Walker, P — development work, 1957

GAS-0118

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, cleaning — TEMP: RT

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

GaAs, (100), Te-doped, n-type wafers used as substrates in a study of leakage caused by cleaning. Cleaning sequence was: (1) degrease in TCE; (2) rinse in acetone; (3) rinse in methanol; (4) wash with HCl and (5) rinse in MeOH. Wafers were then argon ion cleaned 15 min with power varying from 100 to 1000 eV. Both aluminum and gold dots were evaporated for electrical test evaluations.

REF: Kwan, P et al — *Solid State Electron*, 26,125(1983)

GAS-0117

ETCH NAME: Hydrochloric acid, dilute — TIME:

TYPE: Acid, cleaning — TEMP: 70°C

COMPOSITION:

3 .... HCl

7 .... H_2O

DISCUSSION:

GaAs, (100) wafers used as substrates for LPE growth of GaAs, Sn-doped and Si ion implanted thin films. Substrates were cleaned prior to epitaxy by: (1) degrease in boiling TCE; (2) boiling IPA; (3) wash in 15% HCl and DI water rinse; (4) clean in NH_4OH:H_2O_2, RT, 2 min with DI water rinse and (5) N_2 blow dry. Wafers were used in a study of Ni/AuGe and Au/Ni/AuGe evaporated metal contacts.

REF: Marlow, G S et al — *Solid State Electron*, 26,259(1983)

GAS-0001d

ETCH NAME: — TIME:

TYPE: Acid, oxide removal — TEMP: RT

COMPOSITION:

1 .... HCl

1 .... EOH

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DISCUSSION:
GaAs:Cr, (100) (SI) wafers used as substrates for GaAs epitaxy growth. Solution used as the final step in a cleaning sequence of substrates before epitaxy. Wafers were oxidized in boiling water, the oxide stripped with the solution shown. See GAS-0001a for additional discussion.
REF: Ibid.

GAS-0012b
ETCH NAME: Clorox
TYPE: Acid, polish
COMPOSITION:
x .... *NaClO

TIME:
TEMP: RT

*Standard Clorox contains about $5^1/_2$% NaClO

DISCUSSION:
GaAs:Cr, (100) (SI) wafers used for epitaxy growth of GaAs thin films Solution used as a replacement for BRM polishing solutions. See GAS-0012a for added discussion. (*Note:* Clorox is a highly reactive bleaching agent for paper and textiles.)
REF: Ibid.

GAS-0001e
ETCH NAME: Water
TYPE: Acid, oxidation/cleaning
COMPOSITION:
x .... H_2O

TIME:
TEMP: Boiling

DISCUSSION:
GaAs:Cr, (100) (SI) wafers used for epitaxy growth of GaAs thin films. Boiling water used to oxidize substrate surfaces as part of a cleaning sequence prior to epitaxy. The oxide was removed with either 1HCl:1H_2O or 1HCl:1EOH. See GAS-0001a for additional discussion.
REF: Ibid.

GAS-0031
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
50 ml .... 5% NaOH
10 ml .... H_2O_2

TIME:
TEMP:

DISCUSSION:
GaAs wafers. The authors say that this solution mixture will develop grain structure.
REF: Waslgov, R T et al — *J Electrochem Soc*, 129,547(1982)

GAS-0032a
ETCH NAME: Potassium hydroxide
TYPE: Alkali, dislocation
COMPOSITION:
x .... KOH, molten

TIME: 4 min
TEMP: Molten

DISCUSSION:
GaAs, (100) wafers and other orientations. This molten flux was used to develop dis-

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locations and were compared to dislocations obtained by electrolytic etching with H_2SO_4 (the SSA etch).

REF: Nagata, K et al — *J Electrochem Soc,* 128,2347(1981)

GAS-0033: Mo, P et al — *J Cryst Growth,* 65,243(1983)

Used to develop dislocations in GaAs ingots. The "A/B" etch was used to develop stria, applied at RT with light. (See GAS-0059.).

GAS-0034: Katz, L E — *J Electrochem Soc,* 124,425(1977)

GaAs:Cr, (100) (SI), and n-GaAs, (100): Si-doped wafers used as substrates for GaAs, Sn-doped epitaxy thin film growth. GaAs substrates were etch cleaned in $3H_3PO_4$:$1H_2O_2$:$1H_2O$ prior to epitaxy. The molten KOH was used to develop dislocations in the Sn-doped epitaxy layers.

GAS-0157: Kimura, H et al — *J Cryst Growth,* 70,185(1984)

GaAs, (100) wafers. Ingots grown by LEC and HPLEC (20 atm argon) with and without indium doping. Molten KOH used to observe etch pit density (EPD). Pits show a cellular network in un-doped GaAs; whereas pits align in ⟨110⟩ directions with In-doped GaAs. Rosette patterns observed at seed end of ingot, but these figures decrease toward tail.

GAS-0128b: Elliot, A G et al — *J Cryst Growth,* 70,169(1984)

GaAs, (100) wafers with low dislocation density, doped with In, Si, and Te were grown by LEC, and used in a study of dislocation density. Molten flux KOH was used 10 min at 425°C to develop dislocations.

GAS-0163b: Grabmair, J G & Watson, C B — *Phys Status Solidi,* 32,K13(1969)

GaAs:Cr, (100), and (111) wafers used in a study of dislocation density. Wafers were cut from ingots grown by LEC and HB. Molten flux KOH was evaluated for dislocation development between 300 and 450°C. Below 360°C results were poor, possibly due to water in the KOH flux.

GAS-0219b: Mori, H & Takagashi, S — *J Cryst Growth,* 69,23(1984)

GaAs:Cr, (100) (SI) wafers cut $^1/_2$°-off toward (110). Wafers used in a study of dislocations. Chem/mech polish wafers with BRM solution prior to KOH molten flux etching for dislocations.

GAS-0225b: Motsuto, M & Mike, H — *J Electrochem Soc,* 124,441(1977)

GaAs:Cr, (100) (SI), or Si doped wafers used as substrates for epitaxy growth study of tin doped GaAs. Molten flux used to develop dislocations in epitaxy layers.

GAS-0035
ETCH NAME: TIME:
TYPE: Alkali, dislocation TEMP: 160°C
COMPOSITION:
1 .... KOH or x .... KOH
1 .... NaOH
DISCUSSION:

GaAs, (100) wafers and other orientations. The 1KOH:1NaOH mixture is a eutectic molten flux. Authors show that if the wafers are immediately immersed in ethylene glycol for 20 min after molten flux etching the surface oxidation is reduced and the EG slowly dissolves residual KOH/NaOH leaving a less damaged surface for defect/dislocation study.

REF: Lessoff, H & Gorman, R — *J Electron Mater,* 14,203(1985)

GAS-0163b: Grabmair, H J G & Watson, C B — *Phys Status Solidi,* 32,K13(1969)

GaAs:Cr, (100) and (111) (SI) wafers, and n-type wafers used in a dislocation study. The molten flux was in a platinum crucible with wafers held in a platinum wire basket. Etch times were (1) 15—120 sec for (100), and (2) 1—30 sec for (111).

GAS-0119b: Ibid.

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GaAs, (100), and (111) wafers cut within $^1/_2°$ of planes from ingots grown by CZ and LEC methods. Surfaces were polished with $1Br_2$:MeOH, and then etched in KOH at 360°C, 15 min, in a dislocation study. Compare results with the A/B Etch (GAS-0059), and the RC-1 Etch (GAS-0048).

GAS-0183a
ETCH NAME:
TYPE: Acid, preferential
TIME: 2—5 min
TEMP: RT
COMPOSITION:
1—5 .... 2% NaOH
1 .... H_2O_2
DISCUSSION:
GaAs, (111) wafers used in a study of precipitates induced by zinc diffusion. Solution produces sharp triangular etch pits.
REF: Black, J F & Jungbluth, E D — *J Electrochem Soc*, 114,181(1967)

GAS-0185
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
1 .... 15% NaOH
1 .... 5% H_2O_2
DISCUSSION:
GaAs, (100) and (111) wafers doped with Se, Te, Zn, and Pd used in a study of stress effects and electrical measurements. Solution used as a dislocation etch.
REF: Black, J & Lubin, P — *J Appl Phys*, 35,2462(1964)

GAS-0036
ETCH NAME:
TYPE: Alkali, preferential
TIME: 5—20 min
TEMP: Boiling
COMPOSITION:
(1) 250 ml .... 30% KOH
1000 ml .... MeOH
(2) 250 ml .... 30% KOH
100 ml .... ethylene glycol/glycerin
DISCUSSION:
GaAs, (111) wafers. Initial, general study and development of etchants for gallium arsenide. These solutions were shown to be preferential. Spheres were etched to finite crystal form in additional wafer studies.
REF: Walker, P — personal development, 1957

GAS-0017
ETCH NAME:
TYPE: Acid, junction stain
TIME:
TEMP:
COMPOSITION:
x .... KOH
x .... $K_3Fe(CN)_6$
x .... H_2O
DISCUSSION:
GaAs, (100) wafers, zinc diffused. Wafers were cleaved in ⟨110⟩ and stained with the solution shown to develop p-n junctions.
REF: Roedel, R J et al — *J Electrochem Soc*, 131,1726(1984)
GAS-0038a: Radiker R H & Lowen, J — *J Electrochem Soc*, 107,26(1960)
GaAs wafers fabricated as diffused diodes. Solution shown was used as a junction etch.

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GAS-0039
ETCH NAME: TIME:
TYPE: Acid, anisotropic TEMP:
COMPOSITION:
12 g .... KOH
8 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
DISCUSSION:
GaAs, (100) wafers used as substrates for epitaxy growth of InGaAsP layers. Material was cleaved ⟨110⟩ and etched in solution shown to develop layer structure.
REF: Bolkhovityanova, E et al — *J Electron Mater,* 12,525(1983)

GAS-0040
ETCH NAME: TIME: 1 min
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
2 g .... KOH
8 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
DISCUSSION:
GaAs, (100) p-type wafers used as substrates for epitaxy growth of p-InP. After epitaxy, wafers were cleaved ⟨110⟩ and etched to develop layer structure.
REF: Takeda, Y et al — *Jpn J Appl Phys,* 23,84(1983)

GAS-0041
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT and 60°C
COMPOSITION:
1 .... 12 *N* HCl
1 .... 17 *N* CH_3COOH (HAc)
*1 .... 1 *N* $K_2Cr_2O_7$

*14.7 g/100 cm H_2O

DISCUSSION:
GaAs wafers used in a chemical etching study. Authors say there are two etch regions, which they classify as A and B. The A region is rate limited, and the solution is light yellow in color. The B region is diffusion limited and dark brown in color.
REF: Adachi, S & Os, K — *J Electrochem Soc,* 131,126(1984)

GAS-0042
ETCH NAME: Nitric acid TIME:
TYPE: Acid, stain TEMP:
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
GaAs and Si (100) wafers used as substrates for epitaxy growth of Ge/GaAs and GaP/Si. Wafers were cleaved ⟨110⟩ and stained to observe layer structure.
REF: Rosztoczy, F E & Stein, W W — *J Electrochem Soc,* 119,1119(1972)

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GAS-0043
ETCH NAME: Nitric acid, dilute
TIME: $2^1/_2$ h
TYPE: Acid, preferential
TEMP: RT
COMPOSITION:
1 .... HNO_3
2 .... H_2O
DISCUSSION:

GaAs, grown as a (111) ingot oriented 15° off-(111) and Te doped. After growth ingot was cut lengthwise on (110), and solution used to develop growth patterns. Patterns showed anomalous nonconcentric freeze-out structures and high impurity concentration areas indicative of super-cooling of the ingot during growth similar to that observed with both Ge and InSb ingots. Striations observed were caused by Te segregation. The solution was changed every 15 min during the etch period.
REF: LeMay, C Z — *J Appl Phys*, 34,439(1964)
GAS-0044b: Schell, H A — *Z Metallkd*, 48,158(1957)

GaAs, (111) wafers used in a study of surface polarity. Solution will develop dislocation pits on the (111)Ga surfaces but not on $(\overline{1}\overline{1}\overline{1})$As.
GAS-0183b: Black, J F & Jungbluth, E D — *J Electrochem Soc*, 114,181(1967)

GaAs, (111) wafers used in a study of precipitates induced by zinc diffusion. Solution used to develop dislocation pits.
GAS-0211b: Ibid.

GaAs, (100) wafers cut from ingots doped with germanium, and used in a study of a Travelling Solvent growth method. Solution was used for dislocations and defects.

GAS-0044a
ETCH NAME: Schell etch
TIME:
TYPE: Acid, preferential
TEMP: RT
COMPOSITION:
1 .... HNO_3
3 .... H_3O
DISCUSSION:

GaAs, (111) wafers. Solution developed as a dislocation etch for polarity study. Develops dislocation pits on (111)Ga surfaces.
REF: Schell, H A — *Z Metallkd*, 48,158(1957)
GAS-0045a: Richards, J L & Crocker, A J — *J Appl Phys*, 31,611(1960)

GaAs, (111) wafers. Solution developed dislocation on the (111)A surfaces, and terraces on the $(\overline{1}\overline{1}\overline{1})$B. A sphere etched in the solution produce the finite crystal form of a tetrahexahedron, (hk0).

GAS-0044c
ETCH NAME:
TIME:
TYPE: Acid, polish
TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... H_2O
DISCUSSION:

GaAs, (111) wafers. Solution used as a polishing etch prior to dislocation etching of polar surfaces.
REF: Ibid.

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GAS-0006d
ETCH NAME: TIME:
TYPE: Acid, isotropic TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, wafers. Referred to as a rapid polish etch.
REF: Ibid.
GAS-0046: White, J C & Roth, W C — *J Appl Phys*, 30,956(1959)
GaAs, (111) wafers. The solution polishes the (111)A (gallium) surface, and produced etch pits on the $(\overline{1}\overline{1}\overline{1})$B (arsenic) surface.
GAS-0045b: Ibid.
GaAs, (111) wafers. Results as for GAS-0046, above. Sphere etched to finite crystal form was a rhombic dodecahedron, (hh0).

GAS-0047a
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HF
9 .... HNO_3
10 .... H_2O
DISCUSSION:
GaAs, (100) and (111) wafers. The latter orientation used as (111)A and $(\overline{1}\overline{1}\overline{1})$B. All wafers used as substrates for VPE growth of ZnTe and ZnS. Surfaces were mechanically lapped, then prepared as follows: (1) degrease in boiling TCE; (2) rinse in acetone, then MeOH; (3) etch in $3H_2SO_4$:$1H_2O$:$1H_2O$ to remove lap damage. Final etch clean in solution shown prior to epitaxy.
REF: Matsumoto, T & Ishida, T — *J Cryst Growth*, 67,135(1984)

GAS-0045c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HNO_3
3 .... H_2O
+ .... 1% $AgNO_3$
DISCUSSION:
GaAs, (111) wafers. Solution produces etch pits on both (111)A and $(\overline{1}\overline{1}\overline{1})$B surfaces. Sphere etched in solution does not produce a finite crystal form.
REF: Ibid.

GAS-0048
ETCH NAME: RC-1 TIME: 3 min
TYPE: Acid, dislocation TEMP: RT
COMPOSITION:
2 .... HF
3 .... HNO_3
+ .... 22.4 × 10^{-3} *M* $AgNO_3$

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DISCUSSION:

GaAs, (111) wafers. Solution produces triangular etch pits on the $(\overline{111})$B surface similar to the Schell etch. Produces conical etch pits on the (111)A surface. For comparison etched with the Schell etch, 15 min, and the RC-1 etch, for $1^1/_2$ min. They both shown 1-to-1 correspondence of etch pits. Used $1HF:1HNO_3:1H_2O$ solution to polish surfaces and to etch thin specimens.

REF: Abrahams, M S — *J Appl Phys*, 35,3626(1964)

GAS-0119a Ibid.

GaAs, (100) and (111) wafers from ingots grown by LEC and CZ. Solution used in a dislocation study.

GAS-0049a

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

1 .... HF

3 .... H_2O_2

DISCUSSION:

GaAs, single crystal spheres. A sphere etched in this solution produced the finite crystal form of a tetrahexahedron, (hk0).

REF: Richards, J L — *J Appl Phys*, 31,604(1960)

GAS-0050

ETCH NAME: TIME:

TYPE: Acid, isotropic TEMP:

COMPOSITION:

1 .... HNO_3

1 .... HCl

8 .... Glycerol

DISCUSSION:

GaAs, wafers. Used as an etch polish solution. High viscosity etches preferred for chemical polishing as attack tends to reduce high points more evenly, and produces a more planar surface.

REF: Packard, R D — *J Electrochem Soc*, 112,112(1965)

GAS-0006s, Ibid.

GAS-0051: Walker, P — personal development, 1979

GaAs:Cr, (100) (SI) wafers. Etch polished wafers in the solution as shown to remove lapping damage prior to ion implantation with Si^+ ions. Used both glycerin and ethylene glycol in varying amounts for viscosity control to optimize surface planarity.

GAS-0052

ETCH NAME: TIME:

TYPE: Acid, polish TEMP:

COMPOSITION:

1 .... HNO_3

2 .... HCl

2 .... H_2O

DISCUSSION:

GaAs, (111) wafers. Described as a polish etch for both GaAs and GaP.

REF: Uragski, T et al — *J Electrochem Soc*, 123,580(1976)

GAS-0167: Gatos, H C & Lavine, M C — Lincoln Lab Tech Rep 293, Jan 1963

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GaAs, (111) wafers. Etch time 10 min. Mix solution and use fresh. Pits are developed on the (111)A surfaces.

GAS-0044d
ETCH NAME: Aqua regia
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
3 .... HCl
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers. Described as a polishing etch for GaAs.
REF: Ibid.

TIME:
TEMP:

GAS-0053a
ETCH NAME:
TYPE: Acid, step-etch
COMPOSITION:
1 .... HF
1 .... H_2O_2
50 .... H_2O
DISCUSSION:
GaAs, (100) wafers, were Mg^+ ion implanted. This mixture was used to step-etch after ion implantation to study the implantation depth profile.
REF: Yu, P W — *J Appl Phys*, 48,2434(1977)

TIME:
TEMP: 2°C

GAS-0053b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
5 .... HF
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used as substrates for Mg^+ ion implantation. Solution used to etch clean GaAs prior to implantation.
REF: Ibid.

TIME:
TEMP:

GAS-0045d
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... H_2O_2
4—6 .... H_2O
DISCUSSION:
GaAs, (111) wafers. Solution will produce etch pits on the (111)A but only terraces on (111)B. A sphere etched in the solution produce the finite crystal form of a tetrahexahedron, (hk0).
REF: Ibid.

TIME:
TEMP:

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GAS-0054
ETCH NAME: TIME:
TYPE: Acid, structure TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
10 .... H_2O
DISCUSSION:
GaAs, (100) wafers, and other single crystal material substrates used for epitaxy growth of GaAs. After epitaxy, substrates were cleaved ⟨110⟩ and etched to develop layer structure. Authors say that this etch will not develop stria.
REF: Willardson, R K & Beer, A C — *Semiconductors and Metals,* Vol 7, Academic Press, New York, 1971, 160

GAS-0044f
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers. Described as a preferential etch for GaAs.
REF: Ibid.

GAS-0056a
ETCH NAME: Aqua regia TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
GaAs, (111) wafers. Aqua regia can be used as a polish etch.
REF: *S.E.R.L. Tech J,* 10,86(January 1960)

Gas-0057
ETCH NAME: TIME: 4 min
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
2 .... HCl
1 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a defect etching study. The solution will develop macroscopic spiral etch pits and figures on (111)A surfaces, but no figures on $(\overline{1}\overline{1}\overline{1})$B.
REF: Little, C L & McCarty, R T — *J Electrochem Soc,* 120,419(1973)
GAS-0186: White, J G & Roth, W C — *J Appl Phys,* 30,956(1959)
GaAs, (111) wafers used in a study of polar surfaces. Solution used at RT, 10 min. It will develop both dislocations and surface damage etch pits.

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GAS-0047b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:
GaAs, (100) wafers used as substrates for VPE growth of ZnTe and ZnS. Substrate preparation was: (1) mechanical lap/polish; (2) degrease in boiling TCE; (3) rinse in acetone, then methanol. Immediately prior to epitaxy, etch clean with solution shown.
REF: Ibid.

GAS-0056b
ETCH NAME: TIME: 30 sec
TYPE: Acid, junction TEMP: RT
COMPOSITION:
3 .... *"51" etch
2 .... H_2O

*5HCl:1HNO_3

DISCUSSION:
GaAs, (111) wafers. Used to develop p-n junctions.
REF: Ibid.
GAS-0189: Edmonds, J T — *J Appl Phys,* 3,1428(1960)
GaAs, (111) n-type wafers used in a heat treatment study. Solution used as a structure development etch after heat treatment.

GAS-0056c
ETCH NAME: 51 Etch TIME: 30 sec
TYPE: Acid, polish/junction TEMP: RT/cold
COMPOSITION:
1 .... HNO_3
5 .... HCl
DISCUSSION:
GaAs, (111) wafer. Solution used at room temperature is a general polish etch for gallium arsenide. Used cold, it is a p-n junction etch. Solution should be allowed to "age" before using as it is a form of aqua regia. (*Note:* Many acid mixtures become increasingly preferential below RT, and can be used to develop structures, p-n junctions, etc.)
REF: Ibid.
GAS-0190: Cardona, M — *Phys Rev,* 121,752(1961)
GaAs, (111) wafers used in a material study. Solution used as a general etch; follow etching with DI water rinsing. Also used on InAs.

GAS-0038b
ETCH NAME: 1:1:1 TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... HAc

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DISCUSSION:

GaAs, (111) wafers used to fabricate diffused diodes. Etch clean diffused diode surfaces in solution shown. This is a general polishing solution for both silicon and germanium. (*Note:* It is not good practice to "name" an etch solution by the volume of its constituents as there are many 1:1:1 acid mixtures.)

REF: Ibid.

GAS-0059

ETCH NAME: A/B

TYPE: Acid, dislocation

TIME: 10 min

TEMP: 60°C (4× slower at RT)

COMPOSITION:

1 ml .... HF

2 ml .... H_2O

1 g .... CrO_3

8 mg .... $AgNO_3$

DISCUSSION:

GaAs, (111), (100) and (110) wafers. During use the solution requires constant stirring to prevent precipitation of $AgCrO_4$. This was a major study of dislocation etching of GaAs. All wafers were undoped, cut within 0.5° of the surface plane, and ingots were grown by a modified Bridgman method. Alpha- and beta-type dislocation were obtained by bending wafers — positive (+) vs. negative (−) (111) surfaces. It was noted that a cleaved (111) surface etched 1.5× faster than a mechanically lap/polished surface, probably due to the cleavage steps. Eliminate CrO_3 for etching the $(\overline{1}\overline{1}\overline{1})$B surface. Also included is etch study of GaAs/GaAs epitaxy layers. Etch rates shown as a ratio: 1:0.71:0.69:0.5 for (100)-(111)A-(110)-$(\overline{1}\overline{1}\overline{1})$B. (*Note:* This is a widely used dislocation etch commonly referred to as the A/B etch. It should not be confused with the A-B, two-step cleaning etch for silicon developed by Kern & Puotinen, which is variously shown as the A-B Etch, or the RCA Etch.)

REF: Abrahams, M S & Buiocchi, C J — *J Appl Phys,* 36,2855(1965)

GAS-0130a

ETCH NAME: A/B Etch, modified

TYPE: Acid, dislocation

TIME:

TEMP:

COMPOSITION:

1 .... A/B Etch

5 .... H_2O

DISCUSSION:

GaAs, (100) ingot and wafers. Ingot grown by HPLEC and M-LEC (magnetic liquid encapsulated Czochralski). Solution used with a 100 W halogen lamp as a photo etch. Stria were observed on HPLEC grown material, but none on M-LEC.

REF: Namajima, M et al — *Jpn J Appl Phys,* 24,L65(1985)

GAS-0060

ETCH NAME:

TYPE: Acid, mesa etch

TIME:

TEMP:

COMPOSITION:

80 .... HCl

4 .... H_2O_2

1 .... H_2O

DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of heterostructures, as: p-

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GaAs:Zn/p-GaAlAs/n-GaAs/GaAs (100) substrate. Solution was used to form mesa structures in the p-GaAs:Zn doped layer.
REF: Reynolds, R T Jr et al — *J Appl Phys*, 56,1968(1984)
GAS-0226: Kular, S S et al — *Solid State Electron*, 27,83(1984)

GaAs:Cr, (100) (SI) wafers used as substrates for zinc implantation, then coated with Si_3N_4. Nitride patterned with photolithographic techniques and aluminum metallized in fabricating Hall samples. The Hall samples then used in a Hall measurement study. Clean the nitrided surfaces with solution shown prior to aluminum evaporation.

GAS-0061a
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 1 or 10
x .... $C_6H_4O_2$ (Quinone)
x .... $C_4H_6O_2.H_2O$ (Hydroquinone)
DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Lower pH values will etch GaAlAs. Higher pH values will etch GaAs.
REF: Tijburg, R P & Dongen, T — *J Electrochem Soc*, 122,687(1976)

GAS-0061b
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 2
x .... 0.0025 *M*/l $Ce(SO_4)_2.4H_2O$
x .... 0.0025 *M*/l $Ce(NO_3)_3.6H_2O$
DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Solution is selective for p-type GaAlAs.
REF: Ibid.

GAS-0061c
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 7
x .... 0.1 *M*/l $K_3Fe(CN)_6$
x .... 0.1 *M*/l $K_4Fe(CN)_6$
DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Solution is selective for GaAs.
REF: Ibid.

GAS-0061d
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 9.7
x .... 0.225 *M*/l $K_3Fe(CN)_6$
x .... 0.225 *M*/l $K_4Fe(CN)_6$
DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Solution is selective for $Ga_{0.7}Al_{0.5}3As$.
REF: Ibid.

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GAS-0061e
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 9.4
x .... 0.3 *M*/l KI
x .... 0.04 *M*/l I_2
DISCUSSION:
GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Solution is selective for GaAs without aluminum present.
REF: Ibid.

GAS-0061f
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION: pH: 9
x .... 0.3 *M*/l KI
x .... 0.1 *M*/l I_2
DISCUSSION:
GaAs, (100) wafers used as substrates for epitaxy growth of GaAlAs/GaAs. Solution is selective for $Ga_{1-x}Al_xAs$ (x = 0.15). Also used at pH 11 for etching InGaP/GaP or GaAlAs.
REF: Ibid.

GAS-0007b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
x .... H_2SO_4
x .... H_2O_2
x .... H_2O
DISCUSSION:
GaAs wafers. A general etch solution for polishing gallium arsenide. Composition variations are used. Used as an immersion etch; as a chem/mech etch on a polishing pad with rotation; angle etch, etc.
REF: Kern, W — *RCA Rev*, 39,278(1978)
GAS-0063b: Shaw, D W — *J Electrochem Soc*, 128,874(1981)
GaAs wafers used in a study of the reaction of hydrogen peroxide containing solutions on GaAs. Etch solution was used in a beaker at a 30° angle, and rotated at 135 rpm. Solution produced two different angle side slopes in the etched pits, and such pit slope angles vary with changes in the etch composition. (*Note:* See SI-0092a-k & SI-0300 for more details on pit side slope angles vs. etch compositions.)

GAS-0064
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
8 .... H_2O
DISCUSSION:
GaAs, (111) wafers. Solution produced grain structure.
REF: Connell, F et al — *Solid State Electron*, 1, 97(1960)

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GAS-0065
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... H_2SO_4
x .... H_2O_2
x .... H_2O
TIME:
TEMP:
DISCUSSION:
GaAs wafers. Used a beaker at a tilt angle with rotation to polish gallium arsenide.
REF: Sullivan, P T & Pompliano, R S — *J Electrochem Soc,* 122,764(1976)

GAS-0063a
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
1 .... H_2O
TIME:
TEMP: RT
RATE: 14.6 μm/min
DISCUSSION:
GaAs, (100), n-type wafers polished on both sides were used in a study of acid hydrogen peroxide solutions. Parameters were etch rate, morphology, mask undercutting, and relative anisotropy. Silicon nitride was deposited and photolithographically patterned as the etch masks. Patterns were both as strips in ⟨110⟩ direction orientation, for channels; and as circular openings for pits. Etching was with an angled rotation beaker system: beaker angle 30°, with rotation at 135 rpm. Rotation was reversed half way through etch periods. Nine sulfuric acid-hydrogen peroxide, and four hydrochloric acid-hydrogen peroxide solutions were evaluated. Solutions were mixed fresh and used within 2 h. Wafers were ⟨110⟩ cross-sectioned to profile etch pit side slopes, and show the variation obtained for (011) and $(01\bar{1})$.
REF: Shaw, D W — *J Electrochem Soc,* 128,875(1981)

GAS-0063c
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
40 .... H_2O
TIME:
TEMP: RT
RATE: 1.2 μm/min
DISCUSSION:
GaAs, (100), n-type wafers. Solution developed re-entrant double angle (011) and shallow concave, curve $(01\bar{1})$ pit side slopes. See GAS-0063a for added discussion.
REF: Ibid.

GAS-0063d
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
80 .... H_2O
TIME:
TEMP: RT
RATE: 0.54 μm/min

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DISCUSSION:
GaAs, (100), n-type wafers. Solution developed re-entrant double angle (011) and sharp, flat positive slopes (01$\bar{1}$) pit sides. See GAS-0063a for added discussion.
REF: Ibid.

GAS-0063e
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
160 .... H_2O
TIME:
TEMP: RT
RATE: 0.25 μm/min
DISCUSSION:
GaAs, (100), n-type wafers. Solution developed re-entrant double angle (011) and sharp, flat positive slope (01$\bar{1}$) pit sides. See GAS-0063a for added discussion.
REF: Ibid.

GAS-0063f
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
1000 .... H_2O
TIME:
TEMP: RT
RATE: 0.038 μm/min
DISCUSSION:
GaAs, (100), n-type wafers. Solution developed re-entrant double angle (011) and sharp, flat positive slope (01$\bar{1}$) pit sides. The re-entrant leg lengths on these solutions from GAS-00063a to GAS-0063e vary progressively from a long negative upper slope to a long positive lower slope with the 1:8:80 solution showing equal positive/negative lengths. See GAS-0063a for added discussion.
REF: Ibid.

GAS-0063g
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
8 .... H_2O
TIME:
TEMP: RT
DISCUSSION:
GaAs, (100), n-type wafers. Solution developed re-entrant double angle (011) and sharp, flat positive slope (01$\bar{1}$) pit sides. Re-entrant slope angles similar to GAS-0063b with upper leg longer negative slope. See GAS-0063a for added discussion.
REF: Ibid.

GAS-0063h
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
5 .... H_2O
TIME:
TEMP: RT
RATE: 5.0 μm/min

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DISCUSSION:

GaAs, (100), n-type wafers. Solution developed re-entrant angle with soft positive curve at bottom (01$\bar{1}$) and sharp, flat positive slope (011) pit sides. See GAS-0063a for added discussion.

REF: Ibid.

GAS-00631

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

8 .... H_2SO_4

1 .... H_2O_2

1 .... H_2O

TIME:

TEMP: RT

RATE: 1.2 μm/min

DISCUSSION:

GaAs, (100), n-type wafers. Solution developed short, negative upper slope with shallow curved bottom slope (01$\bar{1}$) and sharp, flat positive slope (011) pit sides. See GAS-0063a for added discussion.

REF: Ibid.

GAS-0063j

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

3 .... H_2SO_4

1 .... H_2O_2

1 .... H_2O

TIME:

TEMP: RT

RATE: 5.9 μm/min

DISCUSSION:

GaAs, (100), n-type wafers. Solution developed both pit slopes (011) and (01$\bar{1}$) similar to those of GAS-0061h. See GAS-0063a for added discussion.

REF: Ibid.

GAS-0063k

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

1 .... HCl

4 .... H_2O_2

40 .... H_2O

TIME:

TEMP: RT

RATE: 0.22 μm/min

DISCUSSION:

GaAs, (100), n-type wafers. Both pit slopes (011) and (01$\bar{1}$) similar to those of GAS-0063a. See GAS-0063e for slope comparisons and GAS-0063a for added discussion.

REF: Ibid.

GAS-0063i

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

1 .... HCl

1 .... H_2O_2

9 .... H_2O

TIME:

TEMP: RT

RATE: 0.20 μm/min

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DISCUSSION:

GaAs, (100), n-type wafers. Single, sharp negative slope (011) and single, positive slope (01$\bar{1}$). See GAS-0063a for added discussion.

REF: Ibid.

GAS-0063m

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

40 .... HCl

4 .... H_2O_2

1 .... H_2O

TIME:

TEMP: RT

RATE: 5.0 μm/min

DISCUSSION:

GaAs, (100), n-type wafers. Both (011) and (01$\bar{1}$) show positive curves in pit slopes. See GAS-0063a for added discussion.

REF: Ibid.

GAS-0063n

ETCH NAME:

TYPE: Acid, selective

COMPOSITION:

80 .... HCl

4 .... H_2O_2

1 .... H_2O

TIME:

TEMP: RT

RATE: 11 μm/min

DISCUSSION:

GaAs, (100), n-type wafers. Both (011) and (01$\bar{1}$) show positive curves in pit slopes. In all of these solutions etch undercut was greater on the (011). GAS-0063k solution showed the least undercutting of both (011) and (01$\bar{1}$). See GAS-0063a for added discussion.

REF: Ibid.

GAS-0191

ETCH NAME: Hydrofluoric acid

TYPE: Acid, mask removal

COMPOSITION:

x .... HF

TIME:

TEMP:

DISCUSSION:

GaAs, (100) wafers ion implanted with zinc, then coated with AlN and Si_3N_4 prior to an annealing study. Both coatings were removed with HF after annealing before diffusion depth study of zinc.

REF: Barrett, N J — *J Appl Phys,* 57,5470(1985)

GAS-0192

ETCH NAME:

TYPE: Acid, dislocation

COMPOSITION:

1 .... HF

3 .... CrO_3

2 .... H_2O

TIME:

TEMP: 0°C

RATE: 1.25 μm/min

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DISCUSSION:

GaAs, (100) wafers used as substrates for OMVPE growth of GaInAs and GaInP layers, and used in a defect study of the epitaxy thin films. Solution used to develop dislocations and defects. An He-Ne laser at 0°C was used to illuminate the solution during the etch period.

REF: Kuo, C P — *J Appl Phys*, 57,5428(1985)

GAS-0193: Wayher, J L et al — *J Cryst Growth*, 63,285(1983)

Reference for the etching method shown in GAS-0192.

GAS-0066

ETCH NAME: TIME:

TYPE: Acid, cleaning TEMP:

COMPOSITION:

1 .... H_2SO_4

10 .... H_2O

DISCUSSION:

GaAs:Te, (100) n-type wafer substrates were oxidized with SiO_2, then evaporated with SnO_2 in fabricating MIS solar cells. Substrates were degreased ultrasonically with TCE, then MeOH; and then etch cleaned in the solution shown prior to oxidation/metallization.

REF: Brinker, P J et al — *J Electrochem Soc*, 128,1968(1981)

GAS-0068

ETCH NAME: TIME:

TYPE: Acid, damage removal TEMP:

COMPOSITION:

(1) 18 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

(2) 1 .... H_2SO_4
1 .... H_2O_2
125 .... H_2O

DISCUSSION:

GaAs:Cr, (100) (SI) wafers used as substrates for MBE growth of GaAs/GaAs. Substrates were etched in solution (1) to remove lap/polish damage; then etch cleaned in the slower (2) solution immediately before epitaxy.

REF: Hiyamizu, S et al — *J Electrochem Soc*, 127,1562(1980)

GAS-0069

ETCH NAME: TIME: 30 sec

TYPE: Acid, polish/cleaning TEMP: RT

COMPOSITION:

(1) 3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

(2) 20 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

DISCUSSION:

GaAs:Cr, (100) (SI) wafers. Wafers were etch polished in solution (1). Then after photo resist patterning and acetone removal of the photo resist, surfaces were final cleaned with solution (2).

REF: Tokumitsu, E et al — *J Appl Phys*, 55,3163(1984)

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GAS-0070
ETCH NAME: TIME:
TYPE: Acid, polish/removal TEMP:
COMPOSITION:
90 .... H_2SO_4
5 .... H_2O_2
5 .... H_2O
DISCUSSION:
GaAs, (100) n^+ wafers used as substrates for an anodic etching study. After mechanical polishing, remove 9—11 μm of surface material with the etch solution shown.
REF: Nagata, K et al — *J Electrochem Soc,* 128,2247(1981)

GAS-0006g
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used as substrates for Gunn diode fabrication. This solution was used to selectively etch channels in wafer surfaces. Also used to develop layer structure in ⟨110⟩ cleaved sections of MBE layers deposited in a study of superlattice device structures.
REF: Kern, W — *RCA Rev,* 39,278(1978)

GAS-0071
ETCH NAME: TIME:
TYPE: Acid, step-etch TEMP: RT
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
75 .... H_2O
DISCUSSION:
GaAs, (100) wafers Be diffused. Used Apiezon-W, black wax, to coat surfaces, then used the solution shown to step-etch for development of the Be diffusion depth profile.
REF: McLevige, W V et al — *J Appl Phys,* 48,3342(1977)

GAS-0072a
ETCH NAME: TIME:
TYPE: Acid, selective TEMP: 30°C (20—50°C)
COMPOSITION:
1 .... H_2SO_4
2.5 .... H_2O_2
50 .... H_2O
DISCUSSION:
GaAs:Cr, (100) (SI), or n^+ diffused wafers used in a development study of selectively etched pit shapes. Etching was done through photo resist and/or SiO_2 masks. A 5:1:1 mixture produces rough pit bottoms at mask edges. Mixtures between 3:1:1 and 6:1:1 show preferential etching at mask edges. The composition shown produced good, flat bottomed pits. Etching is linear with both time and temperature, and ultrasonic stirring will increase rate with a nominal rate of 0.38 μm/min at 30°C. MBE growth was done into the etched pits.

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pits. Pits were prepared by etching through an SiO_2 mask, and the SiO_2 overhang remaining after pit forming was removed with HF prior to epitaxy.
REF: Li, A-Z — *J Electrochem Soc,* 130,2027(1983)

GAS-0073
ETCH NAME: TIME:
TYPE: Acid, polish/clean/selective TEMP:
COMPOSITION:
3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100), n-type wafers. Solution used for general polish and cleaning surfaces.
REF: Nakamura, T & Katoda, T — *J Appl Phys,* 55,3064(1984)
GAS-0047c: Matsumoto, T & Ishida, T — *J Cryst Growth* 67,135(1984)

GaAs, (100), (111)A, and $(\overline{111})$B wafers were used as substrates for VPE growth of ZnTe and ZnS. Prepare wafers by: (1) degrease in boiling TCE; (2) rinse in acetone, then MeOH, and (3) etch in solution shown. After etching, follow with a final etch in $1HF:9HNO_3:10H_2O$.
GAS-0075: Serl, J — *J Electrochem Soc,* 120,1417(1973)

GaAs, (100) wafers. As a polish etch the rate shown as 5 μ/min.
GAS-0076: Kohn-Kuhnenfeld, F — *J Electrochem Soc,* 119,1063(1972)

GaAs, (100) wafers used in a photo etching study. Zinc-doped wafers were grown by Float Zone (FZ) and Te- or Cr-doped (SI) wafers were grown by the Czochralski (CZ) method. An HBO 200 W Hg lamp was used as the photo light source during 5 min etching at RT. Material resistivity produced different structures: n-type wafers produced etched pits; whereas p-type wafers formed a mesa; and semi-insulating wafers showed an etch "footprint", but neither a pit nor mesa. The solution will also develop stria and dislocations, and the cone type structures observed can be caused by gas bubbles adhering to surfaces during the etch period.
GAS-0130: Namajima, M et al — *Jpn J Appl Phys,* 24,L65(1985)

GaAs, (100) wafers cut from ingots grown from a BN crucible by HPLEC and M-LEC (magnetic field LEC). Wafers were mechanically polished and etched at 60°C in the 3:1:1 etch solution. The A/B etch as $1A/B:5H_2O$ was used as a photo etch with a 100 W halogen lamp (for A/B Etch, see: GAS-0059). Material used in a study of stria and dislocations.
GAS-0131: Chung, Y et al — *Thin Solid Films,* 104,193(1983)

GaAs, (100), n-type wafers used as substrates. AgSe evaporated on wafer backs for contact, and annealed at 450°C. Then Ge_3N_4 grown on front surface. Before depositions, etch clean at RT with 3:1:1 solution, DI water rinse, and N_2 dry. Material used in a study of interface density of Ge_3N_4/GaAs. The nitride is unstable at high temperature; N_2 anneal is better than H_2 anneal. Latter is leaky. N_2 anneal densifies; H_2 anneal increases film porosity with segregation of free Ge.
GAS-0198: Kraulte, H et al — *J Electron Mater,* 12,215(1983)

GaAs, (100) wafers cut within 1° of plane. Wafers were cleaned: (1) degrease; (2) etch in HCl and (3) etch solution shown.
GAS-0056d: Ibid.

GaAs, (111) wafers. Solution used warm as a polish etch with a removal of 5 μm/min.
GAS-0223: Reep, D H & Ghandi, S K — *J Electrochem Soc,* 131,2697(1984)

GaAs:Cr, (100) wafers cut 3°-off toward (110), and used as substrates for GaAs epitaxy thin film growth. Clean wafers: (1) degrease in TCE, and rinse in acetone, then MeOH; (2) etch in solution shown at 60°C, 1 min; (3) DI H_2O rinse, and (4) N_2 blow dry.
GAS-0224: Ploog, K et al — *J Electrochem Soc,* 128,400(1981)

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GaAs, (100) wafers used as substrates for MBE growth of GaAs thin films doped with S or Be. Material used in a study of structure obtained from periodic impurity doping. Substrate cleaning: (1) diamond paste lap/polish; (2) polish on lens paper saturated with NaClO; (3) rinse in TCE, then MeOH, then double-distilled H_2O; (4) boil in HCl, twice; (5) free etch in solution shown at 48°C, 1 min; (6) rinse in double-distilled H_2O, and (7) N_2 blow dry. The etch solution was allowed to sit after mixing, then used as a "stagnant" etch.

GAS-0225a: Motsuto, M & Mike, H — *J Electrochem Soc,* 124,441(1977)

GaAs:Cr, (100) wafers Si doped. Used as substrates in a study of tin doped GaAs epitaxy layers. Clean in solution shown before epitaxy. Develop epitaxy defects in molten KOH flux at 360°C, 5 min.

GAS-0229: Lafere, W H et al — *Solid State Electron,* 25,389(1982)

GaAs, (100) n-type wafers used as substrates in the study of MIS Schottky barrier type devices. Clean substrates: (1) in DI H_2O with ultrasonic agitation; (2) degrease in boiling TCE, then rinse in acetone, then MeOH; (3) clean in solution shown at 80°C, 90 sec; (4) DI H_2O rinse, and N_2 blow dry. Metallize with Al, Ag, Au, or Sn, and evaluate electron trapping in the native oxide as related to type metal contact deposited.

GAS-0077
ETCH NAME:
TIME:
TYPE: Acid, polish/cleaning
TEMP: RT
COMPOSITION:

n-type	p-type
3	2 .... H_2SO_4
1	1 .... H_2O_2
1	1 .... H_2O

DISCUSSION:

GaAs:Cr, (100) (SI) wafers used in a study of surface cleaning. The two etches shown will leave a thin Ga_2O_3 oxide on surfaces which can be removed by vacuum bake at 550°C, 10—30 min, as Ga oxides decompose between 370 to 570°C. By polishing with Br_2:MeOH and DI H_2O rinse, surfaces will be passivated. The following solutions and operations were evaluated:

(1) H_2O_2 or HNO_3 used, alone, etch and clean is erratic.
(2) Br_2:MeOH; H_2SO_4:H_2O_2:H_2O; HF:HNO_3; and HF:H_2O_2 solutions all leave a slight oxide.
(3) In reducing carbon and oxygen surface contamination prior to vacuum deposition of metals, epitaxy growth, or diffusion the following sequence was used:
    (a) mechanical lap and polish, then:
        (i) TCE — bp
        (ii) HAc — bp
        (iii) EOH — 60°C
        (iv) DI H_2O — 60°C
        (v) HCl — dip
        (vi) H_2SO_4 — 70°C — use ultrasonic with heavy stirring + white light and follow with DI H_2O rinse and immediately into vacuum.

REF: Munzo-Yague, A et al — *J Electrochem Soc,* 128,149(1981)

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GAS-0007h
ETCH NAME: TIME: 3 min
TYPE: Acid, isotropic TEMP: 50°C
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100) wafers. This is a rapid polishing solution and leaves a residual oxide film on surface approximately 5 Å thick. Follow with successive dips in HF, then highly $NaOH:H_2O_2:H_2O$ at 30°C to reduce residual oxide to less than 10 Å thick.
REF: Ibid.
GAS-0079: Langmuir, M E — *J Electrochem Soc,* 129,1704(1982)

GaAs, (100), n-type, Si-doped, and Zn diffused wafers. The solution was used as a general etch polish.
GAS-0080: Takagishi, S & Mori, H — *Jpn J Appl Phys Lett,* 23,L100(1984)

GaAs:Cr, (100) wafer substrates etched cleaned in the solution shown. Time was 2 min at 50°C.
GAS-0193a: Lewis, C R et al — *J Electron Mater,* 12,507(1983).

GaAs, (100) wafers cut within 2° of plane. Wafers were Mg doped during MBE layer growth. Solution used to pre-clean wafers before epitaxy. After epitaxy and Mg junction forming, solution also used to delineate p-n junctions.

GAS-0078
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100) wafers cut within $\pm 1/2°$ of plane, Te-doped. LPE grown wafers were p^+, Ge-doped. CZ grown wafers were p^+, Zn doped and Bridgman (boat) grown wafers were p^+, Cd-doped. 1500 Å of SiO_2 was deposited and photo resist patterned, then "V" channels etched into wafer surfaces with the solution shown. Remove photo resist with acetone, then remove oxide with HF. Follow with epitaxy n-type GaAs growth into "V" channels.
REF: Sankaran, R — *J Appl Phys,* 126,1241(1979)

GAS-0081
ETCH NAME: TIME: $1\,1/2$ min
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100) wafers used in a study of chemical oxidation state depth profiling. Wafers were etch cleaned in the solution shown. Follow with 1 *M* HCl, 1 min; then running DI H_2O, 5 min: MeOH rinse; and N_2 blow dry. Allow wafers to sit in air for 12 months prior to study.
REF: Kohiki, S et al — *Jpn J Appl Phys Lett,* 23,L15(1984)
GAS-0082: Johns, R C — *Thin Solid Films,* 96,285(1982)

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GaAs, (100), n-type wafers. Solution used to etch clean surfaces. Time was 3 min at RT. Follow with Br_2:MeOH, 2 min at RT, and then DI H_2O rinse with N_2 blow dry.
GAS-0083: Yoneda, K et al — *J Cryst Growth*, 67,125(1984)

GaAs:Cr, (100) (SI) and $(\bar{1}\bar{1}\bar{1})$B wafers were used as substrates for MBE ZnS thin film epitaxy. After degreasing use the etch shown to clean surfaces and DI water rinse. Follow with HCl soak, 10 min at 30°C, to remove native oxide. Final clean in vacuum, 15 min at 620°C before epitaxy deposition. Time in the solution shown was 10 min at 60°C.
GAS-0030c: Yu, P W — *J Appl Phys*, 48,2434(1977)

GaAs, (100) wafers used for Mg ion implantation. Wafers cleaned in the solution for 15 sec at RT before ion implant.
GAS-0085: Patterson, A M — *J Electron Mater*, 13,621(1984)

GaAs:Cr, (100) (SI) wafers. Complete cleaning cycle was: (1) Teepol detergent, boiling; (2) DI H_2O, rinse; (3) degrease with hot TCE; (4) etch in solution shown, 30 sec, RT; (5) boiling HCl dip; and (6) DI H_2O rinse. Author says this produces a hydrophobic surface.
GAS-0195b: Ibid.

GaAs, (100) wafers cut within 2—3° of plane. Wafers were cleaned and polished: (1) polish in xNaClO:xH_2O, (2) degrease with solvents; (3) etch in HCl with DI H_2O; and (4) final clean in solution shown with DI H_2O rinse.
GAS-0200: Khiki, S et al — *Jpn J Appl Phys*, 23,L15(1984)

GaAs, (100) wafers used in a study of the chemical states on surfaces. Etch in solution shown $1^1/_2$ min, and DI H_2O rinse. Then clean substrates: (1) 1 *M* HCl, 1 min, RT; (2) wash in running DI H_2O, 5 min, RT; (3) MeOH rinse, and N_2 blow dry. Let wafers sit in air for 12 months before evaluating.
GAS-0165: Bhat, R — *J Electron Mater* 14,433(1985)

GaAs, (100) wafers cut 6°-off plane toward (111)A. Also used (110) and (111) wafers. All wafers were OMCVD deposited with GaAs and AlGaAs epitaxy thin films. Wafers were prepared by: (1) chem/mech polish with Br_2:MeOH to remove subsurface work damage; (2) degrease in solvents; (3) then etch polish in solution shown. Material used in a study of the thin film morphology.

GAS-0086
ETCH NAME:
TYPE: Acid, clean
TIME: 20 sec
TEMP: RT
COMPOSITION:
7 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100), undoped wafers. Degrease with solvents and then etch clean in the above solution prior to MBE growth of a 1000 Å GaAs buffer layer followed by an SrF_2 dielectric coating.
REF: Sullivan, P W — *J Vac Sci Technol*, B2,202(1984)
GAS-0231: Laidiy, W D et al — *J Vac Sci Technol*, B(1),155(1983)

GaAs wafers. Chem/mech polish in BRM solution, then final clean with solution shown.

GAS-8087
ETCH NAME:
TYPE: Acid, clean
TIME:
TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

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DISCUSSION:

GaAs, (100), Te-doped wafer used in a study of oxygenated surfaces. First, clean in MeOH then in HCl to remove native oxide before etching in the solution shown, and DI H_2O rinse. Anneal in UHV 30 min at 800 K before oxidation.

REF: Szuber, J — *Thin Solid Films,* 111,309(1984)

GAS-0262: Leung, S et al — *J Electrochem Soc,* 132,898(1985)

GaAs, (100) n-type wafers cut from ingots grown by LEC under a B_2O_3 atmosphere, or grown by Horizontal Bridgman (HB). Clean substrates: (1) degrease in TCE, rinse in acetone, then MeOH; (2) soak in 1HCl:1H_2O at RT, 5 min, DI H_2O rinse; (3) etch clean in solution shown for 2 min, at RT, and (4) final water rinse and N_2 dry. Co-evaporate Au/Ga for 20 nm thickness. Annealing metallization at 225°C will develop orthorhombic structured Au_2Ga, though material was annealed over a range of 130—400°C. To thin for TEM study: (1) epoxy two metallized wafers face-to-face; (2) section cut in ⟨110⟩ direction; (3) mechanically lap specimen wafer surfaces down, and (3) final thin by Ar^+ ion milling with a 6 KeV power setting for observation of GaAs/metal interfaces.

GAS-0007d
ETCH NAME:
TYPE: Acid, isotropic/thinning
TIME:
TEMP: RT and 40°C
COMPOSITION:

1 .... H_2SO_4
4 .... H_2O_2
1 .... HF

DISCUSSION:

GaAs, (100) wafers and other low index planes. A very rapid polish etch. Also used to remove mechanical lap damage and as a general removal/thinning solution.

REF: Kern, W — *RCA Rev,* 39,278(1978)

GAS-0090
ETCH NAME:
TYPE: Acid, thinning/step-etch
TIME:
TEMP: RT
COMPOSITION:

1 .... H_2SO_4
1 .... H_2O_2
100 .... H_2O

DISCUSSION:

GaAs, (100) wafers ion implanted with Si, Zn, and Be in a capless anneal study. Two, 1000 W tungsten-halogen lamps used for annealing wafers with implant side up covered with an Si wafer, or a substrate of quartz or sapphire to prevent arsenic depositing on test surfaces during anneal in an AsH_3/H_2, or AsH_3/Ar atmosphere. Above solution used to thin or step-etch for SEM study of implanted atom distribution.

REF: Lie, S C & Narayan, S Y — *J Electron Mater,* 13,897(1984)

GAS-0091
ETCH NAME:
TYPE: Acid, polish/cleaning
TIME: 30 sec
TEMP: RT
COMPOSITION:

2 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

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DISCUSSION:

GaAs:CR, (100) (SI), and Si-doped wafers used as substrates for LPE growth of InGaAsP layers. After wafer dicing, individual die were etch cleaned in the solution shown.
REF: Hiramatsu, K et al — *Jpn J Appl Phys,* 23,68(1984)

GAS-0098
ETCH NAME: TIME: 3 min
TYPE: Acid, cleaning/junction TEMP: 50°C
COMPOSITION:

4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

DISCUSSION:

GaAs:Cr, (100) (SI), and Si-doped wafers used as substrates for MOVPE growth of InGaP to produce p-n junction diodes. Substrates were degreased and then etched in the above solution prior to epitaxy. Substrates heated in vacuum in H_2 at 500°C for final cleaning prior to epitaxy deposition.
REF: Iwamoto, T et al — *J Cryst Growth,* 68,27(1984)
GAS-0193b: Ibid.

GaAs, (100), wafers cut 2°-off toward (110), and doped with Sn, Zn, or Cr were used as substrates for epitaxy OMVPE growth of both Mg thin films and Mg-doped GaAs layers to form p-n junctions. The solution shown was used to etch clean substrates prior to epitaxy and to delineate junctions after epitaxy.
GAS-0100: Waldrop, J R — *J Phys Chem Solids,* 45,44(1984)

GaAs, (100), n- and p-doped wafers used in a study of native oxides. The n- and p-type wafers were etched together in the above solution for 30 sec at RT to surface clean. Final cleaning to remove native oxide was done in vacuum at 550°C.

GaAs, (100), wafers cut within ± $^1/_2$°, and (100), 2°-off plane toward (110) from both Horizontal Bridgman (HB) and Czochralski (CZ) grown ingots were used in a dislocation study. The above solution was used for 2 min at 50°C to chem/mech polish substrates. Dislocation pits were developed with molten KOH.
GAS-0222: Hoke, W E & Laborrier, W C — *J Vac Sci Technol,* B2,272(1984)

GaAs, (100) wafers used to grow epitaxy MBE GaAs thin film layers. Clean wafers: (1) chem/mech polish in BRM solution, and MeOH rinse; (2) degrease in TCE, then rinse in acetone, then in MeOH; (3) etch solution shown; (4) DI water rinse, and (5) N_2 blow dry. Epitaxy layers were Si doped n-type; Be doped p-type.

GAS-0072b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:

6 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

DISCUSSION:

GaAs, (100), wafers, Si or Be doped wafers were cleaned in this solution.
REF: Li, A-Z — *J Electron Mater,* 12,71(1983)
GAS-0221: Mitsunaga, K et al — *J Vac Sci Technol,* B2,256(1984)

GaAs:Cr, (100) (SI) wafers used as substrates for MBE growth of heterostructure layers of AlGaAs, and n-type GaAs. Clean wafers: (1) degrease in TCE, then rinse in acetone, then ISO; (2) etch in solution shown. After epitaxy the solution was used to etch-strip epitaxy

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layers, and called a transverse junction strip (TJS) system. (*Note:* TJS is a form of channel etching to measure epitaxy layer thicknesses and observe p-n junctions.)

GAS-0103
ETCH NAME: TIME:
TYPE: Acid, clean TEMP:
COMPOSITION:
90 .... H_2SO_4
5 .... H_2O_2
5 .... H_2O
DISCUSSION:

GaAs, (100) wafers used as substrates for deposition of AlN by CVD. SiO_2 was deposited as a mask using photo resist to pattern, open, and etch with HF. The exposed GaAs in windows was lightly etch clean in the above solution before AlN deposition.
REF: Nake, K & Ozeski, M — *J Cryst Growth,* 68,200(1984)

GAS-0104
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
20 .... HCl
2 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100) wafers as substrates used for gold deposition in a study of the gold/GaAs interface reaction. Substrates were mechanically lapped and then etched in the above solution. Ar^+ ion milling was used for final cleaning prior to gold sputter deposition. Ion milling also used to thin substrates for TEM study. Both the (100) surface and cleaved ⟨110⟩ cross-sections studied.
REF: Yoshie, T et al — *Thin Solid Films,* 111,149(1984)

GAS-0105
ETCH NAME: Phosphoric acid TIME:
TYPE: Acid, removal TEMP: Hot
COMPOSITION:
40 .... H_3PO_4
1 .... H_2O_2
40 .... H_2O
DISCUSSION:

GaAs, (100) wafers used as substrates for LPE growth of p-type, Ge-doped GaAlAs layers. The etch shown was used to etch remove material to near the junction, and the substrates were Ar^+ ion thinned for TEM study.
REF: Veda, O et al — *J Appl Phys,* 50,764(1979)

GAS-0106
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
3 .... H_3PO_4
1 .... H_2O_2
50 .... H_2O

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DISCUSSION:

GaAs, (100) wafers used as substrates for Si^+ and S^+ ion implantation and capless anneal. Even under an As overpressure at 800°C during anneal, thermal etch pits formed. The higher the ion energy dose, the higher the number of pits formed.

REF: Kaskara, J et al — *J Appl Phys,* 50,541(1979)

GAS-0129b: Heiblum, M et al — *Solid State Electron,* 25,185(1982)

GaAs, (100) wafers, and GaAs epitaxy thin film deposited wafers were used in a study of ohmic contacts with AuGe/Ni metallization. After contact deposition as dot structures, surfaces were cleaned in the solution shown. Reaction produced an etched moat around metal contact dots which showed a resistivity variations vs. the adjoining surface.

GAS-0004d

ETCH NAME:

TIME: 1—2 min

TYPE: Acid, dislocation

TEMP: RT

COMPOSITION:

100 .... H_3PO_4

100 .... H_2SO_4

1 .... H_2O_2

DISCUSSION:

GaAs, (100) wafers used as substrates for LPE growth of GaAlAs. This etch used to develop Stacking Faults (SFs) at the substrate interface.

REF: Ibid.

GAS-0108a

ETCH NAME:

TIME: 2 min

TYPE: Acid, selective

TEMP: RT

COMPOSITION:

1 .... H_3PO_4

1 .... H_2O_2

20 .... H_2O

DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of AlGaAs double heterojunction (DH) structures. The etch shown was used to define mesas and channels.

REF: Inoue, K & Sakaki, R — *Jpn J Appl Phys Lett,* L61(1984)

GAS-0108b

ETCH NAME:

TIME:

TYPE: Acid, thinning

TEMP:

COMPOSITION:

3 .... H_3PO_4

1 .... H_2O_2

75 .... H_2O

DISCUSSION:

GaAs, (100) wafers used as substrates for epitaxy growth of AlGaAs double heterojunction (DH) structures. The AlGaAs layers were etch thinned in the solution shown to remove about 200 Å in forming gate patterns.

REF: Ibid.

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GAS-0109
ETCH NAME: TIME: 35 min
TYPE: Acid, via hole TEMP: RT
COMPOSITION:
75 .... H_3PO_4
100 .... H_2O_2
25 .... H_2O
DISCUSSION:
GaAs, (100) wafers were 200 μm thick and etched in the solution shown to develop via holes. Stirring the acid will produce a faster etch rate.
REF: Yengalla, S P & Ghosh, C L — *J Electrochem Soc,* 130,1377(1983)

GAS-0007e
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: 60°C
COMPOSITION:
49 .... H_3PO_4
11 .... HNO_3
DISCUSSION:
GaAs, (111)A and ($\overline{111}$)B wafers. Solution will etch polish both surface orientations equally.
REF: Kern, W — *RCA Rev,* 39,278(1978)

GAS-0007f
ETCH NAME: TIME:
TYPE: Acid, anisotropic TEMP:
COMPOSITION:
1 .... H_3PO_4
1 .... H_2O_2
3 .... MeOH
DISCUSSION:
GaAs, (100) wafers with epitaxy grown heterostructure. Etch will produce selective etch structure.
REF: Ibid.
GAS-0096b: Kukken, N K & Tilburg, R P — *J Electrochem Soc,* 130,1722(1983)
GaAs, (100) wafers selectively etched through a mask to develop pit and via hole structures using positive (+) or negative (−) gravity during the etch period. Brass material also etched in this manner.

GAS-0007i
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
5 .... H_3PO_4
5 .... H_2SO_4
2 .... H_2O_2
DISCUSSION:
GaAs, (100) wafers used as substrates for selective etching of pit structure using an artificial gravity during the etch period. This solution develops pits selectively.
REF: Ibid.

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GAS-0007j
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP: Variable
COMPOSITION:
10 .... *citric acid
1 .... H_2O_2
1 .... *H_2O

*Concentration variable

DISCUSSION:
GaAs, (100), (111), (110), (211) wafers. Rate varies with: (1) plane orientation; (2) solution composition; (3) temperature and (4) agitation of solution. Low concentrations of citric acid are limited by diffusion reaction. Higher concentrations are rate limited.
REF: Ibid.

GAS-0017
ETCH NAME: Hydrofluoric acid, dilute TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... 10% HF
DISCUSSION:
GaAs, (100) n/n^+, Si-doped wafers used in a study of amorphous metal deposition. Substrates were cleaned by degreasing in TCE, then rinsing in IPA. Immediately before placing wafers in vacuum for metallization, HF rinse in the solution shown, water rinse, and N_2 dry.
REF: Wickenden, D K et al — *Solid State Electron,* 27,515(1984)

GAS-0007k
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... NaOCl
x .... H_2O
DISCUSSION:
GaAs wafers of various orientations. Solution concentration can be varied. Used for wafer polishing by rotation on an impregnated pellon-type pad.
REF: Ibid.
GAS-0114: Frese, J W Jr & Morrison, S R — *J Appl Phys,* 126,1235(1979)
GaAs, (111), Cd-doped, and (110), Sn-doped wafers used in an electrolytic oxidation study. Native oxides were removed from surfaces prior to controlled oxidation by soak in 1 *M* HCl, or by: (1) etching 3 min, at 80°C in $3H_2SO_4$:$1H_2O_2$:$1H_2O$, then (2) in HCl, conc. for 15 sec at RT.

GAS-0115
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
1 .... 2% NaOH
1 .... 1.25% H_2O_2
x .... H_2O

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DISCUSSION:

GaS, (100), n-type wafers used as substrates in a surface treatment study. Degrease in boiling TCE. Rinse in acetone and MeOH. Etch rate for the solution shown is 1000 Å/min. Treatments of study were (1) $NaOH/H_2O_2$; (2) HCl, conc.; (3) Ar^+ ion sputter; and (4) sitting in air. Ar^+ ion cleaning produced subsurface damage to 100 Å depth.
REF: Huber, E & Hartnagel, H L — *Solid State Electron*, 27,589(1984)

GAS-0116
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:

10 .... H_2SO_4	to	1 .... H_2SO_4
1 .... H_2O_2		1 .... H_2O_2
1 .... H_2O		16 .... H_2O

TIME: 4 min
TEMP: 20°C

DISCUSSION:

GaAs, wafers used in a general etch study of etch characteristics of solutions containing hydrogen peroxide. Variations in solution concentrations shown above change a pit side-slope/bottom from an edge-groove bottom to a flat edge-bottom with a relative 90° vertical pit slope. A good cleaning/removal solution sequence is: (1) the above solution as an 8:1:1 mixture, 3 min at 60°C; (2) 3 min in HCl, conc.; (3) 3 min in H_2O, and (4) a final wash with hot chloroform. Other etch systems described.
REF: Kohn, E — *J Electrochem Soc*, 127,505(1980)

GAS-0120
ETCH NAME: Schell etch
TYPE: Acid, preferential
COMPOSITION:
3 .... HNO_3
1 .... H_2O

TIME:
TEMP:

DISCUSSION:

GaAs, (111) wafers Cr, Te, and Zn doped. This etch was used to develop dislocations.
REF: Weiss, B L et al — *J Appl Phys*, 48,3614(1977)

GAS-0032b
ETCH NAME: SSA
TYPE: Electrolytic, dislocation
COMPOSITION:
5 .... H_2SO_4
95 .... propylene glycol

TIME: 10—15 min
TEMP:
ANODE: Al strip to GaAs
CATHODE: Pt
POWER: 1.5 mA/cm^3
RATE: 0.3 μm/10 min

DISCUSSION:

GaAs wafers. Etch was used as an anodic dislocation etch on gallium arsenide. Wafers were first mechanically polished; then chemically etch polished in: $90H_2SO_4{:}5H_2O_2{:}5H_2O$ to remove lap damage. All electrolytic, (SSA) etching was done in the dark with solution stirring. A molten KOH etch was used for dislocation etch result comparison.
REF: Ibid.

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GAS-0186
ETCH NAME: TIME:
TYPE: Acid, damage removal TEMP:
COMPOSITION:
20 .... HCl
2 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100) wafers used as substrates for gold evaporation in a study of the Au/GaAs interface. Mechanically lap surfaces and then etch polish in the solution shown. In vacuum system, Ar^+ ion sputter clean prior to gold evaporation. In preparing specimens for TEM study, etch thin by Ar^+ ion sputter removal of the substrate from the back un-alloyed side to near GaAs/Au interface.
REF: Yoshie, T et al — *Thin Solid Films,* 111,201(1984)

GAS-0119a
ETCH NAME: A/B etch TIME: 30 sec to 25 min
TYPE: Acid, dislocation TEMP: RT
COMPOSITION:
1 ml .... HF
1 g .... CrO_3
8 mg .... $AgNO_3$
DISCUSSION:

GaAs, (100) and (111) wafers cut within $^1/_2°$ of plane. Cut from ingots grown by Czochralski (CZ) or Liquid Encapsulated Czochralski (LEC) method. Wafers were polished with $1Br_2$:MeOH to remove lap damage, and then studied for dislocations. Three preferential solutions were evaluated against each other. The solution shown [see GAS-0059] against: molten flux KOH at 360°C, 15 min [see GAS-0032], and the RC-1 Etch, 45 sec, RT [see GAS-0048].
REF: Hope, D A O & Cockayne, B — *J Cryst Growth,* 67,153(1984)

GAS-0125
ETCH NAME: Caro's etch TIME: 5 min
TYPE: Acid, cleaning TEMP:
COMPOSITION:
10 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:

GaAs, (100), n-type wafers grown by LEC as ingots. Clean wafers by: (1) degrease in TCE at 70°C; (2) rinse in acetone, then MeOH: (3) etch clean in solution shown, and (4) DI H_2O rinse. (*Note:* Original Caro's Etch mixture is $1H_2SO_4$:$1H_2O_2$. Once these type solutions are activated they become self-heating, and will reach a steady-state boiling point of about 175°C. See: SI-0104.)
REF: Bhat, I et al — *Solid State Electron,* 27,121(1984)
GAS-0128: Iliadis, A & Singer, K E — *Solid State Electron,* 26,7(1983)

GaAs:Cr, (100) (SI) wafers with thin film S-doped GaAs epitaxy used in a study of Ge reactions from AuGe(13%) metallization. Clean wafers by: (1) etch in solution shown 90 sec, RT; (2) DI H_2O rinse; (2) HCl rinse 90 sec, RT; (3) DI H_2O rinse; (4) N_2 blow dry prior to vacuum metallization of AuGe.
GAS-0127: Kular, S S et al — *Solid State Electron,* 27,83(1984)

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GaAs:Cr, (100) (SI) wafers with Zn^+ ion implantation used in the preparation of Hall samples. Clean wafers in solution shown prior to Si_3N_4 thin film masking, followed by aluminum dot metallization.

GAS-0126
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
x .... H_3O_4
x .... H_2O_2
x .... H_2O
TIME:
TEMP:
DISCUSSION:

GaAs, (100) wafers fabricated as Schottky barrier diodes for a heat treatment study. Wafers were etch thinned in solution shown, then an n-type GaAs buffer layer was grown by VPE, followed by E-beam metallization with Ti, then Al.
REF: Wada, Y & Chino, K I — *Solid State Electron,* 26,559(1983)

GAS-0129
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HF, vapor
TIME:
TEMP: Hot
DISCUSSION:

GaAs:Cr, (100) (SI) wafers used as substrates for epitaxy growth of un-doped (naturally p-type) epitaxy buffer layers, then a doped GaAs layer. Solution shown used to clean epitaxy surfaces before metallization: (1) HF, vapor, (2) DI water rinse, and (3) N_2 blow dry. SiO_2 evaporated as a thin film mask, and photolithographically processed with patterns opened with $1HF:3H_2O$ before metallizing.
REF: Heiblum, M et al — *Solid State Electron,* 25,185(1982)

GAS-0181
ETCH NAME: A/B etch
TYPE: Acid, preferential
COMPOSITION:
12 ml .... HF
24 ml .... H_2O
12 g .... CrO_3
24 mg .... $AgNO_3$
TIME:
TEMP:
DISCUSSION:

GaAs, (111) wafers with zinc diffusion. Solution used as a dislocation etch in studying zinc reactions. Also worked with GaP. (*Note:* See GAS-0059 for original A/B etch.)
REF: Cohon, M M & Bedard, F D — *J Appl Phys,* 39,75(1968)

GAS-0132
ETCH NAME:
TYPE: Halogen, oxide removal
COMPOSITION:
x .... 2% Br_2
x .... MeOH
TIME: 15 sec
TEMP: RT
DISCUSSION:

GaAs, (100), Zn-doped, p-type wafers used as substrates for chemical solution growth of TiO_2 films. Remove native oxide with solution shown, rinse with MeOH and hold under

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MeOH. Plate Ti with Ti-isoproxide, or Ti-ethylhexoxide in isopropyl alcohol for 1 min. Then hold over water (95% RH) for about 1 week to obtain a 500—2000 Å TiO_2 film. Etch film in $2HF:2NH_4F:5H_2O$; rinse in IPA, then in MeOH under a nitrogen atmosphere. Ar^+ ion sputter etch cleaning produced craters and contamination. Chemical etch cleaning may produce some pits.
REF: Bertrand, P A & Fleischauer, P D — *Thin Solid Films,* 103,167(1983)

GAS-0186b
ETCH NAME: Argon
TYPE: Ionized gas, thinning
COMPOSITION:
x .... Ar^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
GaAs, (100) wafers used in a study of the Au/GaAs interface. Argon ion etching was used to thin the wafers for TEM study. See GAS-0186a for additional discussion.
REF: Ibid.

GAS-0187
ETCH NAME:
TYPE: Acid, junction/defect
COMPOSITION:
50 ml .... NaOH
10 ml .... H_2O_2
TIME: 15 sec
TEMP: RT
DISCUSSION:
GaAs wafers. Solution used to develop grain boundaries. Time shown is for use as a junction etch on solar cells devices that were fabricated in a study of spectral characteristics.
REF: Nasledov, D N & Tsarenkov, B A — *Sov Phys Solid State,* 1,1346(1959)

GAS-0141
ETCH NAME:
TYPE: Acid, polish jet
COMPOSITION:
40 .... HCl
4 .... H_2O_2
1 .... H_2O
TIME:
TEMP:
DISCUSSION:
GaAs, (111), n-type and undoped material cut as rectangular bars, used in a study of dislocations induced by compression. Compression in ⟨123⟩ crystallographic directions was 2% at 550°C in argon. After compression, the bar was sliced on ⟨111⟩ and the solution shown was used to jet polish thin the specimen for SEM study. Under microscope, the material was stretched in the ⟨123⟩ direction at 120—500°C, and dislocations were observed to glide. Compression also used to introduce dislocations in Horizontal Bridgman (HB) grown silicon.
REF: Meeda, K et al — *J Appl Phys,* 66,554(1984)

GAS-0142
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
10 ml .... H_2O_2
50 ml .... 5% NaOH
TIME:
TEMP: Boiling
RATE: 10—15 μm/min

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DISCUSSION:

GaAs, (111) wafers used in an etch development study. Etch will develop grain boundaries.

REF: Nasledov, D N et al — *Sov Phys-Tech Phys*, 3,726(1958)

GAS-0140b

ETCH NAME: TIME:

TYPE: Acid, removal TEMP: RT

COMPOSITION:

1 .... 20% NaOH

1 .... H_2O_2

DISCUSSION:

GaAs, (111) wafers used in an etch development study. Solution will attack material at room temperature.

REF: Robbins, H & Schwartz, B — *Tech Rep* 1960

GAS-0049b

ETCH NAME: TIME:

TYPE: *Acid*, polish TEMP:

COMPOSITION:

2 .... HCl

1 .... HNO_3

2 .... H_2O

DISCUSSION:

GaAs, (111) wafers and spheres used in an etch development study of Horizontal Bridgman (HB) grown material. Solution shown used to etch polish wafer surfaces and spheres before dislocation and defect etching.

REF: Richards, J L — *J Appl Phys*, 31,604(1960)

GAS-0005a

ETCH NAME: TIME:

TYPE: Acid, polish TEMP:

COMPOSITION:

2 .... HF

2 .... HCl

3 .... HNO_3

DISCUSSION:

GaAs, (111), n-type, 5—30 Ω cm resistivity wafers used in an etch development study. Initial reaction of solution is slow but after warming during reaction becomes rapid. Add DI H_2O to slow reaction or use cooled (8—10°C) with etch solution in a bath of acetone/ice.

REF: Stopek, S — personal communication, 1956

GAS-0045c

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

1 .... HNO_3

3 .... H_2O

DISCUSSION:

GaAs, (111) wafers and spheres. The (111)A surfaces develop etch pits; and $(\overline{111})$B

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surfaces show terraces, only. A sphere etched to finite crystal form is a tetrahexahedron, (hk0). (*Note:* Solution is called Schell etch.)
REF: Richards, J L & Crocker, A J — *J Appl Phys*, 31,611(1960)

GAS-0045c
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres. Solution will polish both the (111)A and $(\overline{111})$B surfaces. A sphere etched to finite crystal form is a polished tetrahexahedron, (hk0).
REF: Ibid.

GAS-0045d
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HNO_3
1 .... $AgNO_3$
3 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres. Both the (111)A and $(\overline{111})$B surfaces develop pits. A sphere etched in this solution shows no finite crystal form.
REF: Ibid.

GAS-0045e
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
7 .... HNO_3
8—12 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres. Both the (111)A and $(\overline{111})$B surfaces develop pits. A sphere etched to finite crystal form is a highly terraced rhombic dodecahedron, (hh0).
REF: Ibid.

GAS-0045f
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
0—4 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres. The (111)A surface will polish in this solution; whereas the $(\overline{111})$B surface will develop pits. The finite crystal form is a rhombic dodecahedron (hh0).
REF: Ibid.

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GAS-0005b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: 60°C
COMPOSITION:
1 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, (111), n-type, 5—30 Ω cm resistivity wafers used in an etch development study. When used hot, this solution can be very rapid and slightly preferential.
REF: Ibid.

GAS-0147
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in a study of zinc diffusion. Solution used to etch clean wafers prior to diffusion to remove subsurface damage from lapping and polishing. Zinc was diffused at 650—700°C, 3—72 h (66 h gave an 8 μm diffusion depth). A KOH:$K_2Fe(CN)_6$ solution was used as a junction etch on ⟨110⟩ cleaved cross-sections.
REF: Lowen, J & Rediker, R H — *J Electrochem Soc*, 107,26(1960)

GAS-0140c
ETCH NAME: Nitric acid TIME:
TYPE: Acid, removal TEMP: RT and hot
COMPOSITION:
(1) x .... HNO_3 (2) 2 .... HNO_3 (3) 1 .... HNO_3
1 .... H_2O 2 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in an etch development study. Both white and red fuming nitric acid were evaluated. Red fuming nitric etches more rapidly. Both solutions attack GaAs at RT.
REF: Ibid.

GAS-0140d
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT or hot
COMPOSITION:
(1) 1 .... HCl (2) 2 .... HCl
1 .... HNO_3 1 .... HNO_3
DISCUSSION:
GaAs, (111) wafers used in an etch development study. The 1:1 solution is moderate to vigorous at RT. The 2:1 solution shows slow reaction at both RT and hot temperatures.
REF: Ibid.

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GAS-0140e
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:
GaAs, (111) wafers used in an etch development study. Solution will attack GaAs with a moderate to vigorous reaction at RT.
REF: Ibid.

GAS-0149
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
6 .... H_2SO_4
1 .... H_2O
DISCUSSION:
GaAs:Cr, (100) (SI) wafers used as substrates for GaAs growth by MBE. Wafers were etch cleaned in this solution and then edge-cleaved into square blanks in ⟨110⟩ directions to eliminate the etch-curved edges before MBE.
REF: Van Hove, J M et al — *J Vac Sci Technol,* B3,563(1985)

GAS-0150
ETCH NAME: TIME:
TYPE: Acid, cleaning/removal TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
DISCUSSION:
GaAs:Cr, (100) (SI) wafers, or un-doped wafers used as substrates for SrF_2 and CaF_2 thin film deposition in a study of the films growth habit. Prepare wafers by: (1) degrease in solvents; (2) rinse in acetone, then MeOH, then DI H_2O; (3) use etch shown to remove residual lap damage and clean surfaces; (4) rinse in DI H_2O, and (5) N_2 blow dry.
REF: Sullivan P W et al — *J Vac Sci Technol,* B3,500(1985)

GAS-0151
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
7 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in a study of the atomic surface structure of epitaxy GaAs deposited by MBE. Degrease wafers and etch clean with solution shown before MBE.
REF: Croydon, W F et al — *J Vac Sci Technol,* B3,604(1985)
GAS-0249: Wang, W I — *J Vac Sci Technol,* B1(3),630(1983)
GaAs:Cr, (110) wafers used as substrates for epitaxy growth of GaAlAs thin films. Solution used to etch clean surfaces. An Ar^+ ion laser, 1—100 W power, was used for PL measurements.

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GAS-0152
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) and (111) wafers used as substrates for MBE growth of germanium thin films. Etch clean with the solution shown, rinse in H_2O and N_2 blow dry. Argon ion sputter clean in vacuum before Ge deposition.
REF: Katnani, A A et al — *J Vac Sci Technol,* B3,608(1985)

GAS-0153
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
20 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used as substrates for MBE deposition of AlGaAs in a morphology study. Degrease substrates with solvents, then etch with solution shown, and N_2 blow dry.
REF: Stall, R A et al — *J Vac Sci Technol,* B3,524(1985)

GAS-0087b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) Te-doped, n-type wafers used in a study of the oxygenation of surfaces. Degrease with MeOH. Dip in HCl to remove native oxide and then etch in solution shown. Anneal in UHV, 30 min at 800°C before oxidizing.
REF: Szuber, J — *Thin Solid Films,* 112,309(1984)

GAS-0049c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
2 .... H_2O_2
5 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres used in an etch development study. The (111)A surface produces etch pits, and $(\overline{1}\overline{1}\overline{1})$B surface produces terraces.
REF: Ibid.

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GAS-0049d
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... H_2O_2
DISCUSSION:
GaAs, single crystal sphere. Etched in this solution to finite crystal form as a tetrahexahedron, (hk0).
REF: Ibid.

GAS-0049e
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
2 .... H_2O_2
5 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres cut from ingots grown by Horizontal Bridgman (HB). The (111)A surface develops etch pits, and the $(\overline{1}\overline{1}\overline{1})$B develops only terraces.
REF: Ibid.

GAS-0045g
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
2 .... H_2O_2
6 .... H_2O
DISCUSSION:
GaAs, (111) wafers and spheres. The (111)A surface produces pits, and $(\overline{1}\overline{1}\overline{1})$B surface is terraced. The sphere etches to a finite crystal form of a tetrahexahedron, (hk0).
REF: Ibid.

GAS-0155
ETCH NAME: TIME: 2 min
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs:Cr, (100) (SI) wafers used as substrates for MBE thin film growth of GaAs. Degrease substrates in TCE, then rinse in acetone, then MeOH. Etch clean with solution shown, then rinse in DI H_2O, and N_2 blow dry before MBE.
REF: Salerno, J P et al — *J Vac Sci Technol*, B3,618(1985)
AS-0239: Katnani, A A et al — *J Vac Sci Technol*, B3(2),608(1985)
GaAs, (100) and (111) wafers used as substrates for MBE growth of Ge thin films. Clean substrates: (1) etch in solution shown, with DI H_2O rinse and N_2 blow dry, (2) Ar^+ ion sputter clean in MBE vacuum system immediately prior to germanium deposition.

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GAS-0156
ETCH NAME: Vacuum
TYPE: Vacuum, cleaning
COMPOSITION:
x .... vacuum
TIME:
TEMP:
DISCUSSION:
GaAs, (110) wafers were cleaved under UHV to obtain very clean surfaces and, with no further treatment, still in vacuum, were then evaporated with Ag, Al, and Au. (*Note:* Cleaved wafers can have microstructure on surfaces, and are often fine etch polished before metallization.)
REF: Newman, N et al — *J Vac Sci Technol,* A3,996(1985)

GAS-0157
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
2% .... HF
1.2% .... H_2O_2
96.8% .... H_2O
TIME:
TEMP: RT
RATE: 1000 Å/min
DISCUSSION:
GaAs, (100), n-type wafers cleaved and used in a study of etch treatments. Clean wafers: (1) degrease in boiling TCE; (2) rinse in hot acetone, and (3) rinse in hot MeOH. Wafers were dip etched cleaned in concentrated HCl immediately before being placed in vacuum. Wafers were Ar^+ ion cleaned, then stored in air. Wafer backs were AuGe sputter metallized, then re-etched to clean front surfaces. It was noted that Ar^+ ion bombardment produced a damage depth of 100 Å. (*Note:* Care should be taken in using hot acetone due to its fairly low flash ignition point.)
REF: Huber, E & Hartnagel, H L — *Solid State Electron,* 27,589(1984)

GAS-0159
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
2—3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME:
TEMP: 70°C
DISCUSSION:
GaAs, (100) wafers used in a study of preparing carbon free GaAs surfaces. Surfaces analyzed by AES and RHEED. Mix solution fresh and use with heavy ultrasonic stirring.
REF: Munoz-Yagus, A — *J Electrochem Soc,* 128,149(1981)

GAS-0160
ETCH NAME:
TYPE: Acid, photo-selective
COMPOSITION:
1 .... HF
1 .... H_2O_2
10 .... H_2O
TIME: 2 min
TEMP: RT
DISCUSSION:
GaAs, (110), (111), and (211) wafers and GaAs/GaAs epitaxy used in a study of ridge/valley growth structure that shows variable resistivity. Wafers were saw cut, mechanically lapped and polished and then cleaved. Illuminate etch solution during etching with a tungsten

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lamp. Develops "Valley traces type II" striations showing variable resistivity. (*Note:* Similar resistivity variations have been observed in silicon, germanium, and several compound semiconductors. In some cases, as concentric rings of ridge/valley structure. In other cases, as segregation areas of high doping elements. Concentric ring/zone variation can be a problem in critical etching of large volume, small devices on any wafer, particularly, where wafer sizes are greater than 2" in diameter. Resistivity increases from center toward wafer periphery, and etch rates vary across wafer surfaces.)
REF: Lu, Y C & Bauser, E — *J Cryst Growth,* 71,305(1985)

GAS-0161
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
8 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs; Zn, (100) wafers cut 2—3°-off plane toward (110). Wafers were solvent cleaned prior to etch polishing in the solution shown.
REF: Lewis, C R & Ludowise, M J — *J Electron Mater,* 12,749(1984)

GAS-0166
ETCH NAME: TIME:
TYPE: Acid, clean TEMP:
COMPOSITION:
3 .... NH_4OH
1 .... H_2O_2
70 .... H_2O
DISCUSSION:
GaAs, (100) wafers cut 2°-off plane toward (110). Wafers used in an evaluation of the new design of a quartz envelope heater for MBE growth of GaAs/GaAs (100). GaAs substrates were degreased and then etch cleaned in the solution shown before MBE. Substrates were undoped, and cut from ingots grown by LEC. After MBE, cleave wafers ⟨110⟩, and stain in a 1:1:8 A/B solution to develop dislocations and layer structure. (*Note:* See GAS-0059 for A/B solution.)
REF: Boidish, S I et al — *J Electron Mater,* 14,586(1985)

GAS-0167a
ETCH NAME: Superoxol TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a polarity study of III—V compound semiconductors. Solution develops triangle pits on the (111)A, but only variable structure on $(\overline{111})$B. Other compounds studied were: InSb, InAs, and GaSb.
REF: Faust, J W & Sayar, A — *J Appl Phys,* 31,331(1960)

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GAS-0167b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
3 .... HNO_3
1 .... 40% tartaric acid
DISCUSSION:
GaAs, (111) wafers used in a polarity study. Solution develops etch pits on (111)A surfaces.
REF: Ibid.

GAS-0167c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HCl
1 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a polarity study. See GAS-0057 and GAS-0052 for use of similar solutions. The first reference is called preferential; the latter a polish etchant.
REF: Ibid.

GAS-0167d
ETCH NAME: Sodium hydroxide TIME:
TYPE: Alkali, preferential TEMP:
COMPOSITION:
1 .... 40% NaOH
3 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a polarity study. Solution develops etch pits on both positive and negative surfaces.
REF: Ibid.

GAS-0168
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
2 .... H_2O_2
5 .... H_2O
DISCUSSION:
GaAs, specimens cut as cylinders and hemispheres. Specimens were etched preferentially in the solution shown in developing shapes. Modified free energy theorems used to predict equilibrium growth and etching shapes. Also used germanium, etching with superoxol, a 1:1:4 mixture of the solution shown.
REF: Jaccodine, R J — *J Appl Phys*, 33,2663(1962)

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GAS-0169
ETCH NAME: TIME:
TYPE: Acid, junction TEMP: 30°C
COMPOSITION:
1 .... H_2SO_4
50 .... H_2O_2
1000 .... H_2O
DISCUSSION:
GaAs, (100) wafer Zn-doped were used as substrates for epitaxy growth of GaAs to form a p-n junction diode. Solution shown was used to delineate the p-n junction.
REF: Szubor, J M & Singer, K E — *J Vac Sci Technol*, B3,794(1985)

GAS-0170
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
15 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs:Cr, (100) (SI) wafers used for MBE growth of GaAs/GaAs (100). Solution used to etch clean wafer prior to epitaxy.
REF: Kobayashi, K et al — *J Vac Sci Technol*, B3,753(1985)

GAS-0171
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
Ga, (100) wafers used as substrates for selective deposition of tungsten. Cleaning procedure was: (1) chem/mech polish with xBr_2:xMeOH; (2) clean in solution shown; (3) dip in 1HCl:1H_2O, and (4) in vacuum with an As_4 overpressure. Thermally clean at 625°C prior to tungsten deposition for 1000 Å metal thickness. Surface was photo resist processed for pattern openings and the tungsten etched by RF plasma using CF_4:O_2(5%), 3 min at 50 W power, and 1.5 Torr pressure with an additional 10 sec at 0.5 Torr and 100 VDC on the substrate to clean the GaAs surface.
REF: Harbison, J P & Derkits, G E Jr — *J Vac Sci Technol*, B3,743(1985)

GAS-0172
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... H_2SO_4
x .... H_2O_2
x .... H_2O
DISCUSSION:
GaAs:Cr (100) (SI) wafers used as substrates for MBE growth of thin film epitaxy as GaAs/GaAs. Wafer cleaning procedure before MBE was: (1) degrease in solvents; (2) clean

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in solution shown; (3) DI water rinse. Final clean in vacuum at 580°C, 5 min with a 1×10^{-6} Torr back-pressure of As_4.
REF: Shimizu, S et al — *J Vac Sci Technol*, B1,554(1985)

GAS-0173a
ETCH NAME: Sodium hypochlorate TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... NaClO
DISCUSSION:
GaAs, (111)A wafer surfaces used in a study of facet development through holes opened in an SiO_2 mask. After photolithographic opening of the mask, surfaces were etched in the solution shown to develop controlled side slopes in etched pits. On (100) processed wafer surfaces, either $1Br_2$:1000MeOH or 0.7 *M* H_2O_2:1.0 *M* NaOH solutions were used to etch form the pits.
REF: Shaw, D W — *J Electrochem Soc*, 115,777(1968)

GAS-0173b
ETCH NAME: BRM TIME:
TYPE: Halogen, preferential TEMP:
COMPOSITION:
1 .... Br_2
1000 .... MeOH
DISCUSSION:
GaAs, (100) wafers, and other orientations, except (111)A, were used as substrates in a facetted hole etching study. See GAS-0173a for added discussion.
REF: Ibid.

GAS-0173c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... 0.7 *M* H_2O_2
x .... 1 *M* NaOH
DISCUSSION:
GaAs, (100) wafers and other orientations, except (111)A, used in a study of etched pit facet development through a silica mask to define a hole. See GAS-0173a for additional discussion.
REF: Ibid.

GAS-0174
ETCH NAME: TIME: 10 min
TYPE: Acid, preferential TEMP: 82°C
COMPOSITION:
x .... 0.2 *N* $FeCl_3$
x .... 6 *N* HCl
DISCUSSION:
GaAs, (111) wafers used in a study of surface etching characteristics of (111)A vs. $(\overline{111})$B polarity. Other compound semiconductors studied using other specific etchants were InSb, InAs, GaSb, AlSb, InP, and InSb. The direction of positive (+) and negative (−) tetrahedrons (111) pit directions were used to establish the A vs. B wafer face. (*Note:*

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Tetrahedrons show 180°C rotation of their triangle pit orientations on opposed positive and negative wafer sides from (111)A to ($\overline{111}$)B. This is true for all (111) oriented materials.)
REF: Gatos, H C & Lavine, M C — *J Electrochem Soc,* 107,427(1960)

GAS-0175
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: Hot
COMPOSITION:
x .... 4% NaOH
x .... 5% H_2O_2
DISCUSSION:
GaAs, (111) wafers fabricated as Esaki diodes for high frequency applications. Solution used for polishing and finishing diodes. Other solutions evaluated included aqua regia and mixtures of HF:HNO_3. The solution shown gave best polishing and cleaning results.
REF: Burrus, C A — *J Appl Phys,* 32,1031(1961)

GAS-0176
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... HCl
x .... HNO_3
x .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a study of electrical properties. Author says that if the solution shown is used without dilution it will chemically polish.
REF: Detweiler, D P — *Phys Rev,* 97,1575(1955)

GAS-0177
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers used in a polarity etching study. The solution shown develops etch pits on negative ($\overline{111}$)B, arsenic surface, but no pits on the positive (111)A gallium surface.
REF: White, J C & Roth W C — *J Appl Phys,* 31,611(1960)

GAS-0179
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
5 .... HCl
1 .... HNO_3
DISCUSSION:
GaAs, (111) wafers used in a heat treatment study of the material. Solution was used to polish n-type GaAs. Water wash after etching.
REF: Edmonds, J T — *J Appl Phys,* 31,142b(1960)

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GAS-0180
ETCH NAME: Nitric acid
TYPE: Acid, junction
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:
DISCUSSION:
GaAs, as thin film epitaxy grown on germanium substrates to form p-n junctions. The solution shown was used to delineate the junction. Also studied GaAs/GaP and GaP/Ge as epitaxy thin films grown on substrates as devices.
REF: Weinstein, M et al — *J Electrochem Soc*, 111,674(1964)

GAS-0181
ETCH NAME: Potassium hydroxide
TYPE: Alkali, reactivity
COMPOSITION:
(1) x .... 1 *M* KOH + ... O_2
(2) 1 .... NH_4OH 1 .... H_2O + ... O_2/N_2
(3) x .... H_2O 3 .... H_2O + ... O_2/N_2
(4) 1 .... H_2SO_4 + ... O_2/N_2
TIME:
TEMP:
DISCUSSION:
GaAs, (100) wafers used in a study of acid vs. base surface treatment. All solutions shown were used with oxygen or nitrogen bubbled through the etchant during the test period. HCl also was evaluated and was similar to (4). Solution (2) was no better in preventing surface degradation than water, (3), and also produced surface micro-roughness requiring re-polish with acid solutions. Rapid O_2 increase on surfaces with (4) remained unless reduced with a bromine-methanol treatment as re-polishing. Surfaces more susceptible to acid attack than with bases.
REF: Aspenes, D E — *J Vac Sci Technol*, A(3),1018(1985)

GAS-0182a
ETCH NAME:
TYPE: Acid, polish/clean
COMPOSITION:
5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME: 10 min
TEMP: 60°C
DISCUSSION:
GaAs, (100) wafers, Cr-O doped semi-insulating (SI) substrates used for ZnS epitaxy growth. GaAs, $(\overline{111})$B wafers, arsenic doped also used. After chem/mech lap with Br_2:MeOH and degreasing in solvents, wafers were cleaned as follows: (1) etch in solution shown; (2) rinse in DI H_2O; (3) etch 10 min in HCl at 30°C to remove oxide, and (4) final water rinse and drying. Gallium phosphide wafers also were used as substrates.
REF: Yoneda, K et al — *J Cryst Growth*, 67,125(1984)

GAS-0184
ETCH NAME: Sodium hypochlorite
TYPE: Acid, polish/removal
COMPOSITION:
x .... x% NaClO
TIME: 2 h
TEMP: RT
RATE: 3 mils/2 h
DISCUSSION:
GaAs:Cr, (100) (SI) wafers used as substrates for epitaxy growth of InAs. Use solution shown on a paper pad to polish wafers. Just before epitaxy: (1) etch clean in

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$5H_2SO_4$:$1H_2O_2$:$1H_2O$, RT, 5 min then add $5H_2O$ for an additional 5 min all with beaker rotating. After epitaxy, cleave (110) and stain etch, RT, 1 sec in solution shown. To obtain defect density, etch in 1HF:$3HNO_3$.
REF: Cronin, G R et al — *J Electrochem Soc*, 113,1336(1966)

GAS-0187a
ETCH NAME: TIME:
TYPE: Halogen, polish TEMP:
COMPOSITION:
x .... x% Cl_2
x .... MeOH
DISCUSSION:
GaAs, (111) and (100) wafers used in a study of photoluminescence and material growth. Solution used as a polish etch with chlorine gas bubbled through MeOH. Also used $2H_2SO_4$:H_2O.
REF: Panaish, M B et al — *Solid State Electron*, 9,311(1966)

GAS-0187b
ETCH NAME: Sulfuric acid TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... H_2SO_4
x .... H_2O
DISCUSSION:
GaAs, (111) and (100) wafers used in a study of photoluminescence and material growth. Solution used as a polish etch.
REF: Ibid.

GAS-0188a
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
x .... 1 *M* NaOH
x .... 0.7 *M* H_2O_2
DISCUSSION:
GaAs, (111) and (100) wafers used in a study of etching and etch rates through an SiO_2 surface coating mask. All of the following solutions showed etch undercut at the SiO_2 mask edge: (1) $1Br_2$:1000MeOH; (2)$5H_2SO_4$:$1H_2O_2$:$1H_2O$; (3) 3% $HClO_4$; and (4) HCl vapor in vacuum at 800°C. The holes were deeper around and near the SiO_2 mask edges. Solution shown did not etch holes with such undercutting and edge depth variation.
REF: Shaw, D W — *J Electrochem Soc*, 113,958(1966)

GAS-0194
ETCH NAME: TIME:
TYPE: Acid, cleaning sequence TEMP:
COMPOSITION:
(1) degrease
(2) 7 .... H_2SO_4
1 .... H_2O_2
DISCUSSION:
GaAs:Cr, (100) (SI) wafers used as substrates for epitaxy growth of single crystal $ZnGeAs_2$. Substrates were degreased successively in TCE, then rinsed in acetone, and MeOH. Then etch in solution shown, water rinse, and final N_2 jet blow dry. Substrates

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were mounted on $ZnGeAs_2$ coated Mo heater blocks with indium and heated to 450—520°C in the sputter system before MBE growth.
REF: Shah, S I & Greene, J E — *J Cryst Growth,* 68,537(1984)

GAS-0193c
ETCH NAME: TIME:
TYPE: Acid, junction TEMP:
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers within 2° of plane used as substrates for OMVPE growth of Mg-doped GaAs layers. After epitaxy, cleave ⟨110⟩ and use solution shown to stain develop junction. Also used as a cleaning/polishing etch on initial GaAs substrates prior to epitaxy.
REF: Lewis, C R et al — *J Electron Mater,* 12,507(1983)

GAS-0195a
ETCH NAME: Sodium hypochlorate TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... x% NaClO
DISCUSSION:
GaAs, (100) wafers cut within 2—3° of plane. Use solution to polish etch wafers, then clean as follows: (1) degrease; (2) clean in HCl; (3) etch clean in $5H_2SO_4$:$1H_2O_2$:$1H_2O$; and (4) rinse in DI water.
REF: Abrokwah, J I C — *J Electron Mater,* 12,681(1983)

GAS-0197
ETCH NAME: TIME:
TYPE: Acid, dissolve TEMP:
COMPOSITION:
x .... HCl
x .... HNO_3
DISCUSSION:
GaAs wafers grown by Horizontal Bridgman (HB) technique and then dissolved in an aqua regia type solution for a study of iron contamination.
REF: Udagawa, T V et al — *J Electron Mater,* 12,563(1983)

GAS-0028b
ETCH NAME: TIME:
TYPE: Acid, cleaning sequence TEMP:
COMPOSITION:
(1) x .... acetone (2) x .... MeOH, vapor (3) x .... HCl
DISCUSSION:
GaAs, (100) wafers used as substrates for deposition of CVD SiO_2 and SiN_x, then an SiO_2 cap layer used as masks for zinc diffusion into GaAs in a study of pinhole reduction. Wafers were degreased and etch cleaned with solvents as shown.
REF: Blaauw, C et al — *J Electron Mater,* 13,251(1984)

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GAS-0045h
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
1—2 .... H_2O_2
4—6 .... H_2O
DISCUSSION:
GaAs, (111) as single crystal wafers and spheres. The (111)A face developed etch pits; the $(\overline{1}\overline{1}\overline{1})$B, terrace, structure. The sphere etched to a finite crystal form as a tetrahexahedron, (hk0).
REF: Ibid.

GAS-0049e
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
2 .... H_2O_2
5 .... H_2O
DISCUSSION:
GaAs, (111) wafers cut from ingots grown by horizontal zone melting. Solution developed etch pits on (111)A surfaces; terraces on $(\overline{1}\overline{1}\overline{1})$B. (*Note:* Growth method is now called Horizontal Bridgman (HB).)
REF: Ibid.

GAS-0049f
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... H_2O_2
DISCUSSION:
GaAs single crystal spheres. Solution developed a finite crystal form as a tetrahexahedron, (hk0).
REF: Ibid.

GAS-0210
ETCH NAME: Potassium hydroxide TIME:
TYPE: Electrolytic, junction TEMP:
COMPOSITION: ANODE: GaAs
x .... KOH CATHODE:
x .... H_2O POWER:
DISCUSSION:
GaAs, (100) wafers fabricated as diodes in a study of electroluminescent properties with negative resistance. Solution used to electropolish and develop p-n junctions.
REF: Wieser, K & Levitt, R S — *J Appl Phys,* 35,2431(1964)
GAS-0212d; Ibid.
GaAs, (100) wafers used in an X-ray analysis of diffusion induced defects. A 5% KOH solution was used as an anodic junction etch.

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GAS-0211a
ETCH NAME: TIME:
TYPE: Acid, stain (p^+) TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
3 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in a study of growth methods using a Travelling Solvent technique with germanium doping. Solution used to develop structure of the p^+ growth areas. Also used 1HF:2H_2O as a dislocation etch.
REF: Mlavasky, A I & Weinstein, M — *J Appl Phys*, 34,2885(1963)

GAS-0212a
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION
2 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in an X-ray analysis of diffusion induced defects. Solution used as a chem/mech polish etch with wafers in a rotating beaker.
REF: Schwuttke, G H & Rupprecht, H — *J Appl Phys*, 37,167(1966)

GAS-0212b
ETCH NAME: TIME:
TYPE: Acid, junction TEMP: RT
COMPOSITION:
1 .... HF
1 .... H_2O_2
10 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in an X-ray analysis of diffusion induced defects. Solution used to develop p-n junctions.
REF: Ibid.
GAS-0213: Proebsting, R — *Semi Prod Solid State Technol*, November 1964, 33
GaAs, (100) wafers used to fabricate laser diodes. Wafers were zinc diffused at 850°C for 3 h for a 1 mil diffusion depth. After angle lap of portions of wafers, p-n junctions were etched developed as a follows: (1) place a drop of solution across junction at RT; (2) flood specimen surface with intense white light, etching 15—30 sec in solution shown.

GAS-0212c
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: 0°C
COMPOSITION:
3 .... H_2SO_4
1 .... H_2O_2
2 .... H_2O
DISCUSSION:
GaAs, (100) wafers used in an X-ray analysis of diffusion induced defects. Solution

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used to etch section wafers and for general removal in developing cross-section samples for diffusion depth measurement.
REF: Ibid.

GAS-0235
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
50 .... H_2O
TIME:
TEMP: 0°C
DISCUSSION:
GaAs, (100) wafers used in a study of the disorder influence of ion implantation. Prepare wafers: (1) mechanical polish to 0.5 mm thick; (2) chem/mech polish in solution shown prior to I^2.
REF: Anderson, W J & Parks, Y S — *J Appl Phys*, 49,4568(1978)

GAS-0218
ETCH NAME: BRM
TYPE: Halogen, removal/polish
COMPOSITION:
"A" x .... 7.5% Br_2
x .... MeOH
"B" + MeOH cover
TIME: To 10 min
TEMP: RT
DISCUSSION:
GaAs, (100) wafers handled with a special etching technique. "Cover" the BRM solution with a layer of pure MeOH. To etch, slowly lower wafer into BRM through the covering MeOH with minimal disturbance, etch for selected time period, then slowly remove with automatic quenching through the pure MeOH cover layer. Authors note the MeOH cover layer will diffuse downward 1 mm into the BRM solution in 10 min.
REF: Bisaro, R et al — *J Appl Phys*, 40,978(1982)

GAS-0219
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
4 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME: 2 min
TEMP: 50°C
DISCUSSION:
GaAs:Cr (100) (SI) wafers cut $^1/_2$°-off plane toward (110), and used in a study of dislocations. Chem/mech polish wafers in solution shown, then etch in molten flux KOH to develop dislocations.
REF: Mori, H & Takagashi, S — *J Cryst Growth*, 69,23(1984)

GAS-0220
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) 5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
(2) x .... x% Br_2
x .... MeOH
TIME: (1) 3 min (2) 2 min
TEMP: RT RT

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DISCUSSION:

GaAs, (100), n-type wafers prepared as substrates for epitaxy growth of GaAs. Clean in solutions in the order shown with DI H_2O rinse and N_2 blow-dry after each etch step.
REF: Howard, L M et al — *Thin Solid Films,* 96,285(1982)

GAS-0215
ETCH NAME: RIE
TYPE: Ionized gas, structuring
COMPOSITION:

(1) x .... CHF_3 (2) x .... CCl_4

TIME:
TEMP:
GAS FLOW:
PRESSURE
POWER:
(3) x .... CCl_4
x .... Cl_2

DISCUSSION:

GaAs, (100) wafers used in a development study using dry chemical etching (DCE) to form submicron structures. PMMA photo resist used to pattern mesas. Plasma etch (PE) or RIE/RIBE used with gases shown above. CCl_4 develops sloped mesa sides with a bottom trench at the base; with added Cl_2 forms a vertical sided pylon.
REF: Wolf, E D et al — *Proc IEEE* 30,592(1983)

GAS-0227
ETCH NAME:
TYPE: Acid, oxidizing
COMPOSITION:
3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O

TIME:
TEMP:

DISCUSSION:

GaAs, (100) and InSb, (100) wafers used in a cleaning study of surfaces prior to MBE epitaxy growth. After etch cleaning in solution shown, rinse with filtered DI H_2O with wafers on spinner at 3000 rpm. In the MBE vacuum system heat to 590°C to remove residual oxide developed and remaining after etching/rinsing. (*Note:* This is one of several solutions for oxidizing a surface, then stripping the oxide as a surface cleaning step.)
REF: Vasquez, R P et al — *J Vac Sci Technol,* B(3),791(1983)

GAS-0241
ETCH NAME:
TYPE: Molten flux, defect
COMPOSITION:
1 .... KOH
1 .... NaOH

TIME: 1—120 min
TEMP: 325—350°C

DISCUSSION:

GaAs:Cr, (100), (111) (SI), and n-type Si doped wafers used in a defect study. Molten solution as a KOH:NaOH eutectic mixture used in a platinum crucible with wafers in a Pt wire basket. Wafers were cleaned: (1) DI water rinse; (2) acetone rinse; (3) MeOH dip, and (4) 2-propanol (ISO) rinse and, (4) hot N_2 blow drying. GaAs blanks were cut 5 mm square and 0.38 mm thick. The (100) etched 15—120 min; (111), 1—30 min at temperatures shown. Etch rates computed from weight loss: (1) 325°C — (100) 0.02 μm/min; (111), 0.06 μm/min, (2) 350°C — (111) 0.22 μm/min and (100), 0.09 μm/min. Solution develops dislocation pits and other defects. As these alkalies are hygroscopic, repeatability is difficult

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due to variable water inclusion, but results are comparable to other etching systems. There are some rate variations as shown by the references below.
REF: Lessoff, H & Gorman, R — *J Electron Mater,* 13,733(1984)
GAS-0242: Richter, H & Schulz, M — *Krist Tech,* 9,1041(1974)
GaAs, (100) wafers. Rate shown as 1 μm/min at 350°C.
GAS-0243: Iskii, M et al — *Jpn J Appl Phys,* 15,645(1976)
GaAs, (100) wafers. Rate shown as 0.98 μm/min at 350°C.
GAS-0244: Takenenaka, T et al — *Jpn J Appl Phys,* 17,447(1978)
GaAs, (100), n-type, Si doped wafers. Rate shown as 0.15 μm/min at 350°C.
GAS-0245: Wagner, W R & Greene, L I — *J Electrochem Soc,* 128,1091(1981)
GaAs, (100) wafers. KOH, only, with m.p. of 360°C. Etching done from 360 to 365°C. Etching in a dry atmosphere did not develop dislocations. Needs the presence of residual water in the molten KOH?

GAS-0228
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP: RT
COMPOSITION:
1 .... H_2SO_4
10 .... H_2O_2
10 .... H_2O
DISCUSSION:
GaAs, (100), n-type, 0.001—0.04 Ω cm resistivity, wafers used as substrates for 1000 Å Pt evaporation and anneal in a study of interface reactions. Clean substrates: (1) in HCl, conc.; (2) in NaClO solution; (3) and in $1HCl:1H_2O$ with DI water rinse between each step. After metallization and annealing, initially lap thin GaAs substrate back, and final thin with solution shown for interface study by TEM.
REF: Fontaine, C — *J Appl Phys,* 54,1404(1981)

GAS-0230
ETCH NAME: TIME: 90 sec
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
10 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAs, (111)As, (100) and (110) oriented wafers prepared as epitaxy growth substrates for MBE. Clean substrates: (1) degrease; (2) clean with solution shown; (3) 30 sec DI water rinse, and (4) N_2 blow dry. After mounting on moly heater blocks in the MBE vacuum system, desorb residual oxygen on wafer surfaces at 600°C under an As_4 atmosphere before epitaxy growth.
REF: Ballingall, J M — *J Vac Sci Technol,* B(1),163(1983)

GAS-0232
ETCH NAME: Sulfuric acid TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... H_2SO_4, conc.
DISCUSSION:
GaAs:Cr, (100) wafers used to fabricate hi-doped, hot electron devices, as mesa struc-

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tured diodes. Nickel evaporation used as contacts on mesas. Diodes were cleaned in solution shown, and it leaves a thin native oxide.
REF: Harris, J J & Woodcock, J M — *J Vac Sci Technol,* B(1),196(1983)

GAS-0233
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
5 .... NH_4OH
1000 .... H_2O_2
DISCUSSION:
GaAs, (100) wafers used in a study of zinc diffusion at 850°C. Prepare wafers by: (1) chem/mech polish in solution shown, and (2) final clean in solution of $5H_2SO_4$:$1H_2O_2$:$1H_2O$.
REF: Cognetti, C — *J Electrochem Soc,* 128,2198(1981)

GAS-0234
ETCH NAME: BRM TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
(1) 2 ml .... Br_2
1000 ml .... MeOH
(2) $1^1/_2$ ml .... Br_2
1000 ml .... MeOH
DISCUSSION:
GaAs and GaP, (100) and $(\overline{111})$B, high n-type wafers with Te doping used in a solution oxidation reaction study. Prepare wafers by chem/mech polishing in either solution shown using a solution saturated pellon pad. Soak samples 5 to 6 days in the following solvents or acids: (1) MeOH; (2) H_2O at RT and at 60°C; (3) 30% H_2O_2; (4) H_2SO_4; (5) HCl; (6) HNO_3; (7) NaOH, and (8) NaClO. All solutions were used to develop native oxides. These are hydrated type oxides as $Ga_2O_3.H_2O$ with a refractive index on n = 1.7. (*Note:* In the strictest sense of the word, a native oxide is one that forms under natural conditions of oxidation, not a manmade oxide, but any thin film oxide on a material surface is referred to as being a native oxide in Solid State processing.)
REF: Schwartz, B — *J Electrochem Soc,* 118,657(1971)

GAS-0246a
ETCH NAME: Ammonium hydroxide TIME:
TYPE: Base, cleaning TEMP:
COMPOSITION:
x .... NH_4OH
DISCUSSION:
GaAs, (100), p-type wafers used to fabricate light emitting diodes with Al or Au metallized dot contacts. This was a study of the effects of various surface treatments on light emission. Strong acids reduced or eliminated emission; whereas basic solutions show good results; and annealing at 350°C in N_2, 5 min showed improved emission efficiency. Effects may be due to excessive removal of gallium? Arsenic is soluble in HNO_3, and gallium in alkalies. Basic solutions remove Ga_2O_3 and $Ga(OH)_3$ leaving an As enhanced surface. Surfaces also oxidized in AGW solution (see GAO-0005a-b). The study included the crystal planes and their measured angles as etched structures. The following references cite the various solutions evaluated.
REF: Adachi, H & Hartnagel, H L — *J Vac Sci Technol,* 19(3),427(1961)
GAS-0246b: Ibid.

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GaAs, (100), p-type wafers. Chemical surface treatment solution was $1HCl:1H_2O$. See GAS-0246a.

GAS-0246c: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1NaOH:20H_2O_2:50H_2O$. See GAS-0246a.

GAS-0246d: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1NH_4OH:1H_2O$. See GAS-0246a.

GAS-0246e: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $20H_2SO_4:1H_2O_2:1H_2O$. See GAS-0246a.

GAS-0246f: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1H_2SO_4:1H_2O_2:50H_2O$. See GAS-0246a.

GAS-0246g: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1NaOH:1H_2O$. See GAS-0246a.

GAS-0246h: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1NaOH:1H_2O_2:30H_2O$. See GAS-0246a.

GAS-0246i: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1NaOH:3H_2O_2:150H_2O$. See GAS-0246a.

GAS-0246j: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $10H_3PO_4:1H_2O$. See GAS-0246a.

GAS-0246k: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $10H_3PO_4:1H_2O_2:1H_2O$. See GAS-0246a.

GAS-0246l: Ibid.

GaAs, (100), p-type wafers. Chemical surface treatment solution was $1H_3PO_4:2H_2O_2:10H_2O$. See GAS-0246a.

GAS-0251
ETCH NAME: Hydrofluoric acid
TYPE: Acid, selective
COMPOSITION:
x .... HF, conc.
TIME:
TEMP:
DISCUSSION:

GaAs:B, (111) n-type wafers and (100) undoped wafers used as substrates for LPE growth of GaAlAs Be doped thin films for p^+-p-n layer structured solar cells. The p-type GaAlAs films were selectively removed with HF to etch structure the cells.

REF: Masu, J et al — *J Electrochem Soc*, 129,1623(1982)

GAS-0253
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
x .... H_2O_2
x .... NH_4OH
TIME:
TEMP:
DISCUSSION:

GaAs, (100) wafers used as substrates for LPE growth of GaAlAs. The ammonium

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hydroxide was used as a buffering agent, and solution used to selectively remove the GaAs substrate. Swaninathan (GAS-0025) references this work for the solution he and co-workers used.
REF: Ralogan, T & Reinhart, F R — *J Appl Phys,* 44,4127(1973)

GAS-0254
ETCH NAME:
TYPE: Acid, junction
COMPOSITION:
3 .... NH_4OH
1 .... H_2O_2
150 .... H_2O
TIME:
TEMP: RT
RATE: 0.16 μm/min
DISCUSSION:
GaAs, (100) wafers zinc diffused. Solution used for depth profiling by channel or step-etching of the zinc diffused junction for measurement.
REF: Jett-Field, R & Ghandhi, S K — *J Electrochem Soc,* 129,1567(1982)

GAS-0257
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
(1) 5 .... NH_4OH
1000 .... H_2O_2
(2) 5 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME:
TEMP: RT
DISCUSSION:
GaAs, (100) wafers used for zinc diffusion at 850°C. Solution (1) was used as a general removal and chemical polish etch, and solution (2) for final surface polish prior to zinc diffusion.
REF: Chiaretti, O Y & Coonetti, C — *J Electrochem Soc,* 128,2193(1982)

GAS-0258
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
(1) 11 .... HNO_3
49 .... H_3PO_4
(2) 3 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
TIME: (1) 5 min (2) 1 min
TEMP: 60°C 60°C
DISCUSSION:
GaAs, (111) wafers "as-received" with (111)Ga surface polished. The $(\overline{111})$As negative side was additionally mechanically polished with 0.05 μm alumina, then wafers were cleaned in: (1) degrease in TCE; (2) MeOH rinse, and (3) final acetone rinse. Then etch clean in solution (1). Wafers of (100), (110), and $(\overline{111})$As were additionally etch cleaned in solution (2) which was referred to as Caro's etch (See SI-0103). All wafers were used as OMCVD substrates.
REF: Reep, D H & Ghandhi, S K — *J Cryst Growth,* 62,449(1983)

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GAS-0259
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
(1) 1 .... HF (2) x .... laser
1 .... H_2O_2
2 .... H_2O
DISCUSSION:
GaAs, (111) wafers used as substrates for epitaxy growth of Ge and ZnSe. Solution (1) was selective on both (111)Ga and $(\overline{1}\overline{1}\overline{1})$As surfaces. Laser annealing developed both etch pits and growth hillocks. Study involved the development of orientation light figures by etching epitaxy thin films. Authors say that acid and alkali solutions develop etch pits usable as such figures on (111)Ga but not on $(\overline{1}\overline{1}\overline{1})$As.
REF: Owens, S J T & Watt, A H — *Microelectronics,* 5(3),37(1974)

GAS-0261
ETCH NAME: TIME:
TYPE: Acid, stain TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
10 .... H_2O
DISCUSSION:
GaAs:Cr, (100) (SI) wafers cut 2°-off toward (110) for VPE growth of GaAs. To measure epitaxy thickness, angle lap a specimen at 5° and stain with solution shown.
REF: Yoshida, M et al — *J Electrochem Soc,* 132,930(1985)

GAS-0263a
ETCH NAME: TIME:
TYPE: Halogen, cleaning TEMP:
COMPOSITION:
(1) x .... x% Br_2 (2) 1 .... NH_4OH
x .... MeOH 1 .... H_2O_2
10 .... H_2O
DISCUSSION:
GaAs:Be, (110), p-type wafers used as substrates for epitaxy growth of AlGaAs in a comparative LEED study. Substrates were chem/mech polished with solution (1) on lint-free paper; wetted to moly discs with indium, then etch cleaned in solution (2) on a spinner at low speed before being placed in the MBE vacuum system for epitaxy growth.
REF: Kahn, A et al — *J Vac Sci Technol,* 21(2),382(1982)

GAS-0263b
ETCH NAME: Arsenic TIME:
TYPE: Metal, passivation TEMP: 300°C
COMPOSITION:
x .... As
DISCUSSION:
GaAs:Be, (100), p-type wafers used as substrates for epitaxy growth of AlGaAs by MBE. After MBE deposition, wafers coated with a thin layer of arsenic below RT while

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still in the system, held at 10^{-5} Torr in sealed quartz ampoules, and then heated to 300°C to desorb arsenic as a final surface cleaning and stabilization step.
REF: Ibid.

GAS-0248a
ETCH NAME: BRM
TYPE: Halogen, cleaning
COMPOSITION:
(1) 1 .... HCl
9 .... H_2O
(2) x .... 1% Br_2
x .... MeOH
TIME:
TEMP:
DISCUSSION:
GaAs, (100) wafers used in a study of anodic oxidation. Wafers were cleaned in solution (1), then solution (2), followed by MeOH rinse, DI H_2O rinse, and N_2 drying. Anodically oxidize in 1 3% tartaric acid:6 propylene glycol at 0.15 mA/cm² power. See GAS-0248b for surface replication.
REF: Makky, W H et al — *J Vac Sci Technol,* 21(2),417(1982)

GAS-0248b
ETCH NAME:
TYPE: Metal, replication
COMPOSITION:
(1) x .... 4% collodion,
x .... amyl acetate
(2) x .... Pt
(3) x C
TIME:
TEMP:
DISCUSSION:
GaAs, (100) wafers used in a study of anodic oxidation steps. After oxidation, surfaces were replicated: coat surface with solution (1); evaporate (2) as a platinum thin shadow film at a 22° angle; and sputter 200 Å of carbon (3). Remove C/Pt replication film by dissolving collodion with amyl acetate for SEM study of the replication film.
REF: Ibid.

GAS-0248c
ETCH NAME:
TYPE: Electrolytic, oxidation
COMPOSITION:
1 .... 3% tartaric acid
6 .... propylene glycol
TIME:
TEMP:
ANODE: GaAs
CATHODE:
POWER: 0.15 mA/cm²
DISCUSSION:
GaAs, (100) wafers used in a study of anodic oxidation steps. Solution used to grow the oxide.
REF: Ibid.

GAS-0265
ETCH NAME: Acetone
TYPE: Ketone, lift-off
COMPOSITION:
x .... CH_3COCH_3 (acetone)
TIME:
TEMP: RT to warm
DISCUSSION:
GaAs, (100) wafers used for device fabrication and dielectric circuit substrates of alumina, both with fine line metallization patterning. A description of a variety of lift-off techniques applicable to different materials.
REF: Frary, J M & Seese, P — *Semiconductor Int,* December 1981, 7289

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GAS-0266
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
2 .... HF
15 .... HNO_3
5 .... HAc
DISCUSSION:
GaAs, (100) wafers used to fabricate Schottky barrier diodes with low doping for high reverse V_{bd}. Solution used to etch clean wafers with a BHF dip immediately prior to metal evaporation.
REF: Stolt, L et al — *J Solid State Electron,* 26,2195(1983)
GAS-0267: Wheatly, C H & Whelan, J M — *J Phys Chem Solids,* 6,169(1958)
GaAs ingots used in a study of preparation and properties. Solution used as a general etch.

GAS-0268
ETCH NAME: Potassium hydroxide TIME:
TYPE: Molten flux, defect TEMP:
COMPOSITION:
x .... KOH, pellets
DISCUSSION:
GaAs:Cr, (100) (SI), and InP:Fe, (100) (SI) wafers deposited with epitaxy layers of GaAlAs, and InGaAsP, respectively. A study of material defects and contact alloys, and the effect of temperature annealing. Metal alloys were AuGe and InGe. The molten flux shown above was used for defect development of GaAs specimens; Huber's etch on InP (See INP-0072). Describes thread dislocations, grappes, and other type defects.
REF: Chin, A K — *J Cryst Growth,* 70,582(1984)

GALLIUM ALUMINUM ARSENIDE, GaAlAs

General: Does not occur as a natural compound. The compound has no direct use in industrial metal processing, though metallic gallium has several applications as a low temperature alloy. See section on Gallium for further discussion.

Technical Application: GaAlAs thin films are grown on GaAs substrates as p-n or p^+-p-n junction solar cells. Collection efficiency has been as high as 30%, as against about 18% for silicon, but fabrication costs of single crystal gallium arsenide solar cells are some three to four times greater than that for silicon at present.

Thin film growth has been by MBE, OMCVD, and LPE, as a single layer on GaAs substrates, or as a multilayered heterojunction structure with other materials.

Etching: HF:HNO_3 mixed acids or halogens.

GALLIUM ALUMINUM ARSENIDE ETCHANTS

GASA-0001
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF, conc.
DISCUSSION:
(Ga,Al)As:Be, p-type thin films grown on n-type (111) GaAs:B, and (100) GaAs un-

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doped wafers that were n-type. Thin films grown by LPE in fabricating p^+-p-n junction solar cells. HF used for selective removal of (Ga,Al)As.
REF: Masu, K et al — *J Electrochem Soc*, 129,1623(1982)
Note: See previous section on Gallium Arsenide for additional solutions that are selective to either GaAs or GaAlAs:

GAS-0004a-d	*GAS-0061a-f	GAS-0153
GAS-0019	GAS-0060	GAS-0165
GAS-0023	GAS-0105	GAS-0184a
GAS-0025	GAS-0108a-b	GAS-0221

*Selective solutions for both materials.

GALLIUM ARSENIDE PHOSPHIDE ETCHANTS

GASP-0001
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP: RT
COMPOSITION:
8 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
GaAsP wafers as highly p-type doped with Mn. Solution used to develop dislocations.
REF: Fujita, S et al — *Solid State Electron*, 25,359(1982)

GALLIUM IRON OXIDE ETCHANTS

GIO-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
TIME:
TEMP: Hot
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:
$GaFeO_3$, single crystal ingot boat grown. Solution used to remove crystal from boat and clean surfaces after growth. The material is a ferromagnetic and piezoelectric compound. See sections on Ferrite, Iron, Steel, Magnetite, Hematite, and other iron-containing compounds.
REF: Rumeika, J P — *J Appl Phys*, 31,2638(1960)

PHYSICAL PROPERTIES OF GALLIUM NITRIDE, GaN

Classification	Nitride
Atomic numbers	31 & 7
Atomic weight	83.73
Melting point (°C)	800 sub.
Boiling point (°C)	
Density (g/cm^3)	
Energy gap (eV)	3.5

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Coefficient of linear thermal expansion	
(cm/cm) 300—900 K — perpendicular to c-axis	5.59
(cm/cm) to 700 K — parallel to c-axis	3.17
(cm/cm) 700 to 900 K — parallel to c-axis	7.75
Atomic spacing (angstroms)	3.18 or 5.185
Hardness (Mohs — scratch)	6—7
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Silver-grey
Cleavage (basal)	(0001)

GALLIUM NITRIDE, GaN

General: Does not occur as a natural compound. Gallium is a rare element found as traces in other minerals, such as sphalerite, ZnS, and bauxite, a complex hydrated iron/aluminate. As these two minerals are major ores of zinc and aluminum, respectively, gallium is available in usable quantities from recovery during processing of the ores of the two minerals.

There is no use for gallium nitride in industry other than for possible applications in the Solid State and electronics fields.

Technical Application: Gallium nitride is a III—V compound semiconductor. It can be easily grown from a solid gallium source in a nitrogen atmosphere both as an amorphous thin film or as a single crystal compound by CVD and OMCVD techniques. It also has been RF or DC sputtered as a thin film from both a solid GaN target or deposited from gallium in nitrogen atmosphere. The latter being difficult to control due to the low melting point and vapor pressure of gallium (30°C temperature).

It is under evaluation as a thin film surface coating and has been used to fabricate electroluminescent thin film diodes.

Etching: Deliquesces in most single acids. Soluble in alkalies.

GALLIUM NITRIDE ETCHANTS

GAN-0001
ETCH NAME: Sodium hydroxide
TYPE: Electrolytic, selective jet
COMPOSITION:
x .... 0.1 *N* NaOH

TIME:
TEMP:
ANODE: GaN
CATHODE:
POWER:

DISCUSSION:

GaN, (0001) single crystal thin films. Sodium hydroxide is a general etch for gallium nitride. The author says that an insoluble gallium hydroxide, GaOH coating, will form on the surface during etching unless the solution is continually washed away by the jet action.
REF: Pankove, J I — *J Electrochem Soc,* 119,1118(1972)

GAN-0002
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... 30—50% NaOH

TIME:
TEMP: Hot (80°C)

DISCUSSION:

GaN thin films. Described as a general removal etch for gallium nitride. (*Note:* 2—5% concentrations, RT, have been used for pinhole development.)
REF: Chu, T L — *J Electrochem Soc,* 118,1200(1971)

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GAN-0003
ETCH NAME: Hydrochloric acid — TIME: 10—20 sec
TYPE: Acid, removal/clean — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... H_2O
DISCUSSION:
GaO_xN_y surface contamination of gallium arsenide wafers from exposure to air. Solution used to clean wafer surfaces prior to metallization, diffusion, and epitaxy. After etching in solution shown, water rinse and nitrogen blow-dry. Usually followed by a similar cleaning in 1HF:1H_2O, DI water rinse and N_2 dry.
REF: Siracusa, M & Walker, P — personal application, 1978

GAN-0004
ETCH NAME: Phosphoric acid — TIME:
TYPE: Acid, preferential — TEMP: Hot (80°C)
COMPOSITION:
x .... H_3PO_4
DISCUSSION:
GaN, (0001) single crystal thin films. Solution used to develop defects, dislocations, and other etch figures. (*Note:* Solution also used as a general removal etch.)
REF: Shintani, A & Minagawa, S — *J Electrochem Soc,* 123,706(1976)

GAN-0005
ETCH NAME: Heat — TIME:
TYPE: Thermal, cleaning — TEMP: 1200°C
COMPOSITION:
x .... heat
DISCUSSION:
GaN thin films grown by MBE on (0001), and $(01\bar{1}2)$ single crystals sapphire substrates to 1000 Å thickness. Substrates cleaned at temperature shown prior to GaN growth at 700°C. Improved single crystal structure was obtained when GaN was deposited on an AlN thin film previously deposited on the sapphire substrate. As deposited GaN films were n-type.
REF: Yoshida, S et al — *J Vac Sci Technol,* B1(2),250(1983)

PHYSICAL PROPERTIES OF GALLIUM OXIDE, Ga_2O_3

Classification	Metal oxide
Atomic numbers	31 & 8
Atomic weight	187.44
Melting point (°C)	1900
Boiling point (°C)	
Density (g/cm^3)	6.44
Hardness (Mohs — scratch)	5—6
Crystal structure (hexagonal-trigonal pyramid) alpha	$(10\bar{1}1)$ rhomb
(monoclinic — normal) beta	(hk0) prism
Color (solid)	White
Cleavage (basal — poor)	(0001)/(001)

GALLIUM OXIDE, Ga_2O_3
General: Does not occur as a natural compound. The metal gallium is a rare element

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obtained chiefly from sphalerite, ZnS, as a by-product during roasting of the ore for its sulfur and zinc content. Such recovery can be in the form of both gallium and gallium oxide.

The oxide has no use in the metal industry, although the metallic gallium has use in low temperature solders.

Technical Application: Gallium oxide has no current use in Solid State processing. The sub-oxide Ga_2O is unstable above 600°C, but Ga_2O_3 and its hydrate are stable up to a 1900°C boiling point. All of the oxides can occur as native oxides on gallium arsenide semiconductor wafers during processing and, like many other native oxides, considered a surface contaminant in processing. The oxides have been purposely grown on GaAs wafers by boiling in water, then stripping with HCl as a surface cleaning step. The water developed oxide will be relatively soft as a hydrated compound, such as $Ga_2O_3.H_2O$; whereas the normal native oxide that develop naturally on a surface exposed to air form fairly hard type passivation coatings on materials. The gallium oxides formed are commonly a mixture of Ga_2O and Ga_2O_3.

Study of gallium oxide has been primarily concerned with methods of removal from gallium arsenide surfaces during processing.

Etching: Soluble in acids and alkalies, halogens, or by ionized gases.

GALLIUM OXIDE ETCHANTS

GAO-0001a
ETCH NAME: Hydrochloric acid — TIME: 10—30 sec
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... HCl
x .... H_2O
DISCUSSION:
GaAs, (100) wafers prepared as substrates for OMCVD growth of GaAs and AlGaAs. Wafers were boiled in hot water to form an oxide which was removed with this solution as a surface cleaning step.
REF: Lewis, B F et al — *J Phys Chem Solids*, 45,419(1984)

GAO-0001b
ETCH NAME: — TIME: 10—30 sec
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... HCl
x .... EOH
DISCUSSION:
GaAs, (100) wafers. Solution used to remove surface oxide formed by boiling in hot water. Solution shown used to etch clean and remove the oxide.
REF: Ibid.

GAO-0002
ETCH NAME: Hydrochloric acid, dilute — TIME: 10—20 sec
TYPE: Acid, oxide removal — TEMP: RT
COMPOSITION:
1 .... HCl
1 .... H_2O
DISCUSSION:
Ga_2O_3 as a native oxide on gallium arsenide wafers. Solution used to clean surfaces

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prior to metallization. After HCl clean, follow with 1HF:1H_2O, and running DI water rinse, up to 2 min, and nitrogen blow dry.
REF: Siracusa, M — personal communication, 1979

GAO-0003a
ETCH NAME: RIE
TYPE: Ionized gas, removal
COMPOSITION:
4 .... Cl_2
1 .... Ar
TIME: 10 min
TEMP:
GAS FLOW:
PRESSURE: 5 mTorr
POWER: 200 V
DISCUSSION:
Ga_2O_3, as native oxide on GaAs, (100) wafers. Etch removal in pure Cl_2 is slow. Used nichrome as a stencil mask with photo resist to open patterns. Other chlorine/argon ratios as 1:2 and 1:4 were evaluated.
REF: Hu, E C & Howard, R E — *J Vac Sci Technol,* B(2),85(1984)

GAO-0003b
ETCH NAME: RIE
TYPE: Ionized gas, removal
COMPOSITION:
(1) x .... H_2
(2) x .... CCl_2F_2
TIME:
TEMP:
GAS FLOW:
PRESSURE: 5 mTorr
POWER: 60 V
RATE: 150 nm/min
DISCUSSION:
Ga_2O_3 as native oxide on GaAs, (100) wafers. Both gases were evaluated, and hydrogen was preferred for selective removal of native oxides.
REF: Ibid.

GAO-0004
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
Ga_2O_3 doped with iron and grown as single crystal ferrites by the Czochralski (CZ) method. A study of ferrite growth. Also grew ingots of Fe_3O_4, and iron doped: ZnO, CuO, and MnO. Solution shown used for general removal.
REF: Horn, F N — *J Appl Phys,* 32,900(1961)

GAO-0005a
ETCH NAME:
TYPE: Alkali, removal
COMPOSITION:
x .... x% KOH/NaOH
TIME:
TEMP:
DISCUSSION:
Ga_2O_3 and $Ga(OH)_3$ on GaAs, (100), p-type wafers used to fabricate light emitting diodes with Al or Au dot contacts. Both compounds and Ga metal are removed with basic solutions enhancing As surface density. Gave better emission results than strong acid treatment of surfaces.
REF: Adachi, H & Hartnagel, H L — *J Vac Sci Technol,* 19(3),427(1961)

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GAO-0005b
ETCH NAME: AGW
TYPE: Acid, oxidizing
COMPOSITION:
x .... acid
x .... ethylene glycol
x .... water
TIME:
TEMP:
DISCUSSION:
Ga_2O_3 thin film growth of GaAs, (100), p-type wafers used to fabricate light emitting diodes. Solution used to grow 80 or 40 Å thick oxides on diode surfaces in a chemical surface treatment study and their effects on emission.
REF: Ibid.

GALLIUM PHOSPHATE ETCHANT

GAPH-0001
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot
DISCUSSION:
$GaPO_4$ single crystals grown by a hydrothermal temperature gradient process from H_3PO_4 in sealed glass ampoules. Solution used for general removal in a material study.
REF: Requardt, A & Iehmann, G — *J Phys Chem Solids*, 46,107(1985)

PHYSICAL PROPERTIES OF GALLIUM PHOSPHIDE, GaP

Classification	Phosphide
Atomic numbers	31 & 15
Atomic weight	109.7
Melting point (°C)	1480
Boiling point (°C)	
Density (g/cm^3)	4.14
Lattice constant (angstroms)	5.45
Energy gap (eV)	2.4
Refractive index (n =)	3.37
Hardness (Mohs — scratch)	7
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Silver/grey
Cleavage (dodecahedral)	(110)

GALLIUM PHOSPHIDE, GaP

General: Does not occur as a natural metallic compound, and has had no use in the metals industries other than as an additive to iron compounds.

Technical Application: Gallium phosphide is a III—V compound semiconductor, and is a polar compound. The $(\overline{1}\overline{1}\overline{1})$Ga and (111)P wafer surfaces showing different etching characteristics. GaP is one of the few semiconductors that will operate at high temperature (400°C); SiC will operate at 800°C; but the majority of semiconductors do not operate at much above 150°C.

Single crystal ingots are grown by Horizontal Bridgman (HB), Czochralski (CZ), and

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Float Zone (FZ) methods. Epitaxy thin films by Vapor Transport (VT) or CVD. Used as a substrate for epitaxy growth of other compounds, such as zinc sulfides, tellurides, and selenides as heterostructure devices.

Devices fabricated from wafers or thin film epitaxy include rectifiers, electroluminescent diodes, and solar cells.

Also grown as trinary compounds, such as $Ga_{1-x}In_xP$ and $Ga_{1-x}Al_xP$ for similar devices and laser diodes.

Etching: Not soluble in single acids. Aqua regia; HF:HNO_3 with or without HCl, H_2SO_4 and H_2O_2. Alkalies with or without additives, and ionized gases.

GALLIUM PHOSPHIDE ETCHANTS

GAP-0001
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:
GaP, (100), (111)A and $(\overline{111})$B wafers used as substrates for VPE growth of ZnTe, and ZnSe thin films. Wafers were mechanically lapped and polished, then degreased in boiling TCE; rinsed in acetone, then ethanol. The solution shown was used to etch remove lap damage prior to epitaxy.
REF: Matsumoto, T & Ishida, T — *J Cryst Growth*, 67,135(1984)

GAP-0002
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HCl
2 .... HNO_3
1 .... H_2O
DISCUSSION:
GaP, (100) and $(\overline{111})$B, p-type, 0.2 Ω cm resistivity wafers used as substrates for MBE growth of ZnS. Solvent degrease, then etch polish with the solution shown. Wafers were held under vacuum at 620°C, 15 min to remove native oxide prior to ZnS growth.
REF: Yoneda, K et al — *J Cryst Growth*, 67,125(1984)

GAP-0003
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
(1) 2 .... HCl
2 .... H_2SO_4
2 .... H_2O
1 .... HNO_3

(2) 2 .... HNO_3
1 .... HCl

DISCUSSION:
GaP, (100) and (111) wafers. Etch polish in either solution.
REF: Hajkoa, E et al — *Phys Status Solidi*, A10,K35(1972)

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GAP-0004
ETCH NAME: Chlorine
TYPE: Gas, polish
COMPOSITION:
(1) x .... Cl_2
x .... MeOH
(2) x .... Cl_2
x .... H_2O
TIME:
TEMP:
DISCUSSION:
GaP, (100) and (111) wafers. Immerse wafers in either MeOH of H_2O and bubble chlorine gas up through liquid for etching action. Agitate wafers to prevent bubbles adhering to surfaces as they will produce erratic etching results. (*Note:* Intense light is sometimes used in this form of etching.)
REF: Milch, A — *J Electrochem Soc,* 123,1256(1976)
GAP-0022c: Ibid.
GaP, (111) wafers used in a defect, electrical and optical study. Solution etch rate was 1—10 μm/sec, and developed pits only on the $(\overline{1}\overline{1}\overline{1})$B surfaces. Three solutions evaluated were Cl_2:MeOH, Cl_2:H_2O and Br_2:MeOH.

GAP-0005
ETCH NAME:
TYPE: Alkali, polish
COMPOSITION:
x .... 1 *M* $K_3Fe(CN)_6$
x .... 0.5 *M* KOH
TIME:
TEMP: 60 to 95°C
DISCUSSION:
GaP, (111) and (100). Solution used as a general wafer polishing etch. With an evaporated silicon dioxide, SiO_2 or titanium, Ti, thin film as a photo resist patterned mask, solution also used to etch remove and clean dot patterns in forming mesa structures.
REF: Plauger, R — *J Electrochem Soc,* 121,455(1974)

GAP-0006
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 0.05% Br_2
x .... MeOH
TIME: 20 sec + 10 sec
TEMP: RT
DISCUSSION:
GaP, (110) un-doped wafers. Used lens paper wetted with the solution shown for polishing wafer surfaces. After the initial 20 sec etch polishing, dilute with methanol and continue polishing for an additional 10 sec. Rinse in the BRM solution, then in water, then in NH_4OH:H_2O (AMH solution).
REF: Aspnes, D E & Studna, A A — *J Vac Sci Technol,* 20,488(1982)

GAP-0007
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
20% .... Br_2
80% .... MeOH
TIME:
TEMP:
DISCUSSION:
GaP, (111) and GaAs, (111) wafers. Used a pellon pad saturated with the above solution for polishing both of these compound semiconductors.
REF: Fuller, C S et al — *J Electrochem Soc,* 109,880(1962)

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GAP-0008
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: 60°C
COMPOSITION:
2 .... HCl
1 .... HNO_3
2 .... H_2O
DISCUSSION:
GaP, (111) and GaAs, (111)A wafers. Solution used as a polish etch.
REF: Urgaki, T et al — *J Electrochem Soc,* 123,580(1976)

GAP-0009
ETCH NAME: BRM
TYPE: Halogen, polish
TIME:
TEMP:
COMPOSITION:
1 .... Br_2
9 .... MeOH
DISCUSSION:
GaP, (111) and GaAs (111) wafers. Solution used as a general polishing etch for both compounds.
REF: Tuck, E — *J Mater Sci,* 10,321(1976)

GAP-0010a
ETCH NAME: Bromine
TYPE: Halogen, preferential
TIME: 5 min
TEMP: RT
COMPOSITION:
x .... Br_2
DISCUSSION:
GaP, (111) wafers. Bromine alone can be used as a preferential etch that will develop fine pits approximately 20 μm in size. (*Note:* BRM mixtures with greater than 3% Br_2:MeOH also are preferential.)
REF: Kleinman, D A & Spitzer, W G — *Phys Rev,* 118,110(1960)

GAP-0011
ETCH NAME:
TYPE: Acid, polish/selective
TIME: (1)
(2)
TEMP: RT
150—200°C
COMPOSITION:
(1) 3 .... HCl
1 .... HNO_3
(2) x .... H_3PO_4
DISCUSSION:
GaP, $(\overline{1}\overline{1}\overline{1})$B wafers. Solutions used for selective etch grooving of ⟨110⟩ direction channels in GaP surfaces. An evaporated SiO_2 thin film mask, photo resist line patterned, was used with the (1) etch solution (aqua regia). An evaporated thin film gold mask, photo resist line patterned, was etched with the phosphoric acid, solution (2).
REF: Urgkaki, T et al — *Phys Status Solidi,* A10,K38(1972)

GAP-0012
ETCH NAME: Aqua regia
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3

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DISCUSSION:

n-GaP, (111) and p-GaP (111) wafers doped with carbon were surface cleaned with aqua regia.

REF: Scott, W — *J Appl Phys*, 50,472(1979)

GAP-0022b: Ibid.

GaP, (111) wafers used in a defect, electrical and optical study. Hot aqua regia showed a 1—10 μm/sec etch rate, and was preferential on $(\overline{111})$B surfaces.

GAP-0013

ETCH NAME: TIME: 5 min

TYPE: Acid, junction TEMP: 60°C

COMPOSITION:

3 .... H_2SO_4

1 .... H_2O_2

1 .... H_2O

DISCUSSION:

p-GaP, (100) wafers with zinc diffusion to form a p-n junction. Solution was used to step-etch the p-n junction for depth profiling. The p-type is preferential in the solution and the junction will be etch delineated.

REF: Hackett, W H Jr — *J Electrochem Soc*, 119,973(1972)

GAP-0014

ETCH NAME: Hydrochloric acid TIME:

TYPE: Acid, zinc removal TEMP: Boiling

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

GaP, (111) wafers zinc diffused. After diffusion the hot solution was used to remove excess zinc from wafer surfaces.

REF: Wallison, H — *J Appl Phys*, 34,231(1963)

GAP-0022d: Ibid.

GaP, (111) wafers used in a defect, electrical, and optical study. Solution used to clean surfaces prior to preferential etching.

GAP-0015

ETCH NAME: TIME:

TYPE: Acid, stain TEMP:

COMPOSITION:

DISCUSSION:

GaP, (100) wafers used as substrates for LPE growth of tin-doped GaP thin films with formation of p-n junctions. Wafers were cleaved ⟨110⟩ and etch stained to develop the p-n junction. Etchant used not shown.

REF: Fritz, I J et al — *J Electron Mater*, 14,23(1985)

GAP-0016

ETCH NAME: TIME:

TYPE: Acid, polish TEMP:

COMPOSITION:

x .... acids

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DISCUSSION:

GaP, (111), (100), (110) wafers. Reference cited is an excellent review of etchants for gallium phosphide.

REF: Kern, W — *RCA Rev,* 39,278(1978)

GAP-0017

ETCH NAME:

TYPE: Acid, clean

TIME: 30 sec

TEMP: RT

COMPOSITION:

6 .... HNO_3

1 .... HCl

1 .... $HClO_4$

DISCUSSION:

GaP, (100) n-type wafers used in a study of impedance characterization in an electrolyte. Front surface was mechanically polished to a mirror finish and then etched as shown. An Sn:In ohmic contact was alloyed to the back side of wafers at 550°C, 5 min in a nitrogen atmosphere.

REF: Nagami, G et al — *J Electrochem Soc,* 132,1662(1985)

GAP-0018

ETCH NAME:

TYPE: Acid, polish

TIME: 10 sec

TEMP: RT

COMPOSITION:

2 .... HF

1 .... HNO_3

DISCUSSION:

GaP, (111) wafer used in an etch development study. Solution will etch polish both (111)A and $(\overline{111})$B surfaces.

REF: Farren, H — personal communication, 1958

GAP-0019

ETCH NAME:

TYPE: Acid, forming

TIME:

TEMP:

COMPOSITION:

1 .... HF

1 .... HNO_3

*x drops .... Br_2

*x = bromine saturated water.

DISCUSSION:

GaP, (111) wafers fabricated as p-n junction, mesa structured diodes. After diffusion, surfaces were coated with piocin drops to define mesa areas and then etched in the solution shown to form mesa structures. Under 10 V reverse bias electrical leakage was observed on mesa slopes as intense yellow light. Light spots increased in number with increase in voltage. (*Note:* Similar work, observing light emission from p-n junctions, has been done on silicon.)

REF: Iizima, S & Kikuchi, M — *Jpn J Appl Phys,* 1,302(1962)

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GAP-0010b
ETCH NAME: Copper
TYPE: Metal, decoration
COMPOSITION:
x .... Cu
TIME:
TEMP:
DISCUSSION:
GaP, (111) wafers used in a study of infrared lattice absorption. Copper was evaporated on surface, then diffused in to decorate defects. The copper was seen to segregate along grain boundaries and reduced reflectivity.
REF: Ibid.

GAP-0020
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
12 ml .... HF
96 mg .... $AgNO_3$
12 g .... CrO_3
24 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
GaP, (111) wafers used in a study of the electrical properties of gallium phosphide doped with zinc. Solution used to develop defects and structure induced by zinc diffusion.
REF: Cohon, M M & Bedard, F D — *J Appl Phys*, 39,75(1968)

GAP-0022a
ETCH NAME:
TYPE: Halogen, preferential
COMPOSITION:
x .... *I_2
x .... MeOH
+ .... Br_2
TIME: 18 h
TEMP: RT

*Saturate the solution.

DISCUSSION:
GaP, (111) wafers used in a study of defects, electrical and optical effects. This solution was best for developing etch pits. After 18 h both (111)A and $(\bar{1}\bar{1}\bar{1})$B surfaces showed only nodular structure. (*Note:* Such structure is common to bulk, undamaged metal and metallic compound surfaces.)
REF: Gershenzon, M & Mikulyak, R M — *J Appl Phys*, 35,2032(1964)

GAP-0022e
ETCH NAME: Aqua regia, modified
TYPE: Acid, preferential
COMPOSITION:
3 .... HCl
1 .... HNO_3
+ .... Ag or Fe
TIME:
TEMP: Cold and hot
DISCUSSION:
GaP, (111) wafers used in a defect, electrical and optical study. Aqua regia used at RT

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or hot is a rapid etch and will develop pits on the $(\overline{111})$B surface only. Solution used cold with the addition of either silver or iron, will develop dislocation etch pits.
REF: Ibid.

GAP-0023
ETCH NAME: BRM
TYPE: Halogen, cleaning
COMPOSITION:
x .... 0.5% Br_2
TIME: 30 sec
TEMP:
DISCUSSION:
GaP material used for growth of AlGaAsP single crystal ingots. Solution used to clean GaP, GaAs and GaAsP materials prior to mixing for ingot growth. The aluminum was etch cleaned at RT, 15 sec in: $9HCl:3HNO_3:2HF:5H_2O$.
REF: Fujimoto, A — *Jpn J Appl Phys,* 22,109(1984)

GAP-0024
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP: Hot
DISCUSSION:
GaP, polycrystalline material used as a source for LEC growth of single crystals. Boats and tubes were made of SiO_2 or PBN, and cleaned in aqua regia; gallium metal was held under an atmosphere of He, then switched to H_2/PH3, then returned to He and removed. This method developed the GaP source. After GaP single crystal growth, wash crystals in water, and anneal in vacuum at 300—400°C. Excess gallium removed with hot nitric acid. Material as-grown was n-type.
REF: Ringel, C M — *J Electrochem Soc,* 118,609(1971)

PHYSICAL PROPERTIES OF GALLIUM SELENIDE, GaSe

Classification	Selenide
Atomic numbers	31 & 34
Atomic weight	148.68
Melting point (°C)	960
Boiling point (°C)	
Density (g/cm^3)	5.03
Hardness (Mohs — scratch)	6—7
Crystal structure (hexagonal — normal)	$(10\overline{1}0)$ prism
Color (solid)	Steel grey
Cleavage (basal)	(0001)

GALLIUM SELENIDE, GaSe

General: Does not occur as a natural compound, though there are a number of selenides and tellurides of other metal elements, such as lead, copper, silver, and many others as tellurides. Not used in the metal industry.

Technical Application: Gallium Selenide is a III—VI compound semiconductor but is hexagonal, rather than more usual isometric. It can be differentiated by its layered atomic structure similar to cadmium sulfide.

It has been grown as a single crystal for both physical and semiconductor characterization.

Etching: Mixed acids ($HF:HNO_3$), halogens, and alkalies.

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GALLIUM SELENIDE ETCHANTS

GASE-0001
ETCH NAME: TIME:
TYPE: Mechanical, dislocation TEMP: RT
COMPOSITION:
x .... cleave
DISCUSSION:

GaSe, (0001) wafers cleaved and used in a study of dislocations. Authors say the material can be either hexagonal-normal or hexagonal-rhombohedral in structure as an interlayered atomic structure with the gallium layer showing weak van der Waal bonds. Cleaving will create dislocations in the surface, and E-beam annealing is sufficient to create further defects and dislocations. (*Note:* Single crystal cleaved surfaces normally show fine micro-structure on surfaces as ledges, as well as other defects and dislocations. See general section on (galena) lead sulfide, PbS with regard to such ledge-type surfaces.)
REF: Bainski, Z S et al — *J Appl Phys,* 34,469(1963)

GARNETS, $M_3M_2(SiO_4)_3$

General: The general formula shown is for all natural garnets. There are only ten major species of natural garnets, but several form isomorphous series or can have replacement elements such that there are a large number of varieties or subspecies, many with individual names to differentiate color or location occurrence. All garnets are found in the atypical dodecahedron, (110) crystal form, though they may occur as a trapezohedron, (211) in combination with the hexoctahedron, (321) — garnets being one of the few natural minerals that occur with (321) type facets.

There are three prominent groups: (1) aluminum garnet; (2) iron garnet, and (3) chromium garnet. Hardness ranges from H = 6.5—7.5 and specific gravity (density) varies between G = 3.15—4.3 g/cm^3. When a garnet is fused, it can both reduce in density and break down into other minerals with loss of one or more constituent elements.

Garnets are usually an accessory, rock-making mineral with common occurrence in certain rock types, such as chlorites, gneisses, or shists. Garnet is occasionally found in massive beds, but more commonly as individual single crystals, sometimes hundreds of small, deep red crystals (almandite, the iron garnet) in green chlorite beds, along with fine, small octahedrons of coal black magnetite, Fe_3O_4.

There is one special form, not common to other minerals, called a "sand garnet", where the crystal still retains its dodecahedral shape, but has been partly converted by compacted sand grains, with only a small central core of pure garnet. Some sand garnets are 1 to 2 in. in size. Such conversion is largely due to the low fusibility [(F = 3), 1200°C] of most garnets and, under pressure and heat, many garnets are squeezed with elongation in the c-axis direction, such that they are near-tabular in form.

Garnets have little use in metal processing except as lapping and polishing abrasives. They have been used as precious and semiprecious gem stones since ancient times for their range of colors and natural, highly reflective exterior facets. Some of the finest gem stones still come from Southern Asia, the Malay Peninsula, and India. The deep red pyrope garnet is top gem quality, but there are others that, depending upon color, also may be gem quality. Cinnamon-stone (Glossularite) is noted for that color, yet may be white, pale green, amber, honey-yellow, wine-yellow, rose-red, to emerald green. Spessartite is hyacinth-red to violet; andradite, called common garnet, is most often deep red-black, yet can vary in color like glossularite. Uvarovite, the chrome garnet, is a fine emerald green and, when it contains lithium, called the lithium garnet, and is a fine violet color.

As a group, the garnets have a wider range of types, varieties, and subspecies than any other single class of minerals.

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Technical Application: Natural garnets have had little use in Solid State processing other than as lapping and polishing abrasives, but there are an increasing number of applications for artificially developed and grown garnets.

The yttrium iron and yttrium aluminum garnet, YIG and YAG, respectively, were two of the first Solid State laser and masar materials, the laser being more prominent. Note that there are some natural garnets containing yttrium as a replacement element. Where the natural garnet formula is shown as: $M_3M_2(SiO_4)_3$, the artificial formula without silicon is shown as: $M_3M_5O_{12}$ or $A_3B_2C_3O_{12}$ and there are some special mixtures where M_2 and M_3 contain two or more elements.

Where natural garnets are noted for their brilliant colors, the artificial garnets are usually transparent, to slightly yellow-tan in color, and are available as oriented single crystal blanks up to 3″ in diameter.

The artificial garnets have light transmission and frequency characteristics similar to those of quartz, and are used in a like manner as filter elements in microelectronic circuitry, such as GGG garnets. An important application of iron containing garnets, such as YIG, are in the fabrication of bubble memory computer devices with as much as a one million bit capability.

Artificial garnets, when grown by molten flux methods, form as the atypical dodecahedron, (110), but are limited in size to about 1″. They also tend to be contaminated by extraneous elements from the growth flux, such that repeatability control is difficult for consistency in device fabrication. But, like in the growth of semiconductor materials, they are now grown by the Czochralski (CZ) method as ingots up to 5 and 6″ in diameter, and also are grown by modified Czochralski, or Float Zone (FZ). Such ingots are most commonly grown as (100) oriented, sliced, and used with that orientation.

Where garnet is used as an abrasive powder, the W-1 to W-12 types are widely used in semiconductor wafer processing. The W-5 (15 μm) is a common "as received" lap finish. The garnet particles are relatively soft (H = 6), tend to break down under lapping pressure, such that a 600 grit abrasive may give a final finish closer to 400 grit.

Natural garnets have been the subject of much study for centuries, particularly in the jewelry trade and today new artificial garnets are under development for a wide range of applications.

Etching: H_3PO_4, HCl, halogens, variable with type garnet.

The following are the garnets discussed and presented in this section:

Boron Germanium, BGO
Calcium Aluminum Germanium, CAGG
Europium Scandium Iron, ESG
Gadolinium Gallium, GGG
Gadolinium Selenium Gallium, GSGG
Manganese Zinc Yttrium, MZYG
Natural Garnets, GAR
Strontium Gallium, SGG
Yttrium Aluminum, YAG
Yttrium Gallium, YGG
Yttrium Iron, YIG

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GARNET ETCHANTS

BORON GERMANIUM GARNET

BGO-0001
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
DISCUSSION:
$B_4Ge_3O_{12}$ (BGO) single crystal dodecahedron, (110) grown by molten flux. Crystals were transparent and colorless, and were water wash cleaned after removal from the growth flux. The following parameters were established:

TIME:
TEMP:

Specific mass (Kgm^{-3})	7076
Specific heat ($Jkg^{-1}\ K^{-1}$)	303
Thermal diffusivity ($\times 10^{-6} m^2 s^{-1}$)	0.84
Thermal conductivity ($Wm^{-1}\ K^{-1}$)	1.80

REF: Runkin, A Y & Frolou, A A — *J Cryst Growth*, 69,131(1984)

CALCIUM ALUMINUM GERMANIUM GARNET

CAGG-0001
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
DISCUSSION:
$Ca_3Al_2Ge_3O_{12}$ grown as a single crystal ingot by the Czochralski (CZ) method. Requires 2% Y in melt, but there is no yttrium in the final ingot. This was the development of a new garnet type compound.
REF: Rotman, S R et al — *J Appl Phys*, 57,5320(1985)

TIME:
TEMP:

EUROPIUM SCANDIUM IRON GARNET

ESG-0001
ETCH NAME:
TYPE:
COMPOSITION:
DISCUSSION:
$Eu_3Sc_2Fe_3O_{12}$, as single crystal specimens used in a study of atomic location in garnets with the general formula $A_3B_2C_3O_{12}$. Where A = dodecahedral "c" sites; B = octahedral "a" sites; and C = tetrahedral "d" sites.
REF: Stadnik, E M — *J Phys Chem Solids*, 45,133(1984)

TIME:
TEMP:

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GADOLINIUM GALLIUM GARNET

GGG-0001a
ETCH NAME: Phosphoric acid
TYPE: Acid, preferential
COMPOSITION:
x .... H_3PO_4
TIME: Variable
TEMP: RT, hot to boiling
DISCUSSION:
$Gd_3Ga_5O_{12}$ (GGG) garnet fabricated as 0.8 mm spheres; also (001) blanks with structures called "semispheres" (control damaged etched pits or holes in the planar blank surface). Garnets were grown by Molten Flux and Czochralski (CZ) to evaluate the two growth methods. The CZ garnets were more perfect due to less contamination in growth. Spheres were etched to finite crystal form with varied time and temperature. Both a tetrahexahedron, (hk0), and trisoctahedron, (hh1) were obtained as convex dissolutionment forms. The "semispheres" were studied for pit side slope planes as concave surface dissolutionment forms. The solution shown produced smooth exterior facets on finite crystal forms; whereas HBr as an etch solution developed heavy terracing. (*Note:* The use of the term semisphere should not be confused with hemisphere. The latter is a convex surface; whereas the semisphere is a pit in a concave surface. A dissolutionment form is the same thing as a finite crystal form when used to etch a sphere.)
REF: Hartmann, E et al — *J Cryst Growth,* 71,191(1985)

GGG-0001b
ETCH NAME: Hydrogen bromide
TYPE: Halogen, preferential
COMPOSITION:
x .... HBr
TIME: Varied
TEMP: 124°C
DISCUSSION:
$Gd_3Ga_5O_{12}$ (GGG) garnets fabricated as spheres. The finite crystal form was an octahedron, (111) with heavy, multiple (110) terracing on the octahedral faces. See GGG-0001a for additional discussion. (*Note:* The natural garnets grow as a dodecahedron, (110), never as an octahedron, (111).)
REF: Ibid.

GGG-0002
ETCH NAME: Alumina
TYPE: Abrasive, polish
COMPOSITION:
x .... Al_2O_3 powder
TIME:
TEMP: RT
DISCUSSION:
$Gd_3Ga_5O_{12}$, (110) wafers used for LPE growth of $(Gd,Y)_3(Fe,Mn,Ga)_5O_{12}$ thin film garnet layers. Alumina powder can be used to polish substrate surfaces prior to LPE growth. Slow growth developed hillocks. Grown 1°-off (110) developed smooth films. Mn as a doping element constituent can develop $MnCO_3$ or Mn_2O_3 crystallite re-growth. LPE growth was as standard horizontal dip/wipe across the melt rotating at 120 rpm.
REF: Breed, D J et al — *J Appl Phys,* 54,1519(1983)

GGG-0003
ETCH NAME: Alumina
TYPE: Abrasive, polish
COMPOSITION:
x .... alumina, powder
TIME:
TEMP:

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DISCUSSION:

$Gd_3Ga_5O_{12}$ (GGG), (111) wafers used as substrates. Polish substrates with alumina before thin film growth of the following garnet mixtures: $BiTmFeGaO_{12}$; $BiTmPb:TmFeGaO_{12}$, and $BiYPb:YFeGaO_{12}$.

REF: Murthy, V R K & Belt, R F — *Jpn J Appl Phys*, 23,871(1984)

GGG-0004

ETCH NAME: Acetone — TIME:

TYPE: Ketone, cleaning — TEMP: RT to warm

COMPOSITION:

x .... CH_3COCH_3

DISCUSSION:

$Gd_3Ga_5O_{12}$ (GGG), (0001) wafers 3" in diameter with oriented flats. Wafers were mounted on sticky-back mylar sheet, then cut with a resinoid diamond blade as rectangular pieces. After cutting, specimens were soaked in acetone to be removed from the holding mylar paper, then soaked and spray cleaned.

REF: Tarn, W H & Walker, P — personal application, 1983/1984

GGG-0005

ETCH NAME: BRM — TIME:

TYPE: Halogen, cleaning/polish — TEMP:

COMPOSITION:

x .... x% Br_2

x .... MeOH

DISCUSSION:

$Gd_3Ga_5O_{12}$ (GGG), (111) cut wafers used as substrates for bubble memory thin film deposition by LPE of $(Y,Sm,In,Gd)_3(Fe,Ga)_5O_{12}$. Pre-clean the GGG surfaces prior to epitaxy in the solution shown.

REF: Imura, R et al — *Jpn J Appl Phys*, 23,709(1984)

GADOLINIUM SELENIUM GALLIUM GARNET

GSGG-0001

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, cleaning — TEMP: Boiling

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

$Gd_3Se_{1.8}Ga_{3.2}O_{12}$ (GSGG), (0001) wafers cut from Czochralski (CZ) grown ingots. Wafers were diamond saw cut; lapped with 800-grit abrasive; then diamond paste polish in a kerosene carrier. To remove oils and hydrocarbons, final wash in acid shown, then rinse in acetone, then EOH.

REF: Schwartz, K B & Duba, A G — *J Phys Chem Solids*, 8,957(1985)

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MANGANESE ZINC YTTRIUM GARNET

MZYG-0001
ETCH NAME: Silicon carbide
TYPE: Abrasive, polish
COMPOSITION:
x .... SiC, grinder
DISCUSSION:
$Mn_xZn_{1-x}Y_zO_{12}$ single crystal specimens ground as spheres and used in a study of the general material morphology.
REF:
TIME:
TEMP:

NATURAL GARNETS

GAR-0001
ETCH NAME: Phosphoric acid
TYPE: Acid, preferential
COMPOSITION:
x .... H_3PO_4, conc.
DISCUSSION:
Garnets, as natural single crystals used in a study of magnetic interactions and distribution of ions in their structure. Solution can be used to develop defect structure. The following garnets were studied:

Cryolithionite	—	$NaCa_2Mn_2As_3O_{12}$
Berzellite	—	$Ca_3Fe_2Si_3O_{12}$
Andradite	—	$Ca_2Cr_2Si_3O_{12}$ (chrome garnet)
Uvarovite	—	$Na_3Al_2Li_3O_{12}$ (lithium garnet)
Spessartite	—	$Mn_3Al_2Si_3O_{12}$
Almandite	—	$Fe_2Al_2Si_3O_{12}$ (iron or common garnet)

REF: Geller, S — *J Appl Phys*, 31,30S(1960)
TIME:
TEMP:

GAR-0002a
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
1 .... HCl
10 .... H_2O
DISCUSSION:
$Fe_2Al_3Si_3O_{12}$, as natural single crystal almandite. Crystals were deep red, and "squeezed" with elongation in the c-axis direction. Specimens were mounted in resin on glass slides, and mechanically lap thinned with abrasive on a rotating iron platen. Specimens washed in solution shown, then rinsed in water after lapping and used in a microscope structural study. Specimens were found in a green chlorite schist in close association with fine, coal black octahedrons of magnetite, Fe_3O_4.
REF: Walker, P — mineralogy study, 1953
TIME: 10—30 sec
TEMP: RT

GAR-0002b: Ibid.
$Fe_2Al_3Si_3O_{12}$, single crystal specimens as "sand garnets", e.g., outer surface replacement with compacted sand grains. Solution used with steel brush to soak and rub remove loose sand prior to sectioning for study of alteration structure.

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STRONTIUM GALLIUM GARNET

SGG-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP:
DISCUSSION:
$SrGa_{12}O_{19}$ single crystals flux grown as hexagonal, yellow platelets with basal (0001) habit, and cleaved (0001) as wafers. Structure is that of magnetoplumbite, $P6^3/mmc$ space group lattice. Also grew $Sr_2BaGa_{11}O_{20}$ crystals. Solution used to etch remove crystals from flux after slow cooling.
REF: Haberey, F et al — *J Cryst Growth*, 61,284(1983)

YTTRIUM ALUMINUM GARNET

YAG-0001
ETCH NAME: Phosphoric acid
TYPE: Acid, preferential
COMPOSITION:
x .... H_3PO_4, conc.
TIME:
TEMP: 250°C
DISCUSSION:
$Y_3Al_5O_{12}$ (YAG), (110) cut wafers used in a study of impurity diffusion uniformity. Neodymium (Nd) was diffused into specimens as a metal tracer element, and solution shown used to develop segregation locations of neodymium.
REF: Cockayne, B — *Phil Mag*, 12,943(1965)

YTTRIUM GALLIUM GARNET

YGO-0001
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HNO_3
1 .... HAc
3 .... H_2O
TIME:
TEMP:
DISCUSSION:
$Y_2Ga_7O_{12}$ as molten flux grown single crystals with (110) facets using a new flux method. Solution used to clean crystals after removal from flux.
REF: Nielson, J W — *J Appl Phys*, 31,518(1960)

YTTRIUM IRON GARNET

YIG-0001
ETCH NAME:
TYPE:
COMPOSITION:
TIME:
TEMP:
DISCUSSION:
$Y_3Fe_5O_{12}$(YIG), (0001) wafers used to fabricate bubble memory computer devices.

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(*Note:* An excellent article on their use in military equipment vs. disk and tape drive systems.)
REF: Weisenstein, C — *The Bubble Memory Option — Defense Electronics,* September 1, 1985, 97

YIG-0002
ETCH NAME: Hydrochloric acid TIME:
TYPE: Acid, macro-etch TEMP:
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
$Y_3Fe_5O_{12}$, (0001) (YIG) wafers cut from ingots grown by the Float Zone (FZ) technique. Wafers cut used in material study by metallographic sectioning. Solution used to develop macro-structure.
REF: Abernethy, L L et al — *Phys Rev,* S32,276S(1961)

YIG-0004a
ETCH NAME: Phosphoric acid TIME: 10 min
TYPE: Acid, preferential TEMP: 140°C
COMPOSITION:
x .... H_3PO_4, conc.
DISCUSSION:
$Y_3Fe_5O_{12}$, (110) wafers. Material was grown by the top seeded solution growth (TSSG) method using Fe_2O_3 as the melt solvent, as a modified Czochralski (CZ) technique. The method was evaluated against the PbO molten flux growth method. Polish (110) surfaces with 0.01 alumina, then etch in HCl. The solution shown developed rhombohedral shaped pits with elongation that have the appearance of a straw basket weave.
REF: Oka, K & Uncki, H — *J Appl Phys,* 56,436(1984)

YIG-0004b
ETCH NAME: Hydrochloric acid TIME: 4 h
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
20 .... HCl
80 .... H_2O
DISCUSSION:
$Y_3Fe_5O_{12}$, (111) wafers. Solution developed etch pits about 10 μm in size with a density of 10^4—10^6/cm^2. See YIG-0004a for additional discussion.
REF: Ibid.

YIG-0007
ETCH NAME: TIME:
TYPE: Abrasive, polish TEMP:
COMPOSITION:
(1) x .... diamond paste (2) x .... alumina
DISCUSSION:
$Y_3Fe_5O_{12}$ (YIG) single crystal spheres mechanically polished and used to study development of flaws applying ferromagnetic resonance.
REF: Buehler, E & Tanenbaum T — *J Appl Phys,* 31,388(1960)
YIG-0008: Konzler, J E et al — *J Appl Phys,* 31,392(1960)
$Y_3Fe_5O_{12}$ (YIG) single crystal spheres of 1.6 cm diameter with oriented ground flats. Spheres were mechanically polished and used in a study of specific heat and demagnetization.
YIG-0005: Fletcher, P et al — *Phys Rev,* 114,739(1959)

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$Y_3Fe_5O_{12}$ (YIG) single crystal spheres 1.3 cm in diameter and mechanically polished. Used in a study of magnetostatic modes in ferromagnetic resonance of spheres.
YIG-0006: Spencer, E G & LeCraw, R C — *Phys Rev Lett*, 1240(1958)

$Y_3Fe_5O_{12}$ (YIG) single crystal spheres mechanically polished. Used in a study of vibration frequencies (acoustic). Frequency varies inversely, as a ratio of sphere diameters.

YIG-0009
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HNO_3
1 .... HAc
3 .... H_2O
DISCUSSION:
$Y_3Fe_5O_{12}$ (YIG) as a dodecahedron, (110) molten flux grown single crystal. Solution used to clean surfaces after molten flux growth.
REF: Nielsen, J W — *J Appl Phys*, 31,518(1960)

PHYSICAL PROPERTIES OF GERMANIUM, Ge

Classification	Metal
Atomic number	32
Atomic weight	72.60
Melting point (°C)	937.4
Boiling point (°C)	2830
Density (g/cm^3)	5.32
Thermal conductance (cal/sec)(cm^2)(°C/cm) 0°C	0.15
Specific heat (cal/g) 25°C	0.74
Heat of fusion (k-cal/g-atom)	111.5
Heat of vaporization (k-cal/g-atom)	1100
Atomic volume (W/D)	13.6
1st ionization energy (K-cal/g-mole)	187
1st ionization potential (eV)	8.13
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.22
Ionic radius (angstroms)	0.53 (Ge^{+4})
Linear coefficient of thermal expansion ($\times 10^{-8}$ cm/cm/°C)	6.1
Electrical resistivity (micro ohms cm $\times 10^6$) 27°C	47
Vapor pressure (atm $\times 10^{-9}$) 27°C	1.1
Work function (eV)	4.5
Magnetic susceptibility ($\times 10^6$) 20°C	0.22
Debye temperature (K)	362
Cross section (barns)	2.4
Refractive index (n =)	5.67
Extinction coefficient (ks)	0.63
Energy band gap (eV)	0.47
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube (diamond)
Color (solid)	Steel-grey
Cleavage (dodecahedral/cubic)	(110)/(100)

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GERMANIUM, Ge

General: Does not occur in nature as a native element. It is a trace element in several minerals, notably the iron pyrites, and is collected from flue dust during processing of pyrites for the iron and sulfur content. Pyrite, FeS_2, is a major source of iron ore, and representative of the pyrite group as a class of minerals.

There are two known minerals containing germanium: argyrodite, $4Ag_2S.GeS_2$ and germanite, $Cu_3(Fe,Ge)S_4$. Neither mineral occurs in large quantity, but they are associated with the pyrites which represent about 85% of the iron ore mined.

Germanium has had little or no use as a metal in industry until discovery of its semiconducting properties in the mid-1940s.

Technical Application: Germanium was the original semiconductor developed as a wire point contact alloyed diode in the latter part of the 1940s and, by the early 1950s both germanium and silicon, the two elemental semiconductors, had established the semiconductor industry. It is now considered part of the Solid State industry, which includes electronics, quartz crystals, and other allied technologies. Although silicon has become the primary semiconductor, due to its more useful physical and electronic characteristics, germanium is still fabricated as discrete alloyed or diffused devices, and is under development as a constituent in thin film epitaxy, layered devices that contain other compound semiconductors and materials, such as the heterostructure or heterojunction devices.

Both wafers and thin film epitaxy layers of germanium have been used in fabrication of a variety of devices: tunnel diodes, low and high power diodes, varactor diodes, high frequency transistors, solar cells and photodiodes—as a rod or barrel shaped unit, as a lithium-drift alpha-particle radiation detector.

Evaporated germanium has been used in conjunction with photo resist lacquers or alone as an etching and metallization mask on silicon and gallium arsenide. Although germanium oxide, Ge_2O_3, has been grown and used as a surface protectant, it is not as stable and acid resistant as silicon dioxide, SiO_2. The same applies to germanium nitride, Ge_3N_4 vs. silicon nitride, Si_3N_4, though both the pure nitrides and oxynitrides have been studied, and they form an isomorphous series between the two metals as both oxides and nitrides.

Germanium was initially grown as a single crystal ingot using the Bridgman method, now called Horizontal Bridgman (HB). This produces a half-moon-shaped ingot and, as cut wafers, are recognized by that shape. The method is still used for germanium and other materials, such as compound semiconductors, but has a size limitation of about 2—3″ square area. For this reason, most semiconductor ingots are now grown by the Czochralski (CZ) or Float Zone (FZ) methods with ingot/wafer diameters a standard 3″, and approaching 5—6″. Single crystal germanium has been the subject of much study, and is still under development and study. Germanium/silicon single crystal ingots of varying proportional concentrations have been grown and studied. It also is deposited as single crystal thin film epitaxy; as polycrystalline layers, poly-Ge; as amorphous layers, a-Ge, which may be hydrogenated as a-Ge:H.

Etching: Soluble in hot H_2SO_4, but no other single acids. Mixed acids: $HF:HNO_3$; $HF:H_2O_2$ . . . with or without H_2O, HAc, or other additives, alkali + halogen; halogens, DCE ionized gases.

SELECTION GUIDE: Ge

(1) Br_2:MeOH:
  (i) Polish: GE-0038
(2) HF:
  (i) Cleaning: GE-0064: -0126; -0284

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(3) $HF:HNO_3$:
(i) Cleaning: GE-0090
(ii) Polish: GE-0030; -0015b; -0033; -0082; -0159; -0164; -0167; -0168; -0169; -0175; -0189; -0252; -0286
(iii) Structure: GE-0059a; -0077
(iv) Preferential: GE-0085
(v) Junction: GE-0009
(4) $HF:HNO_3$:HAc:
(i) Polish: GE-0088c; -0124; -0253; -0292; -0028; -0027
(ii) Preferential: GE-0220d,i—k; -0032; -0092b
(iii) Thinning: GE-0171
(5) $HF:HNO_3:H_2O$:
(i) Polish: GE-0034; -0079; -0127b; -0036; -0190
(ii) Preferential: GE-0220e
(iii) Removal: GE-0035
(6) $HF:HNO_3:H_2O:Ag(NO_3)_2: +/- H_2O$
(i) Preferential: GE-0220b,c; -0061b
(7) $HF:HNO_3:Cu(NO_3)_2$:
(i) Preferential: GE-0061a
(8) H_2O:
(i) Float-off: GE-0043; -0057; -0203; -0204
(9) H_2O_2:
(i) Cleaning: GE-0001a; -0172; -0210; -0207
(ii) Polish: GE-0211
(iii) Preferential: GE-0005f; -0150a; -0230
(10) $HNO_3: +/- H_2O$
(i) Cleaning: GE-0001b; -0132a; -0241; -0240; -0239; -0207
(ii) Oxidation: GE-0130
(iii) Preferential: GE-0132g
(iv) Polish: GE-0082
(11) HNO_3:Tartaric Acid:
(i) Preferential: GE-0005b
(12) HNO_3:Tartaric Acid:$AgNO_3$:
(i) Preferential: GE-0005a
(13) $HF:HNO_3$:Tartaric Acid:
(i) Polish: GE-0230b
(14) H_2O_2:Tartaric Acid:
(i) Preferential: GE-0005g
(15) Tartaric Acid:Br_2:
(i) Preferential: GE-0005h
(16) $HF:H_2O_2 +/- H_2O$:
(i) Preferential: GE-0220f,h,l; -0223a,h; -0008b,d; -0150a-i; -0058; -0288; -0010a,b; -0032;
(ii) Cleaning: GE-0157
(iii) Passivation: GE-0204b + air
(17) H_2O_2:Citric Acid:
(i) Preferential: GE-0022g
(18) HCl:
(i) Preferential: GE-0132b
(19) H_2SO_4:
(i) Polish: GE-0078

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(20) $KMnO_4$:H_2O:
(i) Oxidation: GE-0158a
(21) KCN:
(i) Cleaning: GE-0122b; -0094b; -0119b; -0159a,b; -0179; -0242
(22) NaClO:H_2O:
(i) Cleaning: GE-0056b
(23) KOH:I_2:
(i) Preferential: GE-0151a; -0221g; -0012a,d; -0206; -0302
(24) KOH:Br_2:
(i) Preferential: GE-0221a,b; -0012b; -0301; -0151b
(25) KOH:$(NH_4)_2S_2O_8$:
(i) Preferential: GE-0012c; -0303; -0220o
(26) KOH:$K_3Fe(CN)_6$:
(i) Preferential: GE-0056; -0134; -0135; -0144c
(27) NaOH:$NaNO_3$:H_2O:
(i) Cleaning: GE-0155
(ii) Preferential: GE-0208
(28) NH_4OH:$Cr(NO_3)_2$:
(i) Preferential: GE-0005d
(29) $Hg(NO_3)_2$:H_2O:
(i) Preferential: GE-0005c
(30) $AgNO_3$:H_2O:
(i) Preferential: GE-0005i

NAMED OR NUMBERED ETCHANTS

(1) Billig's Etch: KOH:$K_3Fe(CN)_6$:H_2O
Preferential: GE-0139a; -0142a
(2) BJ Etch: HF:HNO_3:HAc
Polish: GE-0027
(3) Camp #2 (Superoxol): 1HF:1HNO_3:4HAc
Preferential: GE-0065a; -0007b
(4) Camp #3:
Preferential: GE-0065b
(5) Copper Etch: HF:$CuSO_4$:H_2O
Junction: GE-0149
(6) CP4 (Camp #4): 30HF:50HNO_3:50HAc:0.6Br_2
Note: cleaning/preferential/polish/thinning/structuring
All Applications: GE-0065c (origin); -0015a; -0016; -0017; -0018a; -0019a; -0020; -0022; -0023; -0024; -0025; -0026; -0060b; -0066; -0067; -0069a; -0070a; -0071; -0072; -0073; -0083b; -0091; -0104; -0105; -0111; -0092a; -0093; -0094a; -0095a; -0096; -0097; -0098; -0099; -0100; -0102a; -0112; -0113; -0114; -0115; -0116; -0117; -0118; -0119a; -0120; -0122; -0123; -0138; -0144b; -0150a; -0147a; -0176; -0267; -0227a; -0228; -0253a
(7) CP4A: 30HF:50HNO_3:30HAc
Polish: GE-0014; -0063; -0253b
(8) CP4, varieties:
Note: Br_2 replaced with: xxxx
Preferential: + I_2: GE-0219
Preferential: + Br_2: GE-0213b
(9) Ellis #1:
Preferential: GE-0223b; -0150q

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(10) Ellis #5:
Preferential: GE-0221a; -0150o
(11) Ellis #7 (Superoxol):
Preferential: GE-0221c; -0150i-n, r; -0002
(12) Iodine Etch: $HF:HNO_3:HAc:I_2$
Note: Several formula variations on Ge and other metals as "Iodine Etch", Iodine A Etch, etc. May be as polish/thinning/structuring/cleaning
All Applications: GE-0218; -0139a; -0140; -0203a; -0205; -0083a; -0235; -0266; -0263b; -0267; -0263a
(13) Ferricyanide Etch: $KOH:K_3Fe(CN)_6:H_2O$
Preferential: GE-0150s; -0060d
(14) Peroxide Etch: $HF:H_2O_2:HAc$
Preferential: GE-0060f
(15) WAg Etch: $HF:HNO_3:AgNO_3$ (Westinghouse Silver Etch)
Note: Preferential/polish/thinning/structuring
All Applications: GE-0150p; -0060g; -0066; -0072c; -0075a; -0084; -0144c; -0188; -0225c; -0289
(16) White Etch: $HF:HNO_3:+/-H_2O$
Note: Not recommended as a "name" — solutions are transparent, clear, not white in color, and there are many similar solutions with different formulas
Polish: GE-0015b; -0190
(17) (100) Etch: $HF:HNO_3:H_2O:Cu(NO_3)_2$
Copper Dislocation Etch:
Preferential: GE-0060e; SI-0038a
(18) 1:1:1 Etch: $HF:HNO_3:HAc$
Note: Not recommended as a "name" as there are other constituent 1:1:1 solutions.
Polish: GE-0028
(19) X-1114 Etch: $1HF:1HNO_3$:1 Superoxol:$4H_2O$
Note: Acceptable as a "named etch" as the "X" designates a specific mixture
Polish: GE-0147d
(20) SR4:
Polish: GE-0124
(21) Superoxol: $1HF:1H_2O_2:4H_2O$
Note: Chemically, hydrogen peroxide, H_2O_2 (30%) is called Superoxol
Polish: GE-0226
Preferential: GE-0202; -0002; -0003; -0021b; -0058a,b; -0070b; -0075b; -0095b; -0146; -0185b; -0231; -0218; -0005a; -0007; -0150j
(22) Superoxol:$Ag(NO_3)_2$:
Polish: GE-0078
(23) Aqua Regia: $(3HCl:1HNO_3)$
(i) Polish: GE-0173
(24) Antimony Etch:
(1) Preferential: GE-0257

ABRASIVES
Note: As an acid slurry for removal/polish, or dry in damage studies
(1) Alumina, Al_2O_3: GE-0013
(2) Silicon Dioxide, SiO_2: GE-0295; -0297; -0298

CONTAMINATION
Note: Chemicals applied to a surface in controlled contamination study
(1) Sodium, Na: GE-0282

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(2) NaOH:$Na^{24}CO_3$: GE-0089
(3) HF:HNO_3:HAc:Ag: GE-0128a
(4) HF:HNO_3:HAc:Fe: GE-0234
(5) KOH:$Ge^{71}O_2$: GE-0301

HEAT (THERMAL)
Note: Can be heat in vacuum, only; or furnace heat treatment with gases.
Cleaning: GE-0170
Preferential: GE-0142b; -0146; -0165; -0270; -0278; -0279
Forming: GE-0179

GASES
(1) Chlorine, Cl_2: (preferential): GE-0081
(2) Air, O_2/N_2: (oxidizing): GE-0154
(3) Ar^+ (cleaning): GE-0178; -0201; -0283; -0232

JUNCTION ETCH
Note: Etch/stain/decoration.
All Applications: GE-0031a-d; -0033; -0034; -0212; -0211; -0213; -0019b,c; -0152; -0217; -0080; -0220h; -0127b; -0149; -0009; -0254b; -0254c; -0255; -0271

LASER
Note: As a tool, or germanium as a laser device
(1) Laser (anneal): GE-0286
(2) Laser (device): GE-0299a,b
(3) Laser (cutting): GE-0310

METALS
Note: As a diffusant/preferential etch/defect decoration
(1) Indium (preferential): GE-0127a; -0165c; -0166; -0236; -0275
(2) Indium (decoration): GE-0165b
(3) Copper (I, IV metals), molten: (Preferential): GE-0180
(4) Lithium (diffusion): GE-0270
(5) Barium Titanate (junction): GE-0254b; -0255
(6) Zinc Oxide (junction): GE-0254c
(7) Germanium (optics): GE-0287
LIGHT: GE-0244
ELECTRICITY: GE-0244
ELECTROPLATE: GE-0285
ELECTROLYTIC:
(1) KOH:
  (i) Polish: GE-0088b
  (ii) Preferential: GE-0087; -0147c; -0156; -0300; -0129b
  (iii) Junction: GE-0254a
(2) KOH:H_2O_2:
  (i) Cleaning: GE-0137
  (ii) Preferential: GE-0133b
(3) KOH:GeO_2:
  (i) Removal: GE-0147e
(4) KF:
  (i) Removal: GE-0209

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(5) KF:HNO_3:
(i) Polish: GE-0029b
(6) KCl:
(i) Preferential: GE-0133a
(7) KCl:HNO_3:
(i) Polish: GE-0029a
(8) KCl:GeO_2:
(i) Preferential: GE-0046b; -0133a
(9) H_2SO_4:
(i) Polish/shaping: GE-0088a; -0129d
(10) H_2SO_4:GeO_2:
(i) Removal: GE-0147c
(11) HCl:KI:Oxalic Acid:
(i) Oxidation: GE-0136
(12) HCl:
(i) Preferential: GE-0129c; -0133c
(13) $InSO_4$:
(i) Shaping: GE-0129a
(14) NaCl:
(i) Shaping: GE-0129e
(15) HF:HAc:
(i) Polish/Selective: GE-0212b; -0213
(16) NaOH:
(i) Polish/Selective: GE-0200; -0233

OXIDATION
(1) H_2O: GE-0268a; -0269; -0270; -0271; -0272; -0273; -0277; -0268b; -0255; -0291
(2) HAc:$NaC_2K_3O_2$: GE-0156b; -0255
IRRADIATION:
(1) Neutron: GE-0238; -0262; -0264; -0265; -0274
MOLTEN FLUX:
(1) KCN:NaCN: GE-0163
(2) KOH/NaOH: GE-
CLEAVE:
(i) Cleaved: GE-0310
GROWTH:
(i) Growth: GE-0250; -0249; -0245

SPHERES & HEMISPHERES
Note: Polish, or etching to Finite Crystal Form.
(1) Polish: GE-0150a; -0030
(2) Preferential: GE-0058a; -0006a; -0150a-u; -0007; -0005a,b; -0220a-c; -0223a-h; 0300; -0301; -0302; -0303; -0304; -0010a,b

GERMANIUM ETCHANTS

GE-0001a
ETCH NAME: Hydrogen peroxide
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O_2
TIME:
TEMP: Boiling

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DISCUSSION:

Ge, (111) wafers used in a study of surface conductivity and recombination. Surfaces were cleaned in the solution shown, or in nitric acid.

REF: Razhanov, A U et al — *Zhur Tekh Fiz* 26,2142(1956)

GE-0172: Gouskov, L & Nifontoff, W — *CR Acad Sci (Paris)* 248,1499(1959)

Ge, (111), (100), and (110) wafers used in a study of the effects of surface treatment on material orientation. H_2O_2 was used to clean surfaces prior to oxidation, and it leaves no visible film. Heat wafers in O_2 at two temperature levels: (1) 300—500°C will deposit colored oxides; (2) at 500°C oxide forms a granular structure with raised etch pattern figures, and (3) above 500°C the oxide film is completely granular without growth figures.

GE-0210: Wallis, G & Wang, S — *J Electrochem Soc,* 114,88(1967)

Ge, (111) wafers and other orientations. Wafers used in a study of recombination centers on germanium surfaces subjected to various etches.

GE-0211: Primak, W & Kempwirth, R — *J Electrochem Soc,* 114,88(1967)

Ge, (111) wafers used in a study of H_2O_2 etching on germanium. Preparation etching was done: (1) etch in CP4; (2) polish on micro-cloth with Linde A alumina, 1 min, RT, with H_2O_2 liquid carrier; (3) polish on Pellon pad with NaHClO, then 1—2 sec in CP4. The primary etch study used 100—200 ml of a 3% H_2O_2 solution in a beaker with stirring on a magnetic hot plate. Specimens were held horizontally in the solution with SST forceps during the etch period, then removed and rinsed in running DI water for 2 min, and then N_2 blown dry. Etch rate was 0.21 μm/min.

GE-0005f: Ibid.

Ge, single crystal spheres used in a study of etching convex surfaces to finite crystal form. Finite form was a dodecahedron, (110).

GE-0150a: Holmes, F J — *Acta Metall,* 7,283(1959)

Ge, single crystal hemispheres used in a study of type etch solutions vs. etch patterns, etched pits, and etch rates. Eighteen different preferential solutions evaluated. Hemispheres were first polished and cleaned in 50—70 ml of H_2O_2 before preferential etching.

GE-0230: Rosner, O — *Z Metallkd,* 46,225(1955)

Ge, single crystal sphere and hemispheres used in a study of convex surfaces. Study was similar to that of Holms (GE-0150a-s), Ellis (GE-0005a-h), Batterman (GE-0058), and others.

GE-0001b
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
TIME:
TEMP: Boiling
COMPOSITION:

x .... HNO_3

DISCUSSION:

Ge, (111) wafers used in a study of surface conductivity and recombination. Surfaces were cleaned in boiling HNO_3 or H_2O_2.

REF: Ibid.

GE-0002
ETCH NAME: Superoxol
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:

1 .... HF
1 .... HNO_3
4 .... H_2O

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DISCUSSION:

Ge, (100) wafers. Solution developed as an optical orientation etch for (100) germanium. (*Note:* Also called Camp #2. See: GE-0065a.)

REF: Theuerer, H C — U S Patent #2,542,727

GE-0003: Moss, K T & Hawkins, H L — *J Appl Phys,* 28,1258(1957)

Ge, (111) wafers used in a study of low surface recombination and low absorption levels in germanium.

GE-0021b: Pfann, W G & Vogel, F L Jr — *Acta Metall,* 5,377(1957)

Ge, (111) wafers used in a dislocation and defect study.

GE-0058a: Batterman, S W — *J Appl Phys,* 28,1236(1957)

Ge, (111) wafers and spheres used in a study of pits, hillocks and etch rates. The single crystal sphere finite crystal form was a dodecahedron (hh0) after etching 5 h at RT.

GE-0070b: Della-Pergola, G & Sette, D — *Alta Freq,* 24,499(1955)

Ge, (111) wafers. An evaluation of the effect of different etches on germanium. Other etches were: CP4, silver and copper nitrate.

GE-0075b: Holmes, P J — *Phys Rev,* 119,131(1960)

Ge, (111) dendritic ribbon. Evaluation of etch pits developed with different etch solutions. Authors says that both WAg and ferricyanide give triangle pits pointing upward on dendrites grown in "G" direction (?); whereas superoxol and similar etches show pits pointing downward.

GE-0095b: Schell, A — *Z Metallkd,* 47,614(1956)

Ge, (111) wafers used in an etching study. An evaluation of etch pit development with both CP4 and superoxol.

GE-0141: Dresselhaus, O et al — *Phys Rev,* 98,368(1955)

Ge, (111) wafers 0.5 mm thick and 0.3 mm diameter used in a study of cyclotron resonance of electrons and holes in both germanium and silicon. Solution used as a cleaning etch and preferential etch. Etching time was several minutes.

GE-0185b: Bridgers, H E et al — *Transistor Technology,* Vol I, D Van Nostrand, New York, 1958, 354

Ge, specimens. Describes use of superoxol as an etch.

GE-0231: Rosi, F D — *Acta Metall,* 4,26(1956)

Ge, (111) wafers. A dilute HF:HNO_3 solution was used in studying kink bands in germanium.

GE-0060a: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970, 7—52

Ge, (111) wafers. Solution can be used as a preferential etch. Several other etch mixtures described.

GE-0218: Coblens, A & Ownes, H L — *Transistors — Theory and Applications,* McGraw-Hill, 1955, 211—212

Ge specimens. The use of superoxol as a germanium etchant.

GE-0005a: Ellis, R C Jr — *J Appl Phys,* 28,1068(1957)

Ge, single crystal spheres. Spheres were ground to shape and etch polished prior to finite crystal form (FCF) etching to observe rapid etch planes on convex surfaces. Ten different etchants were used in the two referenced articles, listed here, and the developed finite form is shown in the articles under each etchant evaluated. This was some of the initial work done in studying the convex single crystal planes of semiconductors. Finite crystal form obtained in superoxol was a dodecahedron, (110).

GE-0220a: Ellis, R C Jr — *J Appl Phys,* 25,1497(1954)

Ge, single crystal spheres. See discussion under GE-0005a.

GE-0158b: Batterman, S W — *J Appl Phys,* 28,1236(1957)

Ge and Si single crystal spheres and hemispheres. Material was pedestal grown as

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hemispheres with sections cut and fabricated as complete spheres. Finite crystal form obtained on a sphere was a dodecahedron, (110).
GE-0007: Camp, P R — *J Electrochem Soc,* 102,586(1955)

Ge, single crystal spheres ground to shape and etch polished before preferential etching in a study of convex surfaces. The finite crystal form obtained was a dodecahedron, (110).

GE-0005b
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
3 .... HNO_3
6 .... tartaric acid
DISCUSSION:

Ge, single crystal spheres used in a study of etching convex surfaces to finite crystal form. Finite form obtained was a cube, (100).
REF: Ibid.

GE-0005i
ETCH NAME: Silver nitrate
TYPE: Salt, preferential
TIME:
TEMP:
COMPOSITION:
x .... x% $AgNO_3$
DISCUSSION:

Ge, single crystal spheres used in a study of convex surface planes. Finite crystal form was a cube, (100).
REF: Ibid.

GE-0008
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
3 .... H_2O
DISCUSSION:

Ge, (111) wafers. Solution was used as an optical orientation etch (OOE) for germanium. Etching should be brief, as it also is a polishing etch on germanium. (*Note:* See GE-0002 and additional references under superoxol. The solution shown under GE-0008 is a modification of superoxol.)
REF: Tyler, W W & Dash, W C — *J Appl Phys,* 28,1221(1957)

GE-0147d
ETCH NAME: X-1114
TYPE: Acid, polish
TIME: Seconds
TEMP: RT
COMPOSITION:
1 .... *Superoxol
1 .... HNO_3
1 .... HF
4 .... H_2O

*1HF:1H_2O_2:4H_2O

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DISCUSSION:

Ge, (111) wafers used in an etch development study. Solution shown described as an excellent removal and polish etch for germanium. The removal etch rate for a $^1/_4$" area shown as 25 μm/20 sec.

REF: Bondi, F J — *Transistor Technology,* Vol III, D Van Nostrand, New York, 1958, 15b

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GE-0005c

ETCH NAME: Mercuric nitrate — TIME:

TYPE: Salt, preferential — TEMP:

COMPOSITION:

x .... x% $Hg(NO_3)_2$

DISCUSSION:

Ge, single crystal spheres. Finite form: cube, (100). See GE-0005a for additional discussion.

REF: Ibid.

GE-0005d

ETCH NAME: — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

1 .... $Cr(NO_3)_2$

1 .... NH_4OH

DISCUSSION:

Ge, single crystal spheres. Solution mixed to produce $Cr(NH_3)_4^{++}$ ions. Finite crystal form was a cube, (100). See GE-0005a for additional data.

REF: Ibid.

GE-0005e

ETCH NAME: — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

50 .... HNO_3

50 .... tartaric acid

3 .... x% $AgNO_3$

DISCUSSION:

Ge, single crystal spheres. Finite crystal form is a cube, (100).

REF: Ibid.

GE-0005g

ETCH NAME: — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

1 .... H_2O_2

1 .... tartaric acid

DISCUSSION:

Ge, single crystal spheres. Finite crystal form was a dodecahedron, (110).

REF: Ibid.

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GE-0005h
ETCH NAME: TIME:
TYPE: Halogen, preferential TEMP:
COMPOSITION:
x .... tartaric acid
x .... *Br_2

*Saturate tartaric acid with bromine.

DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a tetrahexahedron, (hk0).
REF: Ibid.

GE-0220b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
37 .... HF
13 .... HNO_3
50 .... H_2O
2 .... x% $AgNO_3$
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a cube, (100).
REF: Ibid.

GE-0220c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
4 .... HF
7 .... HNO_3
87 .... HAc
3 .... x% $AgNO_3$
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a cube, (100).
REF: Ibid.

GE-0220d
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
25 .... HF
45 .... HNO_3
30 .... HAc
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was an octahedron, (111).
REF: Ibid.

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GE-0220e
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
40 .... HF
20 .... HNO_3
40 .... H_2O
2 .... x% $AgNO_3$
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was an octahedron, (111).
REF: Ibid.

GE-0220f
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
50 .... HF
50 .... H_2O_2
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was an octahedron, (111).
REF: Ibid.

GE-0220g
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... H_2O_2
1 .... citric acid
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was an octahedron, (111).
REF: Ibid.

GE-0220h
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
17 .... HF
17 .... H_2O_2
66 .... H_2O
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a dodecahedron, (110).
REF: Ibid.

GE-0220i
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
8 .... HF
13 .... HNO_3
79 .... HAc

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DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a dodecahedron, (110).
REF: Ibid.

GE-0220j
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
13 .... HF
23 .... HNO_3
64 .... HAc
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a trisoctahedron, (hh1).
REF: Ibid.

GE-0220k
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
3 .... HF
5 .... HNO_3
92 .... HAc
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was a tetrahexahedron, (hk0).
REF: Ibid.

GE-0221a
ETCH NAME: TIME: 10—20 min
TYPE: Alkali, preferential TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH(NaOH)
20 g .... I_2
DISCUSSION:
Ge, single crystal spheres fabricated in a "Tornado Sphere Grinder" from $^1/_4$ and $^1/_8$" cubes. Sphere were slow polish etched in 1HF:10HNO_3 prior to preferential etching for finite crystal form of convex surfaces. The crystal form obtained was an octahedron, (111).
REF: Walker, P & Waters, P W — personal development, 1957/1958

GE-0221b
ETCH NAME: TIME: 10—20 min
TYPE: Alkali, preferential TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH(NaOH)
50 ml .... Br_2
DISCUSSION:
Ge, single crystal spheres. Finite crystal form was an octahedron, (111).
REF: Ibid.

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GE-0223a
ETCH NAME: Ellis #5 TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
20 .... HF
3 .... H_2O_2
12 .... H_2O
DISCUSSION:
Ge, spheres and hemispheres. A study of preferential etching of convex surfaces for finite crystal form spheres, and planes on hemispheres. See Holmes, GE-0150a-s for additional data.
REF: Ellis, S O — *J Appl Phys,* 28,1262(1957)

GE-0223b
ETCH NAME: Ellis #1 TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
2 .... HF
1 .... HNO_3
1 .... 10% $AgNO_3$
DISCUSSION:
Ge, spheres and hemispheres used in a study of preferential etching of convex surfaces.
REF: Ibid.

GE-0223c
ETCH NAME: Ellis #7 TIME:
TYPE: Alkali, preferential TEMP: Cold
COMPOSITION:
x .... 0.8 *N* KOH
x .... Cl_2 for pH 8—9
DISCUSSION:
Ge, spheres and hemispheres. Chlorine gas is bubbled through the cold hydroxide solution during the etch period. See Holmes, GE-0150a-s.
REF: Ibid.

GE-0010a
ETCH NAME: TIME: 12 min
TYPE: Acid, preferential TEMP: RT (24°C)
COMPOSITION:
1.5 .... HF
2 .... H_2O_2
4 .... H_2O
DISCUSSION:
Ge, (100) and (110) wafers. Etch used at time and temperature shown as an optical orientation etch (OOE) on (100) surfaces. The (110) surface was etched for 12 min at 20°C for orientation.
REF: Schwuttke, G H — *J Electrochem Soc,* 106,315(1959)

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GE-0010b
ETCH NAME: TIME: 6 min
TYPE: Acid, preferential TEMP: RT (24°C)
COMPOSITION:
1 .... HF
2 .... H_2O_2
4 .... H_2O
DISCUSSION:
Ge, (111) wafers. This solution developed as a light figure orientation etch for (111) surfaces.
REF: Ibid.
GE-0288: Sturge, M D — *Proc Phys Soc*, 73,320(1959)
Ge, (111) wafers used to fabricate p-n junction diodes with boron diffusion. Solution used to etch define the junctions.

GE-0012a
ETCH NAME: TIME: 10—30 min
TYPE: Alkali, preferential TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH
30 g .... I_2
DISCUSSION:
Ge, (111), (100), (110) and (211) wafers. Developed as a light figure orientation etch for germanium. Also used to fabricate controlled etch pit structures and mesas on (111) wafers in device development. Operational diodes and transistors were fabricated.
REF: Walker, P — personal development, 1958
GE-0012d: Ibid.
Both germanium and silicon spheres etched in this solution produce the finite crystal form of a cube, (100).

GE-0012b
ETCH NAME: TIME: 10—30 min
TYPE: Alkali, preferential TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH (450 g)
25 ml .... *Br_2

*Amount of Br_2 varied to obtain specific pit structure.

DISCUSSION:
Ge, (111), (100), (110) and (211) wafers. Solution developed as a light figure orientation etch for germanium. Also used on both n- and p-type (111) germanium to develop controlled-damage pits and mesa structures in device development. Produces a very flat bottomed, sharply triangular pit form within 30 min on (111). Over 30 min etching, pit bottom begins to show terracing. Solution using I_2 (GE-0012a) is very similar and easier to control as bromine dissipates rapidly in hot solutions.
REF: Ibid.
Ge, (111), and (100) wafers. CP4 used as a cleaning etch prior to Ar^+ ion bombardment. Ion cleaning showed anisotropic etching. n-type Ge converted to p-type above 500°C.
GE-0023: Gottaviani, G et al — *J Appl Phys*, 47,626(1976)
Ge, (111) wafers used as substrates for aluminum evaporation and Ge epitaxy for a Ge epi/Al/Ge (111) structure. Substrates were mechanically polished, then polish etched with

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a modified CP4 using 0.5 Br_2. After fabrication, subsequent annealing caused the epitaxy Ge cover to migrate down through the aluminum to the substrate Ge surface.

GE-0024: O'Hara, S — *J Appl Phys,* 35,409(1964)

Ge specimens of ribbon crystal or dendritic germanium grown material used in a study of dislocations and defects. A modified CP4 containing varying amounts of 0.8 g Ge/100 ml HNO_3 added. (*Note:* Etches containing some of the material to be etched have been called "seeded" solutions.)

GE-0025: Crisman, E E et al — *J Electrochem Soc,* 131,1896(1984)

Ge, (111), p-type, 0.1 Ω cm resistivity wafers used as substrates in a germanium oxide study. Degrease wafers in hot TCE, then rinse in hot acetone, and hot MeOH. Remove native oxide in hot 1HF:1H_2O, 30 sec with final rinse in H_2O, and N_2 blow dry. Etch remove about 30% of the specimen thickness with CP4 . . . there was slight orange-peel on the surface after etching. Grow GeO/GeO_2 on surfaces in a pressure bomb, 10 min at 650°C, and 340 atm in an O_2 atmosphere for about 2000 Å of oxide. Anneal at 200°C in forming gas (85% N_2:15% H_2) or in NH_3.

GE-0026: Walker, P — personal development, 1960.

Ge bars cut from (111) grown ingots with grown-in p-n junctions.

GE-0012c
ETCH NAME:
TYPE: Alkali, preferential
TIME: 10—30 min
TEMP: Boiling
COMPOSITION:

250 ml .... 30% KOH (450 g)
45 g .... $(NH_4)_2S_2O_8$

DISCUSSION:

Ge, (111), (100), (110) and (211) wafers. See comments under similar solutions containing Br_2 and I_2 (GE-0012a and GE-0012b). In all three solutions, KOH can be replaced with NaOH.

REF: Ibid.

GE-0065a
ETCH NAME: CP4
TYPE: Acid, polish/preferential
TIME: Variable
TEMP: RT
COMPOSITION:

30 .... HF
50 .... HNO_3
30 .... HAc
0.6 .... Br_2

DISCUSSION:

Ge, (100) wafers and other orientations. CP4 was originally developed as a polishing and preferential etch for (100) germanium surfaces used at RT. Since initial development as Camp #4, the solution has had wide application on germanium, as well as other semiconductors, metals and metallic compounds.

REF: Camp, P R — *J Electrochem Soc,* 102,1415(1955)

GE-0015a: Ingham, H S & McDade, F J — *IBM J,* Jul 1961, p 302

Ge specimens. Used as a general polish for germanium surfaces.

GE-0016: Turner, J — *J Electrochem Soc,* 103,252(1956)

Ge specimens. Recommends using CP4 without bromine for polishing both germanium and silicon wafers. (*Note:* CP4 without bromine is called CP4A.)

GE-0017: Allen, J W & Smith, K C A — *J Electron,* 1,439(1956)

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Ge specimens. Used CP4 to develop edge dislocations in germanium. Authors say that etch rate varies with concentration of electrons and holes in the germanium material.
GE-0018a: Muller, R K — *J Appl Phys,* 32,640(1961)

Ge wafers. CP4 was used to remove saw damage from surfaces in studying grain-boundaries in n-type germanium.
GE-0019a: Weinreich, O et al — *J Appl Phys,* 32,1170(1961)

Ge wafers fabricated with thermally evaporated p-n junction devices. Solution used to develop junctions by etching for 5 min, then with electrical bias across junction, place one drop of KOH solution on wafer across the junction to develop.
GE-0020: Breidt, P Jr et al — *Acta Metall,* 5,60(1957)

Ge wafers. Indented germanium surfaces with a Ta rod at 375°C and used CP4 as a macro-etch to develop dislocations introduced by damaging and accentuated by thermal heating.
GE-0021: Pfann, W G & Vogel, F L Jr — *Acta Metall,* 5,377(1957)

Ge wafers. Solution used at room temperature as a polish etch. Authors say a cone-shaped surface is obtained representative of bulk material is ideal and that p- and n-type surfaces etch similarly. A sphere etched in CP4 produced pole figures, only, at (111) and (100) locations. (*Note:* The mammillary type surface is common to most metals and compounds, when all surface damage depth has been etch removed and the etch solution is slightly preferential. Called either mammillary or botryoidal as a natural mineral structure.)
GE-0022: Forman, R — *Phys Rev,* 117,698(1960)

Bars were cut and lap polished with 600-grit SiC. CP4 was mixed and allowed to age 24 h before use. Bars were forward biased with 0.5 mA power, while being lightly agitated in the solution with removal every 2 min, water quenched and observed until junction was well developed. The p-type junction side etched approximately twice the rate of the n-type forming a sharply defined line trench in 5—7 min.
GE-0060b: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7—52

Ge, (111) wafers. Solution mixture was with 0.3 ml Br_2 and used for 1—3 min as a general cleaning and polishing etch.
GE-0066: Bardsley, W & Bell, R L — *J Electron,* 5,19(1958)

Ge, (111) wafers. Solution used to develop dislocations which were measured for their crystallographic directions and orientation.
GE-0067: Bell, R L — *J Electron,* 3,487(1957)

Ge, (111) wafers. Both CP4 and Dash Etch used in studying dislocation density and defects in semiconductors.
GE-0069: Harnik, E & Margeninski, Y — *J Phys Chem Solids,* 8,96(1959)

Ge, (111) wafers used in a study of surface treatments and the characteristics of fast states on germanium surfaces. Solution used 30 sec at 30°C.
GE-0070a: Della-Pergola, G & Sette, D — *Alta Freq,* 24,499(1955)

Ge, (111), and (100) wafers used in a general study of the effects of different preferential etches. Used CP4, superoxol, WAg, and copper nitrate solutions to develop defects.
GE-0071: Balabanova, L A & Bredov, M M — *Zh Tekh Fiz,* 27,1401(1957)

Ge, (111) wafers used in a study of thermal conversion by irradiation. CP4 + warm DI water rinse was evaluated against a lapped surface with alcohol rinse only. The CP4 treatment reduced conversion 25—50%.
GE-0072: Wehner, G K — *J Appl Phys,* 29,217(1958)

Ge, (111) wafers. Wafers were Hg^+ ion bombarded at 1000 V and etched in CP4 before and after irradiation. Dislocation pits did not correspond before and after irradiation.
GE-0073: Bonfiglioli, G et al — *J Appl Phys,* 31,684(1960)

Ge, (111) wafers. A study of first order structures developed by CP4 on germanium surfaces. CP4 developed conoid etch pits and dislocations, which either disappeared or

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became passive. (*Note:* Those that increase in size and disappear are usually surface damage etch pits; those that remain in place with little size increase, though they too may disappear, are dislocations.)

GE-0083b: Rhodes, E G et al — *J Electron*, 3,403(1957)

Ge, (111) wafers. CP4 used as a polish and damage removal etch before preferential etching. (See GE-0083a.)

GE-0091: Noggles, T S & Stiegler, J O — *J Appl Phys*, 30,1279(1959)

Ge, (111) wafers irradiated and studied under an electron microscope (EM). Solutions used to observe defects before and after irradiation. Both CP4 and CP4A (without bromine) were evaluated.

GE-0104: Handler, P & Portnoy, W M — *Phys Rev*, 116,516(1959)

Ge, (100) wafers used in a study of electron surface states of cleaned surfaces. CP4 was used as a cleaning etch.

GE-0105: Fritzsche, H — *Phys Rev*, 99,406(1955)

Ge, (111) wafers used in a study of electrical parameters at low temperature. CP4 used as a polish etch.

GE-0106: Spears, W E — *Phys Rev*, 112,362(1958)

Ge, (111) wafers, both n- and p-type, 10—22 Ω cm resistivity used in a study of the surface effects of electron irradiation at 80 K. CP4 was used as a polish etch.

GE-0107: Madden, H H & Farnsworth, H E — *Phys Rev*, 112,791(1958)

Ge, (100) wafers used in a high vacuum study of surface recombination velocity. Wafers prepared as follows: (1) Etch thin with CP4 prior to mechanical lapping with A/O 305-grit; (2) polish with MgO on a wax lap; (3) polish etch with CP4, (4) rinse in concentrated KCN and (5) final rinse in double-distilled water.

GE-0108: Brill, P A & Schwartz, R F — *Phys Rev*, 112,330(1958)

Ge, (111) wafers used in a study of radiation recombination. Etch clean surfaces with CP4 or in $2HF:2HNO_3:1HAc$.

GE-0109: Hunter, L P — *IBM Res Dev*, 3,106(1957)

Ge, (111) wafers. A direct measurement of the angular dependence of the atomic scattering factor. CP4 used as a heavy removal etch with at least 20 μm removed and no residual surface damage observed.

GE-0110: Kurtz, A D et al — *Phys Rev*, 101,1285(1956)

Ge, (111) wafers used in a study of the effects of dislocations on minority carrier lifetime. Surfaces were electropolished before preferentially etching with CP4 or superoxol to develop dislocations.

GE-0111: Savage, H — *J Appl Phys*, 31,1472(1960)

Ge, (111) wafers used in a study of copper precipitation on dislocation etch pits. Use a modified CP4 or Ellis #7 (GE-0105r) as a polish and dislocation etch. To copper decorate place drops of $Cu(NO_3)_2$ on surface and heat to 900°C, $^1/_2$ h.

GE-0092a: Faust, J W Jr & John, H F — *J Electrochem Soc*, 108,860(1961)

Ge, (111) dendrites as ribbon crystal growth. Solution used to develop structure and growth patterns. The CP4 solution mixture used was 15 ml HF:25 ml HNO_3:15HAc:0.3% Br_2, RT, 3—10 sec.

GE-0093: Vogel, F L et al — *Phys Rev*, 90,489(1953)

Ge, (111) wafers used in a dislocation study. CP4 solution mixture was $3HF:5HNO_3$:3HAc:0.1% Br_2, RT. Also used on silicon which etches more rapidly.

GE-0094a: Logan, K H & Schwartz, M — *J Appl Phys*, 26,1287(1955)

Ge, (111) wafers used in a study of the restoration of resistivity and lifetime by heat treatment. Both CP4 and KCN solutions used to clean surfaces prior to evaluation.

GE-0095a: Schell, H A — *Z Metallkd*, 47,614(1956)

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Ge, (111) wafers, and other orientations, used in a general defect study. The original CP4 (GE-0065a) used as a dislocation etch.

GE-0096: Harvey, W W & Gatos, H O — *J Electrochem Soc,* 105,654(1958)

Ge, (111) wafers studied for the material reaction in solutions containing dissolved oxygen. Original CP4 solution used at RT, 30—60 sec as a polish etch.

GE-0097: Vogel, F L — *Acta Metall,* 3,95(1955)

Ge, (111) wafers studied for dislocations after mechanical abrasion with 600-grit SiC after temperature stressing. CP4 was used as a polish and dislocation etch.

GE-0098: Faust, J W Jr & John, H F — *J Electrochem Soc,* 107,562(1960)

Ge, (111) wafers, and other orientations. A comparison of etching and fracture techniques for defect study of Ge, Si and III—V compound semiconductors. CP4 with 0.3 parts Br_2 was slightly preferential on (111) surfaces, although it was used primarily as a polish etch.

GE-0099: Patel, J R & Alexander, B H — *Acta Metall,* 4,385(1956)

Ge, (111) wafers. This was a study of plastic deformation of germanium under compression. CP4 was used at RT as a polish etch which also shows slip bands, and also was used hot, at 60°C, as a dislocation etch.

GE-0100: Wallis, G & Wang, S — *J Electrochem Soc,* 106,231(1959)

Ge, (111) wafers used in a study of the effect of various etches on recombination centers in germanium surfaces. CP4 was evaluated against H_2O_2, Iodine "A", electrolytic (KOH), and the Silver Etch.

GE-0102a: Wertheim, O K & Pearson, G L — *Phys Rev,* 107,694(1957)

Ge, (111) wafers used in a study of recombination after plastic deformation. Clean wafers in a solution of KCN, then etch polish in CP4. After deformation at 750°C, re-etch with CP4, RT, 90 sec to develop dislocations. Initial density was 5×10^3 cm^2, increasing to 2×10^7 cm^2 after deformation.

GE-0112: Tweet, A G — *J Appl Phys,* 29,1520(1958)

Ge, (111) wafers as dislocation-free material. Study showed evidence of vacancy clusters. Dislocation free areas etch more rapidly when defect density is greater than 100/cm^2. CP4 used as an electrolytic "pulse" etch to develop dislocations.

GE-0113: Meckel, B B & Swalin, R A — *J Appl Phys,* 30,89(1959)

Ge, (111) wafers. Observation of selective delineation of screw dislocations produced by cathode sputtering as Ar^+ ion bombardment at 300 eV. After bombardment, CP4 was used to develop dislocations.

GE-0114: Heinecke, W J & Ing, S Jr — *J Appl Phys,* 32,1498(1961)

Ge, (111), and (100) wafers used in a study of the reaction of iodine on surfaces. Wafers were etch polished in CP4 prior to iodine treatment at 300—500°C, 5—20 min in an I_2 gas flow of 0.2—6 cm/sec with a partial pressure of 0.004—0.02 atm. Etch rate was directly proportional to iodine partial pressure. Variations in temperature and gas flow rate showed either little effect or erratic results. (*Note:* Etch pits shown in the article are identical to those observed using KOH:I_2 liquid solutions. GE-0151a.)

GE-0115: Dexter, R N et al — *Phys Rev,* 104,637(1956)

Ge, (111) wafers used in cyclotron resonance experiments. CP4 used as a cleaning etch. CP4 does appear to influence photoconduction efficiency, but not scattering frequency. Also studied silicon.

GE-0116: Madden, H H & Farnsworth, H E — *Phys Rev Lett,* 1,346(1958)

Ge, (111) wafers used in high vacuum studies of surface recombination velocity. CP4 used as a surface cleaning etch, but was not as good as ionic bombardment cleaning. Residual oxide layers remaining after etching had little or no effect.

GE-0117: Frank, R C — *J Appl Phys,* 31,1689(1960)

Ge, single crystal seed prepared for ingot growth. The seed was a hollow, polished cylinder. CP4 used as the polish etch and to develop residual dislocations. A cylinder was

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designed, because dislocations are higher in density toward the center of a solid seed. There were traces of radial lineage.

GE-0118: Vook, F L & Balluffi, R W — *J Appl Phys,* 31,1693(1960)

Ge, (111) wafers used in a study of resistivity change from low temperature annealing with deuteron irradiation. CP4A (no bromine) used to remove work damage from mechanically lapped bars.

GE-0119a: Yamashita, T & Ohto, T — *Jpn J Appl Phys,* 16,1565(1961)

Ge, (111) wafers are cut to 1.50 in diameter and mechanically lapped with 1200-grit emory. Etch polish with CP4, then soak in HNO_3, rinse in DI water, then soak in KCN, and DI water rinse. Wafers used in measurement of the Seebeck effect in plastically bent germanium.

GE-0120: Kuczynski, G C & Hochman, R F — *Phys Rev,* 108,946(1957)

Ge, (111) wafers used in a study of induced plasticity. A Knoop point using a Tukon Hardness Tester was used to indent Ge, Si, InSb, and InAs wafer surfaces. Indentation damage results are dependent upon prior surface preparation. Ge, InSb, and InAs surfaces were etch polished with CP4, and silicon with $1HCl:3HNO_3$.

GE-0121: Farnsworth, H E et al — *J Appl Phys,* 29,1150(1958)

Ge, (111) wafers and titanium, silicon, and nickel specimens used in a study of ion bombardment cleaning methods, as evaluated by low-energy electron diffraction. Germanium wafers were cleaned with the following sequence: (1) CP4 etch, (2) HF rinse, then (3) repeat CP4 etch.

GE-0122: Seesger, K — *Phys Rev,* 114,476(1959)

Ge, (111) wafers used in a study of the microwave frequency dependence of drift mobility. CP4 was used to etch polish.

GE-0123: Hogarth, C A & Baynham, H C — *Proc Phys Soc,* 71,647(1958)

Ge, (111) wafers used in a general dislocation study. CP4 used as a preferential etch to develop dislocations.

GE-0138: Davis, W D — *Phys Rev,* 114,1006(1959)

Ge:Si single crystal alloy ingots. CP4 used to develop dislocations.

GE-0144b: Faust, J W Jr & John, H F — *J Electrochem Soc,* 108,825(1961)

Ge, (111) dendrites from material grown as ribbon crystals. CP4 used at RT, 30—45 sec to develop dislocations. Also used the WAg and ferrocyanide etches.

GE-0150a: Holmes, P J — *Acta Metall,* 7,283(1959)

Ge, hemispheres etched in a study of defect patterns, type etch pits, and etch rates on both germanium and silicon. Prior to preferential etching, specimens etch in CP4 to remove lap/polish damage. See GE-0150a-s.

GE-0147a: Bondi, F J — *Transistor Technology,* Vol III, D Van Nostrand, New York, 1958

Ge, specimens. Etch in CP4 for 1—2 min as a polish etch before electrolytic jet etching with 0.1% KOH.

GE-0176: Walter, F J et al — *Rev Sci Instrum,* 31,756(1960)

Ge devices fabricated as large area surface-barrier counters. Etch polished in CP4 prior to processing.

GE-0217: Bridgers, H E et al — *Transistor Technology,* Vol I, D Van Nostrand, New York, 1956, 354

Ge, specimens. Both CP4 and superoxol described as general etchants for germanium.

GE-0227a: Arizumi, T & Akasaki, I — *Jpn J Appl Phys,* 2,143(1963)

Ge, (111), (110), and (100) wafers used in an etching study of structures developed by iodine vapor. Wafers were mechanically lapped and then etched in CP4 to remove work damage and residual oxide prior to etching with hot iodine vapors.

GE-0228: Arizumi, T et al — *Jpn J Appl Phys,* 2,757(1963)

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Ge, (100) wafers and other orientations. Wafers used in studies of impurity doping in vapor grown germanium. CP4 used as a cleaning rinse etch prior to doping.

GE-0217b
ETCH NAME: CP4, variety
TYPE: Acid, polish
COMPOSITION:
15 .... HF
25 .... HNO_3
15 .... HAc
x* .... Br_2

TIME: 3 min
TEMP: RT

*x = 10 drops Br_2/50 ml for a bromine saturated solution.

DISCUSSION:
Ge wafers. This solution is CP4 saturated with bromine, and used as a polishing etch.
REF: Bridgers, H E et al — *Transistor Technology,* Vol I, D Van Nostrand, New York, 1958, 354

GE-0219
ETCH NAME: CP4, modified
TYPE: Acid, dislocation
COMPOSITION:
15 ml .... HF
25 ml .... HNO_3
15 ml .... HAc
x mg .... I_2

TIME:
TEMP: RT

DISCUSSION:
Ge wafers. Solution used to develop screw dislocations. See GE-0218.
REF: Rhodes, R T et al — *J Electron Control,* 3,403(1957)
GE-0220: Walker, P & Waters, P W — personal development, 1957
Ge, (111), (100), (110), and (211) wafers used in a general etching study. CP4 with 1gI_2/200 ml of solution used at RT, cool (8—10°C), and warm (40°C) as a polish and preferential defect development etch.

GE-0221
ETCH NAME:
TYPE: Vacuum, cleaning
COMPOSITION:
x .... vacuum

TIME:
TEMP:

DISCUSSION:
Ge, (100) wafers cleaved in vacuum to obtain clean surfaces and used in a study of oxygen effects on surfaces.
REF: Robinson, P H et al — *J Appl Phys,* 27,962(1956)

GE-0027
ETCH NAME: BJ etch
TYPE: Acid, polish
COMPOSITION:
9 .... HF
15 .... HNO_3
10 .... HAc

TIME:
TEMP:

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DISCUSSION:

Ge, (111) wafers. This is one of several etches developed by the author cited as a good polishing etch for both germanium and silicon.

REF: Stopek, S — personal communication, 1958

GE-0028

ETCH NAME: 1:1:1 TIME:

TYPE: Acid, polish/removal TEMP:

COMPOSITION:

1 .... HF

1 .... HNO_3

1 .... HAc

DISCUSSION:

Ge, (111), and Si, (111) wafers. Solution used as a removal and polish etch on both materials. (*Note:* Although this etch was called a 1:1:1 etch, which it is, such volume nomenclature is not recommended due to the wide variations of possible constituents in such a volume mixture.)

REF: Millea, R P & Hall, R — *J Electrochem Soc,* 105,174(1958)

GE-0030

ETCH NAME: TIME: 1 to 2 h

TYPE: Acid, sphere polish TEMP: RT

COMPOSITION:

5 ml .... HF

75 ml .... HNO_3

DISCUSSION:

Ge, spheres of single crystal germanium and silicon with a 600-grit SiC ground surface were etch polished in this solution prior to preferential etching for finite crystal form and as spherical diffused diodes. Both n- and p-type spheres were used. Etch in a Teflon beaker tilted at about 30° with sufficient rotational agitation to allow spheres to roll freely but not tumble. Time shown is for germanium; silicon time was 10—20 min. Ultrasonically cut cylinders of germanium also were etch polished and fabricated as lithium-drift detectors.

REF: Walker, P — personal development, 1961

GE-0031a

ETCH NAME: TIME:

TYPE: Acid, junction TEMP: RT

COMPOSITION:

20 .... HNO_3

20 .... BJ etch

60 .... H_2O

+ .... $K_2Cr_2O_7$

+ .... light

DISCUSSION:

Ge, (111) rectangular bars with grown p-n junctions. Solution used to delineate the p-n junction.

REF: Walker, P — personal development, 1959

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GE-0032
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... HAc or H_2O
DISCUSSION:
Ge, (111), (100), (110), and (211) wafers. By varying the ratio of HF:HNO_3 the preferential pit shape will vary on germanium surfaces.
REF: Faust, J W — *The Surface Chemistry of Metals and Semiconductors,* John Wiley & Sons, New York, 1950, 151

GE-0015b
ETCH NAME: White etch TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
20 .... HF
80 .... HNO_3
DISCUSSION:
Ge, (111) wafers used as substrates for germanium epitaxy growth. Solution was used to etch polish the epitaxy layers. (*Note:* See comment under GE-0029 with regard to using the term "White" to describe an etch.)
REF: Ibid.

GE-0033
ETCH NAME: TIME:
TYPE: Acid, junction TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
Ge, (111) wafers used to fabricate alloyed p-n junctions with indium. Etch was used to delineate the Ga/In p-n junction.
REF: Newman, R C — *J Appl Phys,* 27,845(1956)
GE-0286: Richards, J L — *J Appl Phys,* 34,3418(1963)
Ge, flash evaporated as a thin film on Ge and GaAs substrates as epitaxy layers. Both substrates were clean etched in 1HF:3HNO_3; rinsed in DI H_2O; then MeOH. CaF_2, (100) substrates were cleaved and used without further processing. All three substrates were used in a study of flash evaporated thin film semiconductors.

GE-0034
ETCH NAME: TIME:
TYPE: Acid, junction TEMP:
COMPOSITION:
5 .... HF
5 .... HNO_3
2 .... H_2O
DISCUSSION:
Ge, (111) wafers used to fabricate alloyed p-n junctions with indium. Etch was used to delineate to Ge/In p-n junction.
REF: Dreiner, A & Garnache, W R — *J Appl Phys,* 27,737(1956)

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GE-0035
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
x .... H_2O
DISCUSSION:
Ge, (111) wafers used in a study of kink bands in the material. Used a dilute HF:HNO_3 etch to remove damage induced by mechanical lapping of germanium surfaces.
REF: Rosi,
TIME:
TEMP:

GE-02201
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
17 .... HF
13 .... HNO_3
50 .... H_2O
2 .... $AgNO_3$
DISCUSSION:
Ge, sphere. A single crystal sphere of germanium was etched to finite crystal form in this solution. Form is a cube, (100).
REF: Ellis, E C Jr — *J Appl Phys*, 25,1497(1954)
TIME:
TEMP:

GE-0038
ETCH NAME: BRM
TYPE: Halogen, polish lap
COMPOSITION:
x .... 0.05% Br_2
x .... MeOH
DISCUSSION:
Ge, (111), (100), and (110) wafers used in a study of surface cleaning. Solution saturated lens paper used as a polishing pad. After initial polish of 20 sec, dilute by flooding with MeOH and continue polishing an additional 10 sec. Follow with rinse in BRM, then MeOH. Final rinse in BHF, then H_2O. Also etch polished with BRM on Si, GaP, GaAs, GaSb, InP, InAs, and InSb.
REF: Aspenes, D E & Studna, A A — *J Vac Sci Technol*, 20,488(1982)
TIME: 20 sec + 10 sec
TEMP: RT

GE-0031b
ETCH NAME:
TYPE: Electrolytic, junction
COMPOSITION:
125 ml .... 0.5 *M* $3K_2S_2O_3.H_2O$
4 g .... I_2
DISCUSSION:
Ge, (111) grown ingot with grown-in p-n junction. Rectangular bars cut and lapped to $^3/_{16} \times {}^3/_{16} \times {}^3/_4$" in size. Etch is milky in color, and copper clips used to hold bars react with etch. Bars were biased during etching with p-type highly polished, and n-type dull grey. The p-type etched faster producing a sharp line at the junction.
REF: Ibid.
TIME: 10 min
TEMP: RT
ANODE: p-Ge
CATHODE: Pt strip
POWER: 60 mA/cm^2

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GE-0031c
ETCH NAME:
TYPE: Electrolytic, junction
COMPOSITION:
250 ml .... 0.5 *M* $Cr_2(SO_4)_3$
2 mg .... Ag
TIME: 15 min
TEMP: RT
ANODE: Pt strip
CATHODE: p-Ge
POWER: 6 mA/cm^2
DISCUSSION:

Ge, (111) grown ingots with grown-in p-n junction. Specimens were cut and lapped as a rectangular bar $^3/_{16} \times {}^3/_{16} \times {}^3/_4$" size. Solution can be used with or without silver. Very slow etch on both p- and n-type areas. Junction appears as a finely etched line.
REF: Ibid.
GE-0212: Lesk, I A & Gonzales, R E — *J Electrochem Soc,* 105,469(1958)

Ge, (111) wafers fabricated as transistors. A selective electrolytic etch used to develop p-n junctions of both silicon and germanium.
GE-0211: Sullivan, M U & Eigler, J H — *J Electrochem Soc,* 103,132(1956)

Ge, (111) wafers electrolytically stream (jet) etched.
GE-0213: Esaki, L — *J Phys Soc Jpn,* 13,1281(1958)

Ge, wafers used to fabricate Esaki p-n junction devices.

GE-0031d
ETCH NAME:
TYPE: Electrolytic, junction
COMPOSITION:
100 ml .... HCl
50 ml .... H_2O
6 g .... $ZnCl_2$
TIME: 15 min
TEMP: RT
ANODE: n-Ge
CATHODE: Pt strip
POWER: 60 mA/cm^2
DISCUSSION:

Ge, (111) ingots with grown-in p-n junction. Rectangular bars were cut and lapped $^3/_{16} \times {}^3/_{16} \times {}^3/_4$" in size. Zinc plates out on Pt cathode. Slight preferential etching with p-type more highly polished. Shows a distinct etched junction line.
REF: Ibid.

GE-0019b
ETCH NAME:
TYPE: Electrolytic, junction
COMPOSITION:
x .... KOH
x .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Ge, (111) wafer with p-n junctions. Specimens lapped with 1800-grit alumina. Etch 5 min, RT with CP4 to remove lap damage and rinse with water, then alcohol. Develop junction by placing a drop of the KOH solution across junction and apply bias.
REF: Ibid.
GE-0254a: Pearson, G J & Feldman, W L — *J Phys Chem Solids,* 9,28(1959)

Ge, (111) wafers used to fabricate indium alloyed p-n junction diodes. Junctions developed in KOH solution, 3 min, 10 mA DC power, with Ge forward biased. This produced micro-pyramids on (110) surfaces. Also studied silicon p-n junctions.

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GE-0018b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... NaOH
x .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Ge, (111) wafers used in a study of current flow across grain boundaries in n-type germanium. First, etch specimens in CP4 to remove lap damage. Electropolish in a sodium hydroxide solution shown.
REF: Ibid.
GE-0052: Jackson, R W — *J Appl Phys,* 27,309(1956)

Ge, (111) wafers with p-n junctions. A 10% solution used to develop junctions. The n-type region will etch; p-type does not etch.
GE-0178: John, H F & Longini, R L — Electrochem Soc Meet, Pittsburgh, PA, October 13, 1955

Ge, specimens used in a study of electrolytic etching. Alkalies are good for long-term etching, reproducibility, and reduction of surface recombination rates.

GE-0043
ETCH NAME: Water
TYPE: Acid, float-off
COMPOSITION:
x .... H_2O (desalted)
TIME:
TEMP:
DISCUSSION:

a-Ge, thin film grown on NaCl, (100) cleave substrates used in a study of amorphous germanium. After deposition, the a-Ge film was floated off the NaCl substrate with water. Under heat and electron impingement of a TEM microscope, there was no effect on the thin film. With a laser beam, and reaction observed under the TEM, the amorphous thin film crystallized into spherical particles.
REF: Pierrard, F et al — *Thin Solid Films,* 111,141(1984)

GE-0044
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 0.1% KOH
x .... 5—25% glycerin
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 0.5 A/in^2
DISCUSSION:

Ge, (111), n-type, 0.004—40 Ω cm resistivity wafers. Solution shown used to polish surface with a removal rate of 0.67 mils/min.
REF: Klein, R C et al — *RCA Rev,* 14,23(1969)

GE-0147b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 0.01—10% KOH
x .... 0.1 *N* NaCl
TIME:
TEMP:
ANODE:
CATHODE:
POWER: $^1/_2$—1 mA/cm^2

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DISCUSSION:

Ge, (111) wafers. Etch with CP4 to remove lap damage, then electropolish in the above solution. Also used: $InSO_4$; H_2SO_4, or HCl as the polishing electrolytes.
REF: Ibid.

GE-0046
ETCH NAME: Potassium fluoride
TYPE: Electrolytic, polish
COMPOSITION:
x .... 10^{-6}—0.1 *N* KF

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

Ge, (111), p- and n-type wafers used in an etching study. The following electrolytes were evaluated: KCl; KI; $NaNO_3$; CaCl; $BaCl_2$, and $LaCl_3$ with the addition of O_2. Below pH 6, there is little or no change in etch rate. Above pH 6, etch rate increases. Rate also increases with acid concentration increase. No observed difference between p- or n-type material with or without illumination.
REF: Harvey, W & Gatos, H C — *J Appl Phys,* 29, 1267(1958)

GE-0047
ETCH NAME: DE-100
TYPE: Ionized gas, RF plasma removal
COMPOSITION:
x *DE-100

TIME:
TEMP: RT to 50°C
GAS FLOW: 300 cc/min
PRESSURE: 1.1 Torr
POWER: 200 W

*CF4:8.5% O_2

DISCUSSION:

Ge, thin films evaporated on silicon, aluminum, alumina, gallium arsenide, and sapphire substrates. Ge film thickness was 250 to 6000 Å. Germanium used as a buffer layer in photo resist applications and as a diffusion drive-in source. After processing, remaining Ge removed with DE-100. Also used for removal of SiO_2; Si_3N_4; or Si, Mo, Ta, TaN, and W films.
REF: Scientific Gas Company Bull, 1972
GE-0048: Walker, P — personal development, 1980

Ge, thin films evaporated as part of a photo resist patterning mask. As evaporated Ge thin film, only, used for drive-in GaAs:Cr,(100) (SI) wafers used in fabricating LN-FETs. Residual germanium removed with DE-100 or RF plasma N_2.

GE-0049
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE
POWER: 500 eV

DISCUSSION:

Ge, (100), wafers cut within 1° of plane, used for silver thin film deposition study. After mechanical polish of wafer, clean with Ar^+ ion bombardment, and follow with 450°C anneal. Repeat until no carbon contamination remains. Silver deposited as a (110) oriented single crystal thin film.
REF: Miller, T et al — *Phys Rev,* B30,520(1984)
GE-232: Farnsworth, H E et al — *J Appl Phys,* 29,1150(1958)

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Ge specimens. Application of ion bonbardment cleaning as an improved method of determined by low-energy electron diffraction. Also evaluated Si, Ti, and Ni.

GE-0063
ETCH NAME:
TYPE: Electrolytic, shaping
COMPOSITION:
15 .... HF
25 .... HNO_3
15 .... HAc
DISCUSSION:

TIME:
TEMP:
ANODE:
CATHODE:
POWER: 20—60 V

Ge, single crystal wire filaments etch formed into tips in a study of surface structure and migration using a field emission microscope (FEM). Different resistivity materials of 1.1, 2.0, and 2.2 Ω cm, n-type were used. During tip forming, stir solution, and illuminate with intense light to prevent "sword-shaping" of tip. For final shaping, reduce power to zero and use as a normal chemical etch. Quench in MeOH without exposure to air to prevent formation of germanium oxides. Also used hydrogen in a vacuum system to remove surface contamination, and used oxygen at 800 K, 20—30 sec to sharpen tips — the latter is difficult to control and is erratic. (*Note:* Solution is CP4A, e.g., CP4 without bromine.)
REF: Arthur, J R Jr — *J Phys Chem Solids,* 25,583(1964)

GE-0008b
ETCH NAME:
TYPE: Acid, orientation
COMPOSITION:
1 .... HF
1 .... H_2O_2
3 .... H_2O
DISCUSSION:

TIME:
TEMP: RT

Ge, (111) wafers, and other orientations. Solution used as a light etch for optical orientation (OO) of surfaces. (*Note:* Also called light figure orientation (LFO) technique.)
REF: Tyler, W W & Dash, W C — *J Appl Phys,* 28,1221(1957)

GE-0008c
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
2 .... HF
4 .... HNO_3
15 .... HAc
DISCUSSION:

TIME: 20—60 sec
TEMP: RT

Ge, (111) wafers, and other orientations. Wafers were lithium diffused, and then etched in this solution shown to develop dislocation arrays generated and decorated by lithium.
REF: Ibid.

GE-0217
ETCH NAME:
TYPE: Acid, junction
COMPOSITION:
1 .... HF
5 .... HNO_3, red fuming

TIME:
TEMP: RT

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DISCUSSION:
Ge, (111) wafers fabricated as p-n junction diodes. Junctions etch cleaned and developed with the solution shown. (*Note:* HNO_3 concentration is 74% for red, fuming.)
REF: Farren, T — personal communication, 1956

GE-0218
ETCH NAME: Iodine etch
TYPE: Acid, polish
TIME: 5 min
TEMP: RT
COMPOSITION:
5 ml .... HF
10 ml .... HNO_3
11 ml .... HAc
30 mg .... I_2
DISCUSSION:
Ge, wafers used as substrates for epitaxy growth of PbS as heterojunctions. The Ge substrates were polished in the solution shown. Use agitation during etch period with specimens immersed in etchant.
REF: Davis, J L & Norr, M K — *J Appl Phys,* 37,1670(1966)

GE-0150a
ETCH NAME: Hydrogen peroxide
TYPE: Acid, preferential
TIME: 2—4 h
TEMP: RT
COMPOSITION:
100 ml .... H_2O_2
DISCUSSION:
Ge, single crystal hemispheres, lap formed or grown by a modified Verneiul process, and used in a preferential etching study to observe etch patterns, type etch pits, and etch rates. The amount of solution used was 50—70 ml unless otherwise shown. Also used on silicon hemispheres. Before preferential etching, etch with CP4 to remove residual mechanical lap damage.
REF: Holmes, P J — *Acta Metall,* 7,283(1959)

GE-0150b
ETCH NAME:
TYPE: Acid, preferential
TIME: 3 h
TEMP: RT
COMPOSITION:
1 .... HF
250 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150c
ETCH NAME:
TYPE: Acid, preferential
TIME: 1 h
TEMP: RT
COMPOSITION:
1 .... HF
100 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

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GE-0150d
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
50 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.
TIME: 30 min
TEMP: RT

GE-0150e
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
8 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etch study.
REF: Ibid.
TIME: 10 min
TEMP: RT

GE-0150f
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.
TIME: 6 min
TEMP: RT

GE-0150g
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.
TIME: 3 min
TEMP: RT

GE-0150h
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
2 .... HF
1 .... H_2O_2
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.
TIME: 20 min
TEMP: RT

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GE-0150i
ETCH NAME: Superoxol, variety
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
x .... H_2O
TIME: 2 min
TEMP: RT
DISCUSSION:
Ge, hemispheres. During the etch period there was a progressive addition of water. Solution used in a preferential etching study.
REF: Ibid.

GE-0150j
ETCH NAME: Superoxol #2
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
TIME: 2 min
TEMP: RT
DISCUSSION:
Ge, hemispheres used in a preferential etch study.
REF: Ibid.

GE-0150k
ETCH NAME: Superoxol #2, dilute
TYPE: Acid, preferential
COMPOSITION:
1 .... Superoxol #2
3 .... H_2O
TIME: 30 min
TEMP: RT
DISCUSSION:
Ge, hemispheres used in a preferential etch study.
REF: Ibid.

GE-0150l
ETCH NAME: Superoxol #2, dilute
TYPE: Acid, preferential
COMPOSITION:
1 .... Superoxol #2
6 .... H_2O
TIME: 2 h
TEMP: RT
DISCUSSION:
Ge, hemispheres used in a preferential etch study.
REF: Ibid.

GE-0150m
ETCH NAME: Superoxol #2, dilute
TYPE: Acid, preferential
COMPOSITION:
1 .... Superoxol #2
8 .... H_2O
TIME: 3 h
TEMP: RT
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

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GE-0150n
ETCH NAME: Superoxol #2, dilute — TIME: 48 h
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
1 .... Superoxol #2
50 .... H_2O
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150o
ETCH NAME: Ellis #5 — TIME: 5 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
20 .... HF
3 .... H_2O_2
12 .... H_2O
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150p
ETCH NAME: WAg etch — TIME: 1 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
2 .... HF
1 .... HNO_3
2—5% .... $AgNO_3$, sat. sol.
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150q
ETCH NAME: Ellis #1 — TIME: 5 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
2 .... HF
1 .... HNO_3
1 .... 10% $Cu(NO_3)_2$, sat. sol.
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150r
ETCH NAME: Ellis #7 — TIME: 3 h
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
"A" x .... 0.8 *N* KOH — "B" x .... 5% KOH
x .... Cl_2 for pH 8—9
Mix: 15 ml "A": 60 ml "B".

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DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0150s
ETCH NAME: Ferric-cyanide etch
TYPE: Acid, preferential
TIME: 2 min
TEMP: RT
COMPOSITION:
6 g .... KOH
4 g .... $K_3Fe(CN)_6$
50 ml .... H_2O
DISCUSSION:
Ge, hemispheres used in a preferential etching study.
REF: Ibid.

GE-0060d
ETCH NAME: Ferric-cyanide etch
TYPE: Acid, preferential
TIME: 1—10 min
TEMP: 80°C
COMPOSITION:
13.7 g .... KOH
9.7 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
DISCUSSION:
Ge, (111) and (100) wafers. Solution used as a preferential etch.
REF: Ibid.

GE-0060e
ETCH NAME: (100) Etch
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
70 ml .... HF
25 ml .... HNO_3
50 ml .... H_2O
3 g .... $Cu(NO_3)_2$
DISCUSSION:
Ge, (100) wafers. This is a general preferential etch, but named for its specific use on the (100) surface in this instance. See SI-0038a for the similar "Copper Dislocation Etch".
REF: Ibid.
GE-0070d: Pergola, G D & Sette, D — *Acta Metall,* 24,499(1955)
Ge, (111) wafers used in a study of the effects of different dislocation etches on germanium. Other etches evaluated were CP4, superoxol, and WAg. See SI-0038a for the "Copper Dislocation Etch" used.

GE-0060f
ETCH NAME: Peroxide etch
TYPE: Acid, preferential
TIME: 1 min
TEMP:
COMPOSITION:
1 ml .... HF
1 ml .... H_2O_2
1 ml .... HAc

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DISCUSSION:

Ge, (100) wafers. Solution used as a preferential etch. (*Note:* In chemistry, the standard 30% concentration of hydrogen peroxide also is called a peroxide etch, when used alone.)
REF: Ibid.

GE-0008c
ETCH NAME:
TYPE: Acid, junction
COMPOSITION:
2 .... HF
4 .... HNO_3
15 .... HAc

TIME: 20—60 sec
TEMP: RT

DISCUSSION:

Ge, (111) wafers with lithium diffused p-n junctions. Solution used to etch develop the p-n junction.
REF: Tyler, W W & Dash, W C — *J Appl Phys*, 28,1221(1957)

GE-0008d
ETCH NAME:
TYPE: Acid, optical orientation
COMPOSITION:
1 .... HF
1 .... H_2O_2
3 .... H_2O

TIME:
TEMP:

DISCUSSION:

Ge, (111) wafers. Solution used as a light etch for optical orientation of the (111) surface.
REF: Ibid.

GE-0220m
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
4 .... HNO_3
2 .... H_2O_2

TIME: 5—30 min
TEMP: RT

DISCUSSION:

Ge, (111) wafers, p-type, 4 Ω cm resistivity used in a general etch development study. Wafers were used after lapping with 600-grit SiC abrasive. The etch solution shown will remove the first mil of material in $1^3/_4$ min; thereafter, the rate is constant at 1 mil/min. The (111) n-type, 10 Ω cm resistivity material evaluated etched at the same constant rate as the p-type material after the first 2 min of etching.
REF: Ibid.

GE-0220n
ETCH NAME:
TYPE: Electrolytic, junction
COMPOSITION:
(1) 250 ml .... 0.5 *M* $FeSO_4.7H_2O$
(2) 250 ml .... 0.5 *M* $ZnSO_4.7H_2O$
(3) 250 ml .... 0.5 *M* $ZnSO_4.7H_2O$
(4) 250 ml .... 0.5 *M* $3K_2S_2O_3.H_2O$

TIME: 15 min
TEMP: RT
ANODE: Pt (Pb & Cu)
CATHODE: p-type Ge
POWER: 6 mA/cm_2

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DISCUSSION:

Ge, (111) ingots with grown-in p-n junction. Specimens cut as bars in an etching study of the material. Both lead and copper were evaluated as anodes but platinum gave best results. All these solutions stain the p-region with good delineation of the junction.
REF: Ibid.

GE-0220o
ETCH NAME:
TYPE: Acid, preferential
TIME: 5—10 min
TEMP: Boiling
COMPOSITION:

175 ml .... 15% KOH
45 g .... $(NH_4)_2S_2O_8$

DISCUSSION:

Ge, (111), (100), (110), and (211) wafers used in an etch development study. The solution develops the typical etch pit patterns associated with each surface orientation within the first 2—3 min, and extended etching enlarges the pits. Solution used as both a light figure orientation etch, and as a general defect and dislocation density etch.
REF: Ibid.

GE-0220p
ETCH NAME:
TYPE: Acid, polish
TIME: 1—20 min
TEMP: RT
COMPOSITION:

50 ml .... CP4 (fresh)
3 mg .... $Fe(NO_3)_2.2H_2O$

DISCUSSION:

Ge, (111) wafers, p-type, 4 Ω cm resistivity used in a general etch development study. Surfaces were mechanically lapped with 600-grit SiC, before using the solution shown as polish etch. Removal rate was about 1 mil in the first 3 min, and about 1 mil/$1^1/_2$ min thereafter.
REF: Ibid.

GE-0056
ETCH NAME:
TYPE: Alkali, preferential
TIME: 5—10 min
TEMP: Boiling
COMPOSITION:

x .... KOH
x .... $K_3Fe(CN)_6$

DISCUSSION:

Ge, (111) wafers used in a study of thermally induced glide. Solution used to delineate defects.
REF: Cummerow, R L — *J Appl Phys*, 30,932(1959)
GE-0134: Alekseeva, V G & Eliseev, P O — *Fiz Tverd Tela*, 1,415(1959)

Ge, specimens used in a study of the effects of bismuth on dislocation density. Solution used to develop dislocations.
GE-0135: Dragoun, Z — *Czech J Phys*, 8,600(1958) (in Russian)

Ge, specimens. A review of dislocation etchants for germanium, both selective and nonselective.
GE-0144c: Faust, J W & John, H F — *J Electrochem Soc*, 108,825(1961)

Ge, (111) dendrites. A ferrocyanide solution used to develop triangle dislocation pits. Also used WAg and CP4 etches.

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GE-0057
ETCH NAME: Water
TYPE: Acid, float-off
TIME:
TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:
a-Ge thin films deposited on NaCl, (100) cleaved substrates. The films were floated-off the substrate by liquefying the NaCl at the a-Ge interface for SEM and TEM study of film morphology.
REF: Nakhodkin, N G et al — *Thin Solid Films*, 112,267(1984)

GE-0058
ETCH NAME:
TYPE: Acid, selective photo
TIME: 3—10 sec
TEMP: RT
COMPOSITION:
2 .... HF
2 .... H_2O_2
5 .... H_2O
DISCUSSION:
Ge, (111), (110), and (211) wafers cut from CZ grown ingots. Wafers were used saw cut, then mechanically lapped and polished, or cleaved. Wafers used in a study of growth habit. During etching, illuminate with an IR Lamp. Etch used to develop "Valley traces Type II" striations that show variable resistivity. (*Note:* Concentric ring increase of resistivity from wafer center has been observed in large 2" diameter (111) silicon wafers.)
REF: Lu, Y C & Bauser, E — *J Cryst Growth*, 71,305(1985)

GE-0059a
ETCH NAME:
TYPE: Acid, structure
TIME:
TEMP:
COMPOSITION:
1 .... HF
5 .... HNO_3
DISCUSSION:
Ge, thin films evaporated on GaAs:Cr (SI) substrates in a diode device study. Photo resist techniques used to form pattern dot structures which were then etched as pedestals (mesas).
REF: Papazian, S A & Reisman, A — *J Electrochem Soc*, 111,961(1968)

GE-0059b
ETCH NAME:
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:
1 .... NaOCl
3 .... H_2O
DISCUSSION:
Ge, thin films evaporated on GaAs:Cr (SI) substrates in a diode device study. Prior to mesa formation the epitaxy germanium surfaces were cleaned in the solution shown.
REF: Ibid.

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GE-0060g
ETCH NAME: WAg etch
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
4 ml .... HF
2 ml .... HNO_3
4 ml .... H_2O
0.2 g .... $AgNO_3$
DISCUSSION:
Ge, (111) wafers. This is a general preferential etch on both germanium and silicon. (*Note:* Full name is the Westinghouse Silver Etch.)
REF: Ibid.
GE-0066: Grubel, R O — *Metallurgy of Elemental and Compound Semiconductors,* Vol 12, Interscience, New York, 1962, 139
Ge, grown as (111) oriented ribbon crystal dendrites. WAg solution used to develop defect and dislocation structure.
GE-0070c: Pergola, C D & Settes, D — *Alta Freq,* 24,499(1955)
Ge, (111) wafers. An evaluation of different etch solutions for developing dislocations. Other etchants were CP4, superoxol, and copper nitrate etch.
GE-0075a: Holmes, P J — *Phys Rev,* 119,131(1960)
Ge, (111) oriented ribbon crystal dendrites. A dislocation etching study of dendritic material. Author says that the triangle pit direction depends on the type solution used. (*Note:* The (111) ribbon crystal dendrites always have a twinned zone down the center of the dendrite with 180° rotation to either side as a positive (+) (111), and a negative (−) (111) surface. The dislocation pits also are rotated, as they are representative of the positive and negative tetrahedron, (111) crystallographic forms common to (111) type surfaces. This dislocation pit structural appearance is true without regard to the type preferential etch solution used.)
GE-0084: Wynne, R H & Goldberg, C — *J Met,* 8,436(1953)
Ge, (111), (100), and (110) wafers. The WAg etch was used as an optical orientation figure etch.
GE-0144c: Faust, J W Jr & John, H T — *J Electrochem Soc,* 108,825(1961)
Ge, (111) ribbon crysal dendrites. Etch used to develop dislocations.
GE-0188: Bennett, A I & Longini, R L — *Phys Rev,* 116,53(1959)
Ge, (111) ribbon crystal dendrites. Solution used to develop dislocations.
GE-0225c: Guatier, K & Kerecman, A J — *Rev Sci Instrum,* 34,108(1963)
Ge, (111) wafers used as substrates for Ge epitaxy growth used in a study of preferential light figure etching. The WAg etch produces very sharp etch pits and hillocks on polished surfaces. Also used hot HCl vapors, and $GeCl_4$ to develop similar structure.

GE-0061a
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
4 .... HF
2 .... HNO_3
4 .... 5% $Cu(NO_3)_2$
DISCUSSION:
Ge, (111) wafers used in a study of the effect of ionic species on the etching of germanium. Solution used as a polishing etch. Without copper nitrate the solution is preferential, developing pyramidal type pits.
REF: Faust, J W Jr — *J Electrochem Soc,* 112,114(1965)

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GE-0061b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
4 .... HF
2 .... HNO_3
4 .... 5% $Ag(NO_3)_2$
DISCUSSION:
Ge, (111) wafers. Solution develops triangular etch pits.
REF: Ibid.

GE-0036
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
4 .... HF
7 .... HNO_3
2 .... H_2O
DISCUSSION:
Ge, (111) wafers used in a study of slow surface relaxation. Specimens were etched in the solution shown and then held for varied periods of time before being treated with water.
REF: Pilkuhn, M H — *J Appl Phys,* 34,3302(1963)

GE-0170
ETCH NAME: Heat TIME:
TYPE: Thermal, cleaning TEMP: 800°C
COMPOSITION:
x .... heat
DISCUSSION:
Ge, (100) very thin films grown by PECVD on NaCl, (100) substrates. The as grown films were p-type, 0.11 Ω cm resistivity with 29 ppm sodium contamination. After vacuum heating contamination was reduced to 3 ppm Na and resistivity increased to 7 Ω cm, p-type. Specimens of 6-cm size were removed from the NaCl by heat melting away the substrate; whereas specimens of 1-cm size were sheared away by cleaving at room temperature.
REF: Outlaw, R A et al — *J Vac Sci Technol,* A3,692(1985)
GE-0142b: Pugh, E H & Samuels, L E — *J Electrochem Soc,* 108,1043(1961)
Ge, (111) wafers were angled lapped to 5°43′ and used in a metallographic study of the effects of abrasion. After abrading surfaces, Billig's etch (GE-0142a) was used to develop damage structure. It showed cleavage cracks, but no dislocations. After heat at 500°C for 15 min, dislocation arrays were developed.
GE-0146: Wolff, G A et al — Electrochem Soc Meet, Pittsburgh, PA, Oct 13, 1955
GE, (111), (113), and (110) wafers used in developing light figure orientation etches. Thermal etching was used to develop etch pit structure. Also etched silicon in HF:I_2 for etch pits.
GE-0165: English, A C — *J Appl Phys,* 31,1498(1960)
Ge, specimens and ingots. Material was heated to 700°C in contact with iron or nickel plates, which developed growth stria. Indium was alloyed into wafers, then dissolved with boiling HCl to study the alloyed pit structure.
GE-0232: Willis, R C et al — *J Appl Phys,* 29,1725(1958)
Ge ingots. Rapid pulling of Czochralski (CZ) ingots causes a high dislocation content,

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and the seed also can introduce dislocations if it has an originally high dislocation density. Slow cooling will reduce pit density to random points, only. Thermal shock produces high density, star-like patterns in the ⟨110⟩ directions.
GE-0233: Wagner, R S — *J Appl Phys*, 29,1678(1958)

Ge ingots. In Czochralski (CZ) growth a too rapid approach of the seed crystal into the molten germanium melt can initiate dislocations due to plastic deformation of the seed. Too rapid cooling (thermal shock) also will create dislocations.

GE-0064
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cover
COMPOSITION:
x .... HF
TIME:
TEMP: RT
DISCUSSION:

Ge, single crystal specimens subject to fracture in a study of the effect of environment on fracture behavior. The study showed that there is a difference between fracturing in air or under HF. (*Note:* Similar work has been done on silicon.)
REF: Johnston, T L et al — *Acta Metall*, 7,713(1959)

GE-0065c
ETCH NAME: Camp #2 (superoxol)
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
TIME:
TEMP: RT
DISCUSSION:

Ge, (111) wafers, and other orientations. Wafers used in a study of etch rates on germanium. (*Note:* Several of the Camp etches are abbreviated: "CP", such as CP4.)
REF: Camp, P R — *J Electrochem Soc*, 102,1147(1955)
GE-0007b: Camp, P R — *J Electrochem Soc*, 102,586(1955)

Ge, oriented wafers and single crystal spheres used in a study of etch rates. Etch referred to as Camp #2 (superoxol). The sphere finite crystal form (FCF) was a dodecahedron, (110).

GE-0065b
ETCH NAME: Camp #3
TYPE: Acid, preferential
COMPOSITION:
56 ml .... HF
56 ml .... HNO_3
12.5 ml .... H_2O
TIME:
TEMP: RT
DISCUSSION:

Ge, (111) wafers. See discussion under GE-0065a.
REF: Ibid.

GE-0077
ETCH NAME:
TYPE: Acid, stress
COMPOSITION:
x .... HF
x .... HNO_3
TIME:
TEMP:
PRESSURE: 7 kg/mm^2 to 47 kg/mm^2 (in air)

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DISCUSSION:

Ge, (111) wafers etched in various mixtures of HF:HNO_3 under varied pressures in a study of the stress fracture of germanium under different environmental conditions. Effect varied with both pressure and specific etchant mixtures.

REF: Breidt, P et al — *J Appl Phys*, 29,226(1958)

GE-0078

ETCH NAME:

TYPE: Acid, polish

COMPOSITION:

(1) x .... HF
x .... HNO_3
x .... H_2O

(2) x .... HF
x .... H_2O_2
x .... H_2O
x .... $Na(NO_3)_2$ + Ag

(3) x .... H_2SO_4

TIME:

TEMP: RT

DISCUSSION:

Ge, (111) wafers used in a study of etching and polishing surfaces. Etch solutions of type (1) were DI water rinsed; type (2), rinsed in KCN to remove Ag and then in DI water. Type (3) sulfuric acid was used at 50°C and DI water rinsed.

REF: Geist, D & Preuss, E — *Z Angew Phys*, 9,526(1957)

GE-0079

ETCH NAME:

TYPE: Acid, polish

COMPOSITION:

3 .... HF
7 .... HNO_3

TIME:

TEMP:

DISCUSSION:

Ge, (111) wafers used in a study of infra-red properties of gold diffused germanium. Solution used to polish samples before gold diffusion. Follow etch by rinsing in double-distilled water.

REF: Johnson, L & Levinstein, H — *Phys Rev*, 117,1191(1960)

GE-0081

ETCH NAME: Chlorine

TYPE: Electrolytic, preferential

COMPOSITION:

x .... Cl_2

TIME:

TEMP: 200—300°C

ANODE: Ge

CATHODE: Graphite (2)

POWER:

DISCUSSION:

Ge, (111) wafers. Two graphite electrodes were used, one with a hole in the side. Chlorine forms GeCl and the vapor, and can be used as a surface polishing system or to fabricate controlled etch pits by jet streaming chlorine through the graphite electrode.

REF: Seiler, K O — U.S. Patent 2,744,000, May 1, 1956

GE-0082

ETCH NAME:

TYPE: Acid, polish

COMPOSITION:

(1) x .... HNO_3

(2) x .... HF
x .... HNO_3

(3) x .... H_2O_2

TIME:

TEMP:

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DISCUSSION:

Ge, (111) wafers used in a study of optical and magnetic surface effects. All three solutions are oxidizers and, after etching, show slow decay of surface conductance. If etching is followed by an HF rinse, there is no decay.

REF: Bray, R & Cunningham, R W — *J Phys Chem Solids,* 8,99(1959)

GE-0083a

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

"A" 160 ml .... HF "B" x .... H_2O

200 ml .... HNO_3

80 ml .... HAc

0.32 g .... I_2

Mix: 1 "A" to 1.5 "B"

DISCUSSION:

Ge, (111) wafers. After mechanical lapping, CP4 was used to remove work damage. Solution shown develops spiral type etch pits on both (111) and (100) surfaces.

REF: Rhodes, E G et al — *J Electron,* 3,403(1957)

GE-0235: Hogarth, C A & Bell, R L — *J Electron,* 3,455(1957)

Ge and Si wafers. A study of the anisotropic diffusion lengths due to the presence of parallel arrays of edge dislocations.

GE-0085

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

1 .... HF

4 .... HNO_3

DISCUSSION:

Ge, (111) wafers used in a study of anisotropic diffusion lengths in germanium and silicon containing parallel arrays of edge dislocations. Solution was used to develop dislocations on both materials after bending under heat to develop defects.

REF: Hogarth, C A & Bell, R L — *J Electron,* 3,455(1957)

GE-0281: Stolwijk, M A et al — *J Appl Phys,* 57,5211(1985)

Ge, (100) wafers cut from Czochralski (CZ) ingots. After chem/mech polish and degreasing, copper was evaporated, then diffused. Solution shown was used to develop decoration structure in a study of diffusion and solubility of copper in germanium.

GE-0046b

ETCH NAME: TIME:

TYPE: Electrolytic, preferential TEMP:

COMPOSITION: ANODE: Ge

x .... 0.1 *N* KCl CATHODE:

x .... 10^{-3} *M* GeO_2 POWER:

DISCUSSION:

Ge, (111) wafers. Study involved electrode potential and the effects of illumination. Results showed that the amount of oxygen dissolved in solution effects etching results.

REF: Harvey, W & Gatos, H C — *J Appl Phys,* 29,1267(1958)

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GE-0087
ETCH NAME: Potassium hydroxide
TYPE: Alkali, preferential
COMPOSITION:
x .... 0.5% KOH

TIME:
TEMP:
ANODE: Ge
CATHODE:
POWER: 5.5 A/cm^2

DISCUSSION:
Ge, (111) n-type wafers. Solution was applied at 5 psi through a 75 mm diameter tube without illumination. Triangle etch figures were developed that were arrayed in a ⟨211⟩ direction. (*Note:* ⟨211⟩ lineation used to be a common defect in Czochralski (CZ) grown ingots in the early 1950s.)
REF: Oberly, J J — *Acta Metall,* 35,122(1957)

GE-0088a
ETCH NAME: Sulfuric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... 0.1 *N* H_2SO_4

TIME:
TEMP:
ANODE: Ge
CATHODE:
POWER: 0.3 mA/cm^2

DISCUSSION:
Ge, (111) wafers used in a study of the effects of aqueous electrolytic solutions on germanium.
REF: Turner, D R — *Acta Metall,* 103,252(1956)

GE-0088b
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, polish
COMPOSITION:
x .... 1 *N* KOH

TIME:
TEMP:
ANODE: Ge
CATHODE:
POWER: 0.3 mA/cm^2

DISCUSSION:
Ge, (111) wafers used in a study of the anodic behavior of germanium in electrolytic aqueous solutions.
REF: Ibid.

GE-0089
ETCH NAME:
TYPE: Alkali, contamination
COMPOSITION:
0.4 ml .... 1% NaOH
0.1 ml .... 7% $^{24}NaCO_3$

TIME:
TEMP:

DISCUSSION:
Ge, single crystal specimens used in a study of adsorption of sodium ions by germanium surfaces. Solution used to introduce contamination.
REF: Robbins, R C — *Acta Metall,* 103,194(1956)

GE-0090
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
10 .... HNO_3

TIME: 11.5 min
TEMP: RT

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DISCUSSION:

Ge, specimens used in a study of Auger electron ejection from silicon and germanium surfaces from the noble gases. The etching and cleaning sequence was (1) etch in solution shown; (2) dip in hot xylene; (3) rinse in acetone; (4) soak in HF, RT, 1 min; (5) clean in $1HNO_3$:$1H_2O$, RT, 30 sec; (6) boil in DI water, 5 min, and (7) air dry.

REF: Hagstrum, H D — *Phys Rev,* 199,940(1960)

GE-0151a

ETCH NAME:

TIME: 15—45 min

TYPE: Alkali, preferential

TEMP: Boiling

COMPOSITION:

250 ml .... 30% KOH (NaOH)

30—40 g .... I_2

DISCUSSION:

Ge, (111), (110), (100), (211) wafers, and single crystal spheres. Solution developed as a light figure orientation etch and general preferential etch for germanium. Used on n-p-n diffused transistors as a step-etch to form transistor vertical structure. The finite crystal sphere form was a cube, (100).

REF: Walker, P — personal development, 1958—1959

GE-0151b

ETCH NAME:

TIME: 10—20 min

TYPE: Alkali, preferential

TEMP: Boiling

COMPOSITION:

125 ml .... 30% KOH (NaOH)

50 ml .... Br_2

DISCUSSION:

Ge, (111), (100), (110), (211) wafers, and single crystal spheres. Solution developed as a light figure orientation etch. Mixture is more difficult to control due to bromine evaporation than is GE-0151a. The finite crystal form of the sphere was a cube, (100).

REF: Ibid.

GE-0124

ETCH NAME: SR4

TIME:

TYPE: Acid, polish

TEMP:

COMPOSITION:

3 .... HF

2 .... HNO_3

1 .... HAc

DISCUSSION:

Ge, (111) wafers used in a study of the variations in surface conductivity of both germanium and silicon. Solution used as a polish etch on both materials.

REF: Ioselevich, M L & Fistul', V I — *Sov Phys (Solid State),* 3,822(1960)

GE-0102b

ETCH NAME: Potassium cyanide

TIME:

TYPE: Acid, cleaning

TEMP:

COMPOSITION:

x .... KCN

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DISCUSSION:

Ge, (111) wafers. The surface was soaked in solution shown to clean prior to etch polishing with CP4 (GE-0102a). Material used in a plastic deformation study.

REF: Ibid.

GE-0094b: Ibid.

Ge, (111) wafers. Etch polish with CP4, then soak in KCN. See GE-0094a.

GE-0119b: Ibid.

Ge, (111) wafers. Etch in CP4, soak in HNO_3, rinse in DI water; then soak in KCN, and DI water rinse. See GE-0119a.

GE-0159b: Hopkins, E L & Clarke, E N — *Phys Rev*, 100,1789(1955)

Ge specimens. Soak in 10% KCN, 1 h to remove metallic ions. Then rinse five times in DI water. See GE-0159a.

GE-0179: Tweet, A G — *Phys Rev*, 99,1245(1955)

Ge, (111) specimens used in a study of electrical properties of plastically deformed germanium. Solution used to clean and etch surfaces.

GE-0142: Wolsky, S F — *J Appl Phys*, 29,1132(1958)

Ge wafers. A study of the preparation and regeneration of clean germanium surfaces.

GE-0092b

ETCH NAME:

TYPE: Acid, dislocation

TIME: 10—45 sec

TEMP: RT

COMPOSITION:

3 .... HF

1 .... HNO_3

1 .... HAc

DISCUSSION:

Ge, (111) dendritic ribbon crystals. This etch solution produces similar dislocation development as does CP4. See: GE-0092a.

REF: Ibid.

GE-0126

ETCH NAME: Hydrofluoric acid

TYPE: Acid, oxide removal

TIME:

TEMP: RT

COMPOSITION:

x .... HF

DISCUSSION:

Ge, (111) wafers used in a study of anodic oxidation. Oxidize in 35% $HClO_4$ with Ge anode and Pt cathode at 45 V. HF used to strip oxide after growth.

REF: Gabor, T — *J Appl Phys*, 32,1361(1961)

GE-0127a

ETCH NAME: Indium

TYPE: Metal, preferential

TIME:

TEMP: Heat

COMPOSITION:

x .... In

DISCUSSION:

Ge, (100), and (111) wafers. Surfaces were oriented precisely from pits formed by alloying metal. After alloying indium, use HCl to etch dissolve the metal to observe pit structure, crystallographic directions, and orientation.

REF: Dreiner, R & Garnache, R — *J Appl Phys*, 33,888(1962)

GE-0165b: Ibid.

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Ge wafers and ingots used in a study of growth striations. Indium alloyed on surfaces and etched away with boiling HCl. See GE-0165a for heat treatment effects.

GE-0166: Dendra, S I — *J Phys Soc Jpn*, 13,533(1958)

Ge, (111) wafers alloyed with indium to develop etch pits. Alloyed at 350°C, 2 min, pits are similar to those observed by etching with CP4. Alloyed at 200°C pits are similar to those observed when etched with superoxol.

GE-0236: Pankore, J I — *J Appl Phys*, 28,1054(1957)

Ge, (111) wafers. A study of the effects of edge dislocations on the alloying of indium in germanium.

GE-0127b
ETCH NAME:
TYPE: Acid, junction
COMPOSITION:
5 .... HF
5 .... HNO_3
2 .... H_2O
TIME:
TEMP:
DISCUSSION:

Ge, (111), and (100) wafers. Indium metal alloyed to produce etch pits for orientation, also forms a p-n junction. Solution shown used as a junction etch.

REF: Ibid.

GE-0128a
ETCH NAME:
TYPE: Acid, contaminating
COMPOSITION:

(1)			(2)		
	5	.... HF		5	.... HF
	8	.... HNO_3		8	.... HNO_3
	15	.... HAc		15	.... HAc
	5 ppb	.... Ag		50 ppb	.... Fe

TIME: 5 sec
TEMP: RT
DISCUSSION:

Ge as surface barrier diodes used in a study of trace impurities on IV characteristics. Solutions shown were used separately; after etching, rinse with DI water and blow dry with air. Specimens were also jet etched electrolytically in the same solutions at RT, 3 sec and 0.15 mA/9 mils power. Silver, Ag, produces p-type channelling; iron, Fe, has little effect, is apparently removed or is inert.

REF: Krembs, G M & Schlacter, M M — *J Electrochem Soc*, 111,417(1964)

GE-0234: Schmidt, P F & Blomgren, M — *J Electrochem Soc*, 106,694(1959)

Ge and Si specimens. A study of electronic reactions using potential measurements during jet etching of p-type materials.

GE-0129a
ETCH NAME: Indium sulfate
TYPE: Electrolytic, shaping
COMPOSITION:
x .... 0.1 $InSO_4$
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Ge specimens. Solution used to electrolytically shape specimens.

REF: Uhiler, A Jr — *Bell Syst Tech J*, 35,333(1956)

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GE-0129b
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, shaping
COMPOSITION:
x .... 10% KOH

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Ge specimens. Solution used to electrolytically shape specimens.
REF: Ibid.

GE-0129c
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, shaping
COMPOSITION:
x .... 2 *N* HCl

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Ge specimens. Solution used to electrolytically shape specimens.
REF: Ibid.

GE-0129d
ETCH NAME: Sulfuric acid
TYPE: Electrolytic, shaping
COMPOSITION:
x .... H_2SO_4
x .... H_2O

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Ge specimens. Solution used to electrolytically shape specimens.
REF: Ibid.

GE-0129e
ETCH NAME: Sodium chloride
TYPE: Electrolytic, shaping
COMPOSITION:
x .... NaCl
x .... H_2O

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Ge specimens. Solution used to electrolytically shape specimens. (*Note:* This is only one use of salt in metal processing.)
REF: Ibid.

GE-0130
ETCH NAME: Nitric acid
TYPE: Acid, oxidizing
COMPOSITION:
(1) x .... HNO_3, conc.
(2) x .... HNO_3
x .... H_2O

TIME:
TEMP:

DISCUSSION:
Ge, (111) wafers, and other orientations. Wafers used in a general study of the reaction of germanium in nitric acid solutions. Various concentrations of nitric acid used to study: I — dissolution and II — passivity.

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REF: Cretella, M C & Gatos, H C — *J Electrochem Soc,* 105,487(1958) I
GE-0131: Cretella, M C & Gatos, H C — *J Electrochem Soc,* 105,492(1958) II
GE-0239: Meigs, P S & Laws, J T — *J Electrochem Soc,* 104,154(1957)
Ge specimens. A study of the oxidation rates on germanium orientation.

GE-0132a
ETCH NAME: Nitric acid
TYPE: Acid, preferential
COMPOSITION:
x .... 18 *N* HNO_3
DISCUSSION:
Ge, (111) wafers used in a general study of preferential etching of surfaces. Solution produces etch pits with closed terrace structure.
REF: Kikuchi, M & Denda, S — *J Phys Soc Jpn,* 11,1127(1956)
GE-0086: Kikuchi, M & Denda, S — *Met Abstr,* 8,818(1958)
GE-0241: Wallis, G & Wang, S — *J Electrochem Soc,* 106,231(1959)
Ge wafers used in a study of the effects of various etches of the recombination centers on germanium surfaces.
GE-0240: Rhodes, E G et al — *J Electron,* 3,403(1957)
Ge specimens. The study of spiral etch pit development in germanium.

TIME:
TEMP:

GE-0132b
ETCH NAME: Hydrochloric acid
TYPE: Acid, preferential
COMPOSITION:
x .... 13 *N* HCl
DISCUSSION:
Ge, (111) wafers used in a general study of preferential etching of surfaces. Solution produces etch pits with closed terrace structure.
REF: Ibid.

TIME:
TEMP:

GE-0133a
ETCH NAME: Potassium chloride
TYPE: Electrolytic, preferential
COMPOSITION:
x .... KCl
DISCUSSION:
Ge, (111) wafers used in a study of surface properties. Anodic etching was used for hole density, and cathodic etching for electron density.
REF: Brattain, W H & Garrett, C G B — *Physica,* 20,885(1954)

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

GE-0133b
ETCH NAME:
TYPE: Electrolytic, preferential
COMPOSITION:
x .... x% KOH
x .... H_2O_2

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

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DISCUSSION:

Ge, (111) wafers used in a study of surface properties. Anodic etching for hole density; cathodic etching for electron density.

REF: Ibid.

GE-0137: Wilkes, J G — *Proc Inst Electr Eng,* 106,199(1959)

Ge, as raw chunk material to be used for ingot growth. Solution was used to clean surfaces.

GE-0133c

ETCH NAME: Hydrochloric acid

TYPE: Electrolytic, preferential

COMPOSITION:

x .... $^{1}/_{10}$ *N* HCl

TIME:

TEMP:

ANODE:

CATHODE:

POWER:

DISCUSSION:

Ge, (111) wafers used in a study of surface properties. Anodic etching for hole density; cathodic etching for electron density.

REF: Ibid.

GE-0136

ETCH NAME:

TYPE: Electrolytic, oxidation

COMPOSITION:

x .... 0.1 *N* HCl

x .... KI

x .... oxalic acid

TIME:

TEMP:

ANODE:

CATHODE:

POWER:

DISCUSSION:

Ge, both p- and n-type specimens used in a study of the anodic oxidation reaction of germanium. Both KI and oxalic acid reduce anodic potential on p-type germanium.

REF: Efimov, E A & Erusalimchik, I G — *Dokl Acad Nauk SSSR,* 128,124(1959)

GE-0139a

ETCH NAME: Iodine etch

TYPE: Acid, dislocation

COMPOSITION:

1 .... HF

2 .... HNO_3

2 .... HAc

+ .... I_2

TIME: 10 sec

TEMP: RT

DISCUSSION:

Ge, thin films grown by MBE on germanium substrates. Polish substrates: (1) lap in silica abrasive solution; (2) mechanically scrub with soap solution, and DI water rinse; (3) degrease in TCE with ultrasonic. Solution shown used to develop defects in deposited thin films. It was noted that scratches on the substrate physically showed through the thin film.

REF: Ota, Y — *J Cryst Growth,* 62,131(1983)

GE-0140: Wang, P — *Sylvania Technol,* 11,2(1958)

Reference for iodine etch shown in GE-0139a.

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GE-0139b
ETCH NAME: Billig's etch
TYPE: Acid, preferential
COMPOSITION:
12 g .... KOH
8 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
TIME:
TEMP: Boiling
DISCUSSION:
Ge, (111) wafers used as substrates to grow (111) oriented thin film germanium by MBE. Solution used to epitaxy layer developed very sharp triangle etch pits.
REF: Ibid.

GE-0142a
ETCH NAME: Billig's etch
TYPE: Acid, preferential
COMPOSITION:
6 g .... KOH
4 g .... $K_3Fe(CN)_6$
50 ml .... H_2O
TIME: 3—5 min
TEMP:
DISCUSSION:
Ge, (111) wafers angle lapped at 5°43′. A metallographic investigation of the damage layer introduced by abrading germanium surfaces. Lapping creates fine cleavage cracks, many as (111) traces, but does not create dislocations. Solution used to develop damage structure. Heating at 500°C, 15 min develops dislocation arrays.
REF: Pugh, E H & Samuels, L E — *J Electrochem Soc,* 1043(1961)

GE-0147c
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, preferential
COMPOSITION:
x .... 0.1% KOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 1.5 A/cm²
DISCUSSION:
Ge specimens jet etched in this solution. Author says that the standard power for immersion etching is 1.5 A/cm².
REF: Bondi, F J — *Transistor Technology,* Vol III, D Van Nostrand, New York, 1958
GE-0156: Zwerdling, S & Sheff, S — *J Electrochem Soc,* 107,338(1960)
Ge specimens used in a study of oxide growth. Grow oxide thin films electrolytically in 0.25 *N* sodium acetate:xHAc at 50—400 μA/cm². Use 0.1 *N* NaOH to remove the oxide.
GE-0350: Tweet, A G — *J Appl Phys,* 30,2002(1959)
Ge, (111) wafers from dislocation-free ingots. A general etching study on the effects of dislocations on vacancies in the lattice structure where they act as energy sinks.

GE-0212b
ETCH NAME:
TYPE: Electrolytic, selective
COMPOSITION:
1 .... HF
1 .... HAc
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Ge, n-p-n transistors. Solution used as a selective junction etch. The 1:1 ratio is best

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though not critical. Requirement is a high conductivity electrolyte. Solution volume was 50 ml, specimens held with tweezers and etched in dimly lit area for best results. A p-type layer may form on surface, as light will forward bias for holes.
REF: Lesk, I A & Gonzalez, R E — *J Electrochem Soc,* 105,469(1958)
GE-0231: Gonzalez, R E & Lesk, I A — *J Electrochem Soc,* 105,402(1958)

Ge and Si devices as p-n-p transistors. The use of selective electrolytic etching for finalizing junction structures.

GE-0149
ETCH NAME: Copper
TYPE: Electrolytic, junction
COMPOSITION:
1 ml .... HF
20 g .... $CuSO_4$
80 ml .... H_2O
DISCUSSION:

TIME: 1 sec every 20 sec
TEMP:
ANODE: Ge, n-type
CATHODE: Ge, p-type
POWER: 15—20 V at 30—50 mA/cm^2

Ge, p-n diffused diode junctions developed by electroplating of copper. Place one drop of solutions across junction and pulse etch electrolytically on a pre-lap bevelled junction. Long etch times will attack n-region, but the p-region will plate with copper. See GE-0039.
REF: Gling, R — *J Electrochem Soc,* 107,356(1960)

GE-0203a
ETCH TIME: Iodine etch
TYPE: Halogen, polish
COMPOSITION:
1 .... HF
2 .... HNO_3
2 .... HAc
x .... I_2
DISCUSSION:

TIME: 2—3 min
TEMP: RT

Ge, (111) wafers used in a study of dislocations and crack formation after indenting the surface with a diamond stylus. An "iodine etch" was used to polish surfaces prior to indenting and dilute CP4 was used to develop defects.
REF: Sugita, Y — *Jpn J Appl Phys,* 2,313(1963)

GE-0203b
ETCH NAME: CP4, dilute
TYPE: Acid, preferential
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... HAc
0.6 .... Br_2
x .... H_2O
DISCUSSION:

TIME:
TEMP:

Ge, (111) wafers. Solution used to develop dislocations and cracks induced by indenting the surface with a diamond stylus.
See GE-0203a.
REF: Ibid.

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GE-0204a
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, passivate
COMPOSITION:
x .... 15% KOH

TIME: (1) 8 sec (2) 10 sec
TEMP:
ANODE: Ge
CATHODE: Ni
POWER: (1) 0.4 A/cm^2
(2) 0.1 A/cm^2 &
0.2 A/cm^2

DISCUSSION:
Ge, p-n-p transistors prepared with indium alloy dots. Solution shown used to oxide passivate the surface in a study of vacuum drying and the properties of germanium surfaces.
REF: Forosho, K & Ono, K — *Jpn J Appl Phys,* 1,148(1962)

GE-0204b
ETCH NAME:
TYPE: Acid, passivation
COMPOSITION:
50 ml .... HF
1 ml .... H_2O_2
x .... air, bubbling

TIME:
TEMP:

DISCUSSION:
Ge, p-n-p transistors prepared with indium alloy dots. Solution shown used to vapor oxidize germanium surfaces by bubbling air through the acid mixture.
REF: Ibid.

GE-0205
ETCH NAME: Iodine etch
TYPE: Halogen, dislocation
COMPOSITION:
2000 mg .... KI
200 mg .... I_2
50 ml .... H_2O

TIME: 70 h; 50 h; 15 h
TEMP: RT 50°C—80°C

DISCUSSION:
Ge wafers of different orientations. Solution shown referred to as a Redox system with formation of GeI_4. Germanium will not etch in KI, only; requires I_2 and rate reduces with evaporation of iodine. Solution used to develop etch pits and structure figures.
REF: Arizumi, T & Akasaki, I — *Jpn J Appl Phys,* 2,350(1963)
GE-0206: Arizumi, T & Akasaki, I — *J Phys Soc Jpn,* 17,712(1962)
Ge specimens. Describes another iodine etch for this material.
GE-0266: Elliot, G — *J Electron Control* 4,456(1958)
Ge, (100) wafers. Used an iodine etch to develop pits within material with 1.2×10^6 dislocation density. Specific observation of spiral etch pits in an apparent polygonized area of the wafer.
GE-0263b: Ibid.
Ge, (100) wafers. Spiral etch pits observed using an iodine etch. Pit density was between 10^5—10^6/cm^2 on both (111) and (100) wafers.
GE-0276: Dorendorf, H — *Z Angew Phys,* 9,513(1957)
GE wafers used in a general study of dislocations.

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GE-0207
ETCH TIME: Hydrogen peroxide — TIME:
TYPE: Acid, cleaning — TEMP: Boiling
COMPOSITION:
(1) x .... H_2O_2 (2) x .... HNO_3
DISCUSSION:
Ge wafers of different orientations. Solutions shown used to clean surfaces prior to oxidation in a study of surface conductivity and recombination. Oxidation was done with both dry O_2 and O_2/O_3, and as wet oxidation. The hydrogen peroxide prepared surface gave best results.
REF: Razhanov, A U et al — *Zh Tekh Fiz,* 26,2142(1956)

GE-0208
ETCH NAME: — TIME:
TYPE: Acid, macro-etch — TEMP: 100°C
COMPOSITION:
x .... 10% NaOH
x .... 15% $NaNO_3$
x .... H_2O
DISCUSSION:
Ge, (111) wafer and spherical shot. Wafers were n-type; shot p-type. Pellet alloyed into wafer about 1 mil deep to form p-n junctions. Solution shown used to etch clean and develop junctions.
REF: Lesk, I A — *J Electrochem Soc,* 107,534(1960)

GE-0154
ETCH NAME: Air — TIME: 24 h
TYPE: Gas, oxidation — TEMP: RT
COMPOSITION:
x .... air
DISCUSSION:
Ge, (111) wafers and other orientations. Rinse surfaces in HF to remove native oxide. Within minutes, a native oxide will regrow sitting in air at RT to about 10—15 Å thick. After 24 h the oxide will stabilize at 25—30 Å thick.
REF: Archer, R J — Electrochem Soc Meet, Washington, D.C., 12—16 May 1957

GE-0147c
ETCH NAME: — TIME:
TYPE: Electrolytic, remove — TEMP: RT
COMPOSITION: — ANODE:
x .... 0.1 *N* H_2SO_4 — CATHODE:
x .... *GeO_2 — POWER: 3.5—50 mA/cm²

*Saturate the solution.

DISCUSSION:
Ge specimens. Germanium is about as electrochemically active as iron, Fe. Cleaned surfaces will react with water forming a hydrated oxide of a $2GeO_3$ type, as stable meta-germanic acid.
REF: Ibid.

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GE-0147e
ETCH NAME:
TYPE: Electrolytic, removal
COMPOSITION:
x .... 1 *N* KOH
x .... *GeO_2

TIME:
TEMP: RT
ANODE:
CATHODE:
POWER: 3.5—50 mA/cm²

*Saturate the solution.

DISCUSSION:
Ge specimens. See discussion under GE-0147c.
REF: Ibid.

GE-0155
ETCH NAME:
TYPE: Alkali, contact etch
COMPOSITION:
x .... 2% $NaClO_4$ ($KClO_4$)
x .... 2% NaOH (KOH)

TIME: 15 min
TEMP: RT

DISCUSSION:
Ge, as devices with evaporated metal contacts. Solution used to etch clean device surfaces.
REF: Bradshaw, S E — U.S. Patent 2,690,383, Sept 28, 1954
GE-0285: Turner, D R — *J Electrochem Soc,* 106,786(1959)
Ge and Si wafers used in a study of electroplated metal contacts.

GE-0157
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HNO_3
x .... H_2O_2

TIME:
TEMP:

DISCUSSION:
Ge specimens used in a study of thermal conductivity at low temperatures. Surfaces were prepared as follows: (1) mechanically lap with emery paper; (2) etch clean in solution shown; (3) soak in KCN solution, and (4) DI water rinse. Specimens were then annealed. Silicon also was studied.
REF: White, G K & Woods, S B — *Phys Rev,* 103,569(1956)

GE-0158a
ETCH NAME: Potassium permanganate
TYPE: Acid, oxidation
COMPOSITION:
x ... x% $KMnO_4$
x .... H_2O

TIME:
TEMP:

DISCUSSION:
Ge specimens used in a study of oxidation. Both single crystal and polycrystalline germanium were evaluated. Solution used to oxidize surfaces. Single crystal surfaces oxidize less rapidly than poly-Ge and rate decreases with material purity. Other oxidizing agents used were (1) water; (2) hydrogen peroxide; (3) sodium peroxide; (4) sodium hypochlorate; (5) air, and (6) carbon dioxide.
REF: Rosner, O — *Semicond Electron,* June 1957, 166

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GE-0159a
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
10 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
Ge specimens used in a study of thermal acceptors in vacuum annealed germanium. Etch clean in this solution and follow with three rinses in DI water. Then soak at RT, 1 h in 10% KCN to remove metallic ions and rinse five times in DI water.
REF: Hopkins, R L & Clarke, E N — *Phys Rev*, 100,1789(1955)

GE-0160a
ETCH NAME: Ferric chloride
TYPE: Acid, cleaning
COMPOSITION:
x .... x% $FeCl_3$
x .... H_2O
TIME: 15 min
TEMP: Boiling
DISCUSSION:
Ge specimens used in a general surface cleaning study. Various etch solutions used. Other etchants were 1HF:1HNO_3, and superoxol.
REF: Coblenz, A & Owens, H L — *Transistors — Theory and Application*, McGraw-Hill, New York, 1955, 211

GE-0161
ETCH NAME:
TYPE: Acid, oxidation
COMPOSITION:
1 .... 10% HF
1 .... 90% HNO_3
TIME:
TEMP:
DISCUSSION:
Ge specimens used in a study of slow surface reactions. Etch in solution shown and age specimens for 4 weeks in air at RT to stabilize oxide.
REF: Morrison, S R — *Phys Rev*, 102,1297(1956)

GE-0162a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... HF
x .... HNO_3
x .... *I_2 (Br_2)

*Saturate the solution.

TIME:
TEMP:
DISCUSSION:
Ge, n-type wafers used to fabricate p-n junctions devices. Wafer preparation sequence was: (1) polish etch in solution shown; (2) rinse in MeOH or 2% HNO_3:MeOH, and (3) wash in 1HF:1HNO_3:8H_2O.
REF: Ditrick, N H — U.S. Patent 2,761,800, Sept 4, 1956

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GE-0163
ETCH NAME:
TYPE: Molten flux, polish
TIME: 20 min then 40 min
TEMP: 590°C—200°C
COMPOSITION:
2 .... KCN
1 .... NaCN
DISCUSSION:
Ge, as alloy junction transistors. Prepare surfaces as follows after material has been alloyed: (1) soak in molten flux at 590°C for 20 min; (2) reduce temperature and continue to soak at 200°C for 40 min; (3) cool to room temperature and (4) DI water wash to remove flux. Then wash in solution shown to final clean, which is called the cyanide treatment. Process gives a lower and flatter collector current.
REF: Dawson, M H — U.S. Patent 2,788,300, April 9, 1957

GE-0009
ETCH NAME:
TYPE: Acid, junction
TIME:
TEMP: RT
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
Ge, as alloyed p-n junctions devices. A study of recombination radiation from deformed junctions at 80 K. Alloy junctions were GeIn or InAs. Solution used as a junction development etch.
REF: Newman, R — *Phys Rev,* 105,1715(1957)

GE-0164
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: RT
COMPOSITION:
1 .... HF
4—5 .... HNO_3
DISCUSSION:
Ge, as single crystal germanium grown by vapor deposition. The (111) oriented seed crystals used were etch polished in the solution shown, which gives a bright mirror finish. Growth rate was slower than average at 0.5—0.7 mils/h.
REF: Ruth, R P et al — *J Appl Phys,* 31,995(1960)

GE-0167
ETCH NAME:
TYPE: Acid, polish
TIME: 4 min
TEMP: RT
COMPOSITION:
15 .... HF
750 .... HNO_3
DISCUSSION:
Ge, as cut cubes oriented (001)/(001):(110)/(110), used in a study of third order elastic modulus. The cube was etch polished in the solution shown.
REF: Bateman, T et al — *J Appl Phys,* 32,928(1961)

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GE-0168
ETCH NAME: TIME: 20 sec
TYPE: Acid, polish TEMP: RT
COMPOSITION:
4 .... HF
21 .... HNO_3
DISCUSSION:
Ge, (111) wafers used in a study of optical constants. Cleaning sequence was: (1) boil in benzene, and reflux with acetone; (2) HF dip, 15 sec, and rinse in acetone, then (3) etch in solution shown with agitation, and DI water rinse.
REF: Archer, R J — *Phys Rev,* 110,354(1958)

GE-0169
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
4 .... HF
7 .... HNO_3
DISCUSSION:
Ge specimens used in a study of thick oxides on surfaces. Etch polish surfaces in solution shown. Oxidation used oxygen dried by passing through a bubbler chilled with ice-acetone to remove moisture.
REF: Lasser, M et al — *Phys Rev,* 105,491(1957)

GE-0170
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... HCl
x .... H_2O_2
DISCUSSION:
Ge, (111) wafers. Solution used to selectively develop left- and right-hand spiral etch pits. Structures were 100 to 1000 times smaller than normal etch pits.
REF: Kikuchi, M & Denda, S — *J Phys Soc Jpn,* 12,105(1957)
GE-0247: Goldberg, F C & Wynne, R H — *J Met,* 5,436(1953)
Ge specimens. Solution used in a general etch study of germanium.
GE-0246: Ellis, S G — *J Appl Phys,* 28,1262(1957)
Ge single crystal material used in a general etch study.
GE-0245: Ellis, S G — *J Appl Phys,* 26,1140(1955)
Ge single crystal material used in a dislocation study of germanium.
GE-0251: Denda, S & Kikuchi, M — *Met Abstr,* 8,818(1958)
Ge single crystal material used in a microscopic study of germanium surfaces.

GE-0171
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
8 .... HAc

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