DISCUSSION:

Ge wafers used in a study of orientation effects of K X-ray absorption spectra. Specimens were etch thinned in this solution for microscope study.

REF: Hussaini, J M & Stephenson, S T — *Phys Rev,* 109,51(1958)

GE-0173

ETCH NAME:

TYPE: Acid, polish/removal

COMPOSITION:

7 .... HCl

1 .... HNO_3

\+ .... glycerin

TIME:

TEMP: 35°C—1000°C

RATE: 75—100 μm/h

775 μm/h

DISCUSSION:

Ge wafers used in an etching study. Rates shown are without glycerin. Addition of glycerin can be used to moderate and control etch rates. $GeCl_4$ that remains on surfaces can be recovered by hydrolyzation.

REF: Wolsky, S P — U.S. Patent 2,734,806, February 14, 1946

GE-0203b

ETCH NAME:

TYPE: Acid, polish

COMPOSITION:

1 .... HF

1 .... HNO_3

1 .... tartaric acid

TIME:

TEMP:

DISCUSSION:

Ge wafers used in an etching study. Solution used to polish surfaces. Boiling water will oxidize germanium as will CO_2 applied to surfaces over 700°C. Improper etching and processing can cause pits that produce instability in transistors and diodes.

REF: Rosner, O — *Z Metallkd,* 46,225(1955)

GE-0175

ETCH NAME:

TYPE: Acid, polish

COMPOSITION:

20% .... HF

80% .... HNO_3

TIME:

TEMP:

DISCUSSION:

Ge wafers doped with copper to fabricate high resistivity photo-conductors. Mechanically lap with 260-grit SiC, then 600-grit abrasive on a glass plate with a water carrier. Etch polish in solution shown and rinse in DI water. (*Note:* See GE-0015. This solution is called white etch.)

REF: Van Heerdren, P J — *Phys Rev,* 108,230(1957)

GE-0177

ETCH NAME:

TYPE: Acid, removal

COMPOSITION:

1 .... HF

2 .... HNO_3

TIME:

TEMP:

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DISCUSSION:

Ge wafers used in a magneto-surface experiment. Solution used as a removal and polishing etch.

REF: Zemel, J N & Petratz, R L — *Phys Rev,* 110,1263(1958)

GE-0178

ETCH NAME: Argon

TYPE: Ionized gas, cleaning

COMPOSITION:

x .... Ar^+ ions

TIME:

TEMP:

GAS:

PRESSURE:

POWER:

DISCUSSION:

Ge, polycrystalline spheres used in a study of cleaning and sputter yield of germanium in rare gases. Other gases studied were Xe, Kr, Ne, and He.

REF: Laegreid, N et al — *J Appl Phys,* 30,374(1959)

GE-0179

ETCH NAME: Heat

TYPE: Thermal, forming

COMPOSITION:

x .... heat

TIME:

TEMP: Elevated

DISCUSSION:

Ge, as polycrystalline spheres. Describes the method of fabrication and evaluation of such spheres as diodes. Produced 40—125 V devices, but other electrical characteristics were poor. (*Note:* This may be the first application of spheres, polycrystalline or single crystal, as a semiconductor device.)

REF: Dunlap, W C Jr — *J Appl Phys,* 25,448(1954)

GE-0276: Wagner, R D — *J Appl Phys,* 29,1678(1958)

Ge wafers. A study of the development of dislocations in germanium by thermal shock.

GE-0278: Logan, K H — *Phys Rev,* 101,1455(1956)

Ge wafers. A study of the introduction of thermally induced acceptors in germanium by heat treatments.

GE-0279: Logan, R A — *Phys Rev,* 91,757(1953)

Ge wafers. Reference for the cleaning solutions used prior to thermal heat treatments used in GE-0278.

GE-0180

ETCH NAME: I—IV metals

TYPE: Molten flux, preferential

COMPOSITION:

x .... Cu

TIME: Variable

TEMP: Molten

DISCUSSION:

Ge, as single crystal spheres etched in liquid metals of the I—IV atomic group at elevated temperatures to develop etch pits. Used light figures developed to explain patterns by atomic radii vs. type metallic solvent. Also studied silicon spheres with these liquidized metals.

REF: Broder, J D & Wolff, G A — Electrochem Soc Meet, Cleveland, OH, 30 September 1956

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GE-0181
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
5 ml .... HF
70 ml .... HNO_3
DISCUSSION:

Ge, as single crystal spheres fabricated using a "Tornado Sphere Grinder". The system is a 2" high, thick-walled aluminum tube section with glue-back Buehler sanding strips attached inside. The tube is screwed down on an aluminum plate with a removable Lucite top. Nitrogen gas is fed into the enclosed tube center area from a tygon tube attached through $^1/_4$" pipe fitting in the Lucite top so that the gas blows against the inner wall. Single crystal materials are cut as cubes, placed in the grinder, and rotated with 3—5 SCFH N_2 flow until spheres are formed. For 10—15 $^1/_4$" diameter germanium cubes, time is about 45 min using 600-grit abrasive paper.

After spheres are formed, etch polish in the solution shown by hand rolling spheres submerged in the etchant using a teflon beaker held at about a 30—45° angle. Spheres should roll, but not tumble. The same solution was used on silicon with starter cubes from $^1/_8$ to $^1/_2$" diameter. Other materials fabricated as spheres were GaAs, GaSb, InAs, InSb, and InP. Spheres used in a study of finite crystal form preferential etching. Diffused spherical devices also have been fabricated from such spheres. (*Note:* There are similar sphere forming systems developed and used with other names, such as the Race-Track grinder. This is the easiest and most rapid way of fabricating single crystals spheres.)

REF: Myers, J & Walker, P — personal development and application, 1956

GE-0211b
ETCH NAME: Iodine A etch TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
15 ml .... HF
30 ml .... HNO_3
33 ml .... HAc
80 mg .... I_2
DISCUSSION:

Ge wafers of various orientations used in a study of the effects of various etchants on recombination centers. WAg, superoxol, CP4, and KOH also studied.

REF: Wallis, G & Wang, S — *J Electrochem Soc,* 106,231(1959)

GE-0190
ETCH NAME: White etch, dilute TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
10 .... HNO_3
6 .... H_2O
DISCUSSION:

Ge wafers cut and polished from germanium single crystals grown by vapor epitaxy in a closed-cycle process. Solution used to produce a polished mirror surface. (*Note:* An example of the use of the term "white etch" for solutions of HF:HNO_3. There are several so called, each as a different concentration mixture, such that the term is not recommended.)

REF: Marinace, J C — *IBM J,* 24,248(July 1961)

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GE-0029a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HNO_3
x .... KCl
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

Ge, (111) wafers used in developing new etching systems. Solutions of HNO_3:KCl will electropolish germanium.
REF: El'kin, B I — *J Metall,* Abstr 3 & 4(1958)

GE-0029b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HNO_3
x .... KF
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

Ge, (111) wafers used in an etch development study. Solutions of HNO_3:KF will electropolish germanium.
REF: Ibid.

GE-0156b
ETCH NAME:
TYPE: Electrolytic, oxidation
COMPOSITION:
x .... *0.25 N* $NaC_2H_3O_2$
x .... HAc
DISCUSSION:
TIME:
TEMP:
ANODE: Ge
CATHODE:
POWER:

Ge specimens used in a study of the growth of anodic oxide films. Solution shown used to anodize germanium. (*Note:* This is anhydrous sodium acetate in glacial acetic acid.)
REF: Zwerdling, S & Sheff, S — *J Electrochem Soc,* 107,338(1960)
GE-0268a: Laws, J T & Meigs, P S — *J Electrochem Soc,* 104,154(1957)

Ge wafers. A study of the oxidation rates of germanium.
GE-0269: de Zuber, N & Pourbiax, M — Rapp Tech #27 (1955)

Ge wafers. A study of the electrochemical behavior of germanium to develop potential pH equilibrium diagrams of the Ge-H_2O system at 25°C. Conclusion was to use H_2O-free electrolytes to reduce germanium oxide formation in hydrogenating Ge:H films.
GE-0375: de Zuber, N & Pourbiax, M — *Semicond Abstr,* 4,203(1956)

Ge wafers. An extension of work done as in GE-0269.
GE-0270: Kikuchi, M — *J Phys Soc Jpn,* 12,756(1957)

Ge wafers. Some experiments on the surface field effects on germanium single crystals. Q values drift toward negative values at RT after etching in CP4, plus growth of an oxide layer.
GE-0271: Laws, J T & Meigs, P S — *J Appl Phys,* 26,419(1955)

Ge and Si wafers with grown-in p-n junctions. A study of the effects of water vapor on the junctions.
GE-0272: Ellis, S G — *J Appl Phys,* 28,1262(1957)

Ge wafers. A surface study on the effects of chemical etching of a controlled oxide, or to minimize oxidation. Both CP4 and superoxol were evaluated.
GE-0273: Chynoweth, A G et al — *Phys Rev,* 118,425(1960)

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Ge and Si wafers with p-n junctions. A study of internal field emission at narrow junctions. Dislocations produce soft PIV, and edge dislocations cause local reduction in the band gap width.

GE-0277: Chynoweth, A G & Pearson, G L — *J Appl Phys,* 29,1103(1958)

Ge and Si wafers with p-n junctions. Additional studies as in GE-0273.

GE-0268b: Ibid.

Ge single crystal spheres with (111), (100), and (110) flats. Oxidize at 450 and 700°C. Above 550°C, oxidation is inversely dependent on pressure, and the amount of oxygen; below, the (110) flat was the only plane to show appreciable oxidation.

GE-0311: Zerdling, J & Sheff, S — *J Electrochem Soc,* 107,388(1960)

Ge wafers. A study of the anodic oxidation of germanium. Best solution was 0.25 *N* anhydrous acetate in acetic acid used at 40—400 $\mu A/cm^2$.

GE-0280: Bray, R & Cunningham, R W — *J Phys Chem Solids,* 8,99(1959)

Ge wafers. An optical and magnetic study. There is a retentive conductance surface effect with oxidizers, such as HNO_3; HF:HNO_3 and H_2O_2. No effect observed with HF, only. Light increases formation of a p-type surface zone.

GE-0200
ETCH NAME: Sodium hydroxide
TYPE: Alkali, cutting
COMPOSITION:
x .... x% NaOH

TIME: Hours
TEMP: Hot
ANODE:
CATHODE:
POWER:

DISCUSSION:

Ge ingot. System used for slicing germanium wafers electrolytically using a 0.003 diameter tungsten wire as the cutting vehicle with the solution shown as an etch assist. Cutting rate maximum was 1730 mils/h.

REF: Shedd, S — *Electrochem Abstr,* 10,15(1961)

GE-0233: Eigler, J H & Sullivan, M U — *J Electrochem Soc,* 103,132(1956)

Ge specimens. A study of electrolytic stream (jet) etching of germanium.

GE-0201
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:

Ge wafers used in a study of Hall mobility of cleaned surfaces. After argon ion cleaning, specimens were annealed in vacuum at 10^{-9} Torr.

REF: Missman, R & Handler, P — *J Phys Chem Solids,* 8,121(1959)

GE-0259: Wolsky, S P — *Phys Rev,* 108,1131(1957)

Ge and Si wafers used in a study of Ar^+ ion bombardment of surfaces for cleaning. Current density was 1—12 $\mu A/cm^2$.

GE-0260: Wolsky, S P — *J Phys Chem Solids,* 8,114(1959)

Ge and Si, (100) wafers used in a surface study. Surfaces were oxidized at RT; Ar^+ ion cleaned; then etched in CP4; and baked in vacuum.

GE-0261: Missman, R & Handler, P — *J Phys Chem Solids,* 8,109(1959)

Ge, (100) wafers used in a study of Hall mobility of cleaned germanium surfaces. Material was 0.2 mm thick, n-type, 20 Ω cm resistivity. Ar^+ ion clean, then anneal at 650°C overnight and cool within 2 h.

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GE-0274: Wagner, E D — *J Appl Phys,* 29,217(1958)

Ge wafers. A study of ion bombardment etching of germanium.

GE-0283: Schlier, K E & Farnsworth, H E — *J Chem Phys,* 30,917(1959)

Ge and Si wafers used in a study of structure and adsorption characteristics of clean surfaces. Ar^+ ion bombardment evaluated.

GE-0202

ETCH NAME: Superoxol

TYPE: Acid, preferential

COMPOSITION:

1 .... HF

1 .... H_2O_2

4 .... H_2O

TIME:

TEMP:

DISCUSSION:

Ge specimens as cut cylinders for the development of dissolutionment diagrams. Modified free energy theorems used to predict equilibrium growth and etching shapes. Solution used to preferentially etch specimens. Also etched GaAs cylinders and hemispheres in $1HF:2H_2O_2:5H_2O$.

REF: Jaccodine, R J — *J Appl Phys,* 33,2663(1962)

GE-0019c

ETCH NAME: Potassium hydroxide

TYPE: Electrolytic, junction

COMPOSITION:

1 drop .... x% KOH

TIME:

TEMP:

ANODE:

CATHODE:

POWER:

DISCUSSION:

Ge, (111), n-type wafers with p-type germanium epitaxy thin films as Ge/Ge (111) to form p-n junctions. Place a drop of solution across the junction and bias to etch delineate.

REF: Ibid.

GE-0209

ETCH NAME: Potassium fluoride

TYPE: Electrolytic, removal

COMPOSITION:

x .... x% KF

TIME:

TEMP:

ANODE:

CATHODE:

POWER:

DISCUSSION:

Ge, (111) wafers and other orientations. A study of the dissolution kinetics of germanium and specific adsorption in aqueous solutions. All solutions were used from concentrations of 10^{-6} to 1 *N*. Below a pH 6, little or no change was observed, but as pH increases above pH 6, etch rate increases. No difference observed between p- or n-type material with or without illumination, as rate increases with concentration increase of solution. Other salts evaluated were KCl, KBr, KI, $NaNO_3$, Na_2SO_4, CsCl, $BaCl_2$, and $LaCl_3$.

REF: Harvey, W W & Gatos, H C — *J Electrochem Soc,* 107,65(1960)

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GE-0013b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
x .... x% NaOH
x .... H_2O_2
x .... 1 μm alumina (Al_2O_3)
DISCUSSION:
Ge, (111), and (100) wafers used as substrates in the preparation of GaAs/Ge and GaP/Ge epitaxially grown heterojunctions. The germanium substrates were polish lapped with the acid slurry shown above using a cotton pad soaked with the solution. The GaAs/Ge junction was delineated using HNO_3:H_2O.
REF: Weinstein, M et al — *J Electrochem Soc*, 111,674(1964)

GE-0203
ETCH NAME: Water TIME:
TYPE: Acid, float-off TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
a-Ge, as thin film material deposited on NaCl, (100) substrates, and used for TEM study of structure. After growth, films were removed from the salt substrates with water using the float-off technique where the NaCl surface at the interface with the a-Ge layer is liquefied with the film floating off.
REF: Nakhotkiu, N G et al — *Thin Solid Films*, 112,267(1984)
GE-0204: Pierrard, P et al — *Thin Solid Films*, 111,141(1984)
a-Ge thin films deposited on NaCl, (100) cleaved substrates. Desalted water was used for float-off to remove films for TEM study. TEM microscope heating did not crystallize films, but using a laser under the TEM produced single crystal spherulitic structures.

GE-0310
ETCH NAME: TIME:
TYPE: Cleave, dislocation TEMP:
COMPOSITION:
x .... cleave
DISCUSSION:
Ge, (111) wafers cleaved and used in a study of electrical states on clean surfaces. Dislocations were present on cleaved surface without any additional processing.
REF: Barnes, G A & Banberg, P C — *Proc Phys Soc*, 71,1020(1958)

GE-0206
ETCH NAME: Potassium hydroxide TIME: 5—60 min
TYPE: Alkali, orientation TEMP: Hot
COMPOSITION:
125 ml .... 5—10% KOH (NaOH)
10 mg .... I_2
DISCUSSION:
Ge, (111) wafers and ingots. Where an ingot is "as-grown" prior to surface grinding to a specific diameter, growth direction can be observed by the hachure growth meniscus marks (3 in ⟨211⟩ directions at 120°) along the ingot length. If they point upwards, it is toward the seed end; if downward, toward the ingot tail. If needed, this gives a ⟨111⟩A and

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$\langle\overline{111}\rangle$B direction. To establish this positive or negative wafer surface direction when wafers are sliced from an ingot ground to specific diameter where these hachure marks are not present, etch lightly with the solution shown. Observe wafer edges for etched triangles for bulk $\langle 110\rangle$ or $\langle 011\rangle$ directions . . . triangle point up or down . . . up is positive, seed end of ingot. For (100) oriented ingot growth, there are four hachure marks in $\langle 110\rangle$ directions at 90°.
REF: Pennington, P & Walker, P — development work, 1957

GE-0165c
ETCH NAME: Indium
TYPE: Metal, decoration
COMPOSITION:
x .... In
TIME:
TEMP: 700°C
DISCUSSION:
Ge, (111) wafers with indium, as a thin sheet or cut pre-form, alloyed and diffused into the wafer to metal decorate and develop growth striations. After alloying, remove excess indium by boiling in HCl. Decorate by heating wafers at 700°C on an iron, nickel or similar metal plate. Indium will develop growth striations and (111) fracture.
REF: English, A C — *J Appl Phys*, 31,1498(1960)

GE-0227b
ETCH NAME: Iodine, vapor
TYPE: Halogen, preferential
COMPOSITION:
x .... I_2, vapor
TIME:
TEMP:
DISCUSSION:
Ge, (111), (110) and (100) wafers used in a study of etch patterns developed by iodine vapor etching. After mechanical lap and etch polishing with CP4, wafers were I_2 vapor etched in both an open and closed tube. In open tube etching was done with 60 cc H_2 gas flow and 10—30 mmHg pressure of iodine.
REF: Arizumi, T & Akasaki, I — *Jpn J Appl Phys*, 2,143(1963)

GE-0226
ETCH NAME: Superoxol
TYPE: Acid, polish
COMPOSITION:
1 .... HF
1 .... H_2O_2
3 .... H_2O
TIME: 2 min
TEMP: RT
DISCUSSION:
Ge, (111) wafers lithium diffused used in a study of lithium precipitation. Wafers were lap polished down to 0.25 μm on microcloth, then polished in solution shown. Under 2000× magnification, 0.2 μm diameter precipitates of lithium were observed in dislocation etch pits.
REF: Blanc, J & Abrahams, M S — *J Appl Phys*, 34,3638(1963)

GE-0225a
ETCH NAME: Germanium chloride
TYPE: Gas, preferential
COMPOSITION:
x .... $GeCl_4$, vapor
TIME:
TEMP:

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DISCUSSION:

Ge, (111) wafers with epitaxy grown Ge layers used in a preferential light figure etch pit development study. Vapor etching developed etch pits and hillocks in the epitaxy layers. Hot HCl vapors also were used with similar results. The WAg etch was used to polish surfaces.

REF: Gualtieri, J G & Kerecman, A J — *Rev Sci Instrum,* 34,108(1963)

GE-0025b

ETCH NAME: Hydrochloric acid, vapor — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

x .... HCl, vapor

DISCUSSION:

Ge, (111) wafers used as substrates for Ge epitaxy growth in a study development of orientation light figures in the epitaxy layers. Hot HCl vapors develop both etch pits and hillocks as does $GeCl_4$ vapor. WAg etch was used to polish surfaces before preferential vapor etching.

REF: Ibid.

GE-0159b

ETCH NAME: Potassium cyanide — TIME: 1 h

TYPE: Acid, cleaning — TEMP: RT

COMPOSITION:

x .... 10% KCN

DISCUSSION:

Ge specimens used in a study of thermal acceptors in vacuum annealed germanium. Etch with 1HF:10HNO_3, and rinse three times with DI water, then soak in the solution shown to removal metallic ions, and rinse five times with DI water.

REF: Ibid.

GE-0300

ETCH NAME: — TIME: 5 to 45 min

TYPE: Alkali, preferential — TEMP: Boiling

COMPOSITION:

387 g .... KOH

250 ml .... H_2O

20 g .... I_2

DISCUSSION:

Ge, (111), 5—10 Ω cm resistivity, n-type wafers used in a controlled pit damage etch study. Solution also used as a light figure orientation etch for (111), (100), (110), and (211) ingots and wafers. Study used both cut dice either randomly edge oriented or bulk plane direction oriented edges: ⟨111⟩ on (111) wafers; ⟨110⟩ on (100) wafers. The former were triangles or diamonds in shape; the latter were squares. See SI-0300 for a description of the diamond stylus damaging system designed. The system was used on germanium and silicon initially, then compound semiconductors in similar studies. The base solution used in all cases was 250 ml of 30% KOH or NaOH, with or without chemical additives. Pit structures obtained were evaluated for shape relative to surface orientation; pit side-slope planes vs. solution mixtures; pit bottom planarity; and pit shape progression with etch time. Pits also were evaluated as concave surfaces against convex sphere surfaces etched to finite crystal form.

Pure solutions of the two hydroxides are cleaning solutions, only, on germanium, but become preferential with chemical additives. Some 50 mixtures were evaluated on silicon,

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but a lesser number on germanium. Germanium, as indium alloy transistors were fabricated and evaluated, similar to the aluminum alloy silicon transistors described in SI-0300 series.

Oriented cut forms of both semiconductor materials were evaluated for type crystallographic planes developed at face edges with variation of additives. The forms studied were cube, (100); cube, (110); octahedron, (111); tetrahedron, (111); and rhomboid, (111). The latter is not a natural crystal form in the isometric system, normal (cubic) class, but contains faces of the octahedron, and both the positive (+) and negative (−) tetrahedrons. Note that calcite in the hexagonal, rhombohedral division shows the atypical rhomboid shape. The solid chemical additives, shown below, were 20—30 g added to the 250 ml 30% KOH/NaOH solution. Liquid bromine was 25 or 50 ml. The etch pit planar surface shape was evaluated after 20 min etch time.

Chemical additive	**Pit shape (111) (20 min etch)**
GE-0301: Iodine, I_2	Triangle & hexagon
GE-0302: Bromine, Br_2	Triangle & hexagon
GE-0303: Ammonium peroxylsulfate, $(NH_4)_2S_2O_8$	Triangle
GE-0304: Potassium ferricyanide, $K_3Fe(CN)_6$	Triangle

Preferential etch pits on (111), (100), (110), and (211) were sufficiently distinctive without controlled pit damage for light figure orientation. The damage induced pits on (111) were flat bottomed similar to those achieved with silicon.
REF: Walker, P & Waters, W P — germanium development, 1956—1958

GE-0243
ETCH NAME: Light
TYPE: Power, plasticity
COMPOSITION:
x .... light
TIME:
TEMP:
DISCUSSION:
Ge specimens. A study of the effects of light induced plasticity in germanium. Intense white light applied to surfaces under strain potentials.
REF: Hochman, R H & Kuczyanski, G C — *J Appl Phys*, 30,267(1959)

GE-0244
ETCH NAME: Electricity
TYPE: Electricity, preferential
COMPOSITION:
x .... current
TIME:
TEMP:
DISCUSSION:
Ge specimens. The use of electric current to determine the positions of dislocation regions in germanium. (*Note:* Method also applied to silicon.)
REF: Hogarth, C A & Baynham, H C — *Proc Phys Soc*, 71,647(1958)
GE-0248: Coffman, R E & Lesk, I A — *J Appl Phys*, 29,1493(1958)
Ge, (111) and (100) wafers fabricated with p-n-p diffused junctions and their use as transistors.

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GE-0238
ETCH NAME: Irradiation
TYPE: Particle, damage
COMPOSITION:
x .... neutron
TIME:
TEMP:
POWER:
DISCUSSION:
Ge samples subjected to irradiation then etched for microscope study of induced defects.
REF: Noggles, T S & Stiegler, J O — *J Appl Phys*, 30,1279(1959)

GE-0250
ETCH NAME: Growth
TYPE: Growth, defects
COMPOSITION:
x .... growth
TIME:
TEMP:
DISCUSSION:
Ge and Si discs as-grown. A development method for growing discs rather than ingots of both materials.
REF: McLaughlin, W A & O'Connor, J — *J Appl Phys*, 29,222L(1958)
GE-0249: Sangster, R C & Carman, J N Jr — *J Chem Phys*, 23,206L(1955)
Ge material growth. A study of the contraction of germanium on being melted.
GE-0245: Bannet, A I & Longini, R L — *Phys Rev*, 116,53(1969)
Ge, dendritic growth as ribbon crystal. A study of the method of growth.

GE-0252
ETCH NAME: CP4
TYPE: Acid, thinning
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc
1% .... Br_2
TIME:
TEMP:
DISCUSSION:
Ge and InP, (100) and (111) wafers used as substrates for thin film growth of CaF_2 and BaF_2. Clean substrates with HF, then heat in vacuum at 300°C for InP and 800°C for Ge. Then deposit thin films. Solution used to thin germanium for TEM study of the thin films. BaF_2 was poor on (100) Ge due to lattice mismatch.
REF: Phillips, J M et al — *J Vac Sci Technol*, B(1),246(1983)

GE-0253
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
(1) 1 .... HF
2 .... HNO_3
1 .... HAc
(2) 10 .... HF
1 .... HNO_3
TIME: (1) 3 min (2) 30 min
TEMP: RT RT
DISCUSSION:
Ge and Si wafers cut from Float Zone (FZ) ingots with 10^4 cm^{-2} grown-in dislocations used in a study of the yield point and mobility of dislocations. Both materials were p-type: Ge, 40 Ω cm, and Si, 200—1000 Ω cm resistivity. After diamond saw cut, lap with 3, then 1 μm diamond paste. Etch polish Ge in solution (1); Si in solution (2).

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REF: Stevens, D S & Tiersten, H F — *J Appl Phys,* 54,1815(1983)
GE-0292: Wallis, G & Wang, S — *J Electrochem Soc,* 106,230(1959)

Ge, (111) wafers and other orientations. A study of the effect of various etchants on recombination centers on germanium surface.

GE-0254b
ETCH NAME: Barium titanate
TYPE: Compound, junction
COMPOSITION:
x .... $BaTi_2O_3$, powder
TIME:
TEMP:
DISCUSSION:

Ge, (111) wafers used to fabricate indium alloyed p-n junction diodes. Brush barium titanate powder across junction, then electrical bias with a small DC battery: n-type to positive (+) and p-type to negative (−) pole. Powder will align along p-n junctions.
REF: Ibid.
GE-0255: Fuller, C S et al — *Phys Rev,* 96,21(1954)

Ge, (111) wafers fabricated with p-n junction diodes. Used barium titanate powder to define junctions.

GE-0254c
ETCH NAME: Zinc oxide
TYPE: Oxide, junction
COMPOSITION:
x .... ZnO_2
x .... silicone (oil)
x .... toluene
TIME:
TEMP:
DISCUSSION:

Ge, (111) wafers fabricated with indium p-n junctions. Paint solution across p-n junction and electrically bias with a small DC battery: n-type is on positive (+) terminal, and p-type negative (−). Developed the p^{-+} junction line more than the actual p-n junction line.
REF: Ibid.
GE-0255: Amick, J A & Goldstein, B — *J Appl Phys,* 30,1471(1959)

Ge, (111) wafers with p-n junctions. Use toluene to thin ZnO_2/silicone solution, and paint on junction. Bias with a 45 V DC battery: n-type for positive terminal; p-type for negative terminal. Also studied silicon p-n junctions in similar work.

GE-0256
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, machining
COMPOSITION:
x .... 10% KOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Ge, (100) specimens. Solution used to chemically machine a square hole through a germanium block with (100) surface orientation.
REF: Uhlir, R T — *Rev Sci Instrum,* 26,965(1955)

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GE-0257
ETCH NAME: Antimony etch
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
4 .... HF
2 .... HNO_3
4 .... H_2O
* .... $SbCl_3$

*0.2 mg per mil of solution.

DISCUSSION:
Ge and Si wafers used in a study of surface states at low temperature after various chemical treatments. Mixture of the HF:HNO_3 system studied in addition to solution shown.
REF: Morrison, S R — *Phys Rev*, 114,437(1959)

GE-0258
ETCH NAME: Indium
TYPE: Metal, structure
TIME:
TEMP: Elevated
COMPOSITION:
x .... In
DISCUSSION:
Ge, (111) wafers used in a study of reactions during micro-alloying. Micropyramids formed during alloying.
REF: Zuleeg, R — *J Appl Phys*, 30,9(1959)
GE-0275: Goldstein, B — *RCA Labs*, RB-85, Dec 1956
Ge wafers. A study of the dissolution of germanium by molten indium.

GE-0262
ETCH NAME: Rhodes etch
TYPE: Irradiation, defects
TIME:
TEMP:
COMPOSITION:
(1) x .... neutron (2) x .... Rhodes etch
DISCUSSION:
Ge wafers studied for neutron irradiation effects. After irradiation, use Rhodes etch to develop defects and structure for microscope examination.
REF: Meckel, B B et al — *J Appl Phys*, 31,1299(1960)
GE-0263a: Rhodes, R G et al — *J Electron Control*, 3,403(1957)
Reference for Rhodes etch, above. (*Note:* See GE-0205.)
GE-0264: Curtis, O L Jr et al — *J Appl Phys*, 28,1161(1957)
Ge specimens used in a study of irradiation effects on the hole lifetime of n-type germanium.
GE-0265: Hunter, L P — *Proc K Ned Akad Wet*, 61,214(1958)
Ge specimens used in a study of the anomalous transmission of X-rays by single crystal germanium. Cu K alpha radiation used. X-ray used to investigate the presence of dislocations in the material.

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GE-0282
ETCH NAME: Sodium
TYPE: Metal, contamination
COMPOSITION:
x .... Na^+ ions
DISCUSSION:
Ge wafers. A study of the adsorption of sodium ions on germanium surfaces.
REF: Wolsky, S P et al — *J Electrochem Soc*, 103,606(1956)

TIME:
TEMP:

GE-0284
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning/removal
COMPOSITION:
x .... HF
DISCUSSION:
a-Ge:H and a-Si:H hydrogenated thin films deposited on (100) silicon substrates and fused quartz blanks. Materials grown in a study of these compounds. HF can be used as a general light cleaning and removal solution. See SI-0420 and QTZ-0009.
REF: Rudder, R A — *Appl Phys Lett*, 43,871(1983)

TIME: 30 sec
TEMP: RT

GE-0286
ETCH NAME: Laser
TYPE: Light, annealing
COMPOSITION:
x .... laser
DISCUSSION:
a-Ge evaporated on fused quartz blanks, then crystallized to a single crystal (111) or (110) oriented thin film, 4000 Å thick by laser annealing. GaAs then grown as 30 μm crystallites by MOCVD for application as an electro-optical device. A developmental study of GaAs deposition on fused quartz.
REF: Shinoda, Y E et al — *IEEE*, 70,132(1982)

TIME:
TEMP:

GE-0295
ETCH NAME:
TYPE: Abrasive, damage
COMPOSITION:
x .... abrasive, powder
DISCUSSION:
Ge, (111) wafers used to fabricate p-n junction diodes in a study of the effects of subsurface residual lapping and polishing damage on device reverse characteristics. Damage depth of a sandblasted surface was 35 μm; a final polished surface was 1 μm.
REF: Buck, T M & McKim, F S — *J Electrochem Soc*, 103,593(1956)
GE-0297: Brophy, J J — *J Appl Phys*, 29,1377(1958)
Ge, (111) wafers fabricated as p-n junction diodes in a study of the effects of an etch polished surface vs. a sandblasted surface on device noise characterization. Polished surfaces showed 40 times less noise.
GE-0298: Baker, D X & Yemm, N — *Br J Appl Phys*, 8,302(1957)
Ge, (111) wafers used in a study of the depth of subsurface damage introduced by abrasive lapping. A 25-μm abrasive powder produced a damage depth of 60 μm with a combination of surface fracture and high dislocation density.

TIME:
TEMP:

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GE-0290
ETCH NAME: Lithium
TYPE: Metal, diffusion
COMPOSITION:
x .... Li, powder
TIME:
TEMP:
DISCUSSION:
Ge, (111) wafers and cylinders. Specimens were initially diffused with nickel, then lithium. A study of the rectification or ohmic effect of Ni or W contact whiskers on a p-n diode. (*Note:* Cylindrical lithium-drift germanium diodes were fabricated for radiation testing of the Van Allen Belt in 1961.)
REF: Tompkins, B E — *Proc IEEE,* 52,1064(1964)

GE-0299a
ETCH NAME: Thallium
TYPE: Metal, laser
COMPOSITION:
x .... Tl
TIME:
TEMP:
POWER:
DISCUSSION:
Ge and Si specimens fabricated as a mirror-cup for laser operation. With thallium and ozone under power introduction against the cup face, reaction will produce a green light as a chemical laser, requiring less power than in an infrared laser operating as a pulsed amplifier.
REF: Peterson, J — *Science News Lett,* 132,257(1987)

GE-0299b
ETCH NAME: Chlorine
TYPE: Halogen, laser
COMPOSITION:
x .... Cl_2
TIME:
TEMP:
POWER:
DISCUSSION:
Ge and Si specimens fabricated as a mirror-cup for laser operation. In the presence of 3-atom clusters of sodium, ionized Cl^+ reduce to 2-atom sodium clusters on a self-sustaining basis to produce visible light as a chemical laser. (*Note:* Reference work done by J L Gole, Ga Inst Technol, Atlanta, GA.)
REF: Ibid.

GE-0351
ETCH NAME:
TYPE: Electrolytic, plating
COMPOSITION:
86 g .... KOH
3.2 g .... $K_2Cr_2O_4.H_2O$
52 g .... *GeO_2
50 ml .... H_2O
TIME:
TEMP: 85°C
ANODE:
CATHODE:
POWER:

*Irradiated for ^{71}Ge.

DISCUSSION:
Ge, (111) wafers used in a study of the effects of heavy doping on the self-diffusion of germanium. The germanium isotope was electroplated as a tracer and was shown to dissolve some oxide, but it was difficult to obtain a uniform deposit.
REF: Valenta, N W & Ramassastry, C — *Phys Rev,* 106,73(1957)

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GE-0287
ETCH NAME: Germanium
TYPE: Metal, optics
COMPOSITION:
x .... Ge
TIME:
TEMP: 116—440 K
DISCUSSION:
Ge specimens cut as 2″ oriented prisms with a refractive angle of 19.55.8 in a study of the material refractive index at 1.8—2.5 wavelength frequency over the temperature range shown. Refractive Index (n = 0.75 nom.) showed a linear rise with temperature increase.
REF: Lukes, F — *Cesk Cas Fys,* 8,262(1958)

GERMANIUM ALLOYS, M_xGe

General: Does not occur in nature as a metallic alloy compound. Germanium is found as a minor constituent in several minerals, notably, sphalerite, ZnS, and is collected as a by-product during ore reduction of this mineral for both its zinc and sulfur content.

There are several germanium alloys used in industry to a minor extent, today, although metallic germanium was of little use until discovery of its semiconducting properties in the late 1940s.

Technical Application: As AuGe(13%) it has wide use in assembly of Solid State microelectronic circuitry in both device and package assembly. As a thin film metallization source it is supplied in small pellets or cylinders of about $^1/_4$-g weight, each. For evaporation from a tungsten boat, pellets are normally "evaporated to completion" for deposit thicknesses between 500—1200 Å. Sputter deposited from a crucible containing as much as a 250-g load, due to vapor pressure differences, gold evaporates first, then germanium, with slow increase of germanium concentration in the evaporating charge. This germanium increase in the pot charge produces an increasingly harder and more brittle Au/Ge compound thin film. In either method of deposition germanium content can vary quite widely as, with evaporation from a tungsten boat, germanium alloys with tungsten, such that the thin film never reaches the 13% initial concentration value, the boat becomes brittle and will shatter after the second or third use.

A widely used multilayer metallization for contact pads in device assemblies is Au/Au:Ge/Ni. After deposition it is annealed to homogenize but, if annealing temperature is high and too long, recrystallization occurs in the otherwise soft gold top layer, and it is impossible to soft gold wire bond to the surface. The Au:Ge(13%) alloy also is supplied as strips that are cut to required size, or as pre-forms in device and circuit substrate fabrication, or for package assemblies and seals.

Other germanium alloys are available, but the AuGe(13%) alloy is the most widely used.

Etching: Tri-iodide; aqua regia; KCN. See Gold section.

GERMANIUM ALLOYS

GOLD GERMANIUM ETCHANTS

AUGE-0001
ETCH NAME: Tri-iodide
TYPE: Halogen, removal
COMPOSITION:
100 g .... KI
50 g .... I_2
500 ml .... H_2O
25 ml .... MeOH
TIME:
TEMP: 40—60°C

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DISCUSSION:

AuGe(13%) alloy as pellets, sheet, or cut pre-forms. Pellets used for contact metallization as ohmic contacts on GaAs:Cr, (100), and Si, (100) n-type wafers in fabrication of microelectronic devices. Multilayer evaporation as nominal thicknesses 1000 Å Au/1200 Å Au:Ge/500 Å Ni; follow with annealing in FG (85% N_2:10—15% H_2), 1—2 min at 350—450°C. Wafers were photolithographically patterned with acetone Lift-off of photo resist excess metal film after evaporation. (AUGE-0001; AUGE-0002). Similar multilayer structure sputter evaporated by E-beam from 200-g load crucibles (AUGE-0003). Alloyed as device contacts or on circuit substrates as contact cut pre-forms (AUGE-0004). The latter includes 50% reduction of AuGe by hole pattern etching to obtain a thinner AuGe film under 0.001 thick, as the 1-mil thickness is the lowest thickness available as rolled sheet. Tri-iodide solutions are standard for etch processing gold, constituent volumes can be varied, and MeOH used to assist in dissolving the I_2 and KI.

REF: Walker, P — personal application, 1972—1985

AUGE-0002: Siracusa, M — personal communication, 1978 (evaporation)

AUGE-0003: Skelly, G — personal communication, 1980 (sputter)

AUGE-0004: Marich, L A — personal communication, 1982 (pre-forms)

AUGE-0006: Marlow, G S & Das, M B — *J Solid State Electron*, 25,91(1982)

AuGe(13%) evaporated on GaAs, (100) n-type wafers and annealed in FB above 350°C showed a sheet resistance between 15—33 Ω/sq.

AUGE-0007: Heiblum, M et al — *J Solid St Electron*, 25,185(1982)

AuGe(13%) evaporated as Au/AuGe/Ni multilayers and annealed 30 seconds at 450°C with a 2000 Å SiO_2 cap, then removed with 1HF:3HNO_3. Layers sputter from a 4-crucible E-gun on GaAs, (100) substrates containing an MBE 2500 Å p-type buffer layer. There is a high resistance layer at the metal/wafer interface due to n^+ Ge penetration (?). Nickel helps adhesion but, after anneal, there were dark Ge/Ni clusters on the soft gold cover surface. (*Note:* Such artifacts have been observed by others, is common to a hardened gold surface that will not accept a soft gold wire bond, and have been referred to as "rosettes".)

AUGE-0008: Iliadis, A & Singer, K E — *J Solid State Electron*, 26,7(1983)

AuGe(13%) deposited as eutectic alloy on n-type GaAs, (100) wafers. Alloying was done in a moly boat with substrate at 110°C during evaporation, then followed by 1000 Å Au. Annealed on a quartz spade in FG, 15 sec at 450°C, then cooled in gas flow 1 min at 300°C. Below 300°C, contact is rectifying; above 300°C, ohmic. This procedure gave minimum resistance with recrystallization of Ge/Ni rectangular particle growth in the soft gold over-layer.

AUGE-0009

ETCH NAME: Potassium cyanide — TIME:

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

x .... x% KCN

DISCUSSION:

AuGe(13%) alloy as Au/AuGe/Ni evaporated multilayered films, or Au/Cr evaporated, and Au/Ni plated coatings on semiconductor wafers, dielectric substrates, and assembly parts. Metallization stripped with solution shown. **CAUTION:** All cyanide solutions are highly toxic, and require controlled disposal.

REF: Valardi, N — personal communication, 1983

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INDIUM GERMANIUM ETCHANTS

INGE-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
InGe used as a deposited Au/InGe alloy contact on (100) InP and GaAs wafers. This was a study of alloy contacts and material defects associated with temperature processing. Other alloy combinations were Pb/Au/Ag and Cu/Ni.
REF: Grovenor, C R M — *Thin Solid Films,* 89,367(1982)

TIN GERMANIUM ETCHANTS

SNGE-0001
ETCH NAME: Aqua regia TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
SnGe(1%) thin films grown on (100) InSb and CdTe substrates in a study of grey-tin as a zero-gap semiconductor material with infrared properties. Lattice parameters of the three materials show a close match: a = 6.49/6.48 Å. Grey tin (alpha-tin) is isometric — normal, diamond structure, is the common form of tin at room temperature, but converts to beta tin at 13.2°C. This reaction is known to produce structural failure under cold weather conditions.
REF: Farrow, R F C — *J Vac Sci Technol,* B(1),244(1983)

GERMANIDES: M_xGe_y

General: Germanides do not occur as natural metallic compounds. Germanium is a trace element in iron pyrites, such as pyrite, FeS_2, and zincblende (sphalerite), ZnS, and collected as a by-product of ore smelting. It was first obtained in any quantity from flue dust collected in the exhaust piping and stacks in iron refineries.

There are two sulfide minerals containing germanium: argyrodite, $4AgS.GeS_2$, and germanite, $Cu_2(Fe,Ge)S_4$. Germanium has had little use in industry until discovery of its semiconducting properties in the late 1940s.

Technical Application: The germanides are treated, here, as a separate unit without regard to germanium alloys, as many have individually distinctive properties, applications in Solid State, and several have been grown as singles crystals. Fewer germanides have been developed and studied than have silicides.

Germanides have been grown as single crystals or deposited as thin films for general morphological study or special characterization of superconductivity, ferromagnetics, photoconductivity. They also have been deposited and annealed like the silicides as possible blocking layers in device construction. See section on Germanium Alloys.

Etching: Mixed acids containing H_2SO_4, HF, HNO_3, alkalies, halogens, and dry chemical etching (DCE) with ionized gases.

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COPPER GERMANIDE ETCHANTS

CUGE-0001
ETCH NAME: Phosphoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Cu:Ge, alloy of different compositions. Specimens used in a study of optical absorption at 4.2 K. Solution is erratic for concentrated alloys as, with greater than 7% Ge, material will not polish. Other alloys were studied.
REF: Raynes, J A — *Phys Rev*, 121,456(1961)

HOLMIUM COPPER GERMANIDE ETCHANTS

HOCG-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3

TIME:
TEMP: (2900°C growth)

DISCUSSION:
$HoCu_2Ge_2$ single crystal specimens grown from mixed powders in an induction furnace by melting under argon. Used in a study of magnetic super-lattices at LHe temperature. RCu_2Ge_2 (R = lanthanides or actinides) materials are body-centered tetragonal structure.
REF: Schobinger-Papamantellos, P et al — *J Phys Chem Solids*, 45,695(1984)

IRON GERMANIDE ETCHANTS

FEGE-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3

TIME:
TEMP:

DISCUSSION:
Fe_3Ge_2 thin films grown on (111) silicon wafers with or without SiO_2 pre-coated surfaces. Grown as both crystalline deposits or as an amorphous structure: a-Fe_xGe_{x-1}. Films show ferromagnetic properties but, with increase in germanium, magnetism is lost.
REF: Terzleff, P et al — *J Appl Phys*, 50,1031(1979)

FEGE-0002
ETCH NAME:
TYPE: Acid, preferential/polish
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc

TIME:
TEMP: 40°C

DISCUSSION:
$FeGe_2$, (100) and (110) wafers cut from a Czochralski (CZ) grown ingot with cobalt or tin doping. Solution used to develop defect structures, and as a general polish etch.
REF: Runkin, A Y & Frolow, A A — *J Cryst Growth*, 69,131(1984)

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MAGNESIUM GERMANIDE ETCHANTS

MGGE-0001a
ETCH NAME: TIME:
TYPE: Halogen, polish TEMP:
COMPOSITION:
4 drops .... Br_2
250 ml .... MeOH
DISCUSSION:
Mg_2Ge, (111) wafers used in a study of semiconducting characteristics of this compound. Polishing was done on a metallographic wheel covered with a cloth saturated with the solution shown. Chem/mech lap at slow speed and quench with MeOH. Gives a bright chemical polish.
REF: Kromer, H et al — *J Appl Phys*, 36,2461(1965)

MGGE-0001b
ETCH NAME: TIME: 30 sec
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
2 .... H_2SO_4
1 .... H_2O_2
200 .... H_2O
DISCUSSION:
Mg_2Ge, (111) wafers. Solution used to clean p-n junction areas, but does not preferentially develop the junction. Material reacts with acids and alkalies. After etch cleaning with solution shown, quench in MeOH. (*Note:* Solution is a highly diluted Caro's etch. See Germanium, Silicon, and Gallium Arsenide.)
REF: Ibid.

MGGE-0002
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
Mg_2Ge, (111) cleaved wafers used in a study of photoconductivity. Specimens were lapped down to 0.2—0.4 mm; below this thickness material fractures. Authors state there is no known etch for this material (?). Also worked with Mg_2Si.
REF: Stella, A & Lynch, D W — *J Phys Chem Solids*, 25,1253(1965)
MGGE-0003: Morris, R G et al — *Phys Rev*, 109,1916(1958)
Mg_2Ge, single crystal specimens. Intrinsic material is n-type; dope with silver for p-type as semiconductor material. Band gap is 0.69 eV. Also worked with Mg_2Si.

MOLYBDENUM GERMANIDE ETCHANTS

MGGE-0001
ETCH NAME: Nitric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
(1) x .... HNO_3 (2) x .... H_2O_2

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DISCUSSION:

Mo_3Ge specimens, Mo_3Ge_2, Mo_2Ge_3, or alpha-$MoGe_2$ used in a general study of these materials. Both acids are rapid etchants. Fused carbonates and nitrates react violently. All of the compounds will resist non-oxidizing solutions.

REF: Brochure: Molybdenum, Climax Molybdenum Company (no date/number)

NIOBIUM GERMANIDE ETCHANTS

NBGE-0001

ETCH NAME: RF plasma
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... Ar

TIME:
TEMP:
GAS FLOW:
PRESSURE: 6 Pa
POWER: 200 V

DISCUSSION:

a-Nb_3Ge compound co-deposited by E-beam evaporation as an amorphous layer on sapphire blanks. Thickness of thin films was 80—100 μm, and they were patterned by standard photolithographic techniques. RF plasma etching is rapid with pure CF_4, but controllable with argon as an inert carrier gas.

REF: Kato, W — *Jpn J Appl Phys*, 23,1536(1984)

NBGE-0002

ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
x .... HAc

TIME:
TEMP:

DISCUSSION:

Nb_3Ge thin films grown on (100) germanium substrates by CVD in a study of high T^c values. Various solution concentrations were used, and will etch both the compound and germanium substrate.

REF: Suzuki, N et al — *Jpn J Appl Phys*, 23,991(1984)

NBGE-0003: Ohishima, S et al — *Jpn J Appl Phys*, 22,264(1983)

Nb_3Ge specimens fabricated by the Shock Sinter method for study of superconducting properties. Material is in space group A15.

TERBIUM COPPER GERMANIDE ETCHANTS

TBCG-0001

ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3

TIME:
TEMP: (2900°C growth)

DISCUSSION:

$TbCu_2Ge_2$ specimens. See discussion under HOCG-0001.

REF: Schobinger-Papamantellos, P et al — *J Phys Chem Solids*, 45,695(1984)

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VANADIUM GERMANIDE ETCHANTS

VGE-0001
ETCH NAME: Kalling's etch
TYPE: Acid, polish
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH
TIME: 10—60 sec
TEMP: RT
DISCUSSION:
V_3Ge and V_3Si arc melted, fabricated and used in a study of different metallic compounds. Solution used as a general removal and polishing etchant. See Cesium Platinide: CEPT-0001 for list of other compounds studied.
REF: Slepowronsky, M et al — *J Cryst Growth*, 65,293(1983)

PHYSICAL PROPERTIES OF GERMANIUM ARSENIDE, $GeAs_2$

Classification	Arsenide
Atomic numbers	32 & 33
Atomic weight	222.42
Melting point (°C)	>800
Boiling point (°C)	
Density (g/cm³)	
Hardness: (Mohs — scratch)	7
Crystal structure (Isometric — normal)	(100) cube
Color (solid)	Steel grey
Cleavage (cubic)	(001)

GERMANIUM ARSENIDE, GeAs

General: Does not occur as a natural metallic compound. Germanium is a trace element in certain sulfites, such as pyrite, FeS_2, and sphalerite, ZnS, obtained during the roasting and reduction process of these ores for their iron and zinc content. Germanite, $Cu_3(Fe,Ge)S_4$, and argyrodite, $4Ag_2S.GeS_2$ are the two known germanium minerals.

There has been no use of the compound in the metal industry to date, other than as an additive in solder alloys.

Technical Application: Germanium Arsenide is a IV—V compound semiconductor. It has been grown and evaluated as a single crystal for both etching and semiconductor characteristics, but has been of little use due to the preeminence of silicon and gallium arsenide.

Etching: H_2O_2, HNO_3, HF:HNO_3 mixtures; aqua regia; alkali.

GERMANIUM ARSENIDE ETCHANTS

GEAS-0001a
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... 20% NaOH
1 .... H_2O_2
TIME:
TEMP: RT

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DISCUSSION:
GeAs, (111) wafer. Cut dice used in an etch development study. The solution shown will etch GeAs at room temperature.
REF: Robbins, H & Schwartz, B — personal communication, 1958

GEAS-0001b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: Hot
COMPOSITION:
2 .... HCl
1 .... HNO_3
DISCUSSION:
GeAs, (111) wafers and cut dice. Solution etches slowly. See GEAS-0001a for additional discussion.
REF: Ibid.

GEAS-0001c
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:
GeAs, (111) wafers and dice. Solution etch reaction is moderate to vigorous. See GEAS-0001a for additional discussion.
REF: Ibid.

GEAS-0001d
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
(1) x .... 3% H_2O_2 (2) x ... 10% H_2O_2
DISCUSSION:
GeAs, (111) wafers and dice. Both concentrations showed little attack at room temperature. See GEAS-0001a for additional discussion.
REF: Ibid.

GEAS-0001e
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT or hot
COMPOSITION:
(1) x .... *HNO_3 (2) 1 .... *HNO_3 (3) 2 .... *HNO_3
2 .... H_2O 1 .... H_2O

*Yellow and red fuming nitric acids evaluated.

DISCUSSION:
GeAs, (111) wafers and dice. All three mixtures shown will react when used hot with moderate to vigorous reaction. Red fuming is the more vigorous. Standard concentration HNO_3, sometimes called White fuming nitric will not etch GeAs. (*Note:* HNO_3 concentrations are 70% (white fuming), 72% (yellow fuming), and 74% (red fuming).)
REF: Ibid.

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PHYSICAL PROPERTIES OF GERMANIUM NITRIDE, Ge_3N_4

Classification	Nitride
Atomic numbers	32 & 7
Atomic weight	273.83
Melting point (°C)	450 del.
Boiling point (°C)	
Density (g/cm^3)	
Refractive index (n =)	2.05
Hardness (Mohs — scratch)	6—7
Crystal structure (hexagonal — normal) alpha	(10$\bar{1}$0) prism
(isometric — normal) beta	(100) cube
Color (solid)	Clear/brownish
Cleavage (none — conchoidal fracture)	None

GERMANIUM NITRIDE, Ge_3N_4

General: Does not occur in nature as a compound. Nitrogen does not form metallic compounds though there are many mineral nitrates and nitrites of primary industrial interest as fertilizers.

There is no major use of this nitride in the metals industry, but surface nitridization is a standard process used for surface hardening and, if there is germanium present in an alloy, some germanium nitride will be formed.

Technical Application: Not used to any extent in Solid State processing to date, but under evaluation as a thin film coating for optical, dielectric, and surface passivation applications similar to other metal oxides and nitrides. Most metal oxides-nitrides form isomorphous series with 100% miscibility of the two compounds, and are studied in that regard. The Ge_3N_4 compound as a thin film has been evaluated for MIS device structures, but shows free Ge separation with temperature annealing such that it is not as stable as its silicon nitride counterpart.

Note that all oxides and nitrides do not show distinct cleavage, but are prone to conchoidal fracture common to all glasses. In most applications as thin films they are amorphous in structure, such as a-Ge_3N_4.

Etching: Soluble in HF, mixed acids and alkalies.

GERMANIUM NITRIDE ETCHANTS

GEN-0001
ETCH NAME:
TYPE: Acid, removal
TIME: 10—20 min
TEMP: Boiling
COMPOSITION:

18 g .... NaOH
5 g .... $KHC_8H_4O_4$
100 ml .... H_2O

DISCUSSION:

Ge_3N_4, and $Ge_3O_{1-x}N_x$. This etch was originally developed for silicon oxynitride. Substrates used were single crystal (111) Si and Ge wafers, quartz crystal AT-cut blanks, and alumina pressed powder blanks. Nitride deposit thickness ranged from 500 to 3500 Å with a nominal 2000 Å for study evaluations, and were grown by DC plasma sputter using a germanium bar in a nitrogen atmosphere with and without oxygen. This was an original developmental study of growing nitride and oxynitride thin films as passivation layers and

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etching masks. The solution shown was specifically developed for compatibility with KMER photo resist pattern processing. See Silicon Nitride section for additional information.
REF: Mann, J E & Walker, P — Electrochem Soc Spring Meet, Dallas, TX, May 1967

GEN-0002
ETCH NAME: Hydrofluoric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
(1) x .... HF, conc. (2) 1 .... HF
10 .... H_2O
DISCUSSION:
Ge_3N_4 and $Ge_3O_xN_y$ thin films DC plasma sputtered on silicon and germanium wafers of different orientations in a developmental deposition and etching study of nitrides and oxynitrides. Other materials studied were Si_3N_4; $Si_3O_xN_y$; and AlN. The dilute solution is more controllable for thin film photo resist lacquer patterning, and both were used for removal. See GEN-0001, and section on Silicon Nitride for additional data. Nitride color chart developed used a refractive index of n = 2.00.
REF: Walker, P — personal development, 1966

GEN-0003
ETCH NAME: Nitrogen — TIME:
TYPE: Gas, densification — TEMP:
COMPOSITION:
x .... N_2
DISCUSSION:
Ge_3N_4 thin films deposited on GaAs, (100) wafers used in fabricating MIS high frequency devices. Deposit nitride in Ar/N_2 at 50 W, and 1.8×10^{-2} Torr pressure at close to RT. Final structure was $Al/Ge_3N_4/GaAs(100)$. Annealing in H_2 produces leakage and nitride phase separation with free Ge. Nitrogen annealing increases density of nitride. Refractive index was n = 2.05.
REF: Chung, Y et al — *Thin Solid Films*, 103,193(1983)

PHYSICAL PROPERTIES OF GERMANIUM OXIDE, Ge_2O_3

Classification	Oxide
Atomic numbers	32 & 8
Atomic weight	104.60
Melting point (°C)	1086
Boiling point (°C)	
Density (g/cm^3)	6.24
Hardness (Mohs — scratch)	6—7
Crystal structure (tetragonal — normal)	(110) prism
Color (solid)	Clear/grayish
Cleavage (none — conchoidal fracture)	None

GERMANIUM OXIDE, Ge_2O_3

General: Does not occur in nature as an oxide compound, though it may appear as a very minor oxidation surface coating on the minerals germanite, $Cu_3(Fe,Ge)S_4$, and argyrodite, $4AgS.GeS_2$, but the oxide is not considered a mineral species. There is no major use in the metals industry. The soluble GeO_2 variety has been used as a pigment and an additive to glass.

Technical Application: No major use in Solid State processing at the present time. In

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fabricating germanium devices the oxides are considered detrimental to electrical characteristics, such that they are removed as native oxides, prior to metallization, diffusion, etc.

As GeO_2 the material has been grown and studied in wafer form in a general glass development study, and deposited on germanium as a thin film for optical properties characterization. The Ge_2O_3 form has been sputter deposited, then converted to the nitride in a study as an isomorphous series. The GeO and Ge_2O_3 forms are insoluble in water; GeO_2 has partial solubility.

Etching: Varies with compound formula: water, acids, alkalies.

GERMANIUM OXIDE ETCHANTS

GEO-0001
ETCH NAME: Methyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... MeOH
DISCUSSION:
GeO_2, as glass blanks used in a study of glass development. Germanium powder was fired in an air furnace at 1200 to 1690°C. Core sections were cut from the glass mass as grown, then cut into blank sections and polished with 400-grit abrasive in a petroleum oil carrier, and rinsed in MeOH. Follow with annealing at 230°C, 30 min.
REF:
TIME:
TEMP: RT

GEO-0002
ETCH NAME: Oxygen
TYPE: Gas, forming
COMPOSITION:
x .... O_2
x .... pressure
DISCUSSION:
GeO_2, grown as thin films on Ge, (111) and other oriented wafers. Growth rate is greatest on the (111). GeO_2 refractive index was maximum n = 2.7 at 340 atm; at 1 atm growth pressure n = 1.6 to 1.9.
REF: Crisman, E E et al — *J Electrochem Soc*, 129,1845(1982)
TIME:
TEMP: 500—550°C
PRESSURE: 680 atm max.

GEO-0003
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... HNO_3
20 .... HAc
DISCUSSION:
Ge_2O_3, DC sputtered thin films with conversion to Ge_3N_4 as an isomorphous series of compounds with variable oxygen content. This was part of original development of DC plasma sputtered thin films and a general study of such films. Also studied SiO_2 with conversion to Si_3N_4, and the Al_2O_3 to AlN, all three oxides/nitrides as ismorphous series. Deposits were on (111) germanium wafers from a germanium bar source. A silicon bar was used with (111) silicon substrates, and an aluminum bar with both silicon and germanium wafers. The solution shown was used as a general etch on all materials and films.
REF: Walker, P & Mann, J E — development work, 1964
TIME:
TEMP: RT

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PHYSICAL PROPERTIES OF GERMANIUM SELENIDE, Ge_2Se_3

Classification	Selenide
Atomic numbers	32 & 34
Atomic weight	181.08
Melting point (°C)	900
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	4—5
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Clear/grayish
Cleavage (cubic)	(001)

GERMANIUM SELENIDE, Ge_2Se_3

General: Does not occur as a natural metallic compound though there are several other minerals as metallic selenides and tellurides. The crystal structure, and hardness shown under physical properties, above, are based on the mineral guanajuatite, Bi_2Se_3.

There has been no use of germanium selenide in the metals industry, to date, though there is possible application in glass making.

Technical Application: The compound is currently under development in Solid State processing as an amorphous thin film for compound characterization. It has been evaporated as a variable Ge_xSe_{1-x} amorphous film, and is a probable IV—VI compound semiconductor.

Etching: Mixed acids, alkalies. Dry chemical etching (DCE) with ionized gases.

GERMANIUM SELENIDE ETCHANTS

GESE-0001a

ETCH NAME:
TYPE: Ionized gas, removal
COMPOSITION:
(1) x .... CF_4
(2) x .... SF_6

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:

Ge_xSe_{x-1} thin films deposited in a structure study. Evaporated layered structures of Ag/Ge_xSe_y and Ag/Se/Ge_xSe_y. Silver was evaporated and used as an etch mask as it will not etch in CF_4, but will etch with SF_6 after photo resist patterning. The CF_4 will etch both selenium and the selenide.

REF: Huggett, P G & Iehmann, H W — *J Electron Mater*, 14,201(1985)

GESE-0001b

ETCH NAME:
TYPE: Alkali, removal
COMPOSITION:
x .... NaOH
x .... Na_2S

TIME:
TEMP:

DISCUSSION:

Ge_xSe_x-1 thin films with silver evaporated as a mask: Ag/Ge_xSe_y and Ag/Se/Ge_xSe_y used in a structure study. Silver will not etch in the solution shown, but germanium dissolves rapidly and selenium slowly.

REF: Ibid.

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PHYSICAL PROPERTIES OF GERMANIUM SULFIDE, GeS

Classification	Sulfide
Atomic numbers	32 & 16
Atomic weight	104.65
Melting point (°C)	530
Boiling point (°C)	
Density (g/cm^3)	3.3—4.0
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — rhombohedral)	(10$\bar{1}$1) rhomb
Color (solid)	Black
Cleavage (rhombohedral)	r(10$\bar{1}$1)

GERMANIUM SULFIDE, GeS

General: Does not occur as a natural compound though there are a number of other metal sulfide minerals.

No use in the metals industry to date. It has application as a black pigment in paints, glass and enamels.

Technical Application: No major use in Solid State processing to date, but is under current morphological study. Material was grown as single crystal platelets by sublimation, and is said to have good (100) cleavage, which would mean the compound as-grown was isometric — normal (cubic) structure rather than hexagonal system. Platelets were doped in the study as a possible IV—VI compound semiconductor. There also is a GeS_2 structure form.

Etching: Mixed acids, alkalies, and NH_4OH.

GERMANIUM SULFIDE ETCHANTS

GES-0001
ETCH NAME: Ammonium hydroxide — TIME:
TYPE: Base, cleaning/removal — TEMP: RT
COMPOSITION:
x .... NH_4OH
DISCUSSION:

GeS single crystal platelets grown by sublimation, and doped with either silver or phosphorus, p- and n-type, respectively. Authors say that platelets are easily cleaved on (100). Material was used in a general morphological study.
REF: Bhatia, K L et al — *J Phys Chem Solids*, 45,1189(1984)

PHYSICAL PROPERTIES OF GERMANIUM TELLURIDE, GeTe

Classification	Telluride
Atomic numbers	32 & 52
Atomic weight	200.20
Melting point (°C)	>1000
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey/black
Cleavage (cubic)	(001)

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GERMANIUM TELLURIDE, GeTe

General: Does not occur as a natural compound though there are a number of other minerals as metallic tellurides and selenides.

There has been no use of the compound in the metals industry to date, other than as a compound semiconductor.

Technical Application: Not used in Solid State processing to any extent, to date. The material has been evaluated as a single crystal IV—VI compound semiconductor with the development of etching solutions, and for general morphological study. More recently, it has been evaporated as a thin film in studying the Tc values and variation of the tellurium fraction.

Etching: Mixed acids of HF:HNO_3:HAc/H_2O, and HNO_3:chromates.

GERMANIUM TELLURIDE ETCHANTS

GETE-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
GeTe as single crystal specimens evaluated for Tc values and change with variation of tellurium fraction.
REF:

PHYSICAL PROPERTIES OF GOLD, Au

Classification	Transition metal
Atomic number	79
Atomic weight	196.9
Melting point (°C)	1063
Boiling point (°C)	2808 (2966)
Density (g/cm^3)	19.3
Thermal conductance (cal/sec)(cm^2)(°C/cm) 0°C	0.743
Specific heat (cal/g) 25°C	0.0312
Latent heat of fusion (cal/g)	14.95
Heat of fusion (k-cal/g-atom)	3.03
Heat of vaporization (k-cal/g-atom)	81.8
Atomic volume (W/D)	10.2
1st ionization energy (K-cal/g-mole)	213
1st ionization potential (eV)	9.223
Electronegativity (Pauling's)	2.4
Covalent radius (angstroms)	1.34
Ionic radius (angstroms)	1.37 (Au^{+1})
Thermal expansion ($\times 10^{-6}$) 0—100°C	14.16
Electrical resistivity (micro ohms-cm) °C	2.125
20°C	2.44
Yield point (psi)	500
Poisson ratio	0.42
Young's modulus (psi $\times 10^6$) — 60% cold worked)	11.2
Tensile strength (psi — annealed)	18,000

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Hall constant (ohms/cm/gauss $\times 10^{-13}$)	6.87
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.15
Cross section (barns)	98.8
Hardness (Mohs — scratch)	2/5—3
(Vicker's — kgf/mm^2)	25
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Yellow gold
(colloidal suspension)	Deep ruby red
Cleavage (none — hackly fracture)	None

GOLD, Au

General: Occurs as a native element and is the chief ore of gold. Ordinary gold contains up to 16% silver and varies in color as yellow- to white-gold depending upon silver content. The purest gold, "sponge gold", comes from Australia and is 99.91% Au:0.09% Ag. Electrum, pale yellow to white, contains 36% silver as a 1:1 mixture and varies from 1.5:1, 2:1 to 2.5:1 and 3:1 (15.1% silver). These mixtures can be differentiated by their specific gravity (density). Orange-red varieties contain up to 20% copper, and the "black-gold" of Australia contains bismuth; also rhodium. Gold is fusible in the Bunsen burner flame at 1100°C, but is not acted upon by fluxes and is insoluble in any single acid. It can be etched in aqua regia, but etching is incomplete if more than 20% silver is present. Gold is widely distributed in the earth's crust and can be extracted from sea water, but is primarily found in quartz veins or alluvial placer deposits in minable quantities. Hydraulic washing of placer deposits is the main method of separation and is used in California, Alaska, Russia, Brazil, Australia, etc. The "quartz reefs" of Australia and Africa are representative of vein mining. The Coeur d'Alene and Randsberg districts — Idaho and California, respectively — are mined for both gold and silver.

Gold was one of the elements known to ancient man and, because of its ductility and malleability — workability — as well as its resistance to acids and atmospheres, has had major use. Initial use was for objets d'art, jewelry, as gold leaf, in barter exchange, and finally, for its monetary value. Today, it is the world-wide base for currency value as set against the U.S. dollar.

Commercially, there are many gold alloys which are measured by carat weighed from 8 to 24, the latter equivalent to pure gold. One carat is approximately 205 milligrams. Depending upon the additive (silver, nickel, zinc, copper, even brass) gold alloys also are classified by color, as white, yellow, grey, red, purple, blue, and green.

Industrial uses of gold are primarily for protective surface coatings to resist corrosion and are applied to most of the known metals and their alloys for this purpose. It can be as gold-cladding, a thin foil of gold being heat and pressure formed on a metal surface; by evaporation in vacuum; or by electrolytic plating. The latter is the more widely used for general surface coating, as first, a nickel flash, followed by a thin gold plating of about 50 micro-inches (μ″). The nickel undercoat may be replaced by chromium, copper, or other metals and is used as a tie-down layer for gold, particularly on polished surfaces. Thicknesses of the gold/nickel vary by application requirements with a minimum amount of gold thickness due to cost. Gold plating baths are either acid or cyanide with gold chloride salts and other metal salts for coloring. The cyanide solutions are more widely used and supplied commercially in 1 to 2 oz Au/gallon solutions. High purity soft gold coatings are 5 9's pure, but decorative or protective coatings contain other metals as hardening agents.

Gold is still widely used for jewelry, with 18 carat being a general standard for rings, earrings, and bracelets. It also is used for decorative purposes on a wide variety of materials in several pleasing forms: stippled, marbleized, antique, royal, and brushed, and as fired onto glass, ceramics, or other metals. Today, brass is used as a low-cost replacement.

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Gold can be reduced to the colloidal state in liquid suspension as a ruby-red solution. It was widely used during the Middle Ages in Europe for staining window glass as gold is unaffected by sunlight and will not fade.

Highly polished gold surfaces have been used as mirrors since ancient times though they have been largely replaced by silver and, today, by aluminum or nickel evaporated on glass.

Technical Application: As a diffusion element in silicon, gold can act as both a donor or acceptor and is used to control electron mobility, T_{rr}, to produce fast switching devices. Its primary use is an evaporated or sputtered metallized electrical contact on semiconductor or similar devices and as a bonding wire or strap in device, circuit substrates and package assemblies. This includes metal thin films or wire on semiconductor devices, proper and discrete components such as capacitors, resistors, and coils. Circuit substrates include pressed powder alumina, beryllia; fused quartz and sapphire; and single crystal quartz and sapphire; in addition to contact pins and package parts. Many of the substrates and parts are gold plated as plating is much lower in cost than evaporation or sputtering.

Pure gold and gold/silver single crystal ingots have been grown and studied for morphological and defect data. One extensive study has been made with single crystals of gold/aluminum as there is major concern and interest in the reaction phenomena between gold and aluminum with regard to device stability.

CAUTION: Gold in contact with aluminum produces what is called "Purple Plague". Several of the Au_xAl_y alloys are brilliant purple in color, and extremely brittle. Such reaction can destroy the electrical contacts of semiconductor devices under operational load as well as during accelerated temperature life tests. Under operational load, the reaction may occur over a period of several months after the device has been assembled with eventual failure in the field.

Etching: Inert in single acids, aqua regia, cyanides, and iodine etchants.

GOLD ETCHANTS

AU-0001a
ETCH NAME: Aqua regia
TYPE: Acid, removal
COMPOSITION:
3 .... HCl
1 .... HNO_3

TIME: Variable
TEMP: RT & 35°C boiling
RATE: 10—15 μm/min @ RT
25—50 μm/min @ 35°C

DISCUSSION:

Au, thin films and specimens. Aqua regia is the oldest known etch for gold dating back to the Middle Ages in Europe. Mix in an open container and allow solution to sit until gas evolution reduces and solution turns a deep transparent red-yellowish color. Used as a general etch for gold. In conjunction with photo resist patterning of thin films used to etch device structures and circuits on substrates. It is a rapid etch and is not as widely used for patterning as are other solutions. (*Note:* Do not store in a closed container due to continuing gas evolution.)

REF: Missel, L I & Glang, R — *Handbook of Thin Film Technology,* McGraw-Hill, New York, 1970

AU-0002: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970

AU-0003a: Walker, P — personal application, 1957—85

Au, thin films and specimens. After gold evaporation on silicon wafers and temperature drive-in, solution used at RT to remove residual gold from surfaces. Solution used to shape or clean gold as a cut pre-form or wire alloy contact on germanium, silicon, and compound semiconductor devices. With evaporated and E-beam sputtered gold thin films on both

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devices and substrates in conjunction with photolithographic patterning. Solution also used as a heavy metal removal etch for cleaning of silicon dioxide and nitride or wafer surfaces prior to diffusion, epitaxy, or metallization. As the cleaning solution of quartz tubing used for diffusion and epitaxy, in the processing of quartz radio frequency blanks with gold electrodes, and in the general cleaning of vacuum internal fixturing. After etching with aqua regia, follow with heavy DI water washing; dry under IR lamps, or with nitrogen blow-off.
AU-0004: Nichols, D R — *Solid State Technol,* December 1979

Au, evaporation film build-up in vacuum evaporators and on fixturing. Etch remove by soaking parts in aqua regia and follow with water washing and drying.

AU-0019
ETCH NAME:
TIME:
TYPE: Thermal, structure
TEMP: to 360°C
COMPOSITION:
x .... heat
DISCUSSION:

Au, thin films deposited on soda-lime glass which was first cleaned with ultrasonic DI water. 300 Å of gold evaporated from a tungsten boat. Gold was polycrystalline with grains up to 500 Å long and preferred (111) orientation parallel to the substrate surface. In vacuum, 1 h at 360°C developed circular pin-holes and hillocks. After 10 min at 630°C, in air, developed either (1) island agglomerates or (2) rod- and bead-like structures to 500 Å thick with some gold color bleached white due to small particle light scattering. Author recommends that for good gold films temperature should be under 630°C. (*Note:* The bleaching effect has been observed on thin films of gold, tungsten, and nickel deposited on alumina, fused quartz and OFHC copper after being subjected to heat treatment up to 400°C on a hot plate in air.)
REF: Zito, R R — *Thin Solid Films,* 114,241(1984)

AU-0003b
ETCH NAME: Aqua regia, dilute
TIME: 5—15 sec
TYPE: Acid, cleaning
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
20—50 .... H_2O
DISCUSSION:

Au, slugs or wire used for evaporation and sputter metallization. Degrease with TCE, RT; wash in DI H_2O; then rinse in MeOH and dry. Etch clean slugs and wire in solution shown, water rinse and hold under MeOH until placed in the vacuum system. After gluing or alloy mounting gold sheet on a sputter target base, dip etch clean, then water wash and wipe with MeOH with a final bake in air oven at 150°C for 8—10 h before installation in the sputter system. Also used with photo resist lacquer pattern etching of thin film gold. (See AU-0003.)
REF: Ibid.

AU-0017
ETCH NAME: Chrome regia
TIME: Variable
TYPE: Acid, removal/preferential
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... 10—20% CrO_3

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DISCUSSION:

Au, thin films and specimens. Used as a general etch for gold similar to aqua regia. On single crystal gold and gold alloys is a preferential etch.

REF: ASTM Pamphlet E701-70

AU-0018

ETCH NAME: Selenic acid — TIME:

TYPE: Acid, removal — TEMP: Hot

COMPOSITION:

x .... H_2SeO_4

DISCUSSION:

Au specimens. Selenic acid is a slow, general etch for gold but not widely used due, in part, to the toxicity of selenium.

REF: Hodgman, C D — *Handbook of Chemistry and Physics,* 27th ed, Chemical Rubber Co, Cleveland, OH, 1943, 588

AU-0003c

ETCH NAME: Potassium cyanide — TIME:

TYPE: Acid, removal — TEMP: RT

COMPOSITION:

x .... KCN

x .... H_2O

DISCUSSION:

Au specimens and thin films. Various concentrations of KCN will dissolve gold. Solutions have been used to strip gold from alumina, quartz, sapphire substrates and metal assembly parts used in semiconductor device assemblies. Also used to strip gold from semiconductor wafers.

REF: Ibid.

AU-0003d

ETCH NAME: Tri-iodide — TIME: 1—10 min

TYPE: Halogen, removal — TEMP: Hot (70°C)

COMPOSITION:

400 g .... KI

200 g .... I_2

1000 ml .... H_2O

DISCUSSION:

Au, specimens and thin films. Constituent quantities can vary and include methyl alcohol to aid in dissolving iodine. Solution is mixed in 5000 ml Pyrex beakers on a magnetic stirring hot plate, requiring up to 1 h for complete mixing unless 100 ml MeOH is added. A single 250 ml beaker of solution can be used hot (40—60°C) for hours to days in processing photo resist patterned thin films in fabricating circuit substrates before solution shows marked depletion and slow reactivity. This is one of the most widely used etchants for gold thin film processing as it is sufficiently slow and controllable for etching fine-line definition (to less than 1 μm line widths) and, when used at about 60°C, will remove 2000 Å of gold in approximately 45 sec. Solutions are nontoxic, as are cyanides, and residual iodine can be removed by washing surfaces with methanol. (*Note:* Tri-iodide solutions with the ethanol replacing water are called tincture of iodine, which is a major medical antiseptic.)

REF: Ibid.

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AU-0008
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
8 g .... KCN
5 g .... $AuCl_3$
4 g .... $K2CO_3$
100 ml .... H_2O
TIME: 4 min
TEMP: RT
ANODE:
CATHODE:
POWER: 10 V
DISCUSSION:
Au foil. Used to polish specimens prior to 8 KeV Ar^+ ion bombardment cleaning. Also used zinc and aluminum with other etchants.
REF: Cunningham, R L et al — *J Appl Phys*, 31,839(1960)

AU-0009
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
100 g .... $K_2Cr_2O_7$
1000 ml .... H_2SO_4
TIME: 2 min
TEMP: 120°C
ANODE: Au
CATHODE:
POWER:
DISCUSSION:
Au specimens used in a study of the cleaning of metal surfaces. (*Note:* This is similar to the standard "glass cleaner" etch used at RT as a wet chemical etching (WCE) solution on laboratory glassware.)
REF: Patzer, L et al — *J Electrochem Soc*, 118,451(1971)

AU-0010
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
5 g .... $(NH_4)_2S_2O_8$
50 ml .... NH_3
100 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
Au, (111) and (100) single crystal blanks. Solution is a preferential etch on these surfaces.
REF: Bowles, J S & Boas W — *J Inst Met*, 501(1947—48)
AU-0014: Gilbertson, L I & Fortner, O W — *Trans Electrochem Soc*, 81,199(1942)
Au, (111) and (100) oriented specimens. Solution shown to be preferential on both orientations.

AU-0011
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
15 ml .... HF
15 ml .... HNO_3
45 ml .... HCl
25 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
Au, (111) wafers and other orientations. Etch pits showed that surfaces were within 1° of orientation as verified by X-ray and Laue photographs.
REF: de Sy, A & Haemiers, H — *Aluminum*, 24,96(1942)

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AU-0012
ETCH NAME: Heat
TYPE: Heat, oxide removal
COMPOSITION:
x .... heat
TIME:
TEMP: 200°C
DISCUSSION:
Au specimens used in a study of photoelectric yield in the vacuum ultraviolet. Heat specimens in vacuum to remove traces of Au_2O_2, Au_2O_3 and Au_2O. Gold oxides are unstable, very thin, and all decompose under 250°C. (*Note:* Gold is considered as inert to oxidation under normal processing conditions but, as shown, oxides can occur. Very spotted and usually under 100—200 Å thick.)
REF: Walker, W C et al — *J Appl Phys,* 26,1366(1955)

AU-0013
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:
Au, single crystal spheres formed by heating the tip of a single crystal wire. Wire was 1—2 mm diameter; spheres, 1—3 mm diameter. Used as electrodes in electrocrystallization studies. Other materials studied were Ag and Cu.
REF: Roe, D K & Gerisder, H — *J Electrochem Soc,* 110,350(1963)

AU-0015
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
3 .... HNO_3
2 .... HAc
TIME:
TEMP:
DISCUSSION:
Au, as ^{199}Au diffused into silicon wafers in a gold diffusion study. Solution used for controlled removal as a form of step-etching to determine the radioactive gold concentration, and crystallographic location of diffused gold.
REF: Spokel, G J & Fairfield, J M — *J Electrochem Soc,* 112,200(1965)

AU-0016
ETCH NAME: CP4
TYPE: Acid, removal
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... HAc
0.6 .... Br_2
TIME:
TEMP:
DISCUSSION:
Au, diffused into silicon in a study of lifetime and capture cross-section. Solution used as a polish etch and step-removal etch in determining depth of gold penetration.
REF: Davis, W D — *Phys Rev,* 114,1006(1959)

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AU-0017
ETCH NAME:
TYPE: Metal, diffusion
COMPOSITION:
x .... Fe, Ni or Co
TIME: Variable
TEMP: 200°C+
DISCUSSION:

Au, thin film deposited by CVD to 300 nm thickness on top of previously deposited Fe, Ni, or Co thin films using fused quartz substrates. Assemblies were then heat treated in air. Borosilicate glass was first used for substrates, but sodium from the glass diffused up into the gold and affected results. All three metals diffuse up through the gold film to the surface by solid-solid diffusion, and showed oxidation products on the gold surfaces. (*Note:* Similar solid-solid diffusion from devices and substrates have been observed with tungsten, zinc from brass, ti-tungsten, cobalt, nickel, and is a basic problem in accelerated life test, and long-term device failure under operating load.)
REF: Swartz, W E et al — *Thin Solid Films,* 114,349(1984)
AU-0018: Parmigiani, F et al — *J Appl Phys,* 57,2524(1985)

Au, thin films 20—200 Å thick deposited on glass substrates used in a study of the optical properties of gold clusters. For TEM study replication, films were prepared by coating the gold surface with a polymer resin (Technevit 4071) dissolved in acetone, the resin then coated with carbon. The replicated carbon thin film can be removed from the glass for TEM study by thermal shock and by dissolving resin in acetone.

AU-0019
ETCH NAME: Water
TYPE: Acid, preparation
COMPOSITION:
x .... H_2O, jet
TIME:
TEMP:
DISCUSSION:

Au, (100) single crystal thin films deposited on NaCl, (100) substrates. A water jet was used to cut a 0.5 mm diameter hole through the sodium chloride from the back side to expose the gold thin film in a study of gold mechanical properties.
REF: Carlin, A & Walker, W P — *J Appl Phys,* 31,2135(1960)

AU-0022
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
67.5 g .... KCN
15 g .... $KFe_2(CN_3)_6$
15 g .... Rochelle salt
19.5 g .... H_3PO_4
2.5 g .... $AgNO_3$
TIME:
TEMP:
ANODE: Au
CATHODE: SS
POWER: 4 V
DISCUSSION:

Au specimens. Solution used to electropolish both gold and silver.
REF: Ruff, A W & Ives, L K — *Acta Metall,* 15,189(1967)

AU-0023
ETCH NAME: Nitric acid
TYPE: Acid, float-off
COMPOSITION:
x .... HNO_3
x .... H_2O
TIME:
TEMP:

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DISCUSSION:

Au, thin films deposited on (0001) muscovite mica substrates and used for structure study of the film. After evaporation, the gold film was removed from the mica with the acid shown using the float-off technique for film study by TEM. See under Mica: MI-0002.
REF: Chopea, K I — *J Appl Phys*, 37,2049(1960)

AU-0024
ETCH NAME: Air
TYPE: Gas, drying
TIME: $^1/_2$—4 h
TEMP: 125°C
COMPOSITION:

x .... air, hot (oven)

DISCUSSION:

Au, thin films evaporated on alumina substrates (2 and 4 μm surface finish) as an Au/TiW(10%) Ti) multilayer films used in a study of blisters occurring with subsequent electrolytic Au up-plating when films are then subjected to a 400°C, 1—5 min soak on a hot plate in air. This heat treatment was evaluated after the following surface treatments: (1) 50% HCl dip, DI H_2O rinse; (2) DI H_2O rinse, only; (3) gold evaporated film, dry, without any further treatment; and (4) surface dried in an air oven, all prior to gold plating. HCl dip gave worst case, large blisters; oven drying showed many small blisters, and did not eliminate blisters. Blistering considered to be due to presence of TiW as the Au/Cr, Au/Ni, or Au/Cu/Mo metallized thin film systems do not blister under similar processing conditions. It also was noted that, after HCl cleaning then gold up-plating, a black, acidic liquid oozed upward onto surfaces at some gold grain boundary locations.
REF: Walker, P & Valardi, N — personal development, 1985

AU-0001b
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:

x .... NaCN
x .... H_2O_2

DISCUSSION:

Au, thin film deposits on silicon wafers. Solution shown as a general removal etch.
REF: Ibid.

AU-0020a
ETCH NAME:
TYPE: Halogen, removal
TIME: 2—3 sec
TEMP: RT
RATE: See discussion
COMPOSITION:

7 g .... KI
25 g .... Br_2
100 ml .... H_2O

DISCUSSION:

Au, thin films. Removal rate for 1000 Å thick film is 2—3 sec. Removal rate for 2500 Å thick film is 30—35 sec.
REF: Bahl, S K & Leach, G L — U.S. Patent 4,190,489, 1980 (Mead Corp.)

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AU-0020b
ETCH NAME:
TYPE: Halogen, removal
COMPOSITION:
18 g .... NaBr
2 g .... Br_2
100 ml .... H_2O
TIME:
TEMP: RT
RATE: See discussion
DISCUSSION:
Au, thin film deposited on glass to 2000 Å thick. Removal time was 30—45 sec.
REF: Ibid.

AU-0020c
ETCH NAME:
TYPE: Halogen, removal
COMPOSITION:
12 g .... KBr
8 g .... Br_2
100 ml .... H_2O
TIME:
TEMP: RT
RATE: See discussion
DISCUSSION:
Au, thin films deposited on glass to 2000 Å thick. After etching, rinse in water. Removal time is 15 sec.
REF: Ibid.

AU-0021
ETCH NAME: Tri-iodine
TYPE: Halogen, removal/pattern
COMPOSITION:
400 g .... I_2
100 g .... KI
400 ml .... H_2O
TIME:
TEMP: 55°C
RATE: 1270 Å/sec
DISCUSSION:
Au, thin film deposits as a multilayer: Au/Ni/Au/TiW/Si(100) substrate or on a gallium arsenide, (100) substrate. Metals sputter evaporated and the top gold surface may be up-plated. Use solution to etch remove Au/Ni/Au layers with time depending on total thickness. Remove from etch and DI water rinse. Continue etching in 1—2 sec dip etch steps to remove any remaining gold traces. Remove TiW with H_2O_2, RT, 6—8 min with a removal rate of 20—30 micro-inches (μ")/min. (See AU-0002c with regard to tungsten oxides on surfaces after etching.)
REF: LaRusso, T — private communication, 1985 (MRC Corp.)

AU-0031
ETCH NAME:
TYPE: Abrasive, polish
COMPOSITION:
x .... emery
TIME:
TEMP: RT
DISCUSSION:
Au, as single crystal blanks. Surfaces mechanically lap polished with emery #2 down to 3/0. Also polished with Buehler #1551 A/B compound in oil on a glass plate. Study was to obtain pressure derivatives of the elastic constants of Zn, Ag, and Cu to 10,000 bars pressure. Materials were etched, but no solution shown.
REF: Daniels, W B & Smith, C S — *Phys Rev*, 111,713(1958)

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AU-0032
ETCH NAME: Pulse plating
TYPE: Gold, plating
COMPOSITION:
75 g .... $(NH_4)_2HC_6H_5O_7$
75 g .... $(NH_4)_2SO_4$
20 g .... $KAu(CN)_2$
1000 ml .... H_2O for pH 5.5—6.0
TIME: 0.9 ms ON — 9 ms OFF
TEMP: 65°C
ANODE: Steel mesh
CATHODE: Alumina
POWER: 0.5 mA/cm²
DISCUSSION:

Au, thin films pulse plated on alumina blanks with 1 μ" finish; grain size of substrates affect gold grain size. E-beam evaporate of metal layers was for the following thicknesses: 750 Å Ti; 3000 Å Pd: 25,000 Å Cu on alumina prior to DC or AC pulse plating of 2000—3000 Å Au. Pulse plating produces higher density, finer grained gold films than straight DC.

REF: Rehrig, D I — *Plating*, January 1974, 43

AU-0033: Olson, R — *Prod Finish*, April 1976

Au, thin films pulse plated with a pulsed rectifier power supply, and pulsed plater system. Pulse 10—75 μsec at 200—5000 Hz frequency with square wave use 1 A average to 500 A (2, 5 to 165 peaks). Article shows effects of gold plating on surfaces of nickel, silver, copper, and Pb/Sn materials.

AU-0036: Mentone, P F — *Prod Finish*, April 1973

Au, pulse plated for fine grain size, and to reduce porocity. A 50 μ" thickness is equivalent to 100 μ" of DC plating with regard to corrosion stability. Chrome pulsed plating improves coverage and hardness of the gold. The finer grains of Ni:Fe alloys gives more uniform magnetic properties.

AU-0034a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
50 ml .... HCl
25 ml .... EOH
250 ml .... glycerin
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Au, thin films plated from a gold cyanide/phosphate bath. Gold plated on copper substrates with substrate dissolved away with $1HNO_3$:$1H_2O$ as a float-off method to obtain the gold film for TEM study. Gold film electropolished and thinned in solution shown small thinned thru-holes in film were due to voids in the deposited film. Films dissolved in aqua regia ($3HCl$:$1HNO_3$) to collect particles of Au(CN) as nonmetallic inclusions, and requires rapid water quench, as particles are soluble in the acid mixture. CoHG films have higher Au(CN) crystal residue than AFHG films, and soft sold films have none. Soft gold deposited at 70°C, and Au(CN) co-deposition with gold is temperature dependent.

REF: Nakahara, S & Okinaka, Y — *J Electrochem Soc.*, 128,264(1981)

AU-0034b
ETCH NAME: Gold plating
TYPE: Metal, plating
COMPOSITION:
44 g .... $KAu(CN)_2$
100 g .... KH_2PO_4
28 g .... KOH
1000 ml .... H_2O
TIME:
TEMP: 40°C
ANODE: Ti w/RuO_2-TiO_2 coating
CATHODE: ST w/Cu sheet wrapping
POWER: 250 mA/cm²

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DISCUSSION:

Au, as hard gold (HG) coatings on copper substrates with a $CoSO_4$ additive for to solution shown for hardening. CoHG gold evaluated against no additive solutions as AFHG films. Grain size: (1) CoHG; 225—275 μm; AFHG: 250—750 μm; (3) soft gold: 1—2 μm. Gold films etch thinned and removed from copper for TEM study, to include presences of Au(CN) nonmetallic crystal contamination in films.

REF: Ibid.

AU-0035: Okinaka, Y & Wolowodiuk, O — *J Electrochem Soc,* 128,288(1981)

Au, thin films plated as CoHG and AFHG hard gold. A study of Au(111) type $Au(CN)_4$ to Au(1) and $Au(CN)_2$ nonmetallic crystal within films. Both AU-0034 and this reference used cylinder electrodes, with cathode rotating, and anode stationary or rotating. A 2.5 μm gold thickness was deposited in 16 min.

AU-0037: Weisberg, A M — Technic Inc., Providence, RI, 1976

Au, thin film plating as soft vs. hard gold. Describes shelf life, and Knoop hardness as related to product usage time of CoAu, NiAu, AgAu, and pure 24 carat gold. Different plating solutions available shown in this brochure.

AU-0025

ETCH NAME: Argon

TYPE: Ionized gas, cutting

COMPOSITION:

x .... Ar^+ ions

TIME:

TEMP:

GAS FLOW:

PRESSURE:

POWER:

RATE: 1 Å/sec

DISCUSSION:

Au, polycrystalline specimens and diffused specimens. Argon used to sputter section cut specimens. Grain boundary areas etched faster during the argon cutting. Ionized argon also used to section iron alloys. Rate shown was for a 0.5 μm cut width.

REF: Perkins, R A — *J Vac Sci Technol,* 13,5(1976)

AU-0026

ETCH NAME: Water

TYPE: Acid, float-off

COMPOSITION:

x .... H_2O

TIME:

TEMP: RT

DISCUSSION:

Au, thin films deposited on (100) NaCl substrates in a study of gold structure. Evaporated at 300°C the gold film was (100) oriented. Evaporated at 150°C gold film was crystalline with random grain orientation. Films removed from sodium chloride by liquefying the salt surface with water for film float-off and TEM microscope study. Tensile properties of thin films studied.

REF: Neugebauer, C A — *J Appl Phys,* 31,1096(1960)

AU-0027

ETCH NAME: Heat

TYPE: Thermal, preferential

COMPOSITION:

x .... heat

TIME:

TEMP:

DISCUSSION:

Au thin films. Deposit studied for the influence of oxidation and reducing atmosphere treatments on vacancy clusters in gold. Gold surfaces were preferentially etched after treatments, but solution not shown.

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REF: Segall, R L & Clarebrough, L M — *Phil Mag*, 8,65(1964)
AU-0028: Silcox, J & Hirsch, P B — *Phil Mag*, 4,72(1959)

Au thin films. Reference for gold etch used in AU-0027. Direct quenching of gold will to develop defects.

AU-0030: Pashley, D W — *Phil Mag*, 4,324(1959)

Au evaporated gold thin films. Observation of dislocations in the films.

GOLD ALLOYS, AuM_x

General: Occurs as native compounds when gold is amalgamated with other element metals, such as silver. The latter is called electrum, $AuAg_x$.

Refined, high purity gold, 5 9's pure (99.999%), is used for contact wires and metallized pads in Solid State semiconductor device fabrication and assembly, but is too soft for general application and use in industry. For commercial applications there are many artificially mixed gold alloys and/or gold plating baths that use other metals or metal salts to improve the hardness of a surface coating or produce a specific color.

In the general formula shown above, AuM_x M = Ag, Cu, Ni, Pt, Pd, Ge, Sn, Cd, In, Fe, Zn, etc., as metal additives, alone, or in combination.

Many of the Au:Ag:Cu mixtures are used in jewelry with the weight measured by carat. Some of the variations by carat and use are shown below:

Carat	Name	Formula	Remarks
24	Pure gold	Au	For any given carat value, the amount of gold and other metals can vary.
22	Dental	92Au:9Ag:3.1Cu	
22	Jewelry	91.66Au:4.16Ag:16Cu	
20	Jewelry	84Au:8.3-11Ag:6—8.3Cu	18 carat gold is a general jewelry standard. Will vary in color as silver, copper, or other metal additives are used in the mixtures.
18	Jewelry	75Au:10-20Ag:5—15Cu	
16	Solder	75Au:17Ag:8.3Cu	
16	Jewelry	67Au:6.6-26Ag:8—27Cu	
15	Jewelry	62Au:11Ag:13Cu	
14	Jewelry	58Au:4-28Ag:14—28Cu	
12	Solder	50Au:15Ag:35Cu	

Some other special gold alloys are

Formula	Name
70Au:21Al	Roberts-Austen purple gold
80Au:20Pd	Palau
60Au:40Pt	White gold (platinum)
75—85Au:8—10Ni:2—9Zn	White gold
75Au:25Fe	Blue gold
90Au:10Cu	Coinage gold

Technical Application: Both high purity gold and gold alloys are used in Solid State processing, device fabrication and assembly. The high purity, 5 9's, gold is evaporated or sputtered onto photo resist patterned wafers and circuit substrates to define contact and electronic function structures in a variety of multilayer metallizations, such as Au/Ni; Au/Cr; Au/AuGe/Ni; Au/Pt/Ni, and may be annealed for interdiffusion of the metals. As alloy pre-forms of AuB or AuP, they are alloyed to p- or n-type surfaces with the 3 to 5% boron or phosphorus improving electrical contact and reducing stress. Although most gold bond wire, 0.001 to 0.0007" diameter, is high purity gold — soft gold — some gold alloys, such

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as AuBe are used to stiffen the wire contact. The latter, AuBe, is recommended for high-speed, automatic bonders.

Electrolytic gold plating, with and without additional evaporated gold, is more often used for metallizing dielectric substrates (alumina, beryllia, quartz, etc.) and on package parts of copper, iron, aluminum. Gold on package parts is primarily for corrosion resistance and is hardened with additional metal additives to withstand general handling, wear and tear.

There are a number of gold and gold alloy pastes as epoxy or polyimide mixtures used for mounting discrete devices and other components in test or final package assemblies. Hardening, or firing temperatures of these pastes range from about 150°C to slightly over 200°C as a maximum, and there is much effort to develop higher temperature capability of such plastic type pastes for improved unit stability.

Although most gold alloys are used in polycrystalline form, several have been grown as single crystals, such as $AuGa_2$, $AuAg_x$ for morphological studies.

Etching: As most gold alloys have a high gold content, they can be etched in the mixed acids shown for gold: aqua regia, cyanides, and iodides.

GOLD ALLOYS

GOLD BISMUTH ETCHANTS

AUBI-0001a
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... KCN
x .... $(NH_4)_2SO_4$
x .... H_2O
DISCUSSION:
Au_2Bi, specimens. Solution used to develop structure. Will darken surfaces for color contrast of defects and structures.
REF: Savas, M A & Smith, R W — *J Cryst Growth*, 71,41(1985)

AUBI-0001b
ETCH NAME: Nitric acid, dilute TIME:
TYPE: Acid, removal/preferential TEMP:
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:
Au_2Bi, specimens as Bi-Au_2Bi. Solution referred to as a "deep" etch for this material. Surfaces were carbon replicated for SEM study.
REF: Ibid.

GOLD CADMIUM ETCHANTS

AUCD-0001
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... 20% KCN
1 .... 20% $(NH_4)_2S_2O_8$

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DISCUSSION:

Au:Cd alloy specimens. Solution used as a polish etch for surfaces in a study of lattice spacing of close-packed hexagonal, hcp, metal alloys.

REF: Massalski, T B — *Acta Metall,* 5,541(1957)

GOLD CESIUM ETCHANTS

AUCS-0001

ETCH NAME: Aqua regia, dilute — TIME:

TYPE: Acid, removal — TEMP: RT

COMPOSITION:

3 .... HCl

1 .... HNO_3

x .... H_2O

DISCUSSION:

Au_2Cs specimens used in a study of the semiconducting properties of the compound.

REF: Spicer, W E et al — *Phys Rev,* 1,55(1959)

GOLD-GALLIUM ETCHANTS

AUGA-0001

ETCH NAME: Tri-iodide — TIME: To 3 min

TYPE: Halogen, removal — TEMP: RT to hot

COMPOSITION:

x .... KI

x .... I_2

x .... H_2O

DISCUSSION:

$AuGa_2$, (100) oriented thin films on NaCl, (100) substrates. The substrate was cleaned: (1) rinse in chloroform, (2) rinse in acetone and (3) final rinse in methanol. Then place substrates in ultra high vacuum (UHV) for co-deposition of gold and gallium. Solution used to etch deposit $AuGa_2$.

REF: Gordon, H T — *J Vac Sci Technol,* A2.535(1984)

AUGA-0002

ETCH NAME: Air — TIME: 25 days

TYPE: Gas, aging defects — TEMP: RT

COMPOSITION:

x .... air

DISCUSSION:

Au:Ga, thin films EB evaporated on NaCl, (100) substrates as a 1:1 alloy with 230 Å Au:270 Å Ga. Gallium formed spherical aggregates on surface when deposition temperature was above the gallium melting point (30°C). After aging as shown: (1) deposit showed 1.5 mm blisters, roughly circular, with T-shaped cracks; (2) silver colored areas showed uniform grain structure of Au:Ga alloy mixture; (3) orange areas were fine-grained, mainly unreacted gold. Alloy area was Au_2Ga with orthorhombic structure like Ni_2Si and there was some interstitial diffusion into amorphous gallium similar to Pd diffusion into Sn forming $PdSn_4$. Cracks were due to Kirkendall voids caused by volume change from interdiffusion.

REF: Nakahara, S & Kinsbron, E — *Thin Solid Films,* 113,15(1984)

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AUGA-0003
ETCH NAME: Argon
TYPE: Ionized gas, thinning
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER: 6 KeV

DISCUSSION:

Au_2Ga, thin films deposited by co-evaporation onto GaAs, (100) substrates and annealed 30 min at RT. Annealing at 225°C produced the Au_2Ga orthorhombic phase. Two wafers were sandwiched together with epoxy, cut in the ⟨110⟩ direction and mechanically lapped to reduce specimen thickness. Finally, thinning was by argon ion bombardment for specimen morphology study under TEM.

REF: Leung, S et al — *J Electrochem Soc*, 132,898(1965)

AUGA-0004: Leung, S et al — *Thin Solid Films*, 104,109(1983)

AuGa and Au_7Ga_2 thin films deposited on GaAs, (100) wafers. The wafers were either Si doped n-type, or Zn doped p-type. After deposition the films were annealed at 400°C by being brought up from RT in 100°C increments. After this heat treatment, twinning was observed.

GOLD GERMANIUM ETCHANTS

AUGE-0001a
ETCH NAME: Tri-iodide
TYPE: Halogen, patterning
COMPOSITION:
400 g .... KI
200 g .... I_2
1000 ml .... H_2O

TIME: 20—30 min
TEMP: 60—70°C

DISCUSSION:

AuGe(13%), alloy ribbon 0.001″ thick, pellets or slugs. The ribbon was used as preforms in microelectronic devices and circuit substrates assembly; pellets were used in multilayer metallization of electric contacts on discrete devices as Au/AuGe/Ni. To clean the alloy: (1) vapor degrease in hot TCE or TCA; (2) dip etch in solution shown, 2—5 sec, 60—70°C; (3) heavy rinse in MeOH to remove residual iodine and (4) N_2 blow dry. Longer etch periods used after photo resist patterning for etch structuring.

REF: Marich, L A et al — personal communication, 1979

GOLD INDIUM ETCHANTS

AUIN-0001
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... 20% KCN
1 .... 20% $(NH_4)_2S_2O_8$

TIME:
TEMP:

DISCUSSION:

Au:In, alloy specimens used in a study of the lattice spacing of close-packed hexagonal, hcp, alloys. Solution used to polish surfaces of Au:In, Au:Cd and Au:Hg.

REF: Massalski, T B — *Acta Metall*, 5,541(1957)

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GOLD MERCURY ETCHANTS

AUHG-0001
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... 20% KCN
1 .... 20% $(NH_4)_2S_2O_8$
DISCUSSION:
AuHg, alloy specimens used in a study of the lattice spacing of close-packed hexagonal, hcp, metal alloys. Solution used to polish surfaces. Also used on AuIn and AuCd.
REF: Massalski, T B — *Acta Metall*, 5,541(1957)
TIME:
TEMP:

GOLD:SILVER ETCHANTS

AUAG-0001
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... KCN
x .... $(NH_4)_2SO_4$
DISCUSSION:
$AuAg_x$, single crystal ingots. Composition varied from pure silver to pure gold with silver content from 10, 25, 50, 75, and 90%. After growth, ingots were subject to strain in a study of stress and deformation. Solution shown was used as a preferential etch to develop defect figures.
REF: Suzucki, H & Barrett, C S — *Acta Metall*, 6,156(1958)
TIME: 2—5 min
TEMP: RT

GOLD TIN ETCHANTS

AUSN-0001a
ETCH NAME: Tri-iodide etch, modified
TYPE: Halogen, cleaning
COMPOSITION:
0.5 g .... KI
0.25 g .... I_2
25 ml .... H_2O
25 ml .... MeOH
DISCUSSION:
AuSn(20%), alloy ribbon 0.001" thick used for alloy mounting contacts of semiconductor devices in microelectronic circuits. Also used as alloy pellets and slugs in metal contact evaporation of wafer surfaces and circuit substrates. To clean AuSn: (1) vapor degrease parts in TCE or TCA; (2) etch clean in solution shown; (3) rinse thoroughly in MeOH to remove residual iodine and (4) air or nitrogen blow dry.
REF: Marich, L A & Porter, R — personal communication, 1978
TIME: 1—2 min
TEMP: 50—70°C

AUSN-0002
ETCH NAME: Aqua regia
TYPE: Acid, patterning
COMPOSITION:
3 .... HCl
1 .... HNO_3
TIME:
TEMP: RT

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DISCUSSION:

AuSn(20%) alloy as an evaporated thin film, or in sheet form strip. Solution used for general removal of thin films (stripping). Solution also used after photolithographic patterning 0.001" thick strips to etch-thru pattern.

REF: Valardi, N & Walker P — personal application, 1985

AUSN-0003

ETCH NAME: Potassium cyanide — TIME: 1—5 min

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

x .... x% KCN

DISCUSSION:

AuSn(20%) alloy as evaporated thin films, or strip pre-forms used for device mounting on substrates. Solution used for general removal and cleaning. Also used for AuGe(13%) alloy and pure gold film removal.

REF: Valardi, N — personal communication, 1984

AUSN-0001b

ETCH NAME: Tri-iodide etch — TIME: 20—30 min

TYPE: Halogen, patterning — TEMP: 60—70°C

COMPOSITION:

400 g .... KI

200 g .... I_2

1000 ml .... H_2O

DISCUSSION:

AuSn(20%), alloy ribbon 0.001" used in contact mounting of semiconductor microelectronic devices in circuit fabrication. Ribbon strips were mounted on glass slides with photo resist and then top surface was coated with photo resist. After air drying 30 min, and 90°C oven cure to harden photo resist, a circular open dot pattern was UV light exposed through an SST mask. Hole pattern in AuSn(20%) strip was etch formed in the solution shown. Similar work done with AuGe(13%), which is more brittle and tends to fracture. Method used to reduce alloy volume of material for thinner alloy joints. See AUGE-0002.

REF: Walker, P — personal application, 1984

GOLD ZINC ETCHANTS

AUZN-0001

ETCH NAME: Tri-iodide — TIME:

TYPE: Halogen, removal — TEMP: RT to hot

COMPOSITION:

x .... KI

x .... I_2

x .... H_2O

DISCUSSION:

Au:Zn, as an evaporated metal contact on InGaAsP/InP(100) (DH) Laser device structures. With photo resist patterning, solution used to etch gold contact pattern or for complete etch removal of the Au:Zn metallization.

REF: Adachi, S et al — *J Electrochem Soc*, 129,1524(1982)

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PHYSICAL PROPERTIES OF GRAPHITE, C

Classification	Ceramic
Atomic number	6
Atomic weight	12.010
Melting point (°C)	3727
Boiling point (°C)	4830
Density (g/cm^3)	2.09—2.23
Hardness (Mohs — scratch)	1—2
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Black
Cleavage (basal — perfect)	(0001)

GRAPHITE, C (Plumbago, Black Lead)

General: Occurs as a native element. It is widely distributed throughout the world and is found in beds, veins and as granules in many types of rock formations: quartzite, limestone, schist, and volcanic rocks, and has been found in meteoric iron. Occasionally may be partly alloyed with iron as Fe_2C. Deposition can be direct, from the breakdown of gases and the natural, slow burning of coal — coking. Although it is hexagonal system, rhombohedral division with a perfect basal (0001) cleavage as a single crystal, it is commonly found in massive form with very distinctive layered structure. See "Carbon" for a more detailed discussion. Graphite has been shown to contain some iron in solid solution — approaching a natural form of steel.

The Bronze Age was followed by the Iron Age (circa 1350 B.C.) which has been in existence for some 3500 years until the present Atomic Age and commencement of the Space Age. The initial discovery and use of iron can be traced back to the Hittite culture in Asia Minor as soft, pure iron — wrought iron — but it was the addition of graphite (carbon) to harden iron that developed the true Iron Age culture: Steel.

Pure graphite (carbon), in addition to its use in the iron industry, has major use as a high temperature refractory for crucibles, furnace linings and similar products. It also is an electrical conductor and used in electrical wiring, as power feed-thrus and so forth. Because of its high melting point and heat carrying capability, it is used as a heater strip. Because of its light producing capability, as a filament in light bulbs. Because it is acid resistant, it has been used as a liner in acid tanks. Because of its low neutron cross section, it has major use as control rods in atomic piles, or as radiation shields. The latter shielding may be as a mixture with alumina and other ceramics.

As a fine dispersion on glass, it will reduce sun glare, such that it is used as a sun screen. In finely powdered form it is dry lubricant. As the product Aqua Dag it is a powdered mixture with alcohol, and is used in the replication of surfaces. It is called "Black Lead", which is a misnomer as it contains no lead, but sticks of graphite have been used as writing implements since ancient times. Sticks are still used for charcoal drawing, and it is the "lead" in pencils. Also as a very fine powder it is stove polished and mixed with grease, black greasepaint, or shoe or stove polish. Added as dry powder to cement or glass and enamels it is a black pigment. As lampblack it is a near-colloidal derivative carbon from the reduction of petroleum, also collected from burning gas (methane cooking gas), or from burning vegetation and coal. See section on Carbon for additional information.

Technical Application: Natural graphite is not used directly in Solid State processing but, as described in the preceding General section, both graphite and carbon parts, natural or artificial, have wide application in equipment as evaporator crucibles, heater strips, power conductors, and the like.

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Pure graphite or graphite/metal mixtures are used to fabricate resistors and special resistive elements in semiconductor circuit assemblies as discrete devices, themselves, for power and frequency control. As Aqua Dag and similar solutions it is used as a mounting medium or to produce surface replication for electron microscope study.

Thin film deposition of graphite and silicon is under development for thin film silicon carbide, SiC, surface protection coatings on semiconductors and on metal cutting tools for wear resistance, and SiC has high temperature capability as a semiconductor device.

Although not natural graphite, amorphous carbon deposited as thin films, a-C, with additional annealing is under development as a conversion structure called diamond-like-carbon, DLC, for use as a chemically inert surface coating. Such coatings, to date, have produced a carbon/diamond crystalline structure, but not single crystal diamond.

Both natural and artificial graphite (e.g., carbon) have been studied as single crystals and the materials, in general, are under continual study and development because of their wide range of use and application.

The etch solutions shown here are those referenced to natural graphite. See the sections on Carbon and Diamond for additional information.

Etching: Very acid resistant. Boiling HNO_3, KOH, H_2SO_4 and H_3PO_4 to dissolve. KOH and NaOH as molten fluxes. Some acid mixtures.

See: "Carbon".

GRAPHITE ETCHANTS

GR-0001
ETCH NAME: Cleave
TYPE: Cleave, preferential
TIME:
TEMP: RT
COMPOSITION:
x .... cleave
DISCUSSION:

C, as single crystal graphite, (0001) cleaved specimens. Cleaved surfaces were relatively strain free and showed dislocation patterns. Also studied natural molybdenite, MoS_2. Both materials are used as dry lubricants.

REF: Boswell, F W C — *J Appl Phys*, 31,1834(1960)

GR-0002: Bacon, R & Sprague, R — *J Appl Phys*, 31,1831(1960)

C, as single crystal graphite, (0001) cleaved specimens. A similar study of defects on cleaved surfaces.

GR-0003
ETCH NAME: Boron
TYPE: Metal, decoration
TIME:
TEMP: 2300°C
COMPOSITION:
x .... B
DISCUSSION:

C, as single crystal graphite specimens. Boron diffused into specimens at the temperature shown produce circular, disc-like figures which change with temperature to disc stacking faults below 2400°C. Discs were 3—6 μm in diameter and, above 2400°C, convert to dislocation loops (loss of boron?).

REF: Hennig, G R — *J Appl Phys*, 34,237(1964)

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GR-0004
ETCH NAME: Oxygen
TYPE: Gas, preferential
COMPOSITION:
x .... O_2
TIME: 2 h
TEMP: 825°C
DISCUSSION:
C, as single crystal graphite specimens. Oxidation of graphite under the conditions shown produce some evidence of nonbasal dislocations.
REF: Thomas, J M et al — *Phil Mag*, 10,325(1964)

GR-0005
ETCH NAME: Sodium peroxide
TYPE: Molten flux, preferential
COMPOSITION:
(1) x .... Na_2O_2 (2) x .... NaOH (3) x .... KNO_3 (4) x .... $KClO_3$
TIME: 5 to 20 min
TEMP: 380°C
DISCUSSION:
C, (0001) specimens cleaved from natural graphite. All etching was done in a platinum crucible at the temperature shown to develop etch pits. Spiral etch pits developed were screw dislocations. Sodium hydroxide gave best results. Time varied 7, 15, and 20 min for pits development. Evaporated with a thin film silver coating for electron microscope (EM) study. (*Note:* Electron microscope for this type of study is now called scanning electron microscopy (SEM). Silver, gold, and nickel are evaporated on graphite for surface replication as graphite and carbon are absorbers of electrons and the metals are needed for reflectivity for electron scanning.)
REF: Patel, A R & Bahl, O P — *Br J Appl Phys*, 16,169(1965)
GR-0006: Kennedy, A J — *Proc Phys Soc*, 75,607(1960)
C, specimens as graphite. A study of dislocations and twinning in graphite. Molten fluxes were used to develop defects.

GR-0007
ETCH NAME:
TYPE: Stress, defect
COMPOSITION:
x .... stress
TIME:
TEMP:
DISCUSSION:
C, as graphite single crystal material. A study of the magnetic field dependence of the Hall effect and magnetoresistance. Stress and strain in the material create defects that will effect the Hall coefficient measurement.
REF: Soule, D E — *Phys Rev Lett*, 1,347(1958)

GR-0008
ETCH NAME:
TYPE: Acid, removal/defect
COMPOSITION:
x .... HNO_3, conc.
TIME: 2—10 min
TEMP: RT to boiling
DISCUSSION:
C, as natural graphite specimens, both massive material and fine single crystals. Massive material was etched by immersion, the single crystal material in hot vapors to develop surface structure and defects. This was a general study of the material from different locations and occurrences.
REF: Walker, P — mineralogy study, 1951—1954

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PHYSICAL PROPERTIES OF HAFNIUM, Hf

Classification	Transition metal
Atomic number	72
Atomic weight	178.49
Melting point (°C)	2222 (2150)
Boiling point (°C)	5400
Density (g/cm^3)	13.09 (13.3)
Thermal conductance (cal/sec)(cm^2)(°C/cm) 50°C	0.0533
Specific heat (cal/g) 25°C	0.035
Heat of fusion (cal/g)	32.4 (29.1)
Heat of vaporization (k-cal/g-atom)	155
Atomic volume (W/D)	13.6
1st ionization energy (K-cal/g-mole)	127
1st ionization potential (eV)	5.5
Electronegativity (Pauling's)	1.3
Covalent radius (angstroms)	1.44
Ionic radius (angstroms)	0.78 (Hf^{+4})
Vapor pressure (atm) 2007°C	10^{-9}
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	5.9
Modulus of elasticity (psi $\times 10^6$) 20°C	19.8
Tensile strength (psi)	86,000
Electron work function (eV)	3.53
Cross section (barns)	105
Hardness (Mohs — scratch)	4—5
(Rockwell B — kgf/mm^2)	95
Crystal structure (hexagonal — normal) alpha <1760°C	$(10\bar{1}0)$ prism, hcp
(isometric — normal) beta >1760°C	(100) cube, bcc
Color (solid)	Grey-silver
Cleavage (basal/cubic)	(0001)/(001)

HAFNIUM, Hf

General: Does not occur free as a native element. Found as a minor constituent in zirconium minerals, such as zircon (zirconia), $ZrSiO_2$, which is found in association with sphalerite, ZnS. Although not a rare element, it is not found in large quantities, but is a recovery metal from zirconium ores, chiefly from zircon. The chemical characteristics of the metal are similar to those of zirconium. It is not used in metal processing, but could act as a desulfurizer in irons and steels as is zirconium.

Technical Application: No use as a metal in Solid State processing though it is under evaluation as a thin film: pure metal, nitride, silicide. The latter as HfSi, Hf_2Si and $HfSi_2$ for blocking layers in heterostructures. The nitride, HfN, is under evaluation as a surface passivation layer as is ZrN and TiN. Metallic hafnium has been grown as a single crystal and deposited as a thin film metal layer for general study.

Both HfS_2 and $HfSe_2$, along with ZrS_2 and $ZrSe_2$, are under evaluation as compound semiconductors with possible application as cathode storage batteries.

Etching: HF and mixed acids.

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HAFNIUM ETCHANTS

HF-0001a
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
10 ml .... HF
45 ml .... HNO_3
45 ml .... H_2O
TIME: Seconds
TEMP: RT
DISCUSSION:
Hf, single crystal wafers and HfN thin films. Solution used to clean surfaces.
REF: Dawson, P T — *J Vac Sci Technol,* 21,36(1982)

HF-0001b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... H_2O_2
20 .... H_2O
TIME:
TEMP:
DISCUSSION:
Hf specimens. Solution shown as a general removal etch.
REF: Ibid.

HF-0002
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, removal
COMPOSITION:
1—2 .... HF
10 .... H_2O
TIME:
TEMP:
DISCUSSION:
Hf, thin films deposited on silicon wafers. Solution shown as a general removal etch for hafnium.
REF: Missel, L I & Glang, R — *Handbook of Thin Film Technology,* McGraw-Hill, New York, 1970

HAFNIUM NITRIDE ETCHANTS

HFN-0001
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
10 ml .... HF
45 ml .... HNO_3
45 ml .... H_2O_2
TIME:
TEMP:
DISCUSSION:
HfN, as a thin film deposit grown from NH_3 pyrolysis. Nitride showed concentric colored bands from wafer center: yellow, blue, red, blue, and yellow. Also studied TiN and ZrN.
REF: Dawson, P T — *J Vac Sci Technol,* 21,36(1982)

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HAFNIUM TIN ETCHANTS

HFSN-0001
ETCH NAME: Nitric acid
TYPE: Acid, tin removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
Hf_5Sn_2, single crystal specimens. After molten flux growth removed excess tin by dissolving with nitric acid.
REF: Bailey, D M & Smith, J F — *Acta Metall*, 14,57(1961)

TIME:
TEMP:

PHYSICAL PROPERTIES OF HELIUM, He

Classification	Inert gas
Atomic number	2
Atomic weight	4.0002
Melting point (°C)	−272.2
Boiling point (°C)	−268.9
Density ($g/cm^3 \times 10^{-3}$)	0.178
(g/l) −270.8°C	0.147
Specific heat (cal/g/°C) 20°C	1.25
Thermal conductivity ($\times 10^{-4}$ cal/cm/cm2/°C/sec)	3.34 @ 20°C
1st ionization potential (eV)	24.58
Cross section (barns)	0.007
Vapor pressure (°C)	−270.3
Critical temperature (°C) C.T.	−267.9
Critical pressure (atms) C.P.	2.26
Hardness (Mohs — scratch)	1—3
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid/liquid/gas)	Colorless
Cleavage (basal)	(0001)

HELIUM, He

General: Helium is a colorless, odorless, tasteless gas that is inert like argon. It does not combine with other elements, nor does argon, although some compounds have been reported, such as HeH, HgHe, and $Ar(HF_3)$.

Helium is an extremely rare gas, only about 0.0005 by volume in standard air (atmosphere), and there is one major gas producing well in the world in Amarillo, Texas that, effectively, produces the world supply of helium. Although hydrogen has better lifting power — 76 pounds per 1000 ft^3 vs. only 65 lb for helium — hydrogen is explosive and flammable, e.g., explosion of the Hindenburg Zeppelin in 1937 at Lakehurst, New Jersey. Since that time, the U.S. has never used hydrogen for zeppelins or balloons — the Germans had to re-strut the war reparation dirigibles transferred to the U.S. after World War I to handle helium rather than hydrogen — all three were lost by accident prior to World War II.

Helium can be reduced to the lowest temperature known to man as a cryogenic liquid, but cannot be reduced to a solid single crystal as can all of the other gases. At 2.2°A (absolute temperature, equivalent to Kelvin, K) helium properties change — thermal conductivity increases, viscosity decreases and it behaves like a gas, rather than a liquid — and it is the only known element that can be reduced to this temperature.

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In industry, helium is used as an inert furnace gas like argon in high temperature processing of metals; has wide application in weather balloons, as well as commercial balloons, both the small party and play types, as well as the larger type used by balloonists, though the latter often use hot air rather than helium.

Perhaps one quarter of all helium produced is used in medicine as the carrier gas with anesthetics, and in the treatment of asthma and other respiratory diseases. As a mixture of He/O_2 it replaces air (N_2/O_2) for deep-sea divers as, when a diver is brought to the surface too rapidly using air, nitrogen forms bubbles in the bloodstream causing the "bends" with severe muscle cramps and spasms. Helium will not form such bubbles in the bloodstream. As an item of interest, when pure helium or He/O_2 mixtures are breathed it affects the vocal cords, producing the "Donald Duck" speech. Note that helium is a by-product of uranium disintegration.

Technical Application: Helium is used as an inert atmosphere in furnaces, although argon and nitrogen are more common as they can be supplied at lower cost for high volume thru-put. Helium is supplied in pressurized cylinders as the pure gas or as gas mixtures, the gas mixtures being used as semiconductor dopant sources of boron or other elements for wafers, or in the single crystal and epitaxy growth of compound semiconductors, ferrites, garnets.

Helium is used as packaging atmosphere, particularly for quartz crystals as it is the lightest of the inert gases and has a minimum frequency loading effect on the quartz. It is under evaluation for the package sealing of high power and high frequency Schottky barrier type devices, such as gallium arsenide, GaAs, for the same reason.

In vacuum evaporators, cryo-pumps are replacing oil diffusion pumps and ion pumps, and they use helium as the chilling agent with chunk graphite as the gas absorbent during chamber pumping for oil-free evaporator operation. Such pumping systems, depending upon usage time, require periodic rejuvenation of graphite to remove collected gases. This is done by vacuum pumping on the cryo-pump itself on a daily or weekly basis with replacement of the graphite about once a year.

In material processing of semiconductors, nitrogen gas is most often used as nitrogen blow-off for drying after etching of parts.

Occasionally other inert gases are similarly used, argon more often than helium, and they can be used from RT to hot (60—80°C). Also, nitrogen is used for a nonoxidizing storage gas in cabinets or working dry boxes, and both argon and helium can be so used. Where a compound such as AlAs reacts with water moisture in the atmosphere, it is held and processed under an inert atmosphere; again, usually nitrogen, but it can be helium or argon.

Etching: N/A

PHYSICAL PROPERTIES OF HEMATITE, Fe_2O_3

Classification	Oxide
Atomic numbers	26 & 8
Atomic weight	159.68
Melting point (°C)	1565
Boiling point (°C)	
Density (g/cm^3)	5.2—5.25
Refractive index (n = −Li)	3.01—2.94
Hardness (Mohs — scratch)	5.5—6.5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb

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Color (single crystal)	Red/black
(massive ocher)	bright red
Cleavage (basal — parting)	(0001)
(rhomb)	$(10\bar{1}1)$

HEMATITE, Fe_2O_3

General: The mineral hematite is a primary ore of iron. Called red iron ore; red ocher; red rouge. Color varies from specular iron (metallic black); massive/fibrous (brown/red to black); red ocher or red hematite; and can be an admixture of brown limonite, $FeO.NH_2O$ and black magnetite, Fe_3O_4. It may appear to be magnetic, but magnetism is due to the presence of magnetite. In reniform masses as kidney ore, similar in appearance to psilomelane, MnO_2, and as a deposit of sedimentary origin, called oolitic hematite, rounded grains with a central sand-grain, of Paleozoic Age and sometimes in extensive beds. Also occurs as red chalk: limestone, $CaCO_3$ — normal white chalk — containing red hematite as coloring. The yellow/brown/red coloring of rocks and earth is due to the presence of iron oxides.

Hematite as iron ore was in use in ancient times from about 1350 B.C. (beginning of Iron Age) and, as red ocher, is still the cosmetic red rouge. The same name, red rouge, also applied when the compound is used as a lapping and polishing abrasive. Red ocher, the geologic name for red rouge, is a pigment coloring for paints, glass, and enamels. Tan or brown rouge may be limonite, black rouge as magnetite.

Technical Application: Not used in Solid State device fabrication or processing. It is occasionally used as a lapping and polishing compound for wafers and parts, and "iron oxide" is used as a pattern coating in the fabrication of photo resist glass masks as a replacement for chromium, nickel and aluminum. As an iron containing material it may be considered a ferrite Solid State compound, and has been studied for magnetic properties.

Both natural and artificially grown single crystals of hematite have been studied for general morphology and other data.

Etching: HCl (all iron oxides).

HEMATITE ETCHANTS

HEM-0001
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HCl
DISCUSSION:

Fe_2O_3, natural single crystals cleaved basal (0001) used in a study of frequency dependence of magnetic resonance. Hydrochloric acid is a slow etch on hematite. (*Note:* Hematite does not show true cleavage, but shows (0001) parting based on its lamellar structure.)
REF: Kumagai, H et al — *Phys Rev*, 99,1116(1955)
HEM-0002: Walker, P — mineralogy studies, 1952

Fe_2O_3, natural single crystal specimens. Solution used as a general cleaning etch in a study of the iron oxides.

PHYSICAL PROPERTIES OF HOLMIUM, Ho

Classification	Lanthanide
Atomic number	67

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Atomic weight	164.94
Melting point (°C)	1461
Boiling point (°C)	2600
Density (g/cm^3)	8.80
Specific heat (cal/g) 25°C	0.039
Heat of fusion (k-cal/g-atom)	4.1
Latent heat of fusion (cal/g)	24.9
Heat of vaporization (k-cal/g-atom)	67
Atomic volume (W/D)	18.7
Electronegativity (Pauling's)	1.2
Covalent radius (angstroms)	1.58
Ionic radius (angstroms)	0.91 (Ho^{+3})
Electrical resistivity (micro ohms cm) 298 K	81.7
Compressibility (cm^2/kg $\times 10^{-6}$)	2.47
Cross section (barns)	64
Magnetic moment (Bohr magnetons)	10.89
Tensile strength (psi)	37,500
Yield strength (psi)	32,100
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	70,200
Transformation temperature (°C)	1428
Hardness (Mohs — scratch)	5—6
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Grey
Cleavage (basal)	(0001)

HOLMIUM, Ho

General: Does not occur in nature as a native element. It is one of the rare earths of the erbium family of the yttrium group, and is found in trace quantities in the mineral gadolinite, $Be_2FeDy_2Si_2O_{10}$, which may contain a high cerium content and, as such, often referred to as gadolinte earth as a source of all of the rare earth elements. Holmium also is found in other yttrium and cerium containing minerals. As the pure metal it is basic akin to the alkali metals but due to scarcity has had little or no application in the general metal industries.

Technical Application: Holmium has had little use in Solid State processing, to date, although it has been grown as a single crystal in general studies of the rare earth elements. It also has been studied as an oxide, a nitride, a ferrite, and an alloy constituent.

Etching: Mixed acids.

HOLMIUM ETCHANTS

HO-0001
ETCH NAME: Heat
TYPE: Thermal, preferential
TIME:
TEMP: <1400°C
COMPOSITION:
x .... heat
DISCUSSION:

Ho, single crystal specimens. The article describes a method of growing rare earth single crystals. After crystal growth, during annealing, thermal etching was used to develop defects, low angle grain boundaries and structure figures. Other metals studied were Dy, Gd, Er, Tb, Tl, and Y.
REF: Nign, H E — *J Appl Phys*, 34,3323(1963)

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HOLMIUM ALLOYS:

HOLMIUM COBALT ETCHANTS:

HOCO-0001
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Ho:Co alloy sputter deposited on glass and NaCl, (100) substrates in a study of this compound. Temperature of deposition was between 60-100°C, and substrates were Ar^+ ion cleaned for 1 h prior to deposition. The oxide is slowly soluble in HCl.
REF: Suzuki, T et al — *Jpn J Appl Phys*, 23,585(1984)

HOLMIUM OXIDE ETCHANTS

HOO-0001
ETCH NAME: Kalling's etch
TYPE: Acid, polish
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH

TIME: 10—30 sec
TEMP: RT

DISCUSSION:
Ho_2O_{17} specimens fabricated by arc melting and used in a study of different metallic compounds. Solution used as a general removal and polishing etchant. See Cesium Platinide: CEPT-0001 for complete list of other compounds studied.
REF: Slepowronsky, M et al — *J Cryst Growth*, 65,293(1983)

HOLMIUM FERRITE ETCHANTS &
HOLMIUM COBALT FERRITE ETCHANTS

HCFE-0001
ETCH NAME: Kalling's etch
TYPE: Acid, polish
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH

TIME: 10—30 sec
TEMP: RT

DISCUSSION:
Ho_2Fe_{17} and $Ho_2Co_{14}Fe_3$ arc melted in fabrication and used in a study of different metallic compounds. Solution used as a general removal and polishing etchant. See Cesium Platinide: CEPT-0001 for complete list of other compounds.
REF: Slepowronsky, N et al — *J Cryst Growth*, 65,293(1983)

HYDRIDES: M_xH

General: Pure metallic hydrides do not occur as natural compounds though there are many hydrated minerals containing either or both water, H_2O, and OH^-, the hydroxyl radical in their formulae. The four elements — oxygen, carbon, nitrogen, and hydrogen — appear

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in many natural compounds in a wide range of combinations and physical forms, from gases, such as methane, CH_4; as simple hydrocarbons, such as the paraffin series $C_nH_{2n} + 2$; amber, 40C:64H:4O, as a ratio; petroleum, as a combination of gas (methane), liquid as the paraffin series, and solid asphaltum or tar with several varieties. Mineral coal as compressed and altered vegetation vary from those still containing vegetation structure (peat, lignite), to the less volatiles containing coals as bituminous and anthracite. Coals and petroleums may have a high sulfur content, but it is the hydrogen content of these minerals that make them useful as fuels.

Hydriding of metal surfaces is done in industrial metal processing and, though it causes embrittlement, it also aids in improving surface hardness as does nitriding. Several metals will absorb and retain large quantities of hydrogen — palladium and platinum as powders — palladium black or platinum black — have been used as hydrogen storage batteries.

Technical Application: Many metals are under development and study in Solid State processing as single crystal hydrides or as hydrogenated thin films as both possible hydrogen storage batteries or as an element in device structuring. Several of these hydrogenated compounds appear in their ordinary metal or compound sections, such as silicon, germanium, silicon carbide, silicon nitride as Si:H, Ge:H, SiC:H, SiN:H, respectively.

Hydriding is done in a furnace under pressure or in an autoclave system, to convert a metal to a hydride, as a separate and distinct operation from hydrogen firing. In this latter case, hot hydrogen gas forms a reducing atmosphere preventing and removing oxides as a surface cleaning function; whereas hydriding is the growth of a new compound form with the addition of hydrogen in the formula. The term hydrogenation has been applied to converting oils to fats for many years, but also could be used with regard to forming metal hydrides, as it is the addition of hydrogen to a compound.

Etching: Acids, alkalies, mixed acids.

HYDRIDE ETCHANTS

HYDR-0001
ETCH NAME: Sulfuric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
NbH, deposited on silicon wafers from a powder mixture in amyl acetate or cellulose nitrate. Paint on surface and fire for 1—10 min at 600—900°C in an inert atmosphere (N_2, Ar). Acid shown used to etch the hydride. Other hydrides evaluated were TaH, ZrH, VH, and TiH.
REF: Sullivan, M V & Eigler, J H — *Acta Metall,* 103,218(1956)

HYDROCARBON, CH_4

General: The formula shown is for methane or marsh gas, CH_4, a major constituent in the formation of petroleum and coal. Although hydrocarbons are derived from organic material not inorganic, this section is included due to the importance and usage of both the hydrocarbons themselves and their derivatives. Methane occurs in swamps and marshes from the decay of vegetation; at night in a swamp it can be seen burning as "fox fire"; it also is the dreaded, explosive firedamp in coal mines. Coal gas, as a household fuel contains 30—40% methane. As a solid at −186°C, methane has the octahedral structure similar to diamond, and is classed as a paraffin compound. It reacts with chlorine to produce hydrochloric acid, HCl, in addition to methyl chloride; methylene chloride; chloroform; and carbon

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tetrachloride. All these additional compounds are used in surface cleaning of metals and metallic compounds.

Petroleum has been known since ancient times. It is believed that "Greek Fire" was a self-igniting mixture of petroleum and quick lime, and it was used in the defense of Constantinople from 330 A.D. to 1453 A.D., when the city fell to the Ottoman Turks. There are surface occurrences of petroleum in the Balkan and Middle East areas. In 1857 Romania was producing over 200 tons of petroleum from hand-dug wells, and oil was first discovered by drilling at Titusville, Pennsylvania, in 1859 when oil was struck.

But even prior to that time, petroleum was being used as a light source replacement for whale-oil lamps. Ancient wooden sailing ships used petroleum as tar from surface tar pits in the Mediterranean area as calking, and the British Navy and merchantmen were using the great tar pit on the island of Martinique in the Caribbean in the 1600 to 1800s.

In geology the hydrocarbons are not considered to be pure mineralogy, although there are a number of named natural minerals as simple hydrocarbons (paraffins); oxygenated hydrocarbons; petroleum and asphaltum; and coals.

Paraffin, as ozocerite and napalite are wax-like substances from oil or coal, and fichtelite comes from fossilized pine. Amber is the oxygenated type of fossilized resin with half a dozen names depending upon type and locale. Amber was known to the ancients for its static electricity reaction and was called electrum, hence electricity. (*Note:* Natural gold:silver amalgam has the mineral name electrum.)

Petroleum grades from a black/brown liquid with or without a high sulfur content, to a black solid called asphaltum (mineral pitch or tar), which is a semi-hard hydrocarbon mixture and amorphous in structure.

The coals are vegetation that has been compacted to a firm solid under pressure and heat. The three primary coals are: anthracite (hard), bituminous (soft), and lignite (brown or bog coal). Peat is not considered a true coal, as it is insufficiently compacted and hardened, but it has been a major fuel source in northern Europe and the British Isles since ancient times. The peat "bricks" are cut from bogs, stacked, and allowed to dry before being used. It produces an intense, hot fire with a fine, flavorful smoke. That smoke is an important ingredient in the making of Scotch whiskey.

Natural gas from both oil and coal has a high methane gas content, which is responsible for the bright blue flame of household stove burners. As it is odorless, colorless and extremely volatile in the presence of air, an odorizer (mercaptan) is added for a distinctive smell.

Other than the fuels from oil and coal (gases, kerosene, gasoline), there are alcohol derivatives, such as methyl alcohol, and solvents, such as toluene and xylene, or benzene and others of the class of aliphatic compounds or aromatics (sweet-smelling). Some black coals have been cut and polished as jewelry. Baltic amber also has been used for jewelry, and studied for the fossilized insects entrapped.

Petroleum derivatives include paraffin as a base of several wax compositions: lampblack as a black pigment; glycerin for the fabrication of rayon and cellophane; synthetic rubbers and plastics, as both saturated and unsaturated hydrocarbon compounds. Although gasoline for ground and air vehicles is a major product of the oil industry, it should be realized that better than half of every barrel of oil is used in the chemical industry and other areas.

Technical Application: Hydrocarbon gases are used for the deposition of thin film carbon for conversion to diamond-like-carbon (DLC), also shown by the acronym i-C. These thin films are discussed further under the section on Carbon. Specific hydrocarbon thin films have been deposited under vacuum conditions using liquefied gases such as nonane or hexane.

Etching: Dissolve with alcohols and solvents.

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HYDROCARBON ETCHANTS

HC-0001
ETCH NAME: Silica gel
TYPE: Mineral, drying
COMPOSITION:
x .... silica gel (c-SiO_2)
DISCUSSION:
Liquid hydrocarbons used for thin film deposition as the material compound under vacuum conditions. Silica gel in an 8-ft column used to dry the liquids before entry into vacuum. Hydrocarbons were nonane, 3-methylpentane and hexane. Outgassing in the vacuum chamber was done by freezing.
TIME:
TEMP:
REF: Berry, W B — *J Electrochem Soc*, 118,597(1971)

PHYSICAL PROPERTIES OF HYDROGEN, H_2

Classification	Reactive gas
Atomic number	1
Atomic weight	2.0162 (H_2)
Melting point (°C)	−258.14
Boiling point (°C)	−252.8
Density ($g/cm^3 \times 10^{-3}$)	0.8988
(g/l liquid)	0.070
Specific heat (cal/g/°C) 20°C	3.34
Latent heat of fusion (cal/g)	15
Thermal conductance ($cal/cm^2/cm/sec$) 20°C	4.05
1st ionization potential (eV)	13.597
Ionic radius (angstroms)	0.180
Cross section (barns)	0.33
Vapor pressure (°C)	−257.9
Critical temperature (°C)	−241 (−239.9)
Critical pressure (atm)	20 (12.8)
Hardness (Mohs — scratch) solid	1—3
Crystal structure (isometric — normal)	(100) cube
(hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	White
(gas/liquid)	Colorless
Solubility (100 ml H_2O) 0°C	1.93 ml
(100 ml EOH) 0°C	6.92 ml
Cleavage (cubic/basal) solid	(001)/(0001)

HYDROGEN, H_2

General: Hydrogen is a colorless, tasteless and odorless naturally occurring gas, highly flammable in the presence of oxygen at standard temperature and up to 180°C will combine only slowly. Above 550°C $2H_2 + O_2$ explosively combines to form water, H_2O. Hydrogen occurs in the free state associated with volcanic eruptions, in some natural gas wells, and as pockets in some mining locations. There is less than 0.000,005% as a free gas in the atmosphere.

Where oxygen is an oxidizing agent, hydrogen is a reducing agent: metal oxides are reduced to pure metals by hydrogen firing; hot hydrogen firing in a furnace or quartz tube

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with nitrogen "end-curtains" to prevent influx of air with additional hydrogen burn-off exists, is used to clean metal surfaces; to anneal material to a specific hardness, such as $^1/_4$-hard, $^1/_2$-hard brass; or as the reducing atmosphere during parts alloying.

The oxy-hydrogen blow torch, invented by Robert Hare in 1801, will produce temperatures in excess of 2500°C, although oxy-acetylene, C_2H_2, torches are more widely used in welding as it will reach temperatures of 3300°C. There is an Atomic Hydrogen Gun, invented by Irving Langmuir in 1933, that splits the hydrogen molecule, H_2, into atomic, H + H atoms, by the gas passing through an electric spark with the production of 104,000 calories of heat. This is a reversible reaction, and the hydrogen molecule re-forms after a short distance.

Other than as free hydrogen, hydrogen combines with almost all substances; it is found as a constituent in minerals, vegetable matter, and is part of mammillary gastric juices in the form of hydrochloric acid (between 0.2 to 0.4%). In minerals, it may be atomic hydrogen, H, as in HBr; as an OH^- radical, such as in gibbsite (hydrargillite), $Al(OH)_3$ . . . aluminum hydroxide as a native mineral, or as H_2O, such as in opal, $SiO_2.nH_2O$, where the water is both in the physical atomic lattice and as an absorbed, interstitial fluid. It is also found in coals and oils, hydrocarbons, in gases, alcohols, esters, and hundreds of chemical compounds to include sugars, starch, cellulose, and plastics.

The hydrogenation process converts liquid vegetable oils to solid fats by adding hydrogen to the formulas; also includes seed oil, such as cottonseed. The production of "water gas" — the obtaining of hydrogen from water by passing steam over coke (carbon) at 1000°C is a major industry, in the manufacture of ammonia, NH_3, water gas and nitrogen are combined at 500°C, and 200 atm of pressure. Ammonia is not only a base for making fertilizers but for nitrate explosives.

A major reason why Berlin, Germany was a military bombing target during World War II were the water-gas and ammonia plants around the outskirts of the city. During World War I, hydrogen was used to inflate Zeppelins and the airships were used to bomb England; but with the explosion of the Hindenburg in 1937 such air travel ceased. Helium was used in place of hydrogen — 15% H_2:He(85%) is nonflammable, as is a similar mixture with nitrogen, known as Forming Gas (FG), 85% N_2:15% H_2.

Hydrogen is absorbed by many metals and there is much current development of hydrogen-storage systems for possible battery applications as well as general storage/release capability. As an example, finely powdered palladium as "palladium black" will absorb between 800 and 900 volumes of hydrogen; powdered platinum about 50 volumes.

Many of the acids used in etch processing contain hydrogen and they can be either reducing or oxidizing acids depending upon the presence of oxygen in the formula. HF, NH_4F are reducing agents; HNO_3, H_2O_2, oxidizing agents; H_3PO_4, HCl, and H_2SO_4 are general removal or cleaning solutions. The hydroxides, KOH and NaOH, are cleaners, preferential etchants or oxidizers; NH_3 and NH_4OH are weak bases as etchants but, as they readily combine with acids to neutralize them (Normal solutions), they are the primary chemicals used to neutralize acid sump disposal systems. Acetic acid, CH_3COOH (HAc), is not only a weak acid etchant for metals but is the acidic element in vinegar.

Technical Application: Hydrogen, as gas, is used as a furnace processing atmosphere for its reducing capabilities, as it will de-oxidize and clean surfaces, and will prevent oxidation products forming during alloying of parts. It also is used in quartz tube diffusion furnaces during semiconductor wafer doping, and in forming metal hydrides in Solid State processing.

High purity hydrogen can be supplied as pressurized single cylinders (Al type under 3600 psi) or as an A2l, interconnected cylinder tank farm, or from a liquid hydrogen, LH_2, source with conversion to gas though heat exchangers. It also is supplied in similar cylinders with other gases as mixtures, such a diborane, B_2H_6, as semiconductor doping sources, or for growth of epitaxy layers.

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Metal hydrides such as TaH, ZrH, and NbH have been used as alloying agents in silicon device assembly, and there is on-going development of metallic hydrides as Si:H, Ge:H, SiC:H, or with additional nitrogen, SiN_x:H. These are grown as both colloidal or amorphous structures.

Etching: N/A

HYDROGEN ETCHANTS

H-0001
ETCH NAME: Pressure
TYPE: Vapor pressure, defect
TIME:
TEMP:
COMPOSITION:

x .... pressure, vapor

DISCUSSION:

H_2, grown as a single crystal under cryogenic vacuum conditions with pressure. Vary vapor pressure in the vacuum system will preferentially etch the single crystal ingot.
REF: Schwentner, N et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1970

HYDROXIDES

All hydroxides contain the OH^- radical and, using the Sorenson pH Scale, are classified as chemical bases with pH values greater than pH 7 (water, neutral). They are the opposite of acids (pH under 7) and, when an acid and base are mixed as Normal solutions, then mixed together, they neutralize each other, producing water and a salt. Base, hydroxide, alkali, all three names are used, and these chemicals will turn litmus paper blue; whereas acids turn the paper red. There are rolls of litmus paper available containing a combination pH numbered color chart ratings that can be used to establish the degree of alkalinity or acidity of solutions.

Almost all metals form natural oxides and may contain both water, as H_2O, or the OH^- hydroxyl ion radical in their formula, and a few are referred to as metal hydroxides. Many metal hydroxides are either sparingly soluble or insoluble in water and are stable under normal pressure and temperature. Bauxite, primarily a colloid of $Al_2O_3.2H_2O$, is the natural aluminum hydroxide; goethite and limonite, FeO(OH) or $Fe_2O_3.H_2O$, are the natural iron hydroxides, and are primarily colloidal; manganite, MnO(OH), the manganese hydroxide; and brucite, $Mg(OH)_2$, is the natural magnesium hydroxide.

The mineral magnesite, MgO, called magnesia, will slowly react with water to form the hydroxide $Mg(OH)_2$, best known as milk of magnesia as a suspension in water. As magnesia, MgO, with a melting point of about 2500°C, it is used as a high temperature ceramic for furnace linings and fire bricks; whereas milk of magnesia, $Mg(OH)_2$, is a medical specific and as powders both materials readily react to neutralize acids, such that they are used as antidotes against poisoning by strong acids. Most laboratories keep these materials available in powder form in chemical processing areas for use against acid burns: mix as a water slurry and apply to the burn area to neutralize the acid. The alkali group of metals are lithium, sodium, potassium, rubidium, and cesium — shown in order of increasing atomic weight, and reduction of both melting and boiling points, in addition to increasing density. Several metals, chemical compounds, and minerals are classified as being like, or similar to an alkali due to their chemical reactions.

As sodium, Na, it is one of the more abundant elements (about 2.5% of the earth's crust), in addition to the mineral halite, NaCl, common salt found in ocean water or saline salt dome deposits, it is found in many other natural minerals. The symbol "Na" comes from the mineral natron, Na_2CO_3, and the name means: metal of soda. An impure form of

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natron was known to the ancient Egyptian priests, and used as part of their embalming fluid in mummification of the pharaohs.

The hydroxide, NaOH, is known as caustic soda, due to its corrosive action on flesh, and is of greater industrial importance than the other alkali compounds due to the abundance of sodium. A major use is in the making of soaps, such as "lye" soap, another term for sodium hydroxide. It is used in the petroleum industry, and in the manufacture of rayon, paper, textiles, and rubber. It also is a major cleaning and etching solution in metals and metallic compounds processing.

As a cleaning/etching solution both sodium and potassium hydroxide, NaOH and KOH, respectively, are the most widely used. The latter, KOH, is preferred where sodium may contaminate the material, such as silicon processing. As a water solution, there are three general concentrations used in material processing: (1) as a 1—15% solution at RT for general surface cleaning; (2) as a 10—20% solution for light removal and surface conditioning/cleaning, and (3) from 20—50% solutions, hot to boiling, as preferential and removal etchants. Several of the chemically inert metals, such as platinum and iridium, can be surface cleaned in boiling hydroxides but, on many others, like single crystal silicon, they are primarily preferential etchants.

As a molten flux, the solid hydroxide pellets liquified at their melting points, they are defect etchants on single crystals, such as KOH at 650°C on silicon. Mixed with other chemicals, such as carbonates and nitrates, molten fluxes are used for single crystal growth: garnets, ferrites, etc.

Another hydroxide, ammonium hydroxide, NH_4OH, as well as ammonia, NH_3, are of major industrial importance as neutralizing solutions. They are widely used to neutralize acid waste from chemical, and metal processing plants. The acids are collected in a sump, then the hydroxide or ammonia added to neutralize before release into a sewage system. They also are used as cleaning and etching solutions alone, or mixed with other acids. In general household, industry, or medical applications they act as both cleaners and disinfectants and, as solid crystals, ammonia is "smelling salts."

The following list of solutions present the hydroxides as etching and cleaning solutions as extracted from aluminum to zirconium. See specific metals and compounds for additional solutions and applications.

HYDROXIDE CONTAINING ETCHANTS

Formula	Material	Use	Ref.
8—10% NaOH/KOH	Al/alloys	Cleaning/pickling/ removal	AL-0003a AL-0002 AL-0062
xKOH:x$K_3Fe(CN)_6$:$K_2B_4O_7.4H_2O$	Al	Removal	AL-0019
2 g NaOH:1000 ml H_2O	Al	Polish	AL-0062
x2.5 *M* NaOH	Al	Electrolytic removal	AL-0064
4 mg NaOH:1000 ml H_2O: 200 ml glycerin	Al	Chem/mech shaping	AL-0077
x30% KOH/NaOH	Al:Be(38%)	Cleaning	ALBE-0001
x10% NaOH	Al:Cu	Removal	ALCU-0001a
x2.5 *M* NaOH	Al:Ni	Removal	ALNI-0001a
x3 *N* NaOH	Al:Ag	Removal/preferential	ALAG-0001
x3 *N* NaOH	Al:Zn	Removal/preferential	ALZN-0001
x10—30% NaOH/KOH	AlN	Removal	ALN-0008b
1—2NH4OH:1—2H_2O_2:4—6H_2O	Al_2O_3	Cleaning	ALO-0004

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Formula	Material	Use	Ref.
5%NaOH:50%HNO_3 + H_2O	Al_2O_3	Electrolytic, anodizing	ALO-0010a
5—20% NaOH	As	Removal	AS-0001a
x30% KOH/NaOH	Be	Cleaning/removal	BE-0001
x10—30% KOH	BeO	Removal	BEO-0004
xKOH, pellet (molten flux)	BC	Removal	BC-0001
xNaOH, pellet (molten flux)	MoB	Removal/preferential	MOB-0001c
xKOH, pellet (molten flux)	Nb_3B_3	Removal/preferential	NBB-0001b
x x%NaOH/KOH	TaB	Removal	TAB-0001a
x x%NaOH/KOH	VB	Removal	VB-0001b
x x%NaOH/KOH	WB_2	Removal	WB-0001c
x x%NaOH/KOH	ZrB_2	Removal	ZRB-0001a
x10% NaOH	BP	Removal/polish	BP-0003
xNH_4OH:xH_2O_2 + H_2O	Brass	Removal, cleaning	BRA-0006
xNH_4OH:xH_2O_2	Bronze	Preferential	BRO-0004b
xNH_4OH	Cd	Cleaning	CD-0006
xNH_4OH	CdO	Cleaning	CDO-0001
x10%NaOH:x$Na_2S_2O_4$:xH_2O	CdTe	Removal (Te)	CDTE-0016a
x50%NaOH	CdTe	Polish	CDTE-0017a
xKOH, pellet (molten flux)	C	Removal	C-0001a
x50%KOH	C	Removal	C-0001b
x1 *N* NaOH	CeO_2	Cleaning	CEO-0001
5 g $KMnO_4$:7.5 g NaOH:30 ml H_2O	Cr	Cleaning	CR-0017c
xNaOH, pellet (molten flux)	Cr_2O_3	Dislocation	CRO-0006a
x x%NaOH	Cu	Cleaning	CU-0001
1NH_4OH:1H_2O_2	Cu	Preferential	CU-0011b
xNH_4OH:xH_2O	Cu:Ga	Preferential	CUGA-0001b
xNH_4OH	Cu_2O	Removal	CUO-0006a
12%NaOH:1H_2O_2	GaSb	Removal	GASB-0001d
xNH_4OH:xH_2O_2	GaAs	Polish	GAS-0007c
1NH_4OH:20H_2O_2	GaAs	Selective removal	GAS-0018
3NH_4OH:1H_2O_2:1H_2O	GaAs	Step-etch	GAS-0022
3NH_4OH:1H_2O_2:150H_2O	GaAs	Junction	GAS-0021
20NH_4OH:7H_2O_2:973H_2O	GaAs	Removal	GAS-0003b
xKOH:xH_2O	GaAs	Electrolytic, junction	GAS-0210
xKOH, pellet (molten flux)	GaAs	Dislocation	GAS-0031
250 ml 30%KOH:100 ml MeOH	GaAs	Preferential	GAS-0036
21 g KOH:8 g $K_3Fe(CN)_6$:100 ml H_2O	GaAs	Preferential, junction	GAS-0039
x4%NaOH:x5%H_2O_2	GaAs	Polish	GAS-0175
x1 *M* NaOH:x0.7 *M* H_2O_2	GaAs	Preferential	GAS-0173c
x30—50% NaOH	GaN	Removal	GAN-0002
x0.1 *N* NaOH	GaN	Electrolytic, selective	GAN-0001
x0.5%KOH:x1 *M* $K_3Fe(CN)_6$	Gap	Polish	GAP-0005
1NH_4OH:1$Cr(NO_3)_2$	Ge	Preferential	GE-0005d
250 ml 30%KOH:20 g I_2	Ge	Preferential	GE-0221a
250 ml 30%KOH:50 ml Br_2	Ge	Preferential	GE-0221b
x x%KOH	Ge	Electrolytic, junction	GE-0019
x x%NaOH	Ge	Electropolish	GE-0042
6 g KOH:4 g $K_3Fe(CN)_6$:50 ml H_2O	Ge	Preferential	GE-0150s

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Formula	Material	Use	Ref.
x0.5%KOH	Ge	Electrolytic, preferential	GE-0087
x 1 *N* KOH	Ge	Electropolish	GE-0088b
x 15%KOH	Ge	Electrolytic, passivation	GE-0204a
x10%NaOH:x15%$NaNO_3$:xH_2O	Ge	Preferential	GE-0208
x2%NaOH:x2%$NaClO_4$	Ge	Cleaning	GE-0155
x x%NaOH:xH_2O_2:x 1μ Al_2O_3	Ge	Chem/mech polish	GE-0210
1 20%NaOH:1H_2O_2	GeAs	Removal	GEAS-0001a
18 g NaOH:5 g $KHC_8H_4O_4$:100 ml H_2O	Ge_3N_4	Removal	GEN-0001
x x%NaOH:xx%Na_2S	GeSe	Removal	GESE-0001
1 20%NaOH:1H_2O_2	InSb	Removal	INSB-0002a
x x%KOH:xHF:xHNO_3	InSb	Polish	INSB-0005b
2.5 g KOH:200 ml MeOH	InP	Cleaning	INP-0048
1 g KOH:1 g $K_3Fe(CN)_6$:1 ml H_2O	InP	Preferential	INP-0064a
4 g KOH:6 g $K_3Fe(CN)_6$:35 ml H_2O	InP	Selective	INP-0064j
140 ml NH_4OH:60 ml HNO_3:10 g H_2Mo_4:240 ml H_2O	Pb	Removal	PB-0009b
5 45%KOH:1H_2O_2:5 EG	PbSe	Electropolish/thinning	PBSE-0002
5 g NaOH:0.2 gI_2:10 ml H_2O	PbTe	Preferential	PBTE-0001a
20 g KOH:45 ml H_2O:20 ml EOH:25 ml Gly	PbTe	Electropolish/ preferential	PBTE-0001b
5 g NaOH:10 ml 0.5%$NaIO_3$	PbTe	Preferential	PBTE-0002a
2 15%NaOH:1 x%$Na_2S_2O_8$	PbTe	Dislocation	PBTE-0005
2 15%NaOH:1$Na_2S_2O_8$, sat. sol.	HgTe	Dislocation	HGTE-0002b
1NH_4OH:2H_2O_2:7H_2O	Mo	Polish/cleaning	MO-0002
100 g NaOH/l:110 g KCN	Mo	Removal/cleaning	MO-0005b
20 g KOH:92 g $K_3Fe(CN)_6$:300 ml H_2O	Mo	Polish	MO-0009
x 10 *N* NaOH	Ni:Cr	Electrolytic, removal	NICR-0005b
xNH_4OH	NiO	Removal	NIO-0001a
x x%NaOH	Quartz	Preferential	QTZ-0014b
100 ml NH_4OH:100 ml H_2O_2:500 ml H_2O	Quartz	Cleaning	QTZ-0012
x 0.1 *N* NaOH	Re	Electropolish	RE-0002
1NH_4OH:1H_2O_2:6H_2O	Sapphire	Cleaning	SAP-0004a
x x%NaOH	Se	Removal	SE-0004b
1NH_4OH:12H_2O_2:4H_2O	$TiSi_2$	Removal	TISI-0003
1—2NH_4OH:1—2H_2O_2:5—7H_2O	Si	Cleaning	SI-0031
1NH_4OH:5H_2O_2	Si	Selective	SI-0021c
x x%KOH	Si	Etch-stop	SI-0084
10—30%KOH	Si	Preferential	SI-0091
250 ml 30%KOH:30 g I_2/50 ml Br_2	Si	Preferential	SI-0092a-g
200 g KOH:10 g $KAu(CN)_6$:800 ml H_2O	Si	Junction plate	SI-0101
x 2 *M* KOH	Si	Electrolytic, oxidation	SI-0146
x 1 *N* KOH: + glycerin: + H_2FSi_6	Si	Electropolish	SI-0245
x 10 *N* NaOH	Si	Selective structuring	SI-0147

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Formula	Material	Use	Ref.
250 ml 30%KOH:30 g KBr/$FeCl_3$	Si	Preferential, pit forming	SI-0198c
3NaOH:1Na_2O_2, pellet, molten	SiC	Polish	SIC-0011
x 2 *M* KOH	SiO_2	Removal	SIO-0002
1—2NH_4OH:1—2H_2O_2:4—6H_2O	SiO_2	Cleaning	SIO-0043
x$NaOH$:x$NaCO_3$:xH_3PO_4	SiO_2	Cleaning	SIO-0039c
18 g NaOH:4 g $KHC_8H_4O_4$:100 ml H_2O	Si_3N_4	Removal	SIN-0008c
1 g KOH:100 ml H_2O	Si_3N_4	Cleaning	SIN-0019
1NH_4OH:1H_2O_2	Ag	Removal	AG-0005
1NH_4OH:1H_2O	Ag	Cleaning	AG-0004a
25 ml NH_4OH:15 ml H_2O_2	Ag	Polish	AG-0012b
1H_2O_2:2EG:2KOH, sat. sol.	Ag_2Se	Polish	AGSE-0001b
3NH_4OH:2H_2O_2	Ag_2Te	Polish	AGTE-0001
xNH_4OH	AgCl	Cleaning	AGCL-0006
180 g NaOH:30 g $KMNO_4$:1000 ml H_2O	Steel	Selective	ST-0015
x x%KOH/NaOH	Ta	Removal	TA-0003f
9 30%KOH:1H_2O_2	TaN	Removal	TAN-0004
20 g KOH:92 g $K_3Fe(CN)_6$:300 ml H_2O	TaN	Removal	TAN-0005a
10 g KOH:10 g $K_3Fe(CN)_6$:100 ml H_2O	TaC	Cleaning	TAC-0001
1 g NaOH:100 $cm^3H_3PO_4$:2 g agar	SnTe	Electropolish	SNTE-0001
1NH_4OH:2H_2O_2	Ti	Removal	TI-0021b
10 g KOH:10 g $K_3Fe(CN)_6$:100 ml H_2O	TiC	Cleaning	TIC-0005
1NH_4OH:2H_2O_2	TiW	Removal	TIW-0001
x 20% NaOH	W	Cleaning	W-0001a
44.5 g NaOH:305 g $K_3Fe(CN)_6$:1000 ml H_2O	W	Removal	W-0001i
10 g NaOH:80 g $KClO_3$:40 g KCO_3:1000 ml H_2O	W	Electropolish/cleaning	W-0003b
xNH_4OH:x 25% $CuSO_4$	W	Polish	W-0006
1 3%NaOH:1 10% $K_2Fe(CN)_6$	W	Removal	W-0030b
1NH_4OH:2H_2O_2	W	Removal	W-0036
5 g KOH:5 g $K_3Fe(CN)_6$:100 ml H_2O	W	Step-etch	W-0035
20—30KOH/NaOH	WO_2	Removal	WO-0001
10 g KOH:10 g $K_3Fe(CN)_6$:100 ml H_2O	WC	Cleaning	WC-0001
x 0.75% NaOH	WRh	Polish	WRH-0001
x x% KOH	Y	Removal	Y-0001
10 ml NH_4OH:50 ml H_2O:2 g $NH_4(NO_3)_2$	Zn	Preferential	ZN-0006c
1—5 2%NaOH:1H_2O_2	Zn	Preferential	ZN-0017a
x 6 *N* NaOH (+ acid?)	ZnO	Removal	ZNO-0007
x 50% NaOH	ZnSe	Preferential	ZNSE-0002a
x 25% NaOH	ZnSe	Cleaning	ZNSE-0002c

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Formula	Material	Use	Ref.
x x% NaOH	ZnSe	Polish	ZNSE-0005
x 30%NaOH	ZnTe	Dislocation	ZNTE-0001a
x 20% NaOH	ZnTe	Removal	ZNTE-0006
1 x%KOH:1 x%NaOH	ZnW	Preferential	ZNW-0001b

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PHYSICAL PROPERTIES OF ICE, H_2O

Classification	Solvent
Atomic numbers	1 & 8
Atomic weight	18
Melting point (°C)	0
Boiling point (°C)	100
Density (g/cm³) 4°C	1.00
Freezing point (°C)	
Phase formation point (amorphous) (K)	80
(hex-to-cubic) (K)	71—76
Plastic deformation point (sphere/block) 0°C	−2.2/−5
Triple point (gas/liquid/solid) °C	4—5
Electrical resistivity (eV) hexagonal	0.84
isometric (cubic)	0.28
hex-cubic (trans.)	0.6
Formation temperature (artificial) (°F)	−4
(natural °F)	+4
Brittleness (psi)	10 (shatters)
Energy band gap (eV) hexagonal	0.85
isometric (cubic)	0.28
Hardness (Mohs — scratch)	3—4
Crystal structure (hexagonal — normal)	Six-rayed platelets
(isometric — normal)	(100) cube
(amorphous)	None
Color (solid)	Colorless to white
Cleavage (basal/cubic)	(0001)/(001)

ICE, H_2O

General: Ice is water in its solid, frozen state and, as it is cooled from 4 to 0°C, it expands, becoming lighter than water. Maximum density of water is 1.00 at 3.98°C, weighs 1 g, and is the unit against which all material specific gravity (density) is measured. Water is the only known substance that has a triple-point — it can exist in the solid/liquid/gas state simultaneously at about 4°C. Eleven volumes of ice will melt to ten volumes of water and, as long as solid ice remains in water as it is heated, temperature will stay at 0°C. The freezing point of ice is 0°C (32°F or 273°A and K) and is nominally clear and transparent, though it may appear slightly bluish to bluish-green by refraction.

Brine is natural salt water containing dissolved salts — halite, NaCl being a major constituent, along with calcium and magnesium chlorides — and artificial brines have been formulated for study of their freezing points. Liquid ammonia, NH_3, sulfur dioxide, SO_2 and, today, Freon, CCl_2F_2 under pressure with a brine solution ($CaCl_2$) are used for refrigeration — boiling points at −33.3, −10, and 29.8°C, respectively.

Ice forms during cold weather by the freezing of water in the ocean or in lakes, rivers and streams on land, and from the compaction of snow, sleet or hail from water vapor in the air. It is estimated that 70% of the fresh water in the world is as frozen ice in the Arctic and Antarctic regions, and it has been suggested that icebergs be driven to the seacoasts of arid desert areas as a fresh water supply.

Under normal atmospheric conditions of pressure, ice forms in the crystallographic hexagonal system, normal class as snowflakes but under increased pressure it will convert to isometric (cubic) system, normal class, as a cube, (100) structure. In some instances, zones of both amorphous and colloidal ice will occur.

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There are several natural and artificial forms of ice with a variety of uses which are described in the following sections:

Natural Forms of Ice

Snow

Annually deposits from water vapor in the air during cold weather in the form of snowflakes — relatively flat, hexagonal platelets of an unlimited variety of lace-like shapes to fairly massive globules of solid ice as pea-size sleet to chunks of hail. The latter can be fist-size or larger and can do physical damage to structures, vehicles and people. Snowflakes can nucleate spontaneously when water vapor in the air reaches the freezing point (self-nucleation) or on dust particles in the air; the latter being more common. Even in the summer time, in the upper reaches of a towering thunderhead cloud that may reach 50,000 ft or more, electric discharge (lightning) or the negative/positive potential that can build due to violent air currents within the cloud can initiate ice formation. (See ICE-0011). Silver iodide, AgI_2, is not water soluble and, as a particulate dust cloud, has been used to seed rain clouds or artificially initiate ice growth.

Annual snowfall is recorded in the temperate zones of the world and calculated for water content of spring run-off from mountain watersheds, ground collection in lakes and dams, and subsurface increase and maintenance of water tables.

At or below freezing, with low humidity, snow can deposit as dry, finely powdered snow and, when high wind occurs simultaneously, blinding snow-fog can be hazardous. Also with wind in winter, with or without snow, the wind-chill factor can drop the temperature below $-30°C$ or more. In early spring, with increased humidity, a snow storm can deposit heavy, wet snow and, in heavily populated areas, snow removal from roads is a major industry throughout the entire winter months. Because of the expansion and contraction of snow and ice it is a major factor in the cracking and reduction of rocks into soil, and can rupture water lines and so forth.

In skiing areas, manmade snow is blown across slopes as chilled water that produces artificial snow. Natural snow has long been used for temporary preservation and packing in the storage and transportation of foodstuff. In the metal industry snow and ice have been mixed with acids or chemicals to obtain cold mixtures at specific temperatures. For special mixtures, see the section on Water: Cold Etchants:

Lake Ice (Ponds, Rivers and Streams)

The fresh water commences to freeze on the surface as scrum ice — then, eventually, as solid ice sheets. Ice thickness varies in depth to 3 or 4 ft on an average. At or near the surface the ice is aerated and can be mixed with compacted snow. With increase in depth and pressure, it becomes solid, nonaerated ice, eventually will convert to cubic structure from its normal hexagonal, and there can be zones of colloidal and amorphous ice.

Before the discovery of refrigeration in the early 1930s, ice was cut from lakes and stored in ice houses for year-round use. Ice houses are thick-walled wooden barn-like structures where the cut slabs of ice are stacked with sawdust layers between blocks to keep them separated and prevent sticking. Lake and river ice is still cut as blocks in many rural areas of the world where there is no or limited electricity for a refrigerator. Properly stored, ice blocks can last year round, even for several years in 90°F weather through the summertime. Ice blocks are normally cut about $2 \times 1 \times 4$ ft in size, then further cut with an ice pick for use as a block of about 25 lb weight . . . with delivery every 2 to 3 days to the home ice box. Note that 1 cubic ft of ice is about 25 lb.

Glacier Ice

The last Ice Age ended about 12,000 B.C. at the end of the Pleistocene Epoch. We are currently in the Quaternary Period, which commenced about 3 million years ago with the

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Eocene Epoch, then the Pleistocene, and our present Holocene Epoch of these last 10,000 years. The last glacial ice sheet in North American extended almost to mid-continent in northern Kansas and, man as we know him today . . . *Homo sapiens, sapien* . . . established his civilization after the last Ice Age. Possibly the earliest city, referred to in ancient writings as the empire of Subir, was only discovered in 1981 in Syria. Artifacts at the site show that the area has been occupied by man for at least 7000 years. As there have been at least four major Ice Ages in the past, geologists believe we may well be between Ice Ages at present. How long before the next one? Estimates range from 10,000 to 500,000 years and, some doomsday environmentalists claim man can create his own Ice Age . . . the "Nuclear Freeze" hypothesis . . . within 100 years?

Regardless, there are still residual, left-over glaciers from the last Ice Age in high mountains and the Polar Regions — in the Swiss Alps; Mount Ranier in the American Northwest; and in Alaska, as only three examples. There is year-round study of these glaciers — their size increase or melt-back — as one factor in determining the variations in world climatic conditions. At depth, some of the ice in these glaciers may be as much as 10,000 years old. Most glaciers move back and forth a few inches a year, but one glacier in Alaska, within the past few years, suddenly has been moving seaward at a rate of 2 to 3 ft/day! This is a local action, does not mean the Arctic ice pack is melting, but is of interest as a singular climatic fluctuation. It is estimated that a 2°C worldwide temperature rise would be required to melt the Antarctic and Arctic ice caps, but the glaciers in the high mountains would probably still remain.

In the 1930s the Chinese claimed the discovery of a frozen Hairy Mammoth in North China which, when thawed, was still edible. Glacial ice contains much detritus — rocks, vegetation, and occasional animal life — and spring-thaw water run-off is often a highly aerated, light green-colored, very cold water.

Glaciers are of little use, other than as water run-off for lakes, rivers, and streams and where they enter the ocean, the glacier face can break off forming icebergs. Greenland in the North Atlantic is still covered by an ancient glacial ice sheet, and is responsible for several of the large icebergs that plague the Atlantic shipping lanes. Since the sinking of the Titanic, there has been a world-sponsored iceberg watch that tracks bergs down the Atlantic during the berg season.

Ice Pack

There are permanent ice packs in the Polar regions of the world. There are year-round study stations in the Antarctic (South Pole) where the snow pack is on underlying rock. The pack in the Arctic (North Pole) is largely on water (some covered rock islands), and study groups enter and leave without a permanent camp. There have been permanent installations built into the Greenland ice since about the late 1930s for research study, and air strips for the Iceberg Service watch. In the Antarctic, there are joint teams of Russian, American, French, and British scientists established in permanent study camps year round, not only studying the ice, but major study of climate conditions. It is here that ice cores — 4″ in diameter and several feet long — are cut to depth, then sections cut and melted to obtain ancient forminifera and radiolaria, which are microscopic sea life that can be used to establish ancient climatic conditions. Some of these ice samples are over 4000 years old from snow laid down at the time the great pyramids of Egypt were being built and man was just establishing his civilization in the Mediterranean area. It is thought that some of the ice at depth could be even older.

It is worth noting that the northern and southern land masses that were covered by the ice sheets during the last Ice Age are still rising, recovering from the massive weight of ice. Great Britain is an example . . . the entire island is tilting . . . the north rising; the south submerging. Norway and Sweden with their fjords and rugged coast line are atypical of a rising land mass, as is the rugged coast of New England in the Americas.

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The polar ice caps are estimated to contain 75% of the fresh water in the world and, if they were to melt completely, the oceans of the world would rise some 2 to 3 ft, inundating many coastal areas. That they have been melting over the past 5000 years is obvious in the Mediterranean area, where there are ancient buildings submerged in the sea.

Icebergs

Common to both the Pacific and Atlantic oceans but of more concern in the North Atlantic due to the heavier shipping traffic in the iceberg zone. These icebergs come mainly off the Greenland glaciers. Icebergs coming out of the Arctic into the Pacific are more low-level ice sheets and are blocked from entering the Pacific Ocean from the Bering Sea by the Aleutian Islands chain that extends across the Pacific from Alaska to near the north Asian mainland. The Antarctic at the South Pole, although it can produce large bergs, these do not travel up into the south Pacific to any extent due to the flow of ocean currents.

Regardless, icebergs can be extremely dangerous as two thirds to three quarters of the bergs are usually underwater, unseen. As they move and melt, they may suddenly "turn-turtle" or break-up into several smaller bergs. In the Arctic, the pack ice breaks into sheet-bergs that can pile up on each other in tremendous ice jams, much like ice jams, in the Mississippi River during spring thaw.

Today there is little use for icebergs, but Saudi Arabia has already suggested the driving of icebergs up from the Antarctic to their desert lands as a source of fresh water. They also could be driven up from the Ross ice shelf below South America to the Atacama Desert in Chile where there has been no known rainfall in recorded history.

Sea Ice

Sea ice forms initially as a near-mush on the ocean surface and, as the ocean water surface is being watched, suddenly solidifies as a thin sheet of ice as far as one can see! It is salt-water ice with a freezing point slightly above that of fresh-water ice. The specific freeze point varies to some degree with concentration of salts, but is usually between 5—6°C, against the 4°C for fresh-water ice. Because of this difference, rock salt is scattered on road ice during winter months to help melt it. Sea ice as permanent pack ice is more common to Arctic ice, it can be layered between snow-derived ice in the pack, rather than in the Antarctic where the ice is on a land mass base. Natural salt water ice is nonpotable and of little use, but specific chemical mixtures of salts are combined artificially for particular below freezing temperature baths in material processing. See the section on Water, and "Cold Etchants".

Sleet/Hail

Sleet is fine, frozen pellets of rain drops; hail is agglomerations of sleet. Both are clear, solid ice, largely amorphous, and occur where there is a rapid change of atmospheric conditions, such as a warm air front meeting a cold front, and can occur at any time of the year under proper conditions. Sleet can occur in the wintertime under similar conditions of rapid atmospheric changes, forming a thin, slick coating on everything it settles upon, and can be particularly dangerous on roads for vehicular traffic.

Black ice is not necessarily sleet, more often the re-freezing of melting snow or ice on roadways, particularly toward the lower road edge or at corners. It may be a mixture of water and road oils, and can be even slicker than pure ice due to the presence of oil. The term "black ice" is used as it is colored by the included dark oils and tars and, on a macadam road, may not be recognized by a driver in a moving vehicle.

There are occasional hail and sleet storms which can cause actual property damage. These occur most often in the U.S. in the mid-continent when frigid arctic air sweeps down from Canada to meet warm tropical air coming up from the Gulf of Mexico.

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Artificial Ice

For Human Use

Natural ice has been used for centuries as a food preservative. Some of the earliest written records refer to its use in the making of sherbet (Arabic: sharbat) . . . a mixture of snow or finely shaved ice with fruit flavoring . . . that may have its origins as far back as 5000 B.C. The Persian satraps used to have runners bring ice down from the mountains for use at the royal courts, and Roman emperors transported ice down from the north Italian Alps. The Eskimos and others who live in high mountains where there is permanent ice have long used ice caves for storage of food.

Refrigeration, as we know it today, was not developed until the early 1930s, though ice houses were in operation making block ice for industry and home use for many years prior to the first refrigerator or Frigidaire (Frig, the wife of the God Odin of Nordic mythology). Ammonia, NH_3, under pressure is still widely used in ice houses for mass production of ice, but Freon, CCl_2F_2, has largely replaced both ammonia and sulfur dioxide for home refrigeration and general storage and transportation of perishable foods. Refrigerated railway cars and trucks were originally developed in the U.S., then shipping refrigeration worldwide.

Refrigeration should be considered one of man's major accomplishments of modern times, as it has taken us away from seasonal reliance for our food supply to include both longer-term storage and transportation. Since ancient times, the seasons of the year . . . planting in the spring . . . harvesting in the fall . . . have controlled our lives. The availability of saltwater fish and shellfish always was in limited supply inland from seacoasts due to spoilage until the advent of refrigeration. Foods that could be dried or salted were the main travelfare.

Quick-freezing, developed as a commercial product after World War II, was another big step — first vegetables and fruit juices — now complete meals. The food is frozen with its liquids; whereas vacuum freezing, or vacuum packed food has little or no liquids. And as an adjunct to quick-freezing, today, nuclear irradiation of foodstuffs is being developed, prior to freezing or not requiring freezing. A recent report said that chicken, irradiated in a sealed bag and without freezing, had a shelf-life of better than a year.

Carbon dioxide, CO_2, as the solid dry ice, bears mention even though it is not "ice" by water definition. Dry ice has a melting point of about $-57°C$ — it sublimes from the solid without passing through a liquid state — and is used as a temporary medium for cold storage of foodstuffs, medical preparations, and industrial items such as epoxies and polyimide pastes. In a closed container it has a working life, or shelf-life, of about 3 days. As gaseous CO_2, it is the natural fermentation in beers and wines, the effervescent bubbles, or is artificially added to wines and soft drinks. Without flavoring it is seltzer water, which can be artificial or natural. A new product may be on the market soon: a flip-top can containing a CO_2 capsule that, when the can is opened, instantly chills the beverage with no need for refrigeration.

Research and Development

In material studies ice has been cut from lakes for determination of crystal structure at depth, and polar ice core samples have already been mentioned. Using high purity water both snowflakes and single crystal ice have been grown in the laboratory using liquid nitrogen, LN_2, cold cryostats, to include silver iodide, AgI_2, as a seeding vehicle. Natural salt water and manmade brines with different salt combinations and concentrations have been frozen and studied with similar cold (cryogenic) cryostats. Some such cryostats have been on a microscope stage to observe ice-forming characteristics directly under the microscope.

Technical Application: Ice has many uses in material processing of metals and metallic compounds in the general metal industries as well as Solid State.

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As refrigeration it is used for cold storage of particular materials, such as gallium (m.p. +30°C); unstabilized hydrogen peroxide, H_2O_2 (m.p. −1.7°C); bromine, Br_2 (m.p. −7.2°C), or epoxy and polyimide resin pastes. Some such resins have a shelf-life of a year at room temperature; others are stored at −40°C for extended shelf-life; others kept frozen as, when brought to room temperature, they harden within seconds or have a working-life of only 6 to 8 h once mixed as an A + B combination.

For a cold liquid in material processing: ice/water (0°C); ice/acetone (+8°C) still are used to chill acid etchants. The ice/acetone mixture also is used to remove water vapor by freeze-out from gases, argon gas from pressurized cylinders in particular. The ice/water mixture also is used as a direct quenching medium in the fabrication or study of many metals and metallic compounds.

As a cooling vehicle ice water or refrigeration coils — even just cool industrial water — is used for heat control in many operations: around furnaces through coils; epitaxy systems; ingot growth systems; water recirc systems; large etchant tanks, and so forth.

There are several "Cold Etchants" using ice or snow as one constituent for specific temperature levels. Several are listed under the section on Water under Cold Etchants.

As already discussed in the General section, ice is under a variety of studies, both natural and artificial, for physical data and electrical parameters. Studied as snowflakes, single crystal blocks, and spheres.

Etching: Water or steam. Pressure variation. Formvar, and heat, only.

ICE ETCHANTS

ICE-0001
ETCH NAME: Water
TYPE: Acid, polish
COMPOSITION:
x .... H_2O
DISCUSSION:
TIME:
TEMP: −5°C or less

H_2O as ice, (0001) single crystals used in a study of ice formation and reactions. Near-freezing water can be used to polish surfaces.
REF: Higuchi, K — *Acta Metall,* 6,636(1958)

ICE-0002: Okliya, M — *Sov Phys-Cryst,* 4,244(1960)

H_2O as ice, (0001) single crystals used in a study of ice formation and reactions. Lap surfaces with emery paper, then on the surface of a ground glass plate with no liquid solution, before polishing with near-freezing water. Cracks in the ice will self-heal at or slightly below −5°C.

ICE-0003: Kingley, W D — *J Appl Phys,* 31,833(1960)

H_2O as ice, (0001) single crystal used in a study of ice formation and reactions. Polish surfaces with near-freezing water. Also studied ice spheres. See ICE-0003b.

ICE-0012: Jellick, H H G — *J Appl Phys,* 32,1793(1961)

H_2O as ice, single crystal hexagonal specimens used in a study of the reactions of various liquid layers on ice surfaces, including freezing power, gripping tension and temperature. Cold water was used as a polishing solution.

ICE-0016: Eisenberg, D & Kadsmann, W — *The Structure and Properties of Water,* Oxford University Press, London, 1969.

H_2O as ice, at normal pressure and temperature (0°C) forms in the Wurtzite structure: hexagonal hemimorphic with no hexagonal plane of principal symmetry, and no horizontal axes of binary symmetry. As there are positive (upper) and negative (down) forms in the hemimorphic class, this accounts for the wide variety of snowflake patterns to a large degree. The high pressure form of ice is isometric normal cube, (100) as a crystal form.

ICE-0017: Dorn, R T et al — *Sci Am,* May 1977

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H_2O as ice from poly-water. As a liquid it is a high density chain of close-packed water molecules formed under special conditions using high purity, DI water. It boils at 150°C and freezes at −40°C to a plastic-like substance which is not like normal water ice.

ICE-0005
ETCH NAME: Liquid helium
TYPE: Gas, freezing
COMPOSITION:
x .... LHe
TIME:
TEMP: Near 2.2 K
DISCUSSION:

H_2O as ice, (0001) single crystals grown as hexagonal platelets in a study of the growth of ice. The water used was doped with KOH (0.1, 0.01 and 0.001 mol/dm^{-3} concentrations). De-aerated the water by repeated solidification and vacuum evacuation using a cryostat with LN_2 and heat exchanger. Operate at 77 K for 10—15 min to crystallize. There is a phase transition at 71—72 K from hexagonal to cubic form (hi-pressure ice). In this study, after ice forming, it was annealed at 60—65 K, then cooled down to LHe temperature.
REF: Tajima, Y — *J Phys Chem Solids*, 45,1135(1984)

ICE-0007
ETCH NAME: Pressure
TYPE: Pressure, dislocation
COMPOSITION:
x .... vapor pressure
TIME:
TEMP: Under 0°C
PRESSURE: Vary vapor pressure
DISCUSSION:

H_2O as ice, (0001) single crystals. A vertical growth system using differential pressure/temperature of a cryostat (LN_2) to solidify water from the vapor phase with a variable "chiller" zone. An ice plate was used to "seed" for growth nucleation, and AgI_2 smoke to initiate growth. Varying the vapor pressure was used to develop dislocations and defects.
REF: Gonda, T & Koke, T — *J Cryst Growth*, 65,36(1983)

ICE-0008a
ETCH NAME: Silver
TYPE: Metal, forming
COMPOSITION:
x .... Ag
TIME:
TEMP:
DISCUSSION:

H_2O as ice, (0001) single crystals used in a study of the hexagonal to cubic transformation with electrical conductivity measurements. A cryostat (LN_2) finger with silver electrodes used to initiate water vapor condensation. Amorphous, a-ice, was formed at 80 K. Sublimation/resublimation between 2 to 220 K used to convert hexagonal ice to cubic ice. Hexagonal band gap: 0.84 eV; cubic band gap: 0.28 eV; transition zone: 0.6 eV. Ice was stored in solid MeOH (−98°C).
REF: Chrzanowski, J & Sujak, B — *Thin Solid Films*, 112,17(1984)

ICE-0003b
ETCH NAME: Liquid nitrogen
TYPE: Gas, forming
COMPOSITION:
x .... LN_2
TIME:
TEMP: −195°C

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DISCUSSION:

H_2O as ice spheres. Spheres formed by spraying water into LN_2 or LOX ($-185°C$). Size was between 0.1 to 3 mm in diameter. Handling spheres at $-2.2°C$ can cause plastic deformation.

REF: Ibid.

ICE-0004

ETCH NAME: Ethylene dichloride — TIME:

TYPE: Acid, dislocation — TEMP:

COMPOSITION:

x .... polyvinyl formal (formvar)

x .... 1% ethylene dichloride

DISCUSSION:

H_2O as ice, (0001) single crystals used in a study of deformation and dislocation development. Pour the mixture over the ice surface, and allow it to dry by evaporation as the formvar solidifies. The water in the ethylene dichloride breaks through to form etch pits in the ice. Small pits form in the larger surface pits, and are crystallographically oriented triangles or hexagons, representative of dislocations(?). The formvar can be peeled from surfaces and used as replicas for SEM study.

REF: Bryant, G W & Mason, B J — *Phil Mag*, 5,1221(1960)

ICE-0009

ETCH NAME: Formvar — TIME:

TYPE: Acid, defect — TEMP:

COMPOSITION:

x .... formvar

DISCUSSION:

H_2O as ice, (0001) platelets grown using a low temperature cryostat (LN_2) built as a microscope sub-stage. Crystals were free-grown in a water bath by cryogenic cooling while under observation with a scanning electron microscope (SEM). After growth, crystals were coated with formvar, and then coated with thin film gold evaporated for reflectivity of the replicated surface. The film was then peeled away for SEM study.

REF: Nenow, D et al — *J Cryst Growth*, 66,489(1984)

ICE-0006

ETCH NAME: Cryogenic gas — TIME:

TYPE: Gas, forming — TEMP: $-195°C$

COMPOSITION:

x .... LN_2

DISCUSSION:

H_2O as ice, (0001) single crystals. An overview of growth techniques of ice forming from vapor phase water.

REF: Icuroda, T — *J Cryst Growth*, 65,27(1985)

ICE-0008b

ETCH NAME: Methyl alcohol — TIME:

TYPE: Alcohol, storage — TEMP: $-98°C$

COMPOSITION:

x .... MeOH, solid

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DISCUSSION:
H_2O as ice, (0001) single crystals. Ice can be held in storage in solid, frozen methyl alcohol. See ICE-0008a.
REF: Ibid.

ICE-0010
ETCH NAME: Brass
TYPE: Metal, polish
COMPOSITION:
x .... brass plate
TIME:
TEMP: Warm
DISCUSSION:
H_2O as ice — hexagonal, amorphous, colloidal and cubic specimens cut from lake ice and used in a study of formation and structure under natural conditions. Specimens were slab-cut using a nichrome wire at red-heat, then polished and thinned by rubbing on a warm brass plate. From the lake surface the ice structure progressed from hexagonal, through variable zones of amorphous and colloidal ice, to cubic ice at depth. There also was a reduction of bubbles, stria and low angle grain boundaries, and such defect density with increasing depth.
REF: Barns, R & Laudise, R A — *J Cryst Growth,* 71,104(1985)

ICE-0011
ETCH NAME: Temperature
TYPE: Temperature, formation
COMPOSITION:
x .... temperature
TIME:
TEMP: −4°F to +14°F
DISCUSSION:
H_2O as ice. A study of the natural growth of ice in clouds during a study of the cause of lightning. Ice forms in clouds as (1) tiny water droplets; (2) super-cooled water droplets well below 32°F; (3) chunk hail; (4) ice pellets called graupels (Ger: "soft hail") — pea-sized, raspberry-like structure formed by super-cooled water droplets freezing together. Ice crystals and graupels bounce off each other attaining a positive (+) or negative (−) charge and, with wind currents and convection within the cloud, charge separation occurs. With sufficient charge accumulation and separation, lightning discharge occurs with energy release up to 100 million volts. The thunderhead clouds, which generate much of the ice, rain and lightning, can extend from 1 mile above the earth surface to better than 10 miles upward as a single cloud. The temperature gradient in such clouds on a hot, humid day may be +90°F at their base — chilling vertically up through the cloud mass — to below −100°F at their top.
REF: Hallett, J — *Science,* Sept 1985, 75

ICE-0013
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, thinning
COMPOSITION:
x .... C_2H_5OH (EOH)
TIME:
TEMP: −20°C
DISCUSSION:
H_2O as ice, (100) cubic single crystals. Initial slices were about 10 mm thick, and lap polish/thinned in solution shown down to 2 mm. Quench in *n*-hexane to stop etching action. Specimens used in a study of voids formed by glide on nonbasal planes.
REF: Maguruma, J et al — *Phil Mag,* 13,625(1966)

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ICE-0014
ETCH NAME: Sodium chloride — TIME:
TYPE: Alkali, inhibitor — TEMP:
COMPOSITION:
x .... 1% NaCl
DISCUSSION:
H_2O as ice, (0001) crystals. The basal plane is the most stable in hexagonal ice. During growth of ice crystals, regardless of surface orientation, if a water solution of NaCl (common salt) is placed on the surface, it will inhibit further pure ice growth. (*Note:* Sea ice freezes slightly above the temperature of pure ice. Addition of NaCl — salt — begins to liquefy a pure ice surface.)
REF: Knight, C A — *J Appl Phys,* 33,1808(1962)
ICE-0015: Hobbs, P V & Mason, B J — *Phil Mag,* 9,181(1964)
H_2O as ice, single crystal spheres or polycrystalline spheres. To form spheres: (1) use a #30 hypodermic needle attached to an earphone diaphragm and use frequency to control water flow through the needle to form spheres 20—300 μm in diameter, or (2) dipping a glasswool fiber into water will cause coalescence at the tip with formation of spheres up to 1 mm in diameter, and (3) water droplets falling down a 2-ft high metal tube packed in solid CO_2 will form spheres that can be collected on a clean glass slide at the bottom. Sintering spheres is less rapid for single crystals under −10°C than for polycrystalline spheres. D_2O ice reacts at −10°C like H_2O ice at −14°C. For single crystal spheres, seed with AgI_2 smoke at slightly above −5°C.

ICE-0018
ETCH NAME: Salt — TIME:
TYPE: Salt, ice forming — TEMP:
COMPOSITION:
x .... $NaMnO_4$
DISCUSSION:
$NaMnO_4$ as a water solution used in a study of the freezing mechanisms of salt solutions. Reactions are similar to those of NaCl water solutions.
REF: Kober Ch & Scheiwem, M W — *J Cryst Growth,* 61,307(1983)

ICE-0019
ETCH NAME: — TIME:
TYPE: Ice, forming — TEMP: −196°C
COMPOSITION:
x .... ice
DISCUSSION:
Ice, used as a substrate for deposition of beryllium in vacuum at LN_2 temperature to produce a "freeze-out" structure of the metal. Thin films can be removed by melting away ice for microscope study as a form of the float-off technique.
REF: Baird, J D et al — *Nature (London),* 182,1660(1958)

PHYSICAL PROPERTIES OF INDIUM, In

Classification	Metal
Atomic number	49
Atomic weight	114.82
Melting point (°C)	156.17 (156.61)

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Boiling point (°C)	2000
Density (g/cm^3)	7.31
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.204
Specific heat (cal/g) 20°C	0.057
Heat of fusion (k-cal/g-atom)	6.8
Latent heat of fusion (cal/g)	6.8
Heat of vaporization (cal/g)	483
Atomic volume (W/D)	15.7
1st ionization energy (K-cal/g-mole)	133
1st ionization potential (eV)	5.785
Electronegativity (Pauling's)	1.7
Covalent radius (angstroms)	1.44
Ionic radius (angstroms)	0.8 (In^{+3})
Coefficient of linear thermal expansion	
Electrical resistivity (micro ohms-cm) 20°C	8.37
Modulus of elasticity (psi $\times 10^6$)	1.57
Tensile strength (psi)	380
Cross section (barns)	194
Hardness (Mohs — scratch)	1
(Brinell — kgf/mm^2)	0.9
Crystal structure (tetragonal — normal)	(110) prism, 1st order
Color (solid)	Silver white
Cleavage (hackly)	None

INDIUM, In

General: Does not occur as a native element and is considered a rare element. It is a minor constituent in sphalerite, ZnS (zincblende) and in the iron pyrites. It is one of the softest of known metals (H = 1) with a low melting point.

The pure metal does not have wide industrial use other than as a surface plating for corrosion resistance against organic acids (food containers). The major use is as a constituent in low melting point alloys of the lead-tin-zinc systems and, as such, these alloys are used in water sprinkler heads for fire protection. In dentistry, when mixed with gold and/or silver, used as a filling amalgam.

Technical Application: The pure metal is not widely used in Solid State device fabrication, but is a constituent of several semiconductor compounds, such as indium antimonide, InSb; indium arsenide, InAs: and indium phosphine, InP. The latter is one of the more widely used compound semiconductors.

Pure indium is used as a "mounting medium", such as for holding moly discs in an MBE system and, by surface alloying, for metal decoration of defects in single crystal wafers. Indium solders are used in device and package assemblies, but are not recommended for space hardware.

The pure metal has been grown for general morphology and defect studies.

Etching: Soluble in acids and mixed acid solutions. Slowly soluble in alkalies.

INDIUM ETCHANTS

IN-0005
ETCH NAME: Nitric acid, dilute
TYPE: Acid, cleaning
TIME: 1—2 min
TEMP: RT
COMPOSITION:
1 .... HNO_3
1 .... H_2O

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DISCUSSION:

In, as pellets used for the epitaxy growth of InP on InP:Fe (100) (SI) wafer substrates. Solution used to clean indium prior to use as an epitaxy metal growth source.

REF: Rhee, J K & Bhattacharya, P E — *J Electrochem Soc,* 130,700(1983)

IN-0001

ETCH NAME: Nitric acid

TYPE: Acid, structure

TIME: 1—4 min

TEMP: RT

COMPOSITION:

x .... HNO_3

x .... H_2O

DISCUSSION:

In, single crystal ingot grown by horizontal zone refining in a Pyrex boat enclosed in a sealed, evacuated glass tube. Five refining passes were made. After each pass ingots were removed and etched in dilute nitric acid to develop grain boundaries.

REF: Flower, S C et al — *J Phys Chem Solids,* 46,96(1985)

IN-0002

ETCH NAME:

TYPE: Electrolytic, structure

TIME:

TEMP: −30°C (dry ice)

ANODE: In

CATHODE: In

POWER: 4 V

COMPOSITION:

1 .... HNO_3

2 .... MeOH

DISCUSSION:

In, single crystal wires used in studying paramagnetic effects in superconductors and the resistance transition in indium wires. Etch in solution shown, rinse in DI water, then alcohol.

REF: Meissner, H & Zdanis, R — *Phys Rev,* 109,681(1958)

IN-0003

ETCH NAME: Hydrochloric acid

TYPE: Acid, removal

TIME:

TEMP: Boiling

COMPOSITION:

x .... HCl

DISCUSSION:

In, preform sheet alloyed on germanium (111) wafer. Metal drive-in was for decoration of defects. Alloy on germanium surface and remove excess indium by boiling in HCl. Heat at 700°C in contact with an iron, nickel or similar metal plate. Indium will develop growth striations and (111) fracture.

REF: English, A C — *J Appl Phys,* 31,1498(1960)

IN-0006: Penna, T C et al — *J Cryst Growth,* 67,27(1984)

In, material used for growth of InGaAs. The raw indium was degreased with solvents, then etch cleaned in HCl. Clean InAs in 1HCl:5glycerin, RT, 10 min. Clean GaAs in boiling HCl, 10 min.

IN-0004

ETCH NAME: Isopropyl alcohol

TYPE: Alcohol, removal

TIME:

TEMP: RT

COMPOSITION:

(1) x .... CH_3-$CHOHCH_3$

(2) x .... EOH

(3) x .... MeOH

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DISCUSSION:

In, specimens used as a solder holder on moly discs in MBE systems. Alcohols will dissolve indium and are used to clean surfaces before use in vacuum applications. After etching, DI water rinse and N_2 blow dry.

REF: Woo, R — personal communication, 1982

INDIUM ALLOYS, InMx

General: Metallic indium is a minor constituent in several minerals, particularly in zinc and iron ores from which it is extracted during ore reduction, but does not occur as a natural metallic alloy.

Pure indium and bismuth, alone, are low temperature alloys and, as mixtures with other metals, form a wide range of low to medium temperature alloys from about 100 to 400°C. Mixtures are compounded for specific temperatures, used for general soldering applications, though not as widely as the lead-tin solders. As indium has a low melting point, and subsequent low vapor pressure, it can show solid-solid diffusion with vaporization at elevated temperatures, similar to the problem encountered with gallium arsenide processing, where both elements can show such reactions.

Technical Application: Some indium solders are used in Solid State device assembly on substrate circuits of alumina, beryllia, etc., or in package sealing and construction but, as cited above, not as widely used as lead-tin solders. Pure indium sheet or alloy sheet are used as sealing gaskets on cryopump vacuum assemblies, as the material makes a firm, soft-seal and can withstand cryogenic temperatures with minimum crystallization or other alteration.

Certain indium alloys, such as InSn and InBi as eutectic alloys, have been evaluated for their superconducting properties.

Etching: Mixed acids and salts, variable with compound.

INDIUM ALLOY ETCHANTS

INDIUM:BISMUTH ETCHANTS

INBI-0001

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

x .... "chromate reagent"

DISCUSSION:

In:Bi, eutectic alloy specimen used in a structure study on the superconducting properties of eutectic alloys. Solution used to develop structure (mixture not shown). Work also done on InSb; PbSn; PbAg and PbTi. (*Note:* Sulfuric acid and sodium dichromate is the standard glass cleaner solution.)

REF: Levy, S A & Kim, Y B — *J Appl Phys,* 37,365(1966)

INBI-0002: Rhines, F N & Grobe, A H — *Trans AIME,* 156,253(1944)

For the "chromate reagent" mixtures.

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INDIUM:TIN ETCHANTS

INSN-0001
ETCH NAME:
TYPE: Electrolytic, preferential
COMPOSITION:
144 ml .... C_2H_5OH (EOH)
16 ml .... *n*-butyl glycol
32 ml .... H_2O
45 g .... $ZnCl_2$
10 g .... $AlCl_3$

TIME:
TEMP:
ANODE: InSn
CATHODE: SS
POWER: 60 V

DISCUSSION:
InSn, alloy specimens (eutectic) used in structure study on the superconducting properties of eutectic alloys. Solution used to develop structure. Work also done on InBi, PbSn, PbAg, and PbTi.
REF: Levy, S A & Kim, Y B — *J Appl Phys*, 37,365(1966)

INDIUM PHOSPHIDE OXIDE ETCHANTS

INPO-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... NH_4OH
x .... H_2O

TIME:
TEMP: RT

DISCUSSION:
InP, (100) wafers used in an anodic oxidation study. Strip oxide with solution shown. See INP-0092a-b for wafer preparation and oxidation procedures.
REF: Gordon, T et al — *J Phys Lett*, 39,965(1981)

RARE EARTH INDIUM ETCHANTS

RIN-0001
ETCH NAME:
TYPE: Halogen, removal
COMPOSITION:
x .... x% Br_2
x .... MeOH

TIME:
TEMP:

DISCUSSION:
R_5In_2 grown as single crystals by melting in an induction furnace in an anti-ferromagnetic susceptibility study. General formula R_5In_2 = rare earths where R = Gd, Ho, Tb, Dy. Ho_5In_2 is tetragonal at room temperature with transition to hexagonal structure at high temperature.
REF: Semitelou, I P & Yakinthes, R K — *J Phys Chem Solids*, 44,31(1983)

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INDIUM SELENIDE ETCHANTS

INSE-0001
ETCH NAME:
TYPE: Acid, defect
TIME: 3 min
TEMP: RT
COMPOSITION:
25 ml .... H_2SO_4
30 g .... $K_2Cr_2O_7$
180 ml .... H_2O
DISCUSSION:

InSe, (0001) as hand cleaved wafers. Material is a III—IV lamellar semiconductor compound with an R3m space group rhombohedral lattice. Ingot grown by Bridgman method in a study of growth mechanisms. As grown material develops cleavage surfaces and indium segregation clusters and zones that precipitate parallel to InSe layers which are perpendicular to the c-axis. Large crystal grain boundaries observed and, like GaSe, there can be defect-free areas. Doping with As (InAs) and In segregation can cause "contamination" defects. Solution shown used to develop dislocations, grain boundaries, and other defects.
REF: Chevy, A — *J Cryst Growth,* 67,119(1984)

INDIUM TELLURIDE ETCHANTS

INTE-0001
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
1 .... Br_2
19 .... HAc
x .... *citric acid

*Saturate the solution.

DISCUSSION:

In_2Te_3 specimens. Solution used as a polishing etch. After etching, use solution — without bromine — to quench reaction and remove residual bromine.
REF: Irving, B A, *The Electrochemistry of Semiconductors,* Holmes, P J, Ed, Academic Press, New York, 1962
INTE-0002: Mooser, E & Pearson, W B — *Phys Rev,* 101,492(1956)

In_2Te_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, $AgInTe_2$, In_2Te_3, and Bi_2Se_3.

INDIUM THALLINIDE ETCHANTS

INTL-0001
ETCH NAME: BRM
TYPE: Halogen, polish
TIME:
TEMP:
COMPOSITION:
x .... x% Br_2
x .... MeOH

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DISCUSSION:

In_2Tl_3 single crystal ingots grown in a study of new semiconductors compounds. See INTE-0001 for other compounds studied.

REF: Mooser, E & Pearson, W B — *Phys Rev*, 101,492(1956)

INDIUM TIN OXIDE ETCHANTS

ITO-0001

ETCH NAME: Nitric acid, dilute — TIME:

TYPE: Acid, flux removal — TEMP: Boiling

COMPOSITION:

x .... HNO_3

x .... H_2O

DISCUSSION:

$InSnO_2$ (ITO) single crystal grown by flux method in $PbO:B_2O_3$ flux with In_2O_3 + SnO_2 at 1200°C, 24 h. Cool at 2—3°C/h to 800—900°C then turn off power. Grow in a platinum crucible. Etch remove ITO crystals with solution shown from flux. Crystals are cubic and black in color; thin crystals are transparent, yellow. With greater than 9% tin in solution, crystals will not grow.

REF: Kani, Y — *Jpn J Appl Phys Lett*, 23,L12(1984)

ITO-0002

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, selective — TEMP:

COMPOSITION:

x .... HCl, conc.

DISCUSSION:

In_2O_3, as a thin film doped with tin, Sn, used for its electro-optical properties. Grown in a $PbO:B_2O_3$ flux. The following elements can be used as donor replacement for indium: Ti, Zr, Hf, Nb, Ta, W, and Ge with similar device applications as ITO material. (*Note:* See Indium Oxide, In_2O_3, for additional etchants.)

REF: Kani, Y — *Jpn J Appl Phys*, 23,127(1983)

PHYSICAL PROPERTIES OF INDIUM ANTIMONIDE, InSb

Classification	Antimonide
Atomic numbers	49 & 51
Atomic weight	216.6
Melting point (°C)	523
Boiling point (°C)	
Density (g/cm^3)	5.80
Refractive index (n =)	3.96
Lattice constant (angstroms)	6.48
Energy band gap (eV)	0.17
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — tetragonal)	(111) tetrahedron
Color (solid)	Grey-silver
Cleavage (dodecahedral)	(110)

INDIUM ANTIMONIDE, InSb

General: Does not occur as a natural compound although there are other metallic anti-

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monides of nickel, iron, copper, arsenic, and silver which may contain sulfur. There is no industrial use other than as a compound semiconductor.

Technical Application: Indium antimonide is a III—V compound semiconductor with the sphalerite, ZnS, structure. It is a (111) surface polar compound with (111)In and ($\overline{111}$)Sb showing different etching characteristics. There has been study of the (111) orientation, but most devices are fabricated with (100) wafer orientation. Single crystal ingots have been grown by the Horizontal Bridgman (HB); Czochralski (CZ); and Float Zone (FZ) methods. Epitaxy thin films are grown by Vapor Transport (VT), and Chemical Vapor Deposition (CVD).

Both single crystal wafers and thin films have been fabricated as devices: microwave mixers; strain transducers; laser diodes; Hall effect devices; and for magnetoresistive applications. Trinary compounds with arsenic or indium have been fabricated as laser and photoluminescent diodes, or photocathodes.

Etching: H_2SO_4, HNO_3. Mixed acids as HF:HNO_3/H_2O_2, HCl:HNO_3. Alkalies and halogens. Dry chemical etching (DCE), ionic gases.

INDIUM ANTIMONIDE ETCHANTS

INSB-0001a
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: RT
COMPOSITION:
10 .... HF
25 .... HNO_3
20 .... CH_3COOH (HAc)
DISCUSSION:

InSb, (111) wafers used in an etch development study of polish and preferential etchants to develop controlled damage-pits using the Pennington Pit Method (PPM) — a diamond stylus with controlled pressure and rotation on a wafer surface that is then etched in a preferential etchant to develop a flat bottom pit. The solution shown is a good polishing etch.

REF: Pennington, P — personal communication, 1957.

INSB-0001b
ETCH NAME:
TYPE: Acid, preferential/polish
TIME:
TEMP: RT
COMPOSITION:
HNO_3 .... 1 .... 1 1
HCl .... 3 .... 5 3
H_2O .... 4 .... 6 8
DISCUSSION:

InSb, (111) wafers. These are possible controlled pit damage preferential etchants. See INSB-0001a for further discussion.

REF: Ibid.

INSB-0041: Eisen, F H & Birchenall, C E — *Acta Metall*, 5,265(1957)

InSb, (111) wafers used in a study of self-diffusion in both InSb and GaSb. Aqua regia used to polish specimens. Also used Vilella's Reagent.

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INSB-0001c
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
25 .... HNO_3
10 .... HCl
20 .... HAc
DISCUSSION:
InSb, (111) wafers used in an etch development study. See INSB-0001a for further discussion.
REF: Ibid.

INSB-0001d
ETCH NAME: Allen's etch TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
x *CP4
x .... HCl
x .... H_2O

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

DISCUSSION:
InSb, (111) wafers used in an etch development study. See INSB-0001a for further discussion.
REF: Ibid.

INSB-0001e
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
1 .... HCl
2 .... $NaClO_3$
3 .... H_2O
DISCUSSION:
InSb, (111) wafers used in an etch development study. See INSB-0001a for further discussion.
REF: Ibid.

INSB-0001f
ETCH NAME: CP4 TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... HAc
0.5 .... Br_2
DISCUSSION:
InSb, (111) wafers used in an etch development study. Solution is a fast chemical polish.
REF: Ibid.
INSB-0019b: Ibid.

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InSb, oriented cylinders were cut in the c-axis direction. CP4 used to polish specimens prior to anodic and air oxidation.

INSB-0023: Bardsley, W & Bell, N A — *J Electron*, 3,103(1957)

InSb, (111) wafers used in an etch pit study. CP4 used to develop etch pits.

INSB-0015: Galaranova, V V & Erokhina, N A — *Fiz Tverd Tela*, 1,1198(1959)

InSb, (111) wafers fabricated as barrier-layer photovoltaic cells with indium or cadmium alloyed junctions. Devices etch cleaned and electrically tuned with CP4.

INSB-0029: Laff, R A & Fan, H Y — *Phys Rev*, 121,53(1961)

InSb specimens. CP4 used to etch thin specimens in a study of carrier lifetime.

INSB-0036: Wertheim, G K — *Phys Rev*, 104,662(1956)

InSb, (111) wafers used in a study of carrier lifetime. CP4 used as a polish etch.

INSB-0039: Haneman, D — *Br J Appl Phys*, 16,411(1965)

InSb, (111) wafers used in a study of strain energy associated with both positive and negative (111) surfaces. Mount specimens in balsam, and mechanically polish with 0.25 μm alumina, then 0.1 μm diamond paste. Remove specimens from balsam by dissolving balsam in xylene. Etch polish surfaces by floating individual wafers on water and adding CP4. The etched side is always concave, and the negative wafer side etches more rapidly.

INSB-0034a: Kuczynski, G C & Hochman, R F — *Phys Rev*, 108,946(1957)

InSb wafers used in a study of light induced plasticity. Specimens were surface damaged using the diamond point of a Knoop Hardness Tester, and then etched in CP4 to develop damage induced defect structure.

INSB-0002a
ETCH NAME:
TIME:
TYPE: Acid, removal
TEMP: Hot
COMPOSITION:
1 .... 20% NaOH
1 .... 30% H_2O_2
DISCUSSION:
InSb, (111) wafers used in an etch development study. Solution will attack when used hot.
REF: Robbins, H & Schwartz, B — Tech Rep, 1960

INSB-0002b
ETCH NAME: Sulfuric acid
TIME:
TYPE: Acid, removal
TEMP: Hot
COMPOSITION:
(1) x .... H_2SO_4, conc.
(2) 2 .... H_2SO_4
1 .... H_2O
DISCUSSION:
InSb, (111) wafers used in an etch development study. Both solutions will attack when used hot.
REF: Ibid.

INSB-0027a
ETCH NAME: Hydrofluoric acid
TIME:
TYPE: Acid, oxide removal
TEMP:
COMPOSITION:
x .... HF

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DISCUSSION:

InSb specimen used in an anodization study. Anodize in a solution of 0.1 *N* KOH with current at about 200 $\mu m/cm^2$. Remove oxide with solution shown which does not etch indium antimonide.

REF: Venables, J D & Brody, R M — *J Electrochem Soc*, 107,296(1960)

INSB-0028a

ETCH NAME:

TIME:

TYPE: Acid, preferential

TEMP:

COMPOSITION:

1 .... HF

1 .... H_2O_2

DISCUSSION:

InSb, (111) used in a study of behavior during heat treatment. Solution is preferential on (111) surfaces. Polish etch with 1HF:2HNO_3: 1HAc. See INSB-0014b.

REF: Haneman, D — *J Appl Phys*, 31,217(1960)

INSB-0027b

ETCH NAME: Potassium hydroxide

TIME:

TYPE: Electrolytic, anodization

TEMP:

COMPOSITION:

x .... 0.1 *N* KOH

ANODE: InSb

CATHODE:

POWER: 200 $\mu A/cm^2$

DISCUSSION:

InSb, (111) wafers used in a study of anodization of surfaces. Solution shown used to anodize.

REF: Ibid.

INSB-0038: Venables, J D & Brody, R M — *J Appl Phys*, 30,1110(1959)

InSb, (111) wafers used in oxidation experiment of surfaces. Flooding solution with light during anodization will increase oxidation rate. Surface replicas of carbon can be made for microscope study.

INSB-0037

ETCH NAME: BRM

TIME:

TYPE: Halogen, polish

TEMP: RT

COMPOSITION:

x .... 0.05% Br_2

x .... MeOH

DISCUSSION:

InSb, (100) wafers to be used as MBE substrates with wafers first studied for surface chemistry. Initially clean in (1) 1HCl:10EOH; (2) EOH rinse/dry, and (3) Cl_2 RF plasma gas clean. For surface studies: (1) apply 1HCl:1HNO_3:25H_2O by pipette with wafer on spinner at 3600 rpm; (2) bubble Cl_2 gas through CCl_4 onto spinning samples working in a dry box; (3) apply either 1HCl:4HNO_3:25H_2O or 1HF:4HNO_3:24 lactic acid. Acids leave C^+ and F^- contamination on surfaces, which can be removed with the BRM solution shown. BRM shown also used to chem/mech polish surfaces with MeOH rinse.

REF: Vasquez, R P et al — *J Appl Phys*, 54,1365(1983)

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INSB-0002c
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
(1) x .... HNO_3
(2) 2 .... HNO_3
1 .... H_2O
(3) 1 .... HNO_3
2 .... H_2O
TIME:
TEMP: RT & hot
DISCUSSION:
InSb, (111) wafers used in an etch development study. Concentrated nitric acid was evaluated with both white and red fuming concentrations and both solutions showed moderate to vigorous reaction at RT. The 2:1 solution is slow at RT but moderate to vigorous used hot. The 1:2 solution shows slow reaction used hot. (*Note:* White fuming nitric is 70%, standard concentration. Yellow fuming is 72%; and red fuming is 74%.)
REF: Ibid.

INSB-0002d
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) 1 .... HCl
1 .... HNO_3
(2) 2 .... HCl
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
InSb, (111) wafers used in an etch development study. The 1:1 solution reacts moderately to vigorously at RT. The 2:1 solution is slow at RT, but used hot it is moderate to vigorous.
REF: Ibid.

INSB-0002e
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
InSb, (111) wafers used in an etch development study. Reaction is moderate to vigorous.
REF: Ibid.
INSB-0018: Venables, J D & Brody, R M — *J Appl Phys*, 29,1025(1958)
InSb, (111) wafers used in an etch study. Solution used at RT, 2—5 sec as a polish etch.

INSB-0003a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
10 .... lactic acid
TIME:
TEMP:
DISCUSSION:
InSb, (111) wafers. Solution used as a polish etch. Also used to polish a single crystal sphere.
REF: Maringer, R E — *J Appl Phys*, 29,1261(1958)

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INSB-0003b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
5 .... HF
10 .... HNO_3
4 .... lactic acid
15 .... H_2O
DISCUSSION:
InSb, (111) wafers. Solution is a preferential etch. A single crystal sphere etched to finite crystal form (FCF) produced (111) pole figures, only.
REF: Ibid.

INSB-0004
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
2 .... HCl
2 .... HNO_3
3 .... H_2O
DISCUSSION:
InSb, (111) wafers used in an etch development study. Solution is a polish etch.
REF: Marsh, O — personal communication, 1958

INSB-0005a
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
6 .... H_2O
DISCUSSION:
InSb, (111) wafers used in an etch development study. The wafers were first polished in an HF:HNO_3:KOH solution. The solution shown produces triangular etch pits on (111)A — indium surfaces. The $(\overline{111})$B — antimony surface — is attacked erratically.
REF: Minamoto, M T — *J Appl Phys*, 33,1826(1962)

INSB-0005b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT & 4°C
COMPOSITION:
x .... HF
x .... HNO_3
x .... x% KOH
DISCUSSION:
InSb, (111) wafers used in an etch development study. Wafers were polished with the solution shown prior to preferential etching to observe the polar structure of this compound. Erratic at 4°C.
REF: Ibid.

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INSB-0006a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
1 .... 1% $Cr_2(SO_4)_3$
TIME:
TEMP: RT
RATE: (111) 9 mg/cm²/min
(111) 17 mg/cm²/min
DISCUSSION:
InSb, (111) wafers used in a defect study. Only low angle boundary dislocation etch pits on (111)A observed. No edge dislocations on $(\overline{1}\overline{1}\overline{1})$B. Solution adjusted for 1% Cr^{+++} ion.
REF: Lavine, M C et al — *J Electrochem Soc,* 108,974(1961)

INSB-0006b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
1 .... 1% $CoSO_4$
TIME:
TEMP: RT
RATE: (111) 8 g/cm²/min
(111) 18 mg/cm²/min
DISCUSSION:
InSb, (111) wafers used in a defect study. Solution will develop edge dislocations on the $(\overline{1}\overline{1}\overline{1})$B surface. Solution adjusted for 1% Co^{++} ion.
REF: Ibid.

INSB-0007
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
2 .... HF
59 .... 20% tartaric acid
39 .... H_2O_2
TIME:
TEMP:
DISCUSSION:
InSb, (100), n-type wafers used in a study of native oxide. Solution shown was used to chem/mech polish surfaces. The native oxide was 2—4 nm thick.
REF: Belyi, V I et al — *Thin Solid Films,* 113,157(1984)

INSB-0008
ETCH NAME:
TYPE:
COMPOSITION:
DISCUSSION:
TIME:
TEMP:
InSb, (100), n-type wafers used in a study of adsorption coefficients. Wafers were wire saw cut from ingots, mechanically and chemical etched (neither solution given). Wafers were etched to 0.04 cm thick.
REF: Brown, E — *J Appl Phys,* 57,2361(1985)

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INSB-0006c
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
DISCUSSION:
InSb, (111) wafers used in a defect study. This solution was used as the "base" polish etch in studying the effect of additives to the solution and their action on surfaces.
REF: Ibid.

TIME:
TEMP: RT
RATE: (111) 11 mg/cm²/min
($\overline{111}$) 17 mg/cm²/min

INSB-0006d
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
1 .... 1% $NiSO_4$
DISCUSSION:
InSb, (111) wafers used in a defect study. Nickel additive was for 1% Ni^{++} ions.
REF: Ibid.

TIME:
TEMP: RT
RATE: (111) 8 mg/cm²/min
($\overline{111}$) 18 mg/cm²/min

INSB-0006e
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
1 .... 0.4% *n*-butylthiobutane
DISCUSSION:
InSb, (111) wafers used in a defect study.
REF: Ibid.

TIME:
TEMP: 4°C
RATE: (111) 3 mg/cm²/min
($\overline{111}$) 8 mg/cm²/min

INSB-0006f
ETCH NAME: CP4, modified
TYPE: Acid, polish
COMPOSITION:
1 .... HF
2 .... HNO_3
1 .... HAc
DISCUSSION:
InSb, (111) wafers used in a defect study. This modified CP4 solution was also used as a "base" polishing and cleaning etch.
REF: Ibid.

TIME:
TEMP: 4°C
RATE: (111) 0.5/cm²/sec
($\overline{111}$) 7.8/cm²/sec

INSB-0035a: Haneman, D — *J Appl Phys*, 31,217(1960)
InSb, (111) wafers. Etch pits developed on (111)Sb, but not on ($\overline{111}$)In with the solution shown. Follow with 1HF:1H_2O_2 and DI water rinse. Also develops preferential etch pits.

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INSB-0006g
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... HNO_3
1 .... HAc
1 .... 0.3% *n*-amylamine
DISCUSSION:
InSb, (111) wafers used in a defect study.
REF: Ibid.

TIME:
TEMP: 2°C
RATE: (111) 0.4/cm²/sec
($\overline{111}$) 0.4/cm²/sec

INSB-0006h
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... HNO_3
1 .... HAc
1 .... 0.05% sodium stearate
DISCUSSION:
InSb, (111) wafers used in a defect study.
REF: Ibid.

TIME:
TEMP: 2°C
RATE: (111) 0.3/cm²/sec

INSB-0028c
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat
DISCUSSION:
InSb, (111) wafers when heat treated below 523°C showed hillock formation with structure alteration due to heat with figure migration across surfaces.
REF: Ibid.
INSB-0035b: Haneman, D — *J Appl Phys*, 31,217(1960)
InSb, single crystal wafers used in a study of the effects of thermal heat treatment.
INSB-0043: Venables, J D & Brody, R M — *J Appl Phys*, 30,122(1959)
InSb wafers. A study of the relation between generation and motion stress in dislocations of the material associated with heat.

TIME:
TEMP: 523°C max.

INSB-0009a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
5 .... H_2O_2
+/− .... H_2O
DISCUSSION:
InSb, (111), p-type wafers used in a study of recombination processes. Solution used to etch polish surfaces.
REF: Zitter, R N & Strauss, A J — *Phys Rev*, 115,266(1959)

TIME:
TEMP:

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INSB-0010a
ETCH NAME: TIME: 3 min
TYPE: Acid, clean TEMP: RT
COMPOSITION:
5 .... HNO_3
1 .... lactic acid
DISCUSSION:
InSb, (111)A, ($\overline{111}$)B, and (100) wafers used as substrates for MBE homoepitaxy growth in an excess Sb_4 atmosphere. Etch polish substrates with Br_2:MeOH; then degrease with solvents, and etch clean with solution shown. In MBE vacuum system, final thermal clean (111) surfaces at 450°C; (100) wafers 430°C due to Sb dissociation.
REF: Okachi, J et al — *J Electron Mater,* 14,419(1985)

INSB-0011
ETCH NAME: Isopropyl alcohol TIME:
TYPE: Alcohol, clean TEMP:
COMPOSITION:
x .... $CH_3CHOHCH_3$ (ISO)
DISCUSSION:
InSb, (001) wafers used as substrates for MBE growth of CdTe thin films. InSb-CdTe form an isomorphous series. Best growth between 50 to 150°C with some dislocations probably due to O_2 and C in the InSb surface. CdTe tends to twin and produce low angle grain boundaries. Before growth, clean InSb by rinsing in alcohol; then Ar^+ ion bombardment at 500 eV in vacuum and anneal at 200°C.
REF: Farrew, R F C et al — *Appl Phys Lett,* 39,954(1981)

INSB-0012a
ETCH NAME: BRM TIME:
TYPE: Halogen, polish TEMP:
COMPOSITION:
x .... Br_2
x .... MeOH
DISCUSSION:
InSb, (100) wafers used as substrates for growth of Cl_2 on surfaces. First, polish with a BRM solution; then dip in 0.5% Br_2:MeOH mixture, and rinse in MeOH. Remove native oxide with 1HCl:10 EOH and rinse in EOH. With wafer on a spinner at 3600 rpm, etch with $1HCl:1HNO_3:25H_2O$ using pipette droplets of etch onto the spinning wafer. Grow chlorinated surface by flooding spinning wafer with CCl_4 saturated with chlorine gas. This was a surface cleaning study.
REF: Vasquez, R P et al — *J Appl Phys,* 54,1337(1983)

INSB-0012b
ETCH NAME: TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
1 .... HCl
10 .... EOH
DISCUSSION:
InSb, (100) wafers used as substrates to grow chlorine on surfaces in a cleaning study. After a BRM surface polish there is a passivating native oxide left, which can be removed with the solution shown. See INSB-0012a.
REF: Ibid.

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INSB-0012c
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HCl
1 .... HNO_3
25 .... H_2O
DISCUSSION:
InSb, (100) wafers used as substrates to grow chlorine on surfaces in a cleaning study. Use a pipette with droplets of the etch solution shown being dropped onto wafer surfaces held on a spinner, and being rotated at 3600 rpm to polish. See INSB-0012a.
REF: Ibid.

INSB-0013
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
8 .... H_2O
X .... 0.4% *n*-butylthiobutane
DISCUSSION:
InSb, (111) wafers. This solution develops beta-type dislocations on both the (111)A and $(\overline{111})$B surfaces.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970, 7
INSB-0026: Gatos, H C et al — *J Appl Phys,* 32,1574(1961)
InSb, (111) wafers used in an etch development and defect study. With *n*-butylthiobutane in solution, pits are flat bottomed similar to those of hot KOH on silicon, and associated with Sb dislocations; without the *n*-butylthiobutane, pits are smooth and conical with a high center point (called a "tit pit"), and associated with indium dislocations. (*Note:* Similar structure has been observed on both germanium and silicon (111) wafers and, as seen on natural minerals, is referred to as mammillary or botryoidal structure.)

INSB-0028a
ETCH NAME: TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
x .... x% I_2
x .... MeOH
DISCUSSION:
InSb, (100) wafers and other orientations. Solution used as a chem/mech polish etch similar to BRM solutions. See INSB-0012a.
REF: Fuller, C S & Allison, H W — *J Electrochem Soc,* 109,880(1962)

INSB-0029
ETCH NAME: CP4A TIME: to 30 sec
TYPE: Acid, polish TEMP: RT
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc

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DISCUSSION:

InSb, (111) wafers and other orientation. Solution used as a general polish etch.

REF: Dewald, J F — *J Electrochem Soc,* 104,244(1957)

INSB-0014a

ETCH NAME: Etch #1 TIME:

TYPE: Acid, preferential TEMP: 10°C

COMPOSITION:

x .... 6 *N* HCl

x .... 0.1 *N* $FeCl_3$

DISCUSSION:

InSb, (100) and (110) wafers used in a study of dislocation and defects on these surfaces. Solution used to develop defects.

REF: Gatos, H C & Lavine, M C — *J Electrochem Soc,* 107,433(1960)

INSB-0025a: Gatos, H C & Lavine, M C — *J Appl Phys,* 31,743(1960)

InSb, (111) wafers. Solution used at 95°C, and will develop dislocation pits on both the (111)A and ($\overline{111}$)B surfaces. Below 82°C solution will only develop pits on the (111)A surface.

INSB-0014b

ETCH NAME: Etch #2 TIME: xx 4 sec

TYPE: Acid, preferential TEMP: 4°C RT

COMPOSITION:

1 .... HF

1 .... HAc

2 .... HNO_3

DISCUSSION:

InSb, (100) and (110) wafers used in a study of dislocation and defects on these surfaces.

REF: Ibid.

INSB-0014c

ETCH NAME: TIME: 20 sec

TYPE: Acid, polish TEMP: RT

COMPOSITION:

5 .... HF

5 .... HNO_3

2 .... H_2O

DISCUSSION:

InS, (100) and (110) wafers used in a study of dislocation and defects on these surfaces. Although this is a polish etch, it shows a dislocation background of pits very similar to those on germanium etched in CP4.

REF: Ibid.

INSB-0015a

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

4 .... HF

5 .... HNO_3

12 .... H_2O

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DISCUSSION:

InSb, (311) wafers used in a study of anodic films. Solution shown will develop etch pits on the $(\overline{3}\overline{1}\overline{1})$B surface but not on the (311)A.

REF: DeWalt, J F — *J Electrochem Soc,* 104,244(1957)

INSB-0025b

ETCH NAME: TIME:

TYPE: Acid, dislocation TEMP:

COMPOSITION:

1 .... HF

1 .... HAc

2 .... HNO_3

x .... *stearic acid

*x = saturate the solution with stearic acid.

DISCUSSION:

InSb, $(\overline{1}\overline{1}\overline{1})$ wafers used in a dislocation etch pit study on (111)A and $(\overline{1}\overline{1}\overline{1})$B surfaces. Solution will develop dislocation pits on both surfaces. With the solution between +2—0°C, and removal rates measured as mg/cm²/sec:

(1) with stearic acid: (111)A = 0.44 (111)B = 0.38

(2) without stearic acid: (111)A = 0.50 (111)B = 7.8

REF: Ibid.

INSB-0025c

ETCH NAME: TIME:

TYPE: Acid, dislocation TEMP:

COMPOSITION:

1 .... HF

1 .... H_2O_2

2 .... H_2O

DISCUSSION:

InSb, (111) wafers used in a study of dislocation etch pits on (111)A and $(\overline{1}\overline{1}\overline{1})$B surfaces. Solution will develop etch pits on both surfaces with those on the (111)A particularly well developed.

REF: Ibid.

INSB-0015b

ETCH NAME: TIME: 5—30 sec

TYPE: Acid, polish TEMP: RT

COMPOSITION:

24 .... HF

40 .... HNO_3

24 .... HAc

DISCUSSION:

InSb, (311) wafers used in an anodic film study. Mechanical lap/polish, then remove residual subsurface damage with the solution shown. Wafers with (110) surfaces were cleaved with a razor blade guillotine system to obtain wafers of 1 cm area, which showed some surface fracture steps present but was within 2° of (110) orientation. Oxide films were formed in a solution of xKOH:2xtartaric acid.

REF: Ibid.

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INSB-0015c
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
10 .... $HClO_4$
40 .... HAc
2 .... H_2O
TIME:
TEMP: 5°C
ANODE:
CATHODE:
POWER: 50 mA/cm^2
DISCUSSION:
InSb, (311) and (110) wafers used in an anodic film study. The black film that forms during polish etching with the solution shown can be removed with running water. Antimony oxides can be dissolved electrolytically with a 0.1 *N* KOH electrolyte, which will not remove In_2O_3.
REF: Ibid.
INSB-0016: Bardsley, W & Bell, R I — *J Electron Control,* 3,103(1957)
InSb, (111) wafers were polished in solution shown before etching for dislocations.
INSB-0017: Aclrytner, J & Kolakowski, B — *Acta Phys Pol,* 17,93(1958)
InSb single crystal surfaces. Several etchants described.

INSB-0019a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1.7 .... HNO_3
1 .... HAc
3.7 .... H_2O
TIME:
TEMP:
DISCUSSION:
InSb, cylinder cut ultrasonically with axis in c-direction. After polishing with CP4, cylinder was anodized at 100 mA/cm^2 or air oxidized at 350°C. After oxidation specimens were etched in the solution shown in a study of crystal orientation and surface reactions.
REF: Lavine, M C et al — *J Appl Phys,* 29,1131(1958)

INSB-0024a
ETCH NAME: Superoxol
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
TIME:
TEMP:
DISCUSSION:
InSb, (111) wafers used in a polarity study of III—V compound semiconductors. Solution used as a preferential etch on (111)A and ($\overline{111}$)B surfaces. Other compounds studied were InAs, GaSb, and GaAs. Superoxol also was evaluated on InAs and GaAs.
REF: Faust, J W & Sagar, A — *J Appl Phys,* 31,331(1960)
INSB-0034b: Ibid.
InSb, (100), n-type wafers, zinc diffused. Cleave on ⟨110⟩ after zinc diffusion to cross-section, and use a superoxol solution to stain the exposed junction.

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INSB-0024b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
(1) 1 .... HF
1 .... HNO_3
4 .... H_2O
(2) 1 .... HF
1 .... HNO_3
DISCUSSION:
InSb, (111) wafers used in a polarity study. The (111)A surface develops triangular pits; the $(\overline{111})$B is erratic. This etch is similar to INSB-0005a and INSB-0002e.
REF: Ibid.

INSB-0026
ETCH NAME: BRM TIME: 20 sec + 10 sec
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
x .... 0.5% Br_2
x .... MeOH
DISCUSSION:
InSb, (110), n-type and (100), p-type wafers used in a cleaning study. Soak lens paper with solution and chem/mech lap surfaces. After lapping flush with MeOH during last 10 sec, then rinse in the BRM solution.
REF: Aspnes, D E & Studna, A A — *J Vac Sci Technol,* 20,488(1982)

INSB-0020
ETCH NAME: CP4, dilute TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x *CP4
x .... H_2O

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

DISCUSSION:
InSb:Zn, (111) wafers used in a study of Cd alloyed p-n junctions and their electrical properties. Solution used to etch-clean junctions.
REF: Lee, C A & Kaminsky, G — *J Appl Phys,* 30,2021(1959)

INSB-0021
ETCH NAME: CP4, dilute TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x *CP4
x .... HAc

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

DISCUSSION:
InSb, thin films used in a study of electrical properties. Films were formed using two quartz plates with lower plate heated above the temperature of the top plate — place a molten

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drop of InSb on the bottom plate and squash into thin film. Wash in CCl_4 and etch clean in solution shown; rinse in DI water and dry under IR lamp.
REF: Bates, G & Taylor, K N R — *J Appl Phys,* 31,991(1960)

INSB-0009b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
5 .... *superoxol
1 .... HF
x .... H_2O

*Superoxol: $1HF:1H_2O_2:4H_2O$

DISCUSSION:
InSb, (100) wafers used in a study of recombination in p-type material. Solution used as a polishing etch although superoxol is primarily a preferential etch.
REF: Zitter, R N et al — *Phys Rev,* 115,266(1959)

INSB-0022a
ETCH NAME: TIME: 2 min
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
1 .... H_2O_2
10 .... lactic acid
DISCUSSION:
InSb:Te, (111), n-type wafers used in a general surface study. Both polar surfaces were studied using the following sequence of etching and cleaning. Three-cleaning classifications: I = hi C; II = hi O_2 and III = hi S:

		Classification		
	Operation step	**I**	**II**	**III**
1.	Degrease & H_2O rinse	*	*	*
2.	$1H_2O_2$:10 lactic acid, 2″, RT		*	*
3.	H_2O rinse	*		*
4.	CP4, 5 sec, RT + H_2O rinse		*	*
5.	10 *M* Na_2S + H_2O rinse			*
6.	H_2O rinse	*	*	*
7.	N_2 blow-dry	*	*	*

In an additional study it was shown that (1) sputter etch; (2) plasma etch and (3) RIE etch all produced a damage layer that created donor sites and leakage in n-type InSb.
REF: Auret, F D — *J Electrochem Soc,* 129,2752(1982)
INSB-0035: Auret, F D — *J Electrochem Soc,* 131,2115(1984)
An extension of the above studies.

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INSB-0030
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... *CP4
1 .... HAc
1 .... H_2O

TIME: 1—2 min
TEMP: RT

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

DISCUSSION:
InSb, (111), (112) and other bulk orientations on (111) or (100) surface oriented wafers. Solution used to develop and polish these orientations.
REF: Venables, J D & Brody, R M — *J Appl Phys,* 29,1025(1958)

INSB-0031
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
2 .... HF
1 .... HNO_3
1 .... HAc

TIME: to 1 min
TEMP: RT

DISCUSSION:
InSb, (111) wafers. Solution will develop etch pits on (111)A indium surface.
REF: Gatos, H C & Lavine, M C — *J Electrochem Soc,* 107,427(1960)

INSB-0032
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
4 .... HNO_3
25 .... lactic acid

TIME:
TEMP: RT

DISCUSSION:
InSb, (100) wafers used as substrates for epitaxy growth of CdTe thin films by MBE. Solution used to polish substrates prior to MBE.
REF: Farrow, R F C et al — *J Vac Sci Technol,* B(3),681(1985)

INSB-0033
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ion

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
InSb, (100) wafers used as substrates for epitaxy growth of CdTe thin films by MBE. Substrates were solvent degreased prior to Ar^+ ion cleaning in vacuum.
REF: Williams, G M et al — *J Vac Sci Technol,* B(3),704(1985)

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INSB-0040
ETCH NAME: BRM
TYPE: Halogen, cleaning
COMPOSITION:
x .... 5% Br_2
x .... MeOH (CH_3OH)
TIME:
TEMP:
DISCUSSION:
InSb, (100), n-type wafers zinc diffused in fabrication of infrared detectors in the 3—5 μm range. Prior to diffusion, wafers were polish cleaned in solution shown.
REF:

INSB-0022b
ETCH TYPE: Degrease
TYPE: Solvent, cleaning sequence
COMPOSITION:
(1)
(i) acetone, hot, rinse three times
(ii) TCE, hot, rinse three times
(iii) acetone, hot, rinse two times, approx. 1 min each
(iv) DI water, rinse three times, approx. 1 min each
(v) Nitrogen blow-dry
TIME:
TEMP:
DISCUSSION:
InSb, (111) n-type, Te doped wafers used in an etching and cleaning study. This degreasing sequence was studied, alone, and used prior to all of the clean/etch sequences described in INSB-0022c thru INSB-0022m. The sequences are classified by carbon content remaining: A = less than 3%; B = 3—30% and C = greater than 30%. Remaining oxide on surfaces after etching was measured by AES using argon ion bombardment of 1 KeV and compared to etch removal of a known thickness of an anodic film. AES profile also shows the $\%O_2$, %In, and %Sb remaining.
REF: Ibid.

INSB-0022c
ETCH NAME: CP4A
TYPE: Acid, removal
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... CH_3COOH (GAA/HAc)
Clean/etch (i) Degrease, INSB-0022b
(ii) Etch in CP4A and DI water rinse
(iii) N_2 blow dry
TIME: # seconds
TEMP: RT
DISCUSSION: InSb, (111) wafers used in an etching and cleaning study. Class: A.
REF: Ibid.

INSB-0022d
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HNO_3
10 .... lactic acid
Clean/etch: (i) Degrease, INSB-0022b
(ii) Etch (shown), and DI water rinse, 3×.
(iii) N_2 blow-dry
TIME: 1, 2, and 20 min
TEMP: RT

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DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: B.
REF: Ibid.

INSB-0022e
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) 30 .... HF
50 .... HNO_3
30 .... HAc
(2) 1 .... HNO_3
10 .... lactic acid

TIME: (1) 5 sec (2) 5 min
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Etch in (2); DI water rinse 2×
(iii) Etch in (1); DI water rinse 3×
(iv) N_2 blow-dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Etch (1) is CP4A from INSB-0022c; etch (2) is from INSB-0022d. Class: A.
REF: Ibid.

INSB-0022f
ETCH NAME: H100
TYPE: Acid, removal
COMPOSITION:
"A" 78 g .... KOH
4 g .... tartaric acid
8 g .... *EDTA
78 g .... H_2O

"B" xml .... H_2O_2

*Ethylenediamine tetraacetic acid

Mix: 5 "A":2 "B" before using

TIME: 30 sec
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Complete INSB-0022e clean/etch
(iii) H100 etch; DI water rinse 2×, 3 min. each
(iv) N_2 blow dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: A.
REF: Ibid.

INSB-0022g
ETCH NAME: acetone, vapor
TYPE: Ketone, cleaning
COMPOSITION:
x .... $(CH_3)_2CO$, vapor

TIME:
TEMP:

Clean/etch: (i) Degrease, INSB-0022b
(ii) Complete INSB-0022e clean/etch
(iii) DI water rinse, 3×, 1 min each
(iv) Acetone dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: C.
REF: Ibid.

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INSB-0022h
ETCH NAME: Sodium sulfide
TYPE: Acid, sulfonation
COMPOSITION:
x .... 10^5 *M* Na_2S

TIME: 1 min
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Complete INSB-0022e clean/etch
(iii) DI water rinse, 3×, 1 min each
(iv) N_2 blow-dry

Note: Approximately 18—20% S detected.

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: A.
REF: Ibid.

INSB-0022i
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O

TIME: 2 min
TEMP: RT

Clean/Etch: (i) Degrease, INSB-0022b
(ii) Etch; DI water rinse 3×, 1 min each
(iii) N_2 blow-dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: B.
REF: Ibid.

INSB-0022j
ETCH NAME: BRM
TYPE: Halogen, removal
COMPOSITION:
x .... 1% Br_2
x .... MeOH

TIME: 10 min
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Etch
(iii) MeOH rinse, 2 min
(iv) DI water rinse 3×, 1 min each
(v) N_2 blow dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: B.
REF: Ibid.

INSB-0022k
ETCH NAME:
TYPE: Acid removal
COMPOSITION:
1 .... HF
2 .... HNO_3
5 .... HAc (GAA)

TIME: 1 min
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Etch
(iii) DI water rinse 3×, 1 min each
(iv) N_2 blow dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: A.
REF: Ibid.

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INSB-0022l
ETCH NAME: CP4, variety
TYPE: Acid, removal
COMPOSITION:
15 .... HF
25 .... HNO_3
15 .... HAc (GAA)
x .... Br_2

TIME: Seconds
TEMP: RT

Clean/etch: (i) Degrease, INSB-0022b
(ii) Etch
(iii) DI water rinse 3×, 1 min each
(iv) N_2 blow-dry

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Class: A.
REF: Ibid.

INSB-0022m
ETCH NAME:
TYPE: Electrolytic, anodizing
COMPOSITION:
15 .... $HClO_4$
60 .... HAc
1.5 .... H_2O

TIME: 90 sec
TEMP: 5°C
ANODE: InSb
CATHODE:
POWER: 15 V

Clean/etch: (i) Degrease, INSB-0022b
(ii) Anodize
(iii) DI water rinse 3×

DISCUSSION:
InSb, (111) wafers used in an etching and cleaning study. Wafers were anodized in the solution shown. This oxide was etched away and the known thickness was used as the standard to evaluate oxide thicknesses developed by the clean/etch sequences shown in InSB-0022b through INSB-0022l. Surface was Class B.
REF: Ibid.

INSB-0041
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
(1) x .... x% Br_2
x .... MeOH
(2) 5 .... HNO_3
1 .... HAc

TIME: (1) variable (2) 5 min
TEMP: RT RT

DISCUSSION:
InSb, (100), (111)A and $(\overline{1}\overline{1}\overline{1})$B oriented wafers used as substrates for MBE of Homo-epi growth of InSb. The $(\overline{1}\overline{1}\overline{1})$B surface developed hillocks in the thin films. Prepare substrates: (1) chem/mech polish in BRM solution; (2) degrease with solvents; (3) etch in solution (2). Thermal heat treat wafers prior to epitaxy: (111) at 450°C, and (100) at 430°C to reduce dislocation content. MBE growth was in an excess Sb_4 atmosphere to study the effects of Sb in InSb.
REF: Okashi, J et al — *J Electron Mater*, 14,4519(1985)
INSB-0042: Brown, E R — *J Appl Phys*, 57,2361(1985)
InSb wire was saw cut, mechanically lapped, then etched down to 0.04 cm diameter in a study of adsorption coefficients.
INSB-0040: Potter, R F — *Phys Rev*, 102,47(1956)
InSb specimens used in a study of electric modulus.

INDIUM GALLIUM ANTIMONIDE, InGaSb

General: Does not occur as a natural compound. Antimony, Sb, occurs as a native metal in small quantity. The mineral stibnite, Sb_2S_3 is a major ore, and there are several antimonates

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and antimonites of Pb, Fe, Ca, Ti, etc. There are no industrial applications of the compound other than in Solid State semiconductor development.

Technical Application: Indium gallium antimonide has been epitaxially deposited as a thin film for general morphological study, and has application in semiconductor heterostructures.

Etching: Mixed acids.

INDIUM GALLIUM ANTIMONIDE ETCHANTS

IGSB-0001
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP:
COMPOSITION:
10 .... HCl
1 .... H_2O_2
10 .... H_2O
DISCUSSION:

InGaSb, deposited as a thin film by epitaxy on the following substrates: BaF_2, (111); NaCl, (100); Corning 7059 glass. Both BaF_2 and NaCl were cleaved in air, and TCE vapor degreased with water rinse. Glass was detergent scrubbed, water washed, and MeOH rinsed. After epitaxy growth the films were etch thinned in the solution shown. Films were then removed by the float-off technique for TEM study. Solutions for float-off removal were: (1) water for NaCl; (2) dilute HCl for BaF_2; and HF for glass.
REF: Eltoukhy, A H & Greene, J E — *J Appl Phys*, 50,505(1979)

PHYSICAL PROPERTIES OF INDIUM ARSENIDE, InAs

Classification	Arsenide
Atomic numbers	49 & 33
Atomic weight	189.8
Melting point (°C)	943
Boiling point (°C)	
Density (g/cm^3)	5.66
Refractive index (n =)	3.42
Lattice constant (angstroms)	6.06
Energy band gap (eV)	0.42
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric—tetrahedral)	(111) tetrahedron
Color (solid)	Grey-silver
Cleavage (dodecahedral)	(110)

INDIUM ARSENIDE, InAs

General: Does not occur as a natural compound, although there are other metallic arsenides of nickel, iron, copper, cobalt, and platinum, which may include sulfur. There is no industrial applications other than as a compound semiconductor.

Technical Application: Indium arsenide is a III—V compound semiconductor with the sphalerite, ZnS structure. It is a (111) surface polar material with (111)In and ($\overline{1}\overline{1}\overline{1}$)As surfaces showing different etching characteristics. Several orientations have been studied, but most devices are fabricated with (100) wafer orientation. Single crystal ingots have been grown by the Horizontal Bridgman (HB); Czochralski (CZ); and Float Zone (FZ) methods.

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Epitaxy thin films have been grown by Vapor Transport (VT), and Chemical Vapor Deposition (CVD).

Some single crystal wafer or thin film devices fabricated include diodes and transistors, laser diodes, and Hall effect devices.

Etching: HCl. Mixed acids of HF:HNO_3/H_2O_2, HCl:HNO_3, and halogens.

INDIUM ARSENIDE ETCHANTS

INAS-0001a
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: 60°C
COMPOSITION:
10 .... 80% lactic acid ($CH_3CHOHCOOH$)
1 .... HNO_3
DISCUSSION:
InAs, (100), n-type wafers used in a study of native oxides. Chem/mech polish. Native oxide is 1—4 nm thick. See GaAs and InSb.
REF: Belyi, V I et al — *Thin Solid Films,* 133,157(1984)

INAS-0001b
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
x .... 1 *M* HCl
DISCUSSION:
InAs, (100), n-type wafers used in a study of native oxides. Chem/mech polish. This solution shows a higher As content in the surface after polishing. The higher electropositive elements tend to pile-up on surfaces, but the reason is presently unknown.
REF: Ibid.

INAS-0002
ETCH NAME: BRM
TYPE: Halogen, polish
TIME: 20 sec + 10 sec
TEMP: RT
COMPOSITION:
x .... 0.05% Br_2
x .... MeOH
DISCUSSION:
InAs, (110), n-type wafers used in a surface cleaning study. Soak lens paper in solution and use as lapping surface. Flush with MeOH during last 10 sec of lap period. Rinse in $NH_4OH:H_2O$; then rinse in BRM; then rinse in H_2O, and final rinse, again, in the $NH_4OH:H_2O$ mixture. Authors say that bromine content is not critical. (*Note:* At the concentration shown it is probably not a critical concentration, but higher concentrations are known to shift from polish etches to preferential.) Also used solution shown on Si, Ge, GaP, GaAs, GaSb, and InSb.
REF: Aspenes, D E & Studna, A A — *J Vac Sci Technol,* 20,488(1982)

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INAS-0003
ETCH NAME: CP4, modified
TYPE: Acid, preferential
COMPOSITION:
75 ml .... HNO_3
15 ml .... HF
15 ml .... HAc
0.06 ml .... Br_2
TIME:
TEMP:
DISCUSSION:
InAs, (111) wafers used in X-ray studies. Surfaces were lightly preferentially etched in the solution shown to differentiate between the (111)A and $(\overline{1}\overline{1}\overline{1})$B surfaces.
REF: Clarke, R L — *J Appl Phys*, 30,959(1959)
INAS-0005c: Ibid.
InAs, (111) wafers. Etch 5 sec. Develops pits on (111)A surfaces.

INAS-0004
ETCH NAME:
TYPE: Acid, clean
COMPOSITION:
1 .... HCl
5 .... glycerin
TIME: 10 min
TEMP: RT
DISCUSSION:
InAs, specimens used as the source material for growing InGaAs. Degrease with TCE, rinse with acetone, then MeOH. Then etch clean with solution shown.
REF: Penna, T C et al — *J Cryst Growth*, 67,27(1984)

INAS-0005a
ETCH NAME:
TYPE: Halogen, dislocation
COMPOSITION:
x .... 5—10% Br_2
x .... MeOH
TIME: 13—30 sec
TEMP:
DISCUSSION:
InAs, (111) wafers. Referred to as a dislocation etch.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw Hill, New York, 1970, 7

INAS-0008
ETCH NAME: CP4
TYPE: Acid, preferential
COMPOSITION:
15 .... HF
25 .... HNO_3
15 .... HAc
0.6 .... Br_2
TIME:
TEMP: RT
DISCUSSION:
InAs, specimens used in a study of light induced plasticity. Wafer surfaces were damaged using the diamond point of a Knoop Hardness Tester and then etching in CP4 to develop damage structure. Also studied Ge and InSb.
REF: Kuczynski, O C & Hochman, R P — *Phys Rev*, 108,946(1957)

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INAS-0005b
ETCH NAME: Hydrochloric acid TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... HCl
DISCUSSION:
InAs, (111) wafers. Solution described as producing etch figures.
REF: Ibid.

INAS-0005d
ETCH NAME: A/B Etch TIME: 10 min
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 ml .... HF
2 ml .... H_2O
8 mg .... $AgNO_3$
1 g .... CrO_3
DISCUSSION:
InAs, (111), (110) and (100) wafers. Used as a preferential etch on both indium arsenide and gallium arsenide. See GAS-0059.
REF: Ibid.

INAS-0006a
ETCH NAME: Hydrochloric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HCl
DISCUSSION:
InAs, (111) wafers used in a polarity study of III—V compound semiconductors. Solution is more of a general removal etch than preferential. See INAS-0001b and INAS-0004. Other compounds studied were InSb, GaSb, and GaAs.
REF: Faust, J W & Sayar, A — *J Appl Phys,* 31,331(1960)

INAS-0006b
ETCH NAME: Superoxol TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
DISCUSSION:
InAs, (111) wafers. Develops triangle pits on (111)A; but is erratic on $(\overline{111})$B.
REF: Ibid.

INAS-0006c
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HNO_3
1 .... H_2O_2
6 .... tartaric acid

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DISCUSSION:
InAs, (111) wafers used in a polarity study.
REF: Ibid.

INAS-0006d
ETCH NAME: CP4, modified
TYPE: Acid, preferential
COMPOSITION:
75 .... HF
75 .... HNO_3
15 .... HAc
0.6 .... Br_2
TIME:
TEMP:
DISCUSSION:
InAs, (111) wafers used in a polarity study.
REF: Ibid.

INAS-0007
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... HCl
x .... 0.4 *N* $FeCl_3$
TIME: 30 min
TEMP: RT
DISCUSSION:
InAs, (111) wafers used in an etch characterization study. Solution used to develop dislocations and defects.
REF: Gatos, H C & Lavine, M C — *J Electrochem Soc,* 107,427(1960)

INAS-0009
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HCl
1 .... HNO_3
TIME:
TEMP:
DISCUSSION:
InAs, (111) wafers used in material studies. Solution used as a general removal and polish etch. Also used on GaAs. (*Note:* A reduced reactivity will be noted for aqua regia; 3HCl:1HNO_3.)
REF: Cardona, M — *Phys Rev,* 121,752(1961)
INAS-0010: Antell, G R & Effer, D — *J Electrochem Soc,* 106,509(1959)
InAs single crystals grown by vapor phase reaction in a study of this method of material growth. Also grew InP, GaAs, and GaP.

INAS-0011
ETCH NAME: Heat
TYPE: Thermal, alteration
COMPOSITION:
x .... heat
TIME:
TEMP: 300°C
DISCUSSION:
InAs, (111) wafers and other orientations. Wafers used in a study of heat treatment effects. Heating to 300°C shows a resistivity change.
REF: Edmond, J T & Hilsom, C — *J Appl Phys,* 31,1300(1960)

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INDIUM ARSENIC PHOSPHIDE ETCHANTS

IASP-0001
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOISITION:
x .... x% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:
$InAs_xP_{x-1}$ polycrystalline ingot grown by the Bridgman method in a study of the material and its oxidation characteristics. Wafers were chem/mech polished in a BRM solution with MeOH rinse prior to oxidation.
REF: Schwartz, G P et al — *J Vac Sci Technol*, A2,1252(1984)

INDIUM BISMUTHIDE ETCHANTS

INBI-0001
ETCH NAME: Soap
TYPE: Solvent, polish
COMPOSITION:
x .... soap
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:
In_5Bi_3, single crystal specimens. Wafers were spark cut from ingot, then mechanically lapped and polished by grinding with abrasives and then polished with diamond paste. Final surface polish was done with a soft cloth saturated with a soap solution. Also etch polished wafers. See INBI-0002.
REF: Schreursl, N W & Weijers, H M — *J Cryst Growth*, 71,155(1985)
INBI-0002: Bhatt, V P et al — *J Pure Appl Phys*, 16,960(1978)
Reference for etch solution used in INBI-0001.

INDIUM GALLIUM ARSENIDE ETCHANTS

IGAS-0001
ETCH NAME:
TYPE: Acid, mesa forming
COMPOSITION:
1 .... H_2SO_4
1 .... H_2O_2
x .... H_2O
TIME: 10—100 sec
TEMP: RT
DISCUSSION:
InGaAs, (001) thin film epitaxy deposit grown by LPE on InP (001) wafer substrates to form very low leakage mesa diodes. Solution shown used to form mesas. See INP-0150 for preparation of InP substrate.
REF: Aspnes, D E et al — *J Vac Sci Technol*, 21,413(1982)

IGAS-0002a
ETCH NAME: Citric acid, dilute
TYPE: Acid, clean
COMPOSITION:
x .... citric acid
x .... H_2O
TIME:
TEMP:

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DISCUSSION:

InGaAs, (100) wafer used as a substrate for MIS device structures with SiO_2 and aluminum. Clean surfaces with citric acid then follow with acid etch before silica deposition. Anneal after SiO_2 deposit at 250°C, 5 min in N_2. Form dot pattern with photo resist, then evaporate aluminum.

REF: Shen, C C & Pande, K P — *J Phys Chem Solids*, 45,314(1984)

IGAS-0002b

ETCH NAME: TIME:

TYPE: Acid, clean TEMP:

COMPOSITION:

1 .... HF

1 .... HCl

4 .... H_2O

DISCUSSION:

AlGaAs, (100) wafer used as a substrate for MIS device structures. After citric acid cleaning, etch clean with the solution shown before SiO_2 deposition.

REF: Ibid.

PHYSICAL PROPERTIES OF INDIUM OXIDE, In_2O_3

Classification	Oxide
Atomic numbers	49 & 8
Atomic weight	277.52
Melting point (°C)	850
Boilint point (°C)	
Density (g/cm^3)	7.18
Hardness (Mohs — scratch)	3—4
Crystal structure (hexagonal — trigonal)	$(10\bar{1}0)$ prism, 1st order
Color (solid — hot/cold)	Red/pale yellow
Cleavage (prismatic)	$(10\bar{1}0)/(01\bar{1}0)$

INDIUM OXIDE, In_2O_3

General: Does not occur as a mineral specie in nature, although it may appear as a very minor encrustation on zinc and iron ores that often contain trace indium. When pure indium metal is burned in air it forms the sequi-oxide In_2O_3 and the mono-oxide, InO, in part. There is no metal processing use in industry, but the oxides are used as coloring agents in glass and enamels.

Technical Application: Indium oxides are III—VI compound semiconductors, and have been evaluated for semiconducting characteristics but, as the pure oxide, have not been used in device fabrication. As the trinary compound of indium tin oxide (ITO), it is fabricated as an opto-electric device.

Etching: HCl, H_2SO_4. Mixed HCl:$FeCl_3$, and halogens.

INDIUM OXIDE ETCHANTS

INO-0001

ETCH NAME: Sulfuric acid TIME:

TYPE: Acid, selective TEMP: 50—60°C

COMPOSITION:

x .... H_2SO_4, conc.

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DISCUSSION:

In_2O_3, $(10\bar{1}0)$ grown as an oriented thin film or as an amorphous film. With tin doping it shows semiconduction. Pattern etching of films was done through a chromium mask with the solution shown.

REF: Fan, J C C & Bachner, F — *J Electrochem Soc*, 122,1719(1975)

INO-0002

ETCH NAME: Hydrochloric acid
TYPE: Acid, selective
COMPOSITION:
x .... HCl, conc.

TIME:
TEMP:

DISCUSSION:

In_2O_3, $(10\bar{1}0)$, deposited oriented thin film or as an amorphous thin film, to include tin doping. Solution used for pattern etching through a mask similar to application shown in INO-0001.

REF: Kane, J et al — *Thin Solid Films*, 29,155(1975)

INO-0003

ETCH NAME: Oxalic acid
TYPE: Acid, selective
COMPOSITION:
x .... 1 *M* oxalic acid

TIME:
TEMP: 50°C

DISCUSSION:

In_2O_3, $(10\bar{1}0)$, oriented thin films or as an amorphous thin film with tin doping. Photolithographic techniques used to pattern surfaces using AZ-1350 photo resist. Solution used to selectively etch films after temperature annealing.

REF: Thornton, J A & Hedgeoth, L V — *J Vac Sci Technol*, 13,117(1976)

INO-0004a

ETCH NAME: Hydrogen iodide
TYPE: Halogen, selective
COMPOSITION:
x .... 55% HI

TIME:
TEMP: RT
RATE: 25 Å/sec

DISCUSSION:

$4In_2O_3$:$1SnO_2$, as thin film surface coatings. Surfaces were patterned using photolithographic techniques with AZ-1350H, post-bake 90 min at 120°C. Insert sample vertically into the solution during etching.

REF: Bradshaw, G & Hughes, A J — *Thin Solid Films*, 33.L5(1976)

INO-0004b

ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
12 .... HCl
1 .... H_2O
x .... Zn, powder

TIME:
TEMP: 20°C
RATE: 150 Å/sec

DISCUSSION:

$4InO_3$:$1SnO_2$ specimens. Coat surface with slurry of zinc:H_2O, immerse horizontally in etch solution of HCl:H_2O. AZ-1350 used as the photo resist pattern lacquer, and the solution shown used to etch pattern.

REF: Ibid.

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INO-0005a
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... 37% HCl
30 g .... $FeCl_3$/l
DISCUSSION:
In_2O_3 specimens. Described as an etch for indium oxide.
REF: Ponjee, J J & Feil, H J — U.S. Patent 4.093,#04 1978 (US Phillips Corp)
TIME: Seconds
TEMP: RT
RATE: 0.1 μm/15 sec

INO-0005b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... 18% HCl
5.5 g .... $FeCl_3$/l
DISCUSSION:
In_2O_3 specimens. Described as an etch for indium oxide.
REF: Ibid.
TIME: Minutes
TEMP: 45°C
RATE: 0.1 μm/10 min

INO-0005c
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... 18% HCl
66 g .... $FeCl_3$/l
DISCUSSION:
In_2O_3 specimens. Removal time will vary with the doping concentration of the indium oxide, as doped with time.
REF: Ibid.
TIME: Minutes
TEMP: 45°C
RATE: 0.1 μm/1.5—8 min

INDIUM GALLIUM ARSENIDE PHOSPHIDE ETCHANTS

IGAP-0001a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
10 .... HBr
DISCUSSION:
InGaAsP, thin film layer grown by LPE as part of a double-heterostructure. Solution is preferential to this material and developed mostly 60° type dislocations. Increase of dislocation density showed both edge, screw, and some pinning types.
REF: Veda, O et al — *Jpn J Appl Phys*, 23,836(1984)
TIME:
TEMP: RT

IGAP-0001b
ETCH NAME: BRM
TYPE: Halogen, preferential
COMPOSITION:
x .... x% Br_2
x .... MeOH
TIME:
TEMP: RT

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DISCUSSION:
InGaAsP, as thin film layers. See IGAP-0001a for discussion.
REF: Ibid.

IGAP-0002
ETCH NAME: BRM
TYPE: Halogen, selective
TIME:
TEMP: RT
COMPOSITION:
x .... 1% Br_2
x .... MeOH
DISCUSSION:
InGaAsP epitaxy thin films grown on InP substrates in a study of ionization coefficients. Solution used to selectively remove portions of the InGaAsP layer as it is not etched by HCl as is GaAs.
REF: Bulman, O E — *Solid State Electron*, 25,1189(1982)

PHYSICAL PROPERTIES OF INDIUM PHOSPHIDE, InP

Classification	Phosphide
Atomic numbers	49 & 15
Atomic weight	145.79
Melting point (°C)	1062
Boiling point (°C)	
Density (g/cm^3)	4.79
Lattice constant (angstroms)	5.87
Refractive index (n =)	3.1
Energy band gap (eV)	1.34
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Grey-silver
Cleavage (dodecahedral)	(110)

INDIUM PHOSPHIDE, InP

General: Does not occur in nature as a native compound. Indium is a soft silver white metal of the aluminum family; whereas, phosphorus is a very reactive acidic non-metal of the nitrogen family with three allotropic forms: yellow (white), red and black. There is no industrial use other than as a compound semiconductor.

Technical Application: Indium phosphide is a III—V binary compound semiconductor, exhibiting the (111)A and (111)B wafer surface polarity effect of these materials. It has the tetrahedral unit cell structure of sphalerite, ZnS, with positive (111)In and negative (111)P atom surfaces which produce different figures and structures when chemically etched. In device processing wafers with (100) surface orientation are used to reduce the polarity effect.

Initially InP ingots were grown by Czochralski (CZ) or Float Zone (FZ) methods with (111) and (100) oriented seeds but, now, also are grown by either vertical or horizontal Vapor Phase Epitaxy (VPE) or Liquid Phase Epitaxy (LPE) technique as thin films. Using the MBE growth method InP substrates and thin films are grown as multilayer heterostructures. There is much on-going development of such heterojunction or heterostructure devices. Like most compound semiconductors it has good ⟨110⟩ cleavage, and surfaces may be used so cleaved.

As discrete elements, indium phosphide has been fabricated as Gunn diodes, solar cells,

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and laser diodes. The substrate wafer, particularly as a heterostructure base, is usually InP:Fe, (100) semi-insulating (SI). Trinary compounds are $InAs_{x-1}P_x$; $In_xAl_{1-x}P$, and $In_{1-x}Ga_xAs_yP$.

Etching: HNO_3, HCl and H_3PO_4. Halogens and mixed acids. Alkalies and dry chemical etching (DCE).

SELECTION GUIDE: InP

(1) Br_2:MeOH (BRM)
- (i) Cleaning: INP-0058; -0012; -0059b
- (ii) Oxide Removal: INP-0066b
- (iii) Polish: INP-0001; -0002; -0003; -0004; -0005; -0006; -0008; -0009; -0010; -0049; -0050; -0011; -0012; -0013; -0058; -0069; -0054b; -0045b; -0061; -0062c; -0067
- (iv) Removal: INP-0006; -0018a,b; -0058
- (v) Selective: INP-0065; -0017; -0064b; -0064f
- (vi) Step-etch: INP-0007; -0014
- (vii) Structure: INP-0057b
- (viii) Thinning: INP-0068; -0016; -0017

(2) H_2O_2
- (i) Oxidation: INP-0019

(3) HCl
- (i) Cleaning: INP-0071
- (ii) Orientation: INP-0065
- (iii) Oxide Removal: INP-0033b; -0066b
- (iv) Polish: INP-0056a
- (v) Removal: INP-0020a; -0056a
- (vi) Selective: INP-0021; -0062d; -0064a,c,e,g,j,l

(4) $HCl:H_2O$
- (i) Cleaning: INP-0053; -0054a
- (ii) Selective: INP-0062e

(5) $HCl:HNO_3$
- (i) Removal: INP-0020b
- (ii) Polish: INP-0070
- (iii) Selective: INP-0062g; -0064a,k,l,m

(6) $HCl:HNO_3:H_2O$
- (i) Polish: INP-0021a

(7) $HCl:H_2O_2$
- (i) Selective: INP-0062e

(8) HCl:HAc
- (i) Selective: INP-0062e

(9) $HCl:FeCl_3$
- (i) Preferential: INP-0055

(10) $HCl:H_2O_2$:HAc
- (i) Removal: INP-0057

(11) $HCl:HNO_3:Br_2$
- (i) Preferential: INP-0021b

(13) HNO_3 +/− H_2O
- (i) Oxidation: INP-0025
- (ii) Removal: INP-0024; -0022b

(14) HIO_3
- (i) Cleaning: INP-0030
- (ii) Polish: INP-0030

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(15) HBr
  (i) Polish: INP-0026; -0062a
(16) HBr:HF
  (i) Preferential: INP-0027
(17) HBr:HNO_3 +/− H_2O
  (i) Defect: INP-0028a; -0062b
(18) HBr:H_2SO_4
  (i) Dislocation: INP-0051; -0061a; -0062b
(19) HBr:HCl
  (i) Selective: INP-0062a
(20) HBr:H_2O_2
  (i) Selective: INP-0062b
(21) HBr:HAc
  (i) Selective: INP-0062a
(22) HBr:H_3PO_4
  (i) Selective: INP-0062a
(23) HBr:Br_2:H_2O
  (i) Polish: INP-0064
(24) HBr:HAc:$K_2Cr_3O_7$
  (i) Preferential: INP-0031a
(25) HBr:H_3PO_4:$K_2Cr_3O_7$
  (i) Oxide Removal: INP-0066b
(26) H_2O_2:HCl:HAc
  (i) Selective: INP-0062f
(27) H_2SO_4
  (i) Cleaning: INP-0067
(28) H_2SO_4:H_2O_2:H_2O
  (i) Removal: INP-0041; -0042; -0063; -0065; -0043b
  (ii) Selective: INP-0062h; -0043a; -0044; -0046a; -0046b; -0064n, m
(29) H_2SO_4:H_2O_2:MeOH
  (i) Cleaning: INP-0047
(30) H_2SO_4:HCl:$K_2Cr_3O_7$
  (i) Selective: INP-0062h
(31) H_3PO_4, Electrolytic
  (i) Selective: INP-0031a; -0052
(32) H_3PO_4:H_2O
  (i) Oxide Removal: INP-0022c
(33) H_3PO_4:HCl
  (i) Grooving: INP-0035
  (ii) Step Etch: INP-0066a
  (ii) Preferential: INP-0066a
  (iv) Removal: INP-0034
  (v) Selective: INP-0057a; -0062e
(34) H_3PO_4:Br_2
  (i) Preferential: INP-0018
(35) H_3PO_4:HBr
  (i) Preferential: INP-0021c
(36) H_3PO_4:HBr:$K_2Cr_3O_7$
  (i) Preferential: INP-0031b
(37) H_3PO_4:HCl:H_2O_2
  (i) Selective: INP-0062f

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(38) H_3PO_4,H_2O_2:H_2O
  (i) Selective: INP-0046a-b
(39) $K_3Fe(CN)_6$
  (i) Staining: INP-0036a
(40) HF +/− H_2O
  (i) Oxide Removal: INP-0045a
(41) HF:Br_2
  (i) Dislocation: INP-0037b
(42) HF:MeOH
  (i) Dislocation: INP-0037a
(43) HF:HNO_3
  (i) Selective: INP-0063
(44) KOH/NaOH
  (i) Cleaning: INP-0056a
(45) KOH:MeOH
  (i) Cleaning: INP-0048
(46) KOH:$K_2Fe(CN)_6$:H_2O
  (i) Preferential: INP-0033d
  (ii) Selective: INP-0040; -0033e; -0064a,d,j,m,n
  (iii) Staining: INP-0039
(47) CF4 (RF Plasma)
  (i) Removal: INP-0059a
(48) Cl_2:O_2 +/− Ar (RF plasma)
  (i) Preferential: INP-0064i
(50) Indium, In
  (i) Etch-back: INP-0049; -0050
(51) Argon, (RF Plasma)
  (i) Cleaning: INP-0062
(52) Heat
  (i) Cleaning: INP-0060
(56) Named/Numbered Etchants:
  (i) Huber Etch (polish): INP-0072
  (ii) Superoxol (polish): INP-0022a
  (iii) A/B Etch (preferential): INP-0051; -0021d
  (iv) CBR Etch (polish): INP-0073; -0075
  (v) BRM (polish/preferential): See: Br_2:MeOH
  (vi) BPK-221 (preferential): INP-0031b
  (vii) H Etch (preferential): INP-0021c; -0051
  (viii) KKI Etch (selective): INP-0064d
  (ix) CP4 (polish/preferential): INP-0056a

INDIUM PHOSPHIDE ETCHANTS

INP-0001
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
  x .... Br_2
  x .... MeOH

TIME:
TEMP:

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DISCUSSION:

InP, (100) cleaved wafers. Degrease with solvents, then free etch in the BRM solution. Rinse in 15% HCl before MOVPE deposition of (GaIn)As.

REF: Hockly, M & White, R A D — *J Cryst Growth,* 68,334(1984)

INP-0002: Long, J A — *J Cryst Growth,* 69,10(1984)

InP, (100) Si doped wafers used as substrates for epitaxy growth. Wafers were chem/mech polished in the solution shown. Hand polish with the same solution immediately before MOCVD deposition of InP:Fe.

INP-0003: Dautremont-Smith, W C & Feldman, L C — *J Vac Sci Technol,* A3,873(1985)

InP, (100), n-type cleaved wafers from an ingot grown by LEC, and used in a study of plasma damage. Polish in the solution shown, then degrease with solvents, and soak in dilute HF.

INP-0004a: Chand, N & Houston, P A — *J Cryst Growth,* 14,9(1985)

InP, (100) wafers used as substrates for epitaxy growth. Solution was used to etch "V" grooves. "V" groove side slopes were (111)A. (*Note:* Controlled groove etching is done by photo resist masking patterned slots in ⟨110⟩ directions.)

INP-0005: Sussmann, R S — *J Electron Mater,* 12,603(1983)

InP:Fe, (100) (SI) wafers cut 2°-off toward (110). Solution used to etch polish surfaces.

INP-0006

ETCH NAME: TIME:

TYPE: Halogen,polish/removal TEMP:

COMPOSITION:

(1) x .... Br_2
x .... MeOH

(2) x .... HCl
x .... H_3PO_4

DISCUSSION:

InP, (100) wafers used as substrates for epitaxy growth of InGaAs layers. Surface mask coating was a silica spin-on rather than SiO_2 or Si_3N_4 by RF or CVD. Spin-on glass at 2500 rpm and anneal 20 min in N_2 at 300°C. Move wafers slowly into furnace heat zone to prevent cracking. InGaAs deposit was 2500 Å thick. Photo resist coat and open slot pattern parallel to ⟨110⟩. Use 1% HF to remove SiO_2 in slots. Then harden remaining SiO_2 mask by annealing at 450°C, 15 min in N_2. Etch "V" grooves with various mixtures of the two solutions shown. Groove side walls are (111)A. After epitaxy deposition, cleaved cross sections on ⟨110⟩ and stain. Etch rates shown as: $(\overline{111})$B>(100)>(111)A.

REF: Chan, N & Houston, P A — *J Electron Mater,* 14,9(1985)

INP-0007

ETCH NAME: BRM TIME:

TYPE: Halogen, step-etch TEMP: RT

COMPOSITION:

x .... 0.5% Br_2
x .... MeOH

DISCUSSION:

InP, (100) n-type wafers used as substrates for diffusion of a p/n junction using CdP_2 at 600°C. For TEM study, the Cd side was step-etched in the solution shown in a study of defect structure induced by Cd diffusion.

REF: Ueda, O — *Jpn J Appl Phys,* 23,1551(1985)

INP-0008: Brown, A S et al — *J Electron Mater,* 14,367(1985)

InP, (100) wafers used as substrates for GaInP epitaxy. Substrates were chem/mech polished in the solution shown. Wafers were then cleaved in half portions. One half of each wafer was annealed in H_2 + Pd, then repolished to remove about 25 μm of surface material.

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Both halves then degreased: acetone — MeOH — H_2O. Then free etched in a solution of: $7H_2SO_4$:$1H_2O_2$:$1H_2O$, RT, 20 sec immediately before epitaxy.

INP-0009
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 1% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:

InP, (110) wafer cleaved under UHV. Wafers (100), (110) and $(\overline{1}\overline{1}\overline{1})$B were saw cut. Chem/mech polish surfaces on a pelon pad and hold under MeOH. The $(\overline{1}\overline{1}\overline{1})$B surface showed signs of orange peel in this solution. Final clean by heating in vacuum at 410°C. Gas bursts were observed at 250°C, 350°C, slight bursts at 380°C, and were probably due to hydrocarbon out-gassing.

REF: Chang, K-H & Meijer, P H E — *J Vac Sci Technol,* 14,789(1977)

INP-0010: Ogura, M et al — *J Cryst Growth,* 68,32(1984)

INP, (100) wafers used as substrates for epitaxy deposition of InGaAsP by MOCVD. Wafers were etch polished in the solution shown before epitaxy. GaAs wafers were used for (AlGa)InP epitaxy thin film growth. GaAs wafers were etch cleaned in $5H_2SO_4$:$1H_2O_2$:$1H_2O$, RT, 2 min.

INP-0049: Tu, C W & Jones, K A — *J Cryst Growth,* 70,117(1984)

InP, (100) wafers used as epitaxy substrates. Chem/mech polish with solution shown. Then degrease in TCE, and soak in 45% KOH, 1 h at RT with final heavy water wash. Re-etch 10 sec with solution shown before loading in vacuum. In CVD system, *in situ* etch with 0.4% HCl hot vapors. After epitaxy, cleave ⟨110⟩ and etch with A/B preferential etch at 60°C, 8 min to develop structure and dislocations.

INP-0050: Gagnaire, A et al — *J Electrochem Soc,* 132,1655(1985)

InP, (100) n-type wafers used in a study of cathodic decomposition. Chem/mech polish in the solution shown; rinse in warm MeOH and blow dry with argon. Solder indium back contacts at 350°C in N_2. The H_2 evolution from electrolyte leaves indium rich film on surfaces.

INP-0065: Smith, N A et al — *J Cryst Growth,* 68,517(1984)

InP ingots grown by LEC and Fe doped. Ingots showed FeP_2 and mixed FeP/FeP_2 segregates. A BRM solution was used to expose the segregates and to dissolve InP and remove precipitates for SEM and X-ray study.

INP-0051
ETCH NAME: A/B Etch
TYPE: Acid, preferential
COMPOSITION:
1 ml .... HF
2 ml .... H_2O
3 g .... CrO_3
8 mg .... $AgNO_3$
TIME:
TEMP: RT
DISCUSSION:

InP, $(\overline{1}\overline{1}\overline{1})$B wafers used as substrates for epitaxy growth of double heterojunction (DH) structure: InP/n-InGaAs/InP/InP$(\overline{1}\overline{1}\overline{1})$B grown by LPE as a photo detector. There is a 25 to 50% mismatch between InGaAs and InP epitaxy layers. The A/B solution was used to

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develop structure and dislocation etch pit density, 10^6 cm^{-2}. Part of mismatch due to use of the $(\overline{111})$B substrate.
REF: Morrien, C B et al — *J Electrochem Soc*, 132,1717(1985)
INP-0080: Zinko, J L et al — *J Electron Mater*, 14,563(1985)

InP:Fe, (100) (SI), and n^+ doped (S/Sn) wafers used as substrates for atmospheric pressure ATMBE growth of InP layers. After epitaxy, cleave ⟨110⟩ and stain with the A/B Etch. (See GAS-0059 for A/B Etch.)

INP-0058
ETCH NAME: BRM
TYPE: Halogen, cleaning
COMPOSITION:
x .... 10% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:

InP:Fe, (100) (SI) wafers used as substrates for epitaxy growth of InP layers. Substrates cleaned as follows: (1) degrease with TCE, then acetone, then isopropyl alcohol (IPA); (2) etch clean in $3H_2SO_4$:$1H_2O_2$:$1H_2O$, and DI water rinse, and (3) etch clean in solution shown. After deposition of SiO_2 use standard photolithography to pattern the mask, and etch open SiO_2 with BHF, and repeat (1) degreasing step. Five mask patterns were used for selective epitaxy deposition of InP.
REF: Oishi, M & Kuroiwa, K — *J Electrochem Soc*, 132,1209(1985)

INP-0011
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
(1) x .... 1% Br_2
x .... MeOH
(2) x .... x% KOH
TIME:
TEMP: RT
DISCUSSION:

InP, (100) wafers cut 3°-off toward (110) used as substrates for epitaxy deposition of various compounds of Ga/Al/As/In by MOCVD. Chem/mech polish in the BRM (1) solution, then soak in the (2) KOH solution to remove native oxide. Before MOCVD use the following cleaning sequence: (1) DI H_2O rinse; (2) etch clean in H_2SO_4, RT, 2 min with ultrasonic; (3) rinse in hot MeOH soak; (4) repeat H_2SO_4, RT, 3 min; (5) hot MeOH rinse and (6) N_2 blow dry.
REF: Cheng, C H — *J Electron Mater*, 13,703(1984)
INP-0012: Kasemset, D et al — *J Electron Mater*, 13,655(1984)

InP, (100) wafers. Clean and etch polish with the BRM solution (1), and soak in KOH solution (2) to remove native oxide.

INP-0013
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
1 .... Br_2
10 .... MeOH
TIME:
TEMP: RT
DISCUSSION:

InP, (100) n-type wafers. Mechanically lap with 0.3 μm alumina. Etch polish surfaces with solution shown.
REF: Nakamura, T & Katoda, T — *J Appl Phys*, 55,3064(1984)

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INP-0014
ETCH NAME: Huber etch (BRM) TIME:
TYPE: Halogen, step-etch TEMP: RT
COMPOSITION:
x .... 1.5% Br_2
x .... MeOH
DISCUSSION:
InP, (100) wafers used as substrates for InP epitaxy. Solution shown was used as a step-etch in a study of the variations of dislocation density with depth of epitaxy layer.
REF: Mahajan, S et al — *J Electrochem Soc*, 129,1556(1982)
INP-0018: Duchemin, J P et al — *Inst Phys Conf Ser*, 45,10(1979)
InP, (100) wafers. After heavy removal of bulk material with a 15% Br_2:MeOH mixture, chem/mech polish surfaces with solution shown above. Rinse in MeOH then in IPA.
INP-0072a: Huber A & Linn, N T — *J Cryst Growth*, 28,80(1975)
InP, (100) wafers. Solution used as a removal etch by dip controlled step-etching. Rate shown as 6—7 μm/min.
INP-0077: Zhu, L A et al — *J Appl Phys*, 57,5486(1985)
InP, (100), Te doped, n-type wafers used as substrates for LPMOCVD growth of InP thin films. Clean substrates as follows: (1) degrease in hot organic solvents; (2) etch in BRM solution shown, RT, 2 min. In epitaxy system, etch both the substrates and epitaxy deposited InP layer with hot HCl gas, *in situ*, to remove surface damage and contamination.

INP-0068
ETCH NAME: BRM TIME:
TYPE: Halogen, thinning TEMP: RT
COMPOSITION:
x .... 1.5% Br_2
x .... MeOH
DISCUSSION:
InP, (100) wafers were etch thinned with the solution shown.
REF: Duh, B V & Bransen, D — *J Electrochem Soc*, 130,207(1983)

INP-0069
ETCH NAME: BRM TIME: To 10 min
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
"A" x .... 7.5% Br_2 "B" x .... MeOH
x .... MeOH
MIX: Cover "A" with "B".
DISCUSSION:
InP, (100) wafers and other III—V compounds evaluated for immersion polishing in solution shown as against chem/mech polishing which can develop sleeks. Immerse wafers in solution, then remove slowly up through over-cover of pure methyl alcohol to quench without exposure to air. The MeOH cover will diffuse into solution in about 10 min.
REF: Risario, R et al — *J Appl Phys*, 53,40(1982)

INP-0054b
ETCH NAME: BRM TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
x .... 0.5% Br_2
x .... MeOH

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DISCUSSION:

InP:Fe (100) (SI) wafers used as substrates for LPE growth of InP epitaxy layers. Rinse in isopropyl alcohol (IPA), then polish in solution shown. Follow with: (1) TCE degreasing, and acetone rinse; (2) 50% HCl, RT, 30 sec, rinse in IPA, and (3) dry in hot IPA.
REF: Ibid.

INP-0059b
ETCH NAME:
TYPE: Halogen, cleaning
TIME: 1 min
TEMP: RT
COMPOSITION:
x .... 2.5% Br_2
x .... MeOH
DISCUSSION:

InP, (100) wafers etch cleaned in this solution.
REF: Hirata, K et al — *J Vac Sci Technol*, 2,44(1984)

INP-0016
ETCH NAME:
TYPE: Halogen, thinning
TIME:
TEMP: RT
COMPOSITION:
x .... 5% Br_2
x .... MeOH
DISCUSSION:

InP, (100) and GaAs, (100) wafers used for gold evaporation and annealing. Black wax was used as a mask to coat wafers and selective etch thin sections for TEM study of line defects.
REF: Nakahara, S et al — *J Electrochem Soc*, 131,1917(1984)
INP-0017: Nakahara, S et al — *Solid State Electron*, 27,557(1984)

InP, (100) wafers used for zinc deposition and anneal. Annealing was done on a carbon strip heater for 30 sec at 250, 300, 350, 375, and 425°C. Used black wax to coat and selectively etch thin wafer portions for TEM study. Thinning included some areas of hole-thru etching.

INP-0018b
ETCH NAME: BRM
TYPE: Halogen, removal
TIME: 15 sec
TEMP: RT
COMPOSITION:
x .... 15% Br_2
x .... MeOH
DISCUSSION:

InP, (100) wafers. Solution used to remove bulk material from both sides of wafers with solution shown, removing 20 μm from each side. Follow with chem/mech surface polish with a 1.5% Br_2:MeOH solution concentration. Rinse in MeOH, then in isopropyl alcohol (IPA).
REF: Duchemin, J P et al — *Inst Phys Conf Ser*, 45,10(1979)

INP-0019
ETCH NAME:
TYPE: Acid, oxidation
TIME: 30 min
TEMP: Boiling
COMPOSITION:
x .... H_2O_2

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DISCUSSION:

InP, (100) wafer used as a substrate for epitaxy growth of the following structure: n-$InPAl^{epi}$/ox-InP/InP^{epi}/InP(100). The hydrogen peroxide was used to form the oxidized-InP layer. The layer was 150—250 Å thick.

REF: Inuishi, M & Wessels, B W — *Thin Solid Films*, 103,141(1983)

INP-0020a

ETCH NAME: Hydrochloric acid — TIME:

TYPE: Acid, removal — TEMP: Hot

COMPOSITION:

x .... HCl

DISCUSSION:

InP, (111) wafers used in an etch development study. Solution shows moderate to vigorous reaction when used hot.

REF: Robbins, H & Schwartz, B — *Tech Rep*, 1960

INP-0081a: Takeda, Y et al — *Jpn J Appl Phys*, 23,84(1984)

InP, (100) wafer used as substrate to epitaxially grow the following structure: p-InGaAs/p-InP/InGaAsP/InP(100). First, etch remove the InGaAs layer to the p-InP buffer layer which is rough, continue etching to the InGaAsP which is very shiny. To remove the InGaAsP layer, etch with $1H_2SO_4$:$1H_2O_2$:$1H_2O$ at RT. The InGaAsP is not as yellow in appearance as the InP substrate.

INP-0020b

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP: RT

COMPOSITION:

(1) 1 .... HCl
1 .... HNO_3

(2) 2 .... HCl
1 .... HNO_3

DISCUSSION:

InP, (111) wafers used in an etch development study. Solution (1) shows moderate to vigorous reaction. Solution (2) is slow at RT.

REF: Ibid.

INP-0021a

ETCH NAME: — TIME:

TYPE: Acid, polish — TEMP: RT

COMPOSITION:

6 .... HCl
1 .... HNO_3
6 .... H_2O

DISCUSSION:

InP, (111) wafers grown by LEC and used as (111)A and $(\overline{111})$B oriented wafer substrates for epitaxy growth of GaInPAs. Substrates were lap polished with Nalaog 1060 (colloidal silica), then etch polished in the solution shown. Epitaxy layers were deposited by a gradient freeze growth (GFG) method. Material was then preferentially etched in a study of dislocation pit density using a 40HCl:80HNO_3:1Br_2 solution, RT, 10 sec.

REF: Thiel, F A & Barns, R L — *J Appl Phys*, 126,1272(1979)

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INP-0021b
ETCH NAME: TIME: 10 sec
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
40 .... HCl
80 .... HNO_3
1 .... Br_2
DISCUSSION:
InP, (111) wafers grown by LEC and used as (111)A and ($\overline{111}$)B oriented substrates for epitaxy growth of GaInPAs. The epitaxy layers were preferentially etched in the above solution in a study of dislocation pit density.
REF: Ibid.

INP-0022a
ETCH NAME: Superoxol, variety TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
1 .... HCl
4 .... H_2O
+12:1 .... H_2O_2
DISCUSSION:
InP, (100), Zn doped p-type wafers. Solution showed used to etch polish surfaces. Follow with 10% H_3PO_4 to remove native oxide.
REF: Pande, K P & Naur, U K R — *J Appl Phys*, 55,3109(1984)
INP-0076: Christon, A et al — *Semiconductor Int*, March 1979, 59
InP, (100) wafers used in a surface contamination and defect study. Cleaning sequence was: (1) acetone rinse; (2) 1% Br_2:MeOH, RT, 5 min; (3) HF:H_2O, RT, 1″, and (4) etch in solution shown above, RT, 10 min. Solution used contained 5 drops of H_2O_2.

INP-0023
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... HCl
x .... HAc
x .... H_2O_2
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Substrates etch cleaned in the solution shown prior to epitaxy.
REF: Kambayashi, T et al — *Jpn J Appl Phys*, 19,79(1980)

INP-0020c
ETCH NAME: TIME:
TYPE: Acid, removal/oxide TEMP: (1) Hot (2) RT
COMPOSITION:
(1) x .... HNO_3, conc. (2) 2 .... HNO_3
1 .... H_2O
DISCUSSION:
InP, (111) wafers used in an etch development study. Solution (2) was used with both

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white and red fuming nitric acid and shows moderate to vigorous reaction in both cases. Concentrated nitric acid shows slow reaction used hot.
REF: Ibid.
INP-0025: Geib, K M et al — *J Phys Chem Solids,* 45,516(1984)

InP, (100) wafers. A concentrated solution used hot to grow an oxide on InP surfaces. Oxide is mainly $InPO_4$.
INP-0086: Wada, O et al — *Solid State Electron,* 25,381(1982)

InP, (100) wafers. Nitric acid used to oxidize surfaces, 50—60°C, 4—5 min by soaking under a microscope light. This formed a 1000 Å thick hydrated oxide. Remove oxide with dilute HCl. (*Note:* This is a method of surface cleaning.)

INP-0022b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... 10% HNO_3
DISCUSSION:

InP, (100) wafers, Zn doped p-type. Wafers processed by (1) degrease in boiling TCE; (2) rinse in MeOH; (3) detergent scrub and (4) DI H_2O rinse. Etch in solution shown to remove lap/polish damage, then etch clean with 1HF:1HCl;$4H_2O$ + I_2:$1H_2O_2$. Final clean to remove native oxide with 10% H_2SO_4.
REF: Ibid.

INP-0026
ETCH NAME: TIME:
TYPE: Halogen, anisotropic TEMP: −15°C
COMPOSITION:
x .... 9 *N* HBr
DISCUSSION:

InP, (100), Sn doped wafers. Pre-clean: (1) ultrasonic TCE; (2) rinse in acetone and (3) rinse in MeOH. Follow with 60% KOH at 50°C, 20 min. Etch to delineate crystallographic directions with 1 HCl(12 *N*): 1 H_2O_2, RT, 30 sec. The $(\overline{1}\overline{1}\overline{1})$B face etches rapidly, and the (100) face shows elongated pits that include line intersection of (111)A and $(\overline{1}\overline{1}\overline{1})$B faces. Coat surfaces with photo resist and open slots in ⟨110⟩ directions. Use solution shown to etch a saw-tooth structure with ridges as (100)/(111)A planes. Solution is not sufficiently preferential at room temperature to etch saw-tooth structure, but will produce the structure when used cold.
REF: Keavney, C J & Smith, H I — *J Electrochem Soc,* 131,452(1984)

INP-0027
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
10 .... HBr
DISCUSSION:

InP, (100) wafers used as substrates for epitaxy growth of a double heterostructure: InP/GaAsP/InP/InP(100). Use a BRM solution to etch remove InP cover. Solution shown is preferential to GaAsP with InP acting as an etch-stop. Most dislocations are 60° type but, with increased density, pure edge, screw and pinning types observed. Solution used to etch thin the epitaxy film for TEM study.
REF: Veda, O et al — *Jpn J Appl Phys,* 23,836(1984)

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INP-0064
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
x .... Br_2
x .... HBr
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:
InP, (100) wafers. Chem/mech polish in solution shown; DI water rinse. Native oxide etch 1 min, RT in 40% HF, water rinse and N_2 blow dry.
REF: Cameron, D C & Foreman, B J — *Solid State Electron,* 27,305(1984)

INP-0028a
ETCH NAME:
TYPE: Acid, defect
COMPOSITION:
1 .... HNO_3
3 .... HBr
TIME: 10 sec
TEMP: RT
DISCUSSION:
InP, (100), p-type wafers used as substrates for epitaxy growth of InGaAsP. Solution developed defects correlated with protrusions observed in the InGaAsP layer.
REF: Lourenco, J A — *J Electrochem Soc,* 131,1914(1984)
INP-0029: Chu, N J et al — *J Electrochem Soc,* 129,352(1982)
InP, (100) wafers used in study similar to INP-0028a.

INP-0030
ETCH NAME: Iodic acid
TYPE: Halogen, polish
COMPOSITION:
x .... 10% HIO_3
TIME: 3 min
TEMP: RT
DISCUSSION:
InP:Fe, (100) (SI) wafers used in a study of optical constants. Chem/mech polish with light scrubbing in solution shown, then final polish with scrubbing; DI water rinse and N_2 blow dry.
REF: Scheps, R J — *J Electrochem Soc,* 131,541(1984)
INP-0085: Hokelek, E & Robinson, G Y — *J Appl Phys Lett,* 40,119(1982)
InP, (100), n- and p-type wafers used in a study of Schottky barrier contacts. Solution used 30 sec, RT, to clean surfaces, and then rinsed in DI water.

INP-0033a
ETCH NAME: Phosphoric acid
TYPE: Electrolytic, selective
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP:
ANODE: GaAs
CATHODE:
POWER:
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of GaInAs. Use solution shown to selectively remove the epitaxy thin film of GaAs. Use 0.5 *M* HCl to remove oxide film remaining after electrolytic etching.
REF: Lyons, M H et al — *J Cryst Growth,* 66,269(1984)

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INP-0022c
ETCH NAME: Phosphoric acid, dilute
TYPE: Acid, oxide:removal
COMPOSITION:
x .... 10% H_3PO_4
DISCUSSION:
InP, (100) Zn doped p-type wafers. After polish etching of surfaces (INP-0022a) use the solution shown to remove native oxide remaining on surface.
REF: Ibid.
TIME:
TEMP:

INP-0033b
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, oxide removal
COMPOSITION:
x .... 0.5 *M* HCl
DISCUSSION:
InP, (100) wafers used as substrates for GaInAs epitaxy growth. After electrolytic selective etch removal of the GaInAs thin film, use the above solution to remove remaining native oxide. See INP-0033a.
REF: Ibid.
TIME:
TEMP:

INP-0034
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HCl
x .... H_3PO_4
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy deposition of thin film InGaAs. Solution used to etch "V" grooves in InP surfaces prior to epitaxy. Groove side slopes are (111)A.
REF: Chand, N & Houston, P A — *J Cryst Growth*, 14,9(1985)
TIME:
TEMP:

INP-0066a
ETCH NAME:
TYPE: Acid, preferential/step-etch
COMPOSITION:
x .... 12 *N* HCl
x .... 15 *N* H_3PO_4
DISCUSSION:
InP:Fe, (100) (SI) wafers cut within 0.5° of the plane, and used in an etch rate study for sub-micron structure fabrication. Wafers were photo resist coated with AZ1350 and step etched to obtain rates. Etching was done with the wafer face down in a glass beaker with stirring and frequent agitation of the wafer during etch period. Etch channels formed were rate measured for (100), (111), (011) surfaces. Face orientation, HCl concentration, and etch rates were as follows:
TIME: 30—120 sec
TIME: 23°C
RATE: See discussion

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Face	HCl (%)	Rate (μm/min)	Etch depth vs. time for the etch solutions shown: Solution	Time/depth (approx.)	
(100)	5	0.09	2.5HCl:7.5H_3PO_4	90 sec	1.28
	10	0.24			
	15	0.40	2HCl:8H_3PO_4	120 sec	1.22
	20	0.70			
	25	1.05	1.5HCl:8.5H_3PO_4	120 sec	0.70
(011)	20	3.40	1HCl:9H_3PO_4	120 sec	0.4+
(111)	20	2.6	0.5HCl:9.5H_3PO_4	140 sec	0.20

REF: Uekusa, S et al — *J Electrochem Soc,* 132,671(1985)

INP-0066b
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, oxide removal
TIME: 60 sec
TEMP: 23°C
COMPOSITION:
x .... 10% HCl
DISCUSSION:
InP:Fe, (100) wafers within 5° of plane used in an etching study for submicron structure fabrication. Solution used to pre-etch wafers prior to AZ1350 photo resist patterning. Wafers were etched in HCl:H_3PO_4 solutions with varied HCl concentrations (INP-0066a) with and without HCl pre-etch of either 10% or 5% HCl. The following etchants were listed as being similar in application to that of the HCl:H_3PO_4 solutions studied:

Solution	Temperature	Content
(1) 2HBr:2H_3PO_4:1$K_2Cr_2O_7$	20°C or 0°C	Solutions containing bromine are rapid with rate dependent on both bromine concentration and the temperature
(2) 0.5Br_2:99.5CH_3OH (MeOH)	−10°C	
(3) 1.5% Br_2:98.5% CH_3OH	−10°C	

REF: Ibid.

INP-0031c
ETCH NAME: BCK-113
TYPE: Acid, selective
TIME: 8 min
TEMP: RT
COMPOSITION:
1 .... 9 *N* HBr
1 .... 17 *N* CH_3COOH (HAc)
3 .... *$K_2Cr_2O_7$

*14.7 g/100 cm^3H_2O

DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Solution will etch both materials and was used in etch forming mesa structures.
REF: Ibid.

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INP-0031d
ETCH NAME: BCK-115 TIME:
TYPE: Acid, selective TEMP: RT
COMPOSITION:
1 .... 9 *N* HBr
1 .... 17 *N* CH_3COOH (HAc)
5 .... *$K_2Cr_2O_7$

*14.7 g/100 cm^3 H_2O

DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Solution will etch both materials and was used in etch forming mesa structures.
REF: Ibid.

INP-0031e
ETCH NAME: BCK-11m TIME:
TYPE: Acid, selective TEMP: RT
COMPOSITION:
1 .... 9 *N* HBr
1 .... 17 *N* CH_3COOH (HAc)
m .... *$K_2Cr_2O_7$ (m = 0.2—2.0)

*14.7 g/100 cm^3 H_2O

DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Solution will etch both materials and was used in etch forming mesa structures. Mirror walls on (110) cleaved planes best with this solution or BCK-221.
REF: Ibid.

INP-0031a
ETCH NAME: BCK-111 TIME: (1) 4 min (2) 2 min
TYPE: Acid, selective/polish TEMP: (1) RT (2) 20°C
COMPOSITION:
1 .... 9 *N* HBr
1 .... 17 *N* CH_3COOH (HAc)
1 .... *$K_2Cr_2O_7$

*14.7 g/100 cm^3 H_2O

DISCUSSION:
InP, (100) wafers used as substrates for MBE growth of InGaAsP. Under condition (1) used to develop defects in epitaxy layers; condition (2) used for a mirror finish surface on InP.
REF: Adachi, S — *J Electrochem Soc*, 129,609(1982)
INP-0032: Adachi, S — *J Electrochem Soc*, 129,1542(1982)
InP, (100) wafers. Similar study as in INP-0031a.

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INP-0031f
ETCH NAME: TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
(1) x .... x% Br_2
x .... MeOH
(2) x .... KI
x .... I_2
x .... H_2O
DISCUSSION:
InP, (100) wafers used as substrates for MBE growth of InGaAsP. Solution (1) used to produce a mirror finish on InP. See BCK-xxx solutions used to selectively etch mesas. Solution (2) was used to etch Au:Zn and AuGe:Ni alloy contacts in conjunction with photolithographic processing with 1350 photo resist in forming mesa contacts.
REF: Ibid.

INP-0035
ETCH NAME: TIME:
TYPE: Acid, grooving TEMP:
COMPOSITION:
3 .... HCl
1 .... H_3PO_4
DISCUSSION:
InP, (100) wafers used as substrates for LPE deposition of InGaAsP. Solution was used to etch grooves in the substrate in ⟨110⟩ directions with groove side slopes $(\overline{111})$B. InGaAsP was deposited in the grooves. After deposition wafer was cleaved ⟨110⟩ and stained to develop layer structure with: 12 g KOH:8 g $K_3Fe(CN)_6$:100 ml H_2O. Surfaces were then studied by SEM.
REF: Ushijima, I et al — *J Cryst Growth*, 69,161(1984)

INP-0021c
ETCH NAME: H etch TIME: 2 min
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
x .... H_3PO_4
x .... HBr
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy deposition of GaInAs. Solution used to develop defect structures. See INP-0051.
REF: Ibid.

INP-0031b
ETCH NAME: BPK-221 TIME:
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
2 .... HBr
2 .... H_3PO_4
1 .... *IN $K_2Cr_3O_7$

*14.7 g/100 cm^3 H_2O

DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Etch rate of epitaxy

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thin film was 2.5 μm/min forming a good mesa structure, and etches InP at a similar rate.
REF: Ibid.

INP-0036a
ETCH NAME: Potassium ferricyanide — TIME:
TYPE: Acid, stain — TEMP:
COMPOSITION:
x .... $K_3Fe(CN)_6$
DISCUSSION:
InP, (100) wafer used as a substrate for epitaxy deposition of InGaAsP. Wafer was cleaved on ⟨110⟩ cross sectioned to observe layer structure. InP substrate was etched back with indium metal prior to epitaxy.
REF: Berman, M A et al — *J Cryst Growth*, 66,480(1984)

INP-0037a
ETCH NAME: — TIME: 1—2 min
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
5 .... HF
1 .... MeOH
DISCUSSION:
InP ingot cut longitudinally on the (112) axis. Ingot etched in a study of growth morphology and defects.
REF: Tohno, S-I et al — *Jpn Appl Phys*, 23,L72(1984)

INP-0037b
ETCH NAME: — TIME: 1—2 min
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
5 .... HF
1 .... Br_2
DISCUSSION:
InP ingot grown by LEC doped with both Ga and Sb. The ingot was cut lengthwise on (112) and etched to observe dislocation pattern.
REF: Ibid.

INP-0072b
ETCH NAME: — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
1 .... Br_2
2 .... H_3PO_4
DISCUSSION:
InP, (100) wafers. Solution used to develop defects and structure.
REF: Ibid.

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INP-0033d
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
8 g .... KOH
0.5 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
+ .... light
TIME: 10 min
TEMP:
RATE: 1.5 μm/h
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of InGaAsP with a cover layer of InP. The InP cover layer was selectively removed with $1HCl:1H_3PO_4$. The InGaAsP layer was etched in the solution shown under light using a 15 W tungsten bulb to develop defects. No defects develop without light and show the same etch rate.
REF: Ibid.

INP-0039
ETCH NAME:
TYPE: Acid, stain
COMPOSITION:
12 g .... KOH
8 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of double-heterostructures (DH) as follows: InP/InGaAsP/InGaAs/InP(100). After deposition the wafer was cleaved on ⟨110⟩ and stained with the solution shown to develop layer structure and defects.
REF: Matsumoto, Y et al — *J Cryst Growth,* 69,53(1984)

INP-0081b
ETCH NAME:
TYPE: Acid, selective/etch-stop
COMPOSITION:
2 g .... KOH
8 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
TIME: 1 min
TEMP: RT
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of double-heterostructures (DH) as follows: pInGaAs/pInP/InGaAsP/InP(100). Growth was by LPE. After epitaxy wafers were cleaved ⟨110⟩ and etched in the above solution to develop layer structures. There is a large etch rate difference between InP and InGaAsP. The latter can be used as a buffer layer for selective etching of InP.
REF: Ibid.

INP-0033e
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
8 g .... KOH
12 g .... $K_3Fe(CN)_6$
100 ml .... H_2O
TIME:
TEMP:

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DISCUSSION:

InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. The etch solution shown was used as a selective etch to remove only the InGaAsP layer.

REF: Ibid.

INP-0020d

ETCH NAME: Sulfuric acid — TIME:

TYPE: Acid, removal — TEMP: Hot

COMPOSITION:

(1) x .... H_2SO_4, conc. (2) 2 .... H_2SO_4

1 .... H_2O

DISCUSSION:

InP, (111) wafers used in an etch development study. Both solutions will attack the material when used hot.

REF: Ibid.

INP-0056b: Ibid.

InP, (100) and other orientations. Wafers used in a general study of material properties. Hot, dilute H_2SO_4 used as a polish and removal etch.

INP-0041

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP: RT

COMPOSITION:

1 .... H_2SO_4

1 .... H_2O_2

1 .... H_2O

DISCUSSION:

InP, (100) wafers used as substrates for epitaxy growth of an Ag/p-InP/p-InGaAs structure. InP is selectively removed with HCl. InGaAsP, part of original deposit structure, is selectively removed with the etch shown.

REF: Takeda, Y et al — *Jpn J Appl Phys,* 23,1341(1985)

INP-0042

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

3 .... H_2SO_4

1 .... H_2O_2

1 .... H_2O

DISCUSSION:

InP:Fe (100) (SI) wafers used as substrates for MISFETT and EMISFET device fabrication. Solution used to etch gate channel for the following structures: (1) Al_2O_3/Al/n-InP:Fe(100), and (2) Al_2O_3/nat.ox,/n-InP/Si(100) substrate. Anodize the aluminum to form the Al_2O_3.

REF: Gordon, R C — *Thin Solid Films,* 103,107(1983)

INP-0063: Kowalsky, W et al — *Solid State Electron,* 27,187(1984)

InP, (100) undoped wafers used to fabricate bar type Gunn diodes. Solution used as a selective etch in forming InP for a metallized structure of Au/Ti/AuGe/InP(100).

INP-0065: Uekusa, S et al — *J Electrochem Soc,* 132,671(1985)

InP:Fe, (100) (SI) wafers used in a selective etching study. Base solution was 12 *N* HCl:15 *N* H_3PO_4, and was varied in pH value with 2—25% HCl. AZ-1350 photo resist was used to pattern wafer, and etch solution was used to step-etch for etch rates of the different

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mixtures. All etching was done at 23°C (effectively RT) in a glass beaker with stirring. Wafers were face down in solutions with frequent agitation during the etch periods.

INP-0033e
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
1 .... H_2SO_4
8 .... H_2O_2
1 .... H_2O
DISCUSSION:
InP, (100) wafer used as substrate for epitaxy deposition of GaInAs or GaInAsP thin films. First, polish substrate in Br_2:MeOH. After epitaxy use solution shown to selectively etch both epitaxy layers.
REF: Lyons, M H et al — *J Cryst Growth*, 66,269(1984)

INP-0033c
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
15 .... H_2SO_4
2 .... H_2O_2
2 .... H_2O
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of GaInAs. Solution used to etch remove the epitaxy deposit.
REF: Ibid.

INP-0044
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
10 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
DISCUSSION:
InP, (100) n-type wafers. Deposit SiO_2 as an etch mask. Photo resist coat and open strips parallel to ⟨110⟩ directions and remove SiO_2 in strip areas with BHF. Use solution shown to etch grooves in InP. Groove side slopes are $(\overline{1}11)$B.
REF: van der Ziel, J et al — *J Appl Phys*, 57,1759(1985)

INP-0045a
ETCH NAME: Hydrofluoric acid, dilute TIME: 30 sec
TYPE: Acid, native oxide removal TEMP: RT
COMPOSITION:
x .... 8% HF
DISCUSSION:
InP, (100) n-type wafers. After chem/mech polish with 2% Br_2:MeOH, etch with solution shown to remove native oxide.
REF: Yamaguchi, E et al — *J Appl Phys*, 55,3098(1984)

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INP-0045b
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
x .... 2% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:
InP, (100) n-type wafers. Chem/mech polish in the solution shown and follow with 8% HF to remove native oxide.
REF: Ibid.

INP-0062
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
InP, (100) wafers, S doped n-type. Surfaces argon ion RF sputter cleaned in fabricating $p^+ - n$ solar cells with gold surface contact metallization.
REF: Ginley, R A — *Solid State Electron*, 27,137(1984)

INP-0046a
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_3PO_4
1 .... H_2O_2
38 .... H_2O
TIME:
TEMP:
TIME: 0.1 μm/min
DISCUSSION:
InP:Fe, (100) (SI) wafers used as substrates for VPE growth of InGaAs doped with either Si or Se after deposition by ion implantation, I^2. Cleave on ⟨110⟩ and profile etch with solution shown. Will etch GaAs with InP acting as an etch-stop.
REF: Penna, J et al — *J Appl Phys*, 57,351(1985)

INP-0046b
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... H_3PO_4
1 .... H_2O_2
76 .... H_2O
TIME:
TEMP:
RATE: 0.05 μm/min
DISCUSSION:
InP:Fe, (100) (SI) wafers used for VPE growth of InGaAs. After deposition epitaxy layer was ion implanted with either Si or Se. Cleave on ⟨110⟩ and profiled etched with this solution. Solution will etch InGaAs with InP acting as an etch-stop.
REF: Ibid.

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INP-0047
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... H_3PO_4
1 .... H_2O_2
3 .... MeOH
DISCUSSION:
InP:Fe, (100) (SI) wafers used as substrates for epitaxy growth by LPE of In/Sn. Wafers first polished in Br_2:MeOH. Immediately before epitaxy etch clean in the solution shown, rinse in MeOH, then in H_2O, and N_2 blow dry.
REF: Chin, B H — *J Electrochem Soc,* 131,1372(1984)

INP-0048
ETCH NAME: TIME: Dip
TYPE: Alkali, cleaning TEMP: RT
COMPOSITION:
2.5 g .... KOH
200 ml .... MeOH
DISCUSSION:
InP:Fe, (100) (SI) n-type wafers. Clean wafers: (1) degrease in TCE, then rinse in MeOH, acetone, then MeOH; (2) dip etch in solution shown; (3) rinse in MeOH, then isopropyl alcohol (IPA) and N_2 blow dry before SiO_2 deposition as a thin surface film mask.

INP-0021d
ETCH NAME: A/B Etch, modified TIME: 30 min
TYPE: Acid, preferential TEMP: 75°C
COMPOSITION:
8 ml .... HF
5 g .... CrO_3
40 g .... $AgNO_3$
10 ml .... H_2O
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of GaInPAs. Solution used to develop dislocations and defects in a study of the epitaxy deposit.
REF: Thiel, F A & Barns, R L — *J Appl Phys,* 126,1272(1979)
INP-0061b: Rokanoar, P J et al — *J Cryst Growth,* 66,317(1984)
InP, (100) and (111) wafers cut from LEC grown ingots either sulfur or zinc doped. Zn-doped wafers were etched in solution shown at RT, 2 min to develop hillocks.

INP-0081c
ETCH NAME: Indium TIME:
TYPE: Metal, etch-back TEMP: >155°C
COMPOSITION:
x .... In
DISCUSSION:
InP, (100) wafers used for epitaxy growth of InGaAs/InGaAsP. During LPE growth, liquid indium was used to lightly etch-back InP prior to epitaxy deposition to clean surface and reduce surface defects.
REF: Ibid.
INP-0036b: Ibid.

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InP, (100) wafers used as substrates for epitaxy growth of InGaAsP. Liquid indium used to etch-back InP during LPE growth to reduce defects in surface.

INP-0051
ETCH NAME: H etch
TYPE: Acid, dislocation
COMPOSITION:
2 .... H_2SO_4
1 .... 4% HBr
TIME: (1) 10—30 sec (2) 2 min
TEMP: RT RT
DISCUSSION:

InP, (100) wafers used in a dislocation study. A study of the "grappe" structure as an impurity at a dislocation. Study was done under a polarized infra-red microscope (PIM) by transmission. Solution used to develop dislocations. Boric acid an impurity?
REF: Stirland, D J et al — *J Cryst Growth*, 61,645(1983)
INP-0061a: Rokanoar, P J et al — *J Cryst Growth*, 66,317(1984)

InP, (100) and (111) wafers cut from LEC grown ingots and either zinc or sulfur doped. Wafer used in a defect study. S-doped wafers developed striations with solution shown within 20 sec at RT, in addition to etch pits.
INP-0062: Fang, D F et al — *J Cryst Growth*, 66,317(1984)

InP, (100) and (111) wafers used in a defect study. Solution used to develop dislocation pits.

INP-0052
ETCH NAME: Orthophosphoric acid
TYPE: Electrolytic, oxidize
COMPOSITION:
x .... 14 *N* H_3PO_4
TIME:
TEMP: 4°C to −30°C
ANODE: InP
CATHODE:
POWER: 40 V
DISCUSSION:

InP, (100) wafers used in a structural defect study by electrolytic etching. Etch polish with Br_2:MeOH before oxidizing with solution shown. With specimen as anode, rotate at 100 rpm. Remove oxide with 2 *N* HCl or 2 *N* HNO_3. For defect development use 0.5 *N* HCl at 400 $\mu A/cm^3$ power.
REF: Elliott, C R & Regnault, J C — *J Electrochem Soc*, 128,113(1981)

INP-0053
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, clean
COMPOSITION:
x .... 10% HCl
TIME: 10 min
TEMP: RT
DISCUSSION:

InP, (100) n-type wafers used in a study of anodized island growth. Degrease in MeOH then acetone. Chem/mech polish on pellon pad with 1% Br_2:MeOH. Then etch with solution shown. Surface replication done with 4% collodion in amyl acetate. After drying, lift-off replica with water. (*Note:* This thin film removal technique is usually called float-off, not lift-off.)
REF: Makky, W H & Wilmsen, G W — *J Appl Phys*, 130,659(1983)
INP-0056a: Reynolds, W N et al — *Proc Phys Soc*, 71,416(1958)

InP, (100) wafers and other orientations used in a general properties study. Both dilute HCl (hot) and concentrated HCl (RT) were used as removal and polish solutions. InP will not etch in NaOH or CP4.

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INP-0054a
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, clean
COMPOSITION:
x .... 50% HCl
TIME: 30 sec
TEMP: RT
DISCUSSION:
InP:Fe, (100) wafers. Clean wafers: (1) degrease in boiling TCE; (2) rinse in acetone, then IPA; (3) etch in HCl and rinse in IPA and, (4) dry in hot IPA vapors. Etch polish cleaned surfaces with 0.5% Br_2:MeOH.
REF: Rhee, J K & Bhattachairya, T — *J Appl Phys*, 130,700(1983)

INP-0059a
ETCH NAME: Carbon tetrafluoride
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
InP, (100) wafers used as substrates for material removal rate study using CF_4 under varying flow conditions. Wafers were first chem/mech polished with 2.5% Br_2:MeOH to remove prior lapping damage before photo resist patterning with AZ-1350 lacquer.
REF: Hirata, K et al — *J Vac Sci Technol*, B(2),44(1984)

INP-0060
ETCH NAME: Heat
TYPE: Thermal, cleaning
COMPOSITION:
x .... heat, in vacuum
TIME:
TEMP: 500°C
DISCUSSION:
InP, (100) wafers used as substrates for MBE of deposition of $Ba_xSr_{1-x}Fe_2$. InP was n-type, S-doped and polished. Clean in vacuum under phosphorus over-pressure prior to MBE growth.
REF: Tu, C W et al — *J Vac Sci Technol*, B(2),24(1984)

INP-0055
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... HCl
x .... 0.4 *N* $FeCl_3$ (for ferric ions)
TIME: 10 min
TEMP: RT
DISCUSSION:
InP, (111) wafers. Solution produces etch figures.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill Book Co., NY, 1970, 7
INP-0058: Gatos, H C & Lavine, M C — *J Electrochem Soc*, 107,427(1960)
InP, (111) wafers used in a surface characterization study.

INP-0057a
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... HCl
1 .... H_3PO_4
TIME:
TEMP:

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DISCUSSION:

InP, (100) tin-doped, n-type wafer used for an InP:Zn, epitaxy thin film deposit as a layer in a buried heterostructure. The solution shown was used to selective etch structure the zinc doped InP layer. Deposition was by Liquid Phase Epitaxy (LPE). Liquid indium used to etch-back surface during film growth. Device structure was InP:Zn/$In_{1-x}Ga_xAs_y:P_{1-y}$/InP:Sn(100). Solution shown used as a mesa etch, and develops (100) facets on mesa walls; 1% Br_2:MeOH develops a cylindrical mesa wall.

REF: DiGiuseppi, M A et al — *J Cryst Growth*, 67,1(1984)

INP-0057b

ETCH NAME: TIME:

TYPE: Halogen, mesa structure TEMP:

COMPOSITION:

x .... 1% Br_2

x .... MeOH

DISCUSSION:

InP:Zn, epitaxy film grown by LPE. Solution used to etch form mesa structures. See INP-0057a for further discussion.

REF: Ibid.

INP-0062a

ETCH NAME: TIME: 1 min

TYPE: Acid, selective TEMP: 20°C

COMPOSITION:

(1) 1 .... HBr
1 .... H_3PO_4

(2) 1 .... HBr
1 .... CH_3COOH (HAc)

(3) 1 .... HBr

(4) 1 .... HBr
1 .... HCl

DISCUSSION:

InP, (100) wafers used as substrates for the growth of double heterostructure (DH) by LPE. Substrates were (1) degreased; (2) DI water rinsed and (3) polished in Br_2:CH_3OH. Substrates were n-type; epitaxy InP n-type and InGaAsP both n- and p-type. Heterostructure used in a selective etching study of InP vs. InGaAsP. The solutions shown will etch InP but not InGaAsP. Specimens cleaved ⟨110⟩ for measurement. SiO_2 was used as a patterned mask as bromine solutions attack photo resist.

REF: Adachi, S et al — *J Electrochem Soc*, 129,1053(1982)

INP-0062b

ETCH NAME: TIME: 1 min

TYPE: Acid, selective TEMP: 20°C

COMPOSITION:

(1) 1 .... HBr
1 .... H_2O_2

(2) 1 .... HBr
1 .... HNO_3

(3) 1 .... HBr
1 .... HNO_3
5 .... H_2O

(4) 1 .... HBr
2 .... HCl

(5) 2 .... HBr
1 .... HCl

DISCUSSION:

InP, (100) wafers used as substrates for LPE growth of double-heterostructures (DH) of InGaAsP:InP in a study of etch selectivity. All of the solutions shown were selective with a ratio of about 10:1 between InGaAsP to InP. See INP-0062a for additional discussion.

REF: Ibid.

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INP-0062c
ETCH NAME: BRM — TIME: 1 min
TYPE: Halogen, selective — TEMP: 20°C
COMPOSITION:

(1)	(2)	(3)	(4)
x .... 4% Br_2	x .... 2% Br_2	x .... 1% Br_2	x .... 0.2% Br_2
x .... MeOH	x .... MeOH	x .... MeOH	x .... MeOH

(5) x .... 0.1% B_2
x .... MeOH

DISCUSSION:
InP, (100) wafers used for LPE growth of double heterostructures (DH) of InGaAsP:InP in a study of etch selectivity. All of the solutions above show a selectivity ratio of about 10:1 between InGaAsP to InP. See INP-0062a for additional information.
REF: Ibid.

INP-0062d
ETCH NAME: Hydrochloric acid — TIME: 1 min
TYPE: Acid, selective — TEMP: 20°C
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
InP, (100) wafers used as substrates for LPE of InGaAsP. Solution will etch InP but not InGaAsP. See INP-0062a for additional discussion.
REF: Ibid.

INP-0062e
ETCH NAME: — TIME: 1 min
TYPE: Acid, selective — TEMP: 20°C
COMPOSITION:

(1)	(2)	(3)	(4)
1 .... HCl	1 .... HCl	1 .... HCl	1 .... HCl
1 .... H_2O_2	1 .... HAc	1 .... H_3PO_4	1 .... H_2O

DISCUSSION:
InP, (100) wafers used as substrates for LPE growth of InGaAsP. Solutions shown will etch InP but not InGaAsP. See INP-0062a for additional discussion.
REF: Ibid.

INP-0062f
ETCH NAME: — TIME: 1 min
TYPE: Acid, selective — TEMP: 20°C
COMPOSITION:

(1)	(2)
1 .... HCl	1 .... HCl
1 .... CH_3COOH (HAc)	1 .... H_3PO_4
1 .... H_2O_2	1 .... H_2O_2

DISCUSSION:
InP, (100) wafers used as substrates for LPE growth of InGaAsP. Solutions shown will etch selectively with a ratio of about 10:1 between InGaAsP and InP. See INP-0062a for additional discussion.
REF: Ibid.

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INP-0062g
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
(1) 1 .... HCl
1 .... HNO_3
(2) 1 .... HCl
2 .... HNO_3
(3) 2 .... HCl
1 .... HNO_3
TIME: 1 min
TEMP: 20°C
DISCUSSION:
InP, (100) wafers used as substrates for LPE growth of InGaAsP. Solutions shown will etch selectively with a ratio of about 10:1 between InGaAsP and InP. See INP-0062a for additional discussion
REF: Ibid.

INP-0062h
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
(1) 1 .... H_2SO_4
1 .... H_2O_2
1 .... H_2O
(2) 1 .... H_2SO_4
2 .... HCl
1 .... 2 *N* $K_2Cr_2O_7$
TIME: 1 min
TEMP: 20°C
DISCUSSION:
InP, (100) wafers used as substrates for LPE growth of InGaAsP. Solution (1) will etch InGaAsP but not InP. Solution (2) is selective with a ratio of about 10:1 between InGaAsP to InP. See INP-0062a for additional discussion.
REF: Ibid.

INP-0063
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
1 .... HF
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
InP,, (111)A and (100) wafers used as substrates for LPE of $Al_xIn_{x-1}As$ and $Al_xGa_yIn_{1-x-y}As$. The (111)A surface produces a smooth epitaxy AlInAs layer grown at 790°C, but shows defects with (100). Selective removal of AlInP from (100) with solution shown. Many small holes observed in (100) surface after film was removed. Also grown as heterostructures.
REF: Nakajima, K et al — *J Electrochem Soc*, 130,1927(1983)

INP-0064a
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
(1) 1 .... HCl
3 .... HNO_3
(2) 6 g .... $K_3Fe(CN)_6$
4 g .... KOH
70 ml .... H_2O
(3) x .... HCl, conc.
TIME: (1) 15 (2) 7 (3) 10 sec
TEMP: RT
DISCUSSION:
InP, (100) wafers used as substrates for epitaxy growth of GaInAsP double heterostructure (DH) used in a study of the controlled development of planar-etched bulk crystal planes with wet chemical etching (WCE) or dry gas etching (DCE) using RIE and combinations of WCE and RIE in channel structuring surfaces. Photo resist patterned deposited surface thin films of Si_3N_4 and Ti/Si_3N_4 were used as the etch masks. Wafers were cleaved

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⟨011⟩. The step etching system shown above was used to develop a near-vertical wall channel with flat bottom down through the active layer to the Q-stop etch layer.
REF: Coldren, L A et al — *J Electrochem Soc*, 130,1918(1983)

INP-0064b
ETCH NAME: BRM
TYPE: Halogen, selective
TIME: See discussion
TEMP: RT
COMPOSITION:
x .... 3% Br_2
x .... MeOH
DISCUSSION:
InP, (100) wafers theta angles controlled toward (011) or $(0\bar{1}1)$. Solution shown used to channel etch InP from the (100) surface to the $(\bar{1}00)$ surface to establish the internal bulk planes etch rates. The approximate etch rates in microns/minute (μm/min) were measured with regard to these surface and relevant bulk planes.
REF: Ibid.

INP-0064c
ETCH NAME: Hydrochloric acid
TYPE: Acid, selective
TIME:
TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
InP, (100) wafers used in a channel etching study. See INP-0064b for additional discussion. This solution produced different theta angle results.
REF: Ibid.

INP-0064d
ETCH NAME: KKI
TYPE: Acid, selective
TIME:
TEMP: RT
COMPOSITION:
1 g .... $K_3Fe(CN)_6$
1 g .... KOH
1 ml .... H_2O
DISCUSSION:
InP, (100) wafers used in a channel etching study. See INP-0064a-c for additional information.
REF: Ibid.

INP-0064e
ETCH NAME: Hydrochloric acid
TYPE: Acid, selective
TIME: 90 sec
TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
In, (100) wafers with channels in ⟨011⟩ or $\langle 01\bar{1}\rangle$ directions using Si_3N_4 as the etch mask. Cross section of the pit slope in the ⟨011⟩ direction shows an initially vertical (011) slope changing to a (111) positive slope. Both channel types had flat bottoms.
REF: Ibid.

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INP-0064f
ETCH NAME: BRM
TYPE: Halogen, selective
COMPOSITION:
x .... 3% Br_2
x .... MeOH
TIME: 120 sec
TEMP: RT
DISCUSSION:
InP, (100) wafers with channels in ⟨011⟩ and ⟨01$\bar{1}$⟩ directions using an Si_3N_4 evaporated film with parallel stripes of 10 μm spacing as etch masks. The (011) orientation developed a shallow cup-like channel; the (01$\bar{1}$) a "V" groove with slight curvature in pit bottom.
REF: Ibid.

INP-0064g
ETCH NAME:
TYPE: Acid, selective
COMPOSITION:
(1) x .... HCl, conc.
(2) x .... Cl_2:O_2 (RIE)
TIME: 10 sec
TEMP: RT
DISCUSSION:
InP, (100) wafers with channels in ⟨011⟩ and ⟨01$\bar{1}$⟩ directions. A titanium etch mask was used for RIE. Results show severe under-cutting of masks with erratic etching results. On ⟨011⟩, reentrant angle side walls with low curvature channel bottom; ⟨011⟩, the upper section was a severely under-cut, shallow positive curve slope with about a 1 μm width deep channel in the center, ending with a point.
REF: Ibid.

INP-0064h
ETCH NAME: RIE
TYPE: Ionized gas, selective
COMPOSITION:
x .... 80% Cl_2
x .... 20% O_2
TIME: 20 min
TEMP: (1) 250°C
(2) 30°C substrate
GAS FLOW:
PRESSURE: (1) 2 mT
(2) 4 mT
POWER: 0.33 W/cm²
DISCUSSION:
InP, (100) wafers with channels in ⟨011⟩ and ⟨01$\bar{1}$⟩ directions. Ti/Si_3N_4 used as the preferred etching mask. Both RIE channels showed similar near-vertical side slopes with flat bottoms. A post HCl, 10 sec etch showed little or no alteration of the slope side configuration of either the (1) or (2) temperature and time conditions.
REF: Ibid.

INP-0064i
ETCH NAME: RIE
TYPE: Ionized gas, preferential
COMPOSITION:
x .... 60% Cl_2
x .... 30% O_2
x .... 10% Ar
TIME: 150 min
TIME: 25°C
GAS FLOW:
PRESSURE: 2 mT
POWER: 0.33 W/cm²
DISCUSSION:
InP, (100) wafers with channels in ⟨011⟩ direction. Both Si_3N_4 for chemical etching and Ti/Si_3N_4 for RIE were evaporated as etch masks. RIE channel slope was a reentrant angle with low curvature channel bottom. Additional etching with HCl, 10 sec, changed slope to

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an upper (111) vertical and medium angle positive lower slope with striations. Specimens were at a 40° angle during RIE.
REF: Ibid.

INP-0064j
ETCH NAME:
TIME: (1) 30 (2) 60 (3) 20 sec
TYPE: Acid, selective
TEMP: RT
COMPOSITION:
(1) x .... HCl, conc.
(2) 6 g .... $K_3Fe(CN)_6$
4 g .... KOH
35 ml .... H_2O
(3) x .... HCl, conc.
DISCUSSION:
InP, (100) wafers with channel in ⟨011⟩ direction. Si_3N_4 used as the etch mask. WCE multi-step etching with or without prior RIE etching. Channel slope was vertical and lower slope positive section similar to HCl after RIE results obtained in INP-0064i. About a 1 μm under-cut of mask against RIE/HCl about 0.5 μm/min.
REF: Ibid.

INP-0064k
ETCH NAME:
TIME: 20 sec
TYPE: Acid, selective
TEMP: RT
COMPOSITION:
(1) 1 .... HCl
1.5 .... HNO_3
(2) 1 .... HCl
2 .... HNO_3
(3) 1 .... HCl
2.5 .... HNO_3
DISCUSSION:
InP, (100) wafers used as substrates for heterostructure of the following configuration: p-GaInAsP/p-InP/i-GaInAs/n-InP (100). Si_3N_4 used as the etching mask with channel (011) oriented. Channel side slopes were: (1) a double near-vertical slope and shallow curved channel bottom; (2) an upper "cliff-like" upper over-hang beneath etch undercut of mask, a vertical slope with a curved positive slope into the bottom channel; (3) upper vertical slope graduating into a positive slope into channel bottom. Striations on vertical slopes. Used with negative photo resist patterning.
REF: Ibid.

INP-0064l
ETCH NAME:
TIME: (1) 20 (2) 10 sec
TYPE: Acid, selective
TEMP: RT
COMPOSITION:
(1) 1 .... HCl
1.5 .... HNO_3
(2) x .... HCl, conc.
DISCUSSION:
InP, (100) wafers used as substrates as described in INP-0064k heterostructure epitaxy. As HCl will not etch GaInP, initial etching is done with solution (1) to establish channel slide slopes, followed by (2) to finalize the InP channel slope and bottom.
REF: Ibid.

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INP-0064m
ETCH NAME: Multi-step etch TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
Step 1: (1) x .... HCl (2) x .... HCl (3) x .... x% Br_2 (4) x .... RIE
x .... HNO_3 x .... HAc x .... MeOH
x .... H_2O_2
Step 2: (1) x .... $K_3Fe(CN)_6$ or x .... H_2SO_4 (3) x .... HNO_3,
x .... KOH x .... H_2O_2 conc.
x .... H_2O x .... H_2O
Step 3: (1) x .... HCl, conc.
Step 4: (i) Repeat 1—3 (ii) repeat 1 & 3 (iii) repeat 2 & 3
DISCUSSION:

InP, (100) wafers used as substrates for DH InGaAsP epitaxy laser channel structure in (001) direction. Any of the Steps (1) will etch all layers and is used to establish initial side-wall facets at near-vertical [RIE also on ⟨011⟩]. Step (1) solutions used as selective Q-layer etchant to recess layers approximately 1000 Å. Step 2 solutions used to planarize the (001) InP. Step 3 solution combinations to improve and finalize facet surfaces for optimum planarity. See other INP-0064a-1 references for specific solution mixtures.
REF: Ibid.

INP-0064n
ETCH NAME: Sequential etch TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
Step 1: (1) x .... $K_3Fe(CN)_6$ (2) x .... H_2SO_4 (3) x .... HNO_3 (4) x .... RIE
x .... KOH x .... H_2O_2 nonselective no undercut
x .... H_2O x .... H_2O
cut Q cap selective
Step 2: (5) x .... HCl (6) x .... x% Br_2 (7) x .... RIE
x .... HNO_3 perpendicular
Step 3: (8) x .... HCl, conc.
cut to Q-active layer
Step 4: (9) x .... $K_3Fe(CN)_6$ (10) x .... H_2SO_4 (11) x .... HNO_3
x .... KOH x .... H_2O_2
x .... H_2O x .... H_2O
Step 5: (12) x .... HCl (13) x .... RIE
x .... HNO_3 5° angle
Step 6: (14) x .... $K_3Fe(CN)_6$ (15) x .... H_2SO_4 (16) x .... HNO_3
x .... KOH x .... H_2O_2
x ..... H_2O x .... H_2O
optional to recess Q after Step 3, (9), (10) or (11)
Step 5: (17) x .... HCl, conc.
etch under Q-layer/planarize (011).
Step 6: (18) repeat 3 thru 5 (19) repeat 3 and 5
planarize facets — optional
DISCUSSION:

InP, (100) wafers used as substrates for DH InGaAsP epitaxy laser channel structure in (011) direction. Basic etching sequence follows: Step 1 — any one of solutions shown; Step 2 — HCl; Step 3 — any one of solutions shown and Step 5 — HCl. Steps 4 and 6, used in order shown, as required. See other INP-0064a-1 references for specific solution mixtures.
REF: Ibid.

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INP-0065
ETCH NAME: Hydrochloric acid
TYPE: Acid, orientation
COMPOSITION:
x .... HCl, conc.
TIME: 20 sec
TEMP: 20°C
DISCUSSION:
InP, (100) wafers with or without thin film InGaAsP epitaxy. The orientation direction of the (100) work surface is important for selective etching of channels and pits related to ⟨011⟩ or ⟨01$\bar{1}$⟩ bulk plane direction; the ⟨0$\bar{1}$1⟩ preferred. Cleave a small section of the wafer and etch in HCl to develop (111)A or ($\bar{1}\bar{1}\bar{1}$)B triangle etch pits in the cleaved surface. If the triangle points away from the upper (100) work surface, the cleavage plane is ⟨011⟩ and a mesa structure will be similar. If the triangle point is toward the (100) work surface, the cleave plane is ⟨01$\bar{1}$⟩ and can show fine-textured, blackish-colored areas after HCl etching.
REF: Stulz, L W & Coldren, I A — *J Electrochem Soc,* 130,1628(1983)
INP-0071: Sagar, A — *Phys Rev,* 117,101(1959)
InP, (100) wafers used in a study of piezoresistance. Concentrated HCl used as a general cleaning etch. An ultrasonic soldering iron was used to activate piezoresistance measurements.

INP-0067
ETCH NAME:
TYPE: Acid, clean/etch sequence
COMPOSITION:
(1) x .... DI H_2O (2) x .... TCE (3) x .... H_2SO_4 (4) x .... MeOH (5) x .... 0.3% Br_2
x .... MeOH
TIME:
TEMP:
DISCUSSION:
InP, (100) wafers used in a study of surface contamination and cleaning in a VPE reactor. Specimens were processed through the sequence shown. (1) rinse several times in DI water; (2) degrease (not shown); (3) ultrasonic clean in sulfuric acid; (4) soak in MeOH and (5) final etch in BRM. Specimens were then thermally annealed at 700°C to include vapor etching. (*Note:* Hot HCl vapor?)
REF: Gautard, B et al — *J Cryst Growth,* 71,125(1985)

INP-0070
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HCl
1 .... HNO_3
TIME:
TEMP:
DISCUSSION:
InP, (111) wafers used in a study of room temperature reflectivity of (111)A and ($\bar{1}\bar{1}\bar{1}$)B surfaces. If cutting and mechanical lapping damage is not removed, reflectivity is sharply reduced and shifted toward lower energy levels. Solution shown used to polish remove subsurface residual damage.
REF: Cardona, M — *J Appl Phys,* 32,958(1961)

INP-0076a
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 1.5% Br_2
x .... MeOH
TIME:
TEMP: RT or −7 to −18°C

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DISCUSSION:

InP, (100) wafer fabricated as Schottky diodes. Solution used to polish wafers prior to Cd diffusion. Etch rate increases by adding drops of the solution during etch period. Better polishing results are obtained using the etchant at the coldest temperature shown. Cleaning sequence was (1) degrease in TCE, then rinse in MeOH, then in acetone, all at 85°C for 10 min, each; (2) boil in 100 g KOH:500 ml H_2O, 80°C, 10 min; (3) DI water rinse several times until no soapy feeling is left.

REF: Aytal, S & Schlachetzki, A — *Solid State Electron,* 25,1135(1982)

INP-0076b

ETCH NAME: TIME: 10 min

TYPE: Halogen, junction stain TEMP: RT

COMPOSITION:

x .... x% Br_2

x .... isopropyl alcohol

x .... acetone

DISCUSSION:

InP, (100) wafers fabricated as Schottky diodes with cadmium diffusion. Solution used as a junction stain with and without acetone. Time is shown with acetone and was evaluated from 1 to 25 min. Also used as a polishing etch. Without acetone is best as a staining etch.

REF: Ibid.

INP-0073a

ETCH NAME: Hydrochloric acid TIME: 1—2 min

TYPE: Acid, polish TEMP: RT

COMPOSITION:

(1) x .... 12 *M* HCl then (2) 1 .... 1 *M* NaOH

1 .... 1 *M* S

1 .... 2.5 *M* NaS_2

DISCUSSION:

InP, p-type single crystal wafers in a study of surface modification of photo-cathodes with polysulfides. Etch polish in solution shown as (1), then modify surface with polysulfide solution (2). InP wafers were Fe and Cr doped with Be implantation and annealed with an Si_3N_4 cap. After anneal, nitride was removed with HF.

REF: Williams, R et al — *J Electrochem Soc,* 129,2082(1982)

INP-0087

ETCH NAME: TIME:

TYPE: Halogen, polish TEMP: RT

COMPOSITION:

x .... x% I_2

x .... MeOH

DISCUSSION:

InP, (100) wafers used in a study of the optical properties of anodic films. Polish substrates in solution shown for strain-free surface. Oxidize in "AGW" solution: 0.5% H_3PO_4:2 ethylene glycol, electrolytically at 1 mA/cm^2 + white light with Ta wire and Pt counter-electrodes; rinse in MeOH and N_2 dry. Strip oxide with NH_4OH:H_2O. Oxide films are hygroscopic — store with zeolite, $CaSO_4$, in closed container for a dry atmosphere.

REF: Studna, A A & Gualtieri, G L — *J Appl Phys Lett,* 39m,965(1981)

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INP-0088
ETCH NAME:
TYPE: Alkali, oxide removal
COMPOSITION:
(1) x .... 45% KOH or (2) x .... 29% NH_4OH
DISCUSSION:

InP, (100) n-type wafers used in a study of electrical properties of dielectric thin films. Clean InP: (1) BRM polish; (2) remove oxide with either solution shown; (3) DI water rinse; (4) N_2 blow dry with filtered N_2 . . . then: etch in 1% Br_2:MeOH; MeOH rinse; DI H_2O rinse; N_2 dry . . . then etch in 1HF:1HC1:4H_2O:0.4% H_2O_2; DI water rinse; N_2 dry . . . then wash in 95% hydrazine; rinse in hexane, and N_2 dry. RF sputter deposit SiO_2 from SiH_4/N_2 and Si_3N_4 from NH_3 at 300°C with a growth rate of 40—50 Å/min.
REF: Meiners, L G — *J Vac Sci Technol,* 19,373(1981)

INP-0074
ETCH NAME: BRM
TYPE: Halogen, grooving
COMPOSITION:
x .... 2% Br_2
x .... MeOH
+ .... wooden stick
TIME: 30 sec soak
TEMP: RT
DISCUSSION:

InP, (100) wafer substrates with InGaP multilayer deposited structure. The following method used to develop damage-free grooves to reveal the quality of the InP/InGaP structures: soak a wooden stick in the solution shown — soak can be repeated — then rub specimen surface to form groove and MeOH rinse. For a 10 μm deep groove, rub 10—30 sec at a time until structure is delineated . . . pressure and stroke control etching depth. Also used a "CJB Etch" and an "HL Etch".
REF: Goods, R L — *J Electrochem Soc,* 129,2082(1982)
INP-0075: Sng Chu, A et al — *J Electrochem Soc,* 129,352(1982)

Reference for CBJ etch shown above.

INP:0072: Huber, A & Linn, N T — *J Cryst Growth,* 28,80(1975)

Reference for HL etch shown above. This INP-0072 reference is also called the Huber etch . . . See under INP-0014.

INP-0092b
ETCH NAME: AGW
TYPE: Electrolytic, oxidizing
COMPOSITION:
1 .... 0.5% H_3PO_4
x .... EG (ethylene glycol)
x .... H_2O
TIME:
TEMP:
ANODE: InP
CATHODE: Pt/Ti wire
POWER: 0.1 mA/cm²

DISCUSSION:

InP, (100) wafers. Solution used to anodically oxidize surfaces in a study of optical properties and water adsorption of the oxide. Ti wire (self-oxidizing) + white light used during oxide growth, followed by rinsing in MeOH. Oxides were stripped with NH_4OH:H_2O. See INP-0092a. (*Note:* Name acronym (AGW) means acid/glycol/water, and can be different acids and glycols.)
REF: Ibid.

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INP-0089
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
(1) x .... x% Br_2
x .... MeOH
(2) x .... HF
x .... NH_4F
x .... H_2O

TIME:
TEMP:

DISCUSSION:
InP, (100) wafers cut within 1° of plane from undoped LEC grown ingot. An extensive study of controlled etch pits formed by etching through a patterned SiO_2 mask. This oxide removed with solution (2), and wafers initially chem/mech polished in (1). Over 30 solutions evaluated and pit slope angles evaluated by cleaving $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ . . . to include concave planes and angles from (100) surface. All etching done in a controlled temperature bath at 25°C, 1 min, except H_3PO_4 solutions used at 60°C up to 20 min. Other solution categories: HCl; H_2SO_4; Br_2; HBr, all with other acid additives.
REF: Adachi, S & Kawaguchi, H — *J Electrochem Soc*, 128,1342(1981)

INP-0090
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
1 .... HCl
4 .... H_2O
1 drop .... H_2O_2/10 ml

TIME:
TEMP:

DISCUSSION:
InP, (100), n-type, 0.3—0.4 Ω cm resistivity, and p-type, 7—8 Ω cm. Wafers used in a study of ion beam etching. Clean wafers: (1) degrease with TCE; (2) rinse in acetone; (3) rinse in MeOH; (4) HF dip, and (5) etch in solution shown. TaSi thin films were sputter deposited.
REF: Wu, C S et al — *J Electrochem Soc*, 132,918(1985)

PHYSICAL PROPERTIES OF IODINE, I_2

Classification	Halogen
Atomic number	53
Atomic weight	253.84
Melting point (°C)	114
Boiling point (°C)	183 (184.35)
Density (g/cm³)	4.93
Thermal conductance ($\times 10^{-4}$ cal/cm²/cm/°C/sec) 20°C	10.4
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	93
Electrical resistivity ($\times 10^{9}$ ohms cm) 20°C	1.3
Latent heat of fusion (cal/g)	14.2
Specific heat (cal/g/°C) 20°C	0.052
1st ionization potential (eV)	10.44
Solubility (100 ml H_2O) 50°C	0.078 ml
Ionic radius (angstroms)	2.20
Heat of vaporization (cal/g)	39.28
Atomic volume (W/D)	25.7

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1st ionization energy (K-cal/g-mole)	241
Electronegativity (Pauling's)	2.5
Covalent radius (angstroms)	1.33
Electrical resistivity ($\times 10^{-6}$ ohm cm) 25°C	5.85
Vapor pressure (mmHg) 25°C	0.31
Critical temperature (°C)	553
Critical pressure (atms)	116
Cross section (barns)	6.4
Refractive index (n=)	3.34
Hardness (Mohs — scratch)	2
Crystal structure (orthorhombic — normal)	(100) a-pinacoid
Color (solid/solution)	Brown-violet/brown
Cleavage (basal)	(001)

IODINE CONTAINING ETCHANTS

Iodine is an oxidizing agent of the halogen family being the heaviest and least reactive of the group. It is the only one that forms as a solid; bromine is a liquid, fluorine and chlorine are gases. Iodine has limited solubility in water but is easily dissolved in alcohols, carbon disulfide, chloroform, and solutions of other iodides, e.g., KI + I_2 goes to KI_3, as a reversible reaction and is an unstable compound known as tri-iodide.

"Tincture of iodine" is a mixture of KI:I_2:EOH, used as a medical antiseptic, and also can be used as a preferential etch on a number of metals and metal compounds. Solutions of iodine in water, alcohols, and iodides are dark brown in color and opaque. In carbon disulfide and chloroform a very distinctive violet color.

Although bromine is more widely used as a bromine:methyl alcohol (BRM) mixture for etch removal, polishing, thinning and defect development on a number of semiconductor materials and other metals, the bromine can be replaced by iodine with similar results. The iodine etchants are more stable and useful where the solutions are used above room temperature as it evaporates less rapidly than bromine.

It should be noted that iodine is used as a disinfectant and germicide; can be introduced into the bloodstream for X-ray evaluation of blood clots and is in the thyroid gland of all mammals in the form of the hormone, thyroxine, which is a metabolic catalyst for carbon dioxide and essential to health. A lack of iodine can produce a goiter and cretinism. Iodized salt is used to help maintain the iodine balance in human beings. Bromine, on the other hand, is a poison if ingested and can cause severe sores on the skin that are difficult to heal, and the vapors can be a severe skin and wet membrane irritant.

The tri-iodide etch for gold is probably the best known of the iodine solutions: KI:I_2:H_2O. It is often preferred over the aqua regia and cyanide etchants, even though it is a brown and opaque solution, as it is more controllable than aqua regia and not toxic like the cyanides. Iodine etchants were in use for several years prior to the advent of the semiconductor and Solid State industries in the mid-1940s, and there are several solutions named "Iodine Etch", "Iodine A", or "Iodine B" etch, with the mixtures varying, depending upon the metal involved even though the "names" may be identical. Although most iodine-containing etchants are probably interchangeable as applied to specific metals and compounds, their reactions can vary such that the term "iodine etch" should be considered as a very general term, not a specific mixture. Iodine etches are used for defect and dislocation development to a large extent though they have been applied as a polish, general removal, passivation, and surface cleaning solution. Also, by varying the molar concentration, they can be used as a selective etch between GaAs and AlGaAs semiconductor material. As an additive to hot hydroxide solutions such etchants are preferential and can be used for light figure orientation of germanium which is unaffected by pure hydroxides. In this case, bromine can

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replace the iodine and both solutions are applicable to silicon and other compound semiconductors as preferential etches.

The following is a selected list of some of the iodine etchants as applied to different metals and compounds and other solutions can be found under the different metals and compounds in this Etchant Section.

Formula	Material	Use	Ref.
10 g I_2:100 ml MeOH	Al	Channel etch	AL-0031
x10% I_2:xMeOH	As	Dislocation	AS-0003a
x0.3 *M* KI:x0.04 *M* I_2	GaAs	Selective (GaAs vs. AlGaAs)	GAS-0061d
x0.3 *M* KI: x 0.3 *M* I_2	GaAs	Selective (AlGaAs vs. GaAs)	GAS-0061e
250 ml 30% KOH:30 g I_2	Ge, Si	Preferential	GE-0012a
160 ml HF:200 ml HNO_3:80 ml HAc: 0.32 g I_2	Ge	Preferential	GE-0083a
1HF:2HNO_3:2HAc: + I_2 "iodine etch"	Ge	Preferential	GE-0139a
xKI:xI_2:xH_2O	Bi	Polish	BI-0003
1% I_2:MeOH	Bi	Dislocation	BI-0006b
10 ml HNO_3:10 ml HCl:40 ml H_2O:1 g I_2	Bi_2Te_3	Preferential	BITE-0001b
400 g KI:200 g I_2:1000 ml H_2O "Tri-Iodide Etch"	Au	Removal/patterning	AU-0007
I_2, vapor	Pt	Passivation	PT-0003
10 ml H_2O:5 g NaOH:2 g I_2 "Iodine Etch"	Pb_2Te_3	Dislocation	PBTE-0002b
5 g NaOH:10 ml 0.5% $NaIO_3$ "Iodate Etch"	Pb_2Te_3	Dislocation	PBTE-0002a
1I_2:2KI:10H_2O "Iodine Etch"	Fe	Preferential	FE-0109
15 ml HF:30 ml HNO_3:33 ml HAc:90 mg I_2 "Iodine A" etch	Ge	Preferential	GE-0151
1 g I_2:50 ml MeOH:100 ml H_2O	Lucite	Clean/disinfect	LU-0001b
xI_2:xMeOH	Ti	Removal	TI-0012b
25 ml HF:100 ml HNO_3:125 ml HAc:2 g I_2 "Iodine Etch"	Si	Preferential	SI-0240
xMeOH:xI_2	Si	Surface preparation	SI-0149
xHF:xI_2	Si	Light figure orientation	SI-0159
10 ml HF:20 ml MeOH:2 mg I_2	Si	Preferential	SI-0204
3 mg I_2:MeOH	SiO_2	Cleaning	SIO-0070
1 g I_2:500 ml MeOH	Si_3N_4	Cleaning	SIN-0002g
400 g KI:100 g I_2:400 ml H_2O	Ag	Removal	AG-0022a
I_2, vapor	U	Cleaning	U-0001b

IODINE, I_2

General: Does not occur as a native element, but there are several iodate minerals of silver, copper and mixed crystals, such as marshite, CuI or idorite, AgI, and miersite 4AgI.CuI. Most iodine is recovered in solution from the oceans and in the soil of some land areas, such as the Piedmont zone along the Atlantic coast. It is still extracted from seaweed along the agar-agar, and dried seaweed is widely eaten in Asia as a general healthful food.

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Pure iodine has little direct use in metal industry processing though, as one of the halogen group, it is used as a mixture with other chemicals in etching and cleaning. In medicine it is a major disinfectant, and has internal uses as already described in the preceding section. In food processing, it imparts the blue color in starch.

Technical Application: Compounds containing iodine are very soft, and have no application in Solid State material processing other than in etch solutions. Iodine as hot vapor has become a major carrier gas in Vapor Transport, VT, growth of metallic compounds, and produces the highest purity chromium metal crystalline ingots.

In a water or alcohol solution it is used as a cleaner and disinfectant of Lucite windows, such as those used in chemical etch sinks, and, as an etch solution is well known as the tri-iodide . . . for gold.

Iodine single crystals have been grown by controlled evaporation from water solutions for study of general morphology and defect structure.

Etching: Alcohols, KI.

IODINE ETCHANTS

I-0001
ETCH NAME: Methyl alcohol — TIME:
TYPE: Alcohol, preferential — TEMP: RT
COMPOSITION:
x .... MeOH (CH_3OH)
DISCUSSION:

I_2, crystalline specimens. Both crystalline and single crystallites were used in conjunction with a silicon etching study. A drop of MeOH was placed on specimen surfaces to develop etch figures and structure. Pieces of iodine were placed on silicon wafer surfaces and the wafer heated to liquefy the iodine in a general study of the iodine etch reaction.
REF: Walker, P & Waters, W P — personal application, 1957

PHYSICAL PROPERTIES OF IRIDIUM, Ir

Classification	Transition metal
Atomic number	77
Atomic weight	192.2
Melting point (°C)	2443 (2454)
Boiling point (°C)	4500 (5300)
Density (g/cm^3)	22.65
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.35
($cal/cm^2/cm/°C/sec$) 20°C	0.14
Specific heat (cal/g) 0°C	0.031
Heat of fusion (k-cal/g-atom)	6.6
Heat of vaporization (k-cal/g-atom)	152
Atomic volume (W/D)	8.54
1st ionization energy (K-cal/g-mole)	212
1st ionization potential (eV)	9.1
Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.27
Ionic radius (angstroms)	0.68 (Ir^{+4})
Vapor pressure (microns @ mp)	3.5
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	6.8
Electrical resistivity (micro ohms-cm) 20°C	5.11

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Young's modulus (psi $\times 10^6$)	76
Magnetic susceptibility (ergs $\times 10^{-6}$)	6.6
Tensile strength (psi — annealed)	160,000
Electron work function (eV)	4.57
Cross section (barns)	460
Hardness (Mohs — scratch)	5—6
(Vicker's — kgf/mm^2)	500
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Silver white
Cleavage (cubic — poor)	(001)

IRIDIUM, Ir

General: Occurs in nature as a native element in small, angular grains. Rare. Found in alluvial deposits of gold sands in Russia, Brazil, the Burma area, and in northern California. Most commonly found as an alloy constituent in platinum and other high temperature metals of the Platinum-Iron group. Native platinum contains up to 2% iridium, and the mineral iridosmine (osmium/iridium) contains up to 30% iridium. As the pure metal it is silver-white in color, both hard and brittle, heavier than gold, and one of the highest melting temperature metals known.

Industrially it is used mainly as an alloy with platinum and osmium for their high temperature and wear characteristics in the fabrication of a variety of small parts: weight standards, ball-point pens, special high-temperature bearings, and compass points. As powdered "Iridium Black" it is a catalyst in chemical processing. It is named after the brilliant colors of its salts that are iridescent reds, blues, and violets. The salts, particularly $IrCl_4$, have important chemical applications.

Technical Applications: Pure iridium metal is not used in Solid State processing to any extent, though platinum (which may contain trace iridium) is sputter evaporated in layered metallization structures. It is under development and study as a silicide: IrSi, $IrSi_2$ and Ir_2Si for application as a buffer in layered heterostructures.

Etching: Very difficult. Very slowly soluble in hot aqua regia.

IRIDIUM ETCHANTS

IR-0001
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, removal — TEMP: Hot
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

Ir, crystalline specimens as wire, rod, sheet. Etch reaction is very slow even when used hot. Solution used for general cleaning and removal.

REF: Dana, E S & Ford, W E — *A Textbook of Mineralogy*, 4th ed, John Wiley & Sons, New York, 1950, 407

IR-0002: Hodgman, C D — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Company, Cleveland, OH, 1943, 329

a-Ir specimens. Soluble in aqua regia.

IR-0003: Brat, T & Fizenberg, M — *J Appl Phys*, 57,264(1985)

Ir, thin films deposited on silicon, (100), n-type, 10 Ω cm resistivity wafers. Silicon wafers were cleaned: (1) degrease with organic solvents; (2) dip in BHF, RT, 5 sec to remove oxides; (3) rinse in H_2O; (4) N_2 blow dry. After metallization deposit SiO_2 as a

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mask for photolithographic patterning. Aqua regia used to etch the Ir thin film. Also co-deposited IrV and $Ir_{80}V_{20}$ thin films.

IR-0004: Brochure: Platinum, Baker & Co., Inc. (no date)

Ir and alloys as metal parts or plating for products. Brochure describes use of the Platinum Group metals in industry: platinum, iridium, osmium, rhodium, palladium. All of these metals can be etched in aqua regia.

IRIDIUM ALLOYS, IrMx

General: Even though iridium is listed as a native element, it more often is found as an alloy with platinum or osmium, and occurs as a mixed alloy with other platinum group metals. The mineral iridosmine, Ir_xOs_y, varies in constituent concentration with locale, and often contains rhodium, platinum, ruthenium, and other metals. Native platinum also is usually as an alloy with trace iridium, rhodium, palladium, osmium, iron, etc.

Due to the high melting point of the primary Platinum Group metals, even when industrially purified, they most often still retain trace elements of each other. As alloy mixtures, they are high temperature brazing alloys, e.g., brazing is above 800°C; whereas soldering is below 800°C as a nominal temperature division.

Technical Application: Probably the best known use of these high temperature alloys is the platinum-platinum:rhodium thermocouple for furnace heat measurement. Iridium alloys are not widely used in Solid State material processing due to high temperature characteristics, though they are occasionally used as brazing alloys in metal package assemblies.

Some iridium alloys have been co-evaporated on silicon as a surface metallization thin film.

Etching: Aqua regia. Halogens.

IRIDIUM ALLOYS

IRIDIUM PLATINUM ETCHANTS

IRPT-0001
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, removal — TEMP: Hot
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

IrPt as alloy mixtures used in the fabrication of high temperature parts. Aqua regia used as a general cleaning, shaping or removal solution.

REF: Pamphlet: Platinum, Baker & Sons, Inc. (no date)

IRPT-0002: Wise, E M — The Platinum Metals — 10M 12-53073 A-20B 117B, 294

IrPt alloy mixtures. A discussion of etching and processing the Platinum Group metals.

IRIDIUM VANADIUM ETCHANTS

IRV-0001
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

IrV and $Ir_{80}V_{20}$ thin films co-deposited on silicon, (100), n-type 10 Ω cm resistivity

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wafers. After metallization, SiO_2 masks were evaporated for photolithographic patterning. Aqua regia used to etch the thin films.
REF: Brat, T & Eizenberg, M — *J Appl Phys*, 57,264(1985)

PHYSICAL PROPERTIES OF IRON, Fe

Classification	Transition metal
Atomic number	26
Atomic weight	55.847
Melting point (°C)	1536
Boiling point (°C)	3000
Density (g/cm^3)	7.87
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.19
Specific heat (cal/g) 100°C	0.12
Heat of fusion (k-cal/g-atom)	3.67
Latent heat of fusion (cal/g)	66.2
Heat of vaporization (k-cal/g-atom)	84.6
Atomic volume (W/D)	7.1
1st ionization energy (K-cal/g-mole)	182
1st ionization potential (eV)	7.896
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.17
Ionic radius (angstroms)	0.74 (Fe^{+2}) 0.64 (Fe^{+3})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	12.6
Electrical resistivity (micro ohms-cm $\times 10^{-6}$)	9.71
Tensile strength (psi)	35,000—45,000
Lattice constant (cm $\times 10^{-8}$)	11.7
Compressibility ($cm^3/kg \times 10^{-11}$)	21
Electron work function (eV)	4.7
Cross section (barns)	2.53
Vapor pressure (°C)	2360
Hardness (Mohs — scratch)	4—5
(Brinell—Kgf/mm^2)	82—100
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Grey black
Cleavage (cubic — perfect)	(001)

IRON, Fe

General: Occurs in nature as a native element, occasionally in large masses, though more common as small aggregates and grains embedded in other rocks and very often containing a small amount of nickel — nickeliferrous iron, $FeNi_2$. Both pure iron and nickeliferrous iron are found as grains associated with gold placers in addition to magnetite, Fe_3O_4, black magnetic iron oxide. Also occurs in meteors as pure iron or $FeNi_2$ with lamellar structure and marked twinning, when etched in dilute nitric acid or iodine. It develops the Widmanstatan figures, when twinning in primarily cubic as fine lines, called Neumann lines.

There are four iron oxides that are primary ores and found in major vein or sedimentary deposits — all of which contribute the tan to red colors of earth, throughout the world. These oxides are

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Limonite, $FeO.nH_2O$ (colloidal)	Bog or brown iron ore
Goethite, FeO.(OH) (crystalline)	Brown or tan iron ore
Hematite, Fe_2O_3 (crystalline)	Red iron ore
Magnetite, Fe_3O_4 (crystalline)	Black iron ore, magnetic

In addition, there is the carbonate mineral siderite, $FeCO_3$, and the group known as the "iron pyrites" — pyrite, FeS_2, being the most common — and pyrite is the most widely mined ore of iron representing as much as 75% of the world production for both its iron and sulfur content. Because of its brassy-yellow color, pyrite is often mistaken for gold, thus the name "Fool's Gold" . . . when struck a sharp blow it shatters to a black powder with the distinctive "rotten egg" odor of sulfur dioxide; whereas gold is malleable and will flatten into thin sheets.

Iron has been in use since about 1350 B.C. when the Hittites in Asia Minor discovered the method of smelting iron ore (requires greater heat than for bronze). With the addition of carbon, iron becomes steel — prior to the Christian Era, Damascus steel and, during the Middle Ages of Europe — Toledo steel from Spain. With the addition of chromium to steel, it becomes stainless steel, SST. Pure iron with minimum carbon is soft and brittle, similar to Wrought Iron, still widely used for decorative purposes, although today there are several hundred forms of both irons and steels designed for specific applications.

Iron and steels are fabricated for specific physical structures which are important to their use and application. The following is a brief description of some of the material phases or compounds that occur as they relate to different types of iron or steel:

- Austentite: (Gamma iron). Stable above 1330°F. Decomposes into ferrite, cementite and pearlite. It is the prominent microstructure in 300 series SST.
- Bainite: Needle-like structure with feathering similar to martensite which has a sharper acicular structure. Forms under moderately rapid cooling.
- Carbide: (Cementite). Hard, intermetallic phase usually associated with grain boundaries, and is colorless. Stands out in high relief from background matrix. Contributes hardness, corrosion and wear resistance, but is difficult to machine and reduces impact strength.
- Ferrite: Soft iron, <0.04% carbon. Light in color and distinctive irregular grain boundaries. Weak structure, highly ductile and easily scratched. The term "ferrite" also refers to a class of iron compounds. See section on Ferrites.
- Graphite: Depending upon the type iron or steel, the included graphite can be in nodular form, as a eutectic dendritic form or as flakes, and may show reaction products as ferrite, pearlite, carbide, or steatite.
- Martensite: Sharp, acicular, needle-like structure that forms with very rapid cooling. Hard and brittle and usually tempered to increase impact strength.

Much of metallographic processing is concerned with the recognition of these materials and structures by macro- and micro-etching, and their direct effect on tool hardness, strength, and corrosion resistance.

Technical Application: In much Solid State device processing, several of the heavy metals such as iron are considered contaminants, and much of the chemical processing involves surface cleaning prior to diffusion, epitaxy, metallization, and other high temperature operations for their removal. On the other hand, iron acts like a dopant element in some compound semiconductors, such as indium phosphide where it is an n-type dopant for InP:Fe, as a semi-insulating (SI) substrate.

Though pure iron is not widely used, iron alloys and steels are part of much processing equipment: vacuum systems, diffusion furnaces, baking ovens, test equipment, and so forth. Stainless steel is usually the base plate in vacuum systems; low-carbon iron, as base plates

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in sputter systems; magnetic steel parts in these systems; soft iron for lapping plates, requiring periodic truing (flattening), as well as lapping cups for surface angling or sphere and lens fabrication (diopter cups) . . . also heater strips, and a multitude of handling parts, such as acid resistant tweezers, spatulas, carrying trays, and the like.

Both pure iron and iron alloy have been grown as single crystal ingots for study of general morphology, stress/strain criteria, defect development, and ferromagnetic properties, the latter in regard to device applications. In addition to manmade irons and steels, both artificial and natural oxides of single crystal iron compounds have been the subject of study for many years, to include corrosion studies under a wide variety of conditions. Wrought iron is probably the most well known as a nearly pure iron product and has been in use since ancient times.

Etching: Easily etched. Soluble in most acids and acid mixtures. See Steel; Ferrites.

IRON ETCHANTS

FE-0001
ETCH NAME: BRM
TYPE: Halogen, oxide removal
TIME:
TEMP:
COMPOSITION:
x .... Br_2
x .... MeOH
DISCUSSION:
Fe, (100) wafers used in a magnetics study to include oxidation. Specimens oxidized in liquid solutions of KNO_3 or $NaNO_3$. Oxide removed with solution shown.
REF: Yamaguchi, S — *J Electrochem Soc,* 107,714(1960)
FE-0022: Mahla, E M & Nielsen, Y E — *J Electrochem Soc,* 19,387(1948)
Fe specimens. Solution used as a general surface cleaning etch.
FE-0023: Osmond, F & Cartlaud, G — *Rev Met,* 811,2(1905)
Fe specimens. Various etch solutions used to develop etch figures and percussion figures.

FE-0021
ETCH NAME:
TYPE: Halogen, cleaning
TIME: 1—3 min
TEMP: RT
COMPOSITION:
x .... 2—5% I_2
x .... H_2O
DISCUSSION:
Fe, as flat soft iron lap platens used for preparing thin section mineral specimens for study. Solution saturated cloth used to wipe clean platen surfaces, followed with water washing and coat with glycerin to prevent rusting.
REF: Weiss, P & Walker, P — mineralogy studies, 1953

FE-0037
ETCH NAME:
TYPE: Halogen, cleaning
TIME: 1—3 min
TEMP: RT
COMPOSITION:
x .... 3% I_2
x .... MeOH
DISCUSSION:
Fe, as flat soft iron lap platens used for polishing Si and GaAs wafers. Wipe platens clean with solution shown using lint-free cloth during platen reconditioning. Follow with water wash and towel drying.

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REF: Walker, P & Menth, M — personal application, 1980
FE-0027a: Walker, P & Bichkowski, M — personal application, 1975

Fe, as soft iron lap platens, both flats and cups, used for processing silicon wafers. Solution used in reconditioning platens. Wipe etch clean with solution shown, then water wash, dry with toweling and coat with glycerin to prevent rusting.

FE-0002
ETCH NAME: Nital
TYPE: Acid, cleaning
COMPOSITION:
x .... 2% HNO_3
x .... EOH
DISCUSSION:

TIME:
TEMP:
ASTM #74

Fe, pure metal samples used in an X-ray study of hydrogen in iron. Solution used to clean surfaces and remove contamination.
REF: Tetelman, A S et al — *Acta Metall,* 9,205(1961)
FE-0017c: ASTM E407-70

Reference for ASTM #74. Solution shown as 1—5 ml HNO_3:100 ml EOH or MeOH.

FE-0013
ETCH TIME: Nital
TYPE: Acid, preferential
COMPOSITION:
x .... 2—3% HNO_3
x .... EOH
DISCUSSION:

TIME:
TEMP:
ASTM #74

Fe, thin films deposited by MBE on GaAs, (110) wafer substrates in an X-ray characterization study of iron saturation in GaAs. Iron thin films were (110) oriented with a 1.34% mismatch. Solution used as a macro-etch on iron films.
REF: Qadri, S B et al — *J Vac Sci Technol,* B(3),718(1985)
FE-0006a: Coleman, E V — *J Appl Phys,* 29,1487(1958)

Fe, single crystal iron whiskers used in a study of dislocations. A 2% Nital solution used to develop dislocations.

FE-0003a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
6% .... $HClO_4$
33% .... butyl cellusolve
59% .... MeOH
DISCUSSION:

TIME:
TEMP:
ANODE: Fe
CATHODE:
POWER:

Fe, polycrystalline specimens used in a study of stacking faults in austenite and its relationship to martensite. Solution used to polish specimens prior to preferential etching.
REF: Motte, H — *Acta Metall,* 5,614(1957)

FE-0003b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
45% .... HCl
5% .... HNO_3
50% .... MeOH

TIME:
TEMP:

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DISCUSSION:
Fe, polycrystalline specimens used in a study of stacking faults in austenite and its relationship to martensite. After polishing specimens (FE-0003a), this solution used to develop stacking fault structures.
REF: Ibid.

FE-0018
ETCH NAME: Marshall's solution
TYPE: Acid, polish
COMPOSITION:
x .... H_2O_2
x .... $COOHCOOH.2H_2O$ (oxalic acid)
TIME:
TEMP:
DISCUSSION:
Fe, specimens. Solution referred to as a "brightening" solution which leaves a thin oxide film on specimen surfaces. Polish rate is affected by film growth. Film can be observed in a static solution. There is gas evolution using a dynamic solution and this minimizes oxide film growth.
REF: Tegart, W J McG — *The Electrolytic and Chemical Etching of Metals*, Pergamon Press, London, 1956

FE-0006b
ETCH NAME: Picral
TYPE: Acid, dislocation
COMPOSITION:
5 .... 4% $(NO_2)_3C_6H_2OH$ (picric acid)
x .... EOH
TIME:
TEMP:
ASTM #29
DISCUSSION:
Fe, single crystal iron whiskers used in a study of dislocations. A 4% Picral solution was used as a dislocation development etch. Also used 2% Nital (FE-0006a).
REF: Coleman, E V — *J Appl Phys*, 29,1487(1958)

FE-0008
ETCH NAME: Heat
TYPE: Thermal, forming (sphere)
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:
Fe, single crystal and polycrystalline spheres formed by splatter arc melting in an He atmosphere from chips and flakes in a water cooled copper pot. Sphere diameters were from 0.1 mm (50% single) and 0.5—1.0 mm (10% single). Other spheres fabricated were Be, V, Zn, NiCr, and AlNi.
REF: Ray, A E & Smith, J F — *Acta Metall*, 11,310(1958)

FE-0009
ETCH NAME: Ferric chloride
TYPE: Electrolytic, forming (sphere)
COMPOSITION:
x .... x% $FeCl_3$
TIME:
TEMP:
ANODE: Fe
CATHODE:
POWER:
DISCUSSION:
Fe, colloidal spheres, 2 mm diameter. Form by electro-deposition of ferric chloride into

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mercury and heat to convert to colloidal state. Spheres were used in a study of loss in exchange coupling in surface layers of ferromagnetic particles.
REF: Luborsky, F E — *Phys Rev,* 109,40(1958)

FE-0004
ETCH NAME:
TYPE: Electrolytic, thinning
COMPOSITION:
x .... $HClO_4$
x .... HAc
DISCUSSION:
TIME:
TEMP:
ANODE: Fe
CATHODE:
POWER:

Fe specimens of alpha-iron used in a study of neutron irradiation damage using an electron microscope. Solution used to polish and thin specimens after irradiation.
REF: Eyre, B L & Bartlett, S F — *Phil Mag,* 12,261(1965)

FE-0005
ETCH NAME: Water
TYPE: Acid, preferential
COMPOSITION:
x .... DI H_2O
DISCUSSION:
TIME:
TEMP:

Fe, single crystal iron spheres $^3/_8$" in diameter with (111), (110), and (110) cutflats oriented and polished. Spheres were soaked in DI water. The (110) plane flat showed the greatest degree of pitting.
REF: Kruger, J — *J Electrochem Soc,* 106,736(1959)
FE-0031: Liss, R B — *Acta Metall,* 7,231(1959)

Fe, as single crystal iron specimens used in a study of etch pits. Dripping water on iron will develop pits.
FE-0032: Dillon, F J Jr — *Phys Rev,* 112,59(1958)

Fe spheres used in a study of magnetostatics and ferromagnetics in iron-containing spheres. Water used to both clean and etch spheres.
FE-0035: Bond, W L — *Rev Sci Instr,* 22,344(1951)

Fe spheres. Describes the tumbling method with a water abrasive slurry to fabricate spheres used in FE-0032.
FE-0033: Carter, T L et al — *Rev Sci Instr,* 30,446(1959)

Fe spheres and ferrites. Used a Buehler polishing wheel with rough to fine abrasives and water. Hold specimens perpendicular to the grinding surface with hollow tubes. (*Note:* Method is similar to that used in facetting gemstones.)
FE-0034: Enck, F D — PhD thesis, University Microfilms Publ #23-264

Fe specimens cut as cylinders. Describes a method using a water coolant with a post grinder tool.
FE-0036: Alexander, E & Many, K A — *Rev Sci Instr,* 26,893(1955)

Fe crystals and other hard crystal materials. Describes a method of wire saw cutting with water, solvents and acids.

FE-0007
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
COMPOSITION:
1 .... HNO_3
1 .... H_2O
TIME:
TEMP:

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DISCUSSION:

Fe, (100) wafers and other orientations. 99.9% pure iron single crystals grown in a study of growth and orientation. Solution used as a general etch and is preferential on the (100).

REF: Stein, D F & Low, J R Jr — *Trans Met Soc AIME*, 221,744(1961)

FE-0024

ETCH NAME: TIME:

TYPE: Acid, cleaning TEMP: RT

COMPOSITION:

1 .... H_2SO_4

1 .... HCl

1 .... H_2O

DISCUSSION:

Fe, as stainless steel tubing. Solution used to polish etch and clean internal bore of tubing. Follow with DI water rinse and then MeOH. Dry with hot air gun. Method used to clean tubing prior to installation in diffusion and vacuum systems.

REF: Mills, T — personal communication, 1966

FE-0025: Walker, P — personal application, 1970

Fe, as stainless steel tubing. Used as described in FE-0024 for tube cleaning prior to installation in epitaxy systems.

FE-0028

ETCH NAME: Iodine etch TIME:

TYPE: Halogen, preferential TEMP:

COMPOSITION:

1 .... I_2

2 .... KI

10 .... H_2O

DISCUSSION:

Fe specimens. Solution described as a preferential etch for iron. (*Note:* Similar mixtures are the tri-iodide etchants for gold; and "tincture of iodine".)

REF: Berglund, T & Deardon, W H — *Metallographer's Handbook of Etching*, Pitman & Sons, London, 1930

FE-0010

ETCH NAME: TIME:

TYPE: Acid, preferential TEMP:

COMPOSITION:

2 .... H_3PO_4

1 .... H_2O_2

DISCUSSION:

Fe, (100) wafers used in a study of latent hardening. Solution used to develop defects and stress figures.

REF: Nakada, W & Sheh, A — *Acta Metall*, 14,961(1961)

FE-0011

ETCH NAME: TIME:

TYPE: Acid, dislocation TEMP:

COMPOSITION:

1 .... HF

10 .... HCl

5 .... HNO_3

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DISCUSSION:

Fe, (100) wafers used in an optical study of passivation films from inorganic inhibitor solutions. Solution used to develop defects induced by passivation.

REF: Horton, M et al — *J Electrochem Soc,* 110,654(1963)

FE-0012

ETCH NAME: Fry's reagent

TYPE: Acid, preferential

COMPOSITION:

40 ml .... HCl
5 g .... $CuCl_2$
30 ml .... H_2O
25 ml .... EOH or MeOH

TIME:

TEMP:

ASTM #79

DISCUSSION:

Fe, (100) wafers and iron alloys used in a study of etch pits and twinning. Both the solution shown and Hahn's modification were used.

REF: Hahn, G T — *Trans Met,* 224,395(1962)

FE-0038: Spreadborough, S et al — *J Appl Phys,* 35,3505(1964)

Fe specimens and 1% Mn doped alloys used in a material study. Fry's reagent used to develop structure and defects.

FE-0014

ETCH NAME: Diamond

TYPE: Compound, polish

COMPOSITION:

x .... diamond paste

TIME:

TEMP:

DISCUSSION:

Fe, (100) and polycrystalline wafers used in a study of nitridization using an E-beam power source. Wafers were polished with diamond paste and chemically etched prior to nitriding of surfaces.

REF: Ebersbach, U et al — *Thin Solid Films,* 112,29(1984)

FE-0015a

ETCH NAME: Soap

TYPE: Acid, cleaning

COMPOSITION:

x .... $3C_{17}H_{35}COO$ (soap)
x .... H_2O

TIME:

TEMP:

DISCUSSION:

Fe specimens as cut and lapped discs were cleaned by washing in a soap/detergent solution, rinsed in water and dried; then followed by flame cleaning. Other metals similarly cleaned were Ti, Zr, Al, Mg, Ag, Au, Cu, Ni, Co, Cd, Zn, and Pb. Metals were evaporated on glass, quartz, and ceramics in a study of frictional adhesion.

REF: Belser, R B — *Rev Sci Instr,* 25,862(1954)

FE-0015b

ETCH NAME: Flame

TYPE: Heat, cleaning

COMPOSITION:

x .... gas flame

TIME:

TEMP: 800—1200°C

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DISCUSSION:

Fe specimens used as an evaporation source for glass, quartz and ceramic. See discussion under FE-0015a.

REF: Ibid.

FE-0016

ETCH NAME: Hydrochloric acid, dilute

TYPE: Acid, cleaning

TIME:

TEMP:

ASTM #16

COMPOSITION:

1 .... HCl

1 .... H_2O

DISCUSSION:

Fe, as residual metal in vacuum systems remaining after iron evaporation. Solution used to clean bell jars and internal fixtures. Can be used on SST, glass, and ceramics.

REF: Nichols, D R — *Solid State Technol*, December 1979

FE-0027b: Walker, P & Menth, M — personal application, 1980

Fe, as SST fixtures and base plates in vacuum systems. Solution used as a general surface cleaning etchant after removal of heavy residual metal evaporation deposits. Surfaces wiped down with lint-free toweling wetted with solution. Follow with water wipe-down, then MeOH wipe down.

FE-0017d: ASTM E407-70

Reference for ASTM #16. Solution shown as 5—10 ml HCl:100 ml H_2O

FE-0019a

ETCH NAME: Al-7

TYPE: Acid, macro-etch

TIME: Dip

TEMP: 160—170°F

COMPOSITION:

50 ml .... HCl

50 ml .... H_2O

DISCUSSION:

Fe specimens. Solution used as a macro-etch to develop structure in irons and steels for metallographic study.

REF: *A/B Metal Digest*, 22(3),14(1983) — Buehler Ltd

FE-0020a

ETCH NAME: Ammonium persulfate

TYPE: Acid, preferential

TIME:

TEMP:

COMPOSITION:

x .... $(NH_4)_2SO_4$, sat. sol.

x .... H_2O

DISCUSSION:

Fe, as grey iron specimens containing eutectic dendritic graphite. Solution used to develop microstructure of carbides and pearlite.

REF: *A/B Metal Digest*, 21(2),17(1983) — Buehler Ltd

FE-0020b

ETCH NAME:

TYPE: Acid, preferential

TIME:

TEMP:

COMPOSITION:

x .... x% $FeCl_3$

x .... EOH

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DISCUSSION:

Fe, as grey iron specimens with high phosphorous content and flake graphite. Solution referred to as "alcoholic ferric chloride" and used as a micro-etch to develop steatite, pearlite, and graphite structures.

REF: Ibid.

FE-0026

ETCH NAME: Heat/hydrogen

TYPE: Thermal, preferential

COMPOSITION:

x .... heat + H_2

TIME:

TEMP: 800—1200°C

DISCUSSION:

Fe, single crystal whiskers used in a study of surface reaction from oxides and thermal etching with hydrogen. Whiskers were oxidized at 700°C, 15 min, then reduced at 900°C, 1 min in H_2. Thermal etching was done in H_2 at temperature range shown for various time periods.

REF: Laukonis, J V — *J Appl Phys,* 32,242(1961)

FE-0028

ETCH NAME: Argon

TYPE: Ionized gas, cutting

COMPOSITION:

x .... Ar^+ ions

TIME:

TEMP:

GAS FLOW:

PRESSURE:

POWER:

RATE: 2 Å/sec

DISCUSSION:

Fe as iron alloy specimens. Argon used to sputter section specimens. Grain boundaries etched faster. Etch rate shown for a 8 μm cut width. Method also used to cut gold specimens.

REF: Perkins, R A — *J Vac Sci Technol,* Al(2),135(1979)

FE-0029a

ETCH NAME:

TYPE: Electrolytic, forming

COMPOSITION:

(1) x .... H_2SO_4 (2) x .... H_2SO_4

TIME:

TEMP:

ANODE: SS 401

CATHODE: SS 305

POWER: 5—15 V

DISCUSSION:

Fe as SST 401 wire 0.020 diameter used in a study of annealing on surface composition. Both solutions used to etch form tips for field ion microscope (FIM) study. Point evaporate metal to tip form by power pulsing.

REF: Krishnasway, S V et al — *J Vac Sci Technol,* 11,5(1974)

FE-0029b

ETCH NAME: Hydrogen

TYPE: Gas, cleaning

COMPOSITION:

(1) x .... TCE (2) x .... H_2 (3) x .... Freon

TIME: 10 min

TEMP: 1100°C

DISCUSSION:

Fe as SST 305. Used a bar electrode for electrolytic forming of SST 401 wire (FE-0029a). Cleaned: (1) TCE; (2) fire in dry H_2; (3) ultrasonically with Freon, RT, 30 min.

REF: Ibid.

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FE-0030
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
25 .... HCl
25 .... HNO_3
50 .... H_2O
DISCUSSION:
Fe, polycrystalline whiskers used in a field ion microscope (FIM) study of whisker structure. Solution used to electropolish specimens.
REF: Lashmore, B & Melmed, A J — *J Appl Phys*, 49,4586(1978)

TIME:
TEMP:
ANODE: Fe specimen
CATHODE:
POWER: 2 V AC

FE-0019b
ETCH NAME: Vilella's Reagent
TYPE: Acid, preferential
COMPOSITION:
5 ml .... HCl
1 g .... picric acid
100 ml .... EOH
DISCUSSION:
Fe, as grey iron flame hardened. Solution used to develop a macro-etched surface which was then observed at 400× with a metallurgical microscope.
REF: Ibid.

TIME:
TEMP:

IRON ALLOYS, Fe_xM_y

General: Native metal elements rarely occur as the completely pure element, but contain other trace metals, such that they are metallic alloys. Native iron is found in small quantities, and often contains nickel. In meteoric iron, this appears as $FeNi_2$ segregates in an iron matrix, and there are two iron nickelides: awarutite and josephinite, both $FeNi_2$ as terrestrial irons alloys. There are many iron-containing minerals as oxides, sulfides, sulfates, phosphates, carbonates, and silicates, several of which are hydrates, and some form as natural colloids, etc.

There are hundreds of iron alloys in industry. The Hittite culture in Asia Minor (now part of Turkey) is thought to be the first to develop iron weapons around 1350 B.C., though iron tools may have been in use by the Egyptians as far back as 3000 B.C. Pure iron is soft: Mohs H = 4—5, but can be hardened with the addition of carbon and silicon. The carbon may segregate to some degree by heat treatment as ferrocarbon compounds. Ferrosilicon is a by-product of the reduction of sand for its silicon content, and there are other ferro-type metal alloy compounds used in the fabrication of irons and steels, such as ferromanganese, ferrophosphorus, ferronickel, etc. These are added to iron for specific characteristics and applications. With added chromium, iron becomes steel and stainless steel, SST; with nickel and cobalt, magnets; "tin cans" are thin sheet steel plated with tin. The world is still in the Iron Age after some 3500 years, and many iron alloys have been developed over that period. See the general introduction to Iron for additional discussion.

Technical Application: Iron and steel alloys have several applications in Solid State material processing and development other than in equipment and parts, e.g., tweezers, crucibles, SST etching cups, etc.

Steel discs and blanks have been used for metal evaporation and adhesion studies of thin film; steel parts, such as saw blades, are coated with carbides to improve wear and cutting time; and there are a number of ferrite resistor materials containing zinc, manganese, and other additive metals for specific frequency levels in microwave device assembly applications. Single crystal ferrite compounds are being developed for both ferromagnetic and

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ferroelectric applications as operating devices, as well as being grown and studied for general morphologic data. There is magnetic stainless steel, and iron magnets have some particular applications in Solid States device construction, such as small ring magnets on silicon diode assemblies or on quartz crystal frequency packages to "pull" and stabilize frequency and/or shift frequency.

Etching: HNO_3, HCl, NaCl, and mixed acids. Nital and Picral. Varies with alloy.

Iron Alloys

Iron Aluminide
Iron Aluminum Sulfide
Iron Beryllium
Iron Carbide
Iron Chromium (Kanthal)
Iron Cobalt Vanadium
Iron Germanium
Iron Manganese
Iron Nickel (+ Alnico)
Iron Silicon

IRON ALLOY ETCHANTS

IRON:SILICON ETCHANTS

FEAL-0001
ETCH NAME: Nital — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... x% HNO_3
x .... EOH
DISCUSSION:
FeAl single crystal specimens used in a study of magnetic structure. Solution shown can be used as a cleaning or slight preferential etch.
REF: Nathans, R et al — *J Phys Chem Solids,* 6,38(1956)

IRON ALUMINUM SULFIDE ETCHANTS

FALS-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
(Fe,Al)S, samples grown in a sealed quartz ampoule for a study of the Fe-Al-S system. Formation of Al_2S_3 under pressure and heat can explode the ampoule. Reaction of Fe-Si formation is rapid, and reduces possible explosion. (*Note:* Etch shown is for pyrite, FeS_2.)
REF: Patinaik, P C & Smeltzer, W W — *J Electrochem Soc,* 131,2688(1984)

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IRON BERYLLIUM ETCHANTS

FEB-0001
ETCH NAME:
TYPE: Electrolytic, cleaning
COMPOSITION:
20 .... HCl
20 .... HNO_3
60 .... MeOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 1—3 V
DISCUSSION:
Fe:Be(20%) polycrystalline wire was etch cleaned and treated in this solution to produce an amorphous surface layer. It was then used as a substrate for further FeBe deposition and conversion to single crystal structure by annealing.
REF: Inal, O T & Goudker, I H — *Thin Solid Films,* 111,149(1984)

IRON CARBIDE ETCHANTS

FEC-0001
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
1 .... HF
4 .... HNO_3
5 .... H_2O
TIME:
TEMP:
DISCUSSION:
FeC, single crystal alloys. Solution used to chemically etch thin, followed by electropolishing. Specimens used in a study of dislocations and structure associated with material fatigue.
REF: McGrath, J T & Bratinn, W J — *Phil Mag,* 12,1293(1965)

FEC-0002
ETCH NAME: Nital
TYPE: Acid, preferential
COMPOSITION:
x .... 2% HNO_3
x .... EOH
TIME:
TEMP: RT
ASTM #74
DISCUSSION:
Fe_3C:Fe specimens. Nital used as a structure development solution on this material.
REF: Savas, N A & Smith, R W — *J Cryst Growth,* 71,66(1985)
FEC-0010c: ASTM E407-70
Fe and Steel alloys. ASTM #74 Nital shown as: 1—5 ml HNO_3:100 ml EOH.
FEC-0004: Dumez, F — *J Vac Sci Technol,* B(1),218(1983)
Fe_3C single crystal cementite grown in a study of single crystal metal alloys. Material as high resistivity at 25°C: 100 Ω cm, and a temperature coefficient of expansion of about 10^{-4} K^{-1}. Also studied TiAl, TiNi, and ZrV, all as metastable alloys. Metallic glasses studied were PdNiP, PtNiP, and PtCuP with structure defined as random packing of spheres in a dense matrix.

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IRON CHROMIUM (KANTHAL ETCHANTS)

KA-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... NaCl
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:
72Fe:5.5Al:22Cr:0.5Co as the metal mixture known as Kanthal. Sodium chloride solutions (sea water, etc.) show strong corrosive attack as do fluorine compounds. Alkalies, nitrates, silicates, and borax attack by destroying oxide fractions in the material.
REF: ASTM E407-70

KA-0002: *Rare Metals Handbook,* Reinhold, New York, 1954
Kanthal, FeCr(22):Al(5.5):Co(0.5) specimens. Salt solutions will attack this alloy. Fluorine, chlorine (gases) and alkali solutions also will etch. Borax will remove oxide, and Kanthal melting point is 1510°C.

IRON:COBALT:VANADIUM ETCHANTS

FECV-0001
ETCH NAME: Nital
TYPE: Acid, defect
COMPOSITION:
x .... 3% HNO_3
x .... EOH
TIME:
TEMP:
ASTM #74
DISCUSSION:
Fe:Co:V alloy used in a study of metallurgical and magnetic properties. Solution used to polish specimens and also to develop grain boundary structure.
REF: Chen, O W — *Phys Rev,* S31,348S(1961)

FECV-0010c: ASTM E407-70
Nital solution as ASTM #74 is 1—5 ml HNO_3:100 ml EOH or MeOH.

IRON GERMANIUM ETCHANTS

FEGE-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
Fe_3Ge_2 as a crystalline deposit, or amorphous thin film as a-Fe_xGe_{1-x}. Films show ferromagnetic properties but with increase of germanium, magnetism is lost. Substrates were silicon wafers with and without SiO_2 pre-coated thin films.
REF: Terzleff, P et al — *J Appl Phys,* 50,1031(1979)

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FEGE-0002
ETCH NAME: CP4A
TYPE: Acid, preferential
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc
TIME:
TEMP:
DISCUSSION:
$FeGe_2$, (100) and (110) wafers cut from Czochralski (CZ) grown ingot with cobalt or tin doping. Solution used as a general polishing etch, and to develop defects preferentially.
REF: Runkin, A Y & Frolow, A A — *J Cryst Growth*, 69,131(1984)

IRON MANGANESE ETCHANTS

FEMN-0001
ETCH NAME: Fry's reagent
TYPE: Acid, preferential
COMPOSITION:
40 ml .... HCl
5 g .... $CuCl_3$
30 ml .... H_2O
25 ml .... EOH or MeOH
TIME:
TEMP:
ASTM #79
DISCUSSION:
Fe:Mn(1%) single crystal specimens. Solution used to develop structure and etch pits. Also used Hahn's modification of Fry's reagent.
REF: Spreadborough, J et al — *J Appl Phys*, 35,3585(1964)
FEMN-0002: Hahn, T — *Trans Met Soc AIME*, 224,343(1962)
Fe specimens. Reference for Hahn's modification of Frey's reagent shown in FEMN-0001.
FEMN-0010c: ASTM E470-70
Reference for ASTM Number shown in FEMN-0001.

IRON NICKEL ETCHANTS

FENI-0030
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
3% .... HCl
2% .... zophiran chloride
95% .... EOH
TIME:
TEMP: 0°C
DISCUSSION:
Fe:Ni(65%) alloy specimens used in a study of the martensite crystal. Cool specimen from RT down to 0°C and continue etching until structure is developed. The etch patterns delineate what appears to be single crystal martensite structure.
REF: Nishyama, Z & Shimiau, K — *Acta Metall*, 6,125(1958)

FENI-0031
ETCH NAME: Nitric acid
TYPE: Acid, structure
COMPOSITION:
x .... HNO_3, conc.
TIME: Days
TEMP: RT

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DISCUSSION:

Alnico V, iron alloy used in a study of transition electron diffraction. Discs, 0.1—0.2 mm were ground down until the edges warped. Soak-etch in concentrated nitric acid for several days to develop phase structure. The etch is very even in its surface attack and structure development.

REF: Kronenberg, K J — *J Appl Phys*, 51,80S(1960)

IRON:SILICON ETCHANTS

FESI-0001

ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HAc
x .... CrO_3

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

Fe:Si(3%) single crystal specimens used in a study of fracture and twinning. Cracks can be nucleated by twinning and dislocations.

REF: Hull, D — *Acta Metall*, 9,11(1961)

FESI-0002: Morris, O E — *Met Prog*, 56,696(1949)

Fe:Si($3^1/_4$%) single crystal specimens.

FESI-0003: Surts, J C & Low, J R Jr — *Acta Metall*, 5,285(1957)

Fe:Si($3^1/_4$%) single crystal specimens.

FESI-0004: Dunn, C O & Daniels, F W — *Trans AIME*, 191,147(1957)

Fe:Si alloy preference for FESI-0001.

FESI-0005: Swets, D E — *J Appl Phys*, 33,1893(1962)

Fe,Si(4%), polycrystalline rods.

FESI-0006: Noble, F W & Aull, D — *Phil Mag*, 12,777(1965)

Fe:Si(3%) single crystal specimens used in a deformation study.

FESI-0005b

ETCH NAME: Nital, variety
TYPE: Acid, preferential
COMPOSITION:
20% .... HNO_3
80% .... EOH

TIME:
TEMP:
ASTM #74

DISCUSSION:

Fe:Si(4%), polycrystalline rods. Solution used to develop single crystal grain structure. Single crystals were cut out of the rods, oriented, and used as seed crystals for single crystal growth.

REF: Swets, D E — *J Appl Phys*, 33,1893(1962)

FESI-0010b: ASTM E407-70

ASTM #74 solution is 1—5 ml HNO_3:100 ml EOH or MeOH.

FESI-0012: Corson, M G — *Iron Age*, 148,45(1941)

FeSi specimens. A general article describing etching techniques for this material.

FESI-0013

ETCH NAME: Argon
TYPE: Gas, preferential
COMPOSITION:
x .... Ar

TIME:
TEMP:

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DISCUSSION:

FeSi specimens. Argon used as a molecular gas and referred to as a thermal etchant for ferrosilicon. The gas will attack both (111) and (100) planes preferentially. Authors say that adsorption of oxygen on different crystallographic planes alters the relative surface energy of such planes.

REF: Dunn, C O & Walters, J L — *Acta Metall*, 7,648(1959)

FESI-0014: Chalmers, B et al — *Proc R Soc*, A193,405(1948)

FeSi specimens. Article referenced by Dunn & Walters (FESI-0013) in their work on this material.

FESI-0007

ETCH NAME:

TYPE: Electrolytic, structure

COMPOSITION:

x .... $HClO_4$

x .... HAc

TIME:

TEMP:

ANODE:

CATHODE:

POWER:

DISCUSSION:

Fe:Si, specimens. Solution used in developing etch patterns in ferrosilicon. Steps observed varied from 10 to 1000 Å in height and were aligned in the ⟨110⟩ direction to a great extent.

REF: Kroupa, F — *Ceskosl Casop Fly*, 8,171(1958)

FESI-0008

ETCH NAME: Fry's reagent

TYPE: Acid, preferential

COMPOSITION:

40 ml .... HCl

5 g .... $CuCl_2$

30 ml .... H_2O

25 ml .... EOH or MeOH

TIME:

TEMP:

ASTM #79

DISCUSSION:

Fe:Si specimens and other iron alloys used in a study of etch pits and twinning. Also used Hahn's modification.

REF: Spreadborough, J et al — *J Appl Phys*, 35,3585(1964)

FESI-0009: Hahn, G T — *Trans Met*, 224,395(1962)

Fe:Si specimens. Reference for Hahn's modification shown in FESI-0008.

FESI-0010c ASTM E407-70

Reference for ASTM number shown in FESI-0008.

FESI-0011

ETCH NAME: Heat

TYPE: Thermal, de-stress

COMPOSITION:

x .... heat

TIME: 1 h

TEMP: 1200°C

DISCUSSION:

FeSi(7.7%), single crystal (100) oriented used for saturation magnetization and anisotropic constant measurements. Wafers cut 3 mm diameter, 0.5 mm thick and annealed to relieve strain from cutting with step-cooling at 10°C/min. Other silicon concentrations were 4.9, 5.4, 6.0, and 6.6%. Also called ferro-silicon.

REF: Arai, K I et al — *J Appl Phys*, 57,460(1985)

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IRON OXIDE, Fe_xO_y

General: There are a number of iron oxide minerals in nature, all in sufficient quantity to be mined as ores of iron. Major deposits are found throughout the world in rocks of all Ages, and much of the brown, yellow, red and black colors of earth are due to their presence in the soil. Origin varies from sedimentary colloidal, to primary volcanic, metamorphic action, and oxidation of other iron bearing minerals. The major oxide ores are

Limonite, $2FeO.nH_2O$ (colloid) — Brownish-yellow
Goethite, FeO(OH) (orthorhombic) — Yellow/brown to black
Hematite, Fe_2O_3 (rhombohedral) — Grey/black red
Magnetite, Fe_3O_4 (isometric) — Black (magnetic)

Though the oxides are important ores, the "iron pyrites" represent 75% of iron ore mined: pyrite, FeS_2, chalcopyrite, $CuFeS_2$ and pyrrhotite, Fe_3S_5. There are carbonates, such as siderite, $FeCO_3$, a colloid with part of the iron coming from anaerobic bacteria. Iron ores, depending upon locale, often contain important percentages of silver, gold, and nickel.

Primary industrial use is as ores for pure iron. Magnetite, in its form of "lodestone", was the original compass for navigation in ancient times, both on the Mediterranean Sea, and on the Sahara and Gobi Deserts (camel caravans, the ships-of-the-desert).

The powdered oxides are lapping and polishing abrasives: tan- or brown rouge; red rouge; and black rouge. Powdered magnetite, and manmade magnetic materials in liquid plastics, as magnetic fluidics, are used for valve operation; dusted on material surfaces to develop magnetic domains for observation of nickel, cobalt, barium titanate, etc.; powder in rubberized plastics, as "magnetic strips", used for door closures and board displays. All of the oxides have been cut and polished as jewelry items and objets d'art. Also as powder for pigments in paints, enamel or glass. In cosmetics, red rouge is hematite (red ocher variety) and the others have been used in oil as face paints.

Technical Application: Iron oxides have several applications in Solid State processing, to include active devices. Chrome glass masks for photolithography are being replaced with an iron oxide, FeO_x, as it is more stable under handling conditions and does not require an antireflective (AR) coating.

There is a range of ferrites — iron (oxide) with additive metals, such as manganese, selenium, etc., supplied as blanks or in bulk forms fabricated as resistor elements, and there are several magnetoresistive compounds used as discrete devices. The yttrium iron garnet (YIG) contains iron oxide, is fabricated as a laser, as a computer bubble-memory device, and has application as an optical filter.

The study and use of natural iron oxides goes back to at least 1350 B.C. when the Hittite culture in Asia Minor (now Turkey) developed the smelting of iron ore, and both natural and artificial single crystals are the subject of morphological studies today.

Etching: Soluble in most acids, but variable with specific oxide. See Hematite, Magnetite, Ferrites, Iron, and Steel.

IRON OXIDE ETCHANTS

FEO-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal
COMPOSITION:
x .... HCl

TIME:
TEMP:

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DISCUSSION:

FeO_x, thin films deposited on soda-lime glass used in the fabrication of photo resist masks. Solution used to clean surfaces and etch patterns masks.

REF: Lipman, R — personal communication, 1981

LIM-0001

ETCH NAME: Nitric acid — TIME: 1—3 min

TYPE: Acid, cleaning — TEMP: RT

COMPOSITION:

x .... HNO_3

DISCUSSION:

$FeO.nH_2O$, the natural mineral limonite as an oxide replacement mineral pseudomorph after pyrite, FeS_2, still in pyrite pseudo-cube form. Solution used to clean and etch surfaces for structure study. Limonite is a natural colloid.

REF: Walker, P — mineralogy study, 1952

MAGT-0005

ETCH NAME: Water — TIME: 2—10 min

TYPE: Acid, cleaning/structure — TEMP: Boiling

COMPOSITION:

x .... H_2O

DISCUSSION:

Fe_3O_4, as fine natural single crystal octahedrons, o(111) found in association with garnet crystals in a green schist. Boiling water used to develop striation figures on the naturally highly polished surfaces with minimum surface alteration.

REF: Walker, P — mineralogy study, 1953

FEO-0002

ETCH NAME: Methyl alcohol — TIME: 1—2 min

TYPE: Alcohol, cleaning — TEMP: RT to hot

COMPOSITION:

(1) x .... MeOH (2) x .... TCE

DISCUSSION:

FeO_x, as thin film evaporation on patterned photo resist glass masks. Both solvents shown used to degrease and clean masks by dipping. Follow with N_2 blow dry. TCE also used as a hot vapor degreaser.

REF: Walker, P — personal application, 1980—1985

HEM-0003

ETCH NAME: — TIME:

TYPE: Molten, flux, removal — TEMP: 1200 K

COMPOSITION:

20—30 g .... H_2SO_4

0.002—0.2 g .... Na_2O_2

DISCUSSION:

Fe_2O_3 specimens and powder used in a solubility study relative to an SO_2/O_2 atmosphere. Developed a phase diagram for Na-Fe-S-O. Na_2O_2 used to establish a pH between 0.5 to 7.5. Also studied NiO, Co_3O_4, Al_2O_3, and Y_2O_3.

REF: Zang, Y S & Rapp, R A — *J Electrochem Soc*, 132,734(1985)

HEM-0005: Gupta, K & Rapp, R A — *J Electrochem Soc*, 127,2194(1980)

Similar work as shown in HEM-0003.

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PHYSICAL PROPERTIES OF IRON PHOSPHIDE, FeP

Classification	Phosphide
Atomic numbers	26 & 15
Atomic weight	86.86
Melting point (°C)	1200
Boiling point (°C)	
Density (g/cm³)	6.1
Hardness (Mohs — scratch)	6—7
Crystal structure (hexagonal — rhombohedral)	(10$\bar{1}$1) rhomb
Color (solid)	Grey-black
Cleavage (basal — poor)	(0001)

IRON PHOSPHIDE, FeP

General: Does not occur as a natural compound although there are several iron phosphate minerals. In the fabrication of irons and steels the compound is an additive as ferro-phosphorus used for a hardening agent. In chemistry there are di- and tri-iron phosphides, as well as the mono-type listed above.

Technical Application: The reference, here, is as FeP_2, which occurs as a crystal segregate in iron doped indium phosphide, along with a sponge FeP form. The material was removed from the single crystal InP matrix for evaluation.

Etching: $HF:HNO_3:H_2O_2$ as mixed acids.

IRON PHOSPHIDE ETCHANTS

FEP-0001
ETCH NAME: BRM — TIME:
TYPE: Halogen, removal — TEMP:
COMPOSITION:
x .... x% Br_2
x .... MeOH
DISCUSSION:

FeP_2, as precipitate growth needles and rhombohedral blocks or lamellae in Fe-doped InP ingots grown by LEC. Segregates can be mixed-phase FeP, sponge-like with hollow center structure. Solution shown was used to etch expose the segregates and to completely dissolve the InP matrix for particle removal for SEM and X-ray study.
REF: Smith, N A et al — *J Cryst Growth*, 68,517(1984)

PHYSICAL PROPERTIES OF IRON DISULFIDE, FeS_2

Classification	Sulfide
Atomic numbers	26 & 16
Atomic weight	119.97
Melting point (°C)	1171
Boiling point (°C)	
Density (g/cm³)	5.00
Hardness (Mohs — scratch)	6—6.5
Crystal structure (isometric — pyritohedral)	(100) pseudo-cube, stria
Color (solid)	Brass-yellow
Cleavage (cubic — poor)	(100)

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IRON SULFIDE, FeS_2

General: The natural mineral pyrite, FeS_2, is the best known of the "iron pyrites" as a mineral group. Marcasite, FeS_2, has orthorhombic structure rather than the isometric structure of pyrite, and can be further distinguished by its lower specific gravity and paler yellow color when fresh. When pyrite forms under alkaline conditions, marcasite forms under acid conditions and is far less stable. Pyrite is widely distributed in rocks of all types and ages, and is found in large deposits. Some 75% of iron ore comes from the pyrites, is important for both iron and sulfur content and, depending upon location, for its percentage of copper, gold, and silver. It is called "fool's gold" from its fine yellow color, but can be distinguished from gold as, when struck, it will shatter to a black powder with the odor of "rotten eggs"; whereas gold can be beaten into very thin sheets of foil. Under oxidizing conditions the sulfur can be leeched and replaced with oxygen, yet still retaining the pseudo-cubic structure of the original pyrite mineral . . . limonite pseudomorphs after pyrite.

Industrially it is the most important ore of iron, and natural pyrite is sometimes added directly to an iron or steel melt with or without subsequent desulfurization.

Technical Applications: Iron pyrites are not directly used in Solid State or semiconductor device fabrication, though both iron and sulfur are, individually, p- and n-type dopants, respectively, for several compound semiconductors.

The pyrite crystal structure — isometric-pyritohedral — is the common type of a number of metallic compounds formed as sulfides, selenides, tellurides, arsenides and antimonides . . . some as compound semiconductors. Pyrite has been artificially grown, and both the manmade and natural single crystals have been studied.

Etching: HNO_3.

IRON SULFIDE ETCHANTS

FES-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:

FeS_2 single crystal ingot artificially growing as the mineral pyrite. Cut specimens mechanically polished with 0.5 μm diamond paste. Etched in nitric acid to polish and remove mechanical cutting damage. Other materials grown in a material study were $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsTe_2$, PtP_2, $PtAs_2$, $PtSb_2$. All ingots show the structure of pyrite. Materials used in an IR spectra study. [*Note:* Authors refer to material structure as "cubic", but it is pseudo-cubic, as pyrite is in the isometric system-pyritohedral class, not isometric-normal class which contains the true cube, (100)]
REF: Lutz, H D et al — *J Phys Chem Solids,* 46,437(1985)
REF: FES-0002: Walker, P — mineralogy study, 1953

FeS_2, as natural single crystals. A dilute solution used in cleaning and etching surfaces in a structural study of the common twinning lamellae on the pseudo-cubic crystal faces.

FES-0003
ETCH NAME: — TIME:
TYPE: Pressure, alteration — TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:

FeS_2, as artificial and natural single crystals used in a study of pressure transition of crystal structure. Both pyrite and marcasite were studied and did not show a transition. The

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mineral hauerite, MnS_2, does show a transition. At RT all three minerals are 4m space group. Materials were powdered and pressurized in a diamond anvil cell for study. (*Note:* Pyrite and hauerite are isometric-pyritohedral; marcasite, orthorhombic — normal.).
REF: Chattopadhyay, T & Von Schering, H G — *J Phys Chem Solids*, 46,113(1985)

IRON PALLADIUM ETCHANTS

FEPD-0001
ETCH NAME: Smog
TYPE: Gas, corrosion
TIME: 30 days
TEMP: RT
COMPOSITION:
x .... H_2O (75% RH)
+ .... Air
+ .... SO_2, NO_2, H_2, Cl_2 traces
DISCUSSION:
FePd, (100) and crystalline thin films co-deposited by E-beam evaporation on a variety of different substrates. The gas/water mixture shown was made artificially to replicate a city atmosphere. The evaporated films contained large area crystallites with cubic structure. The body-centered cubic (bcc) phase that was high in iron showed corrosion cracks. The face-centered cubic (fcc) phase that was high in palladium and inert under test conditions shown above.
REF: Penna, T C et al — *J Cryst Growth*, 67,27(1984)

IRON TITANATE ETCHANTS

FETI-0001
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
TIME:
TEMP: Hot
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
$Fe_{3-x}Ti_xO_4$ single crystal grown by Float Zone (FZ) method for study of this material. (*Note:* Etch shown is for natural minerals arizonite, $Fe_2O_3.3TiO_2$ or pseudobrookite, Fe_2TiO_5. See Titanium Dioxide, TiO_2, this Etchant Section.)
REF: Barabers, V A M et al — *J Cryst Growth*, 69,23(1984)

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PHYSICAL PROPERTIES OF KRYPTON, Kr

Classification	Inert gas
Atomic number	36
Atomic weight	83.8 (83.7)
Melting point (°C)	−157
Boiling point (°C)	−156
Density (g/cm³ — solid)	3.4
(g/l — liquid)	3.7
Thermal conductance (cal/cm²/cm/°C/sec) 20°C	0.21×10^{-4}
1st ionization potential (eV)	14
Cross section (barns)	24
Vapor pressure (°C)	−171.8
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid/gas)	Colorless
Cleavage (cubic — solid)	(001)

KRYPTON, Kr

General: Krypton is one of the rare gases found in the atmosphere. It is inert with a valence of 0 and does not form compounds. There is only 1 ppm in air. It is obtained from the fractional distillation of liquid air, L_{air}, as is LN_2 and the other rare gases in the order of their liquefaction points.

In a vacuum tube the gas produces a yellow-green to green glow and, like neon, Ne, gas (orange-red) is used in electric signs and beacons.

Technical Application: Krypton has had little use in Solid State processing other than as a light source in equipment light bulbs.

Etching: Soluble in LOX.

KRYPTON ETCHANTS

KR-0001
ETCH NAME:
TYPE: Pressure, defect
COMPOSITION:
x .... vacuum pressure
TIME:
TEMP: −158°C
DISCUSSION:

Kr, (100) solid single crystal ingots are formed in vacuum under pressure with liquid helium, LHe, as the freezing vehicle. Surfaces can be preferentially etched by varying the vapor pressure in the vacuum system.

REF: Schwantner, et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1970

KR-0002
ETCH NAME: Krypton
TYPE: Gas, forming
COMPOSITION:
x .... Ar/N_2
x .... 12.7% Kr
TIME:
TEMP:

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DISCUSSION:

Kr, used as a gas ambient component in the RF magnetron sputter deposition of NbN thin films on sapphire substrates. Inclusion of krypton did not appear to improve the resistivity or other electronic functions of the material.

REF: van Dover, R B et al — *J Vac Sci Technol,* A2(3),2219(1984)

KOVAR ETCHANTS

KO-0001a

ETCH NAME:

TYPE: Acid, polish

TIME:

TEMP:

COMPOSITION:

1 .... HNO_3

3 .... HAc

15 ml/l .... HCl

DISCUSSION:

Kovar specimens. Used as a general polishing, removal and cleaning solution.

REF: Westinghouse Report

KO-0001b

ETCH NAME: Hydrochloric acid, dilute

TYPE: Acid, oxide removal

TIME: 1—3 min or 2—10 min

TEMP: 70°C RT

COMPOSITION:

1 .... HCl

1 .... H_2O

DISCUSSION:

Kovar specimens. Solution used to remove native oxide.

REF: Ibid.

KO-0002

ETCH NAME: Ferric chloride

TYPE: Acid, preferential

TIME:

TEMP: Hot

ASTM: #100

COMPOSITION:

x .... 35% $FeCl_3$

DISCUSSION:

Kovar specimens. Solution can be used for general removal or cleaning, and as a slightly preferential etchant. Was used to clean kovar heat-sink substrates for silicon device assembly.

REF: Walker, P — personal application, 1959

KO-0003: ASTM E407-70

Reference for ASTM #100, shown as: 10 g $FeCl_3$:90 ml H_2O

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PHYSICAL PROPERTIES OF LANTHANUM, La

Classification	Transition metal
Atomic number	57
Atomic weight	138.92
Melting point (°C)	920
Boiling point (°C)	3469
Density (g/cm^3)	6.166
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.033
Specific heat (cal/g) 25°C	0.045
Heat of fusion (k-cal/g-atom)	1.5
Heat of vaporization (k-cal/g-atom)	96
Atomic volume (W/D)	22.5
1st ionization energy (K-cal/g-mole)	129
1st ionization potential (eV)	5.61
Electronegativity (Pauling's)	1.1
Covalent radius (angstroms)	1.69
Ionic radius (angstroms)	1.14 (La^{+3})
Electrical resistivity (micro-ohms-cm) 298 K	79.8
Compressibility (cm^2/kg $\times 10^{-6}$)	4.04
Cross section (barns)	8.9
Magnetic moment (Bohr magnetons)	0.49
Tensile strength (psi)	18,900
Yield strength (psi)	18,200
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	101
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Lead-grey
Cleavage (basal)	(0001)

LANTHANUM, La

General: Does not occur as a native element. Though it is not one of the rare earth elements it is found with the cerium group of metals. The chief ores are monazite, (Ce, La, Di)PO_4, a variable phosphate, and allanite (orthite), a cerium/iron silicate containing lanthanum. The latter is found in many igneous rocks of basic types as black grains, often with magnetite, even coated with that magnetic iron ore. The pure metal is lead-grey in color with a metallic luster, and characteristics similar to those of iron, but ignites and burns readily in air to the oxide, La_2O_3. It is kept in benzene to prevent ignition.

The pure metal is not used in the metals industries, but several of the salts have applications in both chemistry and medicine.

Technical Application: Lanthanum has not been used in the Solid State and semiconductor material processing area though, as it resembles iron, it might act as an n-type dopant in compound semiconductors.

Specimens have been studied for general morphological data and, as a sphere, for electrical/resistivity characteristics. As a boride, LaB_6, and as an oxide with strontium and/or iron and cobalt, single crystals have been grown and evaluated.

Etching: Soluble in acids.

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LANTHANUM ETCHANTS

LA-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3
DISCUSSION:
La specimens. Solution shown as a general etch for lanthanum.
REF: Hodgman, C D — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 398
TIME:
TEMP: RT

LA-0002
ETCH NAME:
TYPE: Arc, forming
COMPOSITION:
x .... heat
DISCUSSION:
La specimens were first arc melted as buttons and then machined into spheres $^3/_{16}$ to 2″ in diameter and used in measuring electrical resistivity. Other materials evaluated were Pr, Nd, and Sm.
REF: Alstad, J K et al — *Phys Rev*, 122,1636(1961)
TIME:
TEMP:

LA-0003
ETCH NAME:
TYPE: Pressure, transition
COMPOSITION:
x .... pressure
DISCUSSION:
La, U and Th used as pressed powders in talc to form single crystal specimens in a study of crystal transition and electrical parameters. At RT, La is hexagonal system, dhcp; alters to isometric (cubic), fcc at 23 K bars pressure. Handle materials under oil and wash with hexane. Dry talc at 150°C under pressure and use as the material carrier.
REF: Vijayakumar, V — *J Phys Chem Solids*, 46,17(1985)
TIME:
TEMP:

LANTHANUM BORIDE ETCHANTS

LAB-0001
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
30 .... H_2SO_4
20 .... glycerin
30 .... H_2O
DISCUSSION:
LaB, single crystal filaments to be used as probe tips for electron microscope instruments. Solution used to etch form the probe tips.
REF: Shimizu, R et al — *J Vac Sci Technol*, 15(3),922(1978)
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

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LAB-0002
ETCH NAME: Sulfuric acid
TYPE: Acid, forming
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
LaB_6, single crystal specimens used as cathode filaments formed with a 90° cone and a radius of 15 μm on (100), (210), and (110) orientations.
REF: Kato, T et al — *J Vac Sci Technol*, B(1),100(1983)

TIME:
TEMP:

LANTHANUM BROMIDE ETCHANTS

LABR-0001
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, polish
COMPOSITION:
x .... EOH
DISCUSSION:
$LaBr_3$, (100) wafers, and $LaBr_3$:Sm doped wafers grown as ingots by a modified Bridgman method with a brass inner liner for sharp heat gradient. Material used as the base for Quantum Counters. Specimens were transparent and clear, cut 1—2 mm and 2—5 mm thick for study, and alcohol used to polish faces. Both $SmBr_3$ and $LaBr_3$ are hygroscopic. $LaBr_3$ is orthorhombic; $SmBr_3$, hexagonal.
REF: Krasutsky, N J — *J Appl Phys*, 54,126(1983)

TIME:
TEMP: RT

LANTHANUM STRONTIUM COBALTITE ETCHANTS

LACO-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, preferential
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
$LaSrCoO_3$, single crystals grown by a Float Zone technique using a Xe arc lamp. Cobalt was greater than 0.2% concentration. Material is pseudo-cubic and wafers were cut (001). Mechanically polish with 0.05 μm alumina and etch in solution shown to develop structure. Both twinning and precipitates were observed. Crystal color is black and showed some surface ridging. SEM used for observation.
REF: Matsuura, T et al — *Jpn J Appl Phys*, 23,1172(1984)

TIME: x minutes
TEMP: RT

LACO-0002
ETCH NAME:
TYPE: Salt, polish
COMPOSITION:
x .... 0.05% NaO_3
DISCUSSION:
$LaSrCoO_3$, single crystals cleaved (001). See discussion under LACO-0001. Surfaces were polished with the solution shown and followed with HCl etching to develop structure. Study was to observe martensetic type transformation using a SEM. Twinning was observed.
REF: Matsuura, T et al — *Jpn J Appl Phys*, 23,1197(1984)

TIME:
TEMP: RT

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LANTHANUM STRONTIUM FERRITE ETCHANTS

LAFE-0001
ETCH NAME: Hydrochloric acid — TIME: 1 h
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
$LaSrFeO_3$, single crystals grown by a Float Zone method using a Xe lamp. Iron was <0.02% concentration. Material is pseudo-cubic and wafers were cut (100). Mechanically polish with 0.05 μm alumina and etch in solution shown to develop structure. Both twinning and precipitates were observed. Crystal color was shiny black with smooth surfaces. After etching material was studied under a SEM microscope. Also studied $LaSrCoO_3$.
REF: Matsuura, T et al — *Jpn J Appl Phys,* 23,1172(1984)

PHYSICAL PROPERTIES OF LEAD, Pb

Classification	Metal
Atomic number	82
Atomic weight	207.21
Melting point (°C)	327.43
Boilint point (°C)	1740 (1744)
Density (g/cm^3)	11.35
Thermal conductance (cal/sec)(cm^3)(°C/cm) 20°C	0.083
Specific heat (cal/g) 25°C	0.0306
Latent heat of fusion (k-cal/g-atom)	5.86 (6.26)
Heat of vaporization (cal/g)	203
Atomic volume (W/D)	18.3
1st ionization energy (K-cal/g-mole)	171
1st ionization potential (eV)	
Covalent radius (angstroms)	1.47
Ionic radius (angstroms)	0.84 (Pb^{+4})
Electrical conductance (micro ohms^{-1})	0.046
Thermal conductivity (cal/cm^2/°C/sec) 20°C	0.083
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	29.3
Vapor pressure (°C)	1421
(mmHg) 1167°C	10.0
Magnetic susceptibility ($\times 10^{-6}$ cgs)	0.12
Tensile strength (psi)	3000
Thermal expansion (ppm/°C)	29.3
Cross section (barns)	0.17
Hardness (Mohs — scratch)	1.5
(Brinell — kgf/mm^2)	4.2
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Lead grey
Cleavage (cubic — poor)	(001)

LEAD, Pb

General: Occurs as a native element though it is rare, usually as thin plates and small globular masses. Single crystals are only known from the Harstig mine, Sweden, although

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it has been found in other mines and in gold placer sands. Galena, PbS, is the chief ore of lead which may contain, or be associated with silver and gold, as well as contain trace amounts of selenium, zinc, cadmium, antimony, bismuth, and copper, as sulfides. Galena is one of the most widely distributed metal sulfides and is usually associated with eruptive rocks along with other metal sulfides, such as zinc and iron. It is often closely associated with silver, such that deposits are important for both metals. The chemical symbol Pb is from plumbite, the original name for lead.

Because of its low melting point, and the ease with which galena can be reduced to pure lead, lead was one of the metals known to ancient man. Pure lead is ductile, malleable and soft, like gold, and is also chemically inert as a nonconductor . . . some of the lead drains installed during the Roman Empire period before 1 A.D. are still in use.

In most industrial applications lead is hardened with the addition of other metals and is a constituent in a wide range of alloys. A few of the more important lead alloys are

Formula	Name
99.8Pb:0.2As	Lead shot
94Pb:6Sb	Battery plate
82Pb:15Sb:3Sn	Type metal
99.93Pb:0.08Cu	Chemical lead
87Pb:13Sn:1Cu	Lead foil
67Pb:33Sn	Plumber's solder

As oxides and sulfates (white, red, and yellow) lead is used as paint pigments. Other lead salts are used in medicine as antiseptics and astringents, and tetraethyl lead is used in leaded gasoline. Both "lead" paints and leaded gasoline are being replaced due to their health hazard.

Lead has been found in Egyptian tombs, circa 3500 B.C., and the Romans used lead and lead compounds in their water piping. In soft water lead hydrolyzes to fairly soluble $Pb(OH)_3$ and, as the lead-ion (Pb^{++}) is poisonous it is no longer used for incoming water piping. In the distillation of alcohol, if lead piping is used, lead poisoning is developed in the liquor.

Because of lead's low neutron cross-section like graphite, lead rods can be used for damping atomic piles. As lead shielding, including lead glass, it is used in nuclear generators and facilities construction. Medical technicians and doctors wear lead aprons when working with X-ray equipment for the same reason. In both medicine and industry, where X-ray, van der Graff generators, and similar equipment are in use, the room walls are shielded with lead sheet. This includes lead-glass for sighting windows and as eye shields.

The term "leaded glass" is an old term applied to the assembly of small glass pieces, each piece surround by a lead solder as the holding compound; whereas "lead glass" is a glass to which lead has been added. It is a heavy, clear, relatively soft glass. As already mentioned, the lead glass is used in radiation areas, but also is used in the jewelry industry for objets d'art.

The "lead" pencil is a misnomer . . . the material is graphite (carbon), though a stick of lead drawn across a surface will produce a light grey streak.

Technical Application: Pure lead and lead solders have many uses in Solid State processing, mainly in the assembly of parts and packaging using both wire and cut pre-forms.

Lead also is a constituent of several compound semiconductors, such as lead sulfide, PbS; lead selenide, PbSe; lead telluride, PbTe; lead oxide, and PbO, and there are trinary compounds of both selenides and tellurides.

The most widely used solders are #62 (60Pb:40Sn) the "standard solder", and #63 (38Pb:40Sn:2Ag) with melting points of 185 and 220°C, respectively. They are used in solid

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bar and wire form or as resin-core wire. Wire may be applied directly, such as for wiring parts in place or used as pre-cut forms for mounting discrete devices and circuit elements. Other applications include bulk solder in solder pots for pre-tinning by dip soldering of package device leads and electrical wires. Basic circuit boards, PCBs, are plastic impregnated linen sheets overplated or clad with copper. The boards are drilled and etched to pattern electrical circuits, then pre-tinned with solder prior to discrete elements being assembled on the board. With all items in place, boards are passed through a belt furnace for final soldering.

The fabrication and assembly of PCBs has evolved into its own industry within the Solid State field, and has been a major element in the miniaturization and compaction of electronic equipment, such as computers, microprocessors, TVs, transistor radios, watches, even toys. Much electronic equipment is now designed with computer/board operation, from cutting and dicing equipment to wire bonders, vacuum systems, and machine shop parts design.

Pure lead single crystals, as well as lead alloys, have been grown and studied for morphological and electrical data, and the general study of lead has been in progress since ancient times.

Etching: HNO_3 and hot H_2SO_4. A mixture of glacial acetic acid, HAc, and hydrogen peroxide, H_2O_2 is the most widely used general clean/etch solution.

LEAD ETCHANTS

PB-0001
ETCH NAME: TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
x .... CH_3COOH (HAc)
x .... H_2O_2
DISCUSSION:
Pb specimens. Solution used to clean and remove oxide from lead material used to grow lead telluride.
REF: Sato, V et al — *Jpn J Appl Phys*, 2,688(1963)
PB-0005: Feltham, P — *Acta Metall*, 5,553(1957)
Pb, single crystals used in a study of work hardening in face-centered-cubic (fcc) metals. Solution used to polish surfaces.

PB-0002a
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HAc
1 .... H_2O_2
DISCUSSION:
Pb specimens. Solution used as a general cleaner for lead and removal of lead oxide. Clean in benzene prior to etching. Author references PB-0007 for etch.
REF: Snowden, K V — *Phil Mag*, 6,321(1961)

PB-0002b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
70 .... HAc
30 .... H_2O_2

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DISCUSSION:

Pb, single crystal ingots. Clean in benzene before subjecting specimen to bending fatigue in vacuum. Solution shown used to observe structure developed by fatigue.

REF: Ibid.

PB-0006a: Fleischer, E L — *Acta Metall,* 9,184(1961)

Pb, single crystals. Specimens were flame cut to length, and used in a study of glide. Solution used as a polish etch, and author references the solution to P Strutt, private communication.

PB-0003a

ETCH NAME:

TIME:

TYPE: Acid, polish

TEMP:

COMPOSITION:

3 .... HAc

1 .... H_2O_2

DISCUSSION:

Pb specimens. Used as a cleaning and polishing solution for lead and to remove lead oxide from surfaces.

REF: Rutherford, R J — *Proc Am Soc Test Mater,* 24,739(1924)

PB-0007

ETCH NAME:

TIME: 5—10 sec

TYPE: Acid, preferential

TEMP: 35°C

COMPOSITION:

20 ml .... H_2O_2

80 ml .... HAc

DISCUSSION:

Pb specimens and lead alloys. Solution used in preparing specimens for metallographic and microscopic examination of structure.

REF: Wermer, H K & Wermer, H W — *J Inst Met,* 66,45(1940)

PB-0009a: Tegart, W J McG — *The Electrolytic and Chemical Etching of Metals,* Pergamon Press, London, 1956

Pb specimens. Solution described as an etch for lead. Use was similar to study described under PB-0007.

PB-0008b

ETCH NAME: Potassium cyanide

TIME:

TYPE: Acid, cleaning

TEMP: RT

COMPOSITION:

x .... KCN

DISCUSSION:

Pb, (100) wafers. Polish etch in CP4, then soak in KCN with DI water rinse for a final cleaning.

REF: Ibid.

PB-0003b

ETCH NAME: Hydrochloric acid

TIME:

TYPE: Acid, removal

TEMP:

COMPOSITION:

x .... HCl

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DISCUSSION:
Pb samples. Solution used as a general removal and cleaning etch.
REF: Rutherford, R J — *Proc Am Soc Test Mater*, 24,739(1924)

PB-0004a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HAc
3 .... H_2O_2
TIME: 15—30 sec
TEMP: RT
DISCUSSION:
Pb, (100) wafers and other orientations used in defect etch development study.
REF: Nike, Y — *J Phys Soc Jpn*, 13,970(1958)

PB-0004b
ETCH NAME: Sulfamic acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... $C_5H_{15}NHSO_2OH$
TIME: 45 sec
TEMP: 18°C
ANODE: Pb
CATHODE:
POWER: 2 A/cm^2
DISCUSSION:
Pb, (100) wafers and other orientations used in defect etch development studies.
REF: Ibid.

PB-0006b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HAc
1 .... HNO_3
19 .... MeOH
TIME:
TEMP:
DISCUSSION:
Pb, single crystal specimens were flame cut into lengths and etched in a study of glide. Solution used to polish specimens before being subjected to fatigue.
REF: Fleischer, R L — *Acta Metall*, 9,184(1961)

PB-0008a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... *superoxol
1 .... HNO_3
5 .... H_2O

*1HF:1H_2O_2:4H_2O

TIME:
TEMP:
DISCUSSION:
Pb, (100) wafers. Polish etch in solution shown and follow with KCN soak, then DI water rinse.
REF: Logan, K H & Schwartz, M — *J Appl Phys*, 26,1287(1955)

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PB-0009b
ETCH NAME: TIME: Dip
TYPE: Acid, removal TEMP: RT
COMPOSITION:
140 ml .... NH_4OH
60 ml .... HNO_3
10 g .... H_2MoO_4
240 ml .... H_2O
DISCUSSION:
Pb specimens. Etch by repeat dipping with water rinse between each etch dip period.
REF: Ibid.

PB-0010: ASTE Committee — *Tool Engineers Handbook*, McGraw-Hill, New York, 1949
Pb specimens and Pb alloys. Solution used in process cleaning of lead parts.

LEAD ALLOYS, PbMx

General: Does not occur as a pure metallic alloy in nature although there is the mineral teallite, $PbSnS_2$, and several lead selenides and tellurides. The mineral galena, PbS, was known to ancient man and, as it has a low melting point, lead was extracted by roasting to remove sulfur. Coupled with their knowledge of tin and zinc with copper (bronze and brass), lead alloys were in use as far back as the Egyptian dynastic period around 4500 B.C. (lead artifacts have been found in Egyptian tombs), and engineers of the Roman Empire period (about 500 B.C. to 1000 A.D.) were using lead solders in construction of water piping and aqueduct construction.

Today there are well over a hundred lead-containing solders developed for specific temperature applications in industry, probably the best known and widely used being the lead-tin types for general alloying. A few formulations — as application-named solders — are already shown in the general section under lead.

Technical Application: In addition to the use of lead-tin solders as already described under the technical application section of lead, eutectic lead alloys have been evaluated for their superconducting characteristics, such as those containing tin, silver and titanium.

Etching: HNO_3:HAc, HAc:H_2O_2, variable with alloy.

LEAD ALLOYS

LEAD:SILVER ETCHANTS

PBAG-0001
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HAc
1 .... HNO_3
4 .... glycerin
DISCUSSION:
Pb:Ag, eutectic alloy specimens used in a structure study and their effects on superconducting properties of eutectic alloys. Solution used to develop structures on PbSn, PbAg, and PbTi.
REF: Levy, S A & Kim, Y B — *J Appl Phys*, 37,3659(1966)

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PBAG-0002a
ETCH NAME:
TYPE: Electrolytic, preferential
COMPOSITION:
x .... HAc
x .... $HClO_4$
TIME:
TEMP:
ANODE: PbAg
CATHODE:
POWER:
DISCUSSION:
Pb:Ag, specimen alloys of various compositions. Solution will polish at high current or develop structure at low current.
REF: Heidenreich, R D — *Acta Metall*, 3,78(1955)

PBAG-0002b
ETCH NAME: Molybdic acid
TYPE: Electrolytic, preferential
COMPOSITION:
x .... H_2MoO_4
TIME:
TEMP:
ANODE: PbAg
CATHODE:
POWER:
DISCUSSION:
Pb:Ag specimens of alloys of various compositions. Solution is a preferential etch.
REF: Ibid.

LEAD:TIN ETCHANTS

PBSN-0001
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HAc
1 .... HNO_3
4 .... glycerin
TIME:
TEMP:
DISCUSSION:
Pb:Sn, eutectic alloy specimens used in a structure study and their effects on superconducting properties of eutectic alloys. Solution used to develop structure on PbSn, PbAg, and PbTi.
REF: Levy, S A & Kim, Y B — *J Appl Phys*, 37,3659(1966)

PBSN-0002
ETCH NAME:
TYPE: Alcohol, cleaning
COMPOSITION:
x .... MeOH
TIME:
TEMP: RT to hot
DISCUSSION:
60Pb:40Sn #62 solder as a pure metal solid wire or bulk alloy; as a rosin core wire; or spheretized paste used for general soldering of assembly elements in semiconductor device circuit fabrication, electronic equipment assembly on PCBs, etc. Ethanol and other alcohols or solvents used to clean surfaces prior to and after soldering. Clean surfaces prior to soldering, and to remove residual solder flux after soldering, and included heavy water washing, only.
REF: Walker, P — personal application, 1960—1985

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PBSN-0003
ETCH NAME:
TYPE: Acid, cleaning
TIME: 1 min
TEMP: RT
COMPOSITION:
1 .... HNO_3
10 .... HAc
10 .... H_2O
DISCUSSION:
Pb:Sn alloy contacts on silicon diodes. Solution developed to clean the lead alloy after soldering device contact leads onto silicon wafers and clean the p-n device junctions with minimum etching of either material.
REF: Walker, P — personal development, 1963

PBSN-0004
ETCH NAME:
TYPE: Acid, removal
TIME: 1—3 min
TEMP: RT
COMPOSITION:
1 .... HNO_3
1 .... HAc
1 .... H_2O
DISCUSSION:
Pb:Sn alloys and 50 other lead/metal alloys used in a general study of alloy contacts for silicon. Solution used to remove alloys after firing pellets on wafer surfaces in a hand alloy furnace under nitrogen.
REF: Walker, P — personal development, 1957

LEAD-TITANIUM ETCHANTS

PBTI-0001
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
1 .... HAc
1 .... HNO_3
4 .... glycerin
DISCUSSION:
Pb:Ti, eutectic alloy specimens used in a structure study and their effects on superconducting properties of such alloys. Solution used to develop structure on PbSn, PbAg, and PbTi.
REF: Levy, S A & Kim, Y B — *J Appl Phys*, 37,3659(1966)

PHYSICAL PROPERTIES OF LEAD IODIDE, PbI_2

Classification	Iodide
Atomic numbers	82 & 53
Atomic weight	461.05
Melting point (°C)	402
Boiling point (°C)	954
Density (g/cm^3)	6.16
Hardness (Mohs — scratch)	2—3

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Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Gold yellow
Cleavage (basal)	(0001)

LEAD IODIDE, PbI_2

General: Does not occur as a natural mineral due to fairly high water solubility. There are over 50 lead minerals containing chlorine, but none with fluorine, bromine or iodine, the other three halogen group elements. In chemistry there are both the mono- and di-iodides. There is some use of the di-iodide form as a bronze colored pigment in glass making, and similar uses in printing and photography, but none in the metal industries, other than as an additive to etching and cleaning solutions.

Technical Application: There is no use of these iodide compounds in Solid State processing, other than as additive to etching and cleaning solutions. There are possible filter applications even though the material is fairly water soluble, such that single crystals have been grown by evaporation from alcohol solutions for general study.

Etching: KI and alkalies.

LEAD IODIDE ETCHANTS

PBI-0001
ETCH NAME: TIME:
TYPE: Tape, removal TEMP: RT
COMPOSITION:
x .... adhesive tape
DISCUSSION:

PbI_2, single crystal ingot. After cutting, wafers can be cleaned by cleaving perpendicular to the c-axis using Scotch tape and peeling.

REF: Zielinger, J P et al — *J Appl Phys*, 57,292(1985)

PBI-0002a: Forty, A J — *Phil Mag*, 6,587(1961)

PbI_2, single crystals grown as salt recrystallization in an alcohol solution at 100°C with slow cool to room temperature. Thin crystals that floated on top of the alcohol were collected and used for electron microscope (EM) study. Crystal platelets could be etch thinned in KI.

PBI-0002b
ETCH NAME: Potassium iodide TIME:
TYPE: Halogen, removal TEMP:
COMPOSITION:
x .... x% KI
x .... H_2O
DISCUSSION:

PbI_2, as thin crystal platelets grown from an alcohol solution. Platelets can be etch thinned in this solution for electron microscope study.

REF: Ibid.

PHYSICAL PROPERTIES OF LEAD MOLYBDATE, $PbMoO_4$

Classification	Metal oxide
Atomic numbers	82, 42 & 8
Atomic weight	367.16
Melting point (°C)	800
Boiling point (°C)	

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Density (g/cm^3)	6.7—7.0
Refractive index (n =)	2.402 & 2.304
Hardness (Mohs — scratch)	2.75—3.0
Crystal structure (tetragonal — pyramidal)	(111) pyramid, 1st order
Color (solid)	Yellow/green
Cleavage (pyramidal)	(111)

LEAD MOLYBDATE, $PbMoO_4$

General: Occurs as the mineral wulfenite, $PbMoO_4$, which is of secondary origin being found in the oxidation zone of lead and zinc mines and used as an ore of molybdenum. The primary industrial use is as an ore of molybdenum.

Technical Application: Both molybdate and tungstate single crystals have been studied as artificially grown materials for general morphology, electronic and electrical data, and for crystallographic structure change under pressure and temperature.

Etching: Soluble in acids and alkalies.

LEAD MOLYBDATE ETCHANTS

PBM-0001
ETCH NAME: TIME:
TYPE: Pressure, alteration TEMP:
COMPOSITION:
x .... pressure
DISCUSSION:
$PbMoO_4$ single crystals used in a high pressure chemistry test of materials at above 56 Pa. Other molybdates and tungstates studied were $CaWO_4$, $PbWO_4$, $CaMoO_4$, and $CdMoO_4$.
REF: Hazen, R M et al — *J Phys Chem Solids*, 46,253(1985)

PHYSICAL PROPERTIES OF LEAD MONOXIDE, PbO

Classification	Oxide
Atomic numbers	82 & 8
Atomic weight	223.21
Melting point (°C)	888 (litharge)
Boiling point (°C)	
Density (g/cm^3) — litharge	9.53
(g/cm^3) — massicot	8.0
Refractive index (n =) litharge/massicot	2.65/2.61
Hardness (Mohs — scratch)	2—3
Crystal structure (tetragonal — normal) litharge	(110) prism, 1st order
(orthorhombic — normal) massicot	(100) a-pinacoid
Color (solid) litharge	Yellow/orange
(solid) massicot	Colorless
Cleavage (basal — litharge & massicot)	(001)

LEAD MONOXIDE, PbO

General: It occurs in nature as the mineral massicot, PbO. It is rare, of secondary origin, and usually associated with galena, PbS. It is interesting as the central core of the mineral is a colorless solid, but surfaces are coated with "litharge", the yellow-orange variety of lead oxide. As can be seen from the list of properties, the two varieties have distinctive

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crystal structures even though the mineral appears to be only one form and yellow-orange in color. The mineral plattnerite, PbO_2, is the dioxide form.

In chemical processing, lead can be converted to litharge by heating in air above 600°C, as can all other oxides of lead. Litharge has major use in the glass and pottery industries in the making of flint glass (also called lead glass), and as a coloring agent in pottery glaze. When mixed with glycerin it sets as a hard cement, and has been used as a two-part, colored glue. "Red lead", a lead plumbate, Pb_2PbO_4, is the form used in flint glass, and the red-orange undercoat on iron and steel for fencing and building construction as it is both stable and inert under normal atmospheric conditions so it protects metals against weathering effects.

Because the lead-ion, Pb^{++}, is poisonous, lead piping for drinking water (soft water), lead paints, and leaded gasolines are being replaced due to the health hazard. Lead hydroxide, $Pb(OH)_3$, is the culprit, as it is fairly soluble in soft water and builds up in water piping.

Technical Application: Lead oxide is a IV—VI compound semiconductor with tetragonal system structure rather than isometric-tetragonal, as are several other compound semiconductors. It has the typical (111) polarity of these compounds, such that wafers are normally cut with the (100) orientation for device processing.

It has limited use as a semiconductor, in part due to its softness (H = 2—3, vs. H = 6—7 for most semiconductor materials). It has been grown as a single crystal ingot and as single crystal platelets under pressure with two crystal structures depending upon pressure: under 2200 psi, tetragonal; over 30,000 psi, orthorhombic, respectively, red-orange and yellow-green in color. It has been grown as a single crystal epitaxy thin film and fabricated as photoconductors.

Etching: Litharge is soluble in HNO_3, alkalies and several chloride salts. Massicot is soluble in alkalies.

LEAD OXIDE ETCHANTS

PBO-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
1 .... HAc
1 .... H_2O_2
DISCUSSION:
Pb specimens and single crystal ingots. Solution is a general cleaner and etchant for lead and for removal of lead oxide.
REF: Snowden, K V — *Phil Mag*, 6,321(1961)

PBO-0002
ETCH NAME: TIME:
TYPE: Knife, cleave clean TEMP: RT
COMPOSITION:
x .... knife cut
DISCUSSION:
PbO single crystal plates grown at 400°C under pressure: (1) at less than 2200 psi, structure is tetragonal and orange-red in color; (2) at greater than 30,000 psi structure is orthorhombic and color is yellow-green. Grown in a quartz ampoule in an autoclave with a slurry of NaOH + PbO — crystal platelets grow on ampoule sides. When the orthorhombic form is cleaved with a scalpel some areas of specimen surfaces were converted to tetragonal.
REF: Keezer, R C et al — *J Appl Phys*, 39,2062(1968)

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PBO-0003
ETCH NAME: TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
x .... HAc
x .... H_2O_2
DISCUSSION:
PbO, native oxide removed from lead. Solution used in cleaning lead telluride, $PbTe_2$, surfaces.
REF: Sato, Y et al — *Jpn J Appl Phys*, 2,688(1963)

PHYSICAL PROPERTIES OF LEAD NITRATE, $Pb(NO_3)_2$

Classification	Nitrate
Atomic numbers	82, 7 & 8
Atomic weight	331.23
Melting point (°C)	470
Boiling point (°C)	
Density (g/cm³)	
Refractive index (n =)	1.782
Hardness (Mohs — scratch)	4—5
Crystal structure (isometric — normal) alpha	(100) cube
(monoclinic — normal) beta	(100) a-pinacoid
Color (solid)	Colorless
Cleavage (octahedral/cubic)	(111)/(001)

LEAD NITRATE, $Pb(NO_3)_2$

General: Does not occur as a natural compound although some nitrate fertilizers may be artificially compounded to contain trace lead. No present use in the metal industries, but has chemical and medical applications.

Technical Application: The material has no use in Solid State device development, but has been grown from solution in a structural study, and the effects of irradiation on the development of NO_3^- and other radicals. Similar irradiation effects with development of F^- centers have been done on fluorite, CaF_2, natural crystals, and other transparent crystals, e.g., NaCl, KCl, etc. as ionic and alkaline crystals.

Etching: Water, alcohols.

LEAD NITRATE ETCHANTS

PBNO-0001
ETCH NAME: Water TIME:
TYPE: Solvent, polish TEMP: RT
COMPOSITION:
(1) x .... H_2O or (2) x .... EOH
DISCUSSION:
$Pb(NO_3)_2$ grown as single crystals by slow cooling from a water solution. Crystals were triangular with a (111) base, and were cubic space group T^6n with trigonal axes. Crystals were studied after irradiation to develop for NO_3^-, NO_2^-, and O_3^- centers. Solutions shown used to polish specimens prior to irradiation.
REF: Tagaya, K & Kitagawa, M — *Jpn J Appl Phys*, 23,116(1984)

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PHYSICAL PROPERTIES OF LEAD SELENIDE, PbSe

Classification	Selenide
Atomic numbers	82 & 34
Atomic weight	286.15
Melting point (°C)	1065
Boiling point (°C)	
Density (g/cm^3)	7.6—8.8
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Lead-grey/bluish
Cleavage (cubic)	(001)

LEAD SELENIDE, PbSe

General: Occurs as the natural mineral clausthalite, PbSe, which may contain traces of both mercury and platinum. It looks much like galena, PbS, though with a slightly more bluish cast of color. It is found in small quantities associated with hematite, Fe_2O_3, a primary iron ore, and there are several additional minerals with individual names that contain clausthalite as part of mixed crystals. Due to scarcity, it has no major use in industry other than as a minor ore of selenium and lead.

Technical Application: The material is a IV—VI compound semiconductor with the sphalerite, ZnS, atypical isometric-tetragonal structure. It is a polar compound with (111)Pb and $(\overline{111})$Se wafer surfaces and, because of the difference in etching characteristics of (111) polar surfaces, is normally used with the (100) surface orientation to obviate the polarity effect. As with several of the compound semiconductors, it was originally grown by the Horizontal Bridgman (HB) technique as a single crystal but now is more commonly grown by the Czochralski (CZ) method. Vapor Phase Epitaxy (VPE) has been used to grow single crystal thin films.

It has the same softness problem (H = 2—3) as does lead oxide, PbO, so has not been widely used as a semiconductor ingot-grown product, though epitaxy thin films have been used to fabricate laser devices. Note that selenium and several of its salts are poisonous.

Etching: Easily soluble in halogens and HNO_3. Electrolytically with alkalies.

LEAD SELENIDE ETCHANTS

PBSE-0001a
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
DISCUSSION:
PbSe, (100) wafers and other orientations. Author calls solution an immersion etch for PbSe, PbTe, and PbS.
REF: Swets, D E — *J Electrochem Soc,* 131,172(1984)

TIME:
TEMP:
RATE: 0.37 mg/min

PBSE-0001b
ETCH NAME: Hydrogen bromide
TYPE: Halogen, polish
COMPOSITION:
x .... HBr

TIME: 3 min
TEMP: RT

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DISCUSSION:

PbSe, (100) wafers and other orientations. Used as an immersion polish etch on PbSe, PbTe, and PbS. Also used as a jet/spray etch from a squirt bottle followed with water jet/spray quenching.

REF: Ibid.

PBSE-0001c

ETCH NAME: Hydrogen bromide, dilute

TYPE: Electrolytic, polish

COMPOSITION:

1 .... HBr

3 .... H_2O

TIME:

TEMP:

ANODE: PbSe

CATHODE:

POWER: 20 mA/cm^2

50—100 mV

RATE: 0.2 μm/min

DISCUSSION:

PbSe, (100) wafers and other orientations. Solution used to electropolish both PbSe and PbS. Leaves a yellow film on the surface that can be removed with a dip in nitric acid.

REF: Ibid.

PBSE-0002

ETCH NAME:

TYPE: Electrolytic, polish/thin

COMPOSITION:

5 .... 45% KOH

1 .... H_2O_2

5 .... ethylene glycol (EG)

TIME:

TEMP:

ANODE: PbSe

CATHODE:

POWER:

DISCUSSION:

PbSe, (100) wafers used in a study of dislocations and structure. Solution used to thin specimens for TEM study.

REF: Abrams, H & Tauber, R N — *J Electrochem Soc*, 116,103(1969)

PBSE-0003: Gatos, H C & Lavine, M C — *Prog Semicond*, 9,1(1965)

PbSe, (100) wafers and other orientations. Solution used as a wet chemical etch at 40°C, 3 min.

PBSE-0004

ETCH NAME: Nitric acid, dilute

TYPE: Acid, cleaning

COMPOSITION:

1 .... HNO_3

5 .... H_2O

TIME:

TEMP: RT

DISCUSSION:

PbSe, (100) cleaved wafers. A study of electron and hole mobility between RT and 4.2 K. Material has NaCl cubic structure. Solution can be used to lightly clean surfaces. PbS and PbTe also studied.

REF: Allgaier, R S — Scanlon, W W — *Phys Rev*, 111,1029(1958)

PBSE-0005: Allgaier, R S — *Phys Rev*, 112,828(1958)

PbSe, (100) cleaved wafers. A study of magnetoresistance at 295, 77, and 4.2 K. Solution can be used to clean surfaces. PbS and PbTe also studied.

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LEAD TIN SELENIDE ETCHANTS

PBTS-0001
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... KOH, sat. sol.
1 .... Na_2SO_3, sat. sol.
5 .... glycerin
TIME: 10—15 min
TEMP: 40°C
ANODE: PbSnSe
CATHODE: Pt
POWER: 0.04 A/cm^2
RATE: 1 μm/min
DISCUSSION:

PbSnSe, (100) wafers 1 mm thick, p-type, 100—150 Ω cm resistivity. Use varnish coated SST tweezers to hold specimens to prevent iron contamination during etching. Solution used to polish specimens.
REF: Quadeer, A et al — *J Electrochem Soc*, 129,2145(1982)

PHYSICAL PROPERTIES OF LEAD SULFIDE, PbS

Classification	Sulfide
Atomic number	82 & 16
Atomic weight	239.72
Melting point (°C)	1114
Boiling point (°C)	
Density (g/cm^3)	7.5
Refractive index (n =)	3.912
Hardness (Mohs — scratch)	2.5—2.75
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Lead-grey
Cleavage (cubic — perfect)	(100)

LEAD SULFIDE, PbS

General: The major natural mineral is galena, PbS, often found as single crystal cubes with square, step-fractured faces. It is the most widely distributed metallic sulfide in the world, commonly formed by hydrochemical reactions, and found in large beds and vein ore bodies in both metamorphic and sedimentary rocks. Though 75% of the galena mined in the U.S. is called "soft lead", galena in other areas may contain sufficient gold and silver to make the mineral more valued for its precious metal content. Cerussite, $PbCO_3$, and anglesite, $PbSO_4$, are also important ores of lead, but galena is by far the most widely mined. Well over two million tons are mined annually.

Primarily, industrial use is as an ore of lead. Natural galena single crystals were the first radiofrequency crystals using a wire point contact on the surface. Because specific frequencies are not defined in the mineral, the operator shifted the point probe until he picked up the desired frequency. Alpha-quartz crystals, both natural and now artificial, have replaced galena since the early 1920s, as quartz can be oriented and cut to produce specific frequency ranges as AT, DT, BT, Y, X-cut, etc.

Technical Application: Lead sulfide is a IV—VI compound semiconductor with distinctive isometric — normal (cubic) structure, rather than the more common isometric — tetragonal (zincblende, ZnS) structure of several other compound semiconductors. It is a polar compound with (111)Pb and $(\overline{1}\overline{1}\overline{1})$S surfaces and, as others of this type, is normally used in (100) wafer surface orientation in order to obviate the polarity problems in device processing.

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It can be artificially grown from solutions containing various chemical compounds but, in Solid State semiconductor applications, single crystal ingots are grown by the Bridgman, Czochralski, or Float Zone methods.

Both artificial and natural crystals of galena have been the subject of much study. Like several of the compound semiconductors it can be easily cleaved as a (100) surface, and has been studied as-cleaved or after further polish processing. It has also been grown by Vapor phase epitaxy (VPE) as a single crystal thin film, and such thin film structures have been fabricated as laser and photoconductor diodes. It has the same softness problem as do PbO, PbSe.

Etching: Soluble in acids and halogens. Electrolytic halogens. Slightly soluble in water.

LEAD SULFIDE ETCHANTS

PBS-0001
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
1 .... HCl
3 .... *H_2NCSNH_2

TIME: 1 min
TEMP: 60°C

*Thiourea 100 g/l.

DISCUSSION:

PbS, (100) wafers used in a study of dislocation development as a function of stoichiometry. The authors say that pits obtained from cleaved surfaces are larger and better formed than those from lapped and etch polished surfaces.

REF: Frankin, W M & Wagner, J B Jr — *J Appl Phys,* 34,3121(1963)

PBS-0003: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970, 7

PbS, (100) wafers used in a dislocation etch study. Thiourea (3—10%) in HCl at 60°C, 10 min was used as a preferential etch solution.

PBS-0004: Scanlon, W W — *Phys Rev,* 106,718(1957)

PbS, (100) wafers used in a study of carrier lifetime. Solution used between 60 to 80°C.

PBS-0005: Lyall, K D & Paterson, M S — *Acta Metall,* 14,371(1966)

PbS, (100) cleaved wafers from natural galena used in a study of plastic deformation. Developed edge dislocations and twinning on the (441) plane.

PBS-0002a
ETCH NAME: Nitric acid
TYPE: Acid, removal/polish
COMPOSITION:
x .... HNO_3

TIME:
TEMP: RT
RATE: 23 mg/min

DISCUSSION:

PbS, (100) wafers used in a study of etching to obtain low resistance. Solution used as an immersion etch followed by running DI water rinse. Can also be used to remove yellow stain left on surfaces after electrolytic etching in HBr:H_2O.

REF: Swets, D E — *J Electrochem Soc,* 131,172(1984)

PBS-0006: Walker, P — mineralogy study, 1952—1953

PbS, (100) surfaces as natural single crystal galena specimens used in a general structure study. A 1:1 dilute solution used to clean surface to remove natural discoloration. Specimens also cleaved and studied under a microscope without any surface treatment.

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PBS-0002b
ETCH NAME: Hydrogen bromide
TYPE: Halogen, polish
COMPOSITION:
x .... HBr
DISCUSSION:
PbS, (100) wafers used in a study of etching to obtain low resistance. Solution used as an immersion etch on PbS, PbTe, and PbSe. Also used as a jet-spray from a squirt bottle on PbSnTe and PbSe followed by rinsing in running DI water.
REF: Ibid.

TIME: 3 min
TEMP: RT
RATE: 23 mg/min

PBS-0002c
ETCH NAME: Hydrogen bromide, dilute
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HBr
3 .... H_2O
DISCUSSION:
PbS, (100) wafers used in a study of etching to obtain low resistance. Solution used as a general removal and polishing etch. Yellow film remaining on surfaces removed with nitric acid. Also used on PbSe. This etching gave the lowest surface resistance, Rc.
REF: Ibid.

TIME:
TEMP:
ANODE:
CATHODE: PbS
POWER: 20 mA/cm^2 & 50—100 mV
RATE: 0.2 μm/min

PBS-0007
ETCH NAME: Nitric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HNO_3
5 .... H_2O
DISCUSSION:
PbS, (100) cleaved wafers. A study of electron and hole mobility from RT to 4.2 K. Material has NaCl cubic structure. Solution can be used to lightly clean surfaces. PbSe and PbTe also studied.
REF: Allgaier, R S & Scanlon, W W — *Phys Rev*, 111,1029(1958)
PBS-0008: Allgaier, R S — *Phys Rev*, 122,828(1958)
PbS, (100) cleaved wafers. A study of magnetoresistance at 295, 77, and 4.2 K. Solution can be used to lightly clean surfaces. PbSe and PbTe also studied.

TIME:
TEMP: RT

PHYSICAL PROPERTIES OF LEAD TELLURIDE, PbTe

Classification	Telluride
Atomic numbers	82 & 52
Atomic weight	334.79
Melting point (°C)	>700
Boiling point (°C)	
Density (g/cm^3)	8.16
Hardness (Mohs — scratch)	3
Crystal structure (isometric — normal)	(100) cube

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Color (solid)	Tin-white/yellowish
Cleavage (cubic)	(100)

LEAD TELLURIDE, PbTe

General: Occurs as the mineral altaite, PbTe, usually in massive form but with cubic cleavage, occasionally as cubic or octahedral crystals. Although the color is tin-white, it oxidizes with a yellowish surface coating and can tarnish to deep bronze-yellow. It is found in limited quantities in Russia, Chile, Mexico, and in the U.S. No use in industry other than as a compound semiconductor.

Technical Application: Lead telluride is a IV—VI compound semiconductor and, like other lead compound semiconductors is isometric — normal (cubic) rather than tetrahedral class, as are many other similar compounds, such as gallium arsenide.

It has been grown as single crystal ingots by the Bridgman, Czochralski, and Float Zone methods, and is usually used as a cut or cleaved (100) oriented wafer due to (111) polarity problems. It also has been grown as an epitaxy thin film for device fabrication.

As a thin film it has been used to fabricate both infrared detectors and laser diodes.

Etching: Soluble in acids, mixed acids as well as alkali and halogens.

LEAD TELLURIDE ETCHANTS

PBTE-0001a
ETCH NAME: Iodine etch
TYPE: Halogen, preferential
COMPOSITION:
5 g .... NaOH
0.2 g .... I_2
10 ml .... H_2O
TIME: 5 min
TEMP: 95°C
DISCUSSION:

PbTe, (100) cleaved wafers used in a study of defects and the effect of heat treatment. Solution produced pyramidal etch pits prior to heat treatment. Re-etching after heat treatment would not produce etch pits until surfaces were lapped with SiC abrasive paper and again re-etched.

REF: Sato, Y et al — *Jpn J Appl Phys*, 2,688(1963)

PBTE-0001b
ETCH NAME:
TYPE: Electrolytic, polish/preferential
COMPOSITION:
"A" 20 g .... NaOH/KOH
45 ml .... H_2O
"B" 25 ml .... glycerol
"C" 20 ml .... EOH
TIME: 30 min
TEMP: RT
ANODE: PbTe
CATHODE:
POWER: 1 V & 6 V
RATE: 7 μm/min
DISCUSSION:

PbTe, (100) wafers. To mix the solution: (i) mix solution "A", then (ii) add "B" and "C" and stir to form a miscible solution. Initially polish etch at 6 V with removal rate as shown. Requires about 200 μm removal to eliminate damage induced from SiC lapping of surfaces, e.g., 30 min etching. Reduce voltage to 1 V and continue etching for an additional 15 sec to develop etch pits.

REF: Ibid.

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PBTE-0002a
ETCH NAME: Iodate etch
TYPE: Halogen, preferential
COMPOSITION:
5 g .... NaOH
10 ml .... 0.5% $NaIO_3$
TIME:
TEMP:
DISCUSSION:
PbTe, (100) wafers. Solution applied as a dislocation etch for lead telluride. Also used iodine etch (see PBTE-0002b).
REF: Houston, B & Norr, M K — *J Appl Phys*, 31,616(1960)

PBTE-0002b
ETCH NAME: Iodine etch
TYPE: Alkali, preferential
COMPOSITION:
5 g .... NaOH
2 g .... I_2
10 ml .... H_2O
TIME: 5 min
TEMP: 94—98°C
DISCUSSION:
PbTe, (100) wafers. Used solution as a dislocation etch for PbTe.
REF: Ibid.

PBTE-0003a
ETCH NAME: Hydrogen bromide
TYPE: Halogen, polish
COMPOSITION:
x .... HBr
TIME: 3 min
TEMP: RT
RATE: 0.1 mg/min
DISCUSSION:
PbTe, (100) wafers. Used as an immersion polish solution for PbTe, PbSe, and PbS. PbSnTe and PbSe etched with solution in a squirt bottle, then rinsed with running DI water.
REF: Swets, D E — *J Electrochem Soc*, 131,172(1984)

PBTE-0003b
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP: RT
RATE: 0.1 mg/min
DISCUSSION:
PbTe, (100) wafers. Used as an immersion etch on PbTe, PbSe, and PbS for general removal and cleaning.
REF: Ibid.

PBTE-0004
ETCH NAME:
TYPE: Acid, oxide removal
COMPOSITION:
1 .... HAc
1 .... H_2O_2
TIME:
TEMP:

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DISCUSSION:

PbTe, (100), p-type wafers used in a study of nickel and chlorine diffusion at 700°C. Solution used to remove surface native oxide after lapping and prior to diffusion.

REF: George, T D & Wagner, J B Jr — *J Electrochem Soc,* 115,956(1968)

PBTE-0005

ETCH NAME:

TYPE: Alkali, dislocation

TIME: 10 min

TEMP:

COMPOSITION:

2 .... 15% NaOH

1 .... $Na_2S_2O_8$

DISCUSSION:

PbTe, (100) wafers. Used as a dislocation etch.

REF: Harper, C A — *Handbook of Materials and Processes for Electronics,* McGraw-Hill, New York, 1970, 7

PBTE-0006: Brybick, R F & Scanlon, W W — *J Chem Phys,* 27,607(1957)

PbTe, (100) and other orientations. Several etches described for defect etching of PbTe, PbSe and PbS.

PBTE-0011

ETCH NAME:

TYPE: Acid, polish

TIME:

TEMP: 25°C

RATE: 20—40 μm/min

COMPOSITION:

9 ml .... HNO_3

40 ml .... $K_2Cr_2O_7$, sat. sol.

DISCUSSION:

PbTe, (100) wafers used in development of a good chemical polish solution. Specimens were in a basket and solution agitated on a magnetic stirring hot plate. After etch, rinse in DI water. If a gold colored film appears, etch in 50% NaOH at 100—120°C, from cool (20°C?) up to RT, rinse in dilute HCl, and DI water rinse. See Tin and Germanium Telluride for additional data.

REF: Lorenz, M R — *J Electrochem Soc,* 112,240(1965)

PBTE-0008: Allgaier, R S — *Phys Rev,* 119,554(1960)

PbTe, (100) cleaved wafers used to study field magnetoresistance at room temperature and 77 K.

PBTE-0008

ETCH NAME:

TYPE: Acid, float-off

TIME:

TEMP:

COMPOSITION:

x .... HNO_3

x .... H_2O

DISCUSSION:

PbTe, thin film grown on muscovite mica (0001) substrates. Thin films were removed by the float-off technique using the solution shown for a structure study under a TEM microscope. See Mica: MI-0002.

REF: Chopea, K I — *J Appl Phys,* 37,2049(1960)

PBTE-0009: Allgaier, R S & Scanlon, W W — *Phys Rev,* 111,1029(1958)

PbTe, (100) cleaved wafers. A study of electron and hole mobility between RT and 4.2 K. A $1HNO_3$:$5H_2O$ can be used at RT for light surface cleaning. PbS and PbSe also studied.

PBTE-0010: Allgaier, R S — *Phys Rev,* 122,828(1958)

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PbTe, (100) cleaved wafers. A study of magnetoresistance at 295, 77, and 4.2 K. Material has NaCl cubic structure. A $1HNO_3{:}5H_2O$ solution can be used at RT for light surfaces cleaning. Also studied PbS and PbSe.

PBTE-0012
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... KOH, sat. sol.
1 .... Na_2SO_3, sat. sol.
5 .... glycerol

TIME: 4—7 min or 10—15 min
TEMP: RT or 40°C
ANODE: Pt
CATHODE: PbTe
POWER: 0.04 A/cm^{-2} or 0.09 A/cm^{-2} @ 4 V

DISCUSSION:
PbTe, (100), and PbSnTe, (100) wafers, 1 mm thick with 100—150 μm of damage depth from cutting. Lap specimens as follows: (1) 800-grit SiC:H_2O slurry to remove 150 μm of material; (2) 1200-grit SiC:Glycerol to remove 50 μm; (3) final lap polish with 0.3 μm Linde alumina in paraffin or with "Brasso". For electrolytic etching, hold specimens with varnished tweezers: (1) 10—15 min at lower power to polish; (2) 4—7 min at higher power to develop slightly rounded, square dislocation pits. See: PBTT-0002.
REF: Quadeer, S et al — *J Electrochem Soc,* 129,2181(1982)

LEAD GERMANIUM TELLURIDE ETCHANTS

PBGT-0001
ETCH NAME:
TYPE: Halogen, preferential
COMPOSITION:
5 g .... NaOH
2 g .... I_2
10 ml .... H_2O

TIME:
TEMP:

DISCUSSION:
PbGeTe single crystal ingots grown by Horizontal Bridgman (HB) method using PbTe and Ge pieces as starting materials. The ingots were cubic with a temperature transition to rhombohedral. Transition temperature varies with amount of Ge fraction. Solution used to develop defects and structure.
REF: Tsuji, K — *J Phys Soc Jpn,* 4,1397(1984)

LEAD TIN TELLURIDE ETCHANTS

PBTT-0001
ETCH NAME: Hydrogen bromide
TYPE: Halogen, polish
COMPOSITION:
x .... HBr

TIME: 3 min
TEMP: RT

DISCUSSION:
PbSnTe, (100) wafers. Used as an immersion polish etch on PbS, PbSe, PbTe, and PbSnTe. Also used as a jet/spray from a squirt bottle followed by water jet/spray.
REF: Swets, D E — *J Electrochem Soc,* 131,172(1984)

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PBTT-0002
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... KOH, sat. sol.
1 .... Na_2SO_3, sat. sol.
5 .... glycerin
TIME: 10—15 min
TEMP: RT to 40°C
ANODE: PbSnTe
CATHODE: Pt
POWER: 0.5 A/cm^{-2} & 6 V
DISCUSSION:

PbSnTe, (100) wafers. Solution developed to electropolish specimens prior to dislocation etching. After cutting wafer, the damage layer is 100—150 μm deep. To remove damage: (1) lap on glass plate with 800-grit SiC in H_2O; (2) with 1200-grit SiC for additional 50 μm removal; (3) final mechanical polish with Linde A in paraffin or "Brasso" on Syvelt cloth; (4) rinse in TCE, then MeOH and (5) N_2 blow dry. Using electrolytic solution at 2 V, 4—7 min will produce a rounded cube, (100) finite crystal form (FCF), using small chunk specimens. During electropolishing stir solution and move specimens to prevent flow lines developing. The solution at the 2 V level also acts as a dislocation etch. Material used to fabricate CW laser diodes.
REF: Quadeer et al — *J Electrochem Soc,* 129,2650(1982)

PBTT-0003a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
25 ml .... KOH, sat. sol.
25 ml .... ethylene glycol (EG)
1 ml .... H_2O_2
TIME:
TEMP:
DISCUSSION:

PbSnTe, (100) wafers cut on inner side of doughnut shaped diamond blade. Mechanically polish, then etch with HBr:2% Br_2 to remove lap damage. Ingot was grown by Bridgman method, and solution shown used to develop etch pits in a material study.
REF: Richard, R C — *J Cryst Growth,* 71,192(1985)

PBTT-0003b
ETCH NAME:
TYPE: Halogen, polish/removal
COMPOSITION:
x .... 2% Br_2
x .... HBr
TIME:
TEMP:
DISCUSSION:

PbSnTe, (100) wafers cut from a Bridgman grown ingot. After mechanical lapping, solution shown used to remove residual lap damage before preferential etching to develop defects and pits. See PBTT-0003a.
REF: Ibid.

LEAD ZIRCONATE ETCHANTS

PBZO-0001a
ETCH NAME: Hydrochloric acid
TYPE: Acid, polish
COMPOSITION:
x .... HCl
TIME:
TEMP:

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DISCUSSION:
$PbZrO_3$, single crystal specimens. Solution is an etch for this material. Specimens used in an optical study. Also $NaNbO_3$ single crystals.
REF: Jona, F et al — *Phys Rev*, 97,1584(1955)

PBZO-0001b
ETCH NAME: Lead sulfate — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... $PbSO_4$
DISCUSSION:
$PbZrO_3$ single crystal specimens. Solution is an etch for this material. See PBZO-0001a for further discussion.
REF: Ibid.

PBZO-0001c
ETCH NAME: Sulfuric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
$PbZrO_3$ single crystal specimens. Solution is an etch for this material. See PBZO-0001a for further discussion.
REF: Ibid.

PHYSICAL PROPERTIES OF LITHIUM, Li

Classification	Alkali metal
Atomic number	3
Atomic weight	6.94
Melting point (°C)	180.5
Boiling point (°C)	1336 (1317)
Density (g/cm^3)	0.534
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.17
Specific heat (cal/g) 25°C	0.849
Latent heat of fusion (cal/g)	103.2
Heat of vaporization (cal/g)	5100
Atomic volume (W/D)	13.1
1st ionization energy (K-cal/g-mole)	124
1st ionization potential (eV)	5.39
Electronegativity (Pauling's)	1.0
Covalent radius (angstroms)	1.23
Ionic radius (angstroms)	0.86
Electrical resistivity (micro-ohms-cm) 20°C	9.446
Electron work function (eV)	2.39
Cross section (barns)	71
Vapor pressure (°C)	1097
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	56
Refractive index (n =)	3.16
Hardness (Mohs — scratch)	1—2

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Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Silver white
(flame)	Carmine-red
Cleavage (cubic — poor)	(001)

LITHIUM, Li

General: Does not occur as a free element in nature. There are over a dozen lithium-bearing minerals as silicates, fluorates, and phosphates. Spodumene, $LiAl(SiO_3)_2$, is the primary ore and occurs in acidic pegmatites, occasionally in single crystals of large size — 4 to 5 ft long, over a foot in diameter. The fine, transparent, emerald-green variety is a precious gem stone. Lithium metal is very soft, silver-white in color, and the lightest of all known metals. The metal is classified as an alkaline metal, and its salts are similar to those of sodium and potassium. When ignited, lithium produces a brilliant crimson flame.

In industry it is used with several irons/steels and other metals as an additive to increase tensile strength and for resistance to corrosion. Because of its brilliant red color when burned it is a major component in flares and pyrotechnics. Several salts, notably lithium chloride, LiCl, have important medical applications, and are used in glass to increase ultraviolet transmission. Other lithium compounds improve the gloss in enamels.

Technical Application: The pure metal has limited use in Solid State or semiconductor processing. It has been evaporated along with aluminum on quartz crystal frequency blanks to reduce mass-loading and improve frequency stability and control, and may have similar applications in high frequency microelectronic devices, e.g., gallium arsenide. As a diffusant in germanium, lithium-drift radiation detectors have been fabricated. Lithium reacts with water and moisture in the air, is stored in oil and handled in a dry atmosphere. Single crystals spheres have been fabricated and subjected to study.

Etching: Soluble in acids, but deliquesces in water and alcohols.

LITHIUM ETCHANTS

LI-0001
ETCH NAME: Nitric acid
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... HNO_3
DISCUSSION:
Li, specimens. Lithium is soluble in most single acids. Should be handled in a dry inert atmosphere as it reacts with water vapor in air forming lithium hydroxide.
REF: Hodgman, C D — *Handbook of Chemistry and Physics,* 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 402

LI-0002
ETCH NAME: Heat — TIME:
TYPE: Thermal, forming — TEMP:
COMPOSITION:
x .... heat
DISCUSSION:
Li, single crystal spheres fabricated by melting small pieces of lithium in paraffin with light stirring, and then allowing it to solidify.
REF: Splitstone, P L — Doctoral thesis, Ohio State University, Columbus, 1955
LI-0003: Holcomb, D F — *Phys Rev,* 112,1599(1958)

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Li, single crystal spheres, 50 μm diameter handled in oil and used in a magnetic resonance study.

LI-0004: Holcomb, D F & Norberg, R E — *Phys Rev*, 98,1074(1955)

Li, single crystal spheres in oil? Used in an electronic characterization study.

LI-0005

ETCH NAME: Lithium — TIME:

TYPE METAL: Diffusant — TEMP: 1000°C

COMPOSITION:

x .... Li, in oil

DISCUSSION:

Li, powder in oil used as a diffusant source for germanium. Germanium rods were cut from (111) surface oriented wafers, painted with Li/oil and diffused. After diffusion specimens electrically stabilized in hot oil bath under power load. Devices used to fabricate lithium-drift germanium radiation detectors.

REF: Walker, P — personal development, 1959

LI-0006

ETCH NAME: Methyl alcohol — TIME: 30 sec

TYPE: Alcohol, polish — TEMP: RT

COMPOSITION:

(1) x .... MeOH (CH_3OH) (2) x .... EOH (CH_3CH_2OH) (3) x .... 2-propanol (IPA) ($CH_3CHOHCH_3$)

DISCUSSION:

Li samples cut with a razor blade under oil (also cut sodium and potassium), then into heptane to remove oil, then into tetrahydrofuran to stop heptane removal action. Ten alcohols evaluated with increasing molecular weight which reduces in activity. On lithium, MeOH polished surfaces; on sodium developed grain boundaries, and some brilliantly reflective (hkl) planes, with other planes dull and all pitted; on potassium reaction was violent. Ethyl alcohol, CH_3CH_2OH (EOH) developed grain boundaries and (hkl) polished surface on lithium; on sodium developed grain boundaries with (hkl) planes both brilliant or dull with pitting; on potassium, polished surfaces. 2-Propanol $CH_3CHOHCH_3$ (IPA) on lithium was like EOH; on sodium like EOH but without pitting; on potassium developed polished surfaces. All other alcohols evaluated were not polishing solutions: black surfaces on lithium; grain boundaries with (hkl) planes brilliant to dull with and without pitting on sodium, and dull, pitted surfaces for potassium, in general.

REF: Castellano, R N & Schmidt, P H — *J Electrochem Soc*, 118,653(1971)

LI-0007

ETCH NAME: Diethyl ether — TIME:

TYPE: Organic oxide, polish — TEMP:

COMPOSITION:

x .... $C_4H_{10}O$

DISCUSSION:

Li specimens. Pre-polish surfaces with methanol (MeOH), then final polish with ether. (*Note:* Ether should be handled with caution as it can be flammable and explosive when mixed with air.)

REF: Bowers, R et al — *Material Science Center Rep #3*, Cornell University, Ithaca, NY, 1961

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LI-0008
ETCH NAME: Potassium nitrate
TYPE: Salt, removal
COMPOSITION:
x .... KNO_3, crystals
TIME: x hours
TEMP: 300°C
DISCUSSION:
Li, applied as molten LiOH on rutile, TiO_2 specimens to metal decorate dislocations in rutile. After decoration use the molten flux salt shown to remove excess lithium.
REF: Johnson, O W — *J Appl Phys*, 35,3048(1964)

LITHIUM BISMUTHIDE ETCHANTS

LIBI-0001
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... x% Br_2
x .... MeOH
TIME:
TEMP: RT
DISCUSSION:
Li_3Bi single crystal ingots grown in a study of new semiconducting compounds. Other compounds were Ag_2Se, TlSe, Tl_2Se_3, SnSe, $SnSe_2$, In_2Tl_3, Bi_2Se_3, $AgInTe_2$, In_2Te_3.
REF: Mooser, E & Pearson, W B — *Phys Rev*, 101,492(1956)

PHYSICAL PROPERTIES OF LITHIUM BROMIDE, LiBr

Classification	Bromide
Atomic numbers	3 & 35
Atomic weight	86.36
Melting point (°C)	547
Boiling point (°C)	1265
Density (g/cm³)	3.46
Hardness (Mohs — scratch)	1.5—2
Crystal structure (isometric — normal)	(100) cube
Color (solid)	White
Cleavage (cubic)	(001)

LITHIUM BROMIDE, LiBr

General: Does not occur as a natural mineral although both the bromide and chloride are found in some mineral springs and in the soil. Both beets and tobacco retain lithium, but the solid is deliquescent in air. There are two major minerals containing lithium: petalite, $LiAl(Si_2O_5)_3$ with about 5% lithium and lepidolite mica, chiefly $(OH),F)_2KLiAl_2Si_3O_{10}$, and it is found in other minerals that are characteristic of granite pegmatites, such as spodumene, $LiAl(SiO_3)_2$ with 8.4% lithium.

A primary industrial use, as a mixture of lithium bromide and chloride, is in the electrolysis of lithium minerals for their metal content. Lithium compounds have major use in the glassy industry as a flux, to improve the electrical insulating properties and to increase ultraviolet transmission. They also are used in enamels to improve gloss, and have medical applications.

Technical Application: Lithium bromide is not used in Solid State device processing

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although it could be used in preferential etching solutions. The compound has been grown as a single crystal for general morphology and defect studies.

Etching: Soluble in water, alcohols and ether.

LITHIUM BROMIDE ETCHANTS

LIBR-0001
ETCH NAME:
TYPE: Alcohol, defect
COMPOSITION:
x .... amyl alcohol
x .... $BaBr_2$ (trace)

TIME: 5—10 sec
TEMP: RT

DISCUSSION:

LiBr, (100) cleaved wafers used in a study of slip. After etching in solution shown, rinse in petroleum and air dry. Also studied LiCl.

REF: MacMillan, N H & Smith, D A — *Phil Mag*, 14,869(1966)

PHYSICAL PROPERTIES OF LITHIUM CHLORIDE, LiCl

Classification	Chloride
Atomic number	3 & 17
Atomic weight	42.40
Melting point (°C)	613
Boiling point (°C)	1353
Density (g/cm³)	2.07
Hardness (Mohs — scratch)	1.5—2
Crystal structure (isometric — normal)	(100) cube
Color (solid)	White
Cleavage (cubic)	(001)

LITHIUM CHLORIDE, LiCl

General: Does not occur as a natural compound as it is deliquescent in air. It does occur in some mineral springs and in the soil. Beets and tobacco both contain lithium. There are several minerals containing lithium, such as petalite, $LiAl(Si_2O_5)_3$; lepidolite mica, chiefly $(OH)_2KLiAl_2Si_3O_{10}$; and in granitic pegmatites, the mineral spodumene, $LiAl(SiO_3)_2$ as the primary ore of lithium.

Mixtures of the bromide and chloride are used in the electrolysis of lithium-bearing minerals for the separation of the metal. Lithium compounds are used in the glass industry as a flux, to improve electrical insulating properties and to increase ultraviolet transmission. Also used in enamels to improve gloss, and there are important medical applications. They are the red flame color (lithium) in flares and pyrotechnics.

Technical Application: Lithium chloride is not used in Solid State device processing, although it could be used in etching solutions.

The compound has been grown as a single crystal for general morphology and defect studies.

Etching: Soluble in water, alcohols, and acetic acid.

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LITHIUM CHLORIDE ETCHANTS

LICL-0001
ETCH NAME:
TYPE: Alcohol, defect
COMPOSITION:
x .... isopropyl alcohol
x .... *$BaBr_2$

TIME: 10 sec
TEMP: RT

*Saturate the alcohol.

DISCUSSION:
LiCl, cleaved wafers used in a study of slip. After etching in the solution shown, rinse in CCl_4 and air dry. Also studied LiBr.
REF: MacMillan, N H & Smith, D A — *Phil Mag*, 14,869(1966)

LICL-0002
ETCH NAME:
TYPE: Acid, dislocation
COMPOSITION:
x .... x% $FeCl_3$

TIME:
TEMP:

DISCUSSION:
LiCl wafers. Solution referred to as a dislocation etch for ionic crystals. Used in a study of reduced cohesion due to dislocations.
REF: Gilman, J J — *J Appl Phys*, 32,739(1961)

PHYSICAL PROPERTIES OF LITHIUM FLUORIDE, LiF

Classification	Fluoride
Atomic numbers	3 & 9
Atomic weight	25.94
Melting point (°C)	870
Boiling point (°C)	1676
Density (g/cm^3)	2.3
Hardness (Mohs — scratch)	1.5—2
Crystal structure (isometric — normal)	(100)
Color (solid)	Colorless
Cleavage (cubic — perfect)	(001)

LITHIUM FLUORIDE, LiF

General: Does not occur in nature as a single crystal compound. The fluoride mineral cryolithionite, $2NaF.3LiF.2AlF_2$ occurs in association with cryolite, Na_2AlF_6 as a minor mineral species.

Primary use industrially is as a replacement for natural calcium fluoride in the fabrication of prisms. Like lithium bromide and chloride it is used in the glass industry to improve electrical insulation and ultraviolet transmission characteristics and as a flux. Also used as the red color (lithium) in flares and pyrotechnics. Cryolite is a major flux and growth compound in metal processing.

Technical Application: Lithium fluoride is not used in Solid State device fabrication,

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but it has been grown as an artificial single crystal and studied for general morphology and defects. It is used in the fabrication of prisms and special lenses.

Etching: Slightly soluble in cold water; soluble in acids.

LITHIUM FLUORIDE ETCHANTS

LIF-0001a
ETCH NAME: CP4, modification
TYPE: Acid, dislocation
TIME: 30 sec
TEMP: RT
COMPOSITION:
100 ml .... HF
100 ml .... HAc
160 ml .... HNO_3
2 ml .... Br_2
DISCUSSION:

LiF, (100) cleaved wafers. Used iron forceps to hold specimens. Iron slowly dissolves in the solution and reduces the fast acid reaction. Rinse in ethyl alcohol and then in ether.
REF: Gilman, J J & Johnston, W S — *J Appl Phys*, 27,1018(1956)
LIF-0006: Davisson, J W et al — *J Appl Phys*, 35,3017(1964)

LiF, (111) wafers. Solution used to develop imperfections in specimens that were associated with electrical breakdown.

LIF-0002b
ETCH NAME:
TYPE: Acid, dislocation
TIME: 1 min
TEMP: RT
COMPOSITION:
x .... 2×10^6 *N* FeF_3
x .... H_2O
DISCUSSION:

LiF, (100) cleaved wafers. Mix solution and use immediately with vigorous stirring. Rinse in EOH then ether. Fresh solution will produce 10 μm size pyramid etch pits. An "aged" solution applied to the same specimen develops the old pits only as mounds.
REF: Gilman, J J et al — *J Appl Phys*, 29,747(1958)

LIF-0003a
ETCH NAME: Stearic acid
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
x .... 10^5—10^6 *N* stearic acid
DISCUSSION:

LiF, (100) wafers. Various fatty acids were evaluated as dislocation etchants for lithium fluoride. This is one of the better fatty acids for developing dislocations.
REF: Westwood, A R C et al — *J Appl Phys*, 33,1764(1962)

LIF-0004
ETCH NAME: Hydrogen peroxide
TYPE: Acid, selective
TIME:
TEMP:
COMPOSITION:
x .... 3% H_2O_2

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DISCUSSION:

LiF, (100) wafers studied for defects. Solution used to develop defects and to selectively etch structure.

REF: Urosovskava, A A — *Kristallografiya,* 3,726(1958)

LIF-0005

ETCH NAME: Ultrasonic

TYPE: Vibration, preferential

COMPOSITION:

x .... ultrasonic

x .... H_2O

TIME:

TEMP: RT

POWER: 0.5 W/cm^2 @ 25 Kc

DISCUSSION:

LiF, (111) cleaved wafers subjected to irradiation by ultrasonic vibration in water. Develops triangular etch pits which become rounded with extended time with more pits appearing near wafer edges. KI and KBr also studied. (*Note:* See SI-0048 — ultrasonic etch-stepping patterns.)

REF: Kapustin, A P — *Sov Phys-Cryst,* 4,247(1960)

LIF-0007

ETCH NAME:

TYPE: Acid, preferential

COMPOSITION:

x .... HF

x .... x% $FeCl_3$

TIME:

TEMP:

DISCUSSION:

LiF, (100) single crystal specimens used in a study of pipe diffusion. Solution used as a defect etch. Sodium diffused in along dislocation lines.

REF: Tucker, R et al — *J Appl Phys,* 34,445(1963)

LIF-0008: Gilman, J J & Johnston, W S — *Dislocations in Crystals,* John Wiley & Sons, New York, 1956, 116

Reference for solution used in LIF-0007.

LIF-0009

ETCH NAME: Ferric chloride

TYPE: Acid, preferential

COMPOSITION:

x .... x% $FeCl_3$

TIME:

TEMP:

DISCUSSION:

LiF, (100) wafers. Solutions of ferric chloride referred to as dislocation etchants for ionic crystals.

REF: Gilman, J J — *J Appl Phys,* 32,739(1961)

LIF-0002b

ETCH NAME: "A" etch

TYPE: Acid, preferential

COMPOSITION:

x .... LiF

x .... H_2O

x .... EOH

TIME:

TEMP:

RATE: (100) 5 Å/sec

(111) 34 Å/sec

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DISCUSSION:
LiF, (100) wafers used in a study of dislocations. Also used "W" etch.
LIF-0011a: Ives, M B — *J Appl Phys*, 32,1534(1961)
LiF, (100) and (111) wafers. Used both "A" and "W" etch in a study of orientation dependence dissolutionment. Rates shown under LIF-0010 are from this reference.

LIF-0002c
ETCH NAME: "W" etch
TYPE: Acid, preferential
COMPOSITION:
x .... $HgCl_2$
x .... EOH
TIME:
TEMP:
RATE: (100) 91 Å/sec
(111) 109 Å/sec
DISCUSSION:
LiF, (100) wafers used in a dislocation study. Also used "A" etch.
REF: Ibid.
LIF-0011b: Ives, M B — *J Appl Phys*, 32,1534(1961)
Li, (100) and (111) wafers. See discussion under LIF-0011a.

PHYSICAL PROPERTIES OF LITHIUM NITRIDE, Li_3N

Classification	Nitride
Atomic numbers	3 & 7
Atomic weight	34.83
Melting point (°C)	845
Boiling point (°C)	
Density (g/cm³)	
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — normal)	(100) cube
Color (solid) crystalline	Grey/black
(solid) amorphous	Red-brown
Cleavage (cubic)	(001)

LITHIUM NITRIDE, Li_3N

General: Does not occur as a natural compound as nitrogen does not combine in nature to form metallic compounds, although there are phosphates and chlorates of lithium. There has been no use of the nitride in metal processing, to date.

Technical Application: Lithium nitride has not been used in Solid State processing, but has been studied as a thin film grown on lithium blanks.

Etching: Alcohols.

LITHIUM NITRIDE ETCHANTS

LIN-0001
ETCH NAME: Methyl alcohol
TYPE: Alcohol, removal
COMPOSITION:
x .... MeOH, CH_3OH
TIME:
TEMP:
DISCUSSION:
LiN_x thin films deposited on lithium blank specimens in a nitrogen atmosphere. The nitride deliquesces in alcohols, but they can be used for general etching and removal.
REF: Fremont, M — *Rev Chem Miner*, 4,447(1967)

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LITHIUM NIOBATE ETCHANTS

LINB-0002
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... HNO_3
TIME:
TEMP: Boiling
DISCUSSION:
$LiNbO_3$, single crystal specimens used in a study of domain structure and the Curie temperature. Solution used to develop dislocations and anti-parallel polar domains which are larger than those observed in lithium tantalate.
REF: Levinstein, H J et al — *J Appl Phys*, 37,4585(1966)

LINB-0001
ETCH NAME: Gold
TYPE: Metal, decoration
COMPOSITION:
(1) x .... Au (2) x .... Pt
TIME:
TEMP: 500—700°C
POWER: 250—500 V
DISCUSSION:
$LiNbO_3$, single crystal specimens used in a study of dislocations. Plate gold or platinum on surfaces and use temperatures and powers shown to diffuse metal into the material. Will develop a strain network and defects. This procedure is good for transparent crystals and will develop tilt and twist boundaries. Also used on lithium tantalate, $LiTaO_3$.
REF: Levinstein, H J & Capio, C D — *J Appl Phys*, 38,2761(1967)

LITHIUM TANTALATE ETCHANTS

LITA-0002
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
2 .... HNO_3
TIME:
TEMP: Boiling
DISCUSSION:
$LiTaO_3$ single crystal specimens used in a study of domain structure and the Curie temperature. Solution used as a dislocation etch and will also develop anti-parallel polar domains to a lesser extent than those observed in lithium niobate, $LiNbO_3$.
REF: Levinstein, H J et al — *J Appl Phys*, 37,4585(1966)

LITA-0001
ETCH NAME: Gold
TYPE: Metal, decoration
COMPOSITION:
(1) x .... Au (2) x .... Pt
TIME:
TEMP: 500—700°C
POWER: 250—500 V
DISCUSSION:
$LiTaO_3$, single crystal wafers used in a study of dislocations. Plate gold or platinum on surfaces and use temperatures and electrical powers shown to diffuse metal into the material. Will develop a strain network and defects. This procedure is good for transparent crystals and will develop tilt and twist boundaries. Also used on lithium niobate, $LiNbO_3$.
REF: Levinstein, H J & Capio, C D — *J Appl Phys*, 38,2761(1967)

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LUCITE ETCHANTS

LUC-0001a
ETCH NAME: Acetone
TYPE: Alcohol, dissolve
COMPOSITION:
x .... CH_3COCH_3 (Ace)
TIME:
TEMP: RT
DISCUSSION:
Lucite, sheet and parts. Add acetone to Lucite shavings to form a glue. Use glue to cement Lucite parts together.
REF: Simonds, H R et al — *Handbook of Plastics*, 2nd ed, January 1949
LUC-0002: Walker, P — personal application, 1958/1985
Used this glue to form lucite containers and seals for light pressure box operation (0.5 Torr) and light vacuum operation (10^{-3} Torr). Also used in making three-dimensional electrical power level models of silicon transistors as a display item, and crystallographic structure models using plastic rods and balls. The solid colored plastic balls were drilled using a specially constructed aluminum holding form built for that purpose.

LUC-0001b
ETCH NAME:
TYPE: Halogen, cleaning
COMPOSITION:
(1) 1 g .... I_2
50 ml .... MeOH
1000 ml .... H_2O
(2) 1 tsp .... *tincture of iodine
1 gal .... H_2O
TIME:
TEMP: RT to warm

*xK:xI_2:xEOH

DISCUSSION:
Lucite, sheet and parts. Both solutions can be used to clean and disinfect lucite and polycarbonate plastics.
REF: Ibid.
LUC-0002b: Walker, P — personal application, 1965—1985
Used the methyl alcohol mixture to clean chemical sink plastic hoods in epitaxy system cleanrooms.

LUC-0003
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
x .... glycerin
TIME:
TEMP:
DISCUSSION:
Lucite, sheet and parts can be cleaned in this solution. The liquid mixture has the same refractive index as Lucite: n = 1.49.
REF: Ivanstov, O P — *Dokl Akad Nauk SSSR*, 156,567(1947)

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PHYSICAL PROPERTIES OF LITHIUM SULFIDE, Li_2S

Classification	Sulfide
Atomic numbers	3 & 16
Atomic weight	45.94
Melting point (°C)	450 est.
Boiling point (°C)	
Density (g/cm³)	1.66
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Yellowish
Cleavage (cubic)	(001)

LITHIUM SULFIDE, Li_2S

General: Does not occur as a natural compound. The most important lithium mineral is the mica leipidolite, and there are other silicates and phosphates containing lithium. There is no application in the metals industries for the compound, but there is some use in chemistry and medicine.

Technical Application: The compound, as shown above, has not been used in Solid State processing, but a trinary compound as $LiInS_2$ has been deposited on (001) silicon as a crystalline or glassy thin film.

Etching: Mixed acids of HF:HNO_3.

LITHIUM INDIUM SULFIDE ETCHANTS

LIIS-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

$LiInS_2$, (001) oriented thin films deposited on (111) silicon wafers, or as an amorphous glassy film. Deposition was by evaporation from a moly boat in excess sulfur, or by directional solidification. Solution shown was used as a removal or patterning etch.
REF: Koriyama, K & Saitoh, J — *Solid Thin Films,* 111,331(1984)

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PHYSICAL PROPERTIES OF MAGNESIUM, Mg

Classification	Alkaline metal
Atomic number	12
Atomic weight	24.3
Melting point (°C)	650
Boiling point (°C)	1107
Density (g/cm^3)	1.74
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.37 (0.3867)
Specific heat (cal/g) 20°C	0.245
Latent heat of fusion (cal/g)	82.2 (88)
Heat of vaporization (cal/g)	1260
Atomic volume (W/D)	14.0
1st ionization energy (K-cal/g-mole)	176
1st ionization potential (eV)	7.64
Electronegativity (Pauling's)	1.2
Covalent radius (angstroms)	1.36
Ionic radius (angstroms)	0.66
Linear coefficient of expansion ($\times 10^{-6}$ cm/cm/°C)	26
Electrical resistivity (micro-ohm-cm) 20°C	4.46
Modulus of elasticity (kg/mm^2)	4570
Poisson ratio	0.35
Tensile strength (psi)	33,000
Cross section (barns)	0.063
Vapor pressure (°C)	909
Electron work function (eV)	3.46
Hardness (Mohs — scratch)	2
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Silver-white metal
Cleavage (basal)	(0001)

MAGNESIUM, Mg

General: Does not occur as a native element. It is widely distributed in many minerals, constitutes about 2% of the earth's crust and some 0.5% in sea water as the chloride, $MgCl_2$. Magnesite, $MgCO_3$ — magnesia — is a major ore. Dolomite, $CaMg(CO_3)_2$ and talc (soapstone), $(OH)2Mg_3Si_4O_{10}$, are building stones. In its fibrous form, soapstone is asbestos, which can be carded like flax due to its flexibility. The amphibole minerals tremolite and actinolite contain magnesium and, in their fibrous forms, are also asbestos. When silicified, such asbestos becomes semi-precious to precious gem stones: Cat's Eye.

When the pure metal is exposed to air it becomes slowly coated with carbonate, e.g., becomes magnesite, which stabilizes the surface against further alteration.

As the pure metal it has important applications in the metal industry. Used alone, it is a lightweight construction metal; as an alloy with iron or aluminum it increases structural strength. The aluminum skin of airplanes always contains magnesium. When ignited it burns with a searing white flame — used in flares, tracer bullets, incendiary bombs, and flash bulbs. During wartime it is classified as a strategic material, and has long been used as the white flame color in pyrotechnics.

Magnesium oxide, MgO and the hydroxide, $Mg(OH)_2$ are found in every chemical laboratory, taken internally as an antidote against acid poisoning and, as a water paste, used on the skin to neutralize acids burns. It is milk of magnesia and Maalox, and there are important organic magnesium compounds used in other medical applications.

Technical Application: The pure metal is not widely used in Solid State or the semi-

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conductor industry, though it is used as a dopant element in some compound semiconductors and is under evaluation as a silicide: MgSi, Mg_2Si, and $MgSi_2$. It has been used to grow the compound semiconductor, magnesium selenide, Mg_2Se, and could be used for a similar telluride.

It has been grown artificially as a single crystal and studied for its electrical and physical properties, to include defect structure with and without stress and strain.

Caution should be observed in handling pure magnesium as, when in air, if struck a sharp blow or near an electrical or spark it can ignite. And once ignited it will continue to burn even under water or when smothered with dirt.

Etching: Soluble in mineral acids; HCl, H_2SO_4, and mixed acids. Neon ionic bombardment is preferential.

MAGNESIUM ETCHANTS

MG-0001
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, cutting
COMPOSITION:
1 .... HCl
1 .... H_2O
TIME: 3 h
TEMP: RT
RATE: 75 ft/min cutting rate
DISCUSSION:

Mg, specimens and magnesium alloys. Solution used as an acid-saw cutting system. A mercerized cotton crochet thread was used as the cutting vehicle. Pass the thread through the acid solution, then across the specimen. It required 1 h to cut a 1″ diameter slice at 75 ft/min, cutting speed. Authors say the slice was flat to within 1 mil.

REF: Long, T R & Smith, C S — *Acta Metall*, 25,200(1957)

MG-0004: Reed-Hill, R E & Robertson, W D — *Acta Metall*, 5,717(1957)

Mg, single crystal wafers used in a study of deformation twinning. Specimens were acid machine cut and electropolished, then etched in HCl for dislocation development.

MG-0005: Conrad, H et al — *Acta Metall*, 9,367(1961)

Mg, single crystal specimens used in a study of plastic flow at low temperatures. Solution was 25% HCl, and applied as a polish etch.

MG-0002
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... 1 *N* HNO_3
TIME:
TEMP: RT
DISCUSSION:

Mg, pieces, Solution used to clean magnesium for the growth of single crystal Mg_2Ge. After etch cleaning rinse in DI water three times and final rinse in MeOH, then dry.

REF: Kromar, H et al — *J Appl Phys*, 36,2461(1965)

MG-0003a
ETCH NAME: Nitric acid, dilute
TYPE: Acid, saw
COMPOSITION:
x .... 20% HNO_3
TIME:
TEMP:
DISCUSSION:

Mg, single crystal wafers. Use solution for acid saw cutting of material.

REF: Tsui, R T C — *Acta Metall*, 15,1722(1967)

MG-0009: Shally, J — *Phil Mag*, 13,9(1966)

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Mg, single crystal wafers used in a study of the structure of quenched magnesium. A 5—10% solution used to etch-thin specimens. Used low concentration for large specimens (5 cm^2 size); high concentration for small specimens ($^1/_2$ cm^2 size). After thinning, quench in MeOH and dry.

MG-0003b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HNO_3
4 .... MeOH
TIME:
TEMP: 0°C
ANODE: Mg
CATHODE: SS
POWER: 1 A/cm^2 & 8—10 V
DISCUSSION:
Mg, single crystal wafers. Use solution to electropolish and to etch thin specimens for electron microscope (EM) study.
REF: Ibid:.

MG-0012
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, polish
COMPOSITION:
(1) x .... 20% HCl
(2) x .... 80% HCl
TIME:
TEMP:
DISCUSSION:
Mg, specimens used in a stress evaluation. Both solutions were used as polishing etchants. Also studied aluminum and molybdenum.
REF: Feuerstein, S & John, I W — *J Appl Phys*, 40,3334(1969)

MG-0006
ETCH NAME: Glacial acetic acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... CH_3COOH (HAc)
x .... H_2O
TIME: 1—2 min
TEMP: RT
DISCUSSION:
Mg specimens. Solution used to clean and polish specimens before studying anodic dissolution of magnesium and magnesium alloys in aqueous salt solutions.
REF: Glickman, R — *J Electrochem Soc*, 106,83(1959)
MG-0007: Slutsky, L T & Garland, C W — *Phys Rev*, 107,972(1957)
Mg specimens used in a study of elastic constants. Mechanical lap with 000 emery grit. Then etch with dilute acetic acid, and continue mechanical polish.

MG-0008
ETCH NAME:
TYPE: Electrolytic, polish/thin
COMPOSITION:
20 .... $HClO_4$
80 .... EOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 0.2 A/cm^2 & 10—20 V
DISCUSSION:
Mg, (0001) wafers used in a study of transmission through thin crystals. Solution used to polish and thin specimens. Crystals of MgO and Mo also were studied but thinned with other etch solutions and methods.
REF: Thomas, G & Huftstutler, M C Jr — *J Appl Phys*, 31,1834(1960)

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MG-0010
ETCH NAME: Neon
TYPE: Ionized gas, preferential
COMPOSITION:
x .... Ne^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Mg, single crystal specimens. Neon ion bombardment used to develop structure and orientation figures. Other metals studied were Al, Bi, Cd, Cu, Co, Sn, and Zn.
REF: Yurasova, V E — *Kristallografiya*, 2,770(1957)

MG-0011
ETCH NAME: Sulfuric acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
x .... H_2O
x .... ?(acids)

TIME:
TEMP:

DISCUSSION:
Mg specimens used in a study of neutron-transfer reactions produced by N^+ ion bombardment.
REF: Halbert, M L et al — *Phys Rev*, 106,251(1957)

MG-0014a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
250 g .... CrO_3/l
150 g .... H_2SO_4/l

TIME: x sec
TEMP: 113°F
ANODE: Mg
CATHODE: Steel
POWER: 150—500 A/ft² & 6 V

DISCUSSION:
Mg specimens. Solution used to electropolish material.
REF: ASTE Committee — *Tool Engineers Handbook*, McGraw-Hill, New York, 1949

MG-0014b
ETCH NAME: Acetic acid
TYPE: Electrolytic, polish
COMPOSITION:
12—16 oz .... HAc (5—15%)

TIME: 20—60 sec
TEMP: 85°C
ANODE: Mg
CATHODE: Pb
POWER: 400 A/ft² & 4 V

DISCUSSION:
Mg specimens. Solution used as an electropolishing etchant.
REF: Ibid.

MG-0014c
ETCH NAME: Hydrofluoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... 25% HF

TIME: 10 min
TEMP: RT
ANODE: Mg
CATHODE: Pb
POWER: 400 A/ft² & 45 V

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DISCUSSION:
Mg specimens. Solution used as an electropolishing etchant.
REF: Ibid.

MG-0014d
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:

7.5 oz	.... $NaCO_3$
14 oz	.... $Na_3PO_4.H_2O$
28 oz	.... NaOH
0.1—1 oz	.... ammonium biaurylsulfate

TIME: 1—2 min
TEMP: 140—195°F
ANODE: Mg
CATHODE: steel
POWER: 216 A/ft² & 4 V

DISCUSSION:
Mg specimens. Solution used as electropolish etchant.
REF: Ibid.

PHYSICAL PROPERTIES OF MAGNESIUM FLUORIDE, MgF_2

Classification	Fluoride
Atomic numbers	12 & 9
Atomic weight	62.32
Melting point (°C)	1396 (1263)
Boiling point (°C)	2230 (2227)
Density (g/cm³)	2.9—3.2
Refractive index (n=)	1.378
Surface free energy (ergs cm^{-2}) −173°C	750
Hardness (Mohs — scratch)	5—6
(Knoop — kgf/mm²)	430
Crystal structure (tetragonal — normal)	(110) prism, 1st order
Color (solid)	Colorless
Cleavage (basal)	(001)

MAGNESIUM FLUORIDE, MgF_2

General: Occurs in nature as the mineral sallaite, MgF_2 with an atomic structure similar to rutile, TiO_2. It is of minor occurrence in a glacial moraine in France, and at Vesuvius in Italy. It can be formed artificially by reacting HF with MgO.

There is no application for the natural mineral in metal processing due to scarcity. The metal magnesium is the eighth most abundant element in nature, occurs in many minerals, and is of major importance as a metal. As ribbon or powder, when heated, it burns with an intense white light and is used for flares, incendiary bombs, and in pyrotechnics. It is ligher than aluminum and, as an aluminum alloy, has long been the major construction material for aircraft, in addition to a general construction material, and many, many aluminum products. The fluoride does have medical applications, as do several other magnesium salts. Other magnesium containing minerals, such as talc, soapstone, etc., have wide use, as do the fibrous varieties — asbestos. Note that milk of magnesia, $Mg(OH)_3$, is a medical specific against internal acid poisoning.

Technical Application: The fluoride has had little use thus far in Solid State device processing. It has been used as a single crystal (100) or (110) oriented substrate in the study of optical thin films as evaporated aluminum, chromium, and silver. As a dielectric compound it has application as a lens and filter material based on its optical properties.

Etching: HNO_3. Slowly soluble in other acids.

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MAGNESIUM FLUORIDE ETCHANTS

MGF-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal/polish — TEMP: RT
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
MgF_2, (100) wafers used as substrates for thin film evaporation of aluminum, silver and chromium in a study of mechanical properties of optical films. Solution shown can be used to clean MgF_2 surfaces.
REF: Pulker, H K — *Thin Solid Films*, 89,191(1982)

MGF-0002
ETCH NAME: Sulfuric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2SO_4, conc.
DISCUSSION:
MgF_2, (100) specimens. Solution referred to as a slow etch for this material.
REF: *Encyclopedia of Chemical Technology*, John Wiley & Sons, New York, 1980, 760

PHYSICAL PROPERTIES OF MAGNESIUM NITRIDE, Mg_3N_2

Classification	Nitride
Atomic numbers	12 & 7
Atomic weight	100.98
Melting point (°C)	1500
Boiling point (°C)	
Density (g/cm^3)	2.xx
Hardness (Mohs — scratch)	7—8
Crystal structure (monoclinic — normal)	(100) a pinacoid
Color (solid)	Colorless
Cleavage (basal)	(001)

MAGNESIUM NITRIDE, Mg_3N_2

General: Does not occur in nature as a mineral compound. It can be artificially fabricated by reacting the pure metal in a closed crucible or in a nitrogen atmosphere, e.g., flammable in air when heated to its boiling point as magnesium metal. The nitride, when heated in the presence of water, will separate into ammonia, NH_3 and magnesium hydroxide, $Mg(OH)_3$. The latter being milk of magnesia as a suspension in water.

In the metal industry, magnesium has been nitrided in hot nitrogen gas — the nitridization process — to improve surface hardness against wear and/or flammability if struck or sparked, as well as against corrosion. Note that magnesium metal will burn under water and, once ignited, is nearly impossible to quench . . . smother with dirt . . . and it may still continue to burn.

Technical Application: The compound has had little use in Solid State device processing up to the present, but has been deposited on magnesium specimens is a general study of nitride compounds. Though the nitride is listed as being colorless, the thin films of both magnesium and calcium nitrides were referred to as being black . . . with white spots of their respective oxides . . . if oxygen is present as an impurity in the nitrogen gas. Oxidation of the films will convert them, in part, to their oxides. Caution should be exercised as, with

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sufficient heat, magnesium is flammable in the presence of oxygen in air. As a dielectric it has possible applications as a thin film coating, though it is partly soluble in both water and alcohol.

Etching: Partly soluble in water and alcohols; soluble in linseed oil.

MAGNESIUM NITRIDE ETCHANTS

MGN-0001
ETCH NAME: Methyl alcohol — TIME:
TYPE: Alcohol, removal — TEMP:
COMPOSITION:
x .... CH_3OH(MeOH)
DISCUSSION:

Mg_3N_4, thin films deposited on Mg specimen blanks in a study of the use of high purity nitrogen gas to reduce contamination. Also worked with calcium nitride, Ca_2N_3. The black nitride of both materials will show spots of white oxides, CaO or MgO, respectively, in the presence of O_2 or air.

REF: Aubry, J & Streiff, R — *J Electrochem Soc*, 118,650(1971)

PHYSICAL PROPERTIES OF MAGNESIUM OXIDE, MgO

Classification	Oxide
Atomic numbers	12 & 8
Atomic weight	40.32
Melting point (°C)	800—2500 (2800)
Boiling point (°C)	
Density (g/cm^3)	3.69—3.90 (3.59)
Refractive index (n =)	1.74 (1.736)
Wavelength limits (microns)	0.25—7
Young's modulus (psi $\times 10^6$)	36
Coefficient of linear thermal expansion ($\times 10^6$/cm/cm/°C)	13
Hardness (Mohs — scratch)	6
(Knoop — kgf/mm^2)	690
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Clear/white
Cleavage (cubic)	(001)

MAGNESIUM OXIDE, MgO

General: Occurs in nature as the mineral periclase, MgO, with a crystal structure similar to that of halite, NaCl. It has excellent cubic cleavage which is common to minerals with this structure. It is of minor occurrence in nature as a contact mineral but can be readily grown artificially from a melt containing magnesium chloride and silica.

In industry it has wide application as a high temperature refractory ceramic, often as a mixture with alumina, Al_2O_3.

Technical Application: Not used in Solid State device fabrication and assembly though it has a higher melting point than alumina (2800 vs. about 2500°C). Unfortunately, it has a coefficient of thermal expansion about three times greater than that of silicon (13 vs. 4 $\times$ 10^6/°C). It could be used as a replacement for alumina in package parts where such expansion coefficients are not involved.

As a single crystal or fused periclase it has optical properties similar to those of sapphire and fused quartz and is used in optics and filter applications.

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It can be used as an insulator and as a thin film coating for high temperature surface protection similar to silica or for wear resistance.

Etching: Soluble in most acids and acid mixtures with low solubility in water.

MAGNESIUM OXIDE ETCHANTS

MGO-0001
ETCH NAME: Phosphoric acid — TIME:
TYPE: Acid, thinning — TEMP: 150°C
COMPOSITION:
x .... H_3PO_4
DISCUSSION:

MgO, (100) wafers plastically deformed to produce slip bands. Etch thinned in the solution show for TEM study.

REF: Narayan, J — *J Appl Phys*, 39,2448(1968)

MGO-0002a: Venables, J A — *J Appl Phys*, 34293(1963)

MgO ingot. Cut into rectangular (100) oriented bars by cleaving. Etch thin with the solution shown for 2—3 min at 130°C. Rinse in H_2O, then EOH.

MGO-0011: Thomas, G & Huftstutler, M C Jr — *J Appl Phys* 31,1834(1960)

MgO, (100) wafers used in a study of transmission thorough thin crystals. Wafers were jet-etch thinned with hot acid to a thickness of 1000 Å. Both Mo and Mg wafers also studied, but etch with other acids.

MGO-00214a: Keh, A S — *J Appl Phys*, 31,1538(1960)

MgO, (001) cleaved wafers were polished in phosphoric acid. Surfaces were indented to develop damage points using a square diamond tool. Both symmetrical (square), and asymmetrical (inclined) pits were observed aligned in a ⟨110⟩ direction. Interference patterns showed high points at the four pit corners.

MGO-0002b
ETCH NAME: Ammonium chloride — TIME:
TYPE: Acid, preferential/thinning — TEMP: 80°C
COMPOSITION:
x .... NH_4Cl
DISCUSSION:

MgO, (100) specimens cleaved as rectangles. This solution is a fair polish etch but also develops dislocations. The precipitates observed that do not etch are probably either ZrO_3 or $CaZrO_3$ impurities.

REF: Ibid.

MGO-0003
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... HF
x .... H_2O
DISCUSSION:

MgO specimens. Solution used to develop grain boundaries.

REF:

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MGO-0004a
ETCH NAME: Phosphoric acid, dilute
TYPE: Acid, polish
COMPOSITION:
80% .... H_3PO_4
20% .... H_2O
TIME:
TEMP: 150°C
DISCUSSION:
MgO, (100) wafers used in an irradiation study. Solution used to polish and remove cutting and lapping damage.
REF: Bradley, R — *Phil Mag*, 10, 161(1964)

MGO-0019
ETCH NAME: Gold
TYPE: Metal, decoration
COMPOSITION:
x .... Au
TIME:
TEMP:
DISCUSSION:
MgO, (100) wafers cleaved and diffused with gold to delineate defects and dislocations. Pit side slope angles were measured.
REF: Robins, J L et al — *J Appl Phys*, 37,3893(1966)

MGO-0022b
ETCH NAME: Stoke's etch
TYPE: Acid, dislocation
COMPOSITION:
1 .... H_2SO_4
5 .... NH_4Cl, sat. sol.
1 .... H_2O
TIME:
TEMP:
DISCUSSION:
MgO, (100) wafers used in a plastic deformation study. Solution used to develop defects. Authors say that grown-in dislocations differ from fresh dislocations.
REF: Argon, A S & Orowan, E — *Phil Mag*, 10,1003(1964)

MGO-0023
ETCH NAME:
TYPE: Electron, damage
COMPOSITION:
x .... e^-
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
MgO single crystal specimens used in a study of secondary electron emission from bombardment by relativistic electrons. Material cleaved easily on (100), but if specimens are too thin, they may show internal cracking.
REF: Pomerantz, M A et al — *J Appl Phys*, 31,2036(1960)

MGO-0005
ETCH NAME: Hydrochloric acid
TYPE: Acid, float-off
COMPOSITION:
x .... HCl
TIME:
TEMP:
DISCUSSION:
MgO, (100) substrates cleaved and used for carbon deposition and conversion to diamond

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phase by annealing. Annealing produces a mixture of C, a-C and m-diamond. Mixture of the three forms depends upon deposition parameters and control. HCl was used to float-off deposited thin films for TEM and SEM studies. (*Note:* a- = amorphous. m- = microcrystalline.)
REF: Namba, Y & Mori, T — *J Vac Sci Technol*, A(2),319(1985)

MGO-0006
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions

TIME: 1 h
TEMP: 800°C
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
MgO, (111) cleaved substrates used for deposition of thin film TiN. First, clean in a detergent, then ultrasonic in EOH and N_2 blow dry. Final clean in vacuum system with 2 KeV Ar^+ ion sputter prior to TiN deposition. Used in a study of single crystal growth of TiN.
REF: Johansson, B O et al — *J Vac Sci Technol*, A(2),303(1985)

MGO-0007
ETCH NAME: Phosphoric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_3PO_4

TIME:
TEMP: 100°C

DISCUSSION:
MgO, (100) wafers used in a study of fatigue deformation. Wafers cleaved from ingot — damage and cleavage steps removed by etching with solution shown.
REF: Subtannanian, K N & Washburn, J — *J Appl Phys*, 34,3394(1963)
MGO-0018b: Matkin, D I & Bowen, D H — *Phil Mag*, 12,1209(1965)
MgO, (100) wafers used in a study of whisker growth within single crystal magnesium oxide. Solution used to polish and etch thin specimens.
MGO-0013: Lewis, M H — *Phil Mag*, 13,777(1966)
MgO, (001) cleaved wafers used in an electron microscope (EM) study of precipitates in the material. Solution was used to selectively thin areas on the wafer by jet etching.
MGO-0020: McPherson, R & Swha, H N — *Phil Mag*, 12451(1965)
MgO, bicrystals used in a study of fracture. After mechanical lapping with diamond grit, solution shown was used boiling, 10 min to remove residual sub-surface lap damage.
MGO-0021: Narayan, J — *J Appl Phys*, 35,2448(1964)
MgO, (100) wafers used in a study of plastic deformation and development of slip bands. Solution used at 150°C as a thinning etch.

MGO-0014b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... H_2SO_4
5 .... NH_4Cl, sat. sol.
1 .... H_2O

TIME:
TEMP: RT or hot

DISCUSSION:
MgO, (100) cleaved wafers. Wafer surfaces were deformed by indention and studied for defects generated by this deformation. At room temperature solution produces conical pits; aged and used hot pits are flat bottomed.

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REF: Keh, A S — *J Appl Phys*, 31,1538(1960)
MGO-0009: Mendel, E & Weinig, S — *J Appl Phys*, 31,738(1960)

MgO, (100) cleaved wafers used in a study of dislocations produced by generation of an electric field. Field applied during etching developed a criss-cross pattern of what appear to be slip lines through the entire bulk of the wafer with coronal discharge on the surface during power application.

MGO-0015: Westwood, A R C & Gekha, D L — *J Appl Phys*, 34,3335(1963)

MgO, (100) cleaved wafers used in a study of surface energy. Specimens polish in this solution at RT, 3—10 min.

MGO-0016: Stokes, E J — *Phil Mag*, 3,718(1958)

MgO, (100) wafers used in a dislocation and defect study. Solution referenced as a dislocation etch in this article from MGO-0015.

MGO-0010
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
x .... HF
x .... H_2O
DISCUSSION:

MgO, (100) cleaved wafers used in a study of grain boundary diffusion using nickel and cesium. Prior to metal diffusion etched surfaces did not develop grain boundaries. Grain boundaries observed after metals diffused.

REF: Zaplatynsky, I — *J Appl Phys*, 351353(1964)

MGO-0012a
ETCH NAME: Nitric acid
TYPE: Acid, thinning
TIME:
TEMP: RT
COMPOSITION:
x .... HNO_3
DISCUSSION:

MgO, (100) wafers used in a study of whisker growth within the material. Solution used to etch polish and thin specimens for study.

REF: Matkin, D I & Bowen, D H — *Phil Mag*, 12,1209(1965)

MGO-0017
ETCH NAME: Carbon tetrachloride
TYPE: Solvent, cleaning
TIME:
TEMP: RT
COMPOSITION:
x .... CCl_4
DISCUSSION:

MgO, (100) wafers used in a study of fundamental optical absorption. Cleaved surfaces were cleaned in the solvent shown and follow with alcohol rinse.

REF: Reiling, G H & Hensley, E B — *Phys Rev*, 112,1106(1958)

MGO-0018
ETCH NAME:
TYPE: Acid, dislocation
TIME:
TEMP:
COMPOSITION:
1 .... H_2SO_4
1 .... NH_4Cl, sat. sol.

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DISCUSSION:

MgO, (100) wafers. Specimens were subject to bending and studied for crack nucleation associated with defects. Cracks occur along or in dislocation zones representative of lattice imperfections, impurity lumps, etc.

REF: Briggs, A et al — *Phil Mag*, 10,1041(1964)

MAGNESIUM GERMANIDE ETCHANTS

MGGE-0001a
ETCH NAME: BRM
TYPE: Halogen, polish
TIME:
TEMP: RT
COMPOSITION:

4 drops .... Br_2
250 ml .... MeOH

DISCUSSION:

Mg_2Ge, (111) wafers. Use a metallographic polishing wheel and impregnate a pellon type cloth with solution. Lap at slow speed and quench with MeOH. Gives a bright chemical polish.

REF: Kromer, H et al — *J Appl Phys*, 36,2461(1965)

MGGE-0001b
ETCH NAME:
TYPE: Acid, cleaning
TIME: 30 sec
TEMP: RT
COMPOSITION:

2 .... H_2SO_4
1 .... H_2O_2
200 .... H_2O

DISCUSSION:

Mg_2Ge, (111) wafers. Solution used to clean p-n junction area, but does not develop junction. Material reactions with acids and alkalies. After etch cleaning with the solution shown, quench in MeOH.

REF: Ibid.

MGGE-0002
ETCH NAME:
TYPE: Cleave, cleaning
TIME:
TEMP:
COMPOSITION:

x .... cleave

DISCUSSION:

Mg_2Ge, (111) cleaved wafers used in a study of photoconductivity. Specimens were lapped down to 0.2—0.44 mm — below this thickness material fractures. Authors state there is no known etch for the material? Also worked with Mg_2Si.

REF: Stella, A & Lynch, D W — *J Phys Chem Solids*, 25,1253(1965)

MAGNESIUM SELENIDE ETCHANTS

MGSE-0001
ETCH NAME: BRM
TYPE: Halogen, polish
TIME:
TEMP: RT
COMPOSITION:

(1) x .... x%Br_2
x .... MeOH

(2) x .... H_2SO_4

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DISCUSSION:

MgSe, single crystal evaluated for cohesive energy features of tetrahedral semiconductors. Forty elemental, binary, and trinary materials studied. Solutions shown are general cleaning, removal, and polishing etches for most of the materials studied.

REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

MAGNESIUM TELLURIDE ETCHANTS

MGTE-0001

ETCH NAME: TIME:

TYPE: Acid, removal TEMP:

COMPOSITION:

(1) x .... HF
x .... HNO_3
x .... HNO_3
x .... HAc

(2) 3 .... HCl
1 .... HNO_3

DISCUSSION:

MgTe, single crystals evaluated for adhesive energy features of tetrahedral semiconductors. Forty materials studied. Solutions shown are general cleaning, removal, and polishing etches for most of these materials.

REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

PHYSICAL PROPERTIES OF MAGNESIUM SILICIDE, Mg_2Si

Classification	Silicide
Atomic numbers	112 & 14
Atomic weight	76.70
Melting point (°C)	>1100
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey
Cleavage (cubic)	(001)

MAGNESIUM SILICIDE, Mg_2Si

General: Does not occur as the pure silicide in nature although there are over 50 silicate minerals, which may contain other metals. Many magnesium containing minerals are the basic rock-formers, such as those of the pyroxene and amphibole groups, which include the mineral forms of asbestos. The silicide is an additive to irons, steels, aluminum and copper alloys in the metal industries.

Technical Application: The silicide has been studied in Solid State development of materials as a tetrahedral semiconductor, and is currently under study as a silicide blocking layer in device construction along with several other metal silicides as Mg_2Si, MgSi, and $MgSi_2$. Note that the elemental semiconductors silicon and germanium are referred to as octahedral in crystal classification; whereas many binary silicides and germanides are referred to as tetrahedral. The octahedron, (111) is a crystal form within the isometric system, normal class, and the tetrahedron, (111) is a crystal form within the isometric system, tetrahedral class, such that materials should not be classified by a crystal form within a system or class, but by system/class or by planes of symmetry using the 132 Space Group notations. The tetrahedron is a basic unit cell atomic structure in many semiconductor

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materials. It is the simplest closed form in nature, and the pyramid of geometry. In etching single crystal spheres of these materials, a finite crystal form (FCF) is developed that will vary with solution mixture. See Germanium, Silicon, and Silicides for specific forms obtained.

Etching: Soluble in mixed acids.

MAGNESIUM SILICIDE ETCHANTS

MGSI-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

Mg_2Si, (111) cleaved wafers used in a study of photoconductivity. Specimens were lapped to 0.2—0.44 mm — below this thickness material fractures. Authors state there is no known etch for the material? Also worked with Mg_2Ge. (*Note:* Bromine-methanol should work as a polish/removal etchant.)
REF: Stella, A & Lynch, D W — *J Phys Chem Solids*, 25,1253(1965)

PHYSICAL PROPERTIES OF MAGNESIUM SULFIDE, MgS

Classification	Sulfide
Atomic numbers	12 & 16
Atomic weight	56.38
Melting point (°C)	>200 del
Boiling point (°C)	
Density (g/cm³)	1.6×
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Red brown
Cleavage (cubic)	(001)

MAGNESIUM SULFIDE, MgS

General: Does not occur as a sulfide compound in nature, but there are over ten sulfates with the SO_4^- radical, such as epsomite, $MgSO_47H_2O$, in addition to others with other metal elements — Fe, Al, Zn, Mn — mostly as hydrated minerals. Magnesium is a quite abundant element with many of its natural minerals of industrial importance. See Magnesium for discussion of the metal as an element. The mineral shown above, epsomite, is the natural form of the medical epsom salts.

Technical Application: The sulfide is under evaluation in Solid State development as a binary compound semiconductor.

Etching: Soluble in acids.

MAGNESIUM SULFIDE ETCHANTS

MGS-0001
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
(1) x .... H_2SO_4 (2) x .... HCl

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DISCUSSION:

MgS, single crystals evaluated for cohesive energy features of tetrahedral semiconductors. Forty materials studied. Solutions shown are general, cleaning removal, and polishing etches for most of these materials.

REF: Aresti, A et al — *J Phys Chem Solids*, 45,361(1984)

PHYSICAL PROPERTIES OF MAGNETITE, Fe_3O_4

Classification	Oxide
Atomic numbers	26 & 8
Atomic weight	231.52
Melting point (°C)	1538
Boiling point (°C)	
Density (g/cm^3)	5.16—5.18
Hardness (Mohs — scratch)	5.5—6.5
Crystal structure (isometric — normal)	(111), octahedron
Color (solid)	Iron-black
(thin section)	Colorless/brown
Cleavage (octahedral — indistinct)	(111)
Magnetism (solid — unidirectional)	Strong
(lodestone)	N-S polarity

MAGNETITE, FeO_4

General: Occurs as the natural mineral and called magnetic iron ore. As the variety lodestone it shows N-S polarity, and was used as the first magnetic compass in ancient times, circa 3000 B.C., about the time the island city states of Tyre and Sidon were the major seafaring nations in the Mediterranean Sea. The compass also was in use to guide camel caravans in Asia Minor and across the Gobi Desert in those early times. Some minerals of nickel and cobalt have natural magnetism, but too a lesser degree. Magnetite is widely distributed as grains and small crystals in basic rocks (those low in silica), and is often found in the upper layers of gold placer deposits.

It is found in large magnetic ore bodies — common to the Archaean Shield — the original rocks of the earth's crust where they were first formed by magmatic segregation without further alteration. Sweden is noted for its fine stainless steels, and their magnetite iron comes from such ore bodies which are of particularly high purity.

It has long been used as a lapping and polishing abrasive in the form of emery, Al_2O_3:Fe_3O_4 with Turkish emery considered of highest quality. As the pure magnetite abrasive, it is called Black Rouge. Some of the micas contain Fe_3O_4, which is thought to have been initially deposited as a colloidal precipitate — some other iron oxide ores are so formed as sedimentary deposits.

When heated in oxygen to 220°C it converts to hematite, Fe_2O_3, but retains its magnetism; at 550°C, as hematite without magnetism. Magnetite frequently forms as a furnace by-product during the reduction of other iron ores when the melt is low in silica. It is called ferrosoferric iron, as it contains both Fe^{++} and Fe^{+++} ions in its structure.

It is used directly as the core of electromagnets and, in powder form in liquid plastic, for magnetic fluidic valves; in solid rubberized plastic as a gripping mechanism, such as strips for door closure. There are many artificial magnets as alloy mixtures of Fe/Co/Ni for pure magnetic or electromagnetic action: gripping, moving — magnetic coils control the acceleration in atom smashing tunnel accelerators.

Technical Application: Natural magnetite has had no use in Solid State device devel-

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opment although magnets are used in many equipment operations, and have been used as part of device package assemblies.

Artificial magnetite has been grown from molten fluxes as small single crystals and, as a ferrite material, as larger ingots by the Czochralski (CZ) method. Both the artificial and natural single crystals have been studied for general morphology and, specifically, for ferromagnetic and ferroelectric properties. This includes fabrication as single crystal spheres for etching to finite crystal form (FCF) and in oxidation studies. Spheroids, doughnut shaped forms, also have been studied with regard to magnetic directionality reaction under varying conditions. See Garnet section for use of magnetism in YIG garnets used as computer bubble memory devices.

Etching: HCl, HNO_3, Picric, and Nital mixtures.

MAGNETITE ETCHANTS

MAGT-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, preferential
TIME: 10 sec to 5 min
TEMP: RT
COMPOSITION:
(1) x .... HCl, conc.
(2) 1 .... HCl
5 .... H_2O
DISCUSSION:

Fe_3O_4, (111) single crystals as fine octahedrons of natural magnetite were highly reflective as formed in a green schist deposit, and intimately associated with small iron garnets. Solutions were used in a general etching study to observe structure variations of surfaces.
Walker, P — mineralogy study, 1952

MAGT-0002
ETCH NAME: Lathe
TYPE: Cut, forming
TIME:
TEMP:
COMPOSITION:
x .... lathe cutting
DISCUSSION:

Fe_3O_4, artificial single crystal magnetite. After growth, specimens were lathe cut to an oblate spheroid form and used in a study of magnetization near the Curie Point.
REF: Smith, D O — *Phys Rev*, 102,959(1956)

MAGT-0003
ETCH NAME:
TYPE: Electrolytic, polish
TIME:
TEMP:
COMPOSITION:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Fe_3O_4 specimen cut as a polycrystalline sphere — mainly single crystal — and used in study of g-factors at low temperatures. No etch shown, though magnetite is slowly soluble in acids. Reference shown is for single crystal spheres use in oxidation experiments.
REF: Gwathmey, A T & Lawless, K R — *The Surface Chemistry of Metals and Semiconductors*, Gatos, H C, Ed, John Wiley & Sons, New York, 1960, 483

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MAGT-0004
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:

Fe_3O_4 grown as a single crystal ingot by the Czochralski (CZ), method. A study of the growth of iron ferrites. Also grew ingots of ZnO, Ga_2O_3, CuO, and MnO all doped with Fe. Solution used for general surface cleaning.
REF: Horn, F N — *J Appl Phys*, 32,900(1961)

PHYSICAL PROPERTIES OF MANGANESE, Mn

Classification	Transition metal
Atomic number	25
Atomic weight	54.93
Melting point (°C)	1245
Boiling point (°C)	2150
Density (g/cm³)	7.44
Specific heat (cal/g) 25°C	0.115
Latent heat of fusion (cal/g)	63.7
Latent heat of vaporization (k-cal/g-atom)	537
Atomic volume (W/D)	7.39
Ionization energy (K-cal/g-mole)	171
Electronegativity (Pauling's)	1.5
Covalent radius (angstroms)	1.17
Ionic radius (angstroms)	0.80 (Mn^{+2})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	22
Compressibility ($\times 10^{-7}$)	8.4
Magnetic susceptibility (cgs $\times 10^{-6}$)	8
Electron work function (eV)	3.76
Cross section (barns)	13.3
Vapor pressure (°C)	1792
Hardness (Mohs — scratch)	5
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Grey-pink
Cleavage (cubic — poor)	(001)

MANGANESE, Mn

General: Does not occur as a native element. There are over 150 minerals containing manganese which are widely distributed as silicates, oxides, and carbonates and all of secondary origin. The two most important oxide ores are pyrolucite and psilomelane. MnO_2. The latter is one of the few natural colloids, and pyrolucite may be colloidal in part. The carbonate rhodochrosite, $MnCO_3$, can be a miscible mineral with siderite, $FeCO_3$ up to 40%. Color shifts from brilliant pink/rose to tan with increase of iron content. Pure metallic manganese has characteristics similar to those of iron but is harder and more brittle. This close association of Fe and Mn is further seen in nature with two colloidal "bog" ores: limonite and bog manganese, FeO and MnO, respectively, and both are hydrates.

The metal is of major importance in the metals industries as an additive to iron, copper, nickel, etc. as a hardening agent. Manganous-irons, like ferrosilicon, are starter pig irons

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for fabrication of special steels. The natural oxides, pyrolucite and psilomelane, are highly active oxidizing agents and, when added to glass, will remove the green tint due to iron for fine, clear glass or to produce a faint amethyst color. Both chlorides and permanganates are used as medical antiseptics and in quantitative analysis. The permanganate solutions produce a deep purple color.

It is worth noting that large deposits of psilomelane have been located on the ocean floor in the Pacific Ocean off the coast of California, and may become one of the first major oceanographic mining operations.

Technical Application: Until recently, manganese has had little use in Solid State development but is under evaluation as possible silicides: MnSi, Mn_2Si, $MnSi_2$. It also has been deposited as an amorphous thin film. There are possible applications as a magnetic semiconductor superlattice, such that it has been deposited as a thin film structure in layered CdMnTe crystals. There is no reference here as to its growth and study as a single crystal.

The permanganate, $KMnO_4$, has been used for surface cleaning and as a preferential etching solution on several metals and metallic compounds. Many chemical laboratories maintain the dry chemical available for use as an antiseptic for cuts and abrasions.

Etching: Soluble in dilute acids and halogens.

MANGANESE ETCHANTS

MN-0001
ETCH NAME: Hydrochloric acid, dilute — TIME:
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
x .... HCl
x .... H_2O
DISCUSSION:
Mn, thin film deposits on ruthenium substrates. Manganese surfaces can be etch cleaned in the diluted acid shown.
REF: Heinrich, B et al — *J Vac Sci Technol*, B3(2),766(1985)

MN-0002
ETCH NAME: BRM — TIME:
TYPE: Halogen, removal/polish — TEMP:
COMPOSITION:
x .... x% Br_2
x .... MeOH
DISCUSSION:
Mn, thin films deposited as part of a layer structure in studying a dilute magnetic semiconductor superlattice. GaAs (100) wafers were used as substrates for both CdTe and CdMnTe film deposition. Bromine-methanol solutions can be used as polish and removal etchants on GaAs, CdTe, and CdMnTe.
REF: Kolodziejski, L A et al — *J Vac Sci Technol*, B(3),714(1985)

PHYSICAL PROPERTIES OF MANGANESE DIOXIDE, MnO_2

Classification	Oxide
Atomic numbers	25 & 8
Atomic weight	86.93
Melting point (°C)	−0.54
Boiling point (°C)	

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Density (g/cm^3)	4.73—4.86
Hardness (Mohs — scratch)	2.0—2.5
Crystal structure (orthorhombic — normal)	(100) a-pinacoid
Color (solid)	Brown-black
Cleavage (basal)	(001)

MANGANESE DIOXIDE, MnO_2

General: There are several manganese dioxide minerals in nature, some of wide, others of limited occurrence but all mined as ores of manganese. Pyrolucite and polianite are both single crystal MnO_2, orthorhombic and tetragonal systems, respectively; manganite, Mn_2O_3 is also orthorhombic; whereas psilomelane, MnO_2, is colloidal and is the major ore of manganese. Large deposits have been found on the floor of the Pacific Ocean, and may become one of the first ocean mining operations. The physical data shown, above, is for pyrolucite, which is so soft it will soil the fingers, and has a black streak like graphite, C. As a monoxide, manganosite, MnO is isometric system. Hardness of these different manganese oxides vary widely H = 2 (pyrolucite) to H = 7 (psilomelane).

Other than as ores of manganese, the oxides have important applications in industry, chemistry and medicine: as an oxidizing agent in the manufacture of chlorine, bromine, and oxygen, and as a drier in paints. They are used to remove color from glass (green tint from iron), and to color glass (amethyst). As the chemical $KMnO_4$ it is a powerful oxidizing agent used as a medical antiseptic, as a water clarifier, and in preferential and cleaning etch solutions.

Technical Application: The monoxide and dioxides have had no real application in Solid State processing, though $KMnO_4$ is a constituent in etching solutions. Both manganese nitrides and silicides has been evaluated as have been artificial and native mineral oxides. Pyrolucite has been shown to be an n-type semiconductor compound, and has been evaluated for its infrared as well as semiconducting properties.

Etching: Soluble in HCl.

MANGANESE OXIDE ETCHANTS

MNO-0001a
ETCH NAME: Carbon monoxide — TIME: x h
TYPE: Gas, preferential — TEMP: 1000°C
COMPOSITION:
(1) x .... CO (2) x .... H_2
DISCUSSION:

MnO_2, single crystal specimens used in a study of infrared properties. The CO will produce thermal etch patterns on surfaces. Hot hydrogen gas also produced thermal etch patterns, when applied under similar conditions, but no patterns were obtained with argon as a hot gas.
REF: Loh, E & Newman, R — *J Appl Phys*, 32,470(1961)

MNO-0002
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
(1) x .... HCl, conc. (2) x .... HCl
x .... H_2O
DISCUSSION:

MnO_2, natural crystal specimens. Used as a general etch for psilomelane and other manganese oxides.

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REF: Dana, S E & Ford, W E — *A Textbook of Mineralogy*, 4th ed, John Wiley & Sons, New York, 1950, 509.

MNO-0003: Das, J N — *Z Phys*, 151,395(1958)

MnO_2, as the natural mineral pyrolucite used in a study of semiconducting properties. Material was n-type, and properties were dependent on temperature.

MNO-0004
ETCH NAME: Borax
TIME:
TYPE: Acid, removal
TEMP:
COMPOSITION:
x .... $Na_2B_4O_7.10H_2O$
x .... H_2O
DISCUSSION:

MnO, single crystals doped with iron as ferrites, and grown as ingots by the Czochralski (CZ) method. Other ferrites grown and studied were Fe_3O_4, and iron doped Ga_2O_3, ZnO, and CuO.

MNO-0005: Walker, P — mineralogy study, 1953

MnO_2, as natural psilomelane with highly reflective botryoidal surfaces. A 50% hot solution used to clean and etching surfaces in a general study of swirl structures observed in colloidal minerals. Results compared with natural colloidal silica.

MAGNESIUM STANNIDE ETCHANTS

MGSN-0001
ETCH NAME:
TIME:
TYPE:
TEMP:
COMPOSITION:
DISCUSSION:

Mg_2Sn, single crystal specimens. Authors state that this compound cannot be etched in aqueous solutions as it etches too rapidly. Wafers were cleaved, (001) and used in a study of photoconductivity and photovoltaic effects. Also studied InSb and GaSb.

REF: Frederikse, H P et al — *Photoconductivity Conference*, Brechenridge, R G et al, Eds, John Wiley & Sons, New York, 1956

MGSN-0002
ETCH NAME:
TIME:
TYPE:
TEMP:
COMPOSITION:
DISCUSSION:

Mg_2Sn, (100) cleaved wafers. Wafers were lapped with 600-grit abrasive and used in a study of electrical conductivity at low temperatures. Authors say there is no satisfactory etch for this material because it corrodes too rapidly. (*Note:* BRM type solutions should etch this material, as well as alcohol dilute acids.)

REF: Frederikse, H P R et al — *Phys Rev*, 103,67(1956)

MANGANESE FERRITE ETCHANTS

MNFE-0001
ETCH NAME:
TIME:
TYPE: Abrasive, forming
TEMP: RT
COMPOSITION:
x .... SiC
x .... H_2O

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DISCUSSION:

$MnFe_2$, single crystal sphere 0.8 mm diameter rough ground for nuclear magnetic resonance studies.

REF: Schulman, R G & Jaccarino, V — *Phys Rev*, 108,1219(1957)

MNFE-0002

ETCH NAME: TIME:

TYPE: Abrasive, forming TEMP: RT

COMPOSITION:

x .... SiC

x .... H_2O

DISCUSSION:

$MnFe_2$, single crystal sphere formed in a tornado-type sphere grinder for use in a ferromagnetic resonance study. Spheres were 0.2—0.8 mm diameter. (*Note:* No etch solutions shown, but BRM, Picral, and Nital are used on iron.)

REF: Tannenwald, P E — *Phys Rev*, 100,1713(1955)

MANGANESE TELLURIDE ETCHANTS

MNTE-0001

ETCH NAME: Nitric acid TIME:

TYPE: Acid, polish TEMP:

COMPOSITION:

x .... HNO_3

DISCUSSION:

$MnTe_2$ single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other single crystals grown were FeS_2, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsTe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. Authors say that all crystals are cubic structure like pyrite, FeS_2 and were used in an IR spectra study. (*Note:* Pyrite is in the isometric system, pyritohedral class, and forms as a pseudo-cube with a high degree of facial twinning lamellae of surfaces. It is not "cubic".)

REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

PHYSICAL PROPERTIES OF MERCURY, Hg

Classification	Transition metal
Atomic number	80
Atomic weight	200.69
Melting point (°C)	−38.87
Boiling point (°C)	356.9
Density (g/cm^3)	13.546
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.022
Specific heat (cal/g) 25°C	0.033
Heat of fusion (cal/g)	2.82
Heat of vaporization (cal/g)	65
Atomic volume (W/D)	14.8
1st ionization energy (K-cal/g-mole)	241
1st ionization potential (eV)	10.43
Electronegativity (Pauling's)	1.9
Covalent radius (angstroms)	1.49
Ionic radius (angstroms)	1.10 (Hg^{+2})

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Volume coefficient of expansion ($\times 10^{-6}$) 20°C	182
Electrical resistivity (micro-ohms-cm $\times$ 10^{-6}) 20°C	95.8
Compressibility (atms: 99—493 $\times$ 10^{-6}) 20°C	4
Magnetic susceptibility ($\times 10^{-6}$ cgs) 18°C	0.15
Magnetic moment (nuclear magnetrons)	+0.4993
Electron work function (eV)	4.52
Cross section (barns)	360
Vapor pressure (°C)	261.7
Vaporization point (°C)	350
Hardness (Mohs — scratch) solid	2
Crystal structure (hexagonal — rhombohedral) solid	$(10\bar{1}1)$ rhomb
Color (liquid/solid)	Tin-white
Cleavage (rhombohedral) solid	$(10\bar{1}1)$

MERCURY, Hg

General: Although metallic mercury does occur as a native element it is extremely rare, found only in completely enclosed voids in the primary ore cinnabar, HgS. Mercury (metal) and bromine (semi-metal) are the only two elements that occur in nature as liquids at standard temperature and pressure (22.2°C and 760 mmHg). There are several natural minerals containing mercury, one of the more important being calomel, HgCl — used as a medical specific to stimulate secretory organs. Tiemannite, HgSe and coloradoite, HgTe are natural minerals, which have artificial counterparts grown as compound semiconductors. There is a natural mineral called "amalgam", Ag_2Hg_3 to $Ag_{36}Hg$, the only natural amalgam, although mercury forms amalgams with most metals as artificial compounds.

Mercury is one of the metals that was known to ancient man. The Chinese and Hindu records refer to its use, and it has been found in Egyptians tombs, circa 4500 B.C. The Hg symbol is from hydrargyrum — meaning "liquid silver".

Because mercury has a regular coefficient of expansion, it has long been used for thermometers, barometers, and similar equipment. A column of mercury 760 mm high is the measure of one standard atmosphere of pressure, e.g., 760 mmHg, equal to approximately 30″ with a pressure of about 16 lb/psi.

Industrially, mercury is used in many low temperature alloys as it will form amalgams with most metals. Mercury is poisonous and, as it is normally in the liquid state, will continually release fumes into the air, such that mercury spills can be a severe health hazard.

Mercuric chloride, $HgCl_3$, is a violent poison, though used as an antiseptic; whereas mercurous chloride, HgCl (calomel), is a medical laxative. Mercury fulminate, $Hg(ONC)_2$, is a detonator used for explosives. Because of its brilliant vermillion-red color, the natural mineral cinnabar, HgS, is used as a pigment in paints.

As products using pure mercury, there are high light intensity mercury lamp bulbs and mercury switches — the "silent" switch.

Technical Application: A smear of mercury is occasionally used as a temporary electrical contact or electrically active holding medium in material device testing, and in Solid State and semiconductor processing has been used as a diffusion species for trinary compound semiconductors. It is a major constituent of the binary compound semiconductors: mercuric selenide, HgSe, and mercuric telluride, HgTe.

It can be grown as a single crystal under cold vacuum conditions, and has been frozen as a crystalline solid in LN_2, L_{air} and dry ice, CO_2 (solid). Such freezing liquids themselves, or by varying vacuum pressure, will produce preferential etching action for development of defect structure on solidified mercury.

Solid mercury is sufficiently soft such that it can be sliced with a knife under LN_2. As a smear on any material surface, it can be quick-frozen by a spray of acetone or CO_2.

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Smeared on a metal surface, then allowed to sit with or without slight heating, amalgams formed can be evaluated.

Etching: HNO_3, dilute HCl, and halogen solutions.

MERCURY ETCHANTS

HG-0001
ETCH NAME: Carbon dioxide
TYPE: Gas, preferential
COMPOSITION:
x .... dry ice (solid CO_2)
TIME:
TEMP: −56°C
DISCUSSION:
Hg, liquid frozen into solid form using dry ice and holding at dry ice temperature. CO_2 gas can be used to lightly etch surfaces.
REF: Fickett, F R — *J Appl Phys*, 40,3464(1969)

HG-0002
ETCH NAME: Liquid air
TYPE: Air, preferential
COMPOSITION:
x .... L_{air}
TIME:
TEMP: −70°C and −183°C
DISCUSSION:
Hg, liquid frozen and stressed at the two temperatures shown using liquid air as the freezing agent and preferential etchant. Develops slip and defect structure in single crystal mercury specimens.
REF: Rider, J O & Heckscher, F — *Phil Mag*, 13,678(1966)

HG-0003
ETCH NAME: Liquid nitrogen
TYPE: Gas, preferential
COMPOSITION:
x .... LN_2
TIME:
TEMP: −195°C
DISCUSSION:
Hg, liquid frozen by submersion in LN_2, then sliced under the liquid and pressurized by point contact to develop defect structures. Also used to collect balls of mercury spills by flushing area with LN_2, and recovering mercury with tweezers.
REF: Tarn, W H & Walker, P — mineralogy study/application — 1953/1974

HG-0004a
ETCH NAME: Acetone
TYPE: Ketone, freezing
COMPOSITION:
x .... $(CH_3)_2CO$, spray
TIME:
TEMP: −95°C
DISCUSSION:
Hg, as a smeared surface contact on silicon wafer backs. Acetone used to temporarily solidify mercury during assembly for electrical tests.
REF: Walker, P & Tarn, W H — personal application, 1964

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HG-0004b
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
Hg, applied as a thin film or hemispherical dot on a metal surface for electrical probe contact in device testing. Concentrated acid used to remove mercury after use followed by heavy water washing and air drying.
REF: Ibid.

TIME:
TEMP: RT

PHYSICAL PROPERTIES OF MERCURIC CADMIUM TELLURIDE, HgCdTe

Classification	Telluride
Atomic numbers	80, 48, & 52
Atomic weight	440.59
Melting point (°C)	>900 est.
Boiling point (°C)	
Density (g/cm^3)	
Energy bond gap (eV)	1.75
Hardness (Mohs — scratch)	2—2.5
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Grey/black
Cleavage (octahedral)	(111)

MERCURIC CADMIUM TELLURIDE, HgCdTe

General: Does not occur in nature as a metallic compound although there is a mercuric telluride mineral: coloradoite, HgTe, found sparingly in Colorado in the U.S. and as minable quantities in Australia.

The mineral, HgTe, is used as an ore of both mercury and tellurium in industry in addition to application as a binary semiconductor compound as is the trinary HgCdTe, both as artificially grown materials.

Technical Application: Mercuric cadmium telluride is a II—III—VI trinary compound semiconductor similar in many respects to the binary CdTe II—VI compound as it is grown with varying ratios of $Cd_{1-x}Hg_xTe$. It has the crystal structure of sphalerite, ZnS, as do many of the binary compound semiconductors.

It has been grown as a single crystal for general morphological studies as well as a layered film on CdTe, and has been used to fabricate laser, photoconductor, and photodiode devices.

Etching: Soluble in aqua regia-type solutions, H_2O_2, and halogens.

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MERCURIC CADMIUM TELLURIDE ETCHANTS

HGCT-0001
ETCH NAME: TIME: 30 sec
TYPE: Acid, stain TEMP: RT
COMPOSITION:
1 .... HCl
1 .... HNO_3
1 .... H_2O
DISCUSSION:
HgCdTe, single crystal ingots and wafers. Solution used to stain both ingots and wafers to observe segregation, slip, and other defects.
REF: *J Cryst Growth*, 65,249(1983)

HGCT-0002a
ETCH NAME: TIME:
TYPE: Acid, structure TEMP:
COMPOSITION:
2 .... HCl
1 .... HNO_3
3 .... H_2O
DISCUSSION:
HgCdTe, wafers. Mechanical lap with SiC, then chem/mech polish with an acid slurry of colloidal silica:H_2O_2:H_2O. Then etch with the solution shown to bring out dendritic growth structure. A final light etch in Br_2:MeOH will polish the surface and help delineate the structure.
REF: Boliang, C et al — *J Electron Mater*, 13,47(1984)

HGCT-0003
ETCH NAME: TIME: 3 h
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
2 .... H_2O_2
2 .... H_2O
DISCUSSION:
HgCdTe, (111) thin films grown on CdTe substrates to develop the (111)A and $(\overline{1}\overline{1}\overline{1})$B oriented faces. Solution shown was used to etch surfaces in a study of mis-orientation and structure. The $(\overline{1}\overline{1}\overline{1})$B surface was good with <4° mismatch. The (100) substrate orientation was also evaluated.
REF: Edwall, B D et al — *J Appl Phys*, 55,1453(1984)

HGCT-0004
ETCH NAME: TIME:
TYPE: Halogen, step-etch TEMP: RT
COMPOSITION:
(1) x .... Br_2
x .... MeOH
(2) x .... Br_2
x .... ethylene glycol
DISCUSSION:
HgCdTe, thin films deposited by VPE on CdTe substrates using an open tube with a semi-enclosed slider. Step-etch with solution shown for about 1—2 μm/steps. Removal measured after each step-etch using interference fringes in deposit depth measurement.
REF: Nebirovsky, Y & Kepten, A — *J Electron Mater*, 13,866(1984)

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HGCT-0005
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... 0.1 *N* Br_2
x .... MeOH
DISCUSSION:
HgCdTe, single crystal wafers used in a study of reaction kinetics with Br_2:MeOH. Wafers were hand polished on a pellon pad saturated with the solution shown.
REF: Takasek, R T & Syllaios, A J — *J Electrochem Soc*, 132,656(1985)

TIME:
TEMP:

HGCT-0002b
ETCH NAME:
TYPE: Acid-slurry, polish
COMPOSITION:
x .... colloidal SiO_2
x .... H_2O_2
x .... H_2O
DISCUSSION:
HgCdTe, (111) wafers and other orientations used in a study of growth structure. After mechanical lapping with SiC, wafers were chem/mech polished with the acid-slurry shown. A final light etch with Br_2:MeOH will polish surface and help delineate structure.
REF: Ibid.

TIME:
TEMP: RT

HGCT-0006
ETCH NAME: BRM
TYPE: Halogen, removal
COMPOSITION:
20 .... Br_2
80 .... MeOH
DISCUSSION:
$Hg_{1-x}Cd_xTe$, (111) wafers. Solution used as a general removal etch. After etching rinse in methanol to remove residual bromine.
REF: Parker, S G & Pinnell, J E — *J Electrochem Soc*, 118,1868(1971)

TIME:
TEMP: RT

HGCT-0007
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
x .... 2% Br_2
x .... dimethylformamide
DISCUSSION:
HgCdTe, (111) wafers used in a study of the reduction of native oxide using CVD SiO_2. Wafers were chem/mech polished in the solution shown. They were then oxidized for 700 Å thickness in xKOH:xglycerine:xH_2O, followed by 250—300 Å CVD SiO_2.
REF: Rhiger D R et al - *J Vac Sci Technol*, 21(2)448(1982)

TIME:
TEMP:

HGCT-0008a-b
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
(1) x .... .02% Br_2
x .... MeOH

(2) x .... $NaBH_4$, sat. sol.
x .... MeOH

TEMP: RT

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DISCUSSION:

$Hg_{1-x}Cd_xTe$ single crystal grown in a study of chemical etching and oxidation. Wafers were polished in solution (1), then in solution (2), and (3) again in solution (1). Prior to material growth: (A) clean Cd in HCl; (B) clean Hg in KCN, and (C) clean Te in BRM solution or electrolytically in an $NaBH_4$ solution as shown in (2).

REF: Aspnes, D & Arwin, H — *J Vac Sci Technol*, A(2)3,1309(1984)

HGCT-0009

ETCH NAME: BRM — TIME:

TYPE: Halogen, polish — TEMP:

COMPOSITION:

x .... x% Br_2

x .... MeOH

DISCUSSION:

HgCdTe specimens. After saw cutting of wafers chem-mech polish with a BRM solution using a saturated metallographic type pad. Final etch in BRM solution as a free-etch, e.g., wafers dropped free in solution.

REF: Wu, S Y — *J Vac Sci Technol*, 21,255(1982)

HGCT-0010

ETCH NAME:

TYPE: Acid, slurry removal — TEMP: RT

COMPOSITION:

(1) x .... Al_2O_3, powder
x .... MeOH
x .... HAc

(2) x .... Al_2O_3, powder
x .... I_2
x .... MeOH

DISCUSSION:

HgCdTe (acronym: MCT) single crystal material fabricated as a semiconductor material with a tunable energy gap, After mechanical lapping of surfaces, either slurry solution can be used to etch polish/remove residual lap damage. Solution (2) is a halogen similar to BRM solutions.

REF: Goldstein, M et al — *Metallography* (MEIJAP), 16,321(1983)

PHYSICAL PROPERTIES OF MERCURIC IODIDE, HgI_2

Classification	Iodide
Atomic numbers	80 & 53
Atomic weight	454.45
Melting point (°C)	250
Boiling point (°C)	354
Density (g/cm³)	6.27
Hardness (Mohs — scratch)	1—2
Crystal structure (hexagonal — rhombohedral)	(10$\bar{1}$1) rhomb
(tetragonal — normal)	(100) a-pinacoid
Color (solid)	Yellow-reddish
Cleavage (basal)	(0001)/(001)

MERCURIC IODIDE, HgI_2

General: Does not occur in nature as an iodide compound although it does occur as the chloride: calomel, HgCl — called horn quicksilver — which is found as a coating of

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secondary origin deposited from hot solutions and associated with cinnabar, HgS. The majority of the world's mercury comes from small mines in Spain, and similar deposits are found in the coastal ranges in California. Cinnabar is roasted to obtain the mercury, which is sold commercially by the 50-lb flask.

The yellow form of mercuric iodide occurs when the brilliant red form is heated above 128°C, but reverts to the red form upon cooling and being rubbed or scratched. Sodium nitrate — soda niter, $NaNO_3$ — known as Chile saltpeter, contains sodium iodate, $NaIO_3$; lautarite, $Ca(IO_3)_2$ and dietzeite, $Ca(IO_3)_2.CaCrO_4$ are found in association with Chile saltpeter.

The yellow form of HgI_2 will darken when exposed to light and has been used in photography, and both forms are used in medicine.

Technical Application: Mercuric iodide is not used in Solid State material processing.

Both colored forms may be used in iodine vapor transport growth of mercury containing compound semiconductors such as cadmium mercuric telluride or selenide.

The compound has been grown as a single crystal for general morphological studies.

Etching: Slightly soluble in water, soluble in KI, and other halogens.

MERCURIC IODIDE ETCHANTS

HGI-0001a
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
x .... 0.2% Br_2
TIME:
TEMP: RT
DISCUSSION:
Alpha-HgI_2, single crystal specimens used in a morphology study. Use bromine solution (in MeOH?) to polish. Study under an optical microscope (OM) with an LN_2 cold stage to prevent vaporization.
REF: Kobayshi, T — *J Appl Phys*, 130,1183(1983)

HGI-0001b
ETCH NAME:
TYPE: Halogen, polish
COMPOSITION:
x .... 20% KI
TIME:
TEMP: RT
DISCUSSION:
Alpha-HgI_2, single crystal specimens used in a morphology study. Use a potassium iodide solution (in MeOH?) to polish. Study under an optical microscope (OM) with an LN_2 cold stage to prevent vaporization.
REF: Ibid.

HGI-0002
ETCH NAME: Acetone
TYPE: Ketone, growth
COMPOSITION:
x .... $(CH_3)_2CO$
TIME:
TEMP:
DISCUSSION:
HgI_2 single crystals grown by evaporation from a mixture of powdered 75% HgI_2:25% $HgCl_2$ with acetone as the carrier in an open beaker.
REF:

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PHYSICAL PROPERTIES OF MERCURIC OXIDE, HgO

Classification	Oxide
Atomic numbers	80 & 8
Atomic weight	216.61
Melting point (°C)	100 del.
Boiling point (°C)	
Density (g/cm)	11.14
Refractive index (n =)	2.37—2.65
Hardness (Mohs — scratch)	1.5—2
Crystal structure (orthorhombic — normal)	(100) a-pinacoid
Color (solid)	Orange-red
Cleavage (prismatic — perfect)	(010)

MERCURIC OXIDE, HgO

General: Occurs as the mineral montroydite, HgO. It is a rare species as it is volatile and readily reduced by boiling mercury at close to its vapor point (357°C) in air. The mercury surface becomes coated with a mixed yellow/red mercuric oxide. Caution should be observed in working with mercury and its compounds as both the vapor and finely divided particles are extremely poisonous.

Mercuric oxide has no use in industry, but there are two major chloride compounds: mercurous chloride — calomel, HgCl is a medicinal specific for the stimulation of secretory organs; mercuric chloride, $HgCl_2$ — called corrosive sublimate — is a violent poison, yet is a powerful medical antiseptic. Mercuric fulminate, $Hg(ONC)_2$ is the most used detonator for gunpowder and high explosives. Its discovery led to the development of the percussion cap, which displaced the old flintlock rifles.

Technical Application: Mercuric oxide has no application in Solid State processing. It has little or no use as it is unstable and extremely soft.

Etching: Soluble in acids and water.

MERCURIC OXIDE ETCHANTS

HGO-0001
ETCH NAME: Potassium cyanide — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... x% KCN
DISCUSSION:

HgO, as a native oxide on mercury. Solution used to clean mercury prior to its use in epitaxy growth of HgCdTe. Grown material used in a study of etching and oxidation. (**CAUTION** — The cleaning reaction may produce fulminate of mercury, $Hg(OCN)_2$!)
REF: Aspenes, D E & Arwin, H — *J Vac Sci Technol*, A(2),1309(1984)

PHYSICAL PROPERTIES OF MERCURIC SELENIDE, HgSe

Classification	Selenide
Atomic numbers	80 & 34
Atomic weight	79.57
Melting point (°C)	>900 est.
Boiling point (°C)	
Density (g/cm^3)	8.19 (8.3—8.47)
Hardness (Mohs — scratch)	2—3

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Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Steel-grey
Cleavage (octahedral)	(111)

MERCURIC SELENIDE HgSe

General: Occurs as the natural mineral tiemannite, HgSe, and may be in considerable amounts such as the Utah deposits in the U.S. The mineral onofrite, Hg(S,Se), is of minor occurrence, and both are found in association with sphalerite, ZnS, deposits.

Primary use in industry is as an ore of both mercury and selenium.

Technical Application: Mercuric selenide is a II—IV compound semiconductor with (111) surface polarity common to such compounds: (111)Hg and $(\overline{1}\overline{1}\overline{1})$Se wafer surfaces, respectively. It has had little use as a semiconductor because of its softness (H = 2—3).

It has been the subject of morphological studies as both the natural and artificial single crystal.

Etching: Soluble in aqua regia-type solutions and halogens.

MERCURIC SELENIDE ETCHANTS

HGSE-0001a
ETCH NAME:
TYPE: Acid, polish
TIME: 10—15 min
TEMP: 40°C
COMPOSITION:
1 .... HCl
50 .... HNO_3
10 .... HAc
20 .... 10 *N* H_2SO_4
DISCUSSION:
HgSe, (111) wafers. Described as a polish etch that does not produce pitting. (*Note:* This is a major article on etching II—VI compounds.)
REF: Warekois, E P et al — *J Appl Phys*, 33,690(1962)

HGSE-0001b
ETCH NAME:
TYPE: Acid, preferential
TIME:
TEMP:
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
HgSe, (111) wafers used in an etch study of the polarity effect. The (111)A surface shows pits, initially, but they disappear with etching time. The $(\overline{1}\overline{1}\overline{1})$B surface is coated with a selenium film with no defects apparent. The residual Se film remaining after etching can be removed in H_2SO_4.
REF: Ibid.

HGSE-0001c
ETCH NAME:
TYPE: Acid, preferential
TIME: 5 min, twice
TEMP: RT
COMPOSITION:
6 .... HCl
2 .... HNO_3
3 .... H_2O

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DISCUSSION:

HgSe, (111) wafers used in an etch study of the polarity effect. Wafers were first polish etched (HGSE-0001a). The (111)A surface produces rough craters. The $(\overline{1}\overline{1}\overline{1})$B produces triangular etch figures. Remove residual Se film remaining after etching with polish etch by brush-off under water.

REF: Ibid.

HGSE-0002: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7.

HgSe, (111) wafers. Polish with HGSE-0001a solution which removes Se film, then brush under water; repeat. $(\overline{1}\overline{1}\overline{1})$B surface develops triangle pits.

HGSE-0003

ETCH NAME: Bromine — TIME: 1 min

TYPE: Halogen, polish — TEMP: RT

COMPOSITION:

x .... Br_2

DISCUSSION:

HgSe, single crystal specimens. Follow bromine etching with wash in EOH, then benzene to remove selenium films. (Etch system developed by M C Lavine for Harman.) Specimens used in a magnetoresistance study.

REF: Harman, T O — *J Appl Phys*, 32,1800(1961)

PHYSICAL PROPERTIES OF MERCURIC TELLURIDE, HgTe

Classification	Telluride
Atomic numbers	80 & 52
Atomic weight	327.49
Melting point (°C)	>900 est.
Boiling point (°C)	
Density (g/cm³)	8.07
Hardness (Mohs — scratch)	2.5
Crystal structure (isometric — tetrahedral)	(111) tetrahedron
Color (solid)	Iron-black
Cleavage (octahedral)	(111)

MERCURIC TELLURIDE, HgTe

General: Occurs in nature as mineral coloradoite, HgTe and named for its discovery in sphalerite (ZnS) deposits in the state of Colorado. Major quantities are found in Western Australia and called kalgoorlite, HgTe, as a mineral mixture of coloradoite and petzite, (Ag,Au)Te.

Primary industrial use is as an ore of mercury and tellurium.

Technical Application: Mercuric telluride is a II—VI compound semiconductor with the usual polarity structure of these compounds: (111)Hg and $(\overline{1}\overline{1}\overline{1})$Te wafer surfaces. Like mercuric selenide, HgSe, the compound is relatively soft (H = 2.5) and, as both have very low energy band gaps, they have not been used as semiconductor devices to any extent.

Both the natural and artificial compounds have been studied for morphological data and polarity effects.

Etching: Soluble in aqua regia-type solutions, alkalies, and halogens.

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MERCURIC TELLURIDE ETCHANTS

HGTE-0001a
ETCH NAME:
TYPE: Acid, polish
TIME: 10—15 min
TEMP: RT
COMPOSITION:
1 .... HCl
6 .... HNO_3
1 .... H_2O
DISCUSSION:
HgTe, single crystal wafers. Solution described as a polish etch that does not produce pitting. (*Note:* Article covers etching of II—V compounds.)
REF: Warekois, E P et al — *J Appl Phys*, 33,690(1962)

HGTE-0001b
ETCH NAME:
TYPE: Acid, preferential
TIME: 1 min, 3 times
TEMP: RT
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:
HgTe, (111) wafers used in an etch study of polarity defect development. The (111)A surface produces triangular etch pits with a background of shallow triangular etch figures. The $(\overline{1}\overline{1}\overline{1})$B is flat and grainy in appearance. Etch for three 1-min periods.
REF: Ibid.
HGTE-0002a Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7.
HgTe, (111) wafers. Polish with HGT-0001a solution; then preferential etch for three 1-min periods. (111)A surface develops pits with background figures.

HGTE-0002b
ETCH NAME:
TYPE: Alkali, dislocation
TIME: 10 min
TEMP: RT
COMPOSITION:
2 .... 15% NaOH
1 .... $Na_2S_2O_8$, sat. sol.
DISCUSSION:
HgTe, (111) wafers. Solution used as a general dislocation etch.
REF: Ibid.

METALS, GENERAL

General: Several metals occur in nature as native elements and, like gold, may be the primary source of the metal as an ore. There are metallic types, such as those of the Gold Group (silver, copper, mercury, lead, and amalgam, AgHg); and the Platinum Group (iridium, palladium, and iron). The nonmetals include only graphite (carbon), sulfur, and selenium with zinc considered the connecting link between metals and semi-metals. All of the metals crystallize in the isometric system, normal class; whereas the semi-metals form in the hexagonal system, rhombohedral division. Native tin is an exception, being in the tetragonal system. Osmium occurs as a mixture with iridium in the mineral iridosmine (osmiridium), and all native elements contain traces of other metals, sometimes in fair quantity, such as electrum, AuAg(20%). The semi-metals include tellurium, antimony,

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arsenic, and bismuth which, though they occur as native elements in small quantities, are more common as compounds.

There are some metallic compounds, such as the tellurides and selenides and antimonides, but the majority of metals occur as oxides, sulfides, silicates, carbonates. The silicates comprise over 60% of all known natural minerals. Ancient man is said to have known seven metals — gold, silver, and copper with the most early use, followed by iron, tin, mercury, and sulfur — though he used many compounds in addition: red rouge from red ocher hematite, Fe_2O_3; magnetite, Fe_3O_4, as a compass (lodestone), and as black rouge; silica, SiO_2, as flint or obsidian were some of the first tools; and the Egyptians developed glassmaking, circa 2500 B.C.; not to mention the clays as basic building materials as sun-dried brick, later as kiln-fired brick. Other natural minerals were used as building stone (sandstone, marble, limestone) or as coloring agents for glass, leather, and cloth as shown from Egyptian records, and modern industry today still uses many of the same metals and minerals in a similar manner.

In metal processing there are several aspects related to chemical processing, from ore reduction, through material fabrication, to tests and evaluations utilizing metallographic techniques for study and evaluation. The metal industries, as a group, use more electrolytic etching and cleaning than do the Solid State and electronics industries, in part, due to their handling of the so-called "heavy metals" and their alloys, e.g., iron, steel, molybdenum, tantalum, copper, and tungsten. All processing areas use electrolytic plating on metals for a variety of purposes, from decorative washes to thicker corrosion resistant layers. And organics, such as mylar or other plastics, are coated as sunscreens or other industrial applications. But there is only limited information on plating solutions per se in this book, as it is more concerned with chemical processing using etching and cleaning solutions.

There are many books and articles covering the theory and practice of chemical processing — some general — some on specific metal groups, such as copper and its alloys or irons, steels and their alloys — aluminum and aluminum alloys — molybdenum, tantalum, titanium, and tungsten . . . each metal covered in detail. This includes the handling of solders and brazing alloys, such as the high temperature silvaloys. Because of the broad aspects of such articles and brochures or books, several have been collected as general references and presented in this general Metals section without regard to application of a specific solution, with several appearing elsewhere under a particular metal with a particular solution mixture and application discussion.

Technical Application: See specific metals and metallic compounds in this Etchant Section for more specific applications and discussions.

Etching: See individual formatted materials.

METALS ETCHANTS

MET-0001
ETCH NAME:
TYPE: Electrolytic, polishing
COMPOSITION:
x .... acids

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

All metals. A discussion of the electropolishing of metals for microscopic examination.

REF: von Hamos, I — *Jernkontorets Ann*, 126,568(1942) (in Swedish)

MET-0002: Brovillet, P & Epelboin, I — *Met Rev*, 51,593(1954) (in French)

All metals. A study of results relative to the composition of electrolytic polishing baths.

MET-0003: Michel, P — *Met Rev*, 46,39(1949)

All metals. The use of electrolytic polishing to produce exact geometric forms.

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MET-0004
ETCH NAME:
TYPE: Acid, polishing
COMPOSITION:
x .... acids
TIME:
TEMP:
DISCUSSION:
All metals and alloys. A general discussion of chemical polishing.
REF: de Jong, J J — *Metalen*, 9,2(1954) (in Dutch)

MET-0005
ETCH NAME:
TYPE: Acids, etching
COMPOSITION:
x .... acids solutions
TIME:
TEMP:
DISCUSSION:
Metals. An extensive list of specific etchant mixtures formulated or developed for study and processing of most industrial metals. This pamphlet contains several hundred numbered or named solutions, and several that are unnumbered. It does not describe application or uses, and the list is without regard to any specific metal or metal compounds on which they are used, yet it is probably the most extensive collection of etching and cleaning solutions available, other than this handbook.
REF: Pamphlet: ASTM E407-70 (1971)

MET-0006
ETCH NAME:
TYPE: Electrolytic, dissolution
COMPOSITION:
x .... acids
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
All metals. A general presentation of anodic dissolution etch removal of metals and electropolishing of surfaces.
REF: Niggins, J K — *J Electrochem Soc*, 106,999(1959)

MET-0007
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... acids
TIME:
TEMP:
DISCUSSION:
All metals. A study of grain growth in metals in both bulk materials and thin films. Growth follows a general pattern: initial island growth at low energy points on the substrate surface (defects, etc.); then lateral growth from initially deposited islands until they commence to coalesce; and finally additional thickness growth as complete surface coverage. The initial deposit of islands/lateral expansion may be colloidal to amorphous without structure followed by complete growth coverage as randomly oriented crystallites. Grain size varies with growth rate, temperature, and pressure. Applies to growth of both natural minerals and artificially fabricated metals or alloys.
REF: Feltham, P — *Acta Metall*, 5,97(1957)

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MET-0008
ETCH NAME: TIME:
TYPE: Preparation, metallographic TEMP: RT
COMPOSITION:
(1) x .... mechanical lap/polish
(2) x .... preferential etching
DISCUSSION:
Metals and alloys that are easily oxidized. A discussion of preparation of specimens for photomicrographic study. Large specimens prepared as individual units; small specimens encapsulated in clear Lucite powder under pressure/heat, then rough lapped to expose specimen surface, with final lap/polish and etch of specimen for microscope examination. This is basic metallographic laboratory operation but, as materials are prone to oxidation, work should be done under an inert atmosphere such as nitrogen or argon with solvents and lapping slurries containing nonoxidizing agents, though final specimen finish may include heat tinting by surface oxidation in air on a hot plate.
REF: Boom, E A — *Zavdskaya Lab*, 13,1139,(1947)

MET-0009
ETCH NAME: TIME:
TYPE: Particles, irradiation TEMP:
COMPOSITION:
x .... Ar^+, Xe^+, Cu^+ ions
DISCUSSION:
All metals. A study of the effects of irradiation on metal surfaces that induce damage and structure alteration.
REF: Meckel, B B & Swalin, R A — *J Appl Phys*, 30,89(1959)

MET-0010
ETCH NAME: TIME:
TYPE: Etchants, dislocation TEMP:
COMPOSITION:
x .... acid/acid mixtures
DISCUSSION:
Metals and metallic compounds. A study of the correlation of etch figures with dislocations in a bulk material surface with regard to top surface and bulk crystallographic planes.
REF: Sun, Jui-Fang & Shaskol'skaya, M P — *J Sov Phys-Cryst*, 4,550(1960).
MET-0011: Knuth-Winterfeldt, E — *Rev Alum*, 28,84(1951)
The electropolishing of light metals rich in silicon for electrographic study.

MET-0012
ETCH NAME CP4 TIME:
TYPE: Acid, selective TEMP: RT
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... HAc
0.6 .... Br_2
DISCUSSION:
Metals. A curved steel point was used to scribe 10 μm width lines into substrate surfaces to observe metal plating and etching effects. Plating shows erratic build-up and etching is more rapid along the ruptured lines. Germanium and silicon wafers used as test vehicles; copper, gold, and silver plating as evaluation metals. See SI-0092a.

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REF: Rindner, W & Lavine, J M — *J Electrochem Soc*, 108,809(1961)
MET-0013: Vermilyea, D A — *Acta Metall*, 6,381(1958)
A discussion on the formation of etch pits at dislocations on single crystal metal and semiconductor surfaces.
MET-0014: Ranaldi, M & Ostapkovich, P L — *J Appl Phys*, 31,20)9(1959)
A study of the relationship between optical orientation and etch time.

MET-0015
ETCH NAME: Ion etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
A study of etching surfaces with 8 KeV argon ions. (*Note:* This type of application of ionized gases is now called dry chemical etching (DCE), and is one of the three etchant formats used in this book.)
REF: Cunningham, R L et al — *J Appl Phys*, 31,839(1960)

MET-0016
ETCH NAME: Acid
TYPE: Electrolytic, removal
COMPOSITION:
x .... acid(s)

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Theory and practice of chemical polishing (Part II) covering processes for light metal alloys, the iron group and other metals. (*Note:* The "Iron Group" includes the high temperature precious metals, such as platinum, palladium, osmium, and iridium, in addition to iron.)
REF: Pinner, R — *Electroplating*, 6, 401(1953)

MET-0025
ETCH NAME:
TYPE: Chemical, polishing
COMPOSITION:
x .... acids

TIME:
TEMP:

DISCUSSION:
Theory and practice of chemical polishing of metals. Part I covers copper-base alloys; Part II covers iron-base alloys, and Part III covers general theory of chemical etching.
REF: Pinner, R — *Electroplating*, 6,360(1953) (Part I)
MET-0018: Pinner, R — *Electroplating*, 6,274(1953) (Part II)
MET-0019: Pinner, R — *Electroplating*, 7,127(1954) (Part III)

MET-0020
ETCH NAME: Diamond
TYPE: Abrasive, polish
COMPOSITION:
x .... diamond paste

TIME:
TEMP:

DISCUSSION:
The use of diamond abrasives for metallographic specimen polishing.
REF: Samuel, L E — *J Inst Met*, 81,471(1953)

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MET-0021: Samuel, L E — *Metallurgica*, 50,303(1954)
Similar processing of metals.

MET-0022
ETCH NAME: Brazing TIME:
TYPE: Metal, joining TEMP:
COMPOSITION:
x .... BAg
DISCUSSION:
BAg alloys used as high temperature brazing materials with a discussion of silver brazing techniques, to include the use of pre-forms, design of joints, and methods of application — torch, furnace, resistance, induction, and dip brazing. After brazing, joints are washed in hot water to remove remaining flux, and there are commercial solvent mixtures available (usually an alcohol/water base).
REF: Brochure: *Silvaloy, "A Complete Guide to Successful Silver Brazing"*, Silver Brazing Div., The American Platinum Works, Newark, NJ (no date)

MET-0023
ETCH NAME: Tungsten TIME:
TYPE: Metal, processing TEMP:
COMPOSITION:
(1) x .... chemicals
(2) x .... gases
DISCUSSION:
W, metal specimens and parts. Pamphlet includes physical properties, chemicals and gases evaluated against corrosion, with specific solutions for etching and cleaning tungsten and tungsten alloys.
REF: Pamphlet: *Tungsten*, #395/1./71 — Schwartzkopf Development Corp.

MET-0024
ETCH NAME: Platinum TIME:
TYPE: Metal, processing TEMP:
COMPOSITION:
x .... chemicals
DISCUSSION:
Pt, metal and its alloys. Includes the other Platinum Group metals, such as osmium, indium, and palladium and their physical properties, products fabricated, and applications in chemistry and chemical processing.
REF: Brochure: *Platinum* — Baker & Co., Inc. (no date)

MET-0026
ETCH NAME: TIME:
TYPE: Metals, processing TEMP:
COMPOSITION:
x .... chemicals
DISCUSSION:
Metals and alloys or natural metallic compounds. This series of pamphlets cover most metals and alloys of the general metal industries with regard to metallographic study — preparation of materials — following special testing (corrosion, thermal, stress, etc.) — with specific etching/cleaning formulations applied to specimens with excellent picture results. Also includes metallographic equipment, methods of general processing, and chemical

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processing details. (*Note:* Many of the solutions listed in ASTM E-407-70 are shown here with specific metal or alloy applications.)
REF: Pamphlets: *A/B Metals Digest Series* #/year — Buehler Ltd, 1970—1980s

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MET-0027
ETCH NAME: Potassium chloride
TYPE: Electrolytic, cleaning
COMPOSITION:
x .... KCl, sat. sol.
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

Metals. Solution recommended for removing contamination from metal surfaces and referred to as separating nonmetallic phases from specimens.
REF: Tufts, C F — *J Appl Phys*, 31,1846(1960)

MET-0028
ETCH NAME: Heat
TYPE: Thermal, defect
COMPOSITION:
x .... heat, cycling
DISCUSSION:
TIME:
TEMP:

Metals. A study of strain enhanced diffusion in metals and its interpretation. Cracks in a metal can cause strain which is enhanced with addition heat cycling.
REF: Ruoff, A L — *J Appl Phys*, 34,2862(1963)

MET-0029
ETCH NAME:
TYPE: Mechanical, damage
COMPOSITION:
x .... abrasion
DISCUSSION:
TIME:
TEMP:

Metals, deformed by lapping and polishing of surfaces. A severely deformed zone near the surface that is not characteristic of the bulk material that shows metal flow — the Beilby layer — about 50 Å thick, unknown whether it is amorphous or very fine crystallites. Below the Beilby layer before reaching undisturbed bulk material is a thick transition zone of deformed metal. (*Note:* There is temperature involved in forming the Beilby layer. Damage depth varying with abrasive grit, shape, hardness to some extent, and grit diameter, in particular. Estimates say subsurface damage induced can run from 3 to 5 mils in depth.)
REF: Finch, G I — *Proc Phys Soc*, A63,785(1950)
MET-0030: McAfes, J — *Aust Eng Yearbook*, 1944

Metals. An article on the metallographic polishing and etching of metals.

MET-0031
ETCH NAME:
TYPE: Mechanical, cutting
COMPOSITION:
x .... lubricants
DISCUSSION:
TIME:
TEMP: RT

Metals and hard crystals. A method of wire saw cutting of materials. (*Note:* There are several systems often using an abrasive slurry or acid-slurry, such as abrasive:water:glycerin with or without HCl, HNO_3, HF, KOH. The wire can be metal, single or multiple strand; a linen, rug, or cotton thread; or metal rods.)

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REF: Alexander, E & Many, K A — *Rev Sci Instr*, 26,983(1955)
MET-0013: Enck, F D — Ph.D thesis, *Univ Microfilms*, Publ 23-264.
Describes the use of a tool post grinder in forming cylinders.
MET-0032: Bond, W L — *Rev Sci Instr*, 22,344(1951)
Describes a method of fabricating material spheres by tumbling. (*Note:* There are a number of sphere-forming methods of this type with specific names.)
MET-0034: Carter, J L et al — *Rev Sci Instr*, 30,446(1959)
Describes a sphere grinding technique developed for ferrites. (*Note:* In general metal cutting or shaping a water or oil lubricant with anti-rust agents are used for cooling. Use water-soluble silicones, not mineral oils, for semiconductor or other high-technology materials.)

MET-0035
ETCH NAME: TIME:
TYPE: Growth, structure TEMP:
COMPOSITION:
x .... metal
DISCUSSION:
Metals used in a study of the shape of grain growth. Triangular plane-view grains have an equilibrium 120° angle between sides. If angle is greater, sides will be convex; if less, concave, (+) and (−), respectively. (*Note:* This has been observed by others in single crystal metals and metallic compounds as both naturally grown forms on minerals, and in etched pits.)
REF: Feltham, P — *Acta Metall*, 5,97(1957)
MET-0036: Irving, B A — *J Appl Phys*, 31,109(1960)
Metals and metallic compounds. A study of the shapes of etch hillocks and pits and their correlation with measured etch rates.
MET-0037: Grovenor, C R M — *Thin Solid Films*, 89,367(1982)
Metal contacts. A study of interdiffusion during heating of contacts as diffusion induced boundary migration (DIBM) along deposit grains.

PHYSICAL PROPERTIES OF MOLYBDENUM, Mo

Classification	Transition metal
Atomic number	42
Atomic weight	95.94
Melting point (°C)	2610
Boiling point (°C)	5560
Density (g/cm^3)	10.22
Thermal conductance (cal/sec)(cm^2)(°C/cm)	3.25
Specific heat (cal/g) 20°C	0.062
Latent heat of fusion (cal/g)	67 (70)
Heat of vaporization (cal/mole)	1175
Atomic volume (W/D)	9.4
1st ionization energy (K-cal/g-mole)	166
1st ionization potential (eV)	7.18
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.30
Ionic radius (angstroms)	0.70 (Mo^{+4}) 0.62 (Mo^{+6})

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Vapor pressure (atm $\times 10^{-4}$) 3227°C	8.6
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	5.1
Electrical resistivity (micro-ohms/cm) 0°C	5.17
Magnetic susceptibility (cgs $\times 10^{-6}$) 25°C	0.93
Electron work function (eV)	4.27
Cross section (barns)	2.6
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Silver-white
Cleavage (cubic — poor)	(001)

MOLYBDENUM, Mo

General: Does not occur as a native element. There are half a dozen minerals containing molybdenum, all oxides, other than molybdite, MoS_2. The disulfide is widely distributed in small quantities, and is a major ore of the metal. Because of its softness (H = 1—1.5), dark grey/black color and high specific gravity (G = 4.7—4.8), it was originally confused with lead and graphite. Wulfenite, $PbMoO_4$, is the major oxide ore. The oxide minerals are associated with lead and tin veins and in pegmatites.

The pure metal is a major industrial additive to irons and steels to increase toughness and tensile strength, as well as for its high temperature capabilities. It is softer and more ductile than tungsten, has been used as heater wires or for light filaments, and as plate and rod heating elements for both heat dissipation and its electrical capabilities. The common name is "moly". Moly disulfide, MoS_2, is used as a dry lubricant similar to the applications of graphite and, in stick form, has occasionally been used as a pencil.

Technical Application: In Solid State processing the pure metal has been used as disc and flat heat sinks for device mounting due to its close coefficient of expansion match with semiconductor silicon, it is next only to tungsten in that regard, and more easily processed. As a pressed powder pre-form it has a tough, fibrous structure, but also has been used as an extruded sheet or in single crystal form. It is evaporated as a thin film, often in conjunction with layered structures and the formation of silicides: MoSi, Mo_2Si, $MoSi_2$ used as blocking layers in semiconductor device structuring.

It has been artificially grown as a single crystal and studied for both general morphological and electrical properties. As a deposited thin film on glass, it has been studied for its thin film characteristics.

Etching: Difficult to etch. Soluble in hot HNO_3 and H_2SO_4. Most etching done with mixed acids.

MOLYBDENUM ETCHANTS

MO-0001a
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... H_2O_2
DISCUSSION:
Mo, specimens. Various mixtures of HF:H_2O_2 will etch molybdenum.
REF: Booklet: *Molybdenum*, #406.6.71 Schwartzkopf Development Corp.

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MO-0002
ETCH NAME: TIME:
TYPE: Acid, polish/clean TEMP: RT
COMPOSITION:
1 .... NH_4OH
2 .... H_2O_2
7 .... H_2O
DISCUSSION:
Mo, foil. Solution used to clean moly foil prior to deposition of gallium arsenide as an epitaxy thin film.
REF: Ghandhi, S K & Reep, D H — *J Electrochem Soc*, 129,2778(1982)

MO-0003
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
76 ml .... H_3PO_4
30 ml .... HNO_3
50 ml .... CH_3COOH (HAc)
150 ml .... H_2O
DISCUSSION:
Mo specimens. Solution becomes very hot with heavy evolution of NO and NO_2 fumes. Rinse in running water. Black smut remaining on surfaces can be removed with a dip/soak in HCl, then followed with water rinse and N_2 blow dry.
REF: Bulletin 1116B/Rev-HPD/VB/TM/0883/1K, MRC
MO-0012a: Walker, P — personal application, 1971—1973
Mo, pressed powder discs $^1/_2$ to 2" diameter with 0.090 nominal thickness used as heat sinks for silicon Triacs and SCRs. Discs mounted on strips of acid resistant tape and etched at RT, 1—2 min, water rinse 15—20 sec, soak in HCl 15—30 sec, and water rinse 1—2 min. Dry parts on hot plate at 150°C. Remove from tape, turn over and retape. Repeat etching sequence for second side. Final rinse in MeOH and hot plate dry.

MO-0001b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
x .... H_2SO_4
x .... KF
DISCUSSION:
Mo specimens. Solution will etch molybdenum.
REF: Ibid.

MO-0001c
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... MnO_4
DISCUSSION:
Mo specimens. Solution will etch molybdenum.
REF: Ibid.

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MO-0001d
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2SO_4
x .... $Na_2Cr_2O_7$, sat. sol.
DISCUSSION:
Mo specimens. Solution used to dip clean molybdenum parts.
REF: Ibid.
TIME:
TEMP: 195°F

MO-0001e
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
10 .... formic acid
90 .... H_2O_2
DISCUSSION:
Mo specimens. Used to etch clean molybdenum surfaces.
REF: Ibid.
TIME: 5—10 min
TEMP: RT

MO-0001f
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
Mo specimens. Various mixtures of HF:HNO_3 will attack moly rapidly.
REF: Ibid.
TIME:
TEMP: RT

MO-0001g
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HCl
x .... HNO_3
DISCUSSION:
Mo specimens. Various mixtures of HCl:HNO_3, to include aqua regia (used hot), will attack molybdenum rapidly.
REF: Ibid.
TIME:
TEMP: RT

MO-0001h
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... H_2O
DISCUSSION:
Mo specimens. Pure water used in a high pressure autoclave will etch molybdenum.
REF: Ibid.
TIME:
TEMP: 500°F

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MO-0004
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 12.5% H_2SO_4
x .... MeOH
TIME:
TEMP: −35°C
ANODE: Mo
CATHODE:
POWER:
DISCUSSION:
Mo sheet. Solution used to etch thin moly sheet down to foil.
REF: Whall, I — *J Electrochem Soc,* 129,105(1982)
MO-0005a: Couch D E et al — *J Electrochem Soc,* 105,450(1958)
Mo specimens. 70% H_2SO_4 used to electrolytically clean molybdenum surfaces. May leave a blue stain.
MO-0014: Rao, P & Thomas, G — *Acta Metall,* 15,1153(1967)
Mo specimens. Solution used to electropolish at 0°C and 6—8 V power. Specimens used in a study of neutron irradiation defects.

MO-0006
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
10 .... HCOOH (formic acid)
80 .... H_2O_2
10 .... H_2O
TIME: 2—3 min
TEMP: 60—70°C
RATE: 0.3—0.5 mils/ 2—3 min
DISCUSSION:
Mo specimens. Solution used in a study of cleaning moly surfaces.
REF: Bell Telephone Systems Tech Publ 3143(1958), 61

MO-0007a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
1 .... H_2SO_4
3 .... H_2O
TIME:
TEMP:
DISCUSSION:
Mo specimens. Solution used as a general removal and polish etch.
REF: Grossman, S & Herman, D S — *J Electrochem Soc,* 116,674(1969)

MO-0008a
ETCH NAME: Aqua regia
TYPE: Acid, polish
COMPOSITION:
1 .... HNO_3
3 .... HCl
TIME:
TEMP: 100°C+
DISCUSSION:
Mo specimens. Solution shows very rapid attack above 100°C.
REF: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices,* Reinhold, New York, 1967

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MO-0005b
ETCH NAME: Murakani's reagent
TYPE: Acid, removal/clean
COMPOSITION:
110 g .... KCN
100 g .... NaOH/l
TIME: 10 min, max.
TEMP: 80—90°C
DISCUSSION:
Mo specimens. Used a "diluted" solution. Agitate to prevent formation of a brown film which always forms when solution is used for over 10 min. After etching, water wash. After cleaning, specimens were chromium plated and used in a study of oxidation at high temperatures. (*Note:* An HCl rinse will remove brown moly oxide films.)
REF: Ibid.

MO-0015
ETCH NAME: Moly etch
TYPE: Acid, cleaning
COMPOSITION:
(1) 1145 ml .... HF
1170 ml .... H_3PO_4
550 ml .... HNO_3
570 ml .... HAc
(2) x .... HCl, conc.
TIME: 2—5 min
TEMP: RT
DISCUSSION:
Mo discs. Discs punch-cut from extruded sheet or pressed powder. Material is very tough with an elongated fibrous structure. Disc diameters from $^1/_4$ to 2" and 40 to 60 mils thick used as heat sinks for silicon mounting SCR wafers. Discs mounted on acid resistant tape strips and etch cleaned in solution shown. Solution is highly reactive with release of heavy NO and NO_2 fumes. After etching cleaning removes discs to running DI water for 20—30 sec. Then dip or soak in HCl to remove brown moly oxide stain and water wash. Dry on hot plate in air or under IR heat lamp.
REF: Topas, B & Weinstein, H — personal communication, 1970

MO-0016
ETCH NAME: Sulfuric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP:
ANODE: Mo
CATHODE:
POWER:
DISCUSSION:
Mo specimens. Used as a general anodic removal and polish etch.
REF: Korbslak — *Plating*, 40,1126(1953)

MO-0008b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... 25% HNO_3
TIME:
TEMP: RT
DISCUSSION:
Mo specimens. Concentrated nitric acid forms MoO_3 and can inhibit etching. At 100°C the solution shown is a rapid etch.
REF: Ibid.

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MO-0008c
ETCH NAME: TIME: 10 sec
TYPE: Acid, polish TEMP: 90°C
COMPOSITION:
3.5 ml .... HF
96 ml .... H_2SO_4
0.5 ml .... HNO_3
x .... 18 g/l Cr_2O_3
DISCUSSION:
Mo specimens. Solution is a rapid polishing etch.
REF: Ibid.

MO-0008d
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION
x .... KNO_3
DISCUSSION:
Mo specimens. The solution shown is a violently reactive etch on molybdenum as are the following: KNO_2, NaO_2, KCO_3, Na_2CO_3. KNO_3, KCl_3, and PbO_2.
REF: Ibid.

MO-0007b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
200 g .... $K_3Fe(CN)_6$
20 g .... NaOH
3—3.5 g .... sodium oxalate
1000 ml .... H_2O
DISCUSSION:
Mo specimens. Solution is a rapid polishing etch for molybdenum.
REF: Ibid.

MO-0009
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
92 g .... $K_3Fe(CN)_6$
20 g .... KOH
300 ml .... H_2O
DISCUSSION:
Mo specimens. A general rapid polish etch for molybdenum.
REF: Kodak Data Book, 1966, 91

MO-0010
ETCH NAME: TIME:
TYPE: Acid, clean TEMP:
COMPOSITION:
1 .... HCl
1 .... HNO_3

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DISCUSSION:

Mo poly sheet. Used as an insert on an SiC coated graphite susceptor. Remove after epitaxy deposition and etch clean in solution shown, DI water rinse and towel dry. Bake at 150°C overnight before reuse. Any brown oxide remaining is removed by bake in H_2 at 500°C. Used for MOCVD of deposition of AlGaAs (mp 660.2°C) with full melt at 674°C.
REF: Roberts, J J — *J Vac Sci Technol,* B1,850(1983)

MO-0011
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... KOH
x .... $K_3Fe(CN)_6$
TIME:
TEMP:
DISCUSSION:

Mo specimens used for electroplating. Use solution as an immersion polishing etch. (*Note:* Major article on electroplating of transition metals. Both etch solution and plating solutions are shown.)
REF: Saubestre, E B — *J Electrochem Soc,* 106,305(1959)
MO-0023: Faust, C L & Beach, J G — *Plating,* 43,1134(1950)

Reference shown for solution used above: MO-0011.

MO-0024a
ETCH NAME: Sulfuric acid, dilute
TYPE: Electrolytic, polish/thin
COMPOSITION:
870 ml .... H_2SO_4
30 ml .... H_2O
TIME:
TEMP:
ANODE:
CATHODE:
POWER: 12—20 V & 0.3—0.5 A/cm^2
DISCUSSION:

Mo, (111) wafers used in a study of transmission through thin crystals. Specimens were polished and thinned to about 1000 Å thick. Also, work was done with magnesium and magnesium oxide using other etchants.
REF: Thomas, G & Huftstutler, M C Jr — *J Appl Phys,* 31,1834(1960)

MO-0013a
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
TIME:
TEMP: RT
DISCUSSION:

Mo, (111) wafers. First, clean in solution shown and follow with potassium cyanide.
REF: Logan, K H & Schwartz, M — *J Appl Phys,* 26,1287(1955)

MO-0013b
ETCH NAME: Potassium cyanide
TYPE: Acid, cleaning
COMPOSITION:
x .... KCN
TIME:
TEMP: RT
DISCUSSION:

Mo, (111) wafers. First etch clean in HCl; follow with KCN and DI water rinse.
REF: Ibid.

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MO-0008e
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
250 g .... KOH
100 ml .... H_2O
0.25 g .... $CuSO_4$ or $CuCl_2$
TIME:
TEMP:
ANODE: Ta
CATHODE:
POWER:
DISCUSSION:
Mo specimens. A good general and uniform etch, but is rapid.
REF: Ibid.

MO-0012b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION
55 ml .... HNO_3
57 ml .... HAc
117 ml .... H_3PO_4
115 ml .... HF
TIME:
TEMP: RT
DISCUSSION:
Mo, pressed powder discs used as alloy heat sinks for silicon SCR wafers with diameters from $^1/_2$ to 2". Discs were nominally 0.060 thick. Solution is extremely exothermic with heavy evolution of NO_2 fumes. Black smut remaining on surface is removed by short soak in HCl. The individual acids were evaluated separately on moly and showed the following results: (1) HAc — no reaction in 2 min; (2) H_3PO_4 — no reaction in 2 min; (3) HF — very slow attack with surface cleaning action, only; (4) HNO_3 — turns surface dark grey (oxide). A 1HF:1HNO_3 solution reacts violently leaving a brown or violet-blue moly oxide on surface. After HCl final clean, DI water rinse 2—5 min and air dry on a hot plate — may include MeOH rinse following water.
REF: Ibid.

MO-0017
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal/polish
COMPOSITION:
x .... HF, conc.
TIME:
TEMP:
DISCUSSION:
Mo specimens. Use solution as an immersion etch for general removal and polishing of material.
REF: Runck, R J — *J Electrochem Soc,* 107,74(1957)

MO-0008f
ETCH NAME: Phosphoric acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... 20% H_3PO_4
TIME:
TEMP: 20°C
DISCUSSION:
Mo specimens. Solution is a controllable etch as diluted when used at temperature shown. At 100°C it is extremely rapid.
REF: Ibid.

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MO-0008g
ETCH NAME: Ammonium hydroxide
TYPE: Acid, removal
COMPOSITION:
x .... NH_4OH
DISCUSSION:
Mo specimens. Solution is a very slow removal etch.
REF: Ibid.
TIME:
TEMP:

MO-0008h
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, removal
COMPOSITION:
(1) x .... x% KOH
(2) x .... x% $NaNO_2$
DISCUSSION:
Mo specimens. Both solutions are rapid removal etchants.
REF: Ibid.
TIME:
TEMP:
ANODE: Mo
CATHODE:
POWER:

MO-0008i
ETCH NAME:
TYPE: Electrolytic, removal
COMPOSITION:
x .... NH_4OH
x .... H_2O_2
DISCUSSION:
Mo specimens. Solutions of these two acids are good controllable etchants for this material.
REF: Ibid.
TIME:
TEMP:
ANODE: Mo
CATHODE:
POWER:

MO-0025
ETCH NAME:
TYPE: Acid, removal/step etch
COMPOSITION:
15 .... NH_4OH
10 .... H_2O_2
100 .... H_2O
DISCUSSION:
Mo specimens subjected to Kr^+ ion bombardment. Solution used to step-etch remove molybdenum in studying depth of krypton penetration.
REF: Bartholomew, C Y — *J Appl Phys*, 35,2570(1964)
TIME:
TEMP:

MO-0020
ETCH NAME:
TYPE: Electrolytic, thinning
COMPOSITION:
25 ml .... HCl
10 ml .... H_2SO_4
75 ml .... MeOH
TIME:
TEMP: 10°C
ANODE:
CATHODE:
POWER: 18 V; 4 A/in^2 or 0.6 A/cm^2

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DISCUSSION:
Mo, single crystal specimens used in a study of dislocation channeling from neutron irradiation. Solution used to thin specimens prior to electron microscope observation.
REF: Mastel, B et al — *J Appl Phys*, 34,3637(1963)

MO-001i
ETCH NAME: Aluminum
TYPE: Metal, alloying
TIME:
TEMP: Molten
COMPOSITION:
x .... Al (Fe, Co, Ni & Sn)
DISCUSSION:
Mo, thin films and crystalline specimens. Molten aluminum will rapidly attack molybdenum forming alloys. Molten Fe, Co, Ni, and Sn also will form similar alloys with the material.
REF: Ibid.

MO-0021
ETCH NAME:
TYPE: Acid, polish
TIME: 5 min
TEMP: RT
COMPOSITION:
1 .... HCl
1 .... H_2O_2
DISCUSSION:
Mo, (100) specimens. Used as a general removal and polishing etch. Can be used to etch-pattern epitaxy thin films with photolithography techniques.
REF: Johns, C P — *J Vac Sci Technol*, 13,432(1976)

MO-0022a
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
TIME:
TEMP: Hot
COMPOSITION:
1 .... HNO_3
10 .... H_2O
DISCUSSION:
Mo, thin films evaporated on glass substrates. Solution will slowly attack molybdenum. Solution used to remove the metal and clean the substrate.
REF: *Rare Metals Handbook*, Reinhold, New York, 1954

MO-0022b
ETCH NAME:
TYPE: Acid, removal
TIME:
TEMP: Hot
COMPOSITION:
x .... HCl
x .... HNO_3
DISCUSSION:
Mo, thin films and crystalline specimens. Aqua regia type solutions rapidly attack molybdenum. Solutions used for general removal. Attack rate can be reduced by dilution with water or alcohols.
SEE: MO-0001g.
REF: Ibid.

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MO-0022c
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
Mo, thin films and crystalline specimens. Mixtures of these acids show rapid attack on molybdenum. Solutions used for general removal. Attack rate can be reduced by dilution with water or alcohols.
REF: Ibid.

MO-0023
ETCH NAME: Sodium acid sulfate TIME:
TYPE: Acid, removal/thinning TEMP: Hot
COMPOSITION:
x .... $NaSO_4$
x .... H_2O
DISCUSSION:
Mo, crystalline specimens. Hot pickling in the solution shown used to reduce thickness. A study of the correlation of temperature and grain size effects in the ductile-brittle transition of molybdenum.
REF: Passmore, E M — *Phil Mag*, 12,441(1965)

MOLYBDATES $M_2Mo_3O_8$

General: There are several molybdate and tungstate minerals in nature with the general formula MO_4 and MWO_4 with M = Ca, Pb, Fe, Bi, Cu, Fe, scheelite, $CaWO_4$ or wulfenite, $PbMoO_4$ and ferberite, $FeWO_4$ or hubnerite, $MnWO_4$ are representative of the two crystal classes — the tetragonal scheelite or monoclinic wolframite groups, respectively. These minerals are found in veins and pegmatites formed under pneumatolytic, hydrothermal conditions or by secondary alteration in the oxidation zone of ore deposits.

Most of these minerals are primarily ores of tungsten and molybdenum in industry. See discussion under either molybdenum or tungsten for further information.

Technical Application: Several molybdates have been artificially grown for general crystallographic and morphological study with possible Solid State applications for their ferritic or magnetic properties.

$Fe_2Mo_3O_8$ and others have been grown as fine elongated single crystals by CVD or Vapor Transport (VT) techniques. Structure was referred to squeezed dodecahedrons (isometric system) or elongated hexagonal system, e.g., prisms with elongation in either case on the z-axis. Note that natural garnets often occur with this elongated dodecahedral structure.

Etching: Soluble in HCl, HNO_3, and mixed acids of the $HCl:HNO_3$. $HF:HNO_3$, $HF:H_2O$ and hydroxides.

MOLYBDATE ETCHANTS

FEMO-0001a-b
ETCH NAME: Nitric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
(1) 1 .... HNO_3
1 .... H_2O
(2) 1 .... HCl
2 .... HNO_3

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DISCUSSION:

$Fe_2Mo_3O_8$ single crystals grown by CVD. General formula $M_2Mo_3O_8$ with M = Fe, Mn, Co, Ni. The molybdide Fe_2Mo_4 also was grown. A sealed quartz ampoule used for growth, and crystals grew on tube walls as squeezed dodecahedrons elongated in the z-direction. Solutions shown are general removal etchants for most molybdates.

REF: Strobel, A & LePage, Y — *J Cryst Growth*, 61,328(1983)

PHYSICAL PROPERTIES OF MOLYBDENUM CARBIDE, Mo_2C

Classification	Carbide
Atomic numbers	42 & 6
Atomic weight	203.1
Melting point (°C)	2410 (2300)
Boiling point (°C)	
Density (g/cm³)	9.06
Hardness (Mohs — scratch)	8+
(Vicker's — kgf/mm²)	1950
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	White
Cleavage (basal)	(0001)

MOLYBDENUM CARBIDE, Mo_2C

General: Does not occur as a natural compound. It is fabricated industrially as a high temperature ceramic as both the mono- and dicarbide, but is not as widely used as silicon carbide, SiC.

Technical Application: There has been no use in Solid State development of devices, although it has been studied as a carbide for general morphology.

Etching: HNO_3, HF, hot H_2SO_4, HCl.

MOLYBDENUM CARBIDE ETCHANTS

MOC-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:

Mo_2C, specimens. Material is soluble in nitric acid. Also etch in HF, hot H_2SO_4 and HCl.

REF: *A Dictionary of Carbide Terms*, — Adams Carbide Corp., Kenilworth, NJ

MOLYBDENUM GERMANIDE ETCHANTS

MOGE-0002
ETCH TIME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
(1) x .... HNO_3 (2) x .... H_2O_2
DISCUSSION:

Mo_3Ge specimens and Mo_3Ge_2; Mo_2Ge_3 or alpha-$MoGe_2$ are the germanium equivalents

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of silicides. Both solutions are rapid etchants. Fused carbonates and nitrates react violently. All materials will resist nonoxidizing solutions.
REF: Brochure: *Molybdenum,* Climax Molybdenum Company (No date/number)

MOLYBDENUM NITRIDE ETCHANTS

MON-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
MoN and Mo_2N thin films grown on (100) silicon wafers (p- and n-type, 10 Ω cm resistivity). First, deposit 500—1000 Å SiO_2 on wafers with dry O_2; then sputter deposit 300 Å Mo in argon atmosphere, and anneal at 250°C for good adhesion. Pattern etch and clean Mo film with hot H_3PO_4. Form nitride with NH_3 in dry forming gas (FG) (85% N_2:15% H_2) in and open tube, 10 min for 600 Å MoN. 10% NH_3 in N_2 produces smooth surfaces. MoN cubic, fcc, when formed under 800°C; Mo_2N (hexagonal) forms above 800°C with film cracking. Both nitrides can be etched in the solution shown.
REF: Kim, M J — *J Electrochem Soc,* 130,1196(1983)

PHYSICAL PROPERTIES OF MOLYBDENUM SULFIDE, MoS_2

Classification	Sulfide
Atomic numbers	42 & 16
Atomic weight	143.05
Melting point (°C)	795
Boiling point (°C)	Sublimes
Density (g/cm³)	4.7—4.8
Hardness (Mohs — scratch)	1—1.5
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Lead-grey
Cleavage (basal)	(0001)

MOLYBDENUM SULFIDE, MoS_2

General: Occurs as the mineral molybdenite, MoS_2. It is often a pneumatolitic contact deposit associated with ore veins of tin and tungsten minerals, also in pegmatites. Although it is widely distributed, it is never found in large quantities, yet it is an important ore of molybdenum. The other half dozen molybdenum minerals are oxides containing tungsten, iron, calcium, and bismuth. Because of its low hardness (H = 1—1.5) and lead-grey/black color, it was long thought to be a lead mineral, only established as a separate mineral species in 1778. It can be distinguished from lead and graphite by its color streak on paper or porcelain — blue-grey, rather than greenish grey.

Other than as an ore of molybdenum in industry, the compound is used as a dry lubricant, similar to the usage of graphite.

Technical Application: No use in Solid State or semiconductor processing other than as a dry lubricant in some equipment applications.

It has been grown for many years as an artificial compound by flux growth in the presence of sulfur. In Solid State technology it has been grown by the Vapor Transport (VT)

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method, as fine single crystals and platelets with distinctive basal (0001) planes. Both the natural and artificial crystals have been studied for morphological data.

Etching: Soluble in acids and halogens.

MOLYBDENUM SULFIDE ETCHANTS

MOS-0001
ETCH NAME:
TYPE: Tape, cleaning
COMPOSITION:
x .... adhesive tape
TIME:
TEMP:
DISCUSSION:

MoS_2 single crystal platelets grown by vapor transport. Single crystal specimens can be separated from the growth matrix with a razor blade. To obtain a clean, fresh surface use adhesive tape to peel away a thin surface layer. Method also used on $MoSeS_2$.
REF: Phillips, M L & Spitler, M T — *J Electrochem Soc*, 127,1719(1980)

MOS-0002
ETCH NAME: BRM
TYPE: Halogen, polish
COMPOSITION:
x .... x% Br_2
x .... MeOH
TIME:
TEMP:
DISCUSSION:

MoS_2 single crystal specimens used in a study for photo-anodes. After etch polishing in solution shown, wash in CCl_4 to remove residual bromine. Thin single crystals can be peeled from bulk material. Also evaluated: $MoSe_2$, WSe_2 and WS_2.
REF: Baglio, J A — *J Electrochem Soc*, 129,1461(1982)

MOS-0003
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
COMPOSITION:
x .... TCE
TIME: Minutes
TEMP: RT to hot
DISCUSSION:

MoS_2 as powdered lubricant on equipment gear-trains. Solution used to degrease and remove old lubricant. Gasoline also used. Material can be etch removed with aqua regia and concentrated H_2SO_4.
REF: Fahr, F — personal communication, 1957

MOS-0004
ETCH NAME: Soap
TYPE: Ester, removal
COMPOSITION:
x .... lava soap
TIME:
TEMP: RT
DISCUSSION:

MoS_2, natural single crystal specimens used in a structure study. A solution of lava soap used to clean work areas and hands after handling material. Dilute aqua regia ($3HCl:1HNO_3:5H_2O$) used for controlled removal of specimen.
REF: Walker, P — mineralogy study, 1952—1953

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MOLYBDENUM TELLURIDE ETCHANTS

MOTE-0001
ETCH NAME: TIME:
TYPE: Halogen, polish TEMP: RT
COMPOSITION:
x .... x% Br_2
x .... MeOH
DISCUSSION:
$MoTe_2$, single crystal specimens. Material is a dichalcogenide type semiconductor with a Band Gap of 1.5 eV. There is possible use as a solar cell with about 10% efficiency. Also working with MoS and WSe_2.
REF: Lewerenz, H J et al — *J Electrochem Soc*, 132,700(1985)

PHYSICAL PROPERTIES OF MOLYBDIC OXIDE, MoO_3

Classification	Oxide
Atomic numbers	42 & 8
Atomic weight	143.05
Melting point (°C)	795
Boiling point (°C)	
Density (g/cm^3)	4.5
Hardness (Mohs — scratch)	1.5
Crystal structure (orthorhombic — normal)	(001) fibers
(hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Yellow
Cleavage (basal)	(001)/(0001)

MOLYBDIC OXIDE, MoO_3

General: Originally thought to occur in nature as the mineral molybdenite, MoO_3, but later analysis changed the name to ferricmolybdenite as a mixture of $Fe_2O_3.3MoO_3.8H_2O$. Data shown under Physical Properties are based on this mineral. It is a relatively rare mineral found as fibers and fine needles in association with molybdenum-bearing iron minerals and limonite, $2Fe_2O_3.3H_2O$.

No industrial use as a natural mineral. The metal molybdenum is used in the fabrication of high speed steels, and has been used as a light filament in radio tubes replacing tungsten.

Technical Application: None at present in Solid State processing. It is part of the native oxide formed on molybdenum surfaces, and can be removed with ammonium hydroxide, NH_4OH. It has been observed as a thin film deposit in working with molybdenum metal substrates.

Etching: Soluble in acids and NH_4OH.

MOLYBDENUM OXIDE ETCHANTS

MOO-0001
ETCH NAME: Ammonium hydroxide TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... NH_4OH

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DISCUSSION:

MoO_3, thin film formed during RF ion plating of AlN on molybdenum substrates. AlN deposited at 1000—1200°C, but at 750°C MoO_3 was formed, and above 1200°C, N_2O_3. Solution is a general etch for the material. See ALN-0014.

REF: Ritajima, M et al — *J Electrochem Soc*, 128,1588(1981)

MOO-0002

ETCH NAME: Sulfuric acid — TIME:

TYPE: Acid, removal — TEMP: Hot

COMPOSITION:

x .... H_2SO_4, conc.

DISCUSSION:

MoO_2, as amorphous platelets on steel is a stable black compound with good surface adhesion to about 250°C with fissures between platelets. Film shows solar selectivity, high adsorption, and low thermal emittance. Solution shown used as a slow etch.

REF: Agnihotri, O P et al — *J Thin Solid Films*, 109,193(1983)

MOLYBDENUM SELENIDE ETCHANTS

MOSE-0001

ETCH NAME: BRM — TIME:

TYPE: Halogen, polish — TEMP:

COMPOSITION:

x .... x% Br_2

x .... MeOH

DISCUSSION:

$MoSe_2$, single crystal specimens used in a study for photoanodes. After etch polish in solution shown, wash in CCl_4 to remove residual bromine. Thin single crystals can be peeled from the bulk material. Also evaluated: MoS_2, WS_2 and WSe_2.

REF: Baglio, J A et al — *J Electrochem Soc*, 129,1461(1982)

MOLYBDENUM SELENIUM SULFIDE ETCHANTS

MOSS-0001

ETCH NAME: — TIME:

TYPE: Tape, cleaning — TEMP: RT

COMPOSITION:

x .... adhesive tape

DISCUSSION:

$MoSeS_2$, single crystal platelets grown by Vapor Transport (VT). Single crystal specimens can be separated from the growth matrix with a razor blade. To obtain clean, fresh surfaces use adhesive tape to peel away thin surface layers. Method also used on MoS.

REF: Phillips, M L & Spitler, M T — *J Electrochem Soc*, 127,1719(1980)

MOUNTING MATERIALS

General: There are a number of natural and artificial compounds used for mounting and holding specimens for lapping, polishing, and etching. Such materials can be woods, plastics, metals, minerals, or rocks as well as semiconductor wafers and other artificial compounds.

These mounting materials range in hardness (Mohs) from beeswax, H = 0.2 to natural resins and hydrocarbons, both paraffin or asphalt base, to artificial plastics with H = 3—5. The natural resins, paraffin, etc., melting points range from about 50 to under 200°C; whereas plastics can vary from 800 to 1500°C.

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Brittleness is a major factor in obtaining a desired pliability for a mounting medium and requirements vary with specific application. As three examples: (1) Beeswax was probably the first natural wax used by man as it is extremely soft, with a melting temperature low enough to become pliable when held in the hand, yet is water-repellent as a surface coating. It is worth noting that the honeycomb hexagonal structure is one of the strongest known and, today, is a major construction form for wood, plastic, metal and cardboard. (2) Waxes, such as paraffins derived from petroleum, are not hand temperature pliable, but are sufficiently soft to be rubbed onto surfaces, also as a good water repellent coating. Both beeswax and paraffins are edible, used as a filler and extender in chocolate candy. The Bull Durham tobacco package, coated with paraffin, is still used to wipe the paraffin onto vehicle windshields in rainy weather to produce a slick, water run-off surface on the glass. (3) Resins, such as copal (one of the shellacs) or carnauba wax, are brittle, but with melting points often under that of boiling water (100°C), also alcohol soluble, such that they can be applied as a thin, relative hard and stable surface coating. Carnauba-type waxes were used as a "sealing wax" on letters before the development of glue, and are still used as a seal on some official documents with an imprinted logo.

Most of the mounting "waxes" are a mixture formulated for a specific pliability and temperature. Pitch (beeswax/linseed oil/rosin) — burgandy, green, optical, etc. — and the Apiezons, particularly, Apiezon-W (black wax) which is an asphalt derivative, are examples. The latter, black wax, although slightly brittle, has a melting point of 80°C and is easily removed with TCE. It also is inert to most metals and compounds used in processing, unaffected by acids or alcohols, such that it is used as both a holding medium in addition to a surface coating for etch patterning.

Powdered plastics — lucite and bakalite — are used in preparing metallographic specimens with the solidified powder holding the specimen. There are metallographic laboratory units that, with a combination of heat and pressure, form the plastic/specimen into small cylinders, which are then mechanically lapped and polished to expose the specimen. And the specimen may be preferentially etched to develop structure. Other plastic formulations, such as the Crystalbond or Pliobond series of compounds are liquefiable mounting mediums available in stick form. In addition, there are the putty-type materials as both a natural rubber derivative or plastic compound.

Lacquers constitute another type mounting or coating material. They can be natural tree or plant rosins and resins, or artificially formulated, such as the photo resist type lacquers used in photolithographic patterning of Solid State semiconductor wafers.

Vacuum, alone or in conjunction with waxes or metal masks, has been used as a primary holding mechanism. Even water, alcohol, and glycerin, as liquids, have been used for temporary holding or positioning of parts and, in vacuum metallization of wafers and substrates, they can be physically held in position with metals, such as phosphor-bronze or steel spring clips.

Low melting temperature metals, such as indium or Wood's Metal, are used to mount and hold specimens in MBE vacuum epitaxy or specimens for microscope examination. The latter includes putty as a specimen holder on a microscope stage and, as an extension, the surface replication technique using aqua dag (graphite powder in alcohol) or an evaporated metal thin film, which is then used for study rather than the specimen, proper.

Technical Application: All of the mounting materials and techniques described in the general section above have been used as mounting or handling mediums for Solid State and metal processing.

They are categorized in the following presentation by basic type, such as natural waxes, plastics, metals. The solutions shown are primarily cleaning and removal types, not only for the mounting materials, themselves, but for the material surfaces to which they are applied, as contamination on surfaces is possibly one of the most severe processing problems related to device, part or equipment failure.

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Many of these materials also are used in a finished product assembly, such as a plastic extrusion encapsulated device, as metal or ceramic packages, or as a lacquer surface coated dielectric.

Etching: Acids, alcohols, and solvents. Varies with material.

MOUNTING MATERIAL ETCHANTS

APIEZON ETCHANTS

APZW-0001
ETCH NAME: Trichloroethylene
TYPE: Solvent, removal
TIME:
TEMP: RT to boiling
COMPOSITION:
x .... TCE
DISCUSSION:

Apiezon-W, commonly called "black wax". Melting point 80°C. This is one of the most widely and generally used materials for surface coating or waxing-down semiconductor wafers and other substrate materials or metals prior to etching. This Apiezon wax is a petroleum tar derivative, and is supplied in 1 lb packages of 15 to 20 sticks, about $^1/_4 \times ^1/_4 \times 8''$ in size.

It can be melted and used uncut, or pieces dissolved in TCE. The latter is applied as a brush or spray coating. It is inert to most acids, alcohols and water, and is used as a general protection against etching or, when patterned, as an etching mask like a photo resist lacquer. As a mounting medium it is used to hold wafers on a ceramic substrate for cutting and dicing of parts.

Trichloroethylene (TCE) is a general solvent for most Apiezon waxes, but other chlorinated solvents can be used, such as trichloroethane (TCA).

Other Apiezon formulations are available for specific applications and are shown under APZW-0003, below.

REF: Blankenship, J L & Borkowski, C J — *IRE Trans Nucl Sci* NS-7,190(1960)

APZW-0002: Walker, P — personal application, 1973—1985

Apiezon "W" as patterned coating on nickel shim stock used to etch fabricate nickel masks for vacuum metal evaporation.

APZW-0003: VWR Supply Catalogue, 1984

Other Apiezon waxes are formulated with different characteristics for particular applications with their own letter designations:

Apiezon H: 250 to −15°C. Ground glass joint seals.

Apiezon L: RT to 30°C. Short-term, hi vac grease seal to 10^{-10} Torr vacuum.

Apiezon M: 30°C & 10^{-3} Torr to 200°C & 10^{-7} Torr vacuum grease with low vapor pressure. Used for holding wafers and substrates on the copper plate of ion milling vacuum systems.

Apiezon N: to 200°C & 10^{-9} Torr as a stop-cock grease.

Apiezon Q: to 30°C for semi-permanent seal of vacuum joints.

Apiezon T: Like "W", but m.p. 120°C.

Apiezon W: to 180°C & 10^{-3} Torr, m.p. 80—90°C. Like "Q", but more widely used.

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BEESWAX ETCHANTS

BEEW-0001
ETCH NAME: Trichloroethylene
TYPE: Solvent, removal
COMPOSITION:
x .... TCE
TIME:
TEMP: RT to boiling
DISCUSSION:

Beeswax (*Apis mellifera*) as a natural by-product from beehives. It has a density of 0.96—0.97 g/cm^3, a solidification point of 60—62°C. The natural color is yellow/amber but, as refined, it is semitranslucent white with m.p. about 67°C.

The "lost-wax" processing was developed in the early Bronze Age, perhaps as early as 4000 B.C. An initial form is made of beeswax with a complete and sometimes intricate surface design. The form is then slowly and carefully coated with layers of wet clay, allowed to air-set, then is kiln fired to harden the clay. During the firing, the beeswax drains out of the form, and is recovered for re-use. A liquefied melt of bronze is then poured into the clay mold and allowed to harden. The clay is finally broken away and, as needed, the part finished by cutting, grinding, and polishing. This method was still in use for making bronze parts into the early 1900s, and is still used in the pottery and clay industries, today, and for making objets d'art out of both brass and bronze.

In modern-day industry, beeswax is used by itself as a mounting and holding medium for etching parts where solution heating is below the beeswax melting point; as a surface coating protectant during cutting or dicing of small, thin parts, such as semiconductor wafer dicing, and the fabrication of TiO_2 dielectric capacitors. It occasionally is used as a holding wax for a specimen mounted on a microscope stage.

When mixed with vaseline and rubber, it is used as a stockcock grease. Mixed with rosin in various proportions as a fairly thick coating on a metallographic platen, it is referred to as a "wax-lap". The wax surface is cross-scored in a V-groove square pattern and, with slow rotation speed of the platen and adding a fine abrasive polishing slurry (alumina), material surfaces can be highly polished with optimum planarity. As a beeswax/resin mixture, thinly coated on a lapping platen, semiconductor wafers are slightly heated and pressured into the wax, the circular platen placed face down on a metal flat, and rotated to lap thin and polish as many as half a dozen wafers at a time.

Trichloroethylene (TCE) is a solvent for beeswax, as well as being a general cleaner for metals and metallic compounds. After wax removal, parts should be hot vapor degreased with TCE, TCA or Freons to insure there is no remaining wax contamination.

REF: *Encyclopedia Britannica* — Lost-Wax process
BEEW-0002: Klatskin, W B — personal communication (microscope), 1983
BEEW-0003: Kunitz, A — personal communication (beeswax/rosin), 1974
BEEW-0004: Waters, W P — personal communication ("wax-lap"), 1960
BEEW-0005: Marich, L A — personal communication (wafer cutting), 1980

DIELECTRICS

CER-0001
ETCH NAME: Wet chemical etching
TYPE: Acid, removal
COMPOSITION:
(1) x .... H_2SO_4 (2) x .... HCl (3) x ... H_3PO_4
TIME:
TEMP: RT

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DISCUSSION:

Ceramics, as substrates or as masks for metal evaporation. To clean ceramics prior to use, etch in any of the three solutions shown, following with heavy water washing, and drying. Best drying is done in a vacuum oven (10^{-3} Torr) at 125—150°C to insure removal of all water moisture. A circulating air oven also can be used. Heating time depends upon the porosity of the ceramic, but $^1/_2$ h or longer is recommended. Primary ceramics in use are alumina, Al_2O_3, and beryllia, BeO in Solid State. Surfaces are a standard 4 or 2 μ″ for most device applications, but can be 25 μ″ for general purpose use. The 4 μ″ is the ceramic as-fired condition; 2 μ″ is diamond paste polished, and a 1 μ″ can be furnished on request.
REF: Accumet, Boston, MA

CER-0002
ETCH NAME:
TYPE: Solvent, degreasing
COMPOSITION:
(1) x .... TCE/TCA/Freon, vapor
(2) x .... EOH/MeOH
TIME: 1—5 min
TEMP: Boiling

DISCUSSION:

Ceramics. Solvents (1) are basic vapor degreaser solvents, and (2) are alcohols type solvents. They all can be used as RT or hot liquids or hot vapors for general cleaning of surfaces to remove oil and dirt contamination. Very often solvent cleaning is following by final alcohol rinsing, and drying with nitrogen gas. Solvent cleaning is used, only, or before and after acid cleaning steps in processing of ceramic substrates.
REF:

CER-0003
ETCH NAME: Hydrogen
TYPE: Gas, cleaning
COMPOSITION:
x .... H_2
TIME:
TEMP: >750°C

DISCUSSION:

Ceramics, as substrates or as masks for metal evaporation. The best method of surface cleaning, particularly, if diamond pastes have been used in surface finishing. Forming gas (75% N_2:15% H_2) can be used as a nonexplosive mixture replacement for pure hydrogen. Both are standard for furnace hydrogen firing used in cleaning metal surfaces to remove residual oxidation and/or contamination. They also are used in processing as reducing atmospheres for alloying or soldering of parts.
REF:

GLA-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
(1) x .... HF, conc.
(2) x .... HF, vapor
(3) x .... HF
x .... H_2O/MeOH
(4) 1 .... HF
1 .... NH_4F (40%)
TIME: Seconds/minutes
TEMP: RT to hot

DISCUSSION:

Glass, as cut blanks, cover glasses, microscope slides. Acids with fluorine are the only ones that will physically etch remove glass. Glass when immersed in liquid HF will be polished; held in hot vapor, will be frosted. The dilute HF is used for slower cleaning, rather

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than etching action. All four solutions shown are used in patterning of SiO_2 thin films deposited on surfaces, in addition to general removal or cleaning of the silica.
REF:

GLA-0002
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... H_2SO_4, conc.
(2) 1 .... H_2SO_4
1 .... $Na_2Cr_2O_7$, sat. sol.

TIME: Minutes
TEMP: RT to hot

DISCUSSION:
Glass, as laboratory glassware or quartzware, in addition to cut blanks, microscope and cover slides. Solution (1) is used in cleaning soda-lime glass blanks prior to chromium metallization as Chrome Glass Masks used in photolithography. Solution (2) is one example of the standard "glass cleaner" that has been used in industry for many years. In both cases, parts should be heavily water washed after etch cleaning, followed by drying.
REF:

GLA-0003
ETCH NAME: Soap
TYPE: Solvent, cleaning
COMPOSITION:
x .... $3C_{17}H_{35}COO$
x .... H_2O

TIME:
TEMP: RT to hot

DISCUSSION:
Glass and ceramics. Two of the cleanest, high purity hard soaps are Ivory and Castile, both recommended for cleaning of missile and space hardware. Soft soaps, such as liquid Joy, also have been used on Solid State and electronic parts. Metals in general can be cleaned in such high purity soap solutions or in detergent types, to include de-foaming or foaming agents, and there are many, many specialized formulations used on all materials as ionic or nonionic. Glass blanks, as soda-lime for chrome glass masks, are scrub-cleaned in a soap solution as one part of the cleaning process prior to chromium evaporation. Many metal and ceramic surfaces are similarly cleaned prior to metal plating. After soap cleaning, parts should be thoroughly water washed as, regardless of soap cleaning capability, they are fat, and fatty acid derivatives, such that they also may act as a surface contaminant like an oil.
REF:

EPOXY ETCHANTS

EPOX-0001
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... H_2SO_4
(2) 3 .... HNO_3
1 .... H_2O

TIME: Minutes
TEMP: RT to warm

DISCUSSION:
Epoxy and polyamide type artificial compounds used as un-loaded mounting or loaded electrical contact materials. There are several metal-loaded types with Ag, Au, Cu, Ni, Al, Fe powders added, and the silver epoxy is widely used in Solid State for assembly and testing of semiconductor devices. The epoxies, in general, have lower temperature capability than polyamides, although both, presently, are limited to about 200°C before charring occurs. Acetone is a general cleaning solution for all of these compounds. For removal, either char

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the epoxy at 250°C or higher, and scrape away; or etch using an acid, such as H_2SO_4, conc. or $3HNO_3$:$1H_2O$. Note that these compounds can be a single component kept frozen for best shelf-life, or an A-B component system that, once mixed, has a pot- or working-life of from seconds to 4—8 h.

Most are rated for 6-month shelf-life before requiring replacement although, for general testing using an A-B component system, some have still been satisfactory after 2 years. Single component systems, no, as they slowly harden with time even when kept frozen at −40°C. Neither epoxies nor polyamides are recommended for high reliability final assemblies as, with time, they will continue to harden, may begin to flake, or allow moisture absorption which can eventually destroy an operational device.
REF:

LACQUER ETCHANTS

PR-0001
ETCH NAME: Acetone
TYPE: Ketone, removal
COMPOSITION:
x .... CH_3COOH_3
DISCUSSION:

TIME: 2—5 min
TEMP: RT to hot

Photo resist (P/R) lacquers, all types. Acetone is a general solvent for these artificial compounds. AZ-1350J negative P/R is widely used for general purpose photolithography in addition to COP types, and there are positive P/R versions of both. The negative P/Rs patterns harden the pattern desired with removal of unwanted material; positive P/Rs are the reverse . . . areas are opened, which are then etch structured or metallized. The PMMA P/Rs have been designed for use with electron-lithography patterning, such as for fine-line structuring of a gallium arsenide gate channel for a field effect transistor (FET) fabrication. The PMMAs can be recognized under a microscope (200—400×) as a pink/reddish coating, whereas AZ- and COP-types are tan/brown in color. These latter ones have different formulations for thicker type coatings, such as AZ-1370J, etc. The older KMER type photo resists are no longer used.

Processing should be done under clean room conditions as a Yellow Room: yellow plastic glass, and yellow fluorescent lighting, as photo resists are sensitive to white light. The lacquers are supplied in dark amber bottles, and should be stored in a dark cabinet for best results. The photo resist is used directly from the bottle, though it may be filtered if desired. To apply and process photo resists:

(1) A glass syringe with replaceable needle and 0.2 μm filter (use new filter element at shift start). The syringe can be re-used indefinitely unless broken, but should be thoroughly washed with acetone after every use to remove old photo resist. Fill syringe with filter and needle removed (hold finger over bottom); attach filter and needle; and extrude some photo resist to eliminate air bubbles.
(2) Photo resist spinner: A removable plastic basin surrounding a vertical $^1/_4$" spindle driven by a motor and vacuum unit mounted beneath the spinner body, and an electronic operation console. Flat-surface holders with or without criss-cross and concentric drain patterns of various sizes are commercially available or can be designed. They all have a central vacuum hole that matches over the vertical drive spindle.
(3) Acetone can: A pressurizable (N_2 gas) stainless steel can with a quick-release connection on the side for nitrogen pressuring after the can is filled with acetone, and with a can top spray head for acetone application.
(4) P/R wafer coat: Spray the SST holder with acetone to insure cleanliness. Place a wafer (semiconductor, ceramic substrate etc.) on the flat holder and activate vacuum switch

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for gripping. Active spinner while spraying wafer with acetone to clean wafer surface, and spin surface dry. Apply a large drop(s) at middle of wafer, and activate spinner. For normal coating: set electronic module for 3500 rpm, and 10—15 sec spin time for a nominal 0.5 μm P/R coating thickness using AZ-1350J. P/R should spin out evenly over entire wafer. There can be slight color variations (yellow, green, red, tan) across surface, but a singular tan color is preferred, and without edge thickening. The soft P/R can be acetone spray removed as needed and coating step repeated. Occasionally a double-coating is done for additional thickness . . . about 0.7 μm using 1350J.

(5) Air cure P/R: Place wafer(s) in an open glass Petri dish other similar holder, and allow to air dry 30—45 min. Wafers should not be completely enclosed with a Petri dish lid, but may be partly covered to prevent dust settling on the drying P/R . . . keep sufficiently open for P/R vapor release.

(6) Oven cure: Three small ovens are often used in series: first, 90°C; second, 90 or 100°C; third 120°C. Standard practice is to cure at 90°C for 1 h each, in oven one and two. Where a hard cure is required, an additional hour at 120°C. Place wafer(s) uncovered on a glass or SST flat carrier, introduce into oven one, and transfer to two and three as required.

(7) UV exposure: A small, basic system consists of (1) a base holder for the wafer and pattern mask, then (2) a camera-type shutter with a high intensity mercury UV light bulb housing directly above, and (3) an electronic operation module with power supply. The light intensity should be checked with the light meter supplied with the equipment on a daily basis, such that exposure time can be correct as the intensity drops slowly with bulb usage time. Turn the bulb on at the beginning of a morning shift, and leave on. When a new bulb is inserted, light intensity and focus are adjusted with x-y-z adjustment screws in conjunction with the light meter.

(8) Pattern exposure masks: Permanent masks are glass . . . soda-lime glass . . . as the chrome glass mask or, more recently, the chromium with anti-reflective (AR) coating is being replaced with iron oxide, FeO_x. The latter do not require the AR coating, and are less prone to damage. The glass photo resist mask making is a highly specialized technique, and normally done by outside vendors to the users design pattern specifications. In-house patterns, as well as outside vendor patterns, start with a rubilith (red mylar on clear acetate) that is usually cut for a 1:10 reduction. After cutting the rubilith pattern, reduce to a black and white negative by photoreduction. The negative can be used as a temporary photo resist mask, or transferred to glass. Many patterns are now computer generated, to include cutting the rubilith, itself. This is still high labor intensity operation, as the rubilith pattern must be hand-peeled.

(9) UV exposure: Set exposure time according to requirement of UV light intensity, type P/R and thickness, and cure schedule. Nominal 10—15 sec exposure for a 90°C cured 0.5 μm thick film. Place wafer on exposure plate, position mask on wafer, then activate exposure timer.

(10) Develop pattern: Each supplier's photo resist has its own developer solution, and should be water diluted per directions. Use warm (50—70°C) and watch developing surface, so as not to over-develop with possible under-cutting of pattern. Rinse in water after developing. Up through this operation, if there is any problem with the photo resist, it can be stripped and redone.

Wafers and substrates are of three basic types: (1) a photo resist coating, only; (2) pre-coated with an oxide or nitride thin film, or (3) pre-coated with a metal thin film. In the first case, the wafer surface may be etched for pits or channels; PMMA electron lithography processed; or metallized with subsequent acetone "lift-off" of excess and extraneous metal. In the second case, the oxide/nitride is etch patterned down to the wafer/substrate surface,

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with the oxide/nitride then acting as an etching, metallization or diffusion mask with or without the P/R still present. In the third case, this is a standard method of processing metallized substrate circuits followed by acetone "lift-off" of the photo resist. There are some special cases, such as using a combination of photo resist/metal as metallization or diffusion mask.

In photolithographic processing, after P/R has been applied and cured, the specimen should not sit with the lacquer still on the surface for more than 6—8 h; otherwise, strip and re-coat. The photo resist can become too hardened with time, it will crack and craze, and be all but impossible to remove from surfaces.

A Yellow Room should be maintained with a temperature between 68—74°F, with a relative humidity of 40%. If RH is very much under 30%, photo resist will cure too rapidly and crack or craze; if much over 60% RH, photo resist will not harden or cure properly, and pattern can slump with loss of definition.

REF: Technical Bulletin #401, 1984 — American Hoerchst Corp

PR-0002: Walker P & Valardi, N — personal application, 1985

AZ-1350J used as both a mounting medium and pattern coating on AuSn(20%) and AuGe(13%) alloy strips placed on microscope slides and hole pattern etched to reduce alloy volume.

PR-0003a: Walker, P — personal development, 1974

KMER photo resists used as a patterning and mounting medium painted on brass and nickel shim stock used as vacuum evaporation metallization masks for silicon wafers. Also used Apiezon-W wax for patterning.

PR-0003b: Ibid. (1964)

KMER type photo resists used for patterning (111) silicon wafers in a development study of DC sputtered silicon nitride, oxynitride and silicon dioxide surface thin films. This included development of etch solutions for the nitrides that were compatible with KMERs.

PR-0004a: Brumfield, D & Walker, P — personal development, 1957

Jello used as a mounting and patterning medium on silicon wafers for aluminum evaporation and lift-off with water. This work was done before the development of photo resist lacquers. Orange, lime, and lemon Jello evaluated, and lemon gave best results.

PR-0004b: Ibid.

Collodion used as a mounting and surface patterning medium on silicon, germanium, gallium arsenide, and indium phosphide wafers for metal contact evaporation in material evaluations and lift-off with amyl acetate. Collodion used prior to development of photo resists.

PR-0006: Hackett, R & Walker, P — personal development, 1978

PMMA photo resist used for electron lithography of (100) oriented gallium arsenide wafers in fabricating FET gate channels (Hackett). Device processing of LN-FETs with $^1/_2$ μm gates (Walker) with improved techniques for PMMA removal. (*Note:* PMMA is more difficult to completely remove than AZ-types due to high energy heating during electron lithography. Acetone lift-off used, but warm, and with more critical evaluation prior to metallization in order to prevent later peeling and lifting of metallization due to PMMA organic contamination.)

LAC-0001

ETCH NAME: TIME: Minutes

TYPE: Solvent, removal TEMP: >100°C

COMPOSITION:

(1) x .... acetone (2) x .... benzene (3) x .... turpentine

DISCUSSION:

Canadian balsam is classified as an oleo-resin or lacquer, used for mounting rock and mineral specimens on glass microscope slides. The clear balsam has a low refractive index

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that does not mask study of thin sections by transmitted light under microscope examination. After mounting, the specimens are lapped down as thin sections on an iron lap with a wet slurry abrasive. In most instances, thin sections are kept on file still mounted, but any of the solvents shown can be used to liquify the balsam for both application and removal.
REF: Walker, P — mineralogy studies, 1952—1953

SHE-0001
ETCH NAME:
TYPE: Solvent, removal
TIME: Minutes
TEMP: 80—100°C
COMPOSITION:
(1) x .... acetone (2) x .... amyl alcohol (3) x .... MeOH
DISCUSSION:

Shellac is classified as a resin, but also referred to as a lacquer. It has been used in a similar manner as described for Canadian balsam in preparing rock and mineral thin sections. In Solid State processing a variety of shellacs are used for coating exposed semiconductor device p-n junctions to prevent electrical arcing as exposed to air, only. Shellacs also have been used in mounting discrete elements on a circuit board (PCBs), for coating the wire windings of motors and, alone, or as mixtures for encapsulating. The solvents shown can be used to both liquify shellacs for application and for their removal.
REF: N/A

METALS

IN-0001a
ETCH NAME: Ammonium hydroxide
TYPE: Alcohol, removal
TIME: Minutes
TEMP: RT to boiling
COMPOSITION:
x .... NH_4OH
DISCUSSION:

In, metal smear used as a solder hold-down for semiconductor wafers and substrates mounted on molybdenum discs for epitaxy growth in MBE systems. The solution shown will slowly dissolve and remove indium without affecting either the specimen material or the molybdenum disc. Acids can be used, but should be compatible for no effect on other than the indium. (*Note:* Thin sheet indium is used as vacuum gasket seals in cryo-pumps, and can be cleaned in the solution shown prior to installation.)
REF: Woo, R — personal communication, 1983
IN-0001b: Ibid.

In, as small pellets used to hold material specimens in position on a microscope stage for observation. Pellet can be positioned in a groove cut in a metal plate and, when the specimen is pressed into the groove it both grips the holding plate and the specimen.

SST-0001
ETCH NAME:
TYPE: Alcohol, cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
(1) x .... MeOH/EOH (2) x .... vacuum
DISCUSSION:

SST, bronze, brass, and graphite have all been used as holders for processing Solid State materials in vacuum evaporation systems, diffusion tubes, or belt furnaces. Steel and brass plates as flat holders in vacuum metallization with wafers held in place with phosphor-bronze or SST spring clips; paired and nested brass plates with critically dimensioned pattern holes for sandwiching alpha-quartz crystals for metallizing electrodes, held together with

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brass clips. Graphite plates with a fine hold pattern to hold 0.010 diameter spheres of aluminum have been used for (111) silicon diode fabrication in the Sphere Alloy Zener process. Graphite boats have been used for furnace alloying of (111) silicon wafers in a stack configuration as SCRs and Triacs. Various shim stock metals (steel, brass, nickel, aluminum) have all been fabricated as evaporation masks, held in place over wafer specimens with spring clips or positioning pins. All of these materials can be cleaned with solvents (TCE, Freons) or with alcohols as shown. Graphite parts often include furnace firing for drying or with vacuum for removal of any liquids entrapped in the graphite surface due to material porosity. The graphite also may be cleaned by light rubbing on a rough paper surface, such as Whatman filter paper.
REF: N/A

PLASTICS

CRY-0001
ETCH NAME:
TYPE: Ketone, removal
TIME: Minutes
TEMP: RT to warm
COMPOSITION:
x .... CH_3COOH_3
DISCUSSION:
Crystalbond, #507, and others as a plastic compound series used for mounting semiconductor wafers, ceramics, quartz, and sapphire substrates for dicing. The compound remains viscous when melted (about 80°C) and tends to trap air bubbles. Care must be taken to prevent bubbles forming or cutting integrity can be lost with pop-out of diced elements. The material is slowly soluble in acetone by soaking in a warm solution.
REF: Porter, R — personal communication, 1984

LUC-0001
ETCH NAME: Acetone
TYPE: Ketone, removal
TIME: Minutes
TEMP: RT to warm
COMPOSITION:
(1) x .... CH_3COOH_3
(2) x .... I_2
x .... $MeOH/H_2O$
DISCUSSION:
Lucite as sheet or powder (also called Plexiglas). Powder or shavings can be liquified with acetone (1) and used as a glue for lucite parts assembly. Powder is used in metallographic laboratories as specimen holders by heating and pressuring into small solid plastic cylinders. The cylinder is then lapped to expose the specimen for polishing and/or preferential etching and microscope study. Lucite sheet is used as a clear chemical sink face, and can be cleaned and disinfected with solution (2) or with a diluted tincture of iodine, $xKI:xI_2$:EOH. See section on Lucite. (*Note:* Do not use acetone to clean Lucite, as it is a solvent and will cause severe smearing of surfaces.)
REF:

BAK-0001
ETCH NAME:
TYPE: Ketone, removal
TIME: Minutes
TEMP: RT to warm
COMPOSITION:
(1) x .... CH_3COOCH_3
(2) x .... (MeOH/EOH)
DISCUSSION:
Bakalite, as a cellulose acetate type plastic, commonly dark brown in color. It has been used from powder form for holding specimens as described of Lucite (LUC-0001). It is

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opaque, but can be transparent like Lucite, and is harder and less prone to being scratched or damaged. Acetone is a very slow solvent for bakalite. Bakalite type plastics also are soluble in alcohols (2), such that cleaning should be done with water and soap.
REF:

MYL-0001
ETCH NAME: Acetone
TYPE: Ketone, removal
TIME: Minutes
TEMP: RT to warm
COMPOSITION:
x .... CH_3COOCH_3
DISCUSSION:

Mylar type plastic. Rubilith material is thin red mylar heat laminated to clear acetate (total thickness of 0.003 or 0.005) used in fabricating design patterns for photolithography glass masks or photograph negatives used to fabricate semiconductor devices and circuit substrates. As white (clear) or blue mylar with a cellulose glue sticky-back coating, the mylar is used for holding semiconductor wafers for scribe & break system dicing. The wafer is lightly held by the glue, and individual dice can be removed with tweezers of a pick-and-place system. Clean the mylar surface by wiping with a water dampened soft cloth, and dissolve the glue with acetone.
REF:

DEK-0001
ETCH NAME: Trichloroethylene
TYPE: Solvent, removal
TIME: Minutes
TEMP: Hot
COMPOSITION:
x .... $CHCl{:}CCl_3$ (TCE)
DISCUSSION:

Dekotinsky plastic cement, available in tan colored stick or powder form. Used to mount semiconductor ingots on ceramic blocks for wafer cutting. No longer used as, when heated even slightly above its melting temperature of about 90°C it polymerizes and, once polymerized, it is impossible to completely remove from surfaces even by lapping. Hot to boiling TCE will slowly remove Dekotinsky, but not after polymerization has occurred.
REF: Walker, P — personal application, 1956—1960

GLY-0001
ETCH NAME: Heat
TYPE: Thermal, removal
TIME:
TEMP: Elevated
COMPOSITION:
(1) x .... heat
(2) x .... solvent
x .... alcohol
DISCUSSION:

Glyptal is a rubberized-plastic type compound, either red or black in color, with very low vapor pressure. It is still used for sealing glass and quartz tubing of vacuum systems against pin-point air leaks, and also has been used as a general mounting and holding medium for parts. It hardens slowly (4 to 8 h), and can become brittle with time (months). Heating and chipping away is one method of removal, and there are special solvent/alcohol mixtures available from suppliers.
REF:

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PUT-0001
ETCH NAME: Trichloroethylene
TYPE: Solvent, removal
COMPOSITION:
x .... $CHCl{:}CCl_3$ (TCE)
TIME: Minutes
TEMP: RT to boiling
DISCUSSION:

Putty, as a natural clay or plastic type. The clay form has been largely replaced in Solid State usage with plastic putty. Used to hold small specimens on a microscope stage for observation, such as a (110) cleaved piece of a semiconductor wafer to study thin film epitaxy layer structure and/or p-n junctions that can be stain or etch developed. After removal of putty, wipe surfaces with TCE to remove residual organic or inorganic contamination.
REF: Menth, M — personal communication, 1982

SIL-0001
ETCH NAME: Alcohol
TYPE: Solvent, removal
COMPOSITION:
(1) x .... MeOH/EOH
(2) x .... $CHCl{:}CCl_2$ (TCE)
TIME: Minutes
TEMP: RT to hot
DISCUSSION:

Silicone oils and greases. These are manmade plastic derivative compounds that range from liquids to solids with various temperatures, vapor pressures, electrical characteristics. The liquids are used as vacuum pump oil for (hot) oil diffusion pumps. They can slowly break down to a varnish-like consistency that coats internal pump surfaces. To clean, soak in hot TCE, then rinse in alcohols and blow dry with air from a compressor. Oil should be replaced every 6 to 9 months, depending upon pump usage time, to prevent oil breakdown as varnish. (*Note:* Silicone should not be confused with silicon. The latter being a metal element, and primary semiconductor material.)
REF: Lopez, P — personal communication, 1973

RESINS

RES-0001
ETCH NAME: Benzene
TYPE: Solvent, removal
COMPOSITION:
x .... C_6H_6
TIME: Minutes
TEMP: RT to warm
DISCUSSION:

Resin, as copal (benin). Melting point is from 65—125°C, and solubility varies with copal type, such as the Class I type: amber. Both have been used for mounting specimens on microscope slides for lapping as thin sections. Both Solid State and geology metals, rocks, or minerals.

Benzene as a liquid derivative of petroleum is a solvent. As the benzene ring, it also is a basic building block in chemistry, in particular, the aromatic compounds. It boils at 80°C, has a specific gravity of 0.88, is insoluble in water, and burns with a yellow, smoky flame. It is a general solvent for fats, resins, phosphorus, etc. Two additional solvents, as homologs of benzene that also are used in Solid State processing are methyl benzene (toluene, C_7H_8), and dimethyl benzene (xylene, C_8H_{10}). In addition, these are coal tar distillates that include naphtha; carbolic, anthracene, and creosote oils.

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RES-0002
ETCH NAME: Methyl alcohol
TYPE: Alcohol, removal
TIME: Variable
TEMP: RT to hot
COMPOSITION:
(1) x .... CH_3OH (MeOH)
(2) x .... CH_3COOH (HAc — acetic acid)
(3) x .... $C_{10}H_{16}$ (turpentine)
DISCUSSION:

Resins, Class I (shellacs), to include pine, myrrh, etc., as gum resins. As Class I they have melting points from about 194—213°C. This is the common yellow-tan, translucent type resins supplied to industry in stick form for general purpose mounting and holding applications. These resins are brittle, but can be mixed in various proportions of beeswax for specific pliability. Such mixtures are used for a wax lap and wafer holding on lapping platens. See Beeswax for additional discussion.
REF: Kunitz, A — personal communication, 1974

PICH-0001a
ETCH NAME: Turpentine
TYPE: Solvent, removal
TIME: Variable
TEMP: RT to hot
COMPOSITION:
x .... $C_{10}H_{16}$
DISCUSSION:

Pitch (tar), as an asphalt hydrocarbon, or as a Class I tree-type resin. Both are commonly mixed with beeswax for specific viscosity, melting points and colors with names, such as burgandy, black (Swedish), green or optical pitch. Canadian balsam also is referred to as a "pitch", although it is a Type II oleo-resin. Melting points of pitch mixtures vary between 60 to 150°C, and are widely used for mounting and holding specimens for lapping, polishing, and cutting — woods, rocks, minerals, gem stones — in addition to glass, semiconductors, metals, and metallic compounds. Turpentine is a general solvent for pitch.
REF:

PICH-0001b
ETCH NAME:
TYPE: Solvent, removal
TIME: Variable
TEMP: RT to hot
COMPOSITION:
(1) x .... MEK (methyl ethyl ketone)
(2) x .... $HCCl:Cl_2$ (TCE)
(3) x .... MeOH/EOH
(4) 2 .... NH_4OH
8 .... H_2O
DISCUSSION:

Polishing pitch (blocking wax), as a mixture of beeswax, linseed oil and white rosin. The mixture can be dissolved in all of the solvents shown. Constituent concentrations are varied for specific viscosity, holding, and melting points. These mixtures have been basic in polishing glass lens and prisms for many years.
REF:

VACUUM HOLDING

VAC-0001
ETCH NAME: Vacuum
TYPE: Vacuum, gripping
TIME:
TEMP:
COMPOSITION:
x .... vacuum

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DISCUSSION:

Vacuum, alone, or in conjunction with waxes or metal masks is used as a holding mechanism. There are several types of vacuum units available: (1) a very small, electrically operated vacuum pick-up unit with $^1/_8$ ID tygon line and metal/plastic needle-type inserts. Operating unit about the size of a 500 ml Pyrex beaker with adjustable vacuum level dial on top for up to about 10^{-1} Torr (100 μm) vacuum level. Handles pick-and-place of small alloy pre-forms, semiconductor dice, etc., and may have a finger-release/vacuum hold hole in the pick-up handle. (2) Vacuum/air units about the size of a shoe box capable of almost 10^{-3} Torr (1 micron). These are air-pump operated, and some of the most widely used vacuum units for general purpose, light vacuum operation, such as for electronic slicing and dicing equipment; photo resist spinners; small vacuum ovens and wire bonders. They use $^1/_4$ ID plastic or metal tubing plumbed-in, and either pull a vacuum (oven) or operate as a vacuum holder, such as for a semiconductor wafer on a photo resist spinner. (3) Mechanical or roughing oil pumps rated for 10^{-3} Torr vacuum, and by liter-per-minute rate. These are the standard vacuum system roughing pumps, occasionally used for small vacuum ovens. (4) High vacuum pumps (oil, ion, cryo-, etc.) capable of vacuum to the 10^{-12} Torr level. Rarely used for general holding or pick-up operation.

REF:

WAXES

CAR-0001

ETCH NAME: Turpentine
TIME:
TYPE: Solvent, removal
TEMP: RT to warm

COMPOSITION:

x .... $C_{10}H_{16}$

DISCUSSION:

Carnauba wax (*Croypha cerifera*) has a melting point of 85°C as a natural tree wax like candlenut or coconut. It is brittle like the resins, but was the original base of sealing waxes (SEAW-0001). Although it has been used as a mounting medium, it is more often mixed with other more pliable waxes. See Pitches and Beeswax.

REF:

CAR-0002

ETCH NAME: Heat
TIME: $1^1/_2$ h
TYPE: Thermal, mixing
TEMP: 120°C

COMPOSITION:

x .... heat

DISCUSSION:

Carnauba wax mixtures developed as 0.1 pf capacitors. Mix the following ingredients: 45% carnauba wax:45% resin:10% white beeswax. Anneal mixture for time and temperature shown in an electric field of 1.97 to 15.75 kV/cm^3. The homogenized mixture can be cut to specimen size with an X-Acto knife.

REF: Walker, O K & Jefimenko, O — *J Appl Phys*, 44,3459(1973)

PARA-0001

ETCH NAME: Benzene
TIME:
TYPE: Solvent, removal
TEMP: RT to warm

COMPOSITION:

x .... C_6H_6

DISCUSSION:

Paraffin is a hydrocarbon distillate with a boiling point in the range of 350°C. It is

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derived from paraffin-base as against the asphalt-base petroleum. The solidified, pure paraffin is white with a greasy feel and is sufficiently soft such that it can be cut with a knife. It is used as a general mounting and holding medium, by itself, but with limited application due to the high melting point, such that it is more often mixed with another lower melting point wax like beeswax to reduce the working melt point.

As the pure paraffin it is used as a thin coating for wax papers, some for the water repellent capability of paraffin. It is sometimes used in mold fabrication of parts similar to the "lost-wax" processing using beeswax, but the most important use is in the making of candles. As a commercial product it also is called Ceresine.

REF:

PARA-0002

ETCH NAME: Trichloroethylene

TIME:

TYPE: Solvent, removal

TEMP: RT to boiling

COMPOSITION:

x .... TCE

DISCUSSION:

Lok-wax formulations are basically paraffins with additive white beeswax for specific melting points. They tend to retain bubbles while still liquified as does Crystalbond. The material has been used for mounting semiconductor wafers for both etching and vacuum metallization.

REF: Cochran, L — personal communication, 1980

SEAW-0001

ETCH NAME: Benzene

TIME:

TYPE: Solvent, removal

TEMP: RT to warm

COMPOSITION:

x .... C_6H_6

DISCUSSION:

Sealing wax. Originally a carnauba type wax, but also made from a base of pitch or other tree resins with additive color. The material is both hard and brittle with common colors of red, green, yellow, and brown or black. The name derives from its use in sealing letters and as document seals before the development of glue. Individuals used to have their own sigils with personal designs carved from agates or metals engraved. The wax will melt in a candle flame (>1500°F), such that a drop of wax was melting across the flap of a letter to be sealed, the sigil firmly pressed into the still liquid and hot wax to imprint and solidify the wax to the document. It is still so used on official documents, as a county, state, government department seal, and may include short ribbons.

Using a dop-stick ($^1/_4$—$^1/_2$" diameter wooden dowel) with sealing wax on one end, small rock and mineral specimens are mounted for polishing en cabachon, such as for star sapphires. This was one of the first methods developed in ancient times for polishing stones, and is still in use today. It is not widely used as a mounting medium in Solid State or metal processing due its brittleness, more often mixed with beeswax, paraffin, and other resins for greater pliability.

REF:

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WOOD

WOOD-0001
ETCH NAME: Water
TYPE: Solvent, cleaning
COMPOSITION:
x .... H_2O
x .... CH_3COCH_3 (acetone)
TIME:
TEMP: RT to boiling
DISCUSSION:

Woods have some uses in Solid State material processing as handling parts. Q-tips with either cotton or foam plastic ends water or acetone soaked for light scrub cleaning of wafers and parts. Acetone is the main cleaning solvent for photo resist lacquers. Wooden tongue depressors and similar smaller sticks are used in stirring chemical solutions or for measuring out dry chemicals on a balance pan. The wooden end of a Q-tip has been used as an acid saturated rod to rub-form an etched channel, or the end sharpened, dipped in HF, then a droplet applied to an oxide thin film to etch-form a pit down to the substrate. Under a microscope the color orders within the oxide layer can be observed and measured for thin film thickness. Hard woods have been used as a lapping platen, such as a maple wood lap with diamond or alumina grits in oil or grease for wafer surface polishing.
REF:

CHAR-0001
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP: >100°C
DISCUSSION:

Charcoal, as made from hard woods or as coke made from coals. In both cases, the material it heated below its burning point to drive off volatiles, such as water moisture and entrapped gases. The use of charcoal dates back to the end of the Bronze Age and the beginning of the Iron Age, circa 5000 and 1350 B.C., respectively, for the more intense heat obtained from charcoal that is required for the smelting of iron . . . also glass . . . soda-lime, developed by the Egyptians, circa 3500 B.C. Both charcoal and, primarily, coke are major fuels in the metal processing industries.

In Solid State processing both charcoal and graphite are used as getters and drying agents in vacuum systems (cryo-pumps with graphite); and in various types of gas and air cleaning filters (both charcoal and graphite).

For cleaning granular charcoal, vacuum oven bake above 125°F, $^1/_2$ to 1 h or more to remove entrapped volatiles. . .the charcoal can then be reused.
REF:

PHYSICAL PROPERTIES OF MUSCOVITE, $(OH)_2KAl_2(AlSi_3O_{10})$

Classification	Mica
Atomic numbers	1, 16, 13, 19, & 14
Atomic weight	342.1
Melting point (°C)	1300
Boiling point (°C)	
Density (g/cm^3)	2.7—3
Refractive index (n=)	1.552—1.588
Hardness (Mohs — scratch)	2—2.25

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Crystal structure (monoclinic — normal)	(001) pseudo-hex sheet
Color (solid)	Olive-green variable
(thin section)	Transparent/clear
Cleavage (basal — perfect)	(001)

MUSCOVITE, $(OH)_2Al_2K(AlSi_3O_{10})$

General: The formula shown is for the variety called muscovite (common mica). There are a number of micas and mica-like minerals that are widely distributed throughout the world as an original constituent mineral or as a secondary product from weathering and alternation of aluminum- and potassium-bearing rocks. There are three groups: (1) the Mica Group, proper; (2) the Clinotite Group, brittle micas, and (3) the Chlorite Group. A supplemental group is the hydrated vermiculites, chiefly from alternation of the micas. Talc and serpentine (fibrous variety is asbestos) are associated minerals. There are many mica-bearing rocks, such as mica-granite — the fine yellowish flakes sometimes mistaken for gold. This discussion will be limited to the Mica Group proper, as they are widely used in industry.

The micas are orthosilicates of aluminum and potassium with the various types containing fluorine, lithium, magnesium, iron, calcium, etc. They are all in the monoclinic system of crystallography with perfect basal cleavage, (001) — micaceous cleavage — and can be easily separated into thin sheets. Hardness and specific gravity (density) vary (H = 2.5—3.5 . . . G = 2.5—3), and thin sheets are highly elastic when bent. Muscovite — common or potash mica — and biotite — iron mica — are the two most used varieties and have a high fusibility index: 5 = 1200°C. Lepidolite lithia micas — fusibility is about 100°C, and is a source of lithium. Phlogophite — magnesium mica — is similar to biotite, but in small, exfoliated masses with a much more greasy feeling. They are all acid resistant, have high electrical resistance, and are heat insulators. When muscovite and biotite are found in pegmatites, they can occur in large single crystal masses as much as 6 ft in diameter with hexagonal outline. As such, they can be cleaved into large thin sheets.

Although high temperature glasses, such as Pyrex, have largely replaced mica in most such applications, mica is the Isinglass long used as stove window insulation. It is still used as a see-through window in several industrial applications as both a temporary or permanent heat shield. Sheet mica parts are used in high-power line insulation and, as a powdered compact, to fabricate insulating board. The latter now replaces asbestos. Flaked and mixed with oil, it is an industrial lubricant.

Oriented prisms of mica are used as polarizers for microscopes and, a major industrial product, as mica capacitors — resistance wielding equipment, discrete elements in electronic assemblies, and so forth.

Phlogophite and some of the vermiculites are used as packaging materials. In oil drilling, as a packing around piping, along with montmorillonite, a clay-like mineral, both swell with water absorption and act as sealers against pumping loss of oil. Also used as a container packing material for shipping acids and corrosive gases, as it will absorb any leakage. The material can then be water leeched, dried and reused. In gardening, it is mixed with soil and fertilizers to retain chemicals and water moisture.

Technical Application: Though not directly used in semiconductor or quartz device fabrication, there are discrete mica capacitors and resistors used in circuit assemblies.

Sheet mica is still used as heat resistant windows on small hand furnaces and small washers are punched from the sheet as insulating elements for electrical stand-offs. Powdered and fabricated as blocks and sheets it is machine cut into a variety of insulating parts and is being used to replace asbestos. Block material is classified by heat-resistant capability, such as 800°C, 1200°C, etc. Most micas are transparent to translucent in thin sheets but, in sufficient thickness, dark yellow-tan, and used as observation windows in furnaces where parts are at red heat or above. The exfoliated phlogophite variety is used as a packing material

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for shipment of dangerous chemicals as it is nonflammable, resistant to chemical attack, and a liquid and gas absorber.

As (001) cleaved sheets, both muscovite and biotite have been used as substrates for metal evaporation and epitaxy thin film growth of semiconductor materials and metals in studying the growth kinetics and structure of such thin films. The thin films are then removed by the "float-off" technique for SEM and TEM study. Depending upon the substrate material, water (NaCl, KCl substrates) or acids (micas) are used to lightly attack and liquify the substrate at the substrate/thin film interface to effect "float-off".

Etching: Muscovite is acid resistant but will decompose in molten fluxes of alkaline carbonates. Biotite is soluble in H_2SO_4. Lepidolite is partially dissolved by acids. Phlogophite is acid resistant like muscovite but, once saturated by liquids or gases, can be dried and reused.

MICA ETCHANTS

MI-0001
ETCH NAME: Alconox
TYPE: Alkali, cleaning
COMPOSITION:
(1) x .... Alconox (2) x .... H_2O
DISCUSSION:
TIME:
TEMP: Boiling

Muscovite mica, $(OH)_2KAl_2(AlSi_3O_{10})$ cleaved (001) and used as substrates for epitaxy thin film growth of CdTe, PbTe, and SnTe doped with Bi and Sb. After cleaving mica, clean in boiling Alconox. Follow with boiling in water several times, and final rinse in high purity MeOH immediately before placing in vacuum system for epitaxy growth. Substrates of CdTe, (111) were also used and polished in 1% Br_2:MeOH. Thin films were used in a study of superlattices.
REF: Davenere, A et al — *J Cryst Growth*, 70,452(1984)

MI-0002
ETCH NAME: Freon
TYPE: Gas, cleaning
COMPOSITION:
x .... Freon
DISCUSSION:
TIME:
TEMP: RT

Mica and natural rock salt, NaCl were both cleaved (0001) prior to use as substrates for gold and silver evaporation. Particulate matter blown off with Freon as particulates affect good adhesion of thin films. No liquids used as sodium chloride is etched by water and mica can adsorb liquid along cleavage planes. (*Note:* Mica is (001) basal cleavage.)
REF: Chopea, K I — *J Appl Phys*, 37,2049(1960)

MI-0003
ETCH NAME: Air
TYPE: Gas, drying
COMPOSITION:
x .... air
DISCUSSION:
TIME:
TEMP: 125°C

Phlogophite mica, $H_2KMg_3Al(SiO_4)_3$. Material as exfoliated pieces used as packing as a liquid gas absorbent and fire-retardant (material will not burn). Used in shipping containers handling acids, toxic liquids, and in the annular vacuum space of cryogenic tanks, e.g., LN_2, LOX. For drying small quantities place material in a Pyrex beaker in an air-circulating oven and bake at 125°C to remove water moisture. Time varies with quantity of phlogophite.

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If toxic gases are involved, proper containers and ventilation are required during heat drying. Used by the referenced author in cleaning 2000 gallon LOX and LN_2 tankers. This cleaning included pulling a final vacuum of 10^{-3} Torr on the mica filled, annular space prior to seal-off.
REF: Walker, P — personal application, 1963

MI-0004
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, float-off — TEMP: RT
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:

Muscovite mica, $(OH)_2KAl_2(AlSi_3O_{10})$, cleaved (100) and used for growth of platinum fibers. Fiber grown at 1000 K with axis in the ⟨1000⟩ direction. Platinum thickness was 1000—1200 Å. Metallization removed with dilute nitric acid as a float-off technique for TEM structure study of the platinum films. (*Note:* Micas are hexagonal system, not isometric.)
REF: Dixit, P & Vook, R W — *Thin Solid Films*, 113,151(1984)

MI-0005a
ETCH NAME: Pressure — TIME:
TYPE: Pressure, defect — TEMPT: RT
COMPOSITION:
x .... pressure
DISCUSSION:

Biotite, $H_2K(Mg,Fe)_3Al(SiO_4)_3$ as (0001) cleaved specimens of hexagonal platelets. By striking the surface a sharp blow with a rod of glass, metal, etc., a six-rayed percussion-figure is formed in the surface. The strongest break-line is parallel to the clino-pinacoid plane of symmetry and can be used to orient planes of optical axes. Specimens used for polarizing microscope plates.
REF: Walker, P — mineralogy development, 1952—1953

M-0005b
ETCH NAME: Trichloroethylene — TIME:
TYPE: Solvent, cleaning — TEMP: RT
COMPOSITION:
(1) x .... TCE (2) x .... MeOH
DISCUSSION:

Muscovite, $(OH)_2KAl_2(AlSi_3O_{10})$, cleaved (0001) and cut as 3″ diameter discs with center hole. Used as a cover on a hand alloy, portable furnace. Fresh mica sheets fabricated as insulation and sighting glass as needed. Degrease with TCE, rinse in MeOH, and air dry. Thicker sheets used as sighting glasses in observing hot parts down-tube in diffusion, and both alloy and epitaxy growth furnaces. Mica stand-off insulators for vacuum systems similarly cut and cleaned. Bulk mica sheet or pressed flake blocks used for handling hot parts, surfaces wiped clean with cloth toweling soaked in either solution.
REF: Walker, P et al — personal application, 1955—1959

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PHYSICAL PROPERTIES OF NEODYMIUM, Nd

Classification	Lanthanide
Atomic number	60
Atomic weight	144.24
Melting point (°C)	1024
Boiling point (°C)	3027
Density (g/cm^3)	7.00
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.031
Heat of fusion (k-cal/g-atom)	1.70
Specific heat (cal/g) 25°C	0.045
Latent heat of fusion (cal/g)	11.78
Heat of vaporization (k-cal/g-atom)	69
Atomic volume (W/D)	20.6
1st ionization energy (K-cal/g-mole)	145
1st ionization potential (eV)	6.77
Electronegativity (Pauling's)	1.2
Covalent radius (angstroms)	1.64
Electrical resistivity (micro-ohm-cm) 298 K	64.3
Compressibility (cm^2/kg $\times$ 10^{-6})	3.0
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	6.7 (8.4)
Cross section (barns)	46
Magnetic moment (Bohr magneton)	3.3
Tensile strength (psi)	24,700
Yield strength (psi)	23,900
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	5,650
Transformation temperature (°C)	855
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Yellowish metal
Cleavage (basal)	(0001)

NEODYMIUM, Nd

General: Does not occur as a native element. It is a rare earth of the cerium group. The mineral monazite $(Ce,La,Di)PO_4$ is the major ore. *Note:* "Didymium, Di", was thought to be an element, but in 1885 von Welsbach separated didymium into the elements neodymium, Nd and praseodymium, Pr.

Not used in industry to any extent as the metal due to scarcity. Many of the neodymium salts are pink in color with a characteristic absorption spectrum.

Technical Application: Not used in Solid State device fabrication. Metallic neodymium has been the subject of electrical and morphological studies along with other rare earth elements of the cerium group.

Etching: Deliquesces in water.

NEODYMIUM ETCHANTS

ND-0001
ETCH NAME: TIME:
TYPE: Arc, forming TEMP:
COMPOSITION:
x .... heat

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DISCUSSION:

Nd, specimens were first arc melted as buttons and then machined into cylinders 3/16 to 2″ in diameter and used in measuring electrical resistivity. Other materials used: La, Pr, Sm.

REF: Alstad, J K et al — *Phys Rev,* 122,1636(1961)

PHYSICAL PROPERTIES OF NEON, Ne

Classification	Rare gas
Atomic number	10
Atomic weight	20.183
Melting point (°C)	−248.67
Boiling point (°C)	−245.9
Density (gm/cm³)	0.9 gm/l liq.
Thermal conductivity (cal/cm²/cm/°C/sec) 20°C	1.1×10^{-4}
1st ionization potential (eV)	21.6
Cross section (barns)	0.032
Hardness (Mohs — scratch) solid	2—3
Crystal structure (isometric — normal) solid	(100) cube fcc
Color (gas/solid)	Colorless
Cleavage (cubic) solid	(001)

NEON, Ne

General: Neon is one of the rare gases found in the atmosphere. It is inert with a valance of 0 and does not form compounds, and there is only about 18 ppm neon in air. It is obtained by the fractionation of liquid air, after the removal of LN_2 (−196°C), being distilled from the remaining LOX.

In a vacuum tube it will produce a red-orange to red glow, and as such is widely used in electric signs and beacons. It also is used in small bulbs as a display light in electronic equipment.

Technical Application: Not generally used in Solid State processing other than as a neon light bulb for signs and equipment display panels. Fabricated as a neon or neon/helium laser.

Etching: Soluble in O_2. As a solid under vacuum, vary vapor pressure to "etch".

NEON ETCHANTS

NE-0001
ETCH NAME: Neon — TIME:
TYPE: Gas, forming — TEMP:
COMPOSITION:
x .... Ar/N_2
x .... 12.8% Ne
DISCUSSION:

Ne, used as a component in the gas ambient used in RF magnetron sputter deposition of NbN thin films. Inclusion did not appear to improve resistivity or other electronic functions of the material.

REF: van Dover, R B et al — *J Vac Sci Technol,* A2(3),1257(1984)

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NE-0002
ETCH NAME: TIME:
TYPE: Pressure, defect TEMP: −250°C
COMPOSITION:
x .... vapor pressure
DISCUSSION:
Ne, grown as a single crystal in vacuum at LHe temperature. Ingot surfaces can be preferentially etched by varying the vapor pressure of the system.
REF: Schwentner, N et al — *Rare Gas Solids,* Vol 3, Academic Press, New York, 1970

NE-0003
ETCH NAME: TIME:
TYPE: Exciton, growth TEMP: −250°C
COMPOSITION:
x .... exciton
DISCUSSION:
Ne, grown as a single crystal solid in a study of exciton growth bubbles in the material.
REF: Ossicini, S — *J Phys Chem Solids,* 46,123(1985)

NE-0004
ETCH NAME: Laser TIME:
TYPE: Gas, measuring TEMP:
COMPOSITION:
x .... Ne
x .... He
DISCUSSION:
Ne/He laser used to measure the optical density (O.D.) vs. time response of an electrochromic device fabricated with Li-W,O thin films on ITO coated quartz blanks with measurement between an Au cover film to the ITO layer. See WO-0007 for device details.
REF: Kitabatake, M et al — *J Electrochem Soc,* 132,433(1985)

PHYSICAL PROPERTIES OF NEPTUNIUM, Np

Classification	Actinide
Atomic number	93
Atomic weight	237
Melting point (°C)	637
Boiling point (°C)	
Density (gm/cm^2)	20.45
Ionic radius (angstroms)	1.10 (Np^3)
Half-life ($\times 10^4$ years)	2.14
Cross section (barns)	170
Hardness (Mohs — scratch)	
Crystal structure (orthorhombic — normal)	(100) a-pinacoid
Color (solid)	
Cleavage (basal)	(001)

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NEPTUNIUM ETCHANTS

NP-0001
ETCH NAME: Hydrochloric acid
TYPE: Acid, removal/polish
COMPOSITION:
x .... HCl, conc.
DISCUSSION:
Np specimens. Solution shown as a general etch for the material.
REF: Vossen, J L & Kern, W — *Thin Film Processes,* Academic Press, New York, 1978
TIME:
TEMP:

PHYSICAL PROPERTIES OF NICKEL, Ni

Classification	Transition metal
Atomic number	28
Atomic weight	58.71
Melting point (°C)	1453
Boiling point (°C)	2730 (2732)
Density (g/cm^3)	8.908
Thermal conductance (cal/sec)(cm^2)(°C/cm) 100°C	0.198
Specific heat (cal/g) 200°C	0.1226
Latent heat of fusion (cal/g)	73.8
Heat of vaporization (k-cal/g-atom)	91.0
Atomic volume (W/D)	6.6
1st ionization energy (K-cal/g-mole)	176
1st ionization potential (eV)	7.63
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.15
Ionic radius (angstroms)	0.69 (Ni^{+2})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	13.3
Electrical resistivity (micro-ohms/cm) 20°C	6.844
Lattice constant	3.5168
Modulus of elasticity (psi $\times 10^6$)	30
Magnetic transformation temperature (°C)	357
Tensile strength (psi)	120,000
Compressibility (cm^2/kg $\times$ 10^{-6})	0.531
Electron work function (eV)	5.01
Cross section (barns)	4.6
Vapor pressure (°C)	2364
Hardness (Mohs — scratch	5
(Brinell — annealed)	75 (80—110)
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Silver-grey metal
Cleavage (cubic — poor)	(001)

NICKEL, Ni

General: Does not occur as a native element. There are about 35 minerals containing nickel, the two major ones being millerite, NiS and niccolite, NiAs, both as primary nickel ores. The latter is called "copper-nickel" due to its color, not the presence of copper. Nickel, as an element, always occurs in meteoric iron and — the earth core — is considered to be

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mainly a mixture of these two metals . . . $FeNi_2$. The pure metal it is hard, yet malleable, ductile, and tenacious. It is relatively inert to most atmospheres and is one of the few metals that shows a degree of magnetism.

Nickel is a major metal in industry with many applications such as an alloy with copper and iron as commercially named mixtures, such as Invar, Hastalloys, Iron-Constantan, Permalloy, Nichrome. Also used for armor plate, in low temperature solders (<800°C), and high temperature brazing alloys. It is now one of the coinage metals, is easily electroplated on other metals for corrosion protection. As plated of evaporated on glass, it is a replacement for a silvered mirror.

Technical Application: Nickel has major application in Solid States device fabrication as an electrical contact metal, as Au/Ni (plated), or Au/AuGe/Ni (evaporated/sputtered).

As an electrolytic plating it is used on semiconductor wafers; ceramic, glass, sapphire, or quartz circuit substrates; on package parts, contact wires, leads, or straps; and as a replacement metal in making photo resist chrome masks. As the pure metal or alloy it has been used as a quartz frequency crystal or semiconductor package, as a testing heat sink, to include a magnet as a mixture with magnetic iron and cobalt.

Nickel has been grown as single crystals and studied widely for its physical and electrical properties. There are a wide range of single crystal alloys containing nickel which have been grown and studied, some of which are included in the "Nickel Alloys" section immediately following this section on Nickel.

Etching: HNO_3, HCl, H_2SO_4, HF, their mixtures, and chrome etch. Ionized gases.

NICKEL ETCHANTS

NI-0001a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
30 .... HNO_3
10 .... H_2SO_4
50 .... HAc
10 .... H_2O
TIME: 30 sec
TEMP: 85°C
RATE: 5 μm/30 sec
DISCUSSION:
Ni specimens. Solution used to polish surfaces prior to oxidation experiments.
REF: Graham, W J et al — *J Electrochem Soc,* 119,879(1972)

NI-0001b
ETCH NAME: Sulfuric acid, dilute
TYPE: Electrolytic, polish
COMPOSITION:
4 .... H_2SO_4
3 .... H_2O
TIME: 2 min
TEMP: RT
ANODE: Ni
CATHODE:
POWER: 0.5 A/cm²
DISCUSSION:
Ni specimens. Solution used to polish specimens in a study of nickel oxidation.
REF: Ibid.

NI-0002
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
COMPOSITION:
3 .... HNO_3
7 .... H_2O
TIME: 1 min
TEMP: RT

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DISCUSSION:
Ni, evaporated as an Au:Ni coating on resistors. In evaluating resistors, after etch removal of gold, etch immediately in the solution shown to prevent formation of nickel oxide.
REF: Bulletin 5M 1/1/83C — Hycomp Inc.

NI-0003a
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
50 ml .... HNO_3
50 ml .... CH_3COOH (HAc)
DISCUSSION:
Ni, evaporated thin films. Solution mixtures is a general removal etch for nickel.
REF: Bulletin 1116B/Rev-HPD/VB/TM/0883/1K — MRC

NI-0003b
ETCH NAME: TIME:
TYPE: Acid, removal TEMP: RT
COMPOSITION:
20 g .... $Ce(NH_4)_2(NO_3)_6$
200 ml .... H_2O
DISCUSSION:
Ni, thin film evaporation on glass or semiconductor substrates. Used as a removal and patterning etch.
REF: Ibid.

NI-0004a
ETCH NAME: Jewitt-Wise etch TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... 10% $NH_4(H_2SO_4)_2$
1 .... 10% KCN
DISCUSSION:
Ni specimens. Solution used in preparing nickel and alloys as metallographic sections for study by developing structure.
REF: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices*, Reinhold, New York, 1967

NI-0004b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
10 .... HCl
33 .... HNO_3
67 .... H_2O
DISCUSSION:
Ni specimens. Solution used to clean nickel surfaces.
REF: Ibid.

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NI-0004c
ETCH NAME: Hydrofluoric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
(1) x .... HF, conc. (2) x .... H_3PO_4, conc.
DISCUSSION:
Ni specimens. Both solutions are slow etchants for nickel.
REF: Ibid.

NI-0004d
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
(1) x .... HNO_3, conc. (2) x .... HF
x .... HNO_3
DISCUSSION:
Ni, specimens. Concentrated nitric acid is an extremely rapid etch. Solutions of HF:HNO_3 are fast but more controllable with removal rate reduced by increase of HF.
REF: Ibid.

NI-0004e
ETCH NAME: Meta-phosphoric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... HPO_3
DISCUSSION:
Ni specimens. This acid is a slow etch for nickel. Can be mixed with alcohol.
REF: Ibid.

NI-0005
ETCH NAME: Aqua regia, modified — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
4 .... HCl
1 .... HNO_3
DISCUSSION:
Ni specimens. Used as a general etch for nickel and brass. With increased nitric acid content can be used to etch high-speed steels.
REF: Oberg, E & Jones, F D — *Machinery Handbook,* 4th ed, The Industrial Press, New York, 1951

NI-0006
ETCH NAME: — TIME: 2—10 min
TYPE: Salt, removal — TEMP: Warm (60°C)
COMPOSITION:
x .... 30% $FeCl_3$
DISCUSSION:
Ni, as 0.005 and 0.010 shim stock. Solution is a general etch for nickel. As applied to shim stock was used with Apiezon-W (black wax) patterning to fabricate metal masks used for gold evaporation on silicon SCRs.
REF: Walker, P — personal application, 1964—1974

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NI-0007
ETCH NAME:
TYPE: Acid, cleaning
TIME: 10—20 min
TEMP: 50—60°C or 65—70°C
RATE: 0.1 to 0.2 mils average
COMPOSITION:

(1) 45 .... H_2O_2
10 .... HCOOH (formic acid)
45 .... H_2O

(2) 45 .... H_2O_2
45 .... HCOOH
10 .... H_2O

DISCUSSION:
Ni specimens. Both solutions used in a study of surface cleaning.
REF: Bell Tel Systems Tech Publ, 3143(1958)61

NI-0008
ETCH NAME:
TYPE: Acid, removal
TIME: 60—90 sec
TEMP: RT
COMPOSITION:
50 g .... $2NH_4NO_3.Ce(NO_3)_3.4H_2O$
10 ml .... HNO_3
150 ml .... H_2O
DISCUSSION:
Ni, thin films vacuum evaporated on soda-lime glass used for photo resist masks. Film thickness 2000 to 2500 Å with and without NiO AR coatings. Use NH_4OH to remove nickel oxide, then etch remove or etch pattern with solution shown. Further addition of nitric acid will reduce etch rate. Without nitric acid rate increases. This is a modification of standard "chrome etch" and can also be used on chromium with and without Cr_2O_3 AR coatings.
REF: Walker, P — personal development, 1975

NI-0009a
ETCH NAME: Sulfuric acid, dilute
TYPE: Electrolytic, polish
TIME: 4—6 min
TEMP: RT
ANODE: Specimen
CATHODE: Nickel
POWER: 2 V
COMPOSITION:
390 ml .... H_2SO_4
290 ml .... H_2O
DISCUSSION:
Ni, specimens used in a study of growth habits. During etch polishing agitate electrolyte vigorously due to heavy gas evolution. Remove specimen with current still running. Rinse in dilute nitric acid to remove anodic film; then rinse in DI water, alcohol and dry with warm air.
REF: Cliffe, D R & Farr, J P — *J Electrochem Soc,* 111,299(1964)

NI-0012
ETCH NAME:
TYPE: Electrolytic, dislocation
TIME:
TEMP:
ANODE: Specimen
CATHODE:
POWER:
COMPOSITION:
x .... H_2SO_4
x .... D_2O
DISCUSSION:
Ni, polycrystalline specimens used in a study of ion implantation (I^2) damage. Specimens were Ar^+ ion bombarded at 250 KeV and then etched. The deuterium, D_2O, is trapped in vacancy complexes in the I^2 region. After temperature anneal there are two types of structures:

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(1) dislocation loops at 21 and 250°C and (2) small voids and dislocation loops at 500°C. All defects were in the implanted region.
REF: Frank, R C et al — *J Appl Phys*, 57,414(1985)

NI-0013
ETCH NAME: Sulfuric acid, dilute
TYPE: Electrolytic, thinning
COMPOSITION:
40% .... H_2SO_4
60% .... H_2O
TIME:
TEMP: 10°C
ANODE: Ni
CATHODE:
POWER: 75A/in^2
DISCUSSION:
Ni, single crystals used in a study of induced deformation and imperfections. Solution used to electro-thin samples.
REF: Bhattachernya, A et al — *J Appl Phys*, 37,4441(1966)

NI-0014a-b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
"A" x .... 55% HNO_3 then "B" x .... 25% HCl
x .... $FeCl_3$, sat. sol.
TIME:
TEMP:
DISCUSSION:
Ni, (100) wafers used in a study of secondary electron reaction on (100) faces of copper and nickel. First etch in "A" — nitric is rapid — and follow with "B" which is slower but produces similar pits and structure as obtained by the nitric acid. An alternate method is to etch with the "B" mixture and follow with 50% H_3PO_4 as an electrolytic polish — even with removal of up to $^1/_2$ mm of material the surface maintains planarity with an estimated 2% number of etch pits.
REF: Burns, J — *Phys Rev*, 119,102(1960)

NI-0015
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... NH_4Cl
x .... NH_2CONH_2 (urea)
TIME:
TEMP: 120—135°C
ANODE;
CATHODE:
POWER:
DISCUSSION:
Ni specimens. A study of the use of this solution for polishing nickel.
REF: Hoar, T P & Mowat, JA S — *J Electrodepositors Tech Soc*, 26,7(1950)

NI-0016
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:
Ni single crystal sphere formed from a liquified droplet of nickel in high vacuum. Sphere was oxidized without removal from vacuum to form NiO, and main oxide growth was on the (100) great circle.
REF: Otter, M — *Z Naturforsch*, 14a,355(1959)

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NI-0017
ETCH NAME: Potassium
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... K^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Ni, (100) wafers within ±3° of surface plane. Wafers used in a study of sulfurizing surfaces by S_2 doping. Wafers were first cleaned by resistive heating and chemical etching; then the ion bombardment cleaning as shown, followed by a 10 min anneal at 1370°C.
REF: Godwski, P & Mroz, S — *Thin Solid Films*, 111,129(1984)
NI-0018: Soden, R R Albano, V J — *J Electrochem Soc*, 117,766(1968)
Ni, high purity specimens. A report on material preparation. After cutting wafers, use a $1H_2SO_4$:$1H_2O$ solution to etch remove residual iron on surfaces from cutting. Solution also used as an anodic polishing etch.

NI-0019
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
30 ml .... HNO_3
10 ml .... H_2SO_4
10 ml .... H_3PO_4
50 ml .... HAc

TIME: 30—60 sec
TEMP: 85—95°C

DISCUSSION:
Ni specimens. Described as a very good polish etch for nickel.
REF: Tegart, W J McG — *The Electrolytic and Chemical Etching of Metals*, Pergamon Press, London, 1956

NI-0020
ETCH NAME: Methyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... MeOH

TIME:
TEMP: RT

DISCUSSION:
Ni, crystalline electrode rod. After grinding to shape, specimen was polished with 6, 1, and $^1/_4$ μm diamond paste and ultrasonically cleaned in water, then in methyl alcohol. Gold and platinum were evaporated in a study of their diffusion in nickel. Platinum films were porous and the thin nickel oxide appeared to have no affect on test results.
REF: Van Den Belt, T G M & De Wit, H W — *Thin Solid Films*, 109,1(1983)

NI-0021a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
2 oz .... $NaCO_3$
5 oz .... $Na_2Si_6O_9$
0.5 oz .... NaOH

TIME: 1—2 min
TEMP: 210°F
ANODE: Pb
CATHODE: Ni
POWER: 15 A/ft² & 6 V

DISCUSSION:
Ni specimens. Solution used as an electropolish etchant. Dip 5—10 sec, RT, in 2% H_2SO_4 for final cleaning.
REF: ASTE Committee — *Tool Engineers Handbook*, McGraw-Hill, New York, 1949

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NI-0021b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
2 oz .... $NaCO_3$
1000 ml .... H_2O
TIME: 1—2 min
TEMP: 120°C
ANODE: Steel
CATHODE: Ni
POWER: 10 A/ft² & 6V
DISCUSSION:
Ni, specimens. Solution used as an electropolish etchant. Dip 5—10 sec, RT, 2% H_2SO_4 as final clean.
REF: Ibid.

NI-0022
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
453.6 g .... H_3PO_4
185.6 g .... $Al_2(SO_4)_3.18H_2O$
14.25 g .... $NiSO_4.6H_2O$
TIME: 5 min
TEMP: 80°C
ANODE: Ni
CATHODE:
POWER: 40 A/dm² & 6 V
DISCUSSION:
Ni specimens used in a study of optical properties according to Drude's formula. Solution used to electropolish nickel. Also studied tungsten. Though nickel grains are attacked at different rates, solution will produce a smoothly polished surface.
REF: Roberts, S — *Phys Rev*, 114,104(1959)

NICKEL ALLOYS, NixMyMz

General: There are several metallic nickel metal alloys that occur as natural single crystals, but the majority are artificial formulations tailored for specific characteristics. Some of the naturally occurring alloys are awaruite, $FeNi_2$; josephinite, $FeNi_3$; maucherite, Ni_3As_2; and melonite, $NiTe_3$. Niccolite, NiAs and millerite, NiS are two major ores of nickel and there are several other oxides, silicates, and hydrated minerals that contain cobalt, iron, bismuth, magnesium, aluminum, and other metals. Most meteoric iron is a mixture of iron and nickel, occasionally with some single crystal portions as $FeNi_2$.

In addition to nickel/iron mixtures which are basic in the iron and steel industry, mixtures of nickel/copper are the basis of monel metal, 67Ni:30Cu. See etchant number NICU-0003a for additional monel types. Monel is highly resistant to both fluorine and chlorine gas as well as hydrochloric acid, and is used as tubing for handling such material, as in the construction of HCl cylinder gas regulators with a 9- to 12-month operational life, before replacement parts are installed. Permalloy, 79Ni:17Fe:4Mo is another major nickel alloy and, in addition to normal metal use, also is fabricated as magnets with iron and cobalt.

Technical Application: Many nickel alloys are used in Solid State equipment design, not in direct device development, although as heat sinks and in package construction. Some devices, such as diodes and quartz frequency crystals use magnets in their package construction for operational control.

Several nickel alloys have been grown and studied as both natural and artificial single crystals or ferrites. Several ferrites are used as resistive elements in assemblies with semiconductor elements or as individual resistors.

Etching: H_3PO_4, $FeCl_3$ and mixed acids.

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NICKEL ALLOYS

Nichrome, NiCr
Nickel aluminum, NiAl
Nickel boridem, NiB
Nickel copper, NiCu
Nickel iron, NiFe:O_2
Nickel manganese, NiMn
Nickel sulfide, NiS
Nickel titanium, NiTi
Nickel zirconium, Zr_2Ni
Permalloy, Ni:Fe:Mo

NICKEL ALLOY ETCHANTS

NICHROME ETCHANTS

NICR-0001
ETCH NAME:
TYPE: Acid, removal
TIME: 30—60 min
TEMP: RT
COMPOSITION:
x .... $Ce(NH_4)_2(SO_4)_6$
x .... HNO_3
x .... H_2O
DISCUSSION:
Ni:Cr, thin film deposition as a bimetallic layer of Au/Ni:Cr on semiconductor substrates. After etch removal of gold, the nichrome can be removed with the solution shown. Solution also used on thin film metallization of pure nickel and chromium. (*Note:* This is a "chrome etch" mixture.)
REF: Bulletin #5M1/183C — Hycomp, Inc.
NICR-0002: Walker, P — personal application, 1964—1979
Ni:Cr, pellets and alloy sheet. Used a 50 g ceric ammonium nitrate: 5 ml nitric acid:100 ml water solution, 2—5 sec, RT for surface cleaning. A cotton swab soaked in the solution or an eye dropper of solution was wiped on surfaces, then flushed with water, rinsed in MeOH, and N_2 blown dry. Increase water or nitric acid to reduce solution reaction. Method used to clean material prior to use as alloy contacts on silicon devices.

NICR-0003
ETCH NAME: Aqua regia
TYPE: Acid, removal
TIME:
TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
Ni:Cr, thin films evaporated on (111) and (100) oriented silicon, and (100) gallium arsenide wafers with or without an SiO_2 thin films. Nichrome films were photolithograph patterned, and aqua regia was used to etch the nichrome for a study of adhesion and peeling. Thermal shock into LN_2, heat quenching, and slight etch removal of nichrome can initiate peeling.
REF: Tanielian, H et al — *J Electrochem Soc,* 132,507(1985)

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NICR-0004a
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
45 .... HCl
5 .... HNO_3
50 .... MeOH
TIME:
TEMP:
DISCUSSION:
Ni:Cr, material specimens used in a study of stacking faults. Solution shown used to develop defect structures.
REF: Motte, H — *Acta Metall,* 5,614(1957)

NICR-0004b
ETCH NAME:
TYPE: Alkali, removal
COMPOSITION:
x .... 10% NaOH
TIME:
TEMP: 368 K (114°C)
RATE: 100 nm/h
DISCUSSION:
Ni:Cr, evaporated thin films on (100) silicon wafers used as a mask for etching pits and via holes. After photolithographic patterning, etching was done at temperature shown with minimum undercutting of the nichrome mask. For a pit on one surface, only, etch about $2^1/_2$ h; for via hole with controlled orifice size, etch aligned opposed side a total time of both sides for about $4^1/_2$ h. The rate shown is for nichrome removal. Hot alkalies are preferential on silicon with a more rapid etch rate.
REF: Ibid.

NICR-0004b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
6 .... $HClO_4$
35 .... butyl cellusolve
59 .... MeOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Ni:Cr, specimens used in a study of stacking faults. Solution used to polish specimens prior to preferential etching to develop defects.
REF: Ibid.

NICR-0005a
ETCH NAME: Chrome etch
TYPE: Acid, removal
COMPOSITION:
x .... $2NH_4NO_3.Ce(NO_3)_3.4H_2O$
x .... CH_3COOH (HAc)
x .... H_2O
TIME:
TEMP:
DISCUSSION:
Ni:Cr, as an evaporated thin film on (100) oriented silicon wafers. The nichrome was used as an etch mask against NaOH solutions in etch forming pits and via holes with controlled center orifices. Solution used to remove nichrome after pit/via hole structuring. Solution does not etch silicon. As a form of the chrome etch, see CR-0006, CR-0007, CR-0008, and NI-0008. (*Note:* Nichrome cannot be evaporated as an alloy mixture due to lower vapor pressure of nickel. Nickel evaporates first, followed by chromium, forming a bi-layer with

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a hard chrome top surface. It can be RF sputter evaporated from a solid target of nichrome as a mixed alloy.)

NICR-0006
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HCl
1 .... HNO_3
3 .... H_2O
TIME:
TEMP:
DISCUSSION:

Ni:Cr, residual metals from evaporation of thin films. Solution used to remove metals and clean vacuum system glass bell jars and internal fixturing. Solution can be used on glass, ceramic, SST and copper.
REF: Nichols, D B — *Solid State Technol*, December 1979

NICR-0007a
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, cutting
COMPOSITION:
20 .... HCl
80 .... H_2O
TIME:
TEMP:
ANODE: NiCr
CATHODE: Nozzle
POWER: 60 V
DISCUSSION:

Ni:Cr, specimens used in a study of work hardening and dislocations in fcc single crystals. Solution used with a jet nozzle to slice wafers prior to chemical etch thinning down to foil thickness for microscope study.
REF: Mader, S et al — *J Appl Phys*, 34,3376(1963)

NICR-0007b
ETCH NAME: Hydrochloric acid
TYPE: Electrolytic, thinning
COMPOSITION:
50 .... HCl
50 .... EOH
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Ni:Cr specimens 2.6 mm diameter discs electrolytically thinned with this solution using a nozzle held 0.4 mm away from the surface as a method of jet thinning. The thinned specimens were used in a microscope study of structure and defects in single crystal material.
REF: Ibid.

NICKEL ALUMINUM ETCHANTS

NIAL-0001
ETCH NAME:
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:

NiAl, single crystal and polycrystalline spheres splatter formed from an arc melted in

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an He atmosphere with chips and flakes in a water cooled copper pot. Spheres used in an etching and structure study. Other metal spheres formed were Be, V, Fe, Zr, and NiCu.
REF: Ray, A E & Smith, F J — *Acta Metall,* 11,310(1958)

NIAL-0002
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 10% $HClO_4$
x .... HAc
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

NiAl, single crystal specimens. Material used in a deformation study. Solution used to both electropolish and then thin specimens for electron microscope observation of defects.
REF: Ball, A & Smallman, R E — *Acta Metall,* 14,1349(1966)

NIAL-0003
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 10% $HClO_4$
x .... EOH
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE:
POWER:

NiAl, specimens and alloys. Specimens studied for structure change associated with aging. Solution used to both polish and etch thin material. Final thinning done at higher power with vigorous solution stirring. An electron microscope was used to observe defects.
REF: Ardell, A J & Nicholson, R B — *Acta Metall,* 14,1295(1966)

NICKEL BORIDE ETCHANTS

NIB-0001
ETCH NAME: Boron
TYPE: Metal, forming
COMPOSITION:
x .... B
DISCUSSION:
TIME: 4 h
TEMP: 800°C

Ni_2B, thin film grown as a surface penetration film on 12 mm thick nickel plates used as substrates. After boridizing, substrates were annealed in 100°C increments from 400 to 800°C for 24 h. Annealed at 800°C, 4 h produce single crystal Ni_2B. Metallographic sections were made and studied for material structure. (*Note:* No etch shown. See Nichrome for possible etchants.)
REF: Skibo, M & Greulich, F A — *Thin Solid Films,* 113,225(1984)

NIB-0002
ETCH NAME: Acetone
TYPE: Ketone, cleaning
COMPOSITION:
x .... CH_3COOH_3
DISCUSSION:
TIME:
TEMP:

NiB, thin films grown on nickel blank surfaces in a study of boridings metal surfaces under 670°C. All metals evaluated were processed: (1) mechanically polish with emery cloth; (2) degrease in acetone; (3) soak in a molten flux borate bath at 670°C; (4) heat in air 2 h

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at 670°C. The borates evaluated as bath constituents were first ground to 325 mesh size before being placed in a crucible, and were KBF_4, KF_4:KF, $NaBF_4$ and $NaBF_4$:KBF_4.
REF: Koyama, K et al — *J Electrochem Soc,* 126,147(1978)

NICKEL COBALT ETCHANTS

NICO-0001
ETCH NAME:
TYPE: Electrolytic, thinning
COMPOSITION:
20 .... $HClO_4$
80 .... CH_3COOH (HAc)
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Ni:Co(15%), specimens used in a study of stacking fault energy and their temperature and concentration dependence in this metal alloy system. Solution used to etch remove and thin specimens.
REF: Ericsson, T — *Acta Metall,* 14,853(1966)

NICKEL:COPPER ETCHANTS

NICU-0001
ETCH NAME: Ferric chloride
TYPE: Acid, preferential
COMPOSITION:
x .... $FeCl_3$, sat. sol.
x .... H_2O
TIME:
TEMP: Boiling
DISCUSSION:
NiCu (5%) to NiCu (80%) single crystal wafers used in developing light figure orientation (LFO) etchants. Solution will develop etch pits on (111) and (100) orientations with vicinal (hk0) facets — (410) on 20% Ni:80% Cu crystals and (210) on 95% Ni:5% Cu crystals.
REF: Yamamoto, M & Watanabe, J — *Met Abstr,* 8,94(1958)

NICU-0002
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:
NiCu(30%), single crystal and polycrystalline spheres fabricated by splatter from an arc melter in a helium atmosphere using chips and flakes of material in a water cool pot. Other metal spheres formed were Be, V, Fe, Zr and NiAl. Diameters ranged from 0.1 to 1.0 mm with 5 to 50% single crystal. Spheres used for etching and electrical studies. (*Note:* This is a monel metal.)
REF: Ray, A E & Smith, J F — *Acta Metall,* 11,310(1958)

NICU-0003a
ETCH NAME: Fluorine
TYPE: Gas, removal
COMPOSITION:
x .... F_2, gas
TIME: 30 days
TEMP: 900—975°C
RATE: 2.5—5.0 mils/month
DISCUSSION:
NiCu(30%), polycrystalline blanks used in an etching study. This is a monel metal, as

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67Ni:30Cu. Evaluated for corrosion resistance against fluorine at elevated temperature. Other monel formulations are

"K" monel 66Ni:29Cu:3Al
"H" monel 63Ni:30Cu:3Si
"S" monel 63Ni:30Cu:4Si
Cast monel 63Ni:30Cu:1.5Si

REF:

NICU-0003b
ETCH NAME: Chlorine
TYPE: Gas, removal
COMPOSITION:
x .... Cl_2, gas
DISCUSSION:
NiCu(30%), polycrystalline blanks used in an etch study. Both dry chlorine gas and hydrochloric acid were evaluated; dry HCl temperature was 450—500°C. See NICU-0003a.
REF: Ibid.

TIME: 30 days
TEMP: 750—850°C
RATE: 2.5—5.0 mils/month

NICKEL IRON OXIDE ETCHANTS

ETCH NAME: Nital
TYPE: Acid, polish/preferential
COMPOSITION:
1 .... HNO_3
99 .... EOH
DISCUSSION:
Fe:Ni(5%):O(15%) specimens. Solution used as both a polish and preferential etch in the study of austenite and martensite structure development.
REF: Motte, H — *Acta Metall*, 5,614(1957)
NIFE-0002: Pamphlet ASTM E407-70
ASTM #74 solution is 1-5HNO_3:100 mlEOH/MeOH
NIFE-0003: Walker, P — mineralogy study, 1953
$NiFe_3$, as the natural mineral josephinite, and meteoric $FeNi_2$ iron samples used in a study of comparative structures. A 5HNO_3:100 ml EOH solution used 1—2 min, RT, to develop surface figures.

TIME:
TEMP:
ASTM #74

NIFE-0004
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
1 .... HNO_3
3 .... H_2O
DISCUSSION:
Fe:Ni, thin film evaporations. Solution used to remove residual metals after evaporation from glass bell jars and internal fixtures of vacuum systems. Use solution on SST, but not on ceramics or glass.
REF: Nichols, D R — *Solid State Technol*, December 1979

TIME:
TEMP:

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NICKEL MANGANESE ETCHANTS

NIMN-0001
ETCH NAME:
TYPE: Electrolytic, dislocation
COMPOSITION:
x .... H_3PO_4, conc.

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:

NiMn, single crystal specimens used in a study of low angle grain boundaries and defects. Solution shown used to develop defect structure.
REF: Taoka, T & Sakata, S — *Acta Metall,* 5,230(1957)
NIMN-0002: Marcinkowski, M J & Miller, D S — *Phil Mag,* 6,871(1961)

Ni_3Mn, single crystal specimens used in a study of ordering strength and dislocations in superlattice materials. Solution used to etch polish material. Also studied Cu_3Au.

NICKEL TITANIUM ETCHANTS

NITI-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3

TIME:
TEMP:

DISCUSSION:

NiTi, single crystal specimens used in a study search for electronic phase transitions in this material. Solution is called a heavy etch. Follow etching with DI H_2O quench, MeOH rinse, and dry. Also etched Zr_2Ni.
REF: Lee, H N & Withers, R — *J Appl Phys,* 49,5488(1978)
NITI-0002: Dumez, P — *J Vac Sci Technol,* B(1),218(1983)

NiTi, grown as a metastable single crystal alloy in study of the material morphology. Other materials studied as metal alloys: AlTi and ZrV. As metallic glasses: PdNiP, PtNiP, and PtCuP.

NICKEL ZIRCONIUM ETCHANTS

NIZR-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3

TIME:
TEMP:

DISCUSSION:

Zr_2Ni, single crystals grown in a study of electronic phase transitions. Solutions of HF:HNO_3 are general etch mixtures for this material. Also studied: Ni:Ti and PtSi.
REF: Lee, R N & Withers, R — *J Appl Phys,* 49,5488(1978)
NIZR-0002: Altounian, Z et al — *J Appl Phys,* 55,1430(1978)

$NiZr_2$, deposited as an amorphous thin film in a general study of the compound.

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PERMALLOY ETCHANTS

PMA-0001a
ETCH NAME: Aqua regia
TYPE: Acid, polish
COMPOSITION:
3 .... HCl
1 .... HNO_3
TIME:
TEMP:
DISCUSSION:
79Ni:17Fe:4Mo, Permalloy single crystal specimens used in a study of strain under compression. The material shows slip on (111) surfaces in a ⟨110⟩ direction. Follow aqua regia by electropolishing.
REF: Chin, G Y et al — *Acta Metall,* 14,467(1966)

PMA-0001b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_3PO_4
x .... CrO_3
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
79Ni:17Fe:44Mo, (111) oriented Permalloy wafers. See PMA-0001a for discussion.
REF: Ibid.

PMA-0002
ETCH NAME: Bromine
TYPE: Halogen, defects
COMPOSITION:
x .... Br_2
TIME:
TEMP:
DISCUSSION:
68Ni:31.9Fe:0.1Mg and 63Ni:35Fe:2Mo. The Mg containing Permalloy showed dark grey/black and grey areas after etching in bromine. The Mo containing Permalloy showed bright areas only. Grey/black = heavy faulting; grey = light faulting and bright = no faulting. The greater the amount of oxygen present in the materials, the greater the degree of faulting. Both specimens were single crystal with (100) oriented surfaces.
REF: Nesbitt, E A et al — *J Appl Phys,* 31,228S(1960)

PHYSICAL PROPERTIES OF NICKEL IODIDE, NiI_2

Classification	Iodide
Atomic number	53
Atomic weight	312.53
Boiling point (°C)	>100
Melting point (°C)	
Density (g/cm^3)	5.84
Hardness (Mohs — scratch)	3—4
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Black
Cleavage (cubic)	(001)

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NICKEL IODIDE, NiI_2

General: Does not occur as a natural mineral due to water solubility although it may occur in solution in minor quantity. There are several nickel minerals as arsenides and sulfides. There is no use of the iodide in the metal industry.

Technical Application: Not used in Solid State processing, but could be used as an iodine additive to etching solutions. It has been grown as a single crystal in crystallographic and morphology studies.

Etching: Alcohol.

NICKEL IODIDE ETCHANTS

NII-0001
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, removal
COMPOSITION:
x .... EOH
TIME:
TEMP: RT
DISCUSSION:

NiI grown as a single crystal in a crystallographic study. It is in the cubic space group 43m. The material can be dissolved in alcohols. Reference refers to the material as Boracite? (*Note:* The natural mineral boracite is a borate, not an iodide: $Mg_5Cl_2B_{14}O_{25}$.)
REF: Cook, R et al — *J Appl Phys*, 49,6025(1978)

RARE EARTH NICKELIDE ETCHANTS

RENI-0001
ETCH NAME: Aqua regia, variety
TYPE: Acid, removal
COMPOSITION:
4 .... HCl
1 .... HNO_3
TIME:
TEMP: RT to hot
DISCUSSION:

$RENi_2$. Rare Earth nickelides initially formed as alloy mixtures by arc melting under argon gas, then re-melted as buttons in a thermal expansion study. Wrap specimens in Ta sheet and anneal 3—9 weeks at 600—900°C at 2×10^{-7} Torr vacuum, $SmNi_2$ in a sealed quartz ampoule due to Sm evaporation. All were cubic (Laves) structure. RE = Y, La, Nd, Sm, Tb, Dy, Ho, Er, Th, Pr, Ce, and Gd. The Y, La, Nd, and Sm nickelides showed secondary phases as RENi, $RENi_2$, $RENi_3$ similar to silicides. (*Note:* Etchant shown is for nickel.)
REF: Ibarra, M R et al — *J Phys Chem Solids*, 45,789(1984)

PHYSICAL PROPERTIES OF NICKEL OXIDE, NiO

Classification	Oxide
Atomic numbers	28 & 16
Atomic weight	74.69
Melting point (°C)	2980
Boiling point (°C)	
Density (g/cm³)	6.4—5.8
Refractive index (n =)	2.18/2.23
Hardness (Mohs — scratch)	5.5

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Crystal structure (isometric — normal)	(111) octahedron
Color (solid)	Dark green
Cleavage (cubic — poor)	(001)

NICKEL OXIDE, NiO

General: Occurs in nature as the mineral bunsenite, NiO. Rare and of no importance as a mineral. Two of the more important ore minerals of nickel are millerite, NiS and niccolite, NiAs.

Nickel oxide has no use in industry other than its normal surface passivation of nickel surfaces as a native oxide.

Technical Application: Nickel oxide is not used in Solid State device fabrication, although nickel is an evaporation and plating metal on structures, substrates and parts as well as used in solid form in package assemblies. In all of these cases, where nickel oxide is present, it is referred to as a native oxide, and considered a contaminant in device fabrication.

There has been some limited study of nickel oxide as, in Solid State studies, it shows p-type conduction as intrinsic semiconductor material.

Etching: Soluble in acids and ammonium hydroxide.

NICKEL OXIDE ETCHANTS

NIO-0001a
ETCH NAME: Ammonium hydroxide
TYPE: Base, removal
COMPOSITION:
x .... NH_4OH
TIME: Seconds
TEMP: RT
DISCUSSION:

NiO specimens. Solution used to remove nickel oxide from nickel surfaces. The solution does not etch pure nickel metal.

REF: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices*, Reinhold, New York, 1967

NIO-0002: Walker, P & Menth, M — personal application, 1982

NiO, native oxide on nickel slugs used for evaporation. Solution used to clean nickel surfaces prior to use. After etching, quench in DI water, then rinse in MeOH and N_2 blow dry.

NIO-0001b
ETCH NAME: Argon
TYPE: Ionized gas, thinning
COMPOSITION:
x .... Ar^+ ion
TIME: 10—15 min
TEMP:
GAS FLOW:
PRESSURE:
POWER: 7—8 KVA then
3—5 KVA
DISCUSSION:

NiO, as intrinsic p-type single crystal specimens. Prepare by lapping with SiC abrasive, then polish with diamond paste. Use Ar^+ ions to RF sputter thin material under vacuum. Use high power for heavy removal, then reduce to lower power for final thinning.

REF: Ibid.

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NIO-0002
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat
TIME:
TEMP: 1000 K
DISCUSSION:
NiO, (100) cleaved wafers used in a study of magnetic susceptibility. After cleaving, specimens were annealed to reduce strain. Also studied CoO.
REF: Singer, J R — *Phys Rev*, 104,929(1956)
NIO-0003: Roth, W L — *J Appl Phys*, 31,2000(1960)
NiO, (100) cleaved wafers used in neutron and optical studies of domains. Epoxy resin used for holding specimens was dissolved in $1H_2SO_4$:$1HNO_3$. Glycol phthalate also used and dissolved off with heat.

NIO-0004
ETCH NAME: Nitric acid
TYPE: Acid, removal (nickel)
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP: Hot
DISCUSSION:
NiO, thin film platelets grown on nickel substrates for thermal oxidation. Nickel inclusions observed in the oxide were removed by etching in hot nitric acid.
REF: Downs, R C — *J Electrochem Soc*, 130,807(1983)

PHYSICAL PROPERTIES OF NICKEL SULFIDE, NiS

Classification	Sulfide
Atomic numbers	28 & 16
Atomic weight	90.75
Boiling point (°C)	797
Melting point (°C)	
Density (g/cm^3)	5.3—5.65
Hardness (Mohs — scratch)	3—3.5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Bronze-yellow
Cleavage (rhombic)	$(10\bar{1}1)$ or $(01\bar{1}2)$

NICKEL SULFIDE, NiS

General: Occurs as the natural mineral millerite, NiS (capillary pyrite). Occurs in slender capillary crystals, hence the common name, often in delicate radiating groups; sometimes interwoven like a wad of hair. It is often coated with a grayish translucent coating. The $(01\bar{1}2)$ is a glide plane, such that by exerting pressure in crystals artificial twins can be formed. It is associated with bodies of other nickel ores, has been grown artificially, and has been noted in meteoric iron.

There also is the mineral polidymite, Ni_3S_4, which is probably isomorphous with linnaeite, Co_3N_4, but is isometric — normal, and occurs as fine octahedron, (111), crystals. It also, like millerite, is prone to twinning, in this case, on a (111) glide plane forming bicrystals, but is of minor occurrence.

Millerite is an ore of nickel, and can be used directly as an additive to iron and steels that are being sulfurized.

Technical Application: There has been no use in Solid State processing, but both the

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natural and artificial materials have been studied due to interest in crystallographic and atomic cell structure.

Etching: HNO_3; aqua regia; slow in other acids.

NICKEL SULFIDE ETCHANTS

NIS-0001
ETCH NAME: Aqua regia
TYPE: Acid, cleaning/removal
TIME: 10—30 sec
TEMP: RT
COMPOSITION:
1 .... HF
3—5 .... HNO_3
10—50 .... H_2O
DISCUSSION:

NiS, as the natural mineral millerite. Various concentrations of solution shown used to clean surfaces (dilute), and develop single specimens crystallographic structure, defects, and twinning in a general study of this mineral, to include magnetism as related to nickel, cobalt, and magnetic iron.
REF: Walker, P — mineralogy study, 1952—1954

PHYSICAL PROPERTIES OF NITROGEN, N_2

Classification	Gas
Atomic number	7
Atomic weight	14.0067
Melting point (°C)	−209.86
Boiling point (°C)	−195.8
Density ($g/cm^3 \times 10^{-3}$) 20°C	1.43
(g/cm^3 vs. air = 1)	0.96717
Specific heat (cal/g/°C) 20°C	0.247
Thermal conductance ($cal/cm^2/cm/°C/sec \times 10^{-4}$) 20°C	0.562
1st ionization potential (eV)	14.54
Ionic radius (angstroms)	0.13 (N^{+5})
Cross section (barns)	1.9
Vapor pressure (°C)	−209.7
Critical temperature (C.T.) (°C)	−147
Critical pressure (C.P.) (atms)	33.5
Chemical reactivity (22.2°C & 760 mmHg)	Inert
Hardness (Mohs — scratch) solid	1—2
Crystal structure (hexagonal — normal) solid	$(10\bar{1}0)$ prism, hcp
Color (gas/liquid)	Colorless
(solid)	Whitish
Cleavage (basal — fair) solid	(0001)

NITROGEN, N_2

General: The primary inert gas in the atmosphere as a mixture of about 75% N_2:24% O_2, plus trace gases. It is inert at standard temperature and pressure, but forms many, many nitrite and nitrate minerals in nature, many of which are primary fertilizers. Many such compounds are unstable, readily give up nitrogen to the atmosphere, while others such as ammonia (NH_3) are water soluble. Although nitrogen is not assimilated directly by plant

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and animal life, it is a major building block in living matter as proteins which contain amines with the NH_3^- radical.

The nitrogen fixation cycle is the natural supplying of free nitrogen to the earth from atmospheric rain, dissolving chemical and minerals in water, and from electrical discharge during thunder and lightning storms.

In addition to nitrates use as fertilizers, there are several important industrial compounds, such as in guncotton and trinitrotoluene (TNT). And there is nitric acid, ammonia, and ammonium hydroxide; Chile saltpeter is both an important fertilizer, as well as having medical applications. Other nitrite and nitrate compounds are used as leather and textile dyes.

The French still call it azote (Lavoisier), but the name nitrogen was proposed by Chaptal (1823) from the Greek name for saltpeter, as it is a major element in that compound.

Most of the pure nitrogen today is obtained from the liquifaction of air, as the oxygen boils off, first, at $-183°C$ leaving nitrogen at $-196°C$. Note that further chilling of the nitrogen is done to obtain atmospheric rare gases, such as neon, krypton, etc., as well as a larger quantity of argon. Obtained as cold, liquified gases, this is the field of cryogenics, and both liquid nitrogen and argon — also oxygen, hydrogen and helium — are supplied to industry and medicine in such liquid form. It is used as both a chilling liquid or passed through heat exchangers and converted back to gas by warming and expansion. Other major sources of industrial nitrogen comes as a by-product of making coke (burning of coal to remove volatiles), and from the processing of Chilean saltpeter (soda niter) and niter (potassium niter).

Metal, glass, and ceramic processing all use nitrogen as an inert furnace gas, alone, or as forming gas (FG) $85\%N_2{:}15\%H_2$. The latter as a reducing atmosphere for de-oxidizing surfaces during alloying, or removing scale contamination. At elevated temperatures the nitridization process introduces a nitride surface layer on metal and metallic compounds for corrosion resistance, strength, and a more inert surface under most atmospheric conditions.

There are several important nitrogen compounds, other than those used in explosives and fertilizers, such as ammonia and ammonium hydroxide. As chemical bases they are used to neutralize acid wastes and, in crystalline form, ammonia is medical "smelling salts". Nitric acid is a strong acid, widely used as the oxidizer element in etch solutions, and nitrous oxide, N_2O, is "laughing gas" used as an anesthetic. In deep-sea diving, using air, when a diver is brought to the surface too rapidly, nitrogen will form bubbles in the bloodstream causing the "bends" which causes severe muscle cramps and spasms. Helium, which does not form such bubbles, is used as a replacement for nitrogen in diving tanks as the breathing atmosphere, but causes the larynx muscles to contract which produces the "Donald Duck" speech. Several commercial plastics contain nitrate, such as cellulose nitrate, a thermoplastic, as celluloid.

Metal nitrides are becoming of increasing importance and use, other than for surface nitridization. A major example is (cubic) boron nitride, B_4N, with a Mohs hardness: $H = 9+$. This is a lapping and polishing abrasive, and has recently been fabricated as a high temperature semiconducting diode. Silicon nitride, Si_3N_4, and aluminum nitride, AlN, are used as surface protectants, etching masks, radiation masks on semiconductors as well as other metal surfaces.

Technical Application: Many Solid State plants have an on-site liquid nitrogen, LN_2, storage tank — 500 to 2000 gallon capacity — with a heat exchanger to convert LN_2 back to N_2 gas. Both the liquid and gas can be brought into the plant with copper lines to user locations, or gas lines, only, directly into furnaces, epitaxy systems, vacuum systems, with LN_2 mobile cylinder fill capability at the outside LN_2 storage tank. Such LN_2 cylinders range from a small cone-shaped size holding 25—50 liquid liters, to 200 l barrel-sized containers on wheels. The storage tank is topped-off (filled) every 2 to 4 days from 2000 gallon cryogenic truck trailers. Note that other cryogenic gases are similarly supplied like LN_2,

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such as LOX, LHe, LCl_2, and LH_2. The latter is normally used directly from the 2000 gallon cryogenic trailer, not transferred into an on-site storage tank.

Nitrogen, as an inert gas, is the usual back-fill gas in vacuum systems being brought "up-to-air", rather than air itself in order to reduce oxidation of metallized parts and the evaporation metal source. Such back-fill is about 40 psi; whereas when nitrogen, again, rather than air, is used for valve operation in vacuum systems, pressure is 80 psi. As LN_2 is already used in the vacuum cold trap for chamber pump-down, such that nitrogen is available, it is more cost efficient to use the gas for chamber back-fill and valve operation, than have to pipe in separate pressurized air lines from air compressors. The nitrogen gas also is usually cleaner than compressed air, and there is no possibility of line oil contamination with nitrogen, as there is from an air compressor. Nitrogen is checked with a Dew Point Meter for water moisture, and a figure of 0.72°F (14.3 ppm) is considered optimum for line nitrogen coming off an LN_2 source. Other processing equipment using nitrogen, both as an inert gas, as well as for valve operation include wire bonders, wafer saws, wafer dicing saws or ultrasonic dicers, resistance welding, or coldwelding systems. The wafer sawing systems also used for cutting ceramic or glass circuit substrates or ferrites as discrete resistors, other dielectrics as both resistors and capacitors. Helium leak detectors sometimes use a nitrogen gas or an air equivalent for general testing of parts or package seals.

As a gas nitrogen it is used as the inert atmosphere in semiconductor diffusion furnaces, alloy belt furnaces, in nitrogen dry boxes for alloying assemblies or for storage of critical parts, such as circuit substrates, and as pressurized line nitrogen blow-off in chemical areas for final drying after etching. It also is bubbled through an etching or cleaning solution to obtain a stirring action and, as an ionized gas, N^+ ions, used in RF plasma cleaning systems. As a pure N_2, N_2/Ar, or N_2/O_2 atmosphere at elevated temperatures, it is used to grow thin film nitrides, notably silicon nitride, Si_3N_4, or oxynitride, SiN_xO_y (5% O_2 is a general standard), and AlN. Most nitrides are used as an improved, inert replacement for silicon dioxide, SiO_2, as etching, diffusion or metallization masks, or for final surface passivation.

Nitrogen gas is available in pressurized cylinders from a standard commercial grade to electronic grade dry nitrogen, in addition to gas mixtures. Mixtures are used as diffusion gases, and the high purity N_2/He(30%) is used as a package back-fill in sealing quartz radio frequency crystals. A standard A-1 cylinder is 9" in diameter, about 5 ft high with a shut-off top valve, and gas supply controlled through a dual gas regulator — one meter showing tank pressure — the down-line meter dial controlled for gas output. The A-1 cylinder is normally supplied under 3600 psi pressure, and is the largest that can be commercially transported under pressure. Larger cylinders with higher pressures are filled on-site.

LN_2 also is used as a freezing agent: single crystal materials, such as semiconductors, are cleaved under liquid nitrogen or, frozen, removed, and then cleaved while still frozen. Common cleave planes are cubic (001); basal (001) or (0001), though they can be dodecahedral (110), octahedral (111), prismatic ($10\bar{1}0$) or rhombic ($10\bar{1}1$), and others in special cases. LN_2 is used in high reliability testing by cycling parts from hot-to-cold in evaluating device and package integrity. Another use is the cryogenic microscope stage; yet another, the cryogenic cryostat used for both device tests and evaluations, and the growth of single crystal ice.

CAUTION: Liquid nitrogen at −196°C will freeze any material submerged in the cold liquid in a matter of seconds — a rose frozen in LN_2 can be removed and shattered like glass.

Even though the atmosphere is about 75% nitrogen, the presence of oxygen is essential to sustain life. In a working area where nitrogen is being used, such as in wafer dicing equipment, the area should be well ventilated as, with an increase in nitrogen content in the atmosphere, the operator will become sleepy . . . at the least. In cleaning LN_2 storage and

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transfer tanks, such tanks should be checked for oxygen content before entering for tank cleaning or air tanks should be worn by operators.

Etching: N/A as gas.

NITROGEN ETCHANTS

N-0001
ETCH NAME: Pressure
TYPE: Pressure, defect
COMPOSITION:
x .... pressure, vapor
TIME:
TEMP: −210°C
DISCUSSION:

N_2, grown as a single crystal under vacuum pressure and cryogenic conditions. LHe used as the freezing vehicle, and single crystal gases so grown have been used in a general study of solid gases. By varying the vapor pressure in the vacuum system, structural defects can be observed.

REF: Schwentner, N et al — *Rare Gas Solids*, Vol. 3, Academic Press, New York, 1970

PHYSICAL PROPERTIES OF NIOBIUM, Nb

Classification	Transition metal
Atomic number	41
Atomic weight	92.906
Melting point (°C)	2468
Boiling point (°C)	4927
Density (g/cm^3)	8.57
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.125
Specific heat (cal/g) 25°C	0.065
Heat of fusion (k-cal/g-atom)	6.4
Latent heat of fusion (cal/g)	69
Atomic volume (W/D)	10.8
1st ionization energy (K-cal/g-mole)	156
1st ionization potential (eV)	6.77
Electronegativity (Pauling's)	1.6
Covalent radius (angstroms)	1.34
Ionic radius (angstroms)	0.69 (Nb^{+5})
Coefficient of linear expansion ($\times 10^{-6}$ cm/cm/°C)	7.1
Electrical resistivity (micro-ohms/cm)	15.22
Electron work function (eV)	4.01
Tensile strength (psi-annealed)	50,000
Cross section (barns)	1.1
Refractive index (n =)	1.80
Hardness (Mohs — scratch)	7—8
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Steel-grey metal
Cleavage (cubic)	(001)

NIOBIUM, Nb

General: The names niobium, Nb and columbium, Cb are synonymous, though today, most references use niobium — and there is a crystallographic discrepancy — originally, columbium was listed as being hexagonal system — rhombohedral division; yet niobium is

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isometric — normal with a bcc (body-centered cubic) crystal structure. Regardless, niobium does not occur in nature as a native element though there are some 20 or more minerals containing niobium in association with rare earths (yttrium, erbium, cerium, etc.) as well as tantalum, iron, and calcium. Most niobium bearing minerals are oxides. The minerals pyrochlore, fergusonite, columbite-tantalite, yttrotantalite, and samarskite being the more prominent.

In the making of iron and steel, niobium is of major importance as it combines with carbon increasing the corrosion resistance. See section titled Columbium which is included separately where work done is referred to that name rather than niobium.

Technical Application: Although not used in most Solid State device fabrication or assembly processes, there is one important device known as the Josephson Junction device, as single crystal Nb_3Sn. It also is used as a high temperature anode in electrolytic etching with or without titanium and tantalum coatings.

The pure metal has been grown as a single crystal and, although it has been widely studied and etched, it is difficult to both etch and cut.

Etching: H_2SO_4, HCl, HNO_3 and mixed acids: HF:HNO_3 with H_2O_2 and H_2SO_4.

NIOBIUM ETCHANTS

NB-0001
ETCH NAME: Air — TIME:
TYPE: Gas, oxidation — TEMP:
COMPOSITION:
x .... air
DISCUSSION:
Nb, thin films evaporated on glass in H_2 to form a-Nb:H. Oxidize in hot air at 80°C, 10 min to form Nb_2O_5. Selectively evaporate Pb for Josephson Junctions: Pb/Nb_2O_5/Nb/SiO_2 as an SIS device (superconductor-insulator-substrate).
REF: Kobyashni, T et al — *J Appl Phys*, 57,2583(1985)

NB-0002
ETCH NAME: — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
1 .... HF
4 .... HNO_3
DISCUSSION:
Nb, specimens used in a study of spark-cut damage. Mechanically lap and polish, then etch polish with solution shown. After spark-cutting decorate damage with carbon, as c-C in isopropyl alcohol.
REF: Guberman, H D — *J Appl Phys*, 39,2974(1968)

N8-0003
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2SO_4
x .... HF
x .... H_2O_2
x .... H_2O

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DISCUSSION:
Nb specimens. Solution used as a general etch for niobium.
REF: Bergund, T & Deardon, W H — *Metallographer's Handbook of Etching*, Pitman & Sons, London, 1931

NB-0004a
ETCH NAME: Hydrochloric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
x .... H_2O
TIME:
TEMP: 70°F and 120°F
RATE: 0.00004/ipy
DISCUSSION:
Nb, specimens. Effectively no acid attack but can be used to clean surfaces.
REF:

NB-0004b
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
TIME:
TEMP: 70°F and 120°F
RATE: 0.0001/ipy 0.004/ipy
DISCUSSION:
Nb, specimens. Effectively no acid attack but can be used to clean surfaces.
REF: Ibid.

NB-0005a
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: Hot
DISCUSSION:
Nb specimens. A slow, general etch for niobium.
REF: Hodgman, C D et al — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 616
NB-0012a: Kohl, W H — *Handbook of Materials and Techniques for Vacuum Devices*, Reinhold, New York, 1967, 304
Nb specimens. Solution used at RT will convert surface to Nb(OH) which can be removed with HF, as can be Nb.

NB-0005b
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF
TIME:
TEMP:
DISCUSSION:
Nb specimens. A slow, general etch for niobium.
REF: Ibid.

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NB-0006
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 10% HF
x .... 90% H_2SO_4
TIME: 1 h
TEMP: 25°C
ANODE: Nb
CATHODE:
POWER:
DISCUSSION:
Nb specimens. Mechanically polish surfaces before electropolishing in the solution shown. A study of tantalum diffusion in niobium.
REF: Lawel, R E & Lundy, T S — *J Appl Phys*, 35,435(1964)
NB-0010b: Cathcart, J V et al — *J Electrochem Soc*, 105,442(1958)
Nb, single crystal sphere with (111), (110), and (100) cut flats and single crystal wafers. Wafers and flats mechanically lapped down to 3 μm alumina finish. Solution used to electropolish prior to oxidation studies.

NB-0012b
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3
TIME:
TEMP: 100°C
DISCUSSION:
Nb specimens. Will etch niobium at or above 100°C. Other general etchants are HF:NH_4F; NaOH/KOH, conc.; HF:HNO_3 mixtures; H_3PO_4. Niobium can be electropolished in tantalum solutions. See TA-0003i.
REF: Ibid.

NB-0007
ETCH NAME: Hydrofluoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... HF
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Nb specimens used for electroplating. Use solution shown to AC polish specimens prior to plating. (*Note:* A major article on the electroplating of transition metals. Both etch and plate solutions shown.)
REF: Saubestre, E B — *J Electrochem Soc*, 106,305(1959)
NB-0008: Faust, G L & Beach, J G — *Plating*, 43,1134(1950)
Reference for solution used above in NB-0007
NB-0014: Beach, J G & Faust, C L — MBI 10004(1954 (Commerce Dept., WDC)
Nb specimens. Solution used to AC etch this material.

NB-0009
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
95% .... HNO_3
5% .... H_2O
TIME:
TEMP:
DISCUSSION:
Nb, polycrystalline samples used in a study of yield and fracture. Polish in solution shown and follow with 5% HF.
REF: Adams, M A et al — *Acta Metall*, 8,25(1960)

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NB-0010a
ETCH NAME: Oxygen
TYPE: Gas, oxidation
COMPOSITION:
x .... O_2
DISCUSSION:
Nb, spheres with cut and oriented faces on (111), (110), and (100). The (111) and (100) surfaces oxidize rapidly; the (110) slowly. Cracking was observed which varies in amount with orientation.
REF: Cathcart, J V et al — *J Electrochem Soc,* 105,442(1958)

TIME:
TEMP:

NB-0011
ETCH NAME:
TYPE: Electrolytic, oxidation
COMPOSITION:
65% .... 0.1 *N* H_2SO_4
35% .... EOH
DISCUSSION:
Nb, specimens used in a study of the temperature dependence of the Tafel Slope in thin anodic oxides. Solution used to develop the oxides. Stir continually and replace solution every 8 h.
REF: Adams, G D & Kao, T — *J Electrochem Soc,* 107,640(1960)

TIME:
TEMP: −10 to −70°C
ANODE:
CATHODE:
POWER: 1—100 mA/cm²

NB-0013
ETCH NAME: Kerosene
TYPE: Hydrocarbon, cleaning
COMPOSITION:
x .... C_{10}-C_{16}
DISCUSSION:
Nb, specimens used in a study of surface oxidation between 375 and 700°C. Surfaces cleaned by light abrasion under kerosene.
REF: Gulbransen, E A & Andrews, K F — *J Electrochem Soc,* 1054(1956)

TIME:
TEMP:

NB-0015a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... H_2SO_4
1 .... H_2O
DISCUSSION:
Nb, (100) oriented single crystal rods used in a study of properties and superconduction. Solution used to etch polish specimens.
REF: Ikushima, A et al — *J Phys Chem Solids,* 27,327(1966)

TIME:
TEMP:

NB-0015b
ETCH NAME: Heat
TYPE: Thermal, preferential
COMPOSITION:
x .... heat

TIME:
TEMP: 1800°C

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DISCUSSION:

Nb, (100) oriented single crystal cylinders. When cylinders were annealed at or above 1800°C thermal etching was observed.

REF: Ibid.

NIOBIUM ALLOYS, NbMx

General: Niobium occurs in nature in the mineral columbite-tantalite, $(Fe,Mn)(Nb,Ta)_2O_6$, and similar minerals containing rare earth elements, and as niobates and titanates with uranium or thorium. Does not occur as a metallic alloy in nature, but there are high temperature artificial alloys. It is an additive to irons and steels for strength and corrosion resistance, and alloyed with both titanium and tantalum for high temperature characteristics.

Technical Application: Niobium alloys are not used in Solid State processing to any extent although they are used as electrodes and antennas. The only reference, here, is for the niobium-aluminum system.

Etching: HF, H_2SO_4. Mixed acids HF:HNO_3. Variable with alloy.

NIOBIUM ALLOY ETCHANTS

NIOBIUM ALUMINUM ETCHANTS

NBAL-0001

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Acid, reduction — TEMP:

COMPOSITION:

x .... HF, conc.

DISCUSSION:

$NbAl_y$, as alloy specimens. Solution used to dissolve material before titration of individual constituents in a study of this alloy system.

REF: Shilo, I — *J Electrochem Soc*, 129,1608(1982)

NBAL-0002:

Nb_3Al grown as a single crystal in a study of crystallographic structure. Structure is A15 crystal symmetry space group.

PHYSICAL PROPERTIES OF NIOBIUM CARBIDE, NbC

Classification	Carbide
Atomic numbers	41 & 6
Atomic weight	104.92
Melting point (°C)	2750
Boiling point (°C)	
Density (g/cm³)	15.77
Hardness (Mohs — scratch)	9+
(Vickers — kgb/mm²)	2800
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
(isometric — normal)	(100) cube
Color (solid)	Grey-white
Cleavage (basal/cubic)	(0001)/(001)

NIOBIUM CARBIDE, NbC

General: Does not occur as a natural compound. The only known natural carbide is a

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minor occurrence of the mineral moissanite, SiC. Niobium carbide is one of the high temperature ceramics.

Technical Application: The material is under study in Solid State development, but has not had any major use to date.

Etching: HF, H_2SO_4.

NIOBIUM CARBIDE ETCHANTS

NBC-0001a
ETCH NAME:
TYPE: Acid, removal/clean
COMPOSITION:
x .... HF
DISCUSSION:
NbC specimens. A very slow etch for this material.
REF: *A Dictionary of Carbide Terms*, Adams Carbide Corp., Kenilworth, NJ
TIME:
TEMP:

NBC-0001b
ETCH NAME:
TYPE: Acid, removal/clean
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
NbC, specimens. Solution is a slow etch for the material. Material was used in a general properties study. Density: 15.77 gm/cm^3. Melting point: 2750°C. Vickers hardness: 2800 kg/cmm^2.
REF: Ibid.
TIME:
TEMP: Hot

NBC-0003a-b
ETCH NAME:
TYPE: Acid, removal/cleaning
COMPOSITION:
(1) x .... 20% sulfamic acid or (2) x .... BHF
DISCUSSION:
NbC, thin films grown by electrolytic deposition on different substrates in a study of the compound. Either solution can be used for the times shown for light removal and cleaning of surfaces. (*Note:* BHF mixture not shown. One standard is 1HF:1NH_4F (40%).)
REF: Hockman, A J — *J Electrochem Soc*, 130,221(1983)
TIME: (1) 1 min (2) 4 sec
TEMP: RT RT

NIOBIUM GERMANIDE ETCHANTS

NBGE-0001
ETCH NAME: RIE
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... Ar
DISCUSSION:
Nb_3Ge, single crystal compound co-deposited by E-beam evaporation as an amorphous layer on sapphire. Thickness was 80—100 μm. Material was patterned by standard pho-
TIME:
TEMP:
GAS FLOW: 200 V
PRESSURE: 6 Pa
POWER:

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tolithographic techniques. Deposit was RF plasma etched with CF_4. CF_4 is a rapid etch alone so argon is used as an inert control gas.
REF: Kato, W — *Jpn J Appl Phys*, 23,1536(1984)

NBGE-0002
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
x .... CH_3COOH (HAc)
DISCUSSION:
Nb_3Ge, thin films grown on (100) germanium substrates by CVD in a study of high T_c. Concentrations of the solution shown will etch both the Nb_3Ge thin film and Ge substrate.
REF: Suzuki, M et al — *Jpn J Appl Phys*, 23,991(1984)

NIOBIUM HYDRIDE ETCHANTS

NBH-0001
ETCH NAME: Sulfuric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... H_2SO_4, conc.
DISCUSSION:
NbH, as powder in amyl acetate or cellulose nitrate used as a binder in silicon alloying. Apply to surface and fire for 1—10 min at 600—900°C in an inert atmosphere (N_2 or Ar). Sulfuric acid will etch the hydride. Other hydrides used in this study were TaH, ZrH, VH, and TiH.
REF: Sullivan, M V & Eigler, J H — *Acta Metall*, 103,218(1956)

NBH-0002
ETCH NAME: Hydrogen TIME:
TYPE: Gas, forming TEMP:
COMPOSITION:
x .... H_2
DISCUSSION:
a-Nb:H, as thin films formed by sputter evaporation of Nb on glass substrates in an H_2 atmosphere under pressure. Below 6 Pa the surface is a mirror finish; above, uneven. See NB-0001 and NBO-0002 for conversion to Nb_2O_5 for use as Josephson Junction devices.
REF: Kobnashni, T et al — *J Appl Phys*, 57,2583(1985)

PROPERTIES CF NIOBIUM NITRIDE, NbN

Classification	Nitride
Atomic numbers	41 & 7
Atomic weight	106.92
Melting point (°C)	2050
Boiling point (°C)	
Density (g/cm³)	8.4
Hardness (Mohs — scratch)	5—6

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Crystal structure (isometric — normal)	(100) cube
Color (solid)	Black
Cleavage (cubic — poor)	(001)

NIOBIUM NITRIDE, NbN

General: Does not occur as a natural compound. There are over 20 niobate-tantalate minerals often containing yttrium, cerium, and uranium as well as calcium, iron, manganese, etc. Most of these minerals occur in pegmatite veins where they may be in rather large crystals. The mineral columbite-tantalite, varying in composition from $FeNb_2O_6$ to $FeTa_2O_6$, is a major ore of both tantalum and columbium (niobium).

Niobium metal added to stainless steel reduces corrosion at elevated temperatures and where surfaces are nitrided they show additional wear resistance. Where irons and steels containing niobium are nitrided, some portions of the nitrided layer will be niobium nitride.

Technical Application: Niobium nitride is under evaluation as a thin film deposit for surface coating with possible applications similar to those of other metal nitrides, such as silicon nitride, aluminum nitride as surface coatings.

It has been grown as an oriented (100) thin film for general morphology and defect studies. Niobium stannite, Nb_3Sn and niobium germanate, Nb_3Ge are fabricated as devices for their superconducting capabilities.

Etching: Soluble in mixtures of $HF:HNO_3$.

NIOBIUM NITRIDE ETCHANTS

NBN-0001

ETCH NAME: Neon	TIME:
TYPE: Ionized gas, cleaning	TEMP:
COMPOSITION:	GAS FLOW:
(1) x .... Ne^+ ions	PRESSURE:
(2) x .... Kr	POWER:

DISCUSSION:

NbN, (100), thin films deposited on NaCl, (100) substrates. Niobium was deposited at 90°C in an Ar/N_2 atmosphere. Ionic gases shown can be used to etch the nitride after photo resist patterning.

REF: van Dover, R B — *J Vac Sci Technol*, A(2) 1257(1984)

NBN-0002

ETCH NAME: Oxygen	TIME:
TYPE: Gas, conversion	TEMP:
COMPOSITION:	
x .... O_2	

DISCUSSION:

NbN, thin films deposited on fused silica and sapphire substrates by DC magnetron sputter in a $15\%N_2/Ar$ atmosphere. At 709 K films were amorphous to microcrystalline. At 400°C in air, the nitride converts to Nb_2O_5. NbN_{90} is cubic structure; NbN is hexagonal, and Nb_2O_5 is monoclinic.

REF: Gallagher, P K et al — *J Electrochem Soc*, 130,2045(1983)

PHYSICAL PROPERTIES OF NIOBIUM OXIDE, Nb_2O_5

Classification	Oxide
Atomic numbers	41 & 8

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Atomic weight	265.82
Melting point (°C)	>400
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	6—7
Crystal structure (monoclinic — normal)	(100) a-pinacoid
Color (solid)	Greyish
Cleavage (none)	Conchoidal fracture

NIOBIUM OXIDE, Nb_2O_5

General: Does not occur as a pure oxide compound in nature although it does occur as an iron niobate, $FeNb_2O_6$, as one end fraction of the mineral known as columbite-tantalite, $(Fe,Mn)(Nb,Ta)_2O_6$ which occurs is quantity in pegmatites and is mined as a source of tantalum, as well as niobium.

To date, there has been little use of the oxide in industry, other than as a chemical base compound for deriving other niobium salts.

Technical Application: The material is under evaluation in Solid State development for general characterization with possible applications as a dielectric capacitor or resistor similar to Ta_2O_5.

Etching: H_2SO_4, HCl. Mixed acids HF:HNO_3.

NIOBIUM OXIDE ETCHANTS

NBO-0001
ETCH NAME: Air — TIME: 10 min
TYPE: Gas, forming — TEMP: 80°C
COMPOSITION:
x .... air
DISCUSSION:

Nb_2O_5, as thin film conversion from Nb thin films grown on glass substrates under pressure in an H_2 atmosphere. Below 6 Pa pressure, surface was a mirror finish; above, was uneven. Nb films were anneal in hot air to convert to the oxide, then lead, Pb, was deposited to form Josephson Junctions.

REF: Kobnashni, T et al — *J Appl Phys*, 57,2483(1985)

NBO0002
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP: Hot boiling
COMPOSITION:
(1) x .... H_2SO_4, conc. (2) x .... HCl, conc.
DISCUSSION:

Nb_2O_5, as the natural mineral iron niobate, $FeNb_2O_6$. Both acids will etch the material easily. With addition of metallic zinc with boiling HCl the solution turns a fine blue color. Material used in a general study of niobates.

REF: Walker, P — mineralogy study, 1953

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NIOBIUM SELENIDE ETCHANTS

NBSE-0001
ETCH NAME:
TYPE: Acid, clean
TIME:
TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
10 .... CH_3COOH (HAc)
DISCUSSION:
Nb_3Se. (100) hexagonal platelets grown by Vapor Transport (VT) in an I_2 vapor atmosphere in sealed in quartz ampoules with 950°C at one end, and 1000°C at the other end. Growth time was 3 weeks. Ingots were washed in the solution shown to remove "dust". Solution does not etch external structure of ingot.
REF: Nakada, I & Ishihara, Y — *Jpn J Appl Phys*, 24,31(1983)

NIOBIUM STANNIDE ETCHANTS

NBSN-0001
ETCH NAME: Heat
TYPE: Heat, removal
TIME:
TEMP:
COMPOSITION:
x .... heat
DISCUSSION:
Nb_3Sn, amorphous thin films initially co-deposited by E-beam deposition on sapphire substrates. Anneal at 800°C to form Nb_3Sn. Remove excess tin from surface by heating and evaporation. Material used in forming $Pb/Nb_2O_5/Nb_3S$ as Josephson Junction devices.
REF: Kaster, R N — *J Appl Phys*, 23,2(1964)
NBSN-0002: Tusuge, H et al — *J Appl Phys Lett*, 43,606(1983)
Nb_3Sn single crystal wafers with lead, Pb evaporated to form Josephson Junction devices for use as logic and memory circuits.

NBSN-0003
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP: RT
COMPOSITION:
1 .... HF
1 .... H_2SO_4
1 .... H_2O
x drops .... H_2O_2
DISCUSSION:
Nb_3Sn, as single crystals formed from a high concentration alloy of CuSn in a study of superconductivity of the niobium compound. To prepare Nb_3SN surfaces: (1) mechanical polish with emery cloth, and (2) etch polish with solution shown.
REF: Murase, S et al — *J Appl Phys*, 49,602(1978)

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NIOBIUM TELLURIDE ETCHANTS

NBTE-0001
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
1 .... HF
10 .... H_2O
DISCUSSION:
Nb_3Te_4, grown as single crystal needles by iodine Vapor Transport (VT) in a sealed quartz ampoule at 1000°C. Growth was in the z-axis direction (0001). Specimens used in a study of magnetism and electronic properties. Silver epoxy paste used for electrical contacts. (*Note:* Solution shown can be used to clean material surface prior to epoxy application.)
REF: Ishikawa, K & Tanemuba, M — *Jpn J Appl Phys*, 23,842(1984)

NITRIDES:

General: Metal nitrides do not occur as natural minerals though there are several nitrate compounds containing the NH_4^- radical, and others containing nitrogen in their formulae.

The nitridization process of metal and alloy surfaces has been in use in the metals industries for many years — furnace firing of materials in a hot nitrogen atmosphere between about 800 to 1200°C, depending upon the metal or alloy. The nitrogen forms a thin film layer that increases surface hardness against wear and improves stability against chemical and atmospheric attack and corrosion. The nitrite and nitrate compounds, both natural and artificial, are primary fertilizers with many applications in both chemistry and medicine.

Technical Application: Nitrides as thin film surface coatings in Solid State began development in the early 1960s with the growth of silicon nitride, Si_3N_4, by the Rand Corporation, and silicon oxynitride initially by TRW semiconductors in the mid-1960s (See Silicon Nitride section). TRW also did initial development work on germanium nitride, Ge_3N_4, at the same period and showed it to be isomorphous with Si_3N_4, and also initial work with AlN.

Since that time, many investigators have been involved with development of a wide range of metal nitrides. They are listed in this book following their parent metal, as several have extensive etchants: silicon, titanium, aluminum, and others.

Nitrides are deposited as thin films surface coatings in all structural forms: colloidal, amorphous, crystalline and single crystal by CVD, MOCVD (both from gaseous sources), and RF (magnetron) sputter (solid target). They are used for surface passivation, as chemical etch, diffusion or metallization and epitaxy masks, mostly as amorphous structures like silicon dioxide, SiO_2, and similar oxides. Silicon oxynitride, $Si_3N_xO_y$ (5% O_2, common) is most often used as it is more inert and chemically resistant than the pure oxide, but easier to chemical process than the pure nitride.

Both oxides and nitrides are used as active elements in semiconductor devices, such as MOS and MNOS diodes.

There are over 25 metal nitrides listed with their etchants in this book. Some nitrides are deposited, then converted to the oxide, such as TiN to TiO_2. Others are being applied as layer elements in heterostructure devices, and the TiN with its yellow-gold color is under consideration as a replacement for gold in decorative work. Nitrides appear following their parent metal.

Etching: Varies from extremely difficult to etching with ease, depending upon the metal nitride involved. Both single acids and acid mixtures are used.

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PHYSICAL PROPERTIES OF OSMIUM, Os

Classification	Transition metal
Atomic numbers	76
Atomic weight	190.2
Melting point (°C)	3045 (3050)
Boiling point (°C)	5027 (5000)
Density (g/cm^3)	22.6
Specific heat (cal/g) 0°C	0.031
Heat of fusion (k-cal/g-atom)	6.4
Latent heat of fusion (cal/g)	36.9
Heat of vaporization (k-cal/g-atom)	162
Atomic volume (W/D)	8.43
1st ionization energy (K-cal/g-mole)	201
1st ionization potential (eV)	8.7
Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.26
Ionic radius (angstroms)	0.88 (Os^{+4})
Vapor pressure (microns) m.p.	13.5
Coefficient of linear thermal expansions ($\times 10^{-6}$ cm/cm/°C)	6.1
Electrical resistivity (micro-ohm cm) 20°C	8.12
Young's modulus (psi $\times 10^{-6}$)	81
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.074
Ionization potential (eV)	8.7
Thermal conductivity (cal-cm/sec/cm^2/°C)	0.206
Cross section (barns)	35.3
Electron work function (eV)	4.55
Hardness (Mohs — scratch)	4—5
(Vicker's kg/mm^2 — annealed)	400
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Blue-black metal.
Cleavage (basal)	(0001)

OSMIUM, Os

General: Does not occur as a native element. Usually extracted from the metals of the platinum-iron group which, as native elements, are alloys containing iron, iridium, rhodium, palladium, osmium, and other metals. The mineral iridosmine (osmiridium) is a variable alloy of iridium and osmium with some subspecies containing up to 70% osmium. It can be distinguished from platinum by its greater hardness, lighter color, and different crystal habit, hexagonal system, rhombohedral division, rather than isometric system, normal class. The alloy with iridium is found as grains in association with platinum and gold in placer deposits. Pure osmium is one of the heaviest known forms of matter, extremely hard and quite chemically inert. When burned in air it oxidizes to OsO_4 as a pungent, irritating, and poisonous vapor.

As the pure metal it has industrial use as a light or heating filament. Alloyed with iridium it has many applications due to its hardness and wear resistance as parts and surface coatings. Osmium and its oxides are used in the glass and ceramics industries.

Technical Application: Osmium metal has had no use in Solid State device fabrication due to its extremely high temperature, weight, and chemical inertness. But it is under development and study as a silicide: OsSi, Os_2Si, and $OsSi_2$ for use as a buffer layer in

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semiconductor heterostructures. It has been grown as single crystal osmium sulfide, OsS_2, and as osmium telluride, $OsTe_2$, for general study as possible semiconductor compounds.

It has been grown as single crystal osmium for general studies and deposited as a thin film as an amorphous structure.

Etching: Aqua regia. Slow in HNO_3.

OSMIUM ETCHANTS

OS-0001a
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HNO_3, fuming
DISCUSSION:
Os specimens. Etch cleaned in fuming nitric acid as single crystal material. (*Note:* There are three concentrations of fuming nitric acid: (1) standard 70%, sometimes called "white" fuming; (2) at 72% "yellow" fuming, and (3) 74% "red" fuming. When a fuming nitric acid is called out, it is often as red fuming.)
REF: Pamphlet: *Platinum*, Baker & Co, Inc., (no date)

OS-0001b
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
1 .... HCl
3 .... HNO_3
DISCUSSION:
Os, as amorphous structured specimens. Use aqua regia to etch clean.
REF: Ibid.

PHYSICAL PROPERTIES OF OSMIUM SULFIDE, Os_2

Classification	Sulfide
Atomic numbers	76 & 16
Atomic weight	254.32
Melting point (°C)	>500 subl
Boiling point (°C)	
Density (g/cm^3)	
Hardness (Mohs — scratch)	5—6
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Black
Cleavage (cubic)	(001)

OSMIUM SULFIDE, OsS_2

General: Does not occur as a natural compound although there are many other metallic sulfide minerals. The only osmium mineral is iridosmine, Ir_xOs, and as a trace element in platinum. There are several artificial compounds in chemistry with the toxic oxide OsO_4 used in glass making.

Technical Application: There has been no use in Solid State processing of the sulfide other than being grown with other cubic sulfides, selenides, and tellurides for IR spectra study and general properties.

Etching: HNO_3, H_2O_2, etc.

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OSMIUM SULFIDE ETCHANTS

OSS-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP:
DISCUSSION:
OsS_2, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, $OsTe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2, and were used in an IR spectra study. (*Note:* Pyrite is not isometric (cubic) system, normal class, but pyritohedral class which does not contain a cube, (100) form, only a pseudocube with heavily twinned and striated faces.)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

OSMIUM TELLURIDE ETCHANTS

OSTE-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
$OsTe_2$, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsSe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2, and were used in an IR spectra study. (*Note:* See note comment under OSS-0001 with regard to crystal structure.)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

PHYSICAL PROPERTIES OF OXYGEN, O_2

Classification	Gas
Atomic number	8
Atomic weight	15.9994 (16)
Melting point (°C)	−218.4
Boiling point (°C)	−183.0
Density ($g/cm^3 \times 10^{-3}$ — gas) 0°C	1.429
(g/l — liquid) 0°C	1.420
(g/cm^3 — solid) −183°C	1.140
(g/cm^3 — solid) −2252.5°C	1.420
Thermal conductance ($\times 10^{-4}$ cal/cm²/cm/°C/sec) 20°C	0.572
Specific heat (cal/g/°C) 20°C	0.218
Latent heat of fusion (cal/g)	3.3
1st ionization potential (eV)	13.61
Ionic radius (angstroms)	1.32 (O^{+2})
Cross section (barns)	0.0002
Vapor pressure (°C)	−198.8
Critical temperature (C.T.) (°C — liquefies)	−118
Critical pressure (C.P.) (atms)	50

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Chemical reactivity (22.2°C & 760 mmHg — gas)	Reactive
(LOX — liquid) −185°C	Reactive
Solubility (100 ml H_2O) 0°C	4.89 ml
(100 ml H_2O) 20°C	3.10 ml
Hardness (Mohs — scratch) solid	2—3
Crystal structure (hexagonal — normal) solid	$(10\bar{1}0)$ platelets
(isometric — normal) solid	(100) cube
Color (gas)	Colorless
(liquid/solid)	Pale blue
Cleavage (basal/cubic — solid)	(0001)/(001)

OXYGEN, O_2

General: A natural element in air which is approximately 24% oxygen and 75% nitrogen with additional trace gases, such as argon, neon, etc. It is obtained by the liquefaction of air; nitrogen (−195°C) boils off first, leaving oxygen (−185°C). It also can be obtained by the reduction of metal oxides, but the compression and fractionation of air is the primary commercial method of obtaining oxygen. It can also be obtained by the electrolysis of water, H_2O, and this method is used to obtain very high purity hydrogen.

Oxygen gas is about $^1/_5$ by volume and $^1/_4$ by weight in the atmosphere; as a constituent in water, H_2O, it constitutes about 85% by weight of ocean water and, when mineral oxides and compounds are included, oxygen is the most abundant element in the world and comprises 50% by weight of the earth's crust and atmosphere.

Many of the basic industrial metals are found as oxides: iron, zinc, copper, tin, aluminum, and manganese. Hematite, Fe_2O_3 — red iron ore — has been a primary ore since ancient times and, as a powder, it is red rouge and a pigment in paint. The red, brown, and tan coloring in rocks is due to the presence of iron oxides. Silica, SiO_2 and alumina, Al_2O_3 are the two most stable compounds; the natural compound called emery is a mixture of Al_2O_3:Fe_3O_4 (magnetite, black iron ore) and may include hematite and is used as a lapping and polishing abrasive. Lead monoxide, PbO, called litharge, as an example, is used in making glass and pottery glaze and also is a semiconductor compound.

The glass industry started with the Egyptian discovery and manufacture of soda-lime glass around 3500 B.C. and today the same formula is still in use. Most glass is made using high purity sand as the starting material; natural silica, silicates, and alumina in clay and ceramic . . . all materials containing oxygen.

Both gaseous oxygen and liquid oxygen (LOX) have wide application in industry and medicine. The gas, of various purity levels or mixed with other gases — O_2/N_2, O_2/Ar, etc., is supplied in high pressure cylinders. The liquid, like all liquidized gases, is transported in 2000 gallon LOX truck tanker trailers and railroad box cars. On-site storage tanks, as well as transport cylinders are of special, double-walled construction . . . the inner spacing is filled with vermiculite, a mica that will absorb moisture and will not burn, and the area is sealed under a light vacuum (10^{-3} Torr) to prevent evaporation. Both liquid and gaseous oxygen can be supplied from such tanks. It should be noted that LOX is a primary fuel in space vehicles and in their booster tanks and in many high speed jet aircraft, and requires special handling as it is instantly explosive in contact with grease and oil.

As ozone, O_3, it occurs in nature during thunderstorms when lightning electrolyzes rain drops and it can be recognized by its very pungent odor. It is used as both a water and air cleaner as it is a very high powered oxidizer. It can be produced by subjecting air to ultraviolet (UV) light and several ozone systems are available commercially which have been used for cleaning metal and semiconductor surfaces. Unfortunately, a concentration of 1 ppm in air can be injurious to health. Liquid ozone is blue and high concentrations are explosive. Note the on-going study of variations of the ozone layer above the Antarctic. It is cyclical, but

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controls the amount of dangerous, high-energy particles entering the atmosphere from the sun.

Atmospheric oxygen is responsible for the formation of the natural oxide and silicate minerals which, as a group, form better than $^3/_4$ of the minerals and rocks of the earth's crust.

Needless to say, oxygen is essential for all life forms, with the exception of a few anaerobic bacteria, and all vegetation use the released carbon dioxide from mammals in photosynthesis, returning oxygen to the atmosphere. Note that the Amazon and Congo River basins in South America and Africa, respectively, produce the greatest amount of oxygen being returned to the atmosphere.

Technical Application: The primary use of oxygen in Solid State processing is for the growth of silicon dioxide, SiO_2, as a thin film coating. As silica, another name for silicon dioxide, it is highly chemically resistant (except for fluorine and fluorine compounds). It is an excellent final surface protectant on metals and semiconductor devices. It also is used as an etching, diffusion and selective epitaxy growth mask where the oxide surface is patterned by photolithographic techniques. It should be noted that the term "oxide" has been in general use for a number of years with reference to silicon dioxide use in the semiconductor industry, and is still so used, even though there are a number of other metal oxides now being grown and applied as thin films on metal surfaces, such as aluminum oxide, Al_2O_3 and beryllium oxide, BeO.

Other than as thin film metal oxide coatings, oxygen as an element is undesirable in semiconductor materials. Most single crystal ingots are grown in quartz tubes — Czochralski (CZ), Float Zone (FZ), Horizontal Bridgman (HB), and Vapor Transport (VT) — and oxygen comes off of the hot quartz (SiO_2) walls and diffuses into the growing material. This has been reduced to some extent by jacketing the growth tubes for water cooling and by temperature control during growth. As most of the oxygen is concentrated in the outer "skin" of an ingot, or, as in the Bridgman and Float Zone methods, swept to the ingot ends by multiple passes of a hot coil, these oxygenated zones can be cut away. Most ingots are grown oversized and lathe cut to specific diameter, which, at the same time, removes the undesirable zones. Oxygen can initiate dislocations, form oxygen defect clusters and create electrical noise in an operating semiconductor device.

Oxygen, when used as an ionized RF plasma gas (O^+ ions), is used for material surface cleaning and, with photo resist patterned material, as part of dry chemical etching (DCE) cleaning, etching, and selective structuring. One widely used mixture on many metals is CF_4:O_2(5%).

Etching: N/A as gas. Pressure as solid.

OXYGEN ETCHANTS

O-0001
ETCH NAME: TIME:
TYPE: Pressure, defect TEMP: −190°C
COMPOSITION:
x .... pressure, vapor
DISCUSSION:
O_2, grown as a single crystal under pressure in vacuum and cryogenic conditions (LHe/LN_2). By varying the vapor pressure in the system, structural defects can be observed.
REF: Schwentner, N et al — *Rare Gas Solids*, Vol 3, Academic Press, New York, 1960

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PHYSICAL PROPERTIES OF PALLADIUM, Pd

Classification	Transition metal
Atomic number	46
Atomic weight	106.4
Melting point (°C)	1552 (1549.4)
Boiling point (°C)	2900 (2927)
Density (g/cm^3)	12.02 (11.3—11.8)
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.18
Specific heat (cal/g) 0°C	0.058
Heat of fusion (cal/g-atom)	4.0
Latent heat of fusion (cal/g)	38.6
Heat of vaporization (k-cal/g-atom)	90
Atomic volume (W/D)	8.9
1st ionization energy (K-cal/g-mole)	192
1st ionization potential (eV)	8.33
Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.28
Ionic radius (angstroms)	0.80 (Pt^{+2})
Vapor pressure (microns) m.p.	26
Coefficient of linear thermal expansion ($\times 10^{-6}$/cm/cm/°C)	11.6
Electrical resistivity (micro-ohms-cm) 20°C	9.93
Electron work function (eV)	4.82 (4.99)
Young's modulus (psi $\times 10^6$)	17
Magnetic susceptibility (cgs $\times 10^{-6}$)	5.8
Tensile strength (psi — annealed)	33,000
Poisson's ratio	0.39
Cross section (barns)	8.0
Hardness (Mohs — scratch)	4.5—5
(Vicker's — kgf/mm^2) annealed	37—39
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Grey-silver metal
Cleavage (cubic — poor)	(001)

PALLADIUM, Pd

General: Does not occur as a pure native element and it is mostly found as small grains as an alloy containing traces of platinum and iridium. Platinum contains up to 2% palladium and is a major source of the metal. Both metals are found in minable quantities in the Ural Mountains of Russia and in Brazil, and are often associated with placer gold deposits. Potarite, from the diamond sands in British Guiana, is a palladium-mercury amalgam. Allopalladium is a hexagonal modification found in the Hartz Mountains. Also from Brazil is the mineral porpezite, a gold alloy containing up to 10% palladium, another major source of the element. It also is extracted from ores of nickel.

The pure metal is more basic than the other elements in the platinum family — Ru, Rh, Pd, Os, Ir — along with platinum and gold, known as the precious metals . . . all highly resistant to oxidation. Thin film palladium is widely used as a mirror plating on instruments as it has excellent silver/white reflectivity and does not tarnish like silver.

Powdered palladium, called palladium black, has the ability to absorb large volumes of hydrogen, even as high as 900 volumes under special conditions, and is under development as a hydrogen storage battery. Platinum black also absorbs hydrogen but to a much lesser extent.

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As an alloy, amalgam mixtures of gold-palladium are extensively used in dentistry as a replacement for gold-platinum. There are several other alloy mixtures of palladium as low temperature solders and high temperature brazing alloys and, as solders, are finding increasing application in the electrical and electronic industries as replacements for the more expensive platinum and gold alloys where it is used for its electrical conductivity.

Like other metals of the platinum family it is used as a catalyst, as in the hydrogenation of carbon compounds, and as a reducing agent in association with hydrogen.

One gold alloy, known as palau (20% Pd) and another, rhotanium (10—40% Pd) have both industrial applications and use in the jewelry trade.

Technical Application: Palladium is finding increasing use as an evaporated thin film in metallization layer structure, e.g., Pd:Cr, Pd:Ti, Au:Pd:Ni. Such structures are used as electrical contact pads and circuits on both discrete Solid State devices, such as silicon and gallium arsenide diodes and transistors, as well as hybrid, planar, or heterostructures. It also is used on circuit substrates of alumina, beryllia, quartz, and sapphire in a similar manner. And palladium alloys, such as Pd:Cd, are being used for assembly and contact purposes as replacement for the higher cost gold and platinum type alloys. It also is under development and application as a silicide: PdSi, Pd_2Si, and $PdSi_2$ for use as a buffer layer in semiconductor heterostructures.

It has not only been studied as a thin film, but grown as a single crystal for general physical data and morphological study.

Etching: HNO_3, slow in H_2SO_4, HCl, and aqua regia.

PALLADIUM ETCHANTS

PD-0001
ETCH NAME: Aqua regia
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

Pd, thin film deposits by E-beam in conjunction with chromium, nickel, silver, or other metals and used for semiconductor device contact pads. Aqua regia is a general etch for palladium.

REF: Bulletin 1092 AMD/ID/JBA/SK/0482/GUILD 1982, 72 — MRC

PD-0002: Walker, P et al — personal application, 1980

Pd, thin films as a sequentially evaporated Pd/Cr layer from standard tungsten boats or filaments as part of the gate contact in fabricating LN-FET gallium arsenide devices. Used solution as shown, and also diluted with 10 parts H_2O, RT, 1—3 sec for surface cleaning.

PD-0002b
ETCH NAME: Aqua regia, dilute
TYPE: Acid, cleaning
TIME: 1—3 sec
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
10 .... H_2O
DISCUSSION:

Pd, thin films evaporated as Pd/Cr pads in GAS LN-FET device fabrication. Solution used as a surface cleaner.

REF: Ibid.

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PD-0003
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... H_2SO_4
x .... glycerin
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:

Pd, 99.95% pure single crystal specimens cut as cylinders with axis in a ⟨110⟩ direction. Used to measure elastic constants from 4.2 to 300 K. Cylinders $^3/_8$" diameter and length. Use solution shown to electropolish specimens. No surface mosaic structure observed after etching.
REF: Rayne, J A — *Phys Rev*, 118,1545(1960)

PD-0004
ETCH NAME: Nitric acid
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3, conc.
TIME:
TEMP: RT or hot
DISCUSSION:

Pd, single crystals and thin films. Solution used as a general etch for dissolving palladium in chemical analysis of native minerals.
REF: Dana, E S & Ford, W E — *A Textbook of Mineralogy*, 4th ed, John Wiley & Sons, New York, 1950, 407
PD-0005: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1947, 498

Pd specimens. Solution used to dissolve palladium to form the nitrate, $Pd(NO_3)_2$.
PD-0002c: Ibid.

Pd, thin films deposited on GaAs (100) wafers and alumina substrates in device and circuit fabrication. Solution used to strip palladium. $1HNO_3$:$10H_2O$ solution used to reduce reactivity. Concentrated acid used to observe possible structure in device failure analysis.
PD-0006: Brochure: *Platinum*, Baker & Co. (no date)

Pd, as plating and fabricated parts. A discussion of physical characteristics and uses of the platinum family of metals.

PALLADIUM ALLOYS, PdM_x

General: Pure metallic palladium does not occur in nature, as it has traces of platinum and iridium primarily, as well as gold, osmium, and rhodium, such that it could be considered a natural alloy. The mineral potarite, PdHg, occurs as one of the few natural amalgams (see section on Amalgam).

Palladium has many industrial uses, and certain alloys are becoming increasingly important in the electronic and metal industries as high temperature, corrosion resistance plating and parts.

Technical Application: Only two alloys are shown here as they are under study or being used in Solid State processing for electrical contact materials as a constituted alloy. The use of multilayered thin films, such as Pd/Cr, was previously mentioned under palladium metal. Like platinum, and other platinum family metals, aqua regia is the primary etching solution.

Etching: Aqua regia.

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PALLADIUM GOLD ETCHANTS

PDAU-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal
TIME:
TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

PdAu deposited as a 1:1 mixture on glass, quartz, and sapphire substrates. The thin film shows crinkling on a thick, hard surface indicative of compressive stress. It is not as severe on thin glass or metal strips, as they can bow and relieve stress. Both metals are cubic, fcc. (*Note:* Isometric system, normal class . . . the cube, (100) is a crystal form within this class, not a true crystallographic system or class, although the isometric system is commonly referred to as the cubic system.)
REF: Asai, H & Oe, K — *J Electrochem Soc*, 128,2052(1981)

PALLADIUM HYDRIDE ETCHANTS

PDH-0001
ETCH NAME: Aqua regia
TYPE: Acid, cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
3 .... HCl
1 .... HNO_3
x .... H_2O
DISCUSSION:

Pd:H as powdered "palladium black" with absorbed hydrogen. Powdered palladium can be cleaned with aqua regia with or without water dilution, then furnace dried under vacuum prior to introduction of hydrogen.
REF: Wise, E M — *The Platinum Metals* (brochure), The International Nickel Co., 1954

PALLADIUM SILVER ETCHANTS

PDAG-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal
TIME:
TEMP: RT or warm
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

PdAg alloy used in a pure metallic paste form as an electrical pad contact for microelectronic circuits. It can be screen printed on alumina substrates and fired to about 1000°C. Also as an epoxy type paste with oven curing between 100—125°C. PdAg is being used as a replacement for gold pastes to reduce cost.
REF: Chapman, D — personal communication, 1983

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PHYSICAL PROPERTIES OF PHOSPHORUS, P

Classification	Non-metal
Atomic number	15
Atomic weight	30.97 (P)
	124.08 (P_4)
Melting point (°C — white (yellow))	44.1
(°C — red) @ 43 atms	590
(°C — violet)	593
(°C — black) 12,000 kg/cm^2	200
Boiling point (°C — white (yellow)/red)	280
Density (g/cm^3 — white (yellow))	1.82
(g/cm^3 — red)	2.20 (2.34)
(g/cm^3 — violet)	2.36
(g/cm^3 — black)	2.691
Specific heat (cal/g) 25°C	0.177
Heat of fusion (k-cal/g-atom)	0.15
Latent heat of fusion (cal/g)	5.0
Heat of vaporization (k-cal/g-atom)	2.97
Atomic volume (W/D)	17.0
1st ionization energy (K-cal/g-mole)	2254
1st ionization potential (eV)	11.0
Electronegativity (Pauling's)	2.1
Covalent radius (angstroms)	1.06
Ionic radius (angstroms)	0.35 (P^{+5})
Electrical conductivity (micro-ohms^{-1})	10^{-17}
Electrical resistivity (ohms cm) 20°C	10^{11}
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm^2/cm/°C) 20°C	125
Cross section (barns)	0.19
Vapor pressure (°C)	197.3
Refractive index (n=) yellow/white	2.144
Hardness (Mohs — scratch)	0.5
Crystal structure (isometric — normal) white	(111) octahedron
(isometric — normal) red	(100) cube
(amorphous) red	none
(monoclinic — normal) violet	(100) a-pinacoid
Color (solid)	Variable by type
Cleavage (cubic/basal — poor)	(001)

PHOSPHORUS-CONTAINING ETCHANTS

General: Phosphorus is widely disseminated in the combined state, making up about 0.12% of the earth's crust. The element is of importance to both plant and animal life. The human skeleton contains 1400 g, the muscles 130 g, and the nerves and brain about 12 g, combined. It is essential to vegetable matter, such that phosphorus compounds are important fertilizers.

White (yellow) phosphorus melts in hot water, will burn under water due to presence of air (aerated) in water, and vigorously if oxygen is bubbled through the water. It also reacts with water moisture in the air, such that it is stored under kerosene. This white form is extremely poisonous, and ingestion of 0.15 g can be fatal. White phosphorus is readily converted to red phosphorus by being heated in its own vapors to 235°C, such that it is so converted for most general processing.

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Red phosphorus is the form in which most phosphorus is used as it will not catch fire below 240°C, and can be handled as it is not toxic. The violet and black varieties are fabricated under special conditions, and are rarely seen or used under normal conditions.

There are nine forms of liquid types of phosphoric acid, but the most commonly used in chemical processing of metals and metallic compounds is called phosphoric acid, H_3PO_4. The following A—Z material list of solutions are this form, with the exception of one application of metaphosphoric acid, HPO_3.

PHOSPHORUS, P

General: Does not occur as a native element, but is widely disseminated in a number of minerals. The chief sources of phosphorus are from the mineral phosphorite, $Ca_3(PO_4)_2$ which is a subspecies of the mineral apatite, as fluorapatite, $(CaF)Ca_4(PO_4)_3$ or chlorapatite, $(CaCl)Ca_4(PO_4)_3$. There are some 15 subspecies of apatite with various names which may contain other elements, such as strontium and manganese. Although apatite has a relatively low Mohs hardness: H = 5, some of the colored varieties are used as gem stones: asparagus-stone, yellowish-green; manganapatite, dark bluish-green; and lasurapatite, sky-blue.

A primary use of red phosphorus has been in the fabrication of matches, invented by John Walker in 1827. The original "match" was a mixture of $KClO_3$:P (white), which is poisonous; P_4S_2 was used as a replacement as it is nontoxic. But $KClO_3$ is explosive in the presence of organic matter, and when mixed with phosphorus and struck a sharp blow — will explode.

The "safety match", developed by the Swedish inventor Bottger in 1848, replaced phosphorus with SbS_3 + oxidizer ($KClO_3$, $K_2Cr_2O_7$ etc.), mixed with powdered glass and glue. These matches are ignited by rubbing on the surface mixture of SbS_3:P (red) and glue. Note that although phosphorus is not used in the match head, it is part of the striking surface.

Phosgene, PH_3, is a colorless, poisonous gas with a distinctive rotten fish odor, and was used in gas warfare during World War I. Today, in semiconductor processing, ^{25}phosphine, PH_3, is a primary n-type dopant for silicon wafers, thin film epitaxy layers, as well as oxides and nitrides. As a doped silicon dioxide is has the acronym PSG.

Phosphorus oxychloride, $POCl_3$ — called "pockel" — as a liquid through which nitrogen gas is bubbled, also is used as an n-type dopant in semiconductor processing.

Phosphorus oxides, as solid materials, also are used as n-type dopants in a similar manner, usually in the form of the pentoxide, P_2O_5 as the trioxide P_2O_3, is poisonous. Regardless, processing fumes from diffusion tubes should be properly ventilated during operation as both oxide types will be present, such that operation is hazardous.

P_2O_5 is the anhydride of the three primary phosphoric acids: orthophosphoric, H_3PO_4; pyrophosphoric, $H_4P_2O_7$ and metaphosphoric, HPO_3. Orthophosphoric acid, commonly called phosphoric acid, is the most commonly used of the three and is the major acid for etching of metals and metallic compounds.

Ferrophosphorus is a slag by-product of the production of phosphorus from calcium phosphates (apatite) and is cast into pigs for use in the iron and steel industry and phosphor-bronze is a mixture of Sn:Cu:P, of use for its spring qualities.

Technical Application: Phosphorus is the primary n-type dopant in silicon semiconductor fabrication, although both arsenic and antimony also can be used. As already mentioned, it can be used in the form of PH_3 (gas), $POCl_3$ (liquid), or P_2O_5 (solid).

Red phosphorus is used to grow several compound semiconductors, such as gallium phosphide, GaP and indium phosphide, InP. The latter is used as InP wafer substrates in MBE layered growth of heterostructures. All of the colored forms of phosphorus have been grown as single crystals for study.

All of the colored forms of phosphorus have been grown as single crystals for study.

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Etching: (1) White: CS_2, NH_3, KOH/NaOH, and water.
(2) Red: EOH, absolute.
(3) Violet: insoluble.
(4) Black: insoluble.

Etchants Containing Phosphorus

Formula	Material	Use	Ref.
$2H_3PO_4$:$1H_2O_2$:$3H_2O$	Al	Removal	AL-0007
$70H_3PO_4$:25 ml H_2SO_4:5 ml HNO_3	Al	Polish	AL-0035
$95H_3PO_4$:$5HNO_3$	Al	Cleaning	AL-0036
$80H_3PO_4$:$5HNO_3$:15HAc	Al:Cu	Macro-polish	ALCU-0002
25 ml H_3PO_4:70 ml H_2SO_4:5 ml HNO_3	Al:Si	Polish	ALSI-0002
$95H_3PO_4$:$5HNO_3$	AlSb	Cleaning/oxide removal	ALSB-0010
xH_3PO_4, conc.	AlN	Removal	ALN-0006
xH_3PO_4, conc.	Al_2O_3	Cleaning	ALO-0002a
xH_3PO_4, conc.	Ba_2TiO_3	Polish	BAT-0002
xH_3PO_4, conc.	Be	Preferential	BE-0003
xH_3PO_4, conc.	BeO	Preferential	BEO-0001a
xH_3PO_4:xH_2SO_4	BeO	Removal	BEO-0006b
xH_3PO_4, conc.	BN	Removal	BN-0002
xH_3PO_4:xH_2O	Brass	Preferential	BRA-0013b
12—15% HH_3PO_4	Brass	Cleaning	BRA-0008d
35% H_3PO_4	Brass	Electrolytic, polish	BRA-0009
xH_3PO_4, conc.	$CaWO_4$	Removal	CAW-0001a
$3H_3PO_4$:$1CrO_3$, sat. sol.	$CaWO_4$	Polish	CAW-0003b
xH_3PO_4, conc.	C	Polish	C-0003
xH_3PO_4:CrO_3:xNaCN	C	Removal	C-0006b
$64H_3PO_4$:$15H_2SO_4$:$21H_2O$	Cr	Electrolytic, polish	CR-0001c
xH_3PO_4, conc.	Co	Electrolytic, polish	CO-0005
xH_3PO_4, conc.	Cu	Electrolytic, polish	CU-0005
$1H_3PO_4$:$1HNO_3$:1HAc	Cu	Polish	CU-0045
xH_3PO_4, conc.	Cu:Ge	Electrolytic, polish	CUGE-0004
xH_3PO_4, conc.	CuO	Polish	CUO-0008
33 ml H_3PO_4:33 ml HNO_3:33 ml HAc	CuO	Removal	CUO-0009
$40H_3PO_4$:$1H_2O_2$:$40H_2O$	GaAs	Removal	GAS-0105
$100H_3PO_4$:$100H_2SO_4$:$1H_2O_2$	GaAs	Dislocation	GAS-0107
$1H_3PO_4$:$1H_2O_2$:$20H_2O$	GaAs	Selective	GAS-0108a
$1H_3PO_4$:$1H_2O_2$:$75H_2O$	GaAs	Thinning	GAS-0108b
$75H_3PO_4$:$100H_2O_2$:$25H_2O$	GaAs	Via hole	GAS-0109
$49H_3PO_4$:$11HNO_3$	GaAs	Polish	GAS-0110b
$5H_3PO_4$:$5H_2SO_4$:$2H_2O_2$	GaAs	Preferential	GAS-0110c
xH_3PO_4, conc.	GaN	Preferential	GAN-0004
xH_3PO_4, conc.	Garnet	Preferential (GGG)	GGG-0001a
xH_3PO_4, conc.	Garnet	Preferential (YAG)	YAG-0006
xH_3PO_4, conc.	Garnet	Dislocation (YIG)	YIG-0001b
xH_3PO_4, conc.	InP	Electrolytic, selective	INP-0033a
10% H_3PO_4	InP	Oxide removal	INP-0022c

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Formula	Material	Use	Ref.
xH_3PO_4:xHCl	InP	Removal	INP-0034
$1H_3PO_4$:3HCl	InP	Grooving	INP-0035
xH_3PO_4:xHBr	InP	Preferential	INP-0021c
$1H_3PO_4$:$1H_2O_2$:3MeOH	InP	Cleaning	INP-0047
$1H_3PO_4$:$1H_2O_2$:$76H_2O$	InP	Selective	INP-0046b
x14 *N* H_3PO_4	InP	Electrolytic, oxidizing	INP-0051
$1H_3PO_4$:1HCl	InP	Selective	INP-0057a
$2H_3PO_4$:$1H_2O_2$	Fe	Preferential	FE-0110
xH_3PO_4, conc.	MgO	Thinning	MGO-0001
$80H_3PO_4$:$20H_2O$	MgO	Polish	MGO-0004
117 ml H_3PO_4:55 ml HNO_3:57 ml HAc:115 ml HF	Mo	Removal	MO-0012b
$xHPO_3$, conc.	Ni	Removal	NI-0004d
xH_3PO_4:$xCrO_3$	Permal-loy	Electrolytic, polish	PMA-0001b
xH_3PO_4, conc.	NiMn	Electrolytic, dislocation	NIMN-0001
$1H_3PO_4$:$1H_2SO_4$	Al_2O_3	Cleaning (sapphire)	SAP-0001
xH_3PO_4, conc.	Al_2O_3	Preferential	SAP-0002a
xH_3PO_4:$xHNO_3$	Si	Selective	SI-0131
xH_3PO_4, conc.	SiC	Removal	SIC-0005c
xH_3PO_4:$xNaOH$:$xNaCO_3$	SiO_2	Cleaning	SIO-0039c
xH_3PO_4, conc.	Si_3N_4	Removal	SIN-0001
$2H_3PO_4$:$1H_2O_2$	Steel	Polish (Fe:Ni)	FE-0012b
$63H_3PO_4$:$15H_2SO_4$:$10CrO_3$:$12H_2O$	Steel	Electrolytic, polish	Fe-0011
x1 *N* H_3PO_4:9 *N* H_2SO_4	Th	Electrolytic, polish	TH-0003
100 ml H_3PO_4:1 g NaOH:2 g agar-agar	SnTe	Electrolytic, polish	SNTE-0001
30% H_3PO_4	Ti	Removal	TI-0001d
xH_3PO_4	TiO_2	Removal	TIO-0011
xH_3PO_4:$xHClO_4$	W	Polish	W-0018b
$1H_3PO_4$:$1H_2SO_4$:$1H_2O$	U	Electrolytic, polish	U-0002c
310 ml H_3PO_4:67 ml H_2SO_4:120 ml H_2O:78 g CrO_3	UO_2	Polish	UO-0001
$4H_3PO_4$:1MeOH	UC	Electrolytic, jet-thinning	UC-0001
$4H_3PO_4$:1MeOH	UN	Electrolytic, jet-thinning	UN-0001
$4H_3PO_4$:1MeOH	US	Electrolytic, jet-thinning	US-0001
33% H_3PO_4:67% C_2H_5OH	Zn	Electrolytic, polish	ZN-0007d
xH_3PO_4, conc.	ZnO	Polish	ZNO-0003
xH_3PO_4, conc.	ZnW	Polish	ZNW-0001a

PHOSPHORUS ETCHANTS

P-0001a
ETCH NAME: Carbon disulfide
TYPE: Acid, removal
COMPOSITION:
x .... CS_2
TIME:
TEMP: RT
DISCUSSION:
P, as white phosphorus is stored under toluene or kerosene to prevent combustion in air, but can be dissolved in the solution shown.

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REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1948, 574

P-0001b
ETCH NAME: Water
TIME:
TYPE: Acid, removal
TEMP: Hot
COMPOSITION:
x .... H_2O
DISCUSSION:
P, as white phosphorus specimens can be dissolved in hot water and will burn with free oxygen present in the water. It will burn under water.
REF: Ibid.

P-0001c
ETCH NAME: Turpentine
TIME:
TYPE: Solvent, removal
TEMP: RT
COMPOSITION:
x .... $C_{10}H_{16}$
DISCUSSION:
P specimens as white phosphorus can be dissolved in several organic solvents without burning, such that it is stored in kerosene.
REF: Ibid.

P-0001d
ETCH NAME:
TIME:
TYPE: Spark, ignition
TEMP: 240°C
COMPOSITION:
x .... emery paper
DISCUSSION:
P, as red phosphorus is not air reactive or water reactive as is the white form. In powder form it is used in the fabrication of matches. When the match head is drawn across a rough surface, such as an emery board containing phosphorus, the phosphorus will ignite and burn. Black phosphorus is similar in properties.
REF: Ibid.

PHOTO RESIST ETCHANTS

AZ-0001a
ETCH NAME: Acetone
TIME:
TYPE: Ketone, removal
TEMP: RT
COMPOSITION:
x .... $(CH_3)_2CO$
DISCUSSION:
AZ-type photo resist lacquers used in semiconductor processing. Standard photo resist spinners consist of a removable metal or plastic bowl with bottom hole up through which extends a $^1/_4$" motor driven shaft on which is mounted a wafer holder for vacuum pump hold down of wafers, and an electronic operation control.

Thickness of coating depends upon the type (by number) of resist and spin speed. AZ-1350J is a standard positive photo resist that is spun on at 3600 rpm, RT, 10—15 sec for a 0.5 μm thickness. 1370J will give about 1 μm thickness. The positive photo resists open a required pattern; whereas negative photo resists cover the pattern.

Cure by first air drying at RT, 1 h; then air-oven bake at 90°C for 1 h (120°C for hard

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bake). Follow by UV light exposure with the pattern mask over the wafer and, finally, develop that pattern with the photo resist developer solution designed for the type photo resist being used.

The wafer can then be metal evaporated or the surface etched for pits, channels, via holes, etc., with acetone lift-off after metallization. If the wafer or circuit substrate is already metallized, the pattern is etched, then remaining photo resist remove for acetone spraying.

Acetone is the solvent for cleaning and removal of most photo resists. Apply as a spray from a stainless steel spray can under nitrogen pressure; soak by immersion in a beaker of acetone; lightly scrub surfaces with a Q-tip soaked in acetone. Removal of extraneous metallization is called the lift-off technique.

There are other photo resist formulations, such as COP or PMMA, but all are processed in the same general manner. They are occasionally used as a paint-on coating as a general holding medium.

CAUTION: Acetone has a boiling point of 56.7°C and a low flash point.

REF: Tech. Bull. #401, 1984 — American Hoechst Corp.

AZ-0005: Mizuno, K — *J Phys Rev*, 4,1434(1984)

P/R used to pattern glass substrates for study of aluminum evaporation of different thicknesses. Acetone used to lift-off excess metal after evaporation.

AZ-0006: Walker, P & Valardi, N — personal application, 1985

AZ-1370J used to pattern AuGe (13%) and AuSn (20%) 0.0001 thick alloy strips. Used photo resist to hold alloys on glass microscope slides and to coat and pattern. Acetone used to dissolve and remove photo resist after etch patterning.

AZ-0001b
ETCH NAME: J-100
TYPE: Solvent, removal
COMPOSITION:
x J-100
TIME:
TEMP: Hot

DISCUSSION:

AZ-type photo resists. J-100 is a phenol base solution containing some alkali and is a general remover and solvent for photo resist lacquers. Particularly useful for hard-baked resists. Caution should be observed when using the solution with materials that can be attacked by hot alkalies as well as normal precautions in handling acids. Use as a hot soak for general photo resist removal and patterning.

REF: Ibid.

AZ-0003
ETCH NAME: Carbon tetrafluoride
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4:
x .... O_2 (5%)
TIME:
TEMP: 40°C (holder base)
or 100°C
GAS FLOW:
PRESSURE: 0.3 Torr
POWER: 200 W
(13.56 MHz)

DISCUSSION:

AZ-1350J and other photo and electron beam resists: PGMA, PMMA, PMIPK (E-beam); Novolak type: AZ, OFPR, OMR (photo). Article shows angstrom removal rates and discusses development of submicron lithography.

REF: Tsuda, M et al — *J Vac Sci Technol*, 19(2),259(1981)

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AZ-0007
ETCH NAME: Cotton pad
TYPE: Rubbing, defect removal
COMPOSITION:
x .... cotton pad
TIME:
TEMP: RT
DISCUSSION:
AZ- and PMMA photo resists spun on soda lime glass substrates used in a study of photo resist defects in both positive and negative resists subject to Si^+ ion bombardment at 200 keV, and up to 5×10^{15} cm^{-1} dose level. Inspection was at 400× with transmitted light. Defects were in the 1- to 3-μm size range, some due to ion bombardment and others intrinsic to the spin-on technique. Defects can be eliminated by laser erasure or by light rubbing with a soft pad.
REF: MacIver, B A & Puzio, L C — *J Electrochem Soc*, 129,2384(1982)

AZ-0008
ETCH NAME: Oxygen
TYPE: Gas, removal
COMPOSITION:
x .... O_2
TIME: 2—5 min or 10—15 min
TEMP: RT start
GAS FLOW: 300 cc/min
PRESSURE: 1.5 Torr
POWER: 200 W (13.56 MHz)
DISCUSSION:
AZ-1350J and other AZ- photo resists for 2—5 min; PMMA for 10—15 min. Used to strip photo resists ranging in thickness from 0.5—5 mils (pressed sheet method of application). Also used as a general contamination removal system in processing semiconductor wafers, ceramic and dielectric substrates, and individual semiconductor devices prior to metallization, epitaxy, or device assembly for testing or final packaging. *Note:* Residual photo resist on a metallized wafer or individual device can be recognized under magnification as fine reddish/brownish lines along the edges of the metallized patterns. If present, usually associated with lifting and peeling of the metallization. Where a semiconductor device has been in storage for any period of time — the plastic $2 \times 2 \times {}^1/_4$ box/trays (Fluorware type) — even in a nitrogen storage area, trays can exude oils from their method of fabrication (form release agents), and coat surface with organic contamination that prevents wire bonding to metal pads of the device: 5 to 10 min in an RF oxygen plasma under the conditions shown above will clean such surfaces. System used was an IPC 2000 unit.
REF: Walker, P — personal development and application, 1983—1985

AZ-0004a
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
100 ml .... H_2SO_4
20 ml .... H_2O_2
TIME:
TEMP: Hot
DISCUSSION:
AZ-type photo resists, other photo resists and general contamination removal and cleaning of surfaces. Should not be used on gallium arsenide wafers as hydrogen peroxide is an active etchant for this material. Used on silicon, ceramic and dielectric substrates, and metals. **CAUTION:** These solution mixtures are highly exothermic and self-sustaining once reaction has commenced and will increase in temperature as reaction continues to a boiling point of about 170°C. See Silicon "Caro Etch".
REF: Tech. Bull. #8, 1984 — EKC Technology, Inc.

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AZ-0004b
ETCH NAME: TIME: 10 min minimum
TYPE: Acid, removal TEMP: 125°C
COMPOSITION:
(1) x .... H_2SO_4 (2) x .... H_2SO_4, conc.
x .... $(NH_4)_2S_2O_8$ (SABO)
DISCUSSION:
AZ-type photo resists and other lacquers. Hydrogen peroxide is replaced with "SABO" for better removal and cleaning control. Use just enough SABO to maintain a clear solution. Use the following procedure: (1) soak 5 min in H_2SO_4 solution (2); then (2) soak 5 min in mixture solution (1) and DI water wash. Caution should be used in disposal of sulfuric acid, particularly when hot, as it can react with explosive splatter in contact with water.
REF: Ibid.

PHYSICAL PROPERTIES OF PHOSPHORUS PENTOXIDE, P_2O_5

Classification	Oxide
Atomic numbers	15 & 8
Atomic weight	142.04
Melting point (°C)	563
Boiling point (°C)	347 subl
Density (g/cm^3)	2.39
Hardness (Mohs — scratch)	1—2
Crystal structure (monoclinic — normal)	(100) a-pinacoid
Color (solid)	White
Cleavage (basal)	(001)

PHOSPHORUS PENTOXIDE, P_2O_5

General: Does not occur as a natural compound although there are many minerals containing the PO_4^- radical as phosphates. Two major minerals are apatite and phosphorite, both calcium phosphates. They are of fossil origin with large deposits in the southeastern and Gulf area of the U.S.

There are three oxide forms: trioxide, tetroxide, and pentoxide. The trioxide is poisonous and can be a by-product from the pentoxide when being used as a diffusion source of phosphorus but, as it has a very low melting point (22.5°C) and is soluble in cold water, it is used in making phosphoric acid, H_3PO_4. The pentoxide has been used as a phosphorus bomb or grenade to produce heavy white smoke and choking fumes. If solid pieces contact the skin, severe burns can result.

Technical Application: The pentoxide is used in Solid State processing as a source of phosphorus, n-type doping of silicon wafers. It was the first dopant source used as a solid, but the gas, PH_3, is used in OMCVD and Vapor Transport (VT) systems. Phosphorus doped silicon dioxide has the acronym PSG.

Etching: H_2SO_4, mix acids.

PHOSPHORUS PENTOXIDE ETCHANTS

PO-0001
ETCH NAME: Sulfuric acid TIME: 30—60 min
TYPE: Acid, removal TIME: RT
COMPOSITION:
x .... H_2SO_4

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DISCUSSION:

P_2O_5 used in powder form as an n-type dopant for silicon wafers. Solution shown has been used to clean quartzware used in phosphorus diffusion furnaces.

REF: Crabbs, G — personal communication, 1973

PO-0002

ETCH NAME: TIME:

TYPE: Acid, removal TEMP: RT

COMPOSITION:

1 .... HF

2 .... HNO_3

4 .... HAc

DISCUSSION:

P_2O_5 and other phosphorus compounds remaining in epitaxy tubes after growth of silicon thin films on (111) silicon wafers with heavy phosphorus doping. Used in fabricating SCRs. Cleaning was done in an acid sink designed for tube cleaning with tube lying horizontal. When acid is introduced there is instant flame-out from open tube ends prior to etching action. After internal tube etching, exterior is washed in the acid solution; the entire tube then DI water washed; finally rinsed with MeOH, and allowed to air dry. Cleaned tubes are returned to the epitaxy system for a dry run to seed tube before next growth run.

REF: Walker, P & Hellstein, G — personal development, 1972

PLASTICS

General: Plastics are artificial compounds. Thermoplastics soften when heated and reharden when cooled. Such thermosetting plastics as powder, rods, and sheets can be heated and molded, and when a critical temperature is reached there is a physical structural change (polymerization) that "sets" the plastic, and it cannot be reliquefied or remolded.

Celluloid was one of the first plastics (Hyatt, 1868), incompletely nitrated cellulose (mono- and dinitrate) are pyroxylin, and when mixed with alcohol and ether called collodion. Bakelite (Baekeland, 1909) is produced by mixing phenol and formaldehyde under pressure, and called a condensation plastic as water is removed during the reaction. Polymerization plastics are produced from simple hydrocarbons and their derivatives, such as Lucite, Plexiglas, polyvinyl chloride (PVC), and styrene base plastics. Acetate and mylar are similar derivative materials.

Bakelite and Plexiglas (Lucite) are lightweight construction materials and are used for aircraft, vehicles, or molded as dinner and kitchenware, and clear Plexiglas is a replacement for glass. In powder form, Lucite is used in preparing metallographic metal and mineral specimens for study: the specimen and powder molded into a solid cylinder under pressure and heat, then lapped to expose the specimen surface. Opaque brown bakelite has been used similarly. Plastic resin impregnation of wood, linen cloth, etc. produces sheets of wood veneer, and impregnated linen cloth used as insulating boards for electrical equipment for mounting electronic circuits as PCBs.

Thin film acetate has long been used for photographic film for both still photography and movie film, and in engineering for drawing overlays, map making, and book or paper jackets. Mylar as rubilith (red film coated on clear acetate sheet .003 and .005 thick) is used to design electronic circuits, then reduced in size on photographic film or on glass plates, such as chrome glass masks for photolithographic processing of semiconductor devices and associated substrate circuits. "Sticky-back" mylar sheet (white or blue color) is used to hold wafers — semiconductors, garnets, ceramics etc. — on the sticky surface, with the mylar held in place with a vacuum chuck for saw cutting or scribe and break dicing of parts. Mylar and other plastic sheets are spray coated or vacuum evaporated with a number of

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metals for reflectivity (aluminum, brass, silver, gold, nickel), and carbon coatings are used as sunscreens.

Many plastics are quite weather resistant and inert to most chemical corrosion, but they are relatively soft (H = 4—5) such that they are easily scratched by metal particles, sand, etc. Depending upon the type, they may or may not be soluble in organic solvents, such as turpentine, xylene, toluene — acetone will dissolve Lucite/Plexiglas. The phenol/formaldehydes, such as Bakelite are resistant; whereas ethyl cellulose compounds are very soluble. Heat resistance also varies with the type material . . . acetates are flammable.

It is worth noting that over 50% of every barrel of oil goes into the chemical and plastic industries — not for gasoline — such that oil economy has a far-reaching effect on industrialized nations.

Costwise, plastics are much cheaper to fabricate as parts than are woods, metals, and glasses, such that many products are replacing those materials . . . the colored acrylic paint sprays are an example of a "new" product, as are the modern throw-away baby diapers, and there is also plasticized rubber. Plastics are a viable, expanding industry which is still developing.

Technical Application: Some of the uses of mylar have already been mentioned, as have PCBs and cloth-impregnated insulator material. The latter are used in epitaxy reactor systems, for example, or as test equipment bases. Corrosive acids, such as HF, are supplied in polyethylene bottles, and there is chemical laboratory plasticware: measuring cylinders, stir rods, beakers, etc. This includes Teflon and Kel-F as fluorinated compounds specifically used for handling HF and other fluorine-containing chemicals.

Polystyrene containers are used directly to transport or hold LN_2 for chilling in vacuum systems — CVD, epitaxy growth system, and ion pump evaporators. Similar containers are used in transporting epoxy and polyimide pastes in solid CO_2, e.g., dry ice.

Teflon and many varieties of plastic tubing are used as electric wire insulators in both electronic equipment as well as in semiconductor packaged device assembly, and there is plastic shrink-tubing — heat the tubing, and it will shrink and mold around the wire or part. Plastic spray coatings are used on equipment, occasionally a semiconductor, similar to lacquer coating. The RTV compounds are a plastic/rubber combination used as an exposed junction coating on semiconductor devices, e.g., SCRs.

Polyethylene boxes as small trays with a cover are used for storing and transporting discrete semiconductor dice and similar devices — from, say, 10 to 200 units per tray — particularly with regard to static sensitive devices: Si and GaAs FETs, IMPATTS, etc. Many types of plastic boxes are used for holding parts, such as tote boxes, shaped package containers, shrink molded covers, general shipping boxes or packing, e.g., "bubble" plastic sheeting, loose particle shapes, etc.

Plastic extrusion molding is used as a final package on semiconductors, resistors, capacitors, and similar assemblies. Plastic face shields and gloves, aprons, and so forth are required wear for operators involved with chemical processing or critical device handling. Plastic eyeglasses or goggles are similarly used in chemical processing or in glass and metal welding operations.

A point on the small plastic trays used for handling static sensitive devices: the mold release compounds used in fabrication of these boxes can, with time, exude from the part as an organic surface contamination. This can affect wire bonding on the device metal contact pads — bonds will not hold. With 5—10 min in an RF plasma unit with O_2 or N_2, this organic residue will be removed. This same problem can occur where metallized substrates are shipped in plastic envelopes, and surfaces also can be cleaned by RF plasma treatment.

Many chemical sinks have a plastic sheet front that can be raised and lowered, commonly Lucite. Do not use acetone to clean— it will start dissolving the Lucite/Plexiglas. See LUC-0001b in the following list of etchants. Note that shaving of Lucite can be liquefied with acetone, then used as a glue.

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Some plastic rods or filaments are used in light transmission systems, similar to glass fiber optics, and also as a rod in laser fabrication. A Lucite rod, when rubbed on wool, will create a static charge, such that they have been used in static generators.

Etching: Variable with type of plastic — both acids and solvents. See Mounting Materials section.

PLEXIGLAS ETCHANTS

PL-0001a
ETCH NAME: Acetone
TYPE: Ketone, removal
COMPOSITION:
x .... CH_3COOH_3
TIME: 192 h
TEMP: RT
DISCUSSION:
Plexiglas plastic sheet. Acetone will dissolve Plexiglas in the test period shown.
REF: Simonds, H R et al — *Handbook of Plastics*, 2nd ed, Reinhold, New York, 1979

PL-0001b
ETCH NAME: Carbon tetrachloride
TYPE: Solvent, removal
COMPOSITION:
x .... CCl_4
TIME: 192 h
TEMP: RT
DISCUSSION:
Plexiglas sheet. Solution will dissolve this material. (*Note:* This is called Lucite under a different brand name.)
REF: Ibid.

PL-0001c
ETCH NAME: Toluene
TYPE: Solvent, removal
COMPOSITION:
x .... $C_6H_5CH_3$
TIME: 192 h
TEMP: RT
DISCUSSION:
Plexiglas sheet. Solution will dissolve this material.
REF: Ibid.

PL-0002
ETCH NAME: Acetone
TYPE: Ketone, sealer
COMPOSITION:
x .... CH_3COOH_3
TIME:
TEMP: RT
DISCUSSION:
Lucite plastic. Shavings of Lucite liquefied with acetone to form a Lucite glue. The glue was then used to coat/encapsulate silicon devices or in the assembly of Lucite sheet into boxes and special housings.
REF: Walker, P — personal application, 1956—1985
LUC-0001a: Simonds, H R et al — *Handbook of Plastics*, 2nd ed, Reinhold, New York, 1979
Lucite, sheet and parts. Shavings liquefied with acetone as a glue used for assembling parts.

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PL-0003
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
TIME:
TEMP: 80—85°C
COMPOSITION:
x .... H_2SO_4, conc.
DISCUSSION:
Most encapsulation plastic compounds used in DIP fabrication can be removed by jet etching with sulfuric acid.
REF: Data sheet — B & G Enterprises, ph: (408) 728-3638

PL-0004
ETCH NAME: Water
TYPE: Acid, cleaning
TIME:
TEMP: RT to warm (40°C)
COMPOSITION:
(1) x .... H_2O
(2) 2 mg .... I_2
50 ml .... $MeOH/H_2O$
DISCUSSION:
Mylar thin film as sticky-back sheet used to hold semiconductor and garnet wafers and substrate materials, such as quartz and sapphire, during scribe and break or diamond saw cutting. Wipe the nonsticking surface with warm water with or without a high purity soap, such as Castille, to clean (1). An iodine mixture (2) may also be used. The iodine solution can be used on other plastics, such as Lucite, Plexiglas, and polystyrenes for light cleaning.
REF: Walker, P — personal application, 1956—1982

PVC-0001a
ETCH NAME: Potassium permanganate
TYPE: Salt, cleaning
TIME:
TEMP: RT
COMPOSITION:
x .... 20—30% $KMnO_4$
DISCUSSION:
PVC, DI water piping and steel piping. Solution used to periodically clean DI water storage tanks and incoming lines to laboratory sinks to remove algae build-up. Flush lines until the purple colored permanganate disappears and check with litmus paper for pH 7 neutrality — may be slightly alkaline. Use on PVC DI water lines.
REF: Tarn, W H & Walker, P — personal application, 1978

PVC-0001b
ETCH NAME: Hydrogen peroxide
TYPE: Acid, cleaning
TIME:
TEMP: RT
COMPOSITION:
x .... 30% H_2O_2
DISCUSSION:
PVC and steel DI water piping. Used in a similar manner as described for permanganate cleaning, above. Particular caution should be observed in removing all traces of peroxide where the water is being used on semiconductor wafers for cleaning, as hydrogen peroxide can act as an etching solution. This also applies to potassium permanganate as both are very active oxidizers.
REF: Ibid.

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LUC-0001c
ETCH NAME:
TYPE: Halogen, cleaning
COMPOSITION:

(1) 1 g .... I_2
50 ml .... MeOH
1000 ml .... H_2O

(2) 1 tsp .... *tincture of iodine
1 gal .... H_2O

*KI:I_2:EOH

TIME:
TEMP: RT to warm

DISCUSSION:
Lucite sheet and parts. Both solutions can be used for cleaning and disinfecting Lucite and polycarbonate plastics. (*Note:* Formula (1) with KI added would be a tri-iodide solution for etching gold. The MeOH is used to increase dissolving rate of iodine in water.)
REF: Ibid.

LUC-0003
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
x .... glycerin
DISCUSSION:
Lucite sheet and parts can be cleaned in this solution. The solution has the same refractive index as Lucite: n = 1.40.
REF: Ivanstov, O P — *Dokl Akad Nauk SSSR,* 56,567(1947)

TIME:
TEMP:

POLY-0001a
ETCH NAME: Toluene
TYPE: Solvent, removal
COMPOSITION:
x .... C_7H_8
DISCUSSION:
Polystyrene material. Solution can be used to liquefy polystyrene pieces to be used as a coating or glue and as a general removal solvent. Used as a solvent in fabrication of silicon devices.
REF: Blankenship, J L & Borkowski, C J — *IRE Trans Nuc Sci,* NS-7,190(1960)

TIME:
TEMP: RT

POLYIMIDES

POLM-0001
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
Polyimides are used as a dielectric surface coating. In a study of metallization on device structures and dielectric coatings with a comparison of silica and polyimide parameters, HF was used to remove silica; H_2SO_4 to remove polyimides.

TIME:
TEMP: RT to hot

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Parameter	Silica	Polyimide
Resistivity (ohms-cm)	1016	1016
Dielectric strength (V μm)	200	135
M>P> (°C)	1710	475
Thermal conductivity (cal/cm-sec/°C)	5×10^{-3}	4×10^{-4}
Dielectric constant (K)	3.9	3.5

REF: Mastroianni, S T — *Solid State Technol,* March 1984, 155

PRINTED CIRCUIT BOARD ETCHANTS

PCB-0001
ETCH NAME: Ferric chloride — TIME:
TYPE: Acid, removal — TEMP: Hot
COMPOSITION:
x .... $FeCl_3$ (35°Bé)
DISCUSSION:
PCB, copper laminated plastic impregnated linen. Boards were etched in a rotating barrel system after photo resist patterning. Solution used to remove copper. After etching, DI water wash, MeOH rinse and air dry.
REF: Fahr, F — personal communication, 1978
PCB-0002: Valardi, N — personal communication, 1985
PCB, copper laminates. After pattern etching of boards, the insert contact fingers were gold plated.

PCB-0003
ETCH NAME: Freon TMS — TIME:
TYPE: Solvent, cleaning — TEMP: 97°F
COMPOSITION:
x .... Freon TMS, spray
DISCUSSION:
PCB, copper laminated and circuit etched boards. Boards were cleaned using a conveyor belt system passing the boards through a hot spray of Freon TMS.
REF: Allen Bradley brochure, 1978

PHYSICAL PROPERTIES OF PLATINUM, Pt

Classification	Transition metal
Atomic number	78
Atomic weight	195.09
Melting point (°C)	1769 (1773.5)
Boilint point (°C)	3800
Density (g/cm³)	21.45
Thermal conductance (cal/sec)(cm²)(°C/cm)	0.17
Specific heat (cal/g) 0°C	0.0314
Latent heat of fusion (cal/g)	26.9
Heat of fusion (k-cal/g-atom)	4.7
Heat of vaporization (k-cal/g-atom)	122
Atomic volume (W/D)	9.10
1st ionization energy (K-cal/g-mole)	207
1st ionization potential (eV)	8.96

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Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.30
Ionic radius (angstroms)	0.80 (Pt^{+2})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	9.1
Electrical resistivity (micro-ohms-cm) 20°C	9.85
Electron work function (eV)	5.32 (5.29)
Young's modulus (psi $\times 10^6$)	24.8
Magnetic susceptibility (cgs $\times 10^{-6}$)	1.1
Tensile strength (psi — annealed)	20.000
Poisson's ratio	0.39
Cross section (barns)	8.8
Vapor pressure (°C)	3714
Hardness (Mohs — scratch)	4—4.5
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Whitish steel-grey
Cleavage (fracture)	Hackly

PLATINUM, Pt

General: Occurs in nature as a native element. The major source of platinum is in the Ural Mountains of southern Russia and represents about 80% of the known platinum reserves in the world. In the Urals it occurs in igneous rocks of olivine called dunites as a product of magmatic differentiation. It is only found in small, scattered quantities in rock, the major amounts coming from associated placer deposits. It is found throughout the world in similar rock areas, and in gold placer deposits as fine, rounded grains of platinum. There are a few minerals containing platinum, mainly arsenates and antimonides, but they are not of minable quantity such that platinum metal is considered a rare element and is practically the only ore source. It has long had a higher monetary value than gold by about 20%. It rarely occurs as a pure metal, but contains trace amounts of other platinum family metals, such as osmium, iridium, rhodium, palladium, and iron. In the latter case it may appear to be magnetic, but this is due to the presence of iron, and is not an intrinsic property of platinum.

It has major industrial use as the pure metal due to its high temperature characteristics, electrical resistivity capability, and inertness to acids and atmospheres. Platinum is fabricated as wire, sheet, foil, powder, and special forms such as crucibles and beakers. As a very fine powder it is called "platinum black" with the capability of absorbing and holding large amounts of hydrogen, though palladium black is almost an order of magnitude better.

As paired wires, platinum and platinum:rhodium, it is a high temperature thermocouple and platinum alone is occasionally used as an electrical contact wire in special assemblies. Other uses include a high temperature crucible; wire, sheet, mesh or rod as the cathode in electrolytic plating and etching; rods, beads, and sponge as a catalyst in many chemical reactions; acid resistant tools; special plating on surfaces as a thin film; and others. Several of these uses apply to Solid State processing. It also is used in jewelry and for objets d'art, and occasionally as a coinage metal.

Technical Application: Not used in direct Solid State device fabrication by itself, but is used in thin film metallization in conjunction with silver, gold, nickel, and other metals for contact layers, and in the fabrication of substrate circuits on dielectrics such as alumina, beryllia, quartz, sapphire, etc. It is also used as a powder in conductive epoxy and polyimide pastes for mounting discrete devices in circuit assemblies.

Dielectrics, as capacitors, resistors, etc., use Pt/Au, Pt/Ni/Au, and other metallizations in their fabrication as discrete elements and platinum is used as a constituent in some alloys for high temperature soldering and brazing with application to semiconductor packages.

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Platinum is under development and investigation as a silicide: PtSi, Pt_2Si, and $PtSi_2$ for use as a buffer layer in semiconductor heterostructures.

As a single crystal it has been grown artificially for general physical data and morphological studies, and has been studied as a thin film deposit on silicon with diffusion into the material for electron mobility control similar to applications of gold.

Etching: Difficult to etch. Aqua regia and fused alkalies; possibly chrome regia, with chromic acid replacing nitric acid.

PLATINUM ETCHANTS

PT-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal
TIME:
TEMP: Boiling
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

Pt and Au evaporated on silicon, (111), n-type 35 Ω cm resistivity wafers grown by Float Zone (FZ). Phosphorus was diffused into one side; then boron diffused into the other side for a p-nn$^+$ diode. Pt diffused into p side, then diffused Au into n$^+$ side — both diffusions 40 min in N_2 with various temperatures. Etch clean both Pt and Au with aqua regia and use the solution to etch remove excess Pt and Au after diffusion. Etch clean silicon wafers prior to diffusion with HF:HNO_3.

REF: Saito, R et al — *J Electrochem Soc*, 132,224(1985)

PT-0004: Bulletin 1092 AMD/ID/JBA/5K/0482/GUILD/1982 — MRC

Pt specimens and thin films. Aqua regia used as a general surface cleaning mixture.

PT-0005: Brochure: *Platinum*, Baker & Co. (no date)

Pt, pure metal and alloy parts. Discusses physical characteristics of different alloys, their manufacture, and parts fabrication. Includes uses of platinum black as a thin film plating, and as a catalyst in chemistry. Additional discussion of other platinum family metals.

PT-0006: Wise, E M — *The Platinum Metals* (brochure) — The Int Nickel Co., 1954

Pt, pure metal and alloys as fabricated parts. Aqua regia used as a general etch for all platinum family metals: Ir, Re, Rh, Os, and Pd.

PT-0002
ETCH NAME: Nitric acid, dilute
TYPE: Acid, float-off
TIME:
TEMP:
COMPOSITION:
x .... HNO_3
x .... H_2O
DISCUSSION:

Pt, thin film deposited at 723 K for 1000—1200 Å thickness on muscovite mica. Shows a (111) fibrous axis. For TEM study of film morphology use solution to float-off from mica substrate.

REF: Dixit, P & Vook, R W — *Thin Solid Films*, 113,151(1984)

PT-0003
ETCH NAME: Iodine
TYPE: Halogen, passivation
TIME:
TEMP: >100°C
COMPOSITION:
x .... I_2, vapor

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DISCUSSION:

Pt, single crystal ingot. Specimen was cut on (111) for a six-sided (111) rhomboid solid, and then mechanically polished. Ar^+ ion sputter clean and then deposit iodine on surfaces from hot vapor. Iodine atoms absorb on platinum surfaces and passivate against attack of perchloric acid.

REF: Stickney, S L et al — *J Electrochem Soc*, 131,260(1984)

PT-0006

ETCH NAME: Sulfur — TIME:

TYPE: Metal, removal — TEMP: Molten

COMPOSITION:

x .... S, molten

DISCUSSION:

Pt, as thermocouple wires — paired — Pt and PtRh. Hot liquid sulfur will attack platinum. A steel heat pipe containing liquid sulfur at 800°C broke through a weld joint and etched down through the furnace lining, metal, table, and into the cement floor, destroying a dozen thermocouples in the process. (*Note:* Liquid sulfur and hot sulfur vapors actively attack almost all metals and metallic compounds forming sulfides and sulfates.)

REF: Zelinsky, T — personal communication, 1978

PLATINUM ALLOYS, PtM_x

General: The metal occurs as a native element, rarely, if at all, in a pure state, but usually contains traces of other platinum family elements . . . Os, Re, Pd, and Fe . . . in particular. Even when used in industry it is rarely as high purity platinum due to the difficulty of separating such extremely high temperature elements as osmium, rhenium, and rhodium. It can be said that platinum occurs as a natural metal alloy, in this sense.

There are specific platinum alloys fabricated in industry for particular applications, as already discussed under Platinum.

Technical Application: Platinum alloys are used in Solid State device design and fabrication as multilayer thin films for electrical contact purposes, in addition to being used as high temperature thermocouples, special chemical handling beakers, or molten flux crucibles.

Etching: Aqua regia.

PLATINUM ALLOYS

PLATINUM GOLD ETCHANTS

PTAU-0001

ETCH NAME: Aqua regia, dilute — TIME:

TYPE: Acid, removal/clean — TEMP: RT to hot

COMPOSITION:

3 .... HCl

1 .... HNO_3

20 .... H_2O

DISCUSSION:

Pt thin films used as a multilayer of Au/Pt/Cr evaporated or sputtered metallization electrical contact structure in silicon and gallium arsenide device fabrication. Aqua regia used as general cleaning etch for platinum group metals and gold. Used a highly diluted solution to lightly clean surfaces prior to gold wire bonding. Wash heavily with running DI water after etching, rinse in MeOH, and N_2 blow dry.

REF: Walker, P — personal application, 1979—1983

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PLATINUM PALLADIUM ETCHANTS

PTPD-0001
ETCH NAME: Aqua regia, dilute — TIME:
TYPE: Acid, clean/preferential — TEMP: RT to warm
COMPOSITION:
3 .... HCl
1 .... HNO_3
x .... H_2O
DISCUSSION:
Pt:Pd, thin films co-sputtered on (111) silicon, p-type 1—3 Ω cm resistivity substrates for a study of this alloy thin film. Substrates were cleaned: (1) degrease in solvents; (2) rinse in dilute HF, RT, three times, then (3) oxidize surface with $3HCl:1H_2O_2:1H_2O$ at 90°C, 10 min prior to PtPd deposition. Dilute aqua regia used to clean alloy surfaces with slight preferential attack after metallization.
REF: Kawarada, H — *J Appl Phys,* 57,344(1985)

PLATINUM RHODIUM ETCHANTS

PTRH-0001
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, cleaning — TEMP: RT to hot
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:
PtRh (2—15%), as thermocouple wires, and paired Pt:PtRh wires. Both materials can be etch cleaned with aqua regia. After bead fusion of the two wire ends (borax in electric discharge pot), water wash to remove borax flux, then dip clean in aqua regia with water washing after etch cleaning.
REF: Wise, E M — *The Platinum Metals* (brochure), The Int Nickel Co., 1954

PLATINUM HYDRIDE ETCHANTS

PT-0001
ETCH NAME: Aqua regia — TIME:
TYPE: Acid, clean — TEMP: RT
COMPOSITION:
3 .... HCl
1 .... HNO_3
x .... H_2O
DISCUSSION:
PtH as powdered "platinum black" with absorbed hydrogen. Powdered platinum can be cleaned with aqua regia with or without water dilution, then furnace dried under vacuum prior to introduction of hydrogen.
REF: Wise, E M — *The Platinum Metals* (brochure), The Int Nickel Co., 1954

PHYSICAL PROPERTIES OF PLATINUM ANTIMONIDE, $PtSb_2$

Classification — Antimonide
Atomic numbers — 78 & 51

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Atomic weight	447.6
Melting point (°C)	>1200
Boiling point (°C)	
Density (g/cm^3)	
Hardness: (Mohs — scratch)	6—7
Crystal structure (isometric — pyritohedral)	(100) pyritohedron
Color (solid)	Grey-white metal
Cleavage (cubic)	(001)

PLATINUM ANTIMONIDE, $PtSb_2$

General: Does not occur in nature as a metallic compound, but there are two arsenate minerals: sperrylite, $PtAs_2$ and cooperite, $Pt(As,S)_2$. Both are of minor occurrence and of no commercial use.

There is no use in industry other than its evaluation as a compound semiconductor.

Technical Application: Platinum antimonide is a V—VIII compound semiconductor with the pyrite, FeS_2, structure, and has been grown and doped p- and n-type for semiconductor characterization. Platinum arsenide, $PtAs_2$, along with $PtSb_2$ and several sulfide, selenide, and telluride compounds has been grown as single crystals and evaluated in an IR spectral study.

All metallic compounds in the isometric system, pyritohedral class tend to show stria on crystal plane oriented surfaces similar to natural pyrite. A common form of pyrite is a pseudo-cube (cube, (100) is normal class), but with a stressed lamellar structure. Such structure is less suitable for semiconductor device fabrication than other compound semiconductors that form in the isometric system, normal or tetrahedral classes, referenced to the sphalerite, ZnS, tetrahedron unit cell.

Etching: Soluble in HNO_3 and mixed acids.

PLATINUM ANTIMONIDE ETCHANTS

PTSB-0001a
ETCH NAME:
TYPE: Acid, preferential
TIME: 5 min
TEMP: 65°C
COMPOSITION:
1 .... HCl
1 .... HNO_3
DISCUSSION:

$PtSb_2$, (100), (111) and (110) wafers cut from a (100) grown ingot. The (100) wafers also were cleaved. Wafers used in a dislocation study. The following solutions were evaluated with the results as shown:

HCl, conc.	20 min	Boiling	No reaction
HF, conc.	20 min	Boiling	No reaction
HNO_3, conc.	20 min	Boiling	No reaction
H_2SO_4, conc.	7 min	160°C	Rough surfaces
H_2SO_4, conc.	10 min	100°C	Patterns (?)
H_2SO_4, conc.	14 min	80°C	No reaction

The mixed acid shown above was used as a cleaning solution, developed orientation etch pits on lapped surfaces, and segregation lines on polished surfaces.

REF: Sagar, A & Faust, J W Jr — *J Appl Phys,* 17,813(1966)

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PTSB-0001b
ETCH NAME: Aqua regia, dilute — TIME: 15 min
TYPE: Acid, preferential — TEMP: 70°C
COMPOSITION:
3 .... HCl
1 .... HNO_3
3 .... H_2O
DISCUSSION:
$PtSb_2$, (100), (110) and (111) wafers cut from (100) grown ingots. (100) wafers also were cleaved. Solution shown developed dislocation etch pits with segregation and slip lines on polished surfaces.
REF: Ibid.

PTSB-0001c
ETCH NAME: — TIME: 40 min
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... H_2O
DISCUSSION:
$PtSb_2$, (100), (110) and (111) wafers cut from (100) grown ingots. (100) wafers also were cleaved. Solution produced faint stria and possible etch pits (?), and left a film on surfaces (Sb?) that could be removed with ultrasonic agitation. The same solution used 3 min at 65°C developed a film that could not be removed with ultrasonic agitation.
REF: Ibid.

PTSB-0001d
ETCH NAME: — TIME: 7 min
TYPE: Acid, preferential — TEMP: 80°C
COMPOSITION:
1 .... HCl
1 .... H_2O_2
DISCUSSION:
$PtSb_2$, (100), (110) and (111) wafers cut from (100) grown ingots. (100) wafers also were cleaved. Solution shown produced faint stria but solution decomposition was too rapid for good control.
REF: Ibid.

PTSB-0001e
ETCH NAME: — TIME: 5 min
TYPE: Acid, preferential — TEMP: 60°C
COMPOSITION:
1 .... HF
1 .... H_2O_2
DISCUSSION:
$PtSb_2$, (100), (110) and (111) wafers cut from (100) grown ingots. (100) wafers also were cleaved. Solution showed possible patterns (?).
REF: Ibid.

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PTSB-0001f
ETCH NAME: TIME: Varied
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... CH_3COOH (HAc)
DISCUSSION:
$PtSb_2$, (100), (110) and (111) wafers cut from (100) grown ingots. (100) wafers also were cleaved. Solution shown produced structure on both p- and n-type wafers. Pits enlarged with extended etching and showed 1:1 correspondence. An etch mixture of $1HCl:1H_2O_2:2H_2O$ used 30 min at RT, showed no reaction.
REF: Ibid.

PTSB-0002
ETCH NAME: TIME: 5 min
TYPE: Acid, removal TEMP: 75°C
COMPOSITION:
1 .... HCl
1 .... HNO_3
1 .... H_2O
DISCUSSION:
$PtSb_2$, (100) wafers. Ingots, as grown, doped with Cu or Th are p-type; doped with Te, n-type. Surfaces lapped with 800-grit abrasive before etching. There is no etch action below 70°C.
REF: Miller, R C — *J Appl Phys*, 35,3582(1964)

PTSB-0003
ETCH NAME: Nitric acid TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
$PtSb_2$, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $CsTe_2$, PtS_2, and $PtAs_2$. All crystals have the cubic pyrite, FeS_2, structure and were used in an IR spectra study. (*Note:* Pyrite is not in the normal class of the isometric system, such that it is not "cubic".)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

PHYSICAL PROPERTIES OF PLATINUM ARSENIDE, $PtAs_2$

Classification	Arsenide
Atomic numbers	78 & 33
Atomic weight	345.05
Melting point (°C)	>800 del
Boiling point (°C)	
Density (g/cm^3)	10.60
Hardness (Mohs — scratch)	6—7
Crystal structure (isometric — pyritohedral)	(100) pseudo-cube

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Color (solid)	Tin-white
Cleavage (cubic/octahedral — indistinct)	(001)/(111)
(fracture)	Conchoidal

PLATINUM ARSENIDE, $PtAs_2$

General: Occurs in nature as the minerals sperrylite, $PtAs_2$, and cooperite, $Pt(AsS)_2$. The latter is orthorhombic — normal, H = 4—4.5 and G = 9, and with similar color and fracture as sperrylite. Both are mostly minor in occurrence, but have been found in the platiniferrous dunites of the Transvaal in Africa in minable quantities. Industrially important only as a source of platinum.

Technical Application: No use in Solid State processing other than being studied as a pyrite structured compound, although it may have some electronic characteristics of interest.

Etching: HNO_3, mixed acids $HCl:HNO_3$, $HF:HNO_3$.

PLATINUM ARSENIDE ETCHANTS

PTAS-0001
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:

$PtAs_2$, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsTe_2$, PtP_2, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2 and were used in a TR spectra study. (*Note:* Pyrite is not "cubic". It is in the isometric system, but pyritohedral class, not normal class, which also is referred to as the cubic class, based on the presence of the cube, (100) as one of the forms in this class.)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

PLATINUM OXIDE ETCHANTS

PTO-0001
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, removal/clean — TEMP:
COMPOSITION:
(1) x .... HCl, conc. (2) x .... H_2SO_4, conc.
DISCUSSION:

PtO, crystalline thin films deposited by reactive sputter in a structural study. PtO_2 as alpha-PtO_2 is space group Pnnm and beta-PtO_2 is P3m. Solutions shown are slow etchants for PtO and cleaning etchants for PtO_2.
REF: Westwood, W D & Bennewitz, C J — *J Appl Phys*, 45,2313(1974)
PTO-0002: Canart-Martin, M C et al — *Chem Phys*, 48,283(1980)

PtO, thin films deposited by reactive sputtering in a structural study.
PTO-0003: Moore, W J & Pauling, L — *Am Chem Soc*, 63,1392(1941)

PtO, crystalline bulk growth used for structural study.
PTO-0004: Schwartz, K B & Prewitt, C T — *J Phys Chem Solids*, 45,1(1984)

$PtOM_x$, single crystal material with other element constituents. A review article of the electronic properties of binary and ternary platinum oxides containing Ba, Sr, Tl, K, Ca, Co, H, Cd, Cu, and Zn. Some of these compounds show semiconducting properties.

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PLATINUM PHOSPHIDE ETCHANTS

PTP-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3
DISCUSSION:

TIME:
TEMP:

PtP_2, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsTe_2$, $PtAs_2$, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2, and were used in an IR spectra study. (*Note:* Pyrite is not "cubic", but in the isometric system-pyritohedral class, not normal class which contains the cube, (100) as a crystal form.)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

PHYSICAL PROPERTIES OF PLUTONIUM, Pu

Classification	Actinide
Atomic number	94
Atomic weight	244
Melting point (°C)	639.5
Boiling point (°C)	3235
Density (g/cm^3)	19.74
Specific heat (cal/g/°C) 25°C	0.034
Latent heat of fusion (cal/g)	3
Thermal conductivity ($cal/cm^2/cm/°C/sec$) 25°C	0.020
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	42.3
Electrical resistivity (ohm cm $\times 10^6$) 0°C	146.45
Ionic radius (angstroms)	0.93 (Pu^{+3})
Half-life (years $\times 10^7$)	7.6
Cross section (barns)	1.6
Hardness (Mohs — scratch)	4—5
Crystal structure (monoclinic — normal)	(100) a-pinacoid
Color (solid)	Silver white
Cleavage (basal)	(001)

PLUTONIUM, Pu

General: Plutonium is one of the radioactive decay elements from ^{238}U and ^{235}U. The latter was used as the atomic bomb in the first test in New Mexico and Hiroshima; ^{239}Pu Nagasaki, and the Bikini tests after World War II. Using graphite piles for control, the ^{239}Pu step is the primary operator for atomic piles and nuclear energy plants. Other uranium isotopes can be used, such as ^{233}U for ^{237}Pu from thorium disintegration, and two other elements have been discovered coincident with the development of atomic power: Americium, Am and Curium, Cu.

Since the end of World War I, nuclear research has developed many applications and products. There are over 100 nuclear power plants throughout the world, and their development has given world industry the necessary power to sustain the tremendous expansion of high technology as major electric power was previously from hydroelectric sources. Because atomic fission releases tremendous amounts of heat, nuclear power plants are located

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along large rivers or seacoasts. The radioactive by-products present a disposal problem, such that much effort is involved in developing alternate energy sources: wind, sun, and hydrothermal. Atomic piles are used as engines for nuclear submarines; all industrial nations have and are developing nuclear warheads as weapons. There is radiation therapy in medicine, as well as industrial equipment for radiation testing of materials as part of space hardware requirements, and irradiation is being developed in food preservation and processing.

Technical Application: Plutonium is not used directly in Solid State device processing, but atomic piles — such as Triga facilities — are used in reliability radiation testing of devices, parts, and assemblies. Many metals, alloys, and metallic compounds are subjected to irradiation studies with a wide range of nuclear and ionic particles. Semiconductor silicon radiation detectors have been fabricated for use in space, and radiation "hard" packages have been developed.

Etching: H_3PO_4 and mixed acids (electrolytic).

PLUTONIUM ETCHANTS

PU-0001
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... H_3PO_4
1 .... *$O(CH_2CH_2OH)_2$

TIME: 5—10 min
TEMP:
ANODE:
CATHODE: SST
POWER: 5 A/dm² & 5 V

*Diethylene glycol

DISCUSSION:

Pu specimens. Solution used as an electropolish.

REF: Tegart, W C McG — *The Electrolytic and Chemical Etching of Metals,* 2nd ed, Pergamon Press, London, 1959

POLYVINIDENE FLUORIDE, PVF_2

General: Does not occur as a natural compound. It has been fabricated artificially as a crystalline material with a polyvinyl base by replacing chlorine in polyvinyl chloride (PVC) with fluorine.

Technical Application: The material is under development as a possible lower cost and easily machinable compound as a replacement for ceramic transducers (barium titanate). It is shown to have piezo- and pyroelectric, as well as ferroelectric properties.

Etching: Strong acids and alkalies.

POLYVINIDENE FLUORIDE ETCHANTS

PVF-0001
ETCH NAME:
TYPE: Pressure, forming
COMPOSITION:
x .... pressure

TIME:
TEMP: Elevated

DISCUSSION:

PVF_2, polycrystalline material formed as sheet as a possible replacement for ceramic transducers. At RT the structure is nonpolar with orthorhombic structure. Above RT to 80°C there are beta and delta forms which are polar. The material will charge with application of pressure, heat, or electrical bias and, when poled, develop piezo-, pyro-, and ferroelectric

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characteristics. The material can be easily machined, unlike the more difficult cutting of barium titanate, $BaTiO_3$, a current major transducer used as an ultrasonic generator.
REF: Marcus, M A — *5th Int Meet on Ferroelectrics*, Pennsylvania State University, 17—21 August 1981

PHYSICAL PROPERTIES OF POTASH ALUM, $KAl(SO_4)_2.12H_2O$

Classification	Alum
Atomic numbers	19, 13, 16, 8 & 1
Atomic weight	333.94
Melting point (°C)	92
Boiling point (°C)	
Density (g/cm³)	1.76
Refractive index (n =)	1.43—1.452
Hardness (Mohs — scratch)	2
Crystal structure (isometric — normal)	(111) octahedron
Color (solid)	Colorless
Cleavage (cubic)	(001)

POTASH ALUM, $KAl(SO_4)_2.12H_2O$

General: Occurs in nature as the mineral potash alum, which is isometric with octahedral habit, and as the mineral kalinite, thought to be monoclinic and of the same composition as potash alum. The alum group of minerals are hydrous sulfates of aluminum and an alkali metal with 12 molecules of water (may be 24 if formula is doubled). The potassium (K) can be replaced with NH_4 (tschermigite) or sodium, Na (soda alum). With 22 molecules of water, a similar group of halothrichite alums are magnesia alum (pickeringite); iron alum (halotrichite); and manganese alum (apjohnite). There are over 50 minerals of this general type. The mineral alunite, $K_2Al_6(OH)_{12}(SO_4)_4$ is called "alumstone", and if it contains considerable soda: natroalunite. *Note:* Natron is sodium carbonate, Na_2CO_3, used by the ancient Egyptians for mummification, hence the symbol for sodium, Na.

Most alums are of secondary origin from the weathering of sulfur-bearing rocks and minerals; from sulfuric acid in ground waters, often associated with volcanoes, or from oxidation of sulfur-bearing rocks, and may occur with bituminous and argillaceous materials.

Both natural and artificially grown alums are used in industry as metal growth and alloying fluxes and in textile, leather making, and dying. In medicine they are used as astringents and styptics, and are also used in food preparation. Note that alum is the material that will make the mouth pucker.

Technical Application: No use in Solid State fabrication of devices, although some alums are additives in solder fluxes. Single crystals of different alums have been grown for a variety of studies.

Etching: Completely soluble in hot water and soluble in dilute acids.

ALUM ETCHANTS

ALUM-0001
ETCH NAME: Water — TIME: 1—2 sec
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
x .... H_2O, deionized
DISCUSSION:
Alum, single crystals grown from a saturated solution started at 80°C. Reduce temper-

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ature to 25°C (near RT), and evaporate for 30 h to slowly form large single crystals. Etch pits developed with deionized water (DI H_2O) are very similar to those observed on diamonds as trigonal pits.
REF: Omar, M & Youssef, T H — *Phil Mag*, 6,791(1961)

ALUM-0002
ETCH NAME: Water — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
Alum, (111) wafers used in a study of dissolution kinetics and defects. Water used for general removal and etch pit development.
REF: Van der Hoek, B et al — *J Cryst Growth*, 61,181(1983)

PHYSICAL PROPERTIES OF POTASSIUM, K (POTASH)

Classification	Alkali metal
Atomic number	19
Atomic weight	39.10
Melting point (°C)	63.7
Boiling point (°C)	760 (774)
Density (g/cm^3) 20°C	0.862
(g/cm^3) 62°C	0.83
Thermal conductance (cal/sec)(cm^2)(°C/cm) 200°C	0.107
(cal/sec)(cm^2)(°C/cm) 21°C	0.232
Specific heat (cal/g) 25°C	0.177
Heat of fusion (cal/g)	14.6
Heat of vaporization (cal/g)	496
Atomic volume (W/D)	45.3
1st ionization energy (K-cal/g-mole)	100
1st ionization potential (eV)	4.339
Electronegativity (Pauling's)	0.8
Covalent radius (angstroms)	2.03
Ionic radius (angstroms)	1.33 (K^{+1})
Electrical resistivity (micro-ohms-cm) 20°C	21.85
($\times 10^{-6}$ ohms cm) 0°C	6.15
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	83
Electron work function (eV)	2.15
Cross section (barns)	2.1
Vapor pressure (°C)	568
Hardness (Mohs — scratch)	0.5
Crystal structure (isometric — normal)	(100) cube, bcc
Color (gas — K^+ ion)	Colorless
(solid)	Silver, metal
Flame color (solid/compounds)	Violet
Cleavage (cubic)	(001)

POTASSIUM, K

General: Potassium does not occur free in nature. It is the eighth most abundant element

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in the earth's crust — over 2% — and is found as an element in over 60 minerals and comprises over 300 artificial compounds. The feldspar minerals as a group (orthoclass, $KAlSi_3O_8$) as an example, are major rock-forming minerals, such as in granites, and the weathering of such rocks produces clays, which are a basic constituent of most sedimentary rock formations — earth, e.g., ordinary dirt contains a high percentage of "potash" as potassium is insoluble in water. Most of the potassium-bearing minerals are insoluble and difficult to reduce for potassium removal. Sylvite, KCl, is an exception — it is soluble in water and is similar in many respects to halite, NaCl — both being reversible compounds as they can be easily liquefied and then recrystallized. Both sylvite and the mineral carnallite, $KMgCl_3.6H_2O$, although they are more rare than halite (common salt), occur in extensive salt-beds in Germany, France, and the western U.S. Sylvite, as the mineral, is extensively used as a fertilizer.

Although potassium compounds are not as widely used as sodium compounds due to cost, most of the potassium compounds do not deliquesce as do their corresponding sodium salts. It is interesting to note that soda-lime glass is soft (standard window glass); whereas potash glass is hard. In the soap industry sodium soaps are hard and potassium soaps are soft, as pastes or liquids.

Sylvite, in addition to being a source of potassium and chlorine, is not retained in the body as is common salt — halite, NaCl, such that it is used as a dietary supplement for salt and is called "sea salt".

Potassium nitrate, KNO_3 — the natural mineral soda niter, is called Chile saltpeter or niter — as it occurs in great quantities in the Chilean deserts in addition to many other desert areas of the world. Potassium nitrate is a very active oxidizer, is not deliquescent, and is used in the manufacture of matches, detonators, percussion caps, and pyrotechnics, e.g., the violet color of the potassium flame.

As the pure metal, potassium is soft, with a silvery luster. Chemically, it is similar to sodium, and is more active. In contact with cold water, it reacts explosively with the liberation of hydrogen, and will burn with its characteristic violet flame. It is stored in kerosene.

The name potash is from English, but the chemical symbol, K, comes from the Latin, kalium. An item of interest: the mineral kaolin, $H_4Al_2Si_2O_9$, which is representative of the kaolin division of clays, is named from the Chinese, kauling. Although not potassium containing, the minerals montmorillonite and bentonite — which may be admixtures with kaolinite — are clay minerals that, when dried, will absorb large quantities of water. They are widely used as casing sealers in oil wells as the clay will expand and harden with water adsorption.

Technical Application: Potassium metal is not used in the direct fabrication of Solid State devices, although several potassium compounds are used in etchants as replacements for similar sodium compounds as potassium does not act as a contaminating species as does sodium on silicon wafers.

Some of the more prominent compounds used in etching solutions are potassium hydroxide, KOH; potassium chloride, KCl; potassium nitrate, KNO_3; and potassium permanganate, $KMnO_4$. Both the hydroxide and chloride are also used as molten flux etches or as growth fluxes for some ferrites and similar metallic compounds.

Etching: Burns in contact with water. Deliquesces in alcohol. Soluble in acids and ammonia.

POTASSIUM ETCHANTS

K-0001
ETCH NAME: Ethyl alcohol — TIME: 30 sec
TYPE: Alcohol, polish — TEMP: RT
COMPOSITION:
(1) x .... CH_3CH_2OH (EOH) (2) x .... $CH_3CHOHCH_3$ 2-propanol (ISO, IPA)

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DISCUSSION:

K specimens cut with a razor blade under oil, then into heptane to remove oil, and into tetrahydrofuran to stop heptane action. Ten alcohols evaluated. Increase of molecular weight reduces reaction. Both solutions shown produce brilliant and smooth surfaces within 30 sec. MeOH produces too violent a reaction for control. Other alcohols developed dull and pitted surfaces — one — alpha-alpha dimethylphenethyl, a purple surface. Also worked with lithium and sodium. See LI-0006 and NA-0002.

REF: Castellano, R N & Schmidt, P H — *J Electrochem Soc*, 118,653(1971)

K-0002

ETCH NAME: TIME:

TYPE: Alcohol, polish TEMP:

COMPOSITION:

99% .... $C_6H_4(CH_3)_2$ (*o*-toluene)

1% .... C_3H_7OH (isopropyl alcohol IPA, ISO)

DISCUSSION:

K specimens. Solution used as a polish etch and to develop grain boundaries. Requires critical timing and control.

REF: Grimes, C C — Doctoral dissertation, University of California, 1962

K-0003

ETCH NAME: TIME:

TYPE: Alcohol, polish TEMP:

COMPOSITION:

x .... $C_6H_4(CH_3)_2$ (*o*-xylene)

x .... 2—6% $CH_3CH_2CHOHCH_3$ (2-butyl alcohol)

DISCUSSION:

K specimens. Solution shown as a general and polish etch for potassium.

REF: Hoyte, A F & Mielczarek — *Appl Mater Res*, 4,121(1965)

K-0004: Foster, H J & Meijer, H E — *J Res Mater Stand*, 71A,127(1967)

K, specimens. Solution applied as a general etch for potassium.

K-0005

ETCH NAME: TIME:

TYPE: Keytone, polish TEMP:

COMPOSITION:

x .... methyl ethyl ketone (MEK)

DISCUSSION:

K specimens. MEK used as a polish etch for potassium.

REF: Schmidt, P H & Rupp, L W Jr — unpublished work, 1971

PHYSICAL PROPERTIES OF POTASSIUM BROMIDE, KBr

Classification	Bromide
Atomic numbers	19 & 35
Atomic weight	119
Melting point (°C)	730
Boiling point (°C)	1380 (1435)
Density (g/cm^3)	2.75
Refractive index (n =)	1.559
Wavelength limits (microns)	0.2—32

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Young's modulus (psi $\times 10^6$)	3.9
Coefficient of linear thermal expansion (10^6 cm/cm/°C)	41
Hardness (Mohs — scratch)	1—1.5
(Knoop — kgf/mm^2)	6
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
Cleavage (cubic)	(001)

POTASSIUM BROMINE, KBr

General: Does not occur in nature as a compound although there are some silver bromides and chlorobromides. As pure bromine it is a liquid at room temperature, has a low boiling point, and does not easily form solid compounds; it is extracted from ocean water and ground water in some areas, such as the Piedmont alluvial plains of the eastern U.S. Compounds of chlorine, bromine, iodine, and fluoride are the haloids of mineralogy or the halogens of chemistry.

Not used in the metals industries other than in cleaning and etching solutions. There are medical and chemical applications.

Technical Applications: Not used in Solid State devices design although it is used in some etching solutions.

Like some of the chlorides, potassium bromide has been used as a cleaved, (001) substrate for metal evaporation and semiconductor epitaxy growth of thin films in morphological studies. Also, as a single crystal it is used for its optical properties as special lenses and filters. Requires special housings and handling as it is hygroscopic and very soft.

Etching: Partially soluble in water and alcohols and completely soluble in glycerine. Can be controllably etched in some acids.

POTASSIUM BROMIDE ETCHANTS

KBR-0001
ETCH NAME: Water — TIME:
TYPE: Acid, polish — TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:

KBr, (100), cleave wafers used as substrates for epitaxy growth of materials and metal evaporation studies. The compound is hygroscopic and soft. Polish surfaces with water. In addition to use as a substrate, it is used for its infrared transmission capabilities in studies and as an operational device.

REF:
KBR-0004: Stoloff, N S et al — *J Appl Phys*, 34,3315(1963)

KBr and KBr:KCl single crystals use in a study of temperature effects on deformation. Specimens were acid saw cut with a water soaked string passed through water, then across the boule. Water was then used to lap and mill specimens to size, followed by water polishing of surface.

KBR-0002
ETCH NAME: Glycerin — TIME:
TYPE: Alcohol, removal — TEMP: RT
COMPOSITION:
x .... $C_3H_5(OH)_3$ (glycerine or glycerol)
DISCUSSION:

KBr specimens. This type alcohol can be used to etch remove or polish the bromide.

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REF: Hodgman, C D — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, OH, 1943, 430

KBR-0003a
ETCH NAME: Acetic acid — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... CH_3COOH (HAc)
DISCUSSION:
KBr, (100) cleaved wafers used in a dislocation study. Solution used to develop dislocations. This article includes etchants for other alkali halides: NaCl, KCl, and KI.
REF: Moran, P R — *J Appl Phys*, 29,1768(1958)

KBR-0003b
ETCH NAME: Potassium chloride — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... KCl
x .... H_2O
DISCUSSION:
KBr, (001) wafers cleaved and used in developing dislocation etching techniques. Concentration of solution not shown, but was used to develop dislocations in the material.
REF: Ibid.

KBR-0004
ETCH NAME: — TIME:
TYPE: Solvent, polish — TEMP:
COMPOSITION:
x .... Linde A alumina
x .... kerosene
DISCUSSION:
KBr and KI single crystal specimens used in a study of nuclear magnetic resonance and acoustic absorption. Specimens initially ground down, then lapped with $303^1/_2$ A/O abrasive. Final polish with slurry shown. The Linde A alumina was referred to as sapphire. (*Note:* Alumina, Al_2O_3, is finely powdered from common or ordinary natural single crystal corundum as a mineral; rarely are the highly valued natural gem stones used, such as red ruby or blue sapphire. The colorless manmade artificial sapphire may be the reference for sapphire, above.)
REF: Bulef, D I & Menes, M — *Phys Rev*, 114,1441(1959)

PHYSICAL PROPERTIES OF POTASSIUM CHLORIDE, KCl

Classification	Chloride
Atomic numbers	19 & 17
Atomic weight	74.6
Melting point (°C)	776
Boiling point (°C)	1500 (sublimes)
Density (g/cm³)	1.98
Refractive index (n=)	1.490
Hardness: (Mohs — scratch)	2
Crystal structure (isometric — normal)	(100) cube

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Color (solid)	Clear/white
Cleavage (cubic — perfect)	(001)

POTASSIUM CHLORIDE, KCl

General: Occurs in nature as the mineral sylvite, KCl. It is a water-soluble salt of potassium and is deposited from hot waters associated with fumaroles, volcanoes, and hot springs. It is a major compound in ocean water though not as abundant as halite, NaCl — common salt. Both of these chlorides are found in desert regions in the soil along sporadic stream and river beds, in dry lake deposits and, in some areas, as subsurface, buried "salt" deposits from the dehydration of shallow, ancient sea-beds. Because of their abundance, particularly in arid areas, they have "salted" the ground to the extent that plants and grasses will not grow without heavy leaching of the soil for their removal. With the building of the Aswan Dam on the upper Nile River in Egypt, the river no longer overflows it banks annually depositing a fresh layer of soil, and farming has been drastically reduced due to the effects of "salting". A similar situation exists in the Indus Valley where, in an attempt to increase the subsurface water table for year-round crops, the desert ground has become useless due to an increase in salt content as the high-level water table was established. Although sylvite is called clear/white in color in the Properties table above, it very commonly contains streaks of yellow and red giving the mineral distinctive colors; whereas halite tends to have blue spots and streaks. In either case, it is probably due to concentrations of potassium or sodium atoms, respectively, as well as other impurities.

Mammillary life requires salt — sodium chloride (halite) — as body fluids are an electrolytic solution, but excess salt leads to obesity because the body will retain it in higher and higher concentrations. On the other hand, the body will not accumulate potassium chloride (sylvite), but will eliminate this form of salt. Therefore — sylvite — is used as a dietary control and is often commercially called "sea salt".

In industry both of these salts are used as molten fluxes and as liquid solutions in soldering and as etchants for several metals. They also are used in fertilizers as plant life also requires sodium and potassium in addition to the animals who use the plants as food.

Technical Application: Not used in Solid State device fabrication, proper, though several etchant solutions may contain potassium chloride.

As a single crystal, (001) cleaved substrate, both natural and artificial potassium chloride have been used for metal deposition and epitaxy growth of metallic compounds for morphological studies. The deposited thin films can be easily removed by the float-off technique using water to liquefy the salt substrate/deposit interface.

Single crystals have been the subject of much study. Crystals are transparent and clear, easily deformed physically to produce slip and dislocations, produce color centers by irradiation, and so forth. Such effects can be easily observed and related to similar effects in the solid and opaque metals and metallic compounds. Much of the initial developmental study and theories of the defect state of inorganic matter has been established within the last half century (since about 1940) using both sylvite and halite as the study vehicles.

Etching: Easily etched in water, acids, alkalies.

POTASSIUM CHLORIDE ETCHANTS

KCL-0001

ETCH NAME: Methyl alcohol	TIME:
TYPE: Alcohol, clean	TEMP:

COMPOSITION:

x .... MeOH

DISCUSSION:

KCl, (100) wafers cleaved and used as substrates for Hot Wall Epitaxy (HWE) deposition

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of PbTe thin films. Etch polish and clean KCl surfaces with MeOH immediately before placing in vacuum system for epitaxy growth.
REF: Vaya, P R et al — *Solid State Electron,* 27,553(1984)

KCL-0002a
ETCH NAME: Ethyl alcohol — TIME: Dip
TYPE: Alcohol, polish — TEMP: RT
COMPOSITION:
x .... EOH
DISCUSSION:
KCl, (100) cleaved wafers used in a dislocation etching study. Solution used to polish surfaces. Rinse in CCl_4.
REF: Barr, L W & Morrison, J A — *J Appl Phys,* 31,617(1960)

KCL-0003a
ETCH NAME: Water — TIME:
TYPE: Acid, forming — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
KCl, single crystal specimens used to fabricate filaments and points. Coat areas to become filaments with glyptol, (1) immerse in water for initial forming, and then (2) in a saturated solution of KCl. Rinse in ethyl alcohol (EOH). Also used on other alkaline halide crystals.
REF: McNulty, J et al — *Rev Sci Instr,* 31,904(1960)

KCL-0003b
ETCH NAME: Potassium chloride — TIME:
TYPE: Acid, forming — TEMP:
COMPOSITION:
x .... KCl, sat. sol.
DISCUSSION:
KCl, single crystal specimens used to fabricate filaments and points. See KCl-0003a for discussion. The material can be etched in a concentrated solution of itself.
REF: Ibid.

KCL-0004
ETCH NAME: — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... *25% $BaBr_2$
x .... EOH

*Mix as a saturated solution.

DISCUSSION:
KCl, (001) cleaved wafers used in developing dislocation etching techniques. Use solution shown to develop dislocations. After etching, rinse in ether. (*Note:* There is a question as to what or which is a saturated solution?)
REF: Moran, P R — *J Appl Phys,* 29,1768(1958)

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KCL-0005
ETCH NAME: Moist air
TYPE: Acid, defect
COMPOSITION:
x .... air
TIME:
TEMP:
DISCUSSION:
KCl, formed as dendritic structure by placing a concentrated solution on a glass plate and cooling rapidly, (with LN_2?). NaCl and a 1KCl:1NaCl mixture also studied. Pit structure that develops around dislocations may be due to etching action of moist air. Dark spots at center of dislocations could be due to impurities or other salt nucleating elements.
REF: Forty, A J & Gibson, J G — *Acta Metall*, 6,137(1958)

KCL-0006
ETCH NAME: Ferric chloride
TYPE: Acid, preferential
COMPOSITION:
x .... x% $FeCl_3$
TIME:
TEMP:
DISCUSSION:
KCl, (100) wafers. Solutions of ferric chloride referred to as dislocation etchants for ionic crystals.
REF: Gilman, J J — *J Appl Phys*, 32,739(1961)

KCL-0002b
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
3 g .... $FeCl_3$
1000 ml .... EOH
TIME:
TEMP:
DISCUSSION:
KCl, (100) cleaved wafers used in a dislocation study. After polishing in pure EOH, this solution used to develop etch pits. The OH^- radical locations appear to act as impurity centers (?).
REF: Ibid.

KCL-0002c
ETCH NAME: Chlorine
TYPE: Gas, preferential
COMPOSITION:
x .... Cl_2
TIME: 48 h
TEMP: 700°C
PRESSURE: 500 mmHg
DISCUSSION:
KCl, (100) cleaved wafers used in a dislocation study. Hot chlorine vapors will develop square etch pits along crystal sub-boundaries.
REF: Ibid.

KCL-0007
ETCH NAME: Hydrochloric acid
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... HCl, conc.
(2) x .... C_3H_7OH (isopropyl alcohol, IPA)
TIME:
TEMP:

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DISCUSSION:

KCl, (100) specimens used in a study of laser induced irreversible absorption changes at 10.6 μm. HCl used to clean surfaces, then rinsed in ISO (IPA). Also studied NaCl.
REF: Wu, S T & Bass, H — *J Appl Phys Lett,* 39,948(1981)

KCL-0008
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
TIME:
TEMP:
DISCUSSION:

KCl, (111) and (100) cleaved wafers used as substrates for growth of Al thin films. Some films converted to AlN by N^+ ion implantation. Prepare KCl substrates: (1) mechanical polish; (2) wash and polish in water; (3) rinse in acetone. On (111) KCl Al was wurtzite structure (fcc); on (100), cubic (100). Water also used to float-off aluminum thin films for TEM study.
REF: Kimura, K et al — *Jpn J Appl Phys,* 23,1145(1984)

PHYSICAL PROPERTIES OF POTASSIUM IODIDE, KI

Classification	Iodide
Atomic numbers	19 & 53
Atomic weight	166
Melting point (°C)	723
Boiling point (°C)	1420 (1330)
Density (g/cm^3)	3.13
Refractive index (n =)	1.677
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cubic
Color (solid)	White
Cleavage (cubic)	(001)

POTASSIUM IODIDE, KI

General: Does not occur as a free natural compound as it is very water soluble, but is found in small quantities in seaweed. There are few iodide minerals as most metallic iodides are water soluble, but there are silver and copper minerals: marshite, CuI; iodyrite, AgI; miersite, 4AgI.CuI; and iodobromilite, a mixture of iodine/bromine. Sodium iodate, $NaIO_3$, is a major commercial source of iodine as it is found in Chilean saltpeter, and potassium iodide collected from Pacific kelp.

Both inorganic- and organic-derived iodide are used in medicine, chemistry, and photography with tincture of iodine as a germicide.

There are no major uses in the metal industry other than as a constituent in etch solutions, such as the tri-iodide etch for gold. A mixture of I_2:KI:EOH is tincture of iodine used as a medical antiseptic.

Technical Application: No major use in Solid State processing to date, though single crystal KI blanks have been used as substrates for metal and metallic compound thin film deposition in conjunction with the float-off technique for TEM structural studies of the films. The other use is in the tri-iodide etch solution already mentioned.

The compound has been grown as a single crystal for general morphological study and substrate applications.

Etching: Soluble in water and alcohols or ether.

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POTASSIUM IODIDE ETCHANTS

KI-0001
ETCH NAME: Water
TYPE: Acid, removal
COMPOSITION:
x .... H_2O
TIME:
TEMP:
DISCUSSION:
KI, (100) wafers cleaved in ultra-high vacuum, UHV. Substrates used for thin film evaporation of silicon, 300 Å thick. Silicon film was removed for TEM study from KI substrate by dissolving the substrate in water.
REF: Nugashima, S & Ogura, I — *Jpn J Appl Phys*, 23,1555(1985)

KI-0002
ETCH NAME: Methyl alcohol
TYPE: Alcohol, polish
COMPOSITION:
x .... MeOH
TIME: 30 sec
TEMP: RT
DISCUSSION:
KI, (100) wafers used in a study of X-ray irradiation. Surface was mechanically lapped with Linde B abrasive and MeOH was used to etch remove residual work damage and polish.
REF: Makris, J J — *Jpn J Appl Phys*, 52,1251(1983)
KI-0004: Ma, C H & Makris, J J — *Jpn J Appl Phys*, 53,1930(1984)
KI, (001) wafers used in a study of X-irradiation. Mechanically lap surfaces on 4/0 emery paper and finish with Linde B alumina as a polish until the water slurry is dry. Use alcohol solution to remove residual lap damage and final polish surfaces.

KI-0003
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME: 10 h
TEMP: 723°C
DISCUSSION: KI, growth method used for optical absorption studies. Weld two quartz plates together with about a 0.2 μm gap. Liquefy KI powder and percolate at 723°C allowing surface tension to draw liquid into the quartz plate gap. Anneal 10 h. The KI single crystal sheet developed is about 0.2 μm thick.
REF: Hashimoto, S — *J Phys Soc Jpn*, 53,1930(1984)

KI-0005a
ETCH NAME: Isopropyl alcohol
TYPE: Alcohol, preferential
COMPOSITION:
x .... C_3H_7OH (isopropanol, IPA, ISO)
TIME:
TEMP:
DISCUSSION:
KI, (100) cleaved wafers used in developing dislocation etching techniques. Etch in solution shown and rinse with CCl_4.
REF: Moran, P R — *J Appl Phys*, 29,1768(1958)

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KI-G005b
ETCH NAME: Pyridine TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... N:NCH:CHCH:CHCH:CH
DISCUSSION:
KI, (100) cleaved wafers used in developing dislocation etching techniques. Etch with solution shown and rinse in CCl_4.
REF: Ibid.

KI-0006
ETCH NAME: TIME:
TYPE: Solvent, polish TEMP: RT
COMPOSITION:
x .... Linde A alumina
x .... kerosene
DISCUSSION:
KI and KBr single crystal specimens used in a study of nuclear magnetic resonance and acoustic absorption. Specimens were initially ground down, then lapped with $303^1/_2$ A/O abrasive. Final polish in slurry shown.
REF: Bulef, D I & Menes, M — *Phys Rev,* 114,1441,(1959)

POTASSIUM MANGANESE FERRITE ETCHANTS

KMI-0001
ETCH NAME: Ferric chloride TIME:
TYPE: TEMP:
COMPOSITION:
x .... 35% $FeCl_3$
DISCUSSION:
$KMnFe_3$, single crystal sphere cut from an ingot and oriented by X-ray. Used in a nuclear magnetic resonance study. Solution shown can be used as a general cleaning and partly preferential etchant.
REF: Schulman, R G & Knox, K — *Phys Rev,* 119,99(1960)

POTASSIUM TANTALATE ETCHANTS

KTO-0001
ETCH NAME: TIME:
TYPE: Abrasive, polish TEMP:
COMPOSITION:
x .... c-Al_2O_3
DISCUSSION:
$KTaO_3$, iron doped single crystal wafer sections cut as parallel pipeds used for photochromism characteristics as optical memory devices. Iron doping produces Fe^{+4} and Fe^{+5} centers. After cutting, polish specimens with colloidal alumina. Also studied $SrTiO_3$. Materials were grown by a molten flux method and doped with either iron or nickel. PbSn solder used as electrical contacts.
REF: Yamaichi, E et al — *Jpn J Appl Phys,* 23,867(1984)
KTO-0002: Ohi, K — *J Phys Soc Jpn,* 40,1371(1976)
$KTaO_3$, crystals. Reference for method of flux growth.

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PHYSICAL PROPERTIES OF PRASEODYMIUM, Pr

Classification	Lanthanide
Atomic number	59
Atomic weight	140.9
Melting point (°C)	935
Boiling point (°C)	3127
Density (g/cm^3)	6.78
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.028
Specific heat (cal/g) 25°C	0.048
Heat of fusion (k-cal/g-atom)	1.60
Latent heat of fusion (cal/g)	11.71
Heat of vaporization (k-cal/g-atom)	79
Atomic volume (W/D)	20.8
1st ionization energy (K-cal/g-mole)	133
1st ionization potential (eV)	5.76
Electronegativity (Pauling's)	1.1
Covalent radius (angstroms)	1.65
Ionic radius (angstroms)	1.06 (Pr^{+3})
Electrical resistivity (micro-ohms-cm) 298 K	68
Compressibility (cm^2/kg $\times 10^{-6}$)	3.21
Magnetic moment (Bohr magnetons)	3.56
Tensile strength (psi)	15.900
Yield strength (psi)	14.500
Magnetic susceptibility (emu/mole $\times 10^{-6}$)	5.320
Transformation temperature (°C)	795
Standard electrode potential (eV)	+2.2
Cross section (barns)	12
Electron work function (eV)	2.7
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Pale yellow metal
Cleavage (basal)	(0001)

PRASEODYMIUM, Pr

General: Does not occur as a native element. It is one of the rare earth elements in the lanthenium series, and found in the mineral monazite, a phosphate of cerium metal, essentially (Ce,La,Di)PO_4. Didymium, Di, was considered an element until 1885 when it was separated into two elements: praseodymium and neodymium with their salts, green and pink, respectively. Neither element has had any major use in industry, to date.

Technical Application: The element has not been used in Solid State processing to date, although it has been grown as a single crystal in general materials studies.

Etching: HNO_3, and other acids.

PRASEODYMIUM ETCHANTS

PR-0001
ETCH NAME: Nitric acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... HNO_3
x .... H_2O

TIME:
TEMP:

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DISCUSSION:

Pr, (0001) wafers used in a diffusion study of cobalt, silver, and gold. Solution used to dissolve the material.

REF: Dariel, M F et al — *J Appl Phys,* 40,274(1969)

PR-0002

ETCH NAME: Electricity

TYPE: Arc, forming

TIME:

TEMP: Elevated

COMPOSITION:

x .... heat

DISCUSSION:

Pr, specimens arc melted as buttons then machined into cylinders. Diameters were from $^{3}/_{16}$ to 2″. Used for measurement of electrical resistivity. Other materials evaluated were La, Nd, and Sm.

REF: Alstad, J K et al — *Phys Rev,* 122,1636(1961)

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PHYSICAL PROPERTIES OF QUARTZ, SiO_2

Classification	Oxide
Atomic numbers	14 & 8
Atomic weight	60.06
Melting point (°C)	1470
Boiling point (°C)	2230 (2500)
Density (g/cm³)	2.6—2.66
Refractive index (n =)	1.54418/1.55328
Hardness (Mohs — scratch)	7
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid — rock crystal)	Colorless
Cleavage (rhomb — indistinct)	$r(10\bar{1}1)$
Fracture (solid)	Conchoidal

QUARTZ, SiO_2

General: One of the most abundant natural minerals in the world as water-washed grains of sand and compacted sandstone. The alpha-quartz single crystal variety is far more abundant than is the high temperature beta-quartz form. Clear single crystals of alpha-quartz are called rock crystal; with purple tint, amethyst; tinted yellow, citron; transparent green, emerald quartz; blue, sapphire quartz; with carbon inclusion, smokey quartz, and others. Other than as semi-precious and precious gem stones, massive quartzite is a building stone, as is sandstone, and sand is a constituent of cement.

Other than as a source of silica, SiO_2, in the glass industry, quartz wedges are used in microscopes for color birefringence, and as polarizing lenses and filters.

Since the invention of the radio, using natural galena, PbS, as the frequency crystal, natural alpha-quartz became the replacement in the early 1920s. This natural quartz forms in a left- and right-handed orientation, and is subject to penetration twinning, and such twinning must be removed or frequency is lost. The best placer deposited, water-washed chunks of alpha-quartz come from Brazil, are relatively low in twinning, and have been the major source of quartz frequency blank material for over 60 years.

Artificial alpha-quartz is replacing the natural stone as it can be grown with controlled orientation, be of higher purity, and free of twinning. Crystals are grown in a vertical pressure autoclave with a temperature gradient. The liquidized silica (chips of natural stone, not sand) in a KOH slurry at bottom and better than 800°C, an oriented seed crystal at the top around 500°C, and under pressures from 20,000 to 40,000 psi. It takes about a month to grow a 1 × 2 × 6 in. crystal. Note that sand is not used as it tends to agglomerate as a gel, and does not vaporize well.

See Table 1 for the natural forms of quartz. Only the main modifications with individual names are shown, and the table does not include the some 80 varieties of quartz, as precious and semi-precious gem stones.

Technical Application: Alpha-quartz crystal blanks are cut off Z-axis at different degrees of angle to obtain specific frequency ranges with the "cuts" letter designated: AT, DT, BT, X, Y, and others. The initially square blanks are then lathe ground to a specific diameter or rectangularly cut, followed by mechanical lap and polish, and surface structuring may be involved. As an example, the AT cut is the smallest round blank and the thinner or more highly polished, the higher the frequency (from 1st to 5th order) with 80 MHz capability with relative ease. The BT cut, on the other hand, is about $^1/_2$" in diameter with one side curved like a lens for about 5 MHz. All quartz crystals have a physical atomic motion when electrically activated that can then be converted to an electrical frequency pulse of controlled magnitude. Generally speaking, in a round blank, the motion is vertical; whereas in a

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rectangular blank it is a horizontal push-pull motion. The round types are primarily radio frequency crystals, some of the rectangular blanks, the quartz crystal watch operators.

After mechanical fabrication, the quartz blank is etch-tuned to near its desired frequency, then opposed metal electrodes are evaporated and, finally, metal sputter-tuned to final frequency before package mounting. Gold, silver, and aluminum are the primary metal electrodes, but BeAl and pure beryllium have been used to reduce the mass-loading effect on the crystal operation. The less weight of metal, the better frequency control, where frequency shifts are evaluated to as little as one cycle shift in 5 years!

As already mentioned, quartz blanks, alone, are frequency crystals for radio and watch operation, but can be combined with discrete semiconductor circuits as electronic oscillators, filters, and similar devices. Cadmium sulfide, CdS, single layer, and reversing layers deposited as thin films on quartz blanks, such as CdS:SCd:CdS alternating layers for additional piezoelectric operations and functions.

Artificial single crystal or fused quartz blanks are used as circuit substrates in Solid State processing or in special development, such as SiO_2:H thin film depositions, and are included, here. Silicon dioxide, SiO_2, as a thin film in semiconductor type processing is covered separately, as are some other single crystal forms: Cristobalite, Tridymite, Opal.

Etching: HF and other fluorine compounds. Alkalies as molten fluxes. Mixed acids: HF:HNO_3 type.

TABLE 1
Natural Forms of Quartz

Name & formula	Structure	Formation temperature (°C) (inversion)
Siliceous sinter, $SiO_2.nH_2O$	Amorphous/colloidal	100—150
Silica, SiO_2	Colloidal	150
Opal, $SiO_2.nH_2O$	Amorphous/colloidal	100—150
Alpha-quartz, SiO_2	Hexagonal: Rhombohedral Trapezohedral — tetrahedral	<573
Beta-quartz, SiO_2	Hexagonal: rhombohedral Trapezohedral — hemihedral	573—870
Alpha-tridymite, SiO_2	Orthorhombic Hexagonal	>800 (117 & 163)
Beta-tridymite, SiO_2	Hexagonal	>870 (117 & 163)
Alpha-cristobalite, SiO_2	Tetragonal (pseudo-isometric)	1200 (198 & 275)
Beta-cristobalite, SiO_2	Isometric — normal	>1200 (198 & 275)
Coestite, SiO_2/SiO_4	Hexagonal — normal, hcp	>1200 + pressure
Stisovite, SiO_2/SiO_4	Hexagonal — normal, hcp	>1200 + pressure
Tektite, SiO_2	Amorphous	>1200 (meteoric)
Obsidian, SiO_2	Amorphous (natural glass)	>1200 (volcanic)

QUARTZ ETCHANTS

QTZ-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
1 .... H_2O

TIME: To 25 min
TEMP: RT

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DISCUSSION:

SiO_2, (0001), ($10\bar{1}0$), natural single crystal and artificial fused quartz wafers and blank. Polished surfaces contain a "smear" layer a few angstroms thick under which there are scratches, pits, and microchips. This smear layer was removed with the solution shown in order to study the damage structure beneath. [*Note:* In polishing glass/quartz the smear-layer (Debeye layer) can vary from 500 to 2000 Å and is amorphous in structure . . . silica that physically fills-in low spots . . . rather than producing a planar, truly flat surface.] Polish lapping with an acid-slurry of cerium oxide/potassium hydroxide improves the true polishing finish quality without a smear layer. This same smear-type layer can occur in mechanical polishing of metals and metallic compounds.

REF: Newkirk, J B et al — *J Appl Phys,* 35,1302(1964)

QTZ-0008: Kobayashi, T & Geska, J — *J Cryst Growth,* 67,318(1984)

SiO_2, as fused quartz ampoules cleaned in this solution before encapsulated growth of gallium arsenide by LEC.

QTZ-0002a

ETCH NAME:

TIME: Minutes/hours

TYPE: Acid-slurry, polish

TEMP: RT

COMPOSITION:

x .... CeO_2 (5 μ)

x .... H_2O

x .... glycerin

x .... 10—15% NaOH

DISCUSSION:

SiO_2, AT-cut quartz crystal blanks and other orientations of both natural and artificially grown alpha-quartz. Mechanical polishing using a planetary lap (both blanks surfaces simultaneously lapped) with iron platens and SST shim holders. Slurry applied by drip method onto top rotating platen at about 1 drop/sec. Blanks lapped to rough frequency as high as 60 MHz (3rd order). Requires defect-free, parallel surfaces to $^1/_4$-wavelength (sodium light). Excellent results obtained using acid-slurry mixture shown; whereas without the alkali oversmearing of lap damage masks the true damaged nature of the surface.

REF: Walker, P — personal development, 1966—1969

QTZ-0003

ETCH NAME: Aqua regia

TIME:

TYPE: Acid, cleaning

TEMP: RT

COMPOSITION:

3 .... HCl

1 .... HNO_3

DISCUSSION:

SiO_2, as single crystal natural quartz, artificial quartz, and vitreous silica (fused glass). This primary reference used aqua regia as a wash solution on vitreous silica to remove iron contamination from surfaces prior to a study of the attack rates of HF.

REF: Blumberly, A A & Staurinov, S C — *J Phys Chem Solids,* 54,1438(1960)

QTZ-0004: Walker, P & Folds, W — personal application, 1969

SiO_2, AT-cut alpha-quartz blanks, both natural and artificial single crystal. Solution used to pre-clean quartz blanks prior to electrode metallization. After etch-cleaning soak at RT, 3—5 min, rinse in running DI water, 2—5 min, rinse in MeOH and N_2 blow dry.

QTZ-0018: Zelinsky, T — personal communication, 1980

SiO_2, fused quartz epitaxy tubes, 4" diameter, used for epitaxy growth of gallium arsenide on gallium arsenide. One section of a tube cleaning sink is filled with aqua regia for soak

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cleaning of tubes and associated parts. After cleaning at RT, 1—2, remove; water rinse heavily, MeOH rinse, and dry under infrared heat lamps.

QTZ-0005
ETCH NAME: Water
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2O
DISCUSSION:
SiO_2, as single crystal quartz blanks used in a study of surface conductivity in the presence of adsorbed layers. Water used as the base for evaluation of the effects of alcohol rinses. Conductivity decreases with an increase of the molecular weight of the alcohol.
REF: Abdrakhmanova, I F & Deryagin, B V — *Dokl Akad Nauk SSSR*, 120,94(1958)

TIME:
TEMP: RT

QTZ-0006
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
1 .... HF
1 .... HNO_3
DISCUSSION:
SiO_2, single crystal artificial alpha-quartz blanks. Solution used to thin quartz blanks in a study of defect structure induced by neutron irradiation. Defect clusters increase with time and dose levels. Can be stabilized by annealing at 500°C. (*Note:* Slightly below the 573°C temperature inversion point to beta-quartz.)
REF: Weissman, S & Nakajima, K — *J Appl Phys*, 34,611(1963)

TIME:
TEMP:

QTZ-0007
ETCH NAME:
TYPE: Acid, tuning
COMPOSITION:
1 .... HF
20 .... HNO_3
20 .... CH_4OHCH_2OH (ethylene glycol, EG)
DISCUSSION:
SiO_2, AT-cut quartz blanks and other cut orientations of both natural and artificial alpha-quartz used for radiofrequency crystals. The solution shown is variable and originally used molasses rather than ethylene glycol as the viscosity control agent. Solution used as a dip-type etch: (1) etch, (2) DI water rinse, (3) dry, and (4) frequency test. Repeat as needed to obtain required frequency prior to electrode metallization. (*Note:* Solution developed to prevent carbonization from residual molasses on blanks during metallization.)
REF: Walker, P & Schidler, A M — personal development, 1967

TIME:
TEMP: Warm

QTZ-0009
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... H_2SO_4
x .... CrO_3
DISCUSSION:
SiO_2, single crystal blanks used for growth of a-Si:H and a-Ge:H thin films. Degrease

TIME: 60 sec
TEMP: RT

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blanks in TCE; rinse in acetone; rinse in MeOH and rinse in DI water. Follow with heavy washing in running DI water. (*Note:* Acid mixture that is similar to the standard "glass cleaner" solution using saturated $Na_2Cr_2O_7$.)
REF: Rudder, R A et al — *J Vac Sci Technol*, A2,326(1984)

QTZ-0010
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
SiO_2, as fused quartz ampoules cleaned in this solution before Chemical Vapor Transport (CVT) growth of $CdSiAs_2$ single crystals.
REF: Avirovic, M et al — *J Cryst Growth*, 67,185(1984)

QTZ-0002b
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:
50 ml .... HF
50 g .... $NH_4F.HF$
100 ml .... H_2O
50 ml .... glycerine
DISCUSSION:
SiO_2, single crystal AT-cut, BT-cut as alpha quartz cuts; fused quartz substrate blanks, and quartzware as diffusion tubes, carriers, etc. Solution used as a general cleaning etchant. Glycerine reduces evaporation and improves wettability and can be varied. Also used on thin film SiO_2 and Si_3N_4. Initial development was for pattern etching of silicon oxynitrides on silicon wafers using standard photolithography. The bifluoride replaces the normal ammonium fluoride, and may be more useful where saturated fluorides are used to maximize control in etching tuning quartz frequency blanks.
REF: Ibid.

QTZ-0012
ETCH NAME: RCA Etch (AB Etch) TIME: 15—20 min
TYPE: Acid, cleaning TEMP: 70—80°C
COMPOSITION:

"A"	"B"
100 ml .... NH_4OH	100 ml .... HCl
100 ml .... H_2O_2	100 ml .... H_2O_2
500 ml .... H_2O	500 ml .... H_2O

DISCUSSION:
SiO_2, alpha-quartz frequency crystals, fused quartz substrates, and quartzware. Etch clean in solution "A", then transfer parts still wet to solution "B" each for time and temperature shown. Remove parts and wash in running DI water, rinse in MeOH and dry with either nitrogen or under IR heat lamps. Used for general cleaning of parts and prior to metallization of quartz frequency crystal electrodes, and fused quartz blanks used as circuit substrates, or for general quartzware. (*Note:* This cleaning method was developed for silicon, see SI-0031.)
REF: Walker, P & Marich, L A — personal application, 1983—1985

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QTZ-0013
ETCH NAME: Hydrofluoric acid
TYPE: Acid, preferential
TIME: 15 h
TEMP: RT
COMPOSITION:
x .... HF (48%)
DISCUSSION:
SiO_2, single crystal blanks cut from synthetic quartz. Solution used to develop etch pits. Pits were triangular with an etch line(?). Authors say they saw inclusion blebs containing residual growth liquid. Frequency device Q-loss is related to density of defects. (*Note:* These authors have observed liquid and gas-filled blebs in natural alpha-quartz but not in cultured or synthetic quartz.)
REF: Spencer, W J & Haruta, K — *J Appl Phys*, 37,549(1966)

QTZ-0014a
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
TIME:
TEMP: Boiling
COMPOSITION:
x .... HNO_3, conc.
DISCUSSION:
SiO_2, single crystal artificial alpha-quartz boules and $(10\bar{1}0)$ prism orientation blanks. Boiling nitric acid used to clean surfaces before preferential etching with sodium hydroxide.
REF: Joshi, M S & Vagh, A S — *Br J Appl Phys*, 17,528(1966)

QTZ-0014b
ETCH NAME: Sodium hydroxide
TYPE: Alkali, preferential
TIME:
TEMP: Boiling
COMPOSITION:
x .... x% NaOH
DISCUSSION:
SiO_2, $(10\bar{1}0)$ artificial alpha-quartz blanks. Solution develops dissolutionment figures, highest etch rate planes, as hillocks. Pits are representative of slowest etch rate planes.
REF: Ibid.

QTZ-0015a
ETCH NAME: Hydrochloric acid, vapors
TYPE: Acid, cleaning
TIME:
TEMP: 1100°C
COMPOSITION:
x .... HCl, vapor
x .... H_2, vapor
DISCUSSION:
SiO_2, fused quartz epitaxy tubes of rectangular cross section. Hot HCl vapors in hydrogen used to clean tubes and silicon wafers prior to silicon epitaxy growth. Also used to clean SiC coated graphite susceptors after epitaxy to remove deposited silicon. HCl vapor concentration varied from 10 to 20%.
REF: Topas, B & Walker, P — personal application, 1972
QTZ-0016b: Ibid.
SiO_2, fused quartz tubes cleaned in 9% HCl:O_2, 16 h at 1200°C prior to dry oxidation of (100) silicon wafers at 1000°C.

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QTZ-0016a
ETCH NAME: 1,1,1 Trichloroethane
TYPE: Solvent, cleaning
COMPOSITION:
x .... 3% CH_3CCl_3, vapor
x .... O_2, vapor
TIME: 16 h
TEMP: 1200°C
DISCUSSION:
SiO_2, fused quartz tubes were cleaned with this vapor mixture. Authors say this mixture is equivalent to 9% HCl:O_2 (QTZ-0016b). Tubes were cleaned prior to oxidation of n-type, 2—5 Ω cm resistivity, (100) silicon wafers in dry O_2 at 1000°C. Aluminum dots were then E-beam evaporated through a gold mask. Tubes were also cleaned with HF.
REF: Greeuw, G et al — *Solid State Electron*, 27,77(1984)

QTZ-0015b
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
5 .... HF
10 .... HNO_3
10 .... CH_3COOH (HAc)
TIME:
TEMP: RT
DISCUSSION:
SiO_2, fused quartz tubes of rectangular cross section used for silicon epitaxy growth on silicon wafers. Solution used for maintenance cleaning of tubes after every 15 to 20 deposition runs to remove heavily phosphorus doped silicon deposit from tube walls. Cleaning was done in a deep-welled tube cleaning sink designed for these epitaxy tubes. Cleaning procedure was (1) first, flush tube with heavy water rise jet (tygon tubing) — **CAUTION**: Phosphorus will flame-out, as it burns under water; (2) pour 250 ml of etch solution into tube — caution: phosphorus can ignite and flame-out; (3) water rinse tube interior; (4) etch solution rinse tube exterior; (5) water wash exterior and interior of tube and (6) final rinse with MeOH outside of sink (no alcohol down an acid drain). Wipe down tube with lint-free paper and blow interior dry with nitrogen. After tube is reinstalled in epitaxy system, make a "dummy" run to condition tube. (*Note:* Caution cannot be overemphasized as flame-out can extend 6—8″ beyond tube ends with explosive ignition.)
REF: Ibid.

QTZ-0020
ETCH NAME:
TYPE: Laser, cut
COMPOSITION:
x .... laser
TIME:
TEMP:
DISCUSSION:
SiO_2 as fused or single crystal quartz substrates used in microelectronic assemblies. Laser used to cut rectangular holes in substrates prior to circuit metallization.
REF: Bowman, T — personal communication, 1984

QTZ-0017
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
10—20 .... H_2O
TIME: 1—2 h
TEMP: RT

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DISCUSSION:

SiO_2, fused quartz tubes, 4″ in diameter used for boron diffusion of silicon wafers. Solution used for maintenance cleaning of tubes. Tubes were held vertically over a Teflon container with the bottom, small tube end, closed with a T/S Pyrex stopcock. Pour sufficient solution into the tube to fill within about 1″ of the top, open end. Allow solution to soak-clean tube interior for 1—2 h at RT. Drain and flush with water, then rinse in MeOH. Cleaning was also done in a horizontal tube cleaning sink.

REF: Tarn, W H & Walker, P — personal application, 1963

QTZ-0019: Walker, P — mineralogy study, 1953

SiO_2, as an oolitic form of natural Chert. Study included metallographic bulk and thin section etching study and powder X-ray analysis of this material. Solution used to develop the oolitic structure to observe and determine types of central-core inclusions that formed the oolites. (*Note:* Oolites are initially formed as colloidal segregates during solidification of sedimentary rocks.)

TRI-0001

ETCH NAME: Sodium carbonate — TIME:

TYPE: Salt, removal — TEMP: Boiling

COMPOSITION:

x .... $NaCO_3$

DISCUSSION:

SiO_2, as the natural mineral tridymite as small white octahedrons. Tridymite can be differentiated from alpha- and beta-quartz as it is attacked by boiling sodium carbonate. Solution used as a soaking solution (60°C) will develop defects and structure. Used in a general mineralogic study of various forms of quartz and silica.

REF: Walker, P — mineralogy study, 1952—1954

COE-0001

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

x .... HF, conc.

DISCUSSION:

SiO_2, as the natural mineral coesite is a high pressure modification of quartz as SiO_2/SiO_2 with a tetrahedra ratio of 4:2. Solution used to etch segregation figures with reference to studies done on other high pressure forms as $CrVO_4$ and $FeVO_4$. See stisovite below as another high pressure form of natural quartz, both associated with meteor strikes.

REF: Young, A P & Schwartz, C M — *Acta Crystallogr*, 15,1304(1962)

STI-0001

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Acid, removal — TEMP: RT to hot

COMPOSITION:

x .... HF, conc.

DISCUSSION:

SiO_2/SiO_4 as the natural mineral stisovite is a high pressure modification of quartz with a tetrahedra ratio of 6:3, considered to be the highest density form of quartz. See COE-0001 for additional discussion.

REF: Young, A P & Schwartz, C M — *Acta Crystallogr*, 15,1304(1962)

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OPAL-0001
ETCH NAME: Chromic acid
TYPE: Acid, coloring
COMPOSITION:
150 ml .... CrO_3, sat. sol.

TIME:
TEMP:
PRESSURE: 10—50 psi

DISCUSSION:

$SiO_2.nH_2O$, as the natural mineral opal is a hydrated form of quartz. Opal is amorphous/colloidal in structure with high internal fracturing. There is water in the crystal lattice and residual in the fracture zones which gives the splay of colors. Heating opal to above 125°C will drive off residual entrapped water changing opal colors toward white. By pressurizing the opal in an autoclave containing chromic acid the stone will develop a splay of green colors. This pressurizing method has been applied to other natural minerals and rocks for different colors. In gross leak package evaluation of Solid State elements, a red dye is used, followed by a light vacuum (10^{-1} Torr sufficient) . . . if red dye appears, there is a package leak. (*Note:* To maintain an opal's color it should be occasionally dampened with water.)
REF: Walker, P — mineralogy development, 1986

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PHYSICAL PROPERTIES OF RADIUM, Ra

Classification	Alkali earth
Atomic number	88
Atomic weight	226.05
Melting point (°C)	700
Boiling point (°C)	1040
Density (g/cm^3)	5
1st ionization potential (eV)	5.28
Ionic radius (angstroms)	1.43
Half-life (years)	1590 (1622)
Cross section (barns)	20
Hardness (Mohs — scratch)	2
Crystal structure (isometric — normal)	(100) cubic
Color (solid)	Silver
Cleavage (cubic)	(001)

RADIUM, Ra

General: Radium is the major decay product of the uranium series disintegration with nine isotopes ending in non-radioactive lead. Its discovery by Madame Curie, and separation in 1910, established the field of radioactivity. There is one part radium in 3.3 million parts uranium, such that the amount of radium and helium in a mineral ore sample is used for radioactive dating. This dating has shown the Earth to be at least 1.5 billion years old. There are over 50 minerals containing uranium, the most well known being pitchblende — the mineral uraninite — named for its black color and from which radium was first discovered. Pitchblende is a uranate containing lead, and usually thorium which is another radioactive series. The mineral carnotite is a uranium vanadinite, brilliant yellow and orange in color, and often found as granular masses of yellow/orange/black as a mixture with pitchblends (Colorado plateau region).

Radium is still used in cancer therapy, though high energy X-rays have been developed for more intense gamma rays. Salts of radium emit a yellow-green light that glows in the dark, used on watch and clock faces through the 1930's before the full danger of radioactivity was realized. Today its use is mainly in the medical field.

Technical Application: Radium has little use in metal processing and Solid State device fabrication areas. It is occasionally used as a test vehicle for radiation counters, though radioactivated lead with a half-life of 24 h is more common.

Radium reacts with water with the evolution of hydrogen, such that it should not be stored in a closed container — also continually emits radon gas as a disintegration by-product which, with time, can pressurize and cause explosive rupture of such sealed containers.

Etching: Deliquesces in acids.

RADIUM ETCHANTS

RA-0001
ETCH NAME: Water — TIME:
TYPE: Acid, reduction — TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:
Ra, as a metal will reduce water with evolution of hydrogen.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, 1947, 295

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ROCHELLE SALT ETCHANTS

RS-0001
ETCH NAME: Water
TYPE: Acid, preferential
COMPOSITION:
x .... H_2O
DISCUSSION:
$NaKC_4H_4O_6.4H_2O$, (0001) wafers lapped on filter paper dampened with water to develop square etch pits with pointed bottoms. After X-ray irradiation, pit shapes became "roof-like" with a line at bottom. Subsequent annealing showed little change. Wafers initially cut with a thread wetted with water.
TIME:
TEMP:
REF: Okada, K — *Jpn J Appl Phys*, 2,613(1963)
RS-0002: Wieder, H H — *Phys Rev*, 109,29(1958)
$NaK_4H_4O_6.4H_2O$ wafers used in a study of ferroelectric polarization reversal in Rochelle Salt.

RS-0003
ETCH NAME: Ethyl alcohol
TYPE: Alcohol, cleaning
COMPOSITION:
x .... EOH
DISCUSSION:
$NaK_4H_4O_6.4H_2O$, (0001) wafers were prepared as follows: dry lap with 600-grit SiC, then polish lap on nylon cloth with a slurry of alumina powder in glycerin. Final wash and clean in alcohol. Salt was deuterium-doped in a study of electro-optical effects and polarization reversal.
TIME:
TEMP:
REF: Wieder, H H & Collins, D A — *Phys Rev*, 120,725(1960)

PHYSICAL PROPERTIES OF RADON, Rn

Classification	Rare gas
Atomic number	86
Atomic weight	222
Melting point (°C — solid)	−71
Boiling point (°C — solid)	−61.8
Density ($g/cm^3 \times 10^{-3}$ — gas) 20°C	9.96
(g/l — liquid)	9.73
(g/cm^3 — solid)	4
Latent heat of fusion (cal/g)	2.9
1st ionization potential (eV)	10.745
Half-life (days)	3.823
Cross section (barns)	0.7
Vapor pressure (°C)	99
Hardness (Mohs — scratch)	2
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Colorless
Cleavage (cubic)	(001)

RADON, Rn

General: Radon is a chemically inert, colorless gas elimination by-product of the dis-

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integration of radium, Ra, with a half-life of only 3.85 days as compared to 1590 years for radium. It emits intense alpha particles and has been extensively studied with regard to its relationship to radium decay, and the other radioactive gases. Helium and lead are decay products of uranium with radium/radon being steps in the process, such that the amount of helium in a sample of, say, fergusonite ore is a measure of its age — one sample was concluded to be over 400,000,000 years old — the earth calculated to be more than $1^1/_2$ billion years old.

Though a radioactive by-product, radon is classified as a rare gas as it emanates from the earth's crust into the atmosphere in small quantities. Such emanations occur worldwide, more common in earthquake-prone areas and in the northeastern U.S. appear to be associated with granitic areas. Sudden increased release of radon in fault areas is recognized as a precursor of fault activity. In some hot spring areas radon is found in the upswelling waters, and it has recently been measured collecting in the basement of buildings, and is said to be a cause of lung cancer. It should be noted that radon emits alpha particles, and alpha particle penetration is stopped by the skin, beta particles by muscle tissue, and gamma particles pass completely through the body. It is the latter rays that are thought to cause long-range mutation in animal and plant life.

Most of the radioactive gases react with water and should not be stored in a closed container as build-up of pressure can cause explosive rupture.

Technical Application: Radon has little use in Solid State due its short half-life although it has long been a primary method of studying radium. It can be used as a radiation alpha counter in place of radioactive lead. The latter, with only a 24-h half-life, has been used in testing silicon radiation detectors.

Etching: Soluble in water.

RADON ETCHANTS

RN-0001
ETCH NAME: Water — TIME:
TYPE: Acid, dissolving — TEMP:
COMPOSITION:
x .... H_2O
DISCUSSION:
Rn, as the gas will dissolve in water, as do many of the radioactive gases.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1947, 295

RARE EARTHS (RE)

General: There are many natural minerals containing trace amounts of the rare earth elements (15 elements) and are chemically divided into two groups: cerium sub-group and yttrium sub-group. The chief source of cerium is from the mineral monazite, as a phosphate, but contains up to 30% cerium and 28% thorium as oxides . . . ceria and thorea. The mineral gadolinite is a mixed silicate of yttrium — yttrium is often called a rare earth, though it is not listed as a rare earth in the Periodic Table of Elements. Yttrium, cerium, and neodymium are fairly abundant, but the others are quite rare — elements 61, 63, 65, and 67—71. The rare earths are considered very active metals similar to calcium. They burn in air to the oxide; the oxides dissolve in water, often hissing like quicklime; and hydroxides are alkaline. Cerium sulfate, $Ce(SO_4)_2$ is a powerful oxidizing agent, and ammonium ceric nitrate or sulfate is a major etching solution constituent for certain metals, such as chromium and nickel.

Some of the rare earths are used as alloy constituents in metal processing, but there is

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no extensive application. Several of their salts have use in both chemistry and medicine, mainly as oxidizers.

Technical Application: Some of the rare earths are under evaluation as doping elements in Solid State material processing. Most have been grown and studied as single crystals or thin films to include as nitrides and silicides. See individual element sections for additional data. Nitrides are mentioned here, also see section on silicides and garnets.

The Rare Earths are as follows:

Atomic number	Element/symbol
57	Lanthanum, La
58	Cerium, Ce
59	Praseodymium, Pr
60	Neodymium, Nd
61	Illinium, Il
62	Samarium, Sm
63	Europium, Eu
64	Gadolinium, Gd
65	Terbium, Tb
66	Dysprosium, Dy
67	Holmium, Ho
68	Erbium, Er
*69	Thulium, Tm
*70	Ytterbium, Yb
*71	Lutetium, Lu

In the literature the Rare Earths have been symbolized by both (RE) and (R). The latter is not recommended as "R" is used in mineralogy as the general symbol for a metal constituent in a mineral; whereas the letter "M" is used in Chemistry. Those starred (*) are not in this book for lack of referenced application.

Etching: Water soluble. See individual listings.

RARE EARTH NITRIDE ETCHANTS

REN-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF, conc.
TIME:
TEMP:
DISCUSSION:
(RE)N_{12} specimens grown by arc melting under argon and annealing at 600—900°C for 3—6 weeks. Materials used in a study of magnetostriction. Nitrides grown were Tb, Pr, Dy, and Ho. See Ibarra Ph.D. thesis for metallography.
REF: Moral, A Del & Ibarra, M R — *J Phys Chem Solids,* 46,127(1985)

PHYSICAL PROPERTIES OF RHENIUM, Re

Classification	Transition metal
Atomic number	75
Atomic weight	186.2
Melting point (°C)	3180 (3167)

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Boiling point (°C)	5900 (5627)
Density (g/cm^3)	21.04
Thermal conductance [cal/(sec)(cm^2)(°C/cm)]	0.095
Specific heat (cal/g) 25°C	0.035
Heat of fusion (k-cal/g-atom)	7.9
Latent heat of fusion (cal/g)	42.2
Heat of vaporization (k-cal/g-atom)	152
1st ionization energy (K-cal/g-mole)	182
1st ionization potential (eV)	7.87
Atomic volume (W/D)	48.85
Electronegativity (Pauling's)	1.9
Covalent radius (angstroms)	1.28
Ionic radius (angstroms)	0.56 (Re^{+7})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	6.2
Electrical resistivity (micro-ohms-cm)	1119.3
Thermal conductivity (cal/cm^2/°C/sec) 20°C	0.17
Vapor pressure (mm $\times 10^{-8}$) 2000°C	3
Electron work function (eV)	4.8 (5.1)
Modulus of elasticity (psi $\times 10^6$)	67
Cross section (barns)	85
Hardness (Mohs — scratch)	5—6
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Silver-grey metal
Cleavage (basal)	(0001)

RHENIUM, Re

General: Does not occur in nature as a native element. It is found as a minor constituent element in several of the tantalate minerals such as tantalite and wolframite. It was only discovered in 1925 by Noddack and has characteristics similar to those of manganese and is considered to be one of the eka-manganese. Although it has a very high melting point, it is easily forged and processed much like iron and copper.

It has some industrial use as an alloy constituent in metals such as iron and steel and is used as the pure metal for its high temperature characteristics in the fabrication of a variety of parts. It is also used as a catalyst for dehydrogenation.

Technical Application: Rhenium has been grown as a single crystal for physical data and morphological studies. As a crystalline metal it has been studied for surface reactions under various conditions — oxide, chloride, sulfides. The sulfides are quite inert and ReS_2 acts as a lubricant similar to MoS.

Etching: HNO_3 H_2O_2 and mixed acid as HF:HNO_3 mixtures.

RHENIUM ETCHANTS

RE-0001
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
8 .... HF
2 .... HNO_3

TIME:
TEMP:

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DISCUSSION:

Re, (0001) wafers used in a study of anisotropy in the superconductivity of deformed rhenium. After specimens are annealed, solution will develop deformation structure.

REF: Hauser, J J — *J Appl Phys*, 33,3074(1962)

RE-0002

ETCH NAME:

TYPE: Electrolytic, polish

COMPOSITION:

x .... 0.1 *N* NaOH

TIME:

TEMP:

ANODE: Ni

CATHODE; Re

POWER: 5—10 V/25 V

DISCUSSION:

Rh, (0001) wafers. Field emission study shows hexagonal patterns. In etching use the DC/AC arc potential to rough etch surfaces; then use AC, 0.05 V/second pulses — with arcing — to polish surfaces. Arcing will occur just below the liquid surface.

REF: Barns, O — *Phys Rev*, 97,1579(1955)

RE-0003

ETCH NAME:

TYPE: Electrolytic, thinning

COMPOSITION:

23 .... $HClO_4$

77 .... HAc

TIME:

TEMP: 20°C

ANODE: Re

CATHODE:

POWER: 6—18 V & 0.3 A/cm^2

DISCUSSION:

Re, (0001) wafers. Solution used to thin specimens for electron microscope (EM) study after neutron irradiation.

REF: Brimhall, J L & Mastel, B — *Phil Mag*, 12,419(1965)

RE-0004a

ETCH NAME: Metal

TYPE: Molten flux, preferential

TIME:

TEMP: (1) 1550°C
(2) 1460°C

COMPOSITION:

(1) x .... Fe (2) x .... Ni

DISCUSSION:

Rh specimens. Rhenium is rapidly attacked by both molten metals.

REF: Kohl, W H — *Handbook of Materials Techniques for Vacuum Devices*, Reinhold, New York, 1967

RE-0004b

ETCH NAME: Sulfur, vapor

TYPE: Element, conversion

COMPOSITION:

x .... S, vapor

TIME:

TEMP: 445°C

DISCUSSION:

Re, specimens. Hot sulfur vapors will attack rhenium converting the surface to ReS_2 or Re_2S_7. At elevated temperature ReS_2 acts as a lubricant. Neither sulfur compound can be etched in aqua regia.

REF: Ibid.

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RE-0004c
ETCH NAME: air
TYPE: Gas, oxidation
COMPOSITION:
x .... Air, moist
TIME:
TEMP: RT or 350°C
DISCUSSION:
Re, specimens. Moist air at RT will form $HReO_4$, at elevated temperature, Re_2O_7. Oxides can be removed with acids.
REF: Ibid.

RE-0004d
ETCH NAME: Chlorine
TYPE: Gas, chlorination
COMPOSITION:
x .... Cl_2, vapor
TIME:
TEMP: RT or hot
DISCUSSION:
Re, specimens. Chlorine will form $ReCl_3$ or $ReCl_5$. HCl can be used to remove the chlorides.
REF: Ibid.

RE-0004e
ETCH NAME: Sulfuric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_2SO_4
TIME:
TEMP: RT or hot
DISCUSSION:
Re specimens. Solution shown as a slow etch for rhenium at RT. Used hot it will form $HReO_4$ which can be removed with acids.
REF: Ibid.

RE-0004f
ETCH NAME: Nitric acid
TYPE: Acid, oxidation
COMPOSITION:
x .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
Re specimens. Nitric acid will rapidly oxidize rhenium to $HReO_4$ which can be removed with acids.
REF: Ibid.

PHYSICAL PROPERTIES OF RHODIUM, Rh

Classification	Transition metal
Atomic number	45
Atomic weight	102.9
Melting point (°C)	1966
Boiling point (°C)	4500 (3960)
Density (g/cm^3) 20°C	12.41
Thermal conductance (cal/sec)(cm^2)(°C/cm) 20°C	0.36
Specific heat (cal/g) 0°C	0.059

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Heat of fusion (k-cal/g-atom)	5.2
Heat of vaporization (k-cal/g-atom)	127
Atomic volume (W/D)	8.3
1st ionization energy (K-cal/g-mole)	178
1st ionization potential (eV)	7.7
Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.25
Ionic radius (angstroms)	0.68 (Rh^{+3})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 20°C	8.3
Electrical resistivity (micro-ohms-cm)	4.5
Electron work function (eV)	4.65 (4.80)
Young's modulus of elasticity (psi $\times 10^6$)	60
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.99
Tensile strength (psi — annealed)	110,000
Neutron cross section (barns)	156
Hardness (Mohs — scratch)	4—4.5
(Vickers kgf/mm^2 — annealed)	120
Crystal structure (isometric — normal)	(100) cube, fcc
Color (solid)	Grey-white
Cleavage (cubic)	(001)

RHODIUM, Rh

General: Occurs as a native element in small quantity as grains in gold and platinum alluvial deposits. It is a member of the platinum family of metals, and is found as a constituent in most native platinum from which it is separated.

Because of its high melting point and extreme inertness to chemical attack it has similar applications to those of platinum in industry. The highest temperature thermocouples are made of two wire strands, one pure platinum, the other Pt:Rh (3—15%) bead welded at one end. As an electroplated coating, it is inert to most acids and alkalies with similar applications to those of chrome plating. Several salts are highly colored yellow and black.

Technical Application: The pure metal has had little use in Solid State processing other than as a furnace thermocouple or some plated part applications.

It has been grown as a single crystal for general morphological study.

Etching: Very difficult. Mixed acids of H_2SO_4:HCl and aqua regia.

RHODIUM ETCHANTS

RH-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal/cleaning
TIME:
TEMP: RT to hot
COMPOSITION:
3 .... HCl
1 .... HNO_3
DISCUSSION:

Rh specimens as wire, rods, sheets, and plated coatings. Aqua regia is a general etch for the material.

REF: Pamphlet: *Platinum*, Baker & Sons, Inc. (no date)

RH-0002: Zelinsky, T — personal communication, 1978

Rh as Pt:Rh and Pt thermocouples used for epitaxy growth furnaces. After bead weld assembly of thermocouples by electric arcing in a borax flux; degrease with TCE, rinsed in MeOH, then water. Lightly etch cleaned in aqua regia at RT, water wash and dry under IR heat lamps.

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PHYSICAL PROPERTIES OF RUBIDIUM, Rb

Classification	Alkali metal
Atomic numbers	37
Atomic weight	85.4
Melting point (°C)	38.9
Boiling point (°C)	688
Density (g/cm^3) 20°C	1.532
Thermal conductance [cal(sec)(cm^2)(°C/cm)]	0.07
Specific heat (cal/g) 25°C	0.0792
Specific heat (cal/g) 0°C	0.080
Latent heat of fusion (cal/g)	6.144
Heat of vaporization (cal/g)	212
Atomic volume (W/D)	55.9
1st ionization energy (K-cal/g-mole)	96
1st ionization potential (eV)	4.176
Electronic work function (eV)	2.13 (2.09)
Electronegativity (Pauling's)	0.8
Covalent radius (angstroms)	2.16
Ionic radius (angstroms)	1.47 (Rb^{+1})
Electrical conductance (micro-$ohms^{-1}$)	0.080
Thermal conductivity (cal/cm^2/cm/°C/sec) 39°C	0.07
Neutron cross section (barns)	0.73
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	90
Electrical resistivity (ohms cm $\times 10^{-6}$) 20°C	12.5
Vapor pressure (°C)	514
Hardness (Mohs — scratch)	0.3
Crystal structure (isometric — normal)	(100) cube, bcc
Color (solid)	Silver/reddish
(flame)	Dark red
Cleavage (cubic)	(001)

RUBIDIUM, Rb

General: Does not occur as a native element in nature. It is a rare alkali metal found chiefly in the mica Lipidolite and some other lithium-bearing minerals. On the island of Elba as Castor and Pollux . . . neither listed as mineral species, circa 1950. The metal forms salts similar to those of potassium.

Little or no use in general industry due to rarity although there are over 50 rubidium chemical compounds, and it forms acid compounds with nitric acid. It has some application in pyrotechnics for its deep red flame color.

Technical Application: The pure metal has had little use in Solid State processing, in part, due to it being one of the softest of known metals with H = 0.3.

Rubidium has been grown as a single crystal for general morphological study, and several compounds such as bromide and iodide also have been studied.

Etching: Acids.

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RUBIDIUM ETCHANTS

RB-0001
ETCH NAME: Water
TYPE: Acid, removal
COMPOSITION:
x .... H_2O
DISCUSSION:
Rb metal will dissolve in water. Initial discovery of both cesium and rubidium were from waters in Durkheim by Bunsen 1860/1861. Named for its deep red spectral lines.
REF: Foster, W & Alyea, H N — *An Introduction to General Chemistry*, 3rd ed, D Van Nostrand, New York, 1947, 365
TIME:
TEMP: RT

PHYSICAL PROPERTIES OF RUBIDIUM BROMIDE, RbBr

Classification	Bromide
Atomic numbers	37 & 35
Atomic weight	165.4
Melting point (°C)	682
Boiling point (°C)	1340
Density (g/cm^3)	3.35
Refractive index (n=)	1.5530
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
Cleavage (cubic)	(001)

RUBIDIUM BROMIDE ETCHANTS

RBB-0001
ETCH NAME: Acetone
TYPE: Keytone, polish
COMPOSITION:
10 .... CH_3COCH_3 (acetone)
1 .... H_2O
DISCUSSION:
RbBr, (001) wafers used to measure elastic constants using ultrasonic cw resonance. Mechanically rough lap wafers with A/O 302 grit. Mechanically polish with A/O 303$^1/_2$ grit on a cast iron lap; then Linde A, then sapphire dust on cloth. Use N-amyl alcohol as liquid carrier for all lap and polish. Etch polish with the solution shown and rinse in MeOH. See Rubidium Iodide.
REF: Bulef, D I & Menes, M — *J Appl Phys*, 31,1010(1960)
TIME:
TEMP: RT

PHYSICAL PROPERTIES OF RUBIDIUM IODIDE, RbI

Classification	Iodide
Atomic numbers	37 & 53
Atomic weight	212.4
Melting point (°C)	642
Boiling point (°C)	1300

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Density (g/cm³)	3.55
Refractive index (n =)	1.6474
Hardness (Mohs — scratch)	2—3
Crystal structure (isometric — normal)	(100) cube
Color (solid)	Colorless
Cleavage (cubic)	(001)

RUBIDIUM IODIDE, RbI

General: Does not occur as a natural compound due to scarcity of the element, and water solubility of the iodide. It was first discovered by Bunsen in 1861 from its red spectral lines associated with lithium in the mineral petalite. It is an alkaline metal with characteristics similar to potassium.

Technical Application: The iodide has had no application in Solid State processing, although it has been grown and studied as a single crystal.

Etching: Acetone, water.

RUBIDIUM IODIDE ETCHANTS

RBI-0001
ETCH NAME: Acetone
TYPE: Alcohol, polish
TIME:
TEMP: RT
COMPOSITION:
10 .... CH_3COCH_3 (acetone)
1 .... H_2O
DISCUSSION:

RbI, (001) wafers used to measure elastic constants using ultrasonic cw resonance. Mechanically rough lap with A/O 302 grit. Mechanically polish with $303^1/_2$ A/O grit on a cast iron lap; then Linde A, then sapphire dust on cloth. Use N-amyl alcohol as liquid carrier for lap and polish. Etch polish with the solution shown and rinse in MeOH. See Rubidium bromide.

REF: Bulef, D I & Menes, M — *J Appl Phys*, 31,1010(1960)

PHYSICAL PROPERTIES OF RUBIDIUM SULFIDE, RuS_2

Classification	Sulfide
Atomic numbers	44 & 16
Atomic weight	165.82
Melting point (°C)	>500
Boiling point (°C)	
Density (g/cm³)	6.99
Hardness (Mohs — scratch)	7.5
Crystal structure (isometric — normal)	(111) octahedron
Color (solid)	Iron-black
Cleavage (octahedral)	(111)

RUBIDIUM SULFIDE, RbS_2

General: Occurs in nature essentially as the minor mineral laurite, RuS_2. It is found as small octahedrons, or in grains associated with the gold and platinum washings in placer deposits.

Not used in the metals industry as the natural mineral due to scarcity.

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Technical Applications: No use in Solid State processing at the present time, but under evaluation as the sulfide, selenide, and telluride for general morphology, to include IR spectra and possible semiconductor characteristics. The reference shown is for all three compounds.

Etching: HNO_3.

PHYSICAL PROPERTIES OF RUTHENIUM, Ru

Classification	Transition metal
Atomic number	44
Atomic weight	101.7
Melting point (°C)	2500 (2450)
Boiling point (°C)	4900 (4111)
Density (g/cm^3)	12.45
Specific heat (cal/g) 20°C	0.055
Heat of fusion (k-cal/g-atom)	6.1
Latent heat of fusion (cal/g)	60.3
Heat of vaporization (k-cal/g-atom)	148
Atomic volume (W/D)	8.3
1st ionization energy (K-cal/g-mole)	173
1st ionization potential (eV)	7.5
Electronegativity (Pauling's)	2.2
Covalent radius (angstroms)	1.25
Ionic radius (angstroms)	0.67 (Ru^{+4})
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C)	9.1
Electrical resistivity (micro-ohms-cm) 20°C	7.2 (6.8)
Vapor pressure (microns @ m.p.)	9.8
Young's modulus (psi $\times 10^6$)	60
Magnetic susceptibility (cgs $\times 10^{-6}$)	0.43
Cross section (barns)	2.56
Hardness (Mohs — scratch)	4—5
(Vicker's — kgf/mm^2) annealed	220
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Black
Cleavage (basal)	(0001)

RUTHENIUM, Ru

General: Although the *Handbook of Chemistry and Physics* refers to its occurrence as a native element, Dana's *Textbook of Mineralogy* does not. Regardless, it is a very rare element and does occur as a minor constituent in platinum and iridosmine. The major occurrence of platinum is in the Ural Mountains of Russia, although it is found throughout the world in minor quantities often associated with magnetite in gold sands.

No use as a metal in industry, primarily due to its scarcity, though it has extremely high temperature characteristics similar to platinum, iridium, and osmium.

Technical Application: Ruthenium metal has had no major use in Solid State material processing, although it has been grown as a single crystal for general study. It also has been evaluated as a compound semiconductor, as a selenide, sulfide, and telluride. It also is under evaluation and study as a silicide: RuSi, Ru_2Si, $RuSi_2$, for possible application as a buffer layer in semiconductor devices similar to other metal silicides.

Etching: HCl, H_2SO_4, HNO_3 acid and aqua regia. RF plasma ionized gases.

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RUTHENIUM ETCHANTS

RU-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal
COMPOSITION:
3 .... HCl
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:
Ru specimens. Aqua regia is a general polish and removal etch for this element. It is only slowly soluble in single acids.
REF: Hodgman, C D — *Handbook of Chemistry and Physics*, 27th ed, Chemical Rubber Co., Cleveland, 1943, 446

RU-0002
ETCH NAME: Argon
TYPE: Ionized gas, cleaning
COMPOSITION:
x .... Ar^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE: 10^{-5} Torr
POWER: 1 KeV
DISCUSSION:
Ru, (100) wafers cut within $\pm 2°$ of plane — 8 mm discs spark cut from single crystal ingots. Mechanical polish with diamond paste. In vacuum, RF plasma Ar^+ ion clean at 1 KeV and 10^{-5} Torr and follow by annealing at 750 to 800°C. Manganese was then deposited on surfaces.
REF: Heinrich, B et al — *J Vac Sci Technol*, B3(2),766(1985)

RUTHENIUM SELENIDE ETCHANTS

RUSE-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
COMPOSITION:
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
$RuSe_2$, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other single crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuTe_2$, OsS_2, $OsTe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2 and were used in an IR spectra study. (*Note:* Pyrite is in the pyritohedral class of the isometric system, not the normal class which contains the cube, (100). In addition, the natural mineral laurite is not of pyrite structure.)
REF: Lutz, H D et al — *J Phys Chem Solids*, 46,437(1985)

RUTHENIUM SULFIDE ETCHANTS

RUS-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
TIME:
TEMP:

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COMPOSITION:
x .... HNO_3
DISCUSSION:
RuS_2, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other single crystals grown were FeS_2, $MnTe_2$, $RuSe_2$, $RuTe_2$, OsS_2, $OsTe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. All crystals are cubic structure like pyrite, FeS_2, and were used in an IR spectra study. (*Note:* See discussion under the selenide with regard to material structure.)
REF: Lutz, H D et al — *J Phys Chem Solids,* 46,437(1985)

RUTHENIUM TELLURIDE ETCHANTS

RUTE-0001
ETCH NAME: Nitric acid
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
$RuTe_2$, single crystal specimens. Cut specimens and mechanically polish with 0.5 μm diamond paste. Etch in solution shown to polish and remove lap damage. Other crystals grown were FeS_2, $MnTe_2$, RuS_2, $RuSe_2$, OsS_2, $OsTe_2$, PtP_2, $PtAs_2$, and $PtSb_2$. All crystals are cubic in structure like pyrite, FeS_2 and were used in an IR spectra study. (*Note:* See discussion under the selenide with regard to pyrite crystal structure.)
REF: Lutz, H D et al — *J Phys Chem Solids,* 46,437(1985)

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PHYSICAL PROPERTIES OF SAMARIUM, Sm

Classification	Lanthanide
Atomic number	62
Atomic weight	150.35
Melting point (°C)	1072
Boiling point (°C)	1900
Density (g/cm^3)	7.55
Specific heat (cal/g) 25°C	0.042
Heat of fusion (k-cal/g-atom)	2.1
Latent heat of fusion (cal/g)	17.29
Heat of vaporization (k-cal/g-atom)	46
Atomic volume (W/D)	19.9
1st ionization energy (K-cal/g-mole)	129
1st ionization potential (eV)	5.6
Electronegativity (Pauling's)	1.2
Covalent radius (angstroms)	1.62
Ionic radius (angstroms)	1.0 (Sm^{+3})
Electrical resistivity ($\times 10^{-6}$ ohms cm) 25°C	90 (10^5 @ 298 K)
Compressibility (cm^2/kg $\times 10^{-6}$)	3.34
Magnetic moment (Bohr magnetons)	1.74
Tensile strength (psi)	18,000
Yield strength (psi)	16,200
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	1,275
Transformation temperature (°C)	924
Cross section (barns)	5800
Hardness (Mohs — scratch)	4—5
Crystal structure (hexagonal — rhombohedral)	$(10\bar{1}1)$ rhomb
Color (solid)	Grey
Cleavage (basal)	(0001)

SAMARIUM, Sm

General: Does not occur as a native element. It is one of the more rare of the cerium group rare earths in the lanthanide series, and found primarily in the mineral samarskite, a tantalate containing rare earths with iron, calcium, and niobium. There has been no use of the material in industry due to scarcity, but several salts have interest in chemistry.

Technical Application: Samarium has not had much use in Solid State processing, although it may have applications in garnet formulations like other rare earths. It has been grown as a single crystal for general morphology study and, as a polycrystalline cylinder, for electrical resistivity measurements.

Etching:

SAMARIUM ETCHANTS

SM-0001
ETCH NAME: Heat
TYPE: Thermal, forming
COMPOSITION:
x .... heat
TIME:
TEMP: Elevated
DISCUSSION:
Sm, specimens were arc melted as buttons and then machined into cylinders $^3/_{16}$ to 2″

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in diameter. Used for measuring electrical resistivity. Other materials studied were La, Pr, and Nd.
REF: Alstad, J K et al — *Phys Rev*, 122,1639(1961)

PHYSICAL PROPERTIES OF SAMARIUM BROMIDE, $SmBr_3$

Classification	Bromide
Atomic numbers	62 & 34
Atomic weight	239.5
Melting point (°C)	>70
Boiling point (°C)	
Density (g/cm³)	~3.xx
Hardness (Mohs — scratch)	2—3
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Colorless
Cleavage (basal)	(0001)

SAMARIUM BROMIDE, $SmBr_3$

General: Does not occur as a natural compound. The metal is one of the rare earths of the cerium lanthanide series. There are a few mineral bromides containing silver, such as bromyrite, AgBr, but none containing samarium. There is no industrial use of samarium bromide.

Technical Application: Samarium bromide has been grown as a single crystal by the Horizontal Bridgman (HB) method and general study of material characteristics. It has been fabricated as a Quantum Counter. The material is hygroscopic and should be handled under an inert gas atmosphere.

Etching: Alcohols.

SAMARIUM BROMIDE ETCHANTS

SMBR-0001
ETCH NAME: Ethyl alcohol — TIME:
TYPE: Alcohol, polish — TEMP: RT
COMPOSITION:
x .... EOH
DISCUSSION:
$SmBr_3$ (0001) wafers cut from ingots grown by a modified Bridgman method with a brass inner line for a sharp heat gradient. Material used as a base for Quantum Counters. Polish surface with alcohol. Specimens cut 1—2 cm² and 2—5 mm thick, were clear, transparent crystals. $SmBr_3$ is hexagonal: $LaBr_3$ is orthorhombic crystal structure, and both are hygroscopic.
REF: Krasutsky, N J — *J Appl Phys*, 54,126(1983)

SAMARIUM COBALT ETCHANTS

SMCO-0001
ETCH NAME: Citric acid, dilute — TIME:
TYPE: Acid, cleaning — TEMP: 80°C
COMPOSITION:
x .... citric acid
x .... H_2O

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DISCUSSION:

$SmCo_5$, specimens fabricated as permanent magnets. Solutions of citric acid can be used to etch clean this material.

REF: Buschow, K H L et al — *J Appl Phys*, 40,4029(1969)

PHYSICAL PROPERTIES OF SAPPHIRE, Al_2O_3

Classification	Oxide
Atomic numbers	13 & 8
Atomic weight	102
Melting point (°C)	1800
Boiling point (°C)	2250
Density (g/cm^3)	3.99
Softening point (°C)	2050
Thermal conductance (cal/sec/cm/°C sec) 25°C	0.086
Coefficient of thermal linear expansion	5.4/6.2 (xtl)
($\times 10^{-6}$ cm/cm/°C)	7.3/8.1 (fused)
Specific heat (cal/g/°C) 25°C	0.18
Electrical resistance (ohms mm^2/cm) @ 500°C	10^{11}
@ 1000°C	10^6
@ 2000°C	10^3
Dielectric constant (e =)	7.5—10.5
Refractive index (n =)	1.769—1.759
Transmission (visible light)	Excellent
(infrared)	50—85%
(ultraviolet)	50—80%
Compressive strength (kg/cm^2)	2100
Modulus of rupture (kg/cm^2)	4000
Atomic spacing (angstroms)	a_o 4.748
	c_o 12.99
Hardness (Mohs — scratch)	9
(Knoop — kgf/mm^2)	1800—2200
(Vicker's — kgf/mm^2)	1570—1800
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism
Color (solid)	Colorless/red/blue
Cleavage (basal)	(0001)

SAPPHIRE, Al_2O_3

General: Occurs in nature as a sub-species of the mineral corundum, Al_2O_3. Corundum is an accessory mineral associated with rocks of the chlorite group, limestone and dolomite found embedded as small masses to large beds. The best gem quality material comes from upper Burma — *in situ* in limestone, in the soil, and in gem-bearing gravels of the Irrawaddy River — mostly ruby. In Cambodia and Siam, as fine blue sapphire. In India, light blue stones from Madras and other districts. Gem stone sapphires of different colors are found throughout the world, as are ordinary corundum and emery.

Corundum: all varieties of dark or dull colors and not transparent, with colors from blue to grey, brown, or black. Amadantine spar from India is greyish brown, but greenish/bluish by transmitted light. Major use has been as an abrasive.

Emery: Black to dark grey in color as a mixture of corundum and magnetite, sometimes hematite. Varies from fine-grained emery to coarse grained with distinct corundum crystals embedded. Still widely used as an abrasive.

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Gem Stones: The transparent to translucent varieties as single crystals are all sapphires. True sapphire is blue; true ruby or Oriental ruby, red; Oriental topaz, yellow; Oriental emerald, green; Oriental amethyst, purple. Asteriated or star sapphire, when cut on the z-axis shows a six-rayed star when viewed on the vertical z-axis caused by minute cylindrical cavities parallel to prism planes. Best quality is a fine grey-blue, near-translucent stone with grey-white "star" rays.

Artificial sapphire can be made in several ways: by melt flux growth; by an electric arc; re-melt of corundum chips — add chromium salt for red (ruby) — cobalt for blue. The Vernieul Process for growth of large single crystal boules (ingots) was developed in the late 1800s for artificial ruby. The system consists of a hopper holding powder that is fed down a tube past a hydrogen flame. The flame liquefies the powder into droplets, which with gravity fall through a control orifice into a vacuum chamber, and onto an oriented seed pedestal at the bottom. Single crystal boules $1^1/_2''$ in diameter and up to 6″ long have been grown in this manner. The method also has been used to grow single crystal hemispheres (see Silicon and Germanium), and is still used to grow high temperature melting single crystals, today. A ruby melt also is poured into molybdenum forms for production of rods, sheet, tubes, prisms, and other specialized shapes fabricated, such as spheres for high temperature ball bearings, and wire bonding tips.

Artificial single crystal gem stones of all materials can be differentiated from the natural stones by microscopic examination of internal artifacts. The artificial stones will show curved growth lines; whereas the natural stones, straight and angled growth lines. The artificial stones also may show flow lines, such as the "paste" jewelry made from glass . . . which was being made by the Egyptians as early as 3000 B.C. Natural transparent stones, such as diamonds, quartz (amethyst, rock crystal, etc.), obsidian (natural glass) may contain flecks of graphite (diamond), or other material (rutilated quartz).

Some "picture" agates (a form of quartz), when cut in thin section, show a skyline like picture of trees, etc., such as that found in the Colorado area near the Grand Canyon, and there is "snowflake" obsidian containing flower-like inclusions of calcium carbonate. Natural stones also may have fine cavities and bubbles, some containing gas or entrapped liquid remaining from their growth environment. The gases or liquids in such material, quartz in particular, are used to establish atmospheric and other geologic conditions that existed at the time of formation as far back as 10 million years. Artificial crystals are not grown with such voids, though they can occur during diffusion of an element or gas, or from ionized particle irradiation. The garnet bubble memory devices refer to the ordered location of iron atoms in a solid matrix, not to an actual bubble or void.

As artificial fused (clear) sapphire with a Mohs hardness of H = 9, it is nearly impervious to being scratched, and is widely used as watch and clock faces. And there have been occasional references to the use of powdered sapphire as a lap and polish abrasive, although fine white alumina abrasives are more often ground from common corundum sources.

Technical Application: Artificial sapphires as both fused and single crystal substrates are used in the Solid State field to fabricate microelectronic circuits after thin film metallization (Au/Cr; Au/Ni, etc.). Discrete units as insulators and mounting bases for semiconductor devices, or active elements are fabricated as modulators and filters in circuitry similar to applications of quartz, glass, etc.

Both sapphire and quartz are in the hexagonal system and, as single crystal sapphire, are normal cut and used as basal (0001) oriented substrates or as either first order or second order prisms, $(10\bar{1}0)$ and $(10\bar{2}0)$, respectively. Like the circular semiconductor wafers, a directionally oriented flat is often cut at the sapphire blank periphery . . . on silicon as a $\langle 110 \rangle$ direction flat . . . on sapphire or quartz, when fabricated as a square (0001) blank, a corner orientation $(10\bar{1}0)$ prism is edge cut.

It should be noted that, in dicing sapphire and quartz into square or rectangular shape, the first cut — parallel to a prism face — is easily done but, the second cut at right angles

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is very difficult, as the normal angles between prism faces in the hexagonal system are at 60°, not 90°, as they are with silicon in the isometric system.

In addition to the use of sapphire as circuit substrates or stand-offs, the use of ruby as wire ball bonding tips in semiconductor device fabrication has already been mentioned, the substrates also have been used for deposition and growth studies of thin film materials, such as AlN and GaN.

Single crystal sapphire has been studied in both natural and artificial forms for many years, much work in regard to the cutting and polishing of gem stone materials.

Etching: Difficult. H_3PO_4, molten fluxes. Dry chemical etching (DCE) with ionized gases. See Aluminum oxide.

SAPPHIRE ETCHANTS

SAP-0001
ETCH NAME:
TYPE: Acid, clean
TIME:
TEMP: Hot(?)
COMPOSITION:
1 .... H_3PO_4
1 .... H_2SO_4
DISCUSSION:
Al_2O_3 (0001) wafers used as substrates for MOCVD growth of GaN, AlN and AlGaN. The latter is an n-type to semi-insulating (SI) semiconductor depending upon the ratio of Al:Ga. The AlGaN thin film is smooth and transparent with some hexagonal pyramid growth near the substrate edge with pyramid edges ⟨1021⟩. Prior to MOCVD, degrease the sapphire substrates in solvents and etch clean with the solution shown. Though a temperature was not shown, solution was probably warm to hot.
REF: Matlonbian, M & Gerehenzon, M — *J Electron Mater*, 14,633(1985)

SAP-0002a
ETCH NAME: Phosphoric acid
TYPE: Acid, preferential
TIME:
TEMP: Hot
COMPOSITION:
x .... H_3PO_4
DISCUSSION:
Al_2O_3, (0001) wafers. Solution will develop dislocation etch pits similar to those observed after silicon has been deposited and removed.
REF: Manasevit, H M & Simpson, W I — *J Appl Phys*, 35,1349(1964)

SAP-0002b
ETCH NAME: Silicon
TYPE: Metal, preferential
TIME:
TEMP: >1200°C
COMPOSITION:
x .... Si
DISCUSSION:
Al_2O_3, (0001) wafers. Silicon metal evaporated and then removed from sapphire surfaces will develop dislocation pits in the sapphire.
REF: Ibid.

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SAP-0003
ETCH NAME: Trichloroethylene
TYPE: Solvent, cleaning
TIME: 2—5 min
TEMP: Boiling
COMPOSITION:
x .... $CHCl:CCl_2$ (TCE)
DISCUSSION:
Al_2O_3, clear fused sapphire blanks and (0001) oriented single crystal blanks used as substrates for metallization of microelectronic circuits. Blanks were cleaned in boiling TCE, transferred to fresh TCE with ultrasonic agitation for additional 2—5 min. Rinse in acetone, then MeOH and nitrogen blow dry.
REF: Marich, L A & Porter, R — personal communication, 1980

SAP-0004a
ETCH NAME: RCA Etch (AB Etch)
TYPE: Acid, cleaning
TIME: 10—15 min
TEMP: 70—80°C
COMPOSITION:

(A)	(B)
1 .... NH_4OH	1 .... HCl
1 .... H_2O_2	1 .... H_2O_2
6 .... H_2O	6 .... H_2O

DISCUSSION:
Al_2O_3, clear fused sapphire blanks and (0001) single crystal oriented blanks used as substrates for metallization of microelectronic circuits. The solutions are used separately; clean in solution "A", then transfer to solution "B" while still wet. Solutions should be mixed fresh and heated when ready for use. After cleaning, rinse in MeOH and nitrogen blow dry. Also followed cleaning with 30 sec HF dip, water rinse 30 sec and N_2 blow dry. A third process step included holding blanks under MeOH until placed in an evaporator system still wet with MeOH. This gave best adhesion results of metal films. This cleaning system also used on alumina, pressed powder blanks and fused/single crystal quartz blanks. Holding wafers or substrates under methanol after etching, and until being placed in a diffusion tube or vacuum evaporator, was used by Walker on silicon and other semiconductor materials in 1963.
REF: Walker, P & Porter, R — personal application, 1981

SAP-0004b
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
TIME: 30 sec
TEMP: RT
COMPOSITION:
x .... HF, conc.
DISCUSSION:
Al_2O_3, clear fused sapphire blanks and (0001) single crystal oriented blanks used as substrates for metallization of microelectronic circuits. HF used as a final cleaning dip prior to vacuum metallization. Follow dip with DI water rinse, MeOH rinse and N_2 blow dry or hold under MeOH until placed in a vacuum system still wet. The latter method gave best adhesion results.
REF: Ibid.

SAP-0004c
ETCH NAME:
TYPE: Halogen, surface treatment
TIME: 15—30 sec
TEMP: RT
COMPOSITION:
5 mg .... I_2
150 ml .... MeOH

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DISCUSSION:

Al_2O_3, clear fused sapphire blanks and (0001) single crystal oriented blanks used as substrates for metallization of microelectronic circuits. After previous blank cleaning, rinse in this solution and N_2 blow dry immediately before placing blanks in a vacuum system or a diffusion system. Iodine complexes ionic surface contamination when parts are heated to >100°C producing a molecularly clean surface for metallization or doping diffusion. This method used on single crystal quartz blanks, alumina pressed power blanks and silicon.
REF: Ibid.

SAP-0005
ETCH NAME: Freon 113 TIME: 1—2 min
TYPE: Solvent, degreasing TEMP: Hot
COMPOSITION:

x .... Freon 113, vapor

DISCUSSION:

Al_2O_3, clear fused sapphire blanks and (0001) single crystal oriented blanks used as substrates for microelectronic circuit metallization. Solution used as the vapor degreaser system solvent for sapphire in addition to other substrate materials and assembly parts.
REF: DaLuca, J & Gunshinan, B — personal communication, 1985

SAP-0006
ETCH NAME: Metallization TIME:
TYPE: Metal, thin film coating TEMP: 1950°C
COMPOSITION:

x .... Nb

DISCUSSION:

Al_2O_3, single crystal spheres were metallized with niobium. Article describes experimental method developed for coating a sphere.
REF: Strayer, D M et al — *NASA Tech Briefs,* Fall 1985, 158

SAP-0007
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, cleaning TEMP: RT
COMPOSITION:

1 .... HF
10 .... H_2O

DISCUSSION:

Al_2O_3, as fused sapphire parts in amorphous form (red ruby). A hot liquidized melt of the material is poured into molybdenum metal forms to fabricate rods, tubes, sheets, etc. Spheres, for use as high temperature ball bearings, ground and polished with diamond paste. Solution used for general cleaning of parts. Ruby wire bonding tips also fabricated.
REF: Brochure

SAP-0008
ETCH NAME: Soap TIME:
TYPE: Fatty acid, cleaning TEMP: Warm
COMPOSITION:

x .... Ivory soap
x .... H_2O

DISCUSSION:

Al_2O_3, as natural single crystals as blue sapphires, red rubies, and star sapphires fab-

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ricated as gem stones. A soap solution was used to wash and remove oil of diamond paste polishing compounds after facetting in orientation studies of these materials.
REF: Walker, P — gem stone fabrication (1953—1985)

SAP-0009
ETCH NAME: Potassium hydroxide
TYPE: Alkali, dislocation
TIME: 2 min
TEMP: 300°C
COMPOSITION:
x .... KOH, fused
x .... 10—15% H_2O
DISCUSSION:
Al_2O_3, single crystal sapphire $(10\bar{1}2)$ and (0001) orientations. Solution used to develop etch pits and dislocations in Czochralski (CZ) grown ingot material.
REF: Kim, K M & McFarlande, S H — *J Appl Phys*, 49,6171(1978)
SAP-0010: Forgeng, W D & Webb, W W — *J Appl Phys*, 28,1449(1957)
Al_2O_3 grown as single micro-crystal sapphire in a study of growth mechanisms and defect structure.

SAP-0011
ETCH NAME: Heat
TYPE: Thermal, cleaning
TIME:
TEMP: 1200°C
COMPOSITION:
x .... heat
DISCUSSION:
Al_2O_3, as (0001) or $(01\bar{1}2)$ sapphire blanks used as substrates for growth of AlN and GaN by MBE. Clean sapphire in the vacuum system at temperature shown — reduce to 1100°C at 2×10^{-5} Torr for Al/NH_3 deposition of AlN; then to 700°C at 2×10^{-4} Torr with Ga/NH_3 for a 1000 Å thick GaN final cover thin film. GaN was n-type. GaN has better uniformity deposited on AlN than directly on sapphire. Coefficient of thermal expansion and atomic spacing shown for the three materials.
REF: Yoshida, S — *J Vac Sci Technol*, B1(2),250(1983)

PHYSICAL PROPERTIES OF SCANDIUM, Sc

Classification	Transition metal
Atomic number	21
Atomic weight	44.94
Melting point (°C)	1539
Boiling point (°C)	2730
Density (g/cm^3)	3.0
Thermal conductance $(cal/sec)(cm^2)(°C/cm)$	0.015
Specific heat (cal/g) 25°C	0.13
Latent heat of fusion (cal/g)	84.52
Heat of vaporization (k-cal/g-atom)	81
Heat of fusion (k-cal/g-atom)	3.8
Atomic volume (W/D)	15
1st ionization energy (K-cal/g-mole)	151
1st ionization potential (eV)	6.56
Electronegativity (Pauling's)	1.3
Covalent radius (angstroms)	1.44
Ionic radius (angstroms)	0.81 (Sc^{+3})

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Electrical resistivity (micro-ohms-cm) 298 K	50.9 (61)
Compressibility ($cm^2/kg \times 10^{-6}$)	2.26
Transformation temperature (°C)	1335
Cross section (barns)	23
Hardness (Mohs — scratch)	5—6
Crystal structure (hexagonal — normal)	$(10\bar{1}0)$ prism, hcp
Color (solid)	Silver grey
Cleavage (basal)	(0001)

SCANDIUM, Sc

General: Does not occur as a native element. It is extremely rare and the metal is found as a trace element in rare earth minerals containing cerium and cesium. Although a transition metal, it is sometimes listed as a rare earth. No use in metal industries due to scarcity, but salts are of use in chemistry.

Technical Application: No use in Solid State processing, to date, due to scarcity. It was not separated as a metal until the middle of this century, but has been grown as a single crystal for general morphology study.

Etching: HCl, HNO_3, aqua regia.

SCANDIUM ETCHANTS

SC-0001a
ETCH NAME: Hydrochloric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... HCl
DISCUSSION:
Sc, (0001) wafers. Solution used as a polish etch.
REF: Colvin, R V & Arajs, S — *J Appl Phys*, 34,286(1963)

SC-0001b
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
Sc, (0001) wafers. Solution used as a polish etch.
REF: Ibid.

SC-0001c
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP:
COMPOSITION:
x .... HCl
x .... HNO_3
DISCUSSION:
Sc, polycrystalline rod dissolved in this solution to determine impurity content.
REF: Ibid.

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PHYSICAL PROPERTIES OF SELENIUM, Se

Classification	Non-metal
Atomic number	34
Atomic weight	78.96
Melting point (°C)	217 (grey form)
Boiling point (°C)	685
Density (g/cm^3)	4.79
Thermal conductance (cal/sec)(cm^2)(°C/cm $\times 10^{-4}$)	0.1 (7—18
Specific heat (cal/g) 25°C	0.084
Heat of fusion (k-cal/g-atom)	1.25
Latent heat of fusion (cal/g)	16.4
Heat of vaporization (k-cal/g-atom)	3.34
Atomic volume (W/D)	16.5
1st ionization energy (K-cal/g-mole)	225
1st ionization potential (eV)	9.75
Electronegativity (Pauling's)	2.4
Covalent radius (angstroms)	1.16
Ionic radius (angstroms)	0.05 (Se^{+4})
Coefficient of linear thermal expansion ($\times 10^{-5}$ cm/cm/°C)	3.79 (3.68)
Electrical resistivity (micro $ohms^{-1}$)	0.08
Compressibility ($atm^{-1} \times 10^{-5}$)	12.2
Magnetic susceptibility ($\times 10^{-6}$ emu/mole)	0.32
Cross section (barns)	12
Vapor pressure (°C)	554
Electrical resistivity ($\times 10^6$ ohm cm) 20°C	10
Electron work function (eV)	4.72
Hardness (Mohs — scratch)	2
Crystal structure (hexagonal — normal)	($10\bar{1}0$) prism (grey type)
(monoclinic — normal)	(100) a-pinacoid (red type)
(amorphous)	None (black type)
(colloidal)	None (dark red type)
Color (solid)	Dull grey (Hex)
(flame)	Azure blue
Cleavage (basal)	(0001) or (001)

SELENIUM, Se

General: Does not occur as a native element. It is a rare element and largely found as a trace element in a number of minerals of the pyrite group, e.g., pyrite, FeS_2 and similar sulfide, telluride, arsenide, and antimonide minerals. Selenium is obtained from the flue dust during the roasting of pyrite ores. It is in the sulfur family, which it resembles in its physical forms and compounds. Can be separated and formed as pure metal colloid, amorphous material, or crystallized in the two crystallographic structures shown in the Physical Properties table above. In the colloidal or amorphous forms it is brilliant red in color; whereas the crystalline forms are a dull grey. As a crystal, its electrical conductivity increases with the brightness of light.

In some areas it occurs in the soil in sufficient amounts to be dangerous to animals and plants as it is a toxic substance.

In general industry its major use is in glass and ceramic fabrication in the colloidal red form as a coloring agent. It is occasionally used as a minor constituent in some metal alloys.

Technical Application: Selenium is an n-type dopant in several compound semiconductors, and there are several binary and trinary compound semiconductors such as zinc selenide,

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ZnSe; cadmium selenide, CdSe or cadmium sulfur selenide, CdSSe and lead tin selenide, PbSnSe etc.

As the pure single crystal it has been fabricated as a rectifier in the semiconductor industry for many years as well as a photoelectric cell. It has a very distinctive, unpleasant odor and can produce "selenium breath" similar to that of tellurium.

Etching: H_2SO_4, HNO_3, CS_2, mixed acids and alkalies.

SELENIUM ETCHANTS

SE-0001
ETCH NAME: Sulfuric acid — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... H_2SO_4
DISCUSSION:
Se, deposits remaining on the $(\overline{111})$B surface of HgSe wafers after preferential etching in 1HCl:1HNO_3. Se film can be removed with the etchant shown.
REF: Warekois, E P et al — *J Appl Phys*, 33,690(1962)

SE-0002: Heleskivt, J et al — *J Appl Phys*, 40,2923(1969)
Se, single crystals (called "trigonal" crystals) used to measure the Hall effect. After lapping surfaces, solution used to remove damage.

SE-0003a
ETCH NAME: — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... H_2SO_4
x .... HNO_3
DISCUSSION:
Se, single crystal wafers used in an X-ray topography study of defects. Solution used to develop defects.
REF: Maukkarinen, K & Toomi, T O — *J Appl Phys*, 40,3054(1969)

SE-0003b
ETCH NAME: — TIME:
TYPE: Halogen, preferential — TEMP:
COMPOSITION:
x .... x% Br_2
x .... MeOH
DISCUSSION:
Se, single crystal wafers. See SE-0003a for discussion.
REF: Ibid.

SE-0004a
ETCH NAME: — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... HNO_3
DISCUSSION:
Se, single crystal specimens used in a material study using an electron microscope (EM) to observe defects. Solution used to etch thin specimens for microscope study.
REF: Chihaya, T et al — *Nippon Kinzoku Gakkaishi*, 17,65(1955)

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SE-0004b
ETCH NAME: Sodium hydroxide — TIME:
TYPE: Alkali, removal — TEMP:
COMPOSITION:
x .... x% NaOH
DISCUSSION:
Se, single crystal specimens. Solution used to etch thin specimens. Authors say that bulk properties differ from surface properties.
REF: Ibid.

SE-0004c
ETCH NAME: Carbon disulfides — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
x .... Cs_2
DISCUSSION:
Se, single crystal specimens. Solution used to etch thin specimens.
REF: Ibid.

SE-0005
ETCH NAME: Heat — TIME:
TYPE: Thermal, cleaning — TEMP: 300°C
COMPOSITION:
x .... heat
DISCUSSION:
Se, powder used for epitaxy growth of CdSe and $(Cd,Se)_{1-x}Zn_x$. Clean material by vacuum baking at 300°C and then re-grind to powder. **CAUTION:** Requires proper cleaning and handling as the material can detonate.
REF: Kim, S U & Park, M J — *Jpn J Appl Phys*, 23,1070(1984)

SE-0006
ETCH NAME: — TIME:
TYPE: Acid, removal — TEMP: RT
COMPOSITION:
x .... 0.1 *M* S
x .... 2.5 *M* Na_2S
x .... 1 *M* KOH
DISCUSSION:
Se residual film left on CdSe polycrystalline thin films grown on titanium substrates after surface cleaning with 25% HNO_3. Remove excess selenium in solution shown. CdSe co-evaporated and heat treated at 400°C, 15 min to homogenize film in a study of the material. See CDSE-0008.
REF: Haak, R et al — *J Electrochem Soc*, 131,2709(1984)

SE-0007
ETCH NAME: Water — TIME:
TYPE: Acid, float-off — TEMP: RT
COMPOSITION:
x .... H_2O
DISCUSSION:
Se, thin films grown by epitaxy on KI (100) cleaved substrates, as 300 Å thick films in a study of Se structure. Water used to dissolve the KI/Se interface with film float-off for TEM study.
REF: Nagashima, S & Ogura, I — *Jpn J Appl Phys*, 23,1555(1984)

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SILICIDES, M_xSi_y

General: Silicides do not occur in nature as mineral alloys even though silicon is second only to oxygen in abundance as an element and is a constituent of most rocks as a silicate. Quartz and its many forms, as the oxide, SiO_2, and the metal silicate minerals, with SiO_2^-, SiO_3^-, SiO_4^- type radicals are primary rock-forming minerals, such as granites, clays, asbestos, hornblende, and feldspars.

Ferrosilicon obtained during the reduction of silicon ores is supplied in rough bar (pig) form to the metals industry as a primary material in the fabrication of irons and steels. This could be considered a form of silicide with a high iron content, but the "silicides" as a named group of materials are a combination of transition metals and silicon as developed in the Solid State and semiconductor industry.

Technical Application: Over a dozen silicides have been developed as mono- and di-silicides, such as MoSi, Ta_2Si, WSi_2, etc. In the general formula shown above, M = Co, Cr, Ni, Mo, Pd, Pt, Ir, Rh, Ti, Ta, W, and others. Silicides are fabricated on silicon wafers by thin film metallization (1) directly on silicon, (2) on a pre-deposited SiO_2 or Si_3N_4 layer on silicon, or (3) on a pre-grown polycrystalline layer of silicon on the single crystal silicon or other metals or metallic compounds. The specimens are then temperature annealed to form the silicide as a crystalline layer with temperature, time, atmospheres, and other annealing conditions controlled to develop the desired crystal structure. Laser annealing has been used directly or as a post-anneal step to increase crystallite size.

The primary application of silicides has been as buffer layers in semiconductor device structures to prevent or reduce cross-over diffusion of other structure elements such as aluminum.

There is much on-going development and study of the silicides themselves, to establish structure and morphology . . . deposition under varied conditions to include reaction studies with other layer elements . . . oxidation of the silicides and so forth. Note that temperature level is a major control factor as to structural forms.

Some silicides, such as $CoSi_2$, using a single crystal seed cut from pre-grown poly-crystalline material, have been used as seed crystals to grow the material as single crystal ingots using the Czochralski (CZ) technique for defect and morphological studies.

The following list of silicides is far from complete but presents both wet chemical etching (WCE) solutions that have been applied to the materials, as well as some dry chemical etching (DCE) ionized gases applied.

Etching: Acids, mixed acids. Ionized gases (CF_4:O_2).

SILICIDE BY TYPE

Aluminum Silicide (See Aluminum Alloys)
Boron Silicide
Cerium Silicide
Chromium Silicide
Cobalt Silicide
Erbium Silicide
Iron/Tungsten Silicide
Magnesium Silicide
Molybdenum Silicide
Nickel Silicide
Palladium Silicide
Platinum Silicide
Praseodymium/Cobalt Silicide
Tantalum Silicide
Terbium/Cobalt Silicide
Titanium Silicide
Titanium/Tungsten Silicide
Tungsten Silicide
Vanadium Silicide

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BORON SILICIDE ETCHANTS

BSI-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
B_4Si, specimens. HF:HNO_3, solutions attack this crystal form of boron silicide very slowly. The form as B_6Si is not etched.
REF: Matkovich, V I — *Acta Metall,* 11,679(1960)

TIME:
TEMP:

CERIUM SILICIDE ETCHANTS

CESI-0001
ETCH NAME: Kalling's etch
TYPE: Acid, polish
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH
DISCUSSION:
$CeSi_2$ specimens arc melted and used in a study of metallic compounds. Solution used as a general removal and polishing etchant. See cerium platinide CEPT-0001 for other compounds studied.
REF: Slepowronsky, M et al — *J Cryst Growth,* 63,293(1983)

TIME: 10—60 sec
TEMP: RT

CHROMIUM SILICIDE ETCHANTS

CRSI-0001
ETCH NAME: Oxygen
TYPE: Gas, oxidation
COMPOSITION:
x .... O_2
DISCUSSION:
$CrSi_2$, thin films deposited on silicon substrates and used in a study of dry oxidation kinetics. Other silicides referenced: Ti, Co, Ni, Mo, Rh, Ta, Ir, W, Pt, Pd, Os, Ru, Fe, Re, Te, Mn, Nb, V, Hf, and Zr.
REF: Bartur, M & Nicolet, M-A — *J Electrochem Soc,* 131,371(1984)

TIME:
TEMP: >1000°C

COBALT SILICIDE ETCHANTS

COSI-0001
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (5%)

TIME:
TEMP:
GAS FLOW:
PRESSURE
POWER:

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DISCUSSION:

$CoSi_2$ thin films grown on Si substrates. All of the following silicides can be etched by DCE in the mixture shown: $MoSi_2$; WSi_2; $TiSi_2$; $TaSi_2$; $CoSi_2$; NiSi.

REF: CRSI-0001

COSI-0002: Lied, G D et al — *J Electron Mater*, 13,95(1984)

CoSi, Co_2Si, and $CoSi_2$ grown on silicon substrates. Si substrates were first: thin film evaporated with SiO_2, which was then polycrystalline evaporated with silicon, Si^e. Cobalt was then evaporated on the Si^e layer and annealed at different temperatures to form the different silicide structures shown.

COSI-0003

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

x .... HF

DISCUSSION:

$CoSi_2$ thin film grown on substrates of Si, (111) and (100), n-type, 0.01 and 0.02 Ω cm resistivity. Co, Ti, Ni, Pd, and Pt evaporated to 1 K Å thickness. Surfaces thermally oxidized, both wet and dry, prior to metallization. Annealed NSi_2, $CoSi_2$, and PdSi at 800°C. $PdSi_2$ and PtSi annealed at 450°C. All other silicides annealed at 650°C. Authors say that all silicides are inert in HF; then say that Ni and Co silicides can be etched in HF(?).

REF: Bartur, M & Nicolet, M-A — *J Electron Mater*, 13,81(1984)

COSI-0004

ETCH NAME: Hydrofluoric acid, dilute — TIME:

TYPE: Acid, dislocation — TEMP:

COMPOSITION:

1 .... HF

1 .... H_2O

DISCUSSION:

$CoSi_2$, (100) wafers. Ingots grown from a $CoSi_2$ seed crystal, initially cut from crystalline material grown as thin films on (111) and (100) silicon wafers. During ingot growth, rotate crucible and seed in opposite directions. Solution used to develop the normal square dislocation etch pits on the (100) surfaces. Low angle grain boundaries observed are probably due to carbon and oxygen contamination.

REF: Ditchek, B B M — *J Cryst Growth*, 69,207(1984)

ERBIUM SILICIDE ETCHANTS

ERSI-0001

ETCH NAME: Heat + FG — TIME:

TYPE: Thermal, forming — TEMP:

COMPOSITION: — GAS FLOW:

x .... heat — PRESSURE:

x .... FG — POWER:

DISCUSSION:

$ErSi_2$ thin films grown on Si, (100), p-type, 1—10 Ω cm resistivity wafers used as substrates with deposit layer structure: a-Si/Er/Si(100). Anneal in forming gas (FG) at 450°C, 30 min to develop: $ErSi_2$. Barrier height changes with annealing temperature, from an initial 0.68 eV to 0.77 eV at 380°C to 0.74 eV at 500°C. Lowest was 0.72 eV (best?) when held at 400—450°C. Surface pits observed at 380°C and increased with additional time at tem-

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perature. There was an SiO_2 barrier observed between Er/Si as Er/SiO_2/Si during barrier height annealing. Acronym c-Si used to denote single crystal silicon. (*Note:* The c-Si acronym for a single crystal is in conflict with colloidal silicon, c-Si.)
REF: Wu, C S et al — *Thin Solid Films,* 104,175(1983)

IRON/TUNGSTEN SILICIDE ETCHANTS

IWSI-0001
ETCH NAME: Hydrogen peroxide
TYPE: Acid, removal
COMPOSITION:
(1) x .... H_2O_2 (2) x .... HNO_3 (3) x .... HCl
DISCUSSION:
FeWSi, thin films deposited on silicon, (100) wafers with and without thin film SiO_2 pre-deposited. FeW films were 1000 Å thick and were overcoated with 1000 Å of aluminum, gold, copper, palladium, or platinum. Used in a study of a-FeW thin films annealed crystallinity, and their application as a buffer layer against the upper metal layer cross-diffusion. Under experimental conditions, the a-FeW was a good barrier up to 650°C for 30 min. (*Note:* a- is the acronym for amorphous structure.)
REF: Suni, I et al — *Thin Solid Films,* 107,73(1983)

TIME:
TEMP:

MAGNESIUM SILICIDE ETCHANTS

MGSI-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
10 .... HF
2 .... HNO_3
DISCUSSION:
Mg_2Si, single crystals. Intrinsic material is n-type semiconducting; dope p-type with Ag or Cu. Band gap varies: 0.69—0.78 eV. Also worked with Mg_2Ge.
REF: Morris, R G et al — *Phys Rev,* 109,1909(1958)

TIME:
TEMP:

MOLYBDENUM SILICIDE ETCHANTS

MOSI-0001
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (5%)
DISCUSSION:
$MoSi_2$ thin films deposited on silicon substrates. All of the following silicides can be etched by DCE in the mixture shown: $MoSi_2$; WSi_2; $TiSi_2$; $TaSi_2$; $CoSi_2$ and NiSi.
REF: CRSI-0001

TIME:
TEMP:
GAS FLOW: 190 cm^3/min
PRESSURE: 0.6—2.0 Torr
POWER:

MOSI-0002. Inoue, S et al — *J Electrochem Soc,* 130,1603(1983)
$MoSi_2$, thin films deposited on silicon, (1000), p-type substrates containing a 1000 Å thick SiO_2 layer pre-deposited at 1000°C with dry O_2. RF plasma etching used to form dot patterns of silicide.

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MOSI-0003
ETCH NAME: CAIBE
TYPE: Ionized gas, selective
COMPOSITION:
x .... Ar
x .... Cl_2
DISCUSSION:

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

$MoSi_2$, the films deposited on silicon substrates, and silicon coated with polycrystalline silicon. Etching was done (DCE) by chemically assisted ion beam etching (CAIBE) in a study of etch rates, material structure, defects, and reactions. Other silicides evaluated were Ti, Ta, and Pt. (*Note:* CAIBE is a specialized form of RF plasma etching as a reactive ion etch (RIE) system.)

REF: Chinn, J D et al — *J Electrochem Soc,* 131,375(1984)

MOSI-0004: Neppl, F et al — *J Appl Phys,* 130,1174(1983)

MoSi and Mo_2Si thin films co-evaporated on silicon (100) substrates in a study of their application in silicon gate structured device technology. Films must be annealed to lower resistivity that substrates and oxygen in air will tarnish surfaces. $MoSi_2$ is tetragonal; Mo_3Si is isometric (cubic), and shows tensile stress due to atomic lattice shrinkage.

MOSI-0005
ETCH NAME:
TYPE: Gas, forming
COMPOSITION:
x .... Ar
x .... CCl_4
DISCUSSION:

TIME:
TEMP: 900°C
GAS FLOW: 5 sccm
PRESSURE: 1—2 × 10^{-4} Torr
POWER:

$MoSi_2$ thin films grown by co-deposition of silicon and molybdenum substrates in argon at 3 × 10^{-3} Torr. Si, (100) substrates used, and deposit showed 55 Ω^2 resistivity. Anneal, as shown above, and resistivity reduces to 5 Ω^2.

REF: Powell, R A — *J Appl Phys,* 130,1164(1983)

NICKEL SILICIDE ETCHANTS

NISI-0001
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (5%)
DISCUSSION:

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

NiSi thin films deposited on silicon substrates. All of the following silicides can be etched by DCE in the mixture shown: $MoSi_2$; WSi_2; $TiSi_2$; $TaSi_2$; $CoSi_2$, and NiSi. (*Note:* This is a form of RF plasma etching.)

REF: CRSI-0001

NISI-0002
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF

TIME:
TEMP:

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DISCUSSION:
$NiSi_2$ thin films grown on silicon substrates. See COSI-0003 for discussion.
REF: Bartur, M & Nicolet, M-A — *J Electron Mater*, 13,81(1984)

NISI-0003
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
x .... O_2
x .... H_2O
DISCUSSION:
$NiSi_2$ thin films deposited on silicon wafers. Also worked with $HfSi_2$. This work referenced to that of Baglin TISI-0005.
REF: Bartur, M — *J Appl Phys Lett*, 40,175(1982)

PALLADIUM SILICIDE ETCHANTS

PDSI-0001
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
DISCUSSION:
PdSi and $PdSi_2$ thin films grown on silicon substrates. See: COSI-0003 for discussion.
REF: Bartur, M & Nicolet, M-A — *J Electron Mater*, 13,81(1984)

PLATINUM SILICIDE ETCHANTS

PTSI-0001
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
x .... HF
DISCUSSION:
PtSi, thin films grown on silicon substrates. See COSI-0003 for discussion.
REF: Bartur, M & Nicolet, M-A — *J Electron Mater*, 13,81(1984)

PTSI-0002
ETCH NAME: Platinum TIME:
TYPE: Metal, deposition TEMP: 1000°C
COMPOSITION:
x .... Pt
DISCUSSION:
Pt_2Si, thin films formed on silicon, (111) and (100) n-type wafers, 1—10 Ω cm resistivity. Silicon wafers were ultrasonically cleaned in acetone; EOH rinse; oxide etched in a BHF solution, then flood with EOH without exposure to air. Wafer backs were coated with tantalum metal for use as a resistance heater control of the substrates. Platinum was evaporated from a resistively heated wire at 1000°C followed by annealing to form Pt_2Si.
REF: Matz, R et al — *J Vac Sci Technol*, A(2),253(1984)

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PTSI-0003
ETCH NAME: CAIBE
TYPE: Ionized gas, removal
COMPOSITION:
x .... Ar
x .... Cl_2
DISCUSSION:
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

PtSi, thin films deposited on silicon and poly-silicon coated wafers. Chemically assisted ion beam etching (CAIBE) used to establish etch rates of the material and for studying defects and structure. Other silicides studied were Mo, Ti, and Ta.
REF: Chinn, J D et al — *J Electrochem Soc*, 131,375(1984)

PTSI-0004
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
TIME:
TEMP:

PtSi specimens used in a study of electronic phase transitions. Various mixtures of solution shown were used for general material etching. Also studied Ni:Ti and Zr_2Ni. See PTSI-0004.
REF: Lee, R N & Wither, R — *J Appl Phys*, 49,5488(1978)

PRASEODYMIUM/COBALT SILICIDE ETCHANTS

PRCS-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
TIME:
TEMP:

$PrCo_2Si_2$, single crystals grown from mixed powders in an induction furnace. Powdered samples used in a study of magnetic super-lattices. These types of materials are body-centered tetragonal (bct) structure. See section on Germanides for similar structured materials.
REF: Yakinthros, J K & Routsi, Ch — *J Phys Chem Solids*, 45,689(1984)

TANTALUM SILICIDE ETCHANTS

TASI-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
COMPOSITION:
1 .... HF
20 .... H_2O
DISCUSSION:
TIME:
TEMP:

$TaSi_2$, thin films deposited on silicon (100), n-type, 10 Ω cm resistivity wafers. Silicon wafers were cleaned in the solution shown to remove native oxide before titanium metal evaporation and annealing.
REF: CRSI-0001

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TASI-0002
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (5%)
DISCUSSION:
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

$TaSi_2$, thin films deposited on silicon substrates. All of the following silicides can be etched in the gas mixture shown: $MoSi_2$, WSi_2, $TiSi_2$, $CoSi_2$ and NiSi.
REF: CRSI-0001

TASI-0003
ETCH NAME: CAIBE
TYPE: Ionized gas, removal
COMPOSITION:
x .... Ar
x .... Cl_2
DISCUSSION:
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

$TaSi_2$, thin films deposited on silicon and poly-silicon deposited wafers. Chemically assisted ion beam etching (CAIBE) was used to establish etch rates and study defects and structure. Other silicides studied were titanium, molybdenum, and platinum.
REF: Chinn, J I et al — *J Electrochem Soc,* 131,375(1984)

TASI-0004
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF
DISCUSSION:
TIME:
TEMP: RT

$TaSi_2$, thin films grown on poly-Si deposited on oxidized silicon wafers or on fused and single crystal sapphire substrates. Ta magnetron sputter and reacted under argon to form 2000 Å silicide. In measuring sheet resistance with a 4-point probe, $TaSi_2$ was etched in HF. Grain boundary diffusion of tantalum into silicon or out-diffusion of phosphorus changes resistivity in poly-Si specimens. A cap oxide reduces the effect.
REF: Maa, J S et al — *J Vac Sci Technol,* B1,1(1983)

TASI-0005
ETCH:
TYPE: Acid, removal
COMPOSITION:
90 .... BHF (1BHF:30H_2O)
5 .... HNO_3
5 .... CH_2OHCH_2OH [ethylene glycol (EG)]
DISCUSSION:
TIME: 2 min
TEMP: RT

$TaSi_2$ thin films 2500—2800 Å used in a study of diffusion contamination. Solution used for general removal or step-etch of the films. Etch rate: 100 Å/min.
REF: Pelleg, J & Muarka, S P — *J Appl Phys,* 54,1337(1983)

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TASI-0006a
ETCH NAME:
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (x%)
DISCUSSION:
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

$TaSi_2$ as thin films grown on poly-Si as mushroom cap structure or cap portion of "T" channel structure. Plasma etch referred to as a fast isotropic etch for metal silicides. $MoSi_2$, WSi, and WSi_2 showed compressive stresses. This was a study of refractory metal silicides for VLSI application.
REF: Sinha, A K — *J Vac Sci Technol,* 19,778(1981)

TASI-0006b
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... HF
30 .... H_2O
DISCUSSION:
TIME:
TEMP: RT

$TaSi_2$ thin films. Solution shown as a rapid etch for material. A BHF mixture also used, but not shown. (*Note:* 1HF:1NH_4F (40%) is one standard.)
REF: Ibid.

TERBIUM/COBALT SILICIDE ETCHANTS

TBCS-0001
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:
TIME:
TEMP:

$TbCo_2Si_2$ specimens. See PRCS-0001 for discussion.
REF: Yakinthros, J K & Routsi, Ch — *J Phys Chem Solids,* 45,689(1984)

TITANIUM SILICIDE ETCHANTS

TISI-0001
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (x%)
DISCUSSION:
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

Si, wafers used as substrates for growth of silicides. All of the following silicides can be dry chemical etched (DCE) in the mixture shown: $MoSi_2$; WSi_2; $TiSi_2$; $TaSi_2$; $CoSi_2$, and NiSi. (*Note:* 5% O_2 is fairly standard.)
REF: CRSI-0001

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TISI-0002
ETCH NAME: Hydrofluoric acid
TYPE: Acid, removal
COMPOSITION:
x .... HF
DISCUSSION:
$TiSi_2$ thin film grown on Si substrates. See COSI-0003 for discussion.
REF: Bartur, M & Nicolet, M-A — *J Electron Mater*, 13,81(1984)

TIME:
TEMP:

TISI-0003
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
1 .... NH_4OH
1 .... H_2O_2
4 .... H_2O
DISCUSSION:
$TiSi_2$, thin film formed on silicon (100) substrates in the fabrication of MOSFET devices. Silicon wafers were dip cleaned in HF prior to sputter evaporation of titanium and titanium was overcoated with molybdenum to reduce oxidation. After photo resist patterning both the Mo and excess Ti remaining after anneal conversion to $TiSi_2$ were selectively removed with the solution shown.
REF: Parks, H K et al — *J Vac Sci Technol*, A(2), 264(1984)

TIME: 10—15 min
TEMP: RT

TISI-0007
ETCH NAME: Kalling's etch
TYPE: Acid, polish
COMPOSITION:
100 ml .... HCl
5 mg .... $CuCl_3$
100 ml .... EOH
DISCUSSION:
$TiSi_2$ arc melted in fabrication and used in a study of metallic compounds. Solution used as a general removal and polishing etchant. See Cesium Platinide: CEPT-0001 for other compounds studied. Also studied the silicide $MoSi_2$.
REF: Slepowronsky, M et al — *J Cryst Growth*, 65,293(1983)

TIME: 10—60 sec
TEMP: RT

TISI-0004
ETCH NAME: CAIBE
TYPE: Ionized gas, removal
COMPOSITION:
x .... Ar
x .... Cl_2
DISCUSSION:
$TiSi_2$, thin films deposited on silicon wafers and wafers coated with poly-Si. Chemically assisted ion beam etching (CAIBE) was used to establish etch rates and to study defects and structure. Other silicides studied were tantalum, molybdenum, and platinum.
REF: Chinn, J D et al — *J Electrochem Soc*, 131,375(1984)

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

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TISI-0005
ETCH NAME:
TYPE: Acid, oxidation
COMPOSITION:
x .... O_2
x .... H_2O
TIME:
TEMP: 100°C
DISCUSSION:

$TiSi_2$ thin films grown on silicon substrates in a study of SiO_2 used to form silicides. Oxidize substrates by bubbling O_2 through hot water at 100°C (wrap beaker with heater tape). Evaporate 2000 Å of metal, and anneal in He 1 h at 1000°C. $TiSi_2$ then annealed at 750°C in wet O_2 develops a porous TiO_2 surface; above 900°C converts to SiO_2 with no Ti or Si metal. Other silicides evaluated: WSi_2, $TaSi_2$, RhSi, Rh_3Si_4, and IrSi as layered semiconductors with 1 eV band gaps. For $NiSi_2$ and $HfSi_2$ reference was made to NISI-0003.
REF: Baglin, J E et al — *J Appl Phys*, 54,1849(1983)

TISI-0006
ETCH NAME: Hydrofluoric acid
TYPE: Acid, oxide removal
COMPOSITION:
1 .... HF
20 .... H_2O
TIME:
TEMP: RT
DISCUSSION:

TiSi thin films grown on (100) silicon wafers, n-type, 10 Ω cm resistivity with p^+ ion implantation. After I^2 native oxide was removed with solution shown prior to evaporation of 100 Å Ti and annealing. A study of the growth of TiSi on ion implanted Si.
REF: Revesz, P et al — *J Appl Phys*, 54,1860(1983)

TITANIUM/TUNGSTEN SILICIDE ETCHANTS

TWSI-0001
ETCH NAME: Aqua regia
TYPE: Acid, removal
COMPOSITION:
3 .... HCl
1 .... HNO_3
TIME:
TEMP: RT
DISCUSSION:

$Ti_{0.3}W_{0.7}Si_2$, thin films. Silicon wafers (111), (110), and (100) oriented were used as substrates for RF deposition from a composite Ti/W target. The thin film was annealed at 700°C to form the silicide and showed no change at temperatures up to 900°C. The silicide was unaffected by hot H_2O_2, HF, or CP4 and only slowly dissolved in aqua regia.
REF: Harris, J M et al — *J Electrochem Soc*, 123,120(1976)

TUNGSTEN SILICIDE ETCHANTS

WSI-0001
ETCH NAME: Dry chemical etching
TYPE: Ionized gas, removal/selective
COMPOSITION:
x .... CF_4
x .... O_2 (5%)
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

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DISCUSSION:

WSi_2, thin films grown on silicon substrates. RF plasma etching can be used for removal and selective etching of most silicides. Also called dry chemical etching (DCE). This gas mixture was used to etch all of the following silicides: $MoSi_2$, $TiSi_2$, $TaSi_2$, and NiSi.
REF: CRSI-0001

WSI-0002
ETCH NAME: Hydrogen peroxide
TYPE: Acid, removal
COMPOSITION:
x .... H_2O_2
TIME:
TEMP:
DISCUSSION:

WSi_2, thin films reacted from CVD tungsten deposited on silicon (100) wafers. Annealing temperatures were 750 and 675°C, 30 min. Solution used for general removal and study of crystallite structures. Deposited material crystallites were tetragonal crystal structure.
REF: Green, M L & Levy, R A — *J Electrochem Soc*, 132,1243(1986)

WSI-0003
ETCH NAME:
TYPE:
COMPOSITION:
TIME:
TEMP:
DISCUSSION:

WSi_2, thin films selectively deposited on poly-Si coatings on silicon wafers for VLSI gate and interconnect structures. Poly-Si was isotropically etched for device patterns prior to tungsten deposition by CVD. WSi_2 on poly-Si produces good adhesion; deposited on SiO_2 there is poor bonding unless the deposit is rich in silicon oxide, Si_xO_y. Tungsten silicide can be etched in CF_4:O_2 gas mixtures. (See WSI-0001).
REF: Miller, N E & Beingglass, I — *Solid State Technol*, December 1982, 85

VANADIUM SILICIDE ETCHANTS

VSI-0001a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
1 .... H_2O_2
4 .... H_2O
TIME:
TEMP:
DISCUSSION:

V_3Si, (111) and (100) wafers used in a dislocation study. Solution used as a chemical polish.
REF: Levinstein, H J et al — *J Appl Phys*, 37,164(1966)

VSI-0001b
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 10% H_2SO_4
TIME: 1—5 min
TEMP: RT
ANODE: V_3Si
CATHODE:
POWER: 5 V

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DISCUSSION:
V_3Si, (111) and (100) wafers used in a dislocation study. Solution used to electropolish surfaces.
REF: Ibid.

VSI-0001c
ETCH NAME: TIME:
TYPE: Acid, dislocation TEMP:
COMPOSITION:
15 .... HF
4 .... H_2O_2
DISCUSSION:
V_3Si, (111), (100) wafers and other orientations. Solution will develop dislocations on both the (111) and (100) wafer surfaces.
REF: Ibid.

VSI-0002
ETCH NAME: TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
15 ml .... HF
100 ml .... HNO_3
DISCUSSION:
V_3Si, specimens used in a study of lattice softening. Solution used as a polishing and cleaning etch.
REF: Vaneo, E R & Finlayson, T R — *J Appl Phys*, 39,1980(1968)

VSI-0004
ETCH NAME: TIME:
TYPE: TEMP:
COMPOSITION:
DISCUSSION:
VSi_2 thin films. Vanadium deposited on (100) and (111) silicon n-type wafers, then annealed at 500°C for 5 min to convert to VSi_2 or as VSi at 350°C. Schottky barrier height was shown to be under 0.55 eV. (*Note:* See other vanadium silicides for etchants.)
REF: Clabes, J G & Roldoff, G W — *J Vac Sci Technol*, 19(2),262(1981)

VSI-0003
ETCH NAME: TIME: 10—60 sec
TYPE: Acid, polish TEMP: RT
COMPOSITION:
100 ml .... HCl
5 g .... $CuCl_3$
100 ml .... EOH
DISCUSSION:
V_3Si and V_3Ge arc melted in fabrication and used in a study of metallic compounds. Solution used as a general removal and polishing etchant. See Cesium Platinide CEPT-0001 for complete list of other compounds.
REF: Slepowronsky, M et al — *J Cryst Growth*, 65,293(1983)

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PHYSICAL PROPERTIES OF SILICON, Si

Classification	Non-metal
Atomic number	14
Atomic weight	28
Melting point (°C)	1412 (1410)
Boiling point (°C)	2878 (2355)
Density (g/cm^3)	2.33
Thermal conductance (cal/sec)(cm^2)(°C/cm)	0.353
Specific heat (cal/g) 25°C	0.162
Heat of fusion (k-cal/g-atom)	11.1
Latent heat of fusion (cal/g)	395
Heat of vaporization (k-cal/g-atom)	71
Atomic volume (W/D)	12.1
1st ionization energy (K-cal/g-mole)	188
1st ionization potential (eV)	8.15
Electronegativity (Pauling's)	1.8
Covalent radius (angstroms)	1.11
Ionic radius (angstroms)	0.42 (Si^{+4})
Electrical conductance (micro ohms — cm^{-1})	0.10
(ohm — cm) 0°C	10
Intrinsic resistivity ($\times 10^{-3}$ ohms cm)	64
Critical pressure (°C)	1450
Critical temperature (C.T.) (°C)	4920
Thermal expansion (ppm/°C)	2.8—7.3
Cross section (barns)	0.16
Vapor pressure (°C)	2083
Electron work function (eV)	4.52
Energy band gap (eV)	1.12
Lattice constant (angstroms)	5.43
Refractive index (n=)	3.6
Hardness (Mohs — scratch)	7
Crystal structure (isometric — normal)	(100) cube ("diamond")
Color (solid)	Grey silver/black
Cleavage (dodecahedral)	(110)

SILICON, Si

General: Does not occur as a native metal like gold, silver, or copper, though next to oxygen, it is the most abundant element in nature. About three quarters of all known minerals are silicates. There are over 3000 single crystal compounds and they make up about one fourth of the earth's crust. The most abundant, pure form is as silicon dioxide, SiO_2 — colloidal, amorphous, single crystal, and crystalline structures as rock-forming deposits, and there are colloidal silica beds formed from the exoskeletons of ancient sea life. Opal also is amorphous. Quartz, in clear single crystal form, is called rock crystal and, with color tints, several precious and semi-precious gem stones; the crystalline varieties include chalcedony, agates, and chert. Flint and chert are largely formed under sedimentary deposition conditions as nodular segregates to extensive beds from siliceous material, to include sea life skeletons. Volcanic obsidian is natural glass, and the volcanic rock, tufa, is a lightweight solidified silica froth.

The major source of silicon metal comes from the reduction of high purity, ancient sand beds, colloidal silica beds, and recently from ashed rice hulls. It is classified as a nonmetal similar to carbon (graphite), has several allotropic forms, and is one of the two semiconductor

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elements, the other being germanium as the two elemental semiconductor materials. Both of the elements are often referred to as being "diamond" structure . . . octahedron, (111) crystal form, of the isometric (cubic) system, normal class . . . but, since that diamond term definition was applied in the 1940s, it has been shown that both silicon and germanium have a tetrahedral unit cell similar to that of compound semiconductors, such that "diamond structure" is erroneous. (See the variety of finite crystal forms (FCF) that have been etched from single crystal spheres under Etchant Formats in both the Silicon and Germanium sections.)

In the heavy metal industries silicon is widely used in the form of ferro-silicon in the manufacture of irons and steels. With 14% silicon content in iron it is a brittle alloy that is highly acid resistant. There are several silicon chemical compounds of importance, such as sodium silicate (water glass) and silicon fluorides used in a variety of commercial processing applications.

The most important and widely used compound is glass, SiO_2 with a variety of additives. See the sections on Silicon Dioxide and Quartz for further details on glasses.

Technical Application: Although germanium was the first semiconductor developed in the late 1940s, it is the silicon semiconductor that has been the primary vehicle in establishing the electronics industry as we know it today; semiconductors being the Solid State equivalent of the glass vacuum tube and, although semiconductors have replaced many vacuum tubes in the low to medium power range (up to about 3000 V and 8 W) they have not reached, and may never reach, the high power capability of some vacuum tubes. A key factor in semiconductor development and processing is the ability to miniaturize, which has led to the microelectronic phase of the industry, well represented by the computer industry in addition to TV, light control, power appliances, microprocessors, and computers, all of continually smaller and smaller design as circuit size is reduced.

It is not within the scope of this small discussion to describe the vast number of silicon devices in any detail as this book is primarily concerned with the chemical processing of semiconductors rather than the electronic functions and characterization of devices, but a few bear mention, such as alloyed or diffused diodes and transistors; silicon-controlled rectifiers (SCRs), MOS, MNOS, IGFETS, FETS, ICs, etc. There are over 100 active silicon semiconductor devices, not including as a family of devices, such as alloy zeners and diffused zeners, which represent over 100 discrete voltage/power level devices alone.

In addition to semiconductor applications, silicon also is being used as a physical material without regard to semiconducting properties. Such application can be divided into two general areas: (1) bulk material used as diffusion tubes and parts carriers, epitaxy susceptor plates, infrared cones, and lenses etc., and (2) physical parts: strain gauges, ink dot heads, circuit boards, fiber optics couplers, as a gas chromatograph or heat sinks, and many other specialized physical structure elements.

Silicon is still the primary semiconductor, but is no longer used just as a single crystal element. Polycrystalline silicon, poly-Si, was initially developed for solar cell application, but also is a thin film deposit — used in conjunction with photolithographic techniques — for improved device structural rigidity or as a buffer or electrically active element in layered structures. Amorphous silicon, a-Si, is under development as a thin film structure, and colloidal silicon, c-Si, is under similar development and application, as is c-Si:H, hydrogenated colloidal silicon, which also may contain nitrogen as c-SiN:H, etc.

Poly-Si is further divided by grain size, with much effort involved to increase grain size for improved solar cell efficiency from its present 13 to 18%. Large crystallite material is grown by a modified Czochralski (CZ) freeze-out method, and by laser annealing.

A bi-crystal form of both silicon and germanium with (111) surface orientation — the ribbon crystal — is under ongoing development. It also is called dendritic growth. Grown as a continuous thin ribbon from a melt, there is always a twinned zone down ribbon center with 180° surface rotation to either side as a positive (111) and negative (111) surface.

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Unfortunately, such ribbon crystals contain low-angle grain boundaries, are highly stressed and, subsequently, contain a high dislocation content. There is much effort in progress to improve these crystals for cost reduction of single crystal growth. They also would eliminate the need of slicing ingots, and reduce the lapping and polishing requirements in processing.

Though silicon has long been used in its (111) surface orientation, with the development of high energy ion implantation (I^2) replacing gaseous diffusion, the (100) surface is more compatible, such that ribbon crystals may now be a thing of the past.

In semiconductor processing, silicon also is used as a constituent in other metallic compounds, such as aluminum-silicon as a p-type alloy. Two extremely important compounds are silicon dioxide, SiO_2 and silicon nitride, Si_3N_4. They are both used in photolithographic processing as masks against diffusion and etching, as a final surface protective coating, or as an active element in device layer construction (MOS and MNOS type devices). Silicides, mainly as blocking layer structures, are in use and under further development: MoSi, W_2Si, $TaSi_2$, and many others. The silicides are not limited to silicon devices alone, but are increasingly applied in compound semiconductor heterostructures.

As silicon has infrared characteristics, it has been fabricated as heat-seeking nose cones for missiles, as silicon lenses for Snooperscope rifles, or part of infrared night-sight eyeglasses. The latter are used for both military applications and air-sea rescue operations. It also is a lens in infrared microscopes, and is even used as a cigarette lighter. As a silicon controlled rectifier, (SCR) it is the operation element in most of the cordless hand tools for variable speed operation, as well as in light-dimming switches.

Single crystals are grown up to 6″ in diameter with 3″ a generally available size. The Czochralski (CZ) method for growing was developed primarily for silicon in the early 1950s, followed by Float Zone (FZ) where the CZ grown ingot is swept with a hot filament melt-zone to improve resistivity homogenization and remove oxygen contamination which in the 1950s was a problem with Czochralski ingots. Growth as polycrystalline silicon, colloidal or amorphous bulk material and thin films has already been mentioned.

Etching: HF:HNO_3, HF:H_2O_2 mixtures with or without H_2O, HAc, or other additives. Hot alkalies, molecular fluorine, and chlorine gases. Ionized gas as dry chemical etching (DCE).

SELECTION GUIDE

Note: The "A" section lists solutions by chemical formula; the "B" section by individual names.

A. Solutions by formula

(1) Br_2:MeOH (BRM)

Note: See Gallium Arsenide and Indium Phosphide for solution variations.

Polish: SI-0001

(2) HF, conc.

Cleaning: SI-0066d; -0235; -0407; -0420; -0414; -0430b

Oxide Removal: SI-0002g; -0005; -0006; -0007; -0008; -0120; -0143; -0211

Passivation: SI-0234

Stain: SI-0188a

(3) HF, vapor

Cleaning: SI-0009; -0027g; -0181b

(4) HF:H_2O

Cleaning: SI-0004a; -0031; -0032b; -0169a; -0191; -0108b; -0283a; -0010; -0011a; -0012; -0013; -0014; -0108a; -0245; -0169b; -0230; -1262; -1260; -0045b; -0132c; -0399; -0429

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Oxide Removal: SI-0132a; -0015; -0135a; -0136; -0144; -0180b; -0211
Step Etch: SI-0135b; -0132c
Thinning: SI-0121a

(5) HF:H_2O: +/− Glycerin (electrolytic)
Polish: SI-0083; -0225; -0245b

(6) HF:AgF
Preferential: SI-0187

(7) HF:CrO_3 (See Section B)
Preferential: SI-0182; -0139

(8) HF:$Cu(NO_3)_2$
Stain: SI-0186c

(9) HF:H_3PO_4
Selective: SI-0130

(10) HF:I_2
Preferential: SI-0125

(11) HF:MeOH
Cleaning: SI-0016

(12) HF:MeOH:I_2
Preferential: SI-0214; -0205

(13) HF:NH_4F/NaF:H_2O (BHF)
Cleaning: SI-0257; -0400; -0413; -0414; -0434
Nitride Removal: SI-0026; -0028
Oxide Removal: SI-0020; -0022; -0023; -0024; -0025; -0027; -0028; -0029; -0222; -0211
*Polish: SI-0021a; -0174a; -0174b; -0174c; -0041b; -0123; -0185
Preferential: SI-0174c; -0174d
*Removal: SI-0212
*May be electrolytic

(14) HF:H_2O_2:NaF_2
Junction: SI-0280

(15) HF:H_2O_2:H_2O
Preferential: SI-0165

(16) HNO_3, conc.
Cleaning: SI-0237
Stain: SI-0003

(17) HNO_3:H_2O_2
Cleaning: SI-0177b

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(18) $HF:HNO_3$
Float-off: Si-0255
Junction: SI-0069; -0223
Pinhole: SI-0060
Polish: SI-0102h; -0056; -0046b; -0052; -0288; -0057; -0201; -0061; -0289; -0058; -0063; -0102c; -0066a; -0092b; -0177a; -0181a; -0068; -0157a; -0121b; -0126; -0127; -0218; -0129; -0130; -0249; -0296; -0154; -0190a; -0161; -0166; -0178; -0180a; -0201b; -0063c
Preferential: SI-0140; -0189; -0168
Removal: SI-0245
Stain: SI-0140; 0189; -0168
Thinning: SI-0059; -0065; -0121b; -0162a; -0163a; -0440; * -0164
*Electrolytic

(19) $HF:HNO_3:H_2O$
Forming: SI-0173b; -0173a
Polish: SI-0073; -0126; -0127; -0128; -0129; -0130; -0249; -0296

(20) $HF:HNO_3$:HAc:
Polish: SI-0072; -0076; -0077; -0079; -0038a; -0080; -0124; -0126; -0127; -0128; -0129; -0130; -0297; -0249; -0296; -0194; -0150; -0160; -0162a; -0170; -0172; -0197a; -0030b; -0393
Preferential: SI-0075; -0246; -0173a
Stain: SI-0167
Step-Etch: SI-0078; -0263b
Thinning: SI-0074; -0124; -0148; -0163a; -0404; -0394; -0434

(21) $HF:HNO_3:AgNO_3:Hg(NO_3)_2$
Polish: SI-0081; -0082

(22) $HF:HNO_3:KNO_3$
Preferential: SI-0064

(23) $HF:H_2O_2:KMnO_3$
Polish: SI-0125

(24) H_2O, boiling
Cleaning: SI-0066c; -0184 (vapor)

(25) H_2O
Float-off: SI-0232

(26) H_2O, steam
Cleaning: SI-0239; -0184

(27) HCl, conc.
Cleaning: SI-0017

(28) HCl, vapor
Cleaning: SI-0221a
Structure: SI-0258; -0259

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(29) HCl, electrolytic
Cleaning: SI-0018

(30) HCl:HNO_3 (See Aqua Regia)
Cleaning: SI-0108a; -0108c; -0392
Preferential: SI-0171

(31) HCl:H_2O_2:H_2O
Cleaning: SI-0233

(32) H_2O_2, conc.
Cleaning: SI-0177b; -0430b
Preferential: SI-0254a; -0282a

(33) H_2SO_4:H_2O
Cleaning: SI-0236; -0256; -0138

(34) H_2SO_4:H_2O_2
Cleaning: SI-0103; -0104; -0105; -0106; -0107; -0108a; -0260

(35) Hydrazine/Diamine/Catechol
Preferential: SI-0115a; -0115b; -0116; -0117; -0118; -0119; -0121a

(36) H_2O_2:NH_4OH
Cleaning: SI-0109
Preferential: SI-0021c

(37) KCl:H_2O
Removal: SI-0102a

(38) KCN:H_2O
Cleaning: SI-0112; -0245

(39) KOH/NaOH:H_2O
Polish: SI-0021b
Preferential: SI-0102b; -0038e; -0088; -0091; -0092a; -0092b; -0206; -0208; -0092c; -0093; -0092d; -0094; -0092e; -0100; -0145; -0217; -0281c; -0253
Etch-Stop: SI-0084; -0085
Structure: SI-0089; -0090; -0091; -0147
Selective: SI-0095; -0243
Junction: SI-0100; -0101

(40) KOH:H_2O:Br_2/I_2
Light Figure Orientation: SI-0092f; -0092g; -0092h

(41) KOH:H_2O, electrolytic
Junction: SI-0195
Oxidation: SI-0097; -0098; -0146; -0271; -0238; -0381; -0223b
Polish: SI-0245
Removal: SI-0096

(42) KOH, molten flux
Preferential: SI-0099

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(43) $KOH:H_2O$: + xxx
Preferential:

(i) + $FeCl_3$:SI-019bb
(ii) + KBr:SI-0198c
(iii) + S:SI-0300
(iv) + $Al(OH)_3$:SI-0301
(v) + Zn:SI-0302
(vi) + $Ba(OH)_2$:SI-0303
(vii) + As_2O_3:SI-0304
(viii) + I_2:SI-0192f
(ix) + Br_2:SI-0092g
(x) + $Ca(OH)_2$:SI-0305
(xi) + $Sr(OH)_2.8H_2O$:SI-0306
(xii) + $AlCl_3.6H_2O$:SI-0307
(xiii) + NH_4 Cl:SI-0308
(xiv) + $CaCl_3.2H_2O$:SI-0205
(xv) + LiCl:SI-0310
(xvi) + $NiCl_2.6H_2O$:SI-0311
(xvii) + $K_2Cr_2O_7$:SI-0312
(xviii) + $KClO_3$:SI-0313
(xix) + $Mg(NO_3)_2.6H_2O$:SI-0314
(xx) + H_3BO_3:SI-0315
(xxi) + HPO_3:SI-0316
(xxii) + $KHCOH_4O_4$:SI-0317
(xxiii) + $K_4Fe(CN)_3.3H_2O$:SI-0318
(xxiv) + KI:SI-0319
(xxv) + $(NH_4)_2C_4H_4O_6$:SI-0320
(xxvi) + $Al_2(SO_4)_3SO_4.24H_2O$:SI-0321
(xxvii) + $3CdSO_4.8H_2O$:SI-0322
(xxviii) + Benzene: SI-0323
(xxix) + Ethyl Alcohol: SI-0324; -0281b; -0281e
(xxx) + Methyl Alcohol: SI-0325; -0281f
(xxxi) + Ethylene Glycol: SI-0326
(xxxii) + Glycerine: SI-0327; -0281a

(44) $KOH:H_2O$: + xxx: + xxx
Preferential:

(i) + CHI_3:Glycerine: SI-0128; -0198a
(ii) + $K_3CO_3.1.5H_2O$:$Ce(OH)_4$:SI-0329
(iii) + Na_2CO_3:$Ce(OH)_4$: SI-0330
(iv) + KCN:I_2: SI-0331

(45) $KBr:H_2O$
Cleaning: SI-0196

(46) $MeOH:I_2$
Cleaning: SI-0149; -0293

(47) $NaCr_2O_7:H_2O$
Cleaning: SI-0066b

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(48) KF:KCl:H_2O (electrolytic)
Polish: SI-0186a

(50) KOH:H_2O:
Step-etch: SI-0085; -0011c

(51) H_2SO_4 +/− H_2O:
Cleaning: SI-0045b; -0138; -0407

(52) NaOH:H_2O:
Removal: SI-0406

(53) H_2SO_4:H_2O_2:
Cleaning: SI-0043b; -0298; -0108a; -0399; -0414; -0420a

(54) NH_4OH:H_2O_2:
Cleaning: SI-0407

(55) HAc:I_2:
Thinning: SI-0440

B. Solutions by Name/Application:
(50) Cleaning: (See Gases)

- (i) RCA (AB): SI-0031; -0032; -0033; -0122; -0173; -0261; -0407; -0406; -0441
- (ii) Caro's Etch: SI-0103; -0169b; -0104; -0105; -0106; -0108a; -0269
- (iii) Solvents: SI-0111; -0114
- (iv) Heat: SI-0113

(51) Preferential: (Named Etchants)

- (i) Chrome Dislocation: SI-0038a
- (ii) Copper Dislocation: SI-0038b; -0153c; -0153d
- (iii) Dash Etch: SI-0153b; -0178; -0179; -0213; -0044; -0038c; -0426a; -0154a
- (iv) Dash Copper Decoration: SI-0154b
- (v) Erhard's Etch: SI-0158; -0182
- (vi) Iodine Etch: SI-0240; -0241; -0244; -0242a; -0242b
- (vii) Landyren's Etch: SI-0120f; -0035
- (viii) Schimmel Etch: SI-0037; -0051; -0294g; -0043; -0139
- (ix) Secco Etch: SI-063a; -0270; -0274; -0402; -0043; -0139; -0036b
- (x) Silver Etch: SI-0209
- (xi) Silver Glycol: SI-0041a; -0042
- (xii) Sirtl Etch: SI-0030; -0039; -0004; -0153a; -0152; -0184; -0249; -0132; -0133; -0134; -0043; -0090; -0364; -0139; -0425; -0426a; -0438
- (xiii) Sopori Etch: SI-0043
- (xiv) Vogel's Etch: SI-0034
- (xv) Wright's Etch: SI-0045; -0264a; -0279; -0043; -0419; -0418; -0421; -0422; -0400; -0397
- (xvi) Chrome Regia: SI-0019; -0242
- (xvii) Aqua Regia: SI-0400; -0434
- (xviii) Superoxol: SI-0165; -0383; -0388

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(52) Preferential: (Acronyms)
- (i) BHF: See Section "A" (13)
- (ii) BF-3: SI-0281d
- (iii) BRM: See Section "A" (1)
- (iv) CP2 (Superoxol): SI-0165; -0067
- (v) CP4/CP4A: SI-0173; -0047; -0048; -0050; -0051; -0052; -0053; -0054; -00173; -0175; -0176a; -0102e; -0002; -0199; -0200; -0202; -0203; -0112; -0242; -0243; -0254b; -0102d; -0011b; -0055; -0437; -0370; -0434; -0076b
- (vi) CP8: SI-0062
- (vii) SR4: *SI-0172

*Polish

(56) Metal Decoration:
- (i) Arsenic: SI-0156; -0157b
- (ii) Copper: SI-0154b; -0178; -0197b; -0112
- (iii) Graphite (Carbon): SI-0110
- (iv) Gold: SI-0101; -0064; -0218; -0434
- (v) Silver: SI-0087; -0280
- (vi) Cobalt: SI-0233
- (vii) Selenium: SI-0120b

(57) Electric Current — preferential
- (i) Defect: SI-0247
- (ii) Decorate: SI-0401(+HF)

(58) Abrasive — polish
- (i) Al_2O_3 slurry: SI-0280b; -0290
- (ii) Al_2O_3:CrO_3 slurry: SI-0016
- (iii) SiO_2 slurry: SI-0280a; -0291a

(59) Shaping/Forming:
- (i) Square/Rectangle: SI-0401
- (ii) Triangles/Diamonds: SI-0208
- (iii) Wafers: SI-0402
- (iv) Cubes/Bars/Cylinders: SI-0093b; -0092a-h
- (v) Grooves: SI-0137; -0243
- (vi) Mesas: SI-0094
- (vii) Spheres: SI-0092a; -0092b; -0092c; -0158
- (viii) Special Cutting: SI-0155; -0156; -0157
- (ix) Surface pattern (Jello): SI-0292
- (x) Surface pattern (photo resist/metals): See etchant discussions.
- (xi) Pylons: SI-0173a-c
- (xii) Junction (melt): SI-0382
- (xiii) Via holes: SI-0415

(60) Gases:
- (A) Dry Chemical Etching (DCE): (ionized gas)
  - (i) Ar^+: SI-0207
  - (ii) CF_4^+:O_2^+: SI-0262; -0285; -0286c

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(B) Wet Chemical Etching (WCE): (molecular gas)
- (iii) Argon$^+$ H_2O vapor: SI-0419; -0437
- (iv) Oxygen: SI-0365
- (v) Helium: SI-0417

(C) Thinning: (ionized gas)
- (i) Ar^+: SI-0193; -0299; -0141

(D) Selective/Preferential/Structure:
- (i) Ar^+: SI-0141; -0297; -0260
- (ii) Ar^+ Laser: SI-0221
- (iii) Ar^+:O_2 +: SI-0222
- (iv) Neutron: SI-0224g; -0389
- (v) H^+: SI-0253; -0231
- (vi) H_2 (O_2 contamination): SI-0220
- (vii) CHF_3^+:O_2^+: SI-0273; -0430b
- (viii) ClF_3^+: SI-0253
- (ix) Cl_2, vapor: SI-0221b; -0221a; -0407 (+He); -0398 (+He)
- (x) SF_6^+:Ar^+: SI-0273; -0274; -0283b
- (xi) SF_6^+:O_2^+: SI-0273; -0274
- (xii) H_2 (defects): SI-0231
- (xiii) CF_4:H_2: SI-0405; -0430b
- (xiv) CF_4:O_2: SI-0430b
- (xv) NF_3:O_2: SI-0408

(E) Polish:
- (i) CF_3Cl^+:$C_2F_6^+$: SI-0286b

(61) Oxidation:
- (i) $HF/NO_2/H_2O$: SI-0142; -0395
- (ii) KOH:H_2: See Section "A" (41)
- (iii) H_2O: See Section "A" (24), (26)
- (iv) HNO_3: See Section "A" (16)
- (v) SiO_2: SI-0403
- (vi) H_2SO_4:H_2O: SI-0396

(70) Silicon (material types):

Note: Structures other than single crystal, and special uses.
- (1) a-Si:H: SI-0406; -0420; -0402; -0247
- (1a) a-Si: SI-0232
- (2) a-, uc-SI:F:H: SI-0239
- (3) Poly-Si: SI-0263c; -0397; -0408; -0398; -0401; -0431; -0439; -0236a; -0274; -0093; -0051; -0076a-b; -0077; -0263b; -0043b; -0158(sphere); -0072; -0297
- (4) As structural material: SI-0091
- (5) Hi-pressure xtls forms: SI-0416
- (6) Ribbon xtls: SI-0425; -0421; -0074; -0148; -0074
- (7) Whisker: SI-0156
- (8) Si ingot grown in space: SI-0132

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(71) Controlled damage (structuring, pits):
Note: Mechanical damage for study or devices.
(1) Diamond stylus: SI-0092a-t; -0418
(2) Knoop hardness tester (diamond): SI-0171

(72) Spheres: (hemispheres):
Note: Studies for convex facets, etch rates, and for device fabrication.
Forming: SI-0156; -0157; -0158; -0154
Polish: SI-0061a-b; -0154; -0254b
Finite form: SI-0092a-t; -0145; -0154; -0254t; GE-0150a-u(hemispheres, Si, Ge)

SILICON ETCHANTS

SI-0001
ETCH NAME: BRM
TYPE: Halogen, polish
TIME: 20 sec + 10 sec
TEMP: RT
COMPOSITION:
x .... 0.5% Br_2
DISCUSSION:
Si, (111), (100) and (110) wafers used in a surface cleaning study. Lens paper was used as a pad wetted with solution shown. Hand polish for 20 sec, dilute with MeOH, and continue polishing an additional 10 sec. After this initial polish, the different orientations were further cleaned as follows: (1) (111): rinse in BRM, then MeOH. Then rinse in 5% HF:MeOH (HFS) solution and MeOH rinse. Then rinse in $1NH_4OH:1H_2O$ (AMH) solution with DI water rinse and then repeat the HFS sequence. (2) (100): rinse in BRM, then MeOH. Then rinse in BHF (buffered hydrofluoric acid solution — not shown) and follow with a final MeOH rinse. (3) (110): rinse in BRM, then in MeOH. Then rinse in HFS sequence. Similar cleaning and polishing was done on the following materials: Ge, GaP, GaAs, GaSb, InP, InAs, and InSb.
REF: Aspenes, D E & Studna, A A — *J Vac Sci Technol,* 20,488(1982)

SI-0102a
ETCH NAME: Nitric acid
TYPE: Acid, cleaning
TIME:
TEMP: Hot
COMPOSITION:
x .... 16 *N* HNO_3
DISCUSSION:
Si wafers: Nitric acid alone will not etch silicon or germanium, but when used hot at or near the boiling point, it is an excellent contamination removal agent for residual surface water. Surfaces should be water flushed for a minimum period of 10 min after nitric acid cleaning. (*Note:* Since this developmental work, boiling nitric acid has been used to oxidize silicon surfaces, followed by an HF strip and DI water rinse as a surface cleaning step.)
REF: Turner, D R — *J Electrochem Soc,* 107,810(1960)

SI-0102h
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
1 .... HF
9 .... HNO_3

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DISCUSSION:

Si, wafers. Author says that if the etch rate is sufficiently rapid, light will not affect the rate. The solution shown is such a composition. Also in general, etch rate of silicon is 10:1 times faster than on germanium with $HF:HNO_3$ etchant mixtures. (*Note:* $HF:HNO_3$ mixtures, either high in HF or HNO_3 content, are used as stain etchants to observe diffusion profiles.)

REF: Ibid.

SI-0003

ETCH NAME: Nitric acid — TIME:

TYPE: Acid, stain — TEMP:

COMPOSITION:

x .... HNO_3, conc.

DISCUSSION:

Si, (100) and GaAs, (100) wafers used as substrates for epitaxy growth of GaP/Si and Ge/GaAs. After epitaxy, cleave wafers ⟨110⟩ and stain to develop layer structure. (*Note:* The stain is by oxide colors.)

REF: Rosztoczy, F E & Sterin, W W — *J Electrochem Soc*, 119,1119(1972)

SI-0004a

ETCH NAME: Hydrofluoric acid, dilute — TIME:

TYPE: Acid, clean — TEMP:

COMPOSITION:

1 .... HF

10 .... H_2O

DISCUSSION:

Si, (100) wafers, p-type, 150 Ω cm resistivity, used as substrates for CVD growth of Beta-SiC. First clean with solution shown, then etch in $3HF:4HNO_3:3HAc$ and DI water rinse prior to SiC deposition.

REF: Addaniano, A & Klein, P H — *J Cryst Growth*, 70,291(1984)

SI-0131: Shih, W et al — *J Vac Sci Technol*, A3,967(1985)

Si, (100), p-type, 14—23.5 Ω cm resistivity wafers of 4″ diameter used as substrates for deposition of thermal SiO_2, then poly-Si doped with $POCl_3$. The resulting PSG oxide remaining on the poly-Si surface was removed with the solution shown at 30°C prior to depositing a thermal SiO_2 cap.

SI-0132b: Ibid.

Si, (100) wafers used as substrates for epitaxy deposition of high n^+ poly-Si doped with phosphorus, followed by $TaSi_2$ and an SiO_2 cap. Step-etch with the solution shown at 30°C for $SiO_2:TaSi_2$ removal with a selectivity of 20:1, respectively. After etch structuring, wafers were cleaved ⟨110⟩ for TEM study.

SI-0169a: Wu, S Y — *J Appl Phys*, 62,1415(1963)

Si, (100) wafers, p-type used for antimony diffusion from a doped, ASG glass surface film. Wafers cleaned in solution shown at RT, 1 min, spin-rinsed in UPDI, and then blown-dry with hot nitrogen. ASG glass was spun-on at various rotation speeds and fired at 150 or 400°C in N_2, 30 min. Also used $7H_2SO_4:3H_2O_2$ at 110°C, 10 min to clean surfaces.

SI-0191: Archer, R J — Electrochem Soc Meet, WDC, 11—16 May 1957.

Si wafers used in a study of optical measurements of films grown on silicon and germanium surfaces in room air. An HF dilute solution was used to initially clean surfaces.

SI-0108b: Ibid.

Si, (111) and (100) wafers used as substrates in a study of pyrogenic oxidation of silicon at high pressure with dry oxygen (800—1000°C and 1—20 atm). Substrates were cleaned:

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(1) H_2SO_4:H_2O; (2) aqua regia and (3) 1HF:10H_2O then spun dry in nitrogen.
SI-0283a: Eisele, K M — *J Electrochem Soc,* 128,123(1981)

Si, (100) wafers with SiO_2 thin films used in a study of RF plasma etching with SF_6. Plasma etching produced rough surfaces and high etch rates due to residual photo resist from patterning if silicon surfaces were not cleaned in 10% HF prior to plasma etching.

SI-0002g
ETCH NAME: Hydrofluoric acid
TYPE: Acid, oxide removal
COMPOSITION:
x .... HF, conc.
TIME:
TEMP:
DISCUSSION:

Si, wafers of different orientations. Concentrated HF used to remove native oxide from surfaces. Used on both silicon and germanium for cleaning as HF alone does not attack these materials. (*Note:* HF does etch silicon but at rates of under 1 Å/min. Primarily used as an oxide remover.)
REF: Ibid.
SI-0005: Akiyama, W et al — *J Cryst Growth,* 68,21(1984)

Si, (100) wafers used as substrates for MOCVD epitaxy growth of GaAs/GaAs/Si and GaAlAs/GaAs/Si. Substrates cleaned in HF to remove native oxide prior to epitaxy. After epitaxy wafers were cleaved ⟨110⟩ and lightly etched in molten KOH to develop domain structure.
SI-0006: Rudder, R A — *J Vac Sci Technol,* A2,326(1984)

Si, (100) wafers used as substrates for thin film deposition of a-Si:H and a-Ge:H. Degrease substrates in TCE, then acetone, MeOH, and DI water rinse. Final dip in HF with DI water rinse.
SI-0007: Liou, L et al — *J Electrochem Soc,* 131,672(1984)

Si, (100) wafers used as substrates for ion implantation of Si^+ and As^+. The amorphous layers after implant were called: Type aI. After annealing at 400 to 600°C called: Type aII. These amorphous zones were etched with HF by immersion: (1) with ultrasonic and (2) with stirring rod at 200 rpm. The stirred solutions etch the fastest. Immersion/ultrasonic etch rate was 42.5 Å/h; immersion/stir etch rate was 80 Å/h. Type aI etching was nonuniform; Type aII etched uniformly up to 6 and 7 h.
SI-0008: Bicknell, R N — *J Vac Sci Technol,* A2,423(1984)

Si, (100) and (111) wafers used as substrates for MBE growth of oriented CdTe thin films. Sapphire substrates as prism ($1\bar{1}02$) and ($1\bar{2}10$) or (0001) basal also were evaluated. All substrates were etch cleaned in HF immediately prior to introduction into the vacuum system. The (0001) basal sapphire plane gave the best orientation fit of CdTe films.
SI-0120: Dev, B N et al — *J Vac Sci Technol,* A3,946(1985)

Si, (111) and (100) wafers used in a study of Se adsorption along (111) and (220) bulk planes. Polish substrates on Syton pad, then degrease with TCE and MeOH rinse. HF soak and water quench without exposure to air, then immediately into a solution of 0.5 mg Se/ 50 ml MeOH. While under Se solution cleave wafers ⟨110⟩. Remove and rinse wafers in MeOH and blow dry with argon.

SI-0009
ETCH NAME: Hydrofluoric acid, vapor
TYPE: Acid, cleaning
COMPOSITION:
x .... HF, vapor
TIME: 10 sec
TEMP: RT to hot

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DISCUSSION:

Si, (111) wafers within $^1/_4°$ of plane, n- and p-type; (111) 2—4° toward (110) wafers used as substrates in formation of $NiSi_2$ and $CoSi_2$ silicides. Wafers were vapor cleaned in HF prior to deposition of 3000—5000 Å of SiO_2. Oxide was patterned by photolithography for selective metallization. In vacuum, prior to metal deposition, wafers were heat cleaned at 1000°C, 2 min at 1×10^{-10} Torr.

REF: Tung, R T — *J Phys Chem Solids,* 45,465(1984)

SI-0027g: Beyer, K D & Kastl, R H — *J Electrochem Soc,* 129,1027(1982)

Si, (111), n- and p-type wafers used in a copper tracer study. Wafer surfaces were treated by dipping in a solution of $1HF:10H_2O:10\%$ ^{64}Cu which is similar to copper concentration in commercial buffered HF solutions. Hang wafers vertically above the HF solution in a closed container for 1 min at RT and do not water rinse after treatment. Native oxide removal rate was shown as 100 nm/min.

SI-0181b: Ibid.

Si, (111) wafers, n-type 5—10 Ω cm resistivity used in fabrication of boron diffused diodes using diborane, B_2H_6 gas in initial development of this process. HF vapor at 35—40°C used on clean surfaces after boron diffusion. Follow with DI water rinse and IR lamp dry.

SI-0132a

ETCH NAME: Hydrofluoric acid, dilute — TIME:

TYPE: Acid, native oxide removal — TEMP:

COMPOSITION:

1 .... HF

16 .... H_2O

DISCUSSION:

Si, (100) wafers used as substrates for epitaxy growth of high n^+ doped poly-Si using phosphorus. Native oxide left on poly-Si as PSG was removed with the solution shown prior to deposition of $TaSi_2$ and an SiO_2 cap.

REF: Palik, E D et al — *J Vac Sci Technol,* B3,492(1985)

SI-0010

ETCH NAME: Hydrofluoric acid, dilute — TIME:

TYPE: Acid, clean — TEMP:

COMPOSITION:

x .... HF

x .... H_2O

DISCUSSION:

Si, (111) p-type wafers used as substrates for deposition of Pt and Pt:Pd metal films. Wafers were degreased, then surface cleaned in solution shown. An oxide was grown on surfaces with $3HCl:1H_2O_2:1H_2O$ at 90°C, 10 min before alloy deposition. The Pt:Pd alloy was both co-deposited and sequentially deposited.

REF: Kawarada, H — *J Appl Phys,* 57,244(1985)

SI-0011a

ETCH NAME: Hydrofluoric acid, dilute — TIME: 20—40 min

TYPE: Acid, clean — TEMP: RT

COMPOSITION:

1 .... HF

1 .... H_2O

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DISCUSSION:

Si, (111) wafers with high boron doping ($>10^{20}$ cm^3). Surface cleaning in the solution shown leaves a blue-green stain. Deposit 50 Å of SiO_2 then etch strip the oxide with HF to remove stain.

REF: Palik, E D et al — *J Electrochem Soc,* 129,2051(1982)

SI-0012

ETCH NAME: Hydrofluoric acid, dilute — TIME: 2 min

TYPE: Acid, clean — TEMP: RT

COMPOSITION:

1 .... HF

30 .... H_2O

DISCUSSION:

Si, (100) wafers used as substrates for LPCVD deposition of tungsten from WF_6. After HF rinse in the above solution, rinse in 18 MΩ water for 10 min and spin-dry. This treatment leaves about 20 Å of native oxide on silicon. Deposit SiO_2 and open windows with photo resist lithography as a mask for selective deposition of 2000 Å tungsten as poly-W. (*Note:* An excellent discussion of stress and adhesion of tungsten films.)

REF: Green, M L & Levy, R A — *J Electrochem Soc,* 123,1243(1985)

SI-0013

ETCH NAME: Hydrofluoric acid, dilute — TIME:

TYPE: Acid, clean — TEMP:

COMPOSITION:

1 .... HF

100 .... H_2O

DISCUSSION:

Si, (100) As-doped, 10 Ω cm resistivity wafers used as substrates for deposition of tungsten, then PtSi. Clean silicon wafers with solution shown. In vacuum system, back-sputter silicon with Ar^+ ionized gas prior to tungsten deposition.

REF: Sinha, A R & Smith, T E — *J Appl Phys,* 44,3465(1973)

SI-0014: Adams, A C et al — *J Electrochem Soc,* 127,1787(1980)

Si, (100), p-type, 8—30 Ω cm resistivity wafers used as substrates in a study of oxidation. First, clean in "acidic H_2O_2" (H_2SO_4:H_2O_2?), then in solution shown to remove native oxide. Various thicknesses of SiO_2 deposited and the same solution used as a step-etch solution to determine oxide etch rates.

SI-0015a

ETCH NAME: Hydrofluoric acid, dilute — TIME: 5 min

TYPE: Acid, oxide removal — TEMP: RT

COMPOSITION:

(1) x .... 20% HF (2) x .... 6% HF

DISCUSSION:

Si, (111) n-type, 1.5—2.5 Ω cm resistivity wafers used as substrates for silicide study as Si/Pd/Pd_2Si/Si. First, degrease substrates in TCE with ultrasonic agitation; then acetone and MeOH rinse. Etch in the 20% HF solution to remove native oxide and DI water rinse. Oxidize surface with "RCA" etch (1HN_4OH:1H_2O_2:6H_2O) and re-etch in the 6% HF solution for 5 min before initial Pd evaporation and anneal at 400°C, 90 min to form Pd_2Si. Follow with Pd metallization, then a 140 Å SiO_2. Anneal at 275°C for various times. The pure Pd will diffuse through the Pd_2Si.

REF: Lien, C-D et al — *J Appl Phys,* 57,224(1985)

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SI-0016
ETCH NAME:
TYPE: Acid, clean
COMPOSITION:
x .... HF
x .... MeOH
TIME:
TEMP:
DISCUSSION:
Si, wafers. Wafers were etched in 1HF:5HNO_3 and then in the solution shown to remove native oxide. Work by Turner (SI-0102a) shows that HF-HNO_3 solutions leave about 10 Å of oxide on silicon surfaces.
REF: Wajda, E S et al — *IBM J*, 36,288(1961)

SI-0017
ETCH NAME: Hydrochloric acid
TYPE: Acid, clean
COMPOSITION:
x .... HCl
TIME: 30 sec × 2
TEMP: RT
DISCUSSION:
Si, (111) wafers used as substrate for deposition of a-C for MIS device study. Degrease substrates in TCE, then rinse in acetone and MeOH. Etch in HCl, rinse in DI H_2O and N_2 dry. DC sputter carbon in argon.
REF: Khan, A A et al — *Solid State Electron*, 27,385(1984)

SI-0018
ETCH NAME: Hydrochloric acid, vapor
TYPE: Electrolytic, clean/vapor
COMPOSITION:
(1) x .... HCl
(2) x .... Cl_2
TIME:
TEMP: Si: 300—400°C & Ge: 200—300°C
ANODE: Ge or Si
CATHODE: C (Ge); Ceramic (Si)
POWER:
DISCUSSION:
Si and Ge wafers. Hot vapors (chlorine content) used to clean both silicon and germanium surfaces. Author states that reaction forms either $GeCl_4$ or $SiHCl_3$. Blow Cl_2 gas through a hole in the graphite mask for Ge; use a ceramic mask with hole for silicon.
REF: Seiler, K O — U.S. Patent #2,744,000, May 1, 1956

SI-0019
ETCH NAME: Chrome regia
TYPE: Acid, clean
COMPOSITION:
500 ml .... HCl
100 ml .... 10% CrO_3
TIME: 1—5 min
TEMP: RT
ASTM: #101
DISCUSSION:
Si, wafers both Float Zone ingot material and epitaxy thin film deposit. Solution used to remove heavy metal ion contamination from surfaces.
REF:
SI-0247: ASTM E407-70
Reference for ASTM Number shown under SI-0019. Solution used on irons and steels as a preferential etchant.

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SI-0020
ETCH NAME: BHF
TYPE: Acid, oxide removal
COMPOSITION:
1 .... HF
5 .... NH_4F (40%)
TIME: $2^1/_2$ min
TEMP: RT
DISCUSSION:
Si substrates used for deposition of a-Si:H by glow discharge decomposition of SiH_4. Native oxide removed from a-Si:H by: (1) soak in hot isopropyl alcohol vapor for "several" hours; (2) etch in BHF solution shown and (3) soak 10 min in fresh chlorine water before deposition of 30 monolayers of cadmium stearate ($CdSt_2$). Store in nitrogen for 2—3 days. Then evaporate gold to form MIS device structure. a-Si:H films are slightly n-type. (*Note:* Chlorine water is made by bubbling gaseous chlorine into water.)
REF: Lloyd, J P et al — *Solid Thin Films*, 89,367(1982)

SI-0021a
ETCH NAME: BHF
TYPE: Acid, isotropic
COMPOSITION:
1 .... HF
7 .... NH_4F(40%)
TIME: 15 min
TEMP: RT
RATE: 250 Å/15 min — Si(111), p-type; 0.3 Å/1 min — Si(111), n-type
DISCUSSION:
Si, (111), n- and p-type. Solution shown will etch silicon at rates shown. Some of the etch action is attributed to impurities in the ammonium fluoride.
REF: Kern, W — *RCA Rev*, 39,278(1978)

SI-0022
ETCH NAME: BHF
TYPE: Acid, oxide removal
COMPOSITION:
1 .... HF
9 .... 40% NH_4F
TIME: 60 sec
TEMP:
RATE: 0.01—0.02 μ/sec (Si_2O)
DISCUSSION:
Si, (100), p-type, 2 Ω cm resistivity wafers used as substrates. First, clean wafer in H_2O_2; then in "acidic" H_2O_2 (H_2SO_4:H_2O_2?); then in HF; then in BHF solution shown. Both SiO_2 and Si_3N_4 were then RF plasma deposited. After sitting for several days, SiO_2 etch rate increases to 0.02—0.03 μm/sec.
REF: Reisman, A et al — *J Electron Mater*, 13,504(1984)

SI-0023
ETCH NAME:
TYPE: Acid, oxide removal
COMPOSITION:
2 .... HF
13 .... NH_4F
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers. Solution used to remove SiO_2. Concentration of ammonium fluoride not shown.
REF: Ralaauw, C — *J Appl Phys*, 131,1114(1984)

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SI-0024
ETCH NAME: BHF
TYPE: Acid, oxide removal
COMPOSITION:
x .... HF
x .... NH_4F
x .... H_2O
TIME:
TEMP:
DISCUSSION:
Si, (111), n-type, 1—10 Ω cm resistivity wafers used as substrates for PtSi formation. Degrease wafer in acetone with ultrasonic agitation, rinse in EOH. Then clean in BHF solution and flood with EOH so that surfaces do not come in contact with air. Deposit 1 KÅ SiO_2 on back of wafer and resistance heat in vacuum at 1000°C. Evaporate Pt from wire by resistive heating and anneal to form PtSi.
REF: Matz, R et al — *J Vac Sci Technol*, A2(2),253(1984)
SI-0025: Walker, R T — *J Appl Phys*, 127,1432(1979)
Si, (111), n-type wafers. Etch cleaned surfaces 4 min at RT.

SI-0026
ETCH NAME: BHF
TYPE: Acid, nitride removal
COMPOSITION:
5 ml .... HF
20 g .... NH_4F
300 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
Si, (111), (100) wafers as substrates for deposition of Si_3N_4 in a study of nitride composition and etch rates. Increased heating of substrate during nitriding slows etch rate and higher film density lowers etch rate (less H_2 in film). Solution used to etch clean wafers and to etch nitrides. Before nitride deposition, wafers were baked in vacuum at 400°C.
REF: Zhou, N S et al — *J Electron Mater*, 14,55(1985)

SI-0027
ETCH NAME: BHF
TYPE: Acid, oxide removal
COMPOSITION:
5 ml .... HF
20 g .... NH_4F
30 ml .... H_2O
TIME:
TEMP:
DISCUSSION:
Si, (100) wafers. Solution used to remove native oxide from wafers prior to deposition of Al_2O_3. After alumina deposition slots were opened in the material by photo resist techniques for use as an etch mask, and grooves etched in silicon prior to SiO_2 plasma deposition.
REF: Ho, V & Seguano, T — *Solid Thin Films*, 95,315(1982)

SI-0028
ETCH NAME: BHF
TYPE: Acid, oxide/nitride removal
COMPOSITION:
x .... HF
x .... NH_4F
x .... H_2O
TIME:
TEMP:

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DISCUSSION:

Si, (100) wafers used as substrates in a study of oxide and nitride etch rates under different deposition conditions. Solution shown used to etch native oxide from wafers, and to etch thin film oxide and nitride after growth.

REF: Kato, I et al — *J Electron Mater,* 13,913(1984)

SI-0029: Brat, T & Eizenberg, M — *J Appl Phys,* 5,264(1985)

Si, (100), n-type, 10 Ω cm resistivity wafers used as substrates in a metallization study. Degrease with organic detergents; then in BHF solution, rinse with H_2O and N_2 blow dry. Evaporate iridium; co-deposit $Ir_{80}V_{20}$ or 1 Ir:1 V. Also used SiO_2 mask, photo resist patterned for selective metal deposition.

SI-0030

ETCH NAME:

TIME:

TYPE: Acid, defect

TEMP:

COMPOSITION:

1 .... HF

x .... 1.5 *M* CrO_3

1 .... H_2O

DISCUSSION:

Si, (111), n-type and (110), p-type wafers used in a defect study. Other CrO_3 concentrations evaluated: 0.5; 1—2; 2.5 and 3 *M*. Solution shown above is close to Sirtl etch.

REF: Yang, K H — *J Appl Phys,* 131,1141(1984)

SI-0431: Ciszeic, T F — *J Electrochem Soc,* 132,963(1985)

Si, polycrystalline ingot grown by Stockbarger-Bridgman method by solidification from a cold crucible. Grain size was about 5 mm evaluated against Czochralski (CZ) and sheet grain size. Edge Supported Pull (ESP) method for sheet as a continuous ingot casting with a square silicon outline with grains. Solution used to develop defects.

SI-0031

ETCH NAME: RCA etch (AB etch)

TIME: 10—20 min

TYPE: Acid, cleaning

TEMP: 75—85°C

COMPOSITION:

"A"	1—2 .... NH_4OH	"B"	1—2 .... HCl
	1—2 .... H_2O_2		1—2 .... H_2O_2
	5—7 .... H_2O		6—8 .... H_2O

DISCUSSION:

Si wafers of all major plane orientations. "A" solution will remove organics and Group I and II metals. "B" solution will remove heavy metals and soluble complexes that do not plate out. Rinse in DI H_2O and N_2 blow dry. This cleaning system was originally developed for cleaning silicon (this reference), but since then has been applied to many other materials. (*Note:* The two etch names shown have both been used. The AB etch designation should not be confused with the A/B etch of Abrahams & Buiocchi.)

REF: Kern, W & Puotinen, W — *RCA Rev,* 70,187(1969)

SI-0032a: Walker, P — personal application, 1970—1985

Si, (111) and (100) wafers used as SCRs (n-type 10—120 Ω cm resistivity with diameters from 0.250 to 2.00″). Silicon, (111) wafers used for high voltage diodes (p-type, 100 to 10,000 Ω cm resistivity). Alumina, quartz, and sapphire substrates used for microwave circuits.

Direct transfer of wafers from solution "A" to "B" still wet. SCRs were water rinsed and IR lamp dried after cleaning. Diode wafers, after DI H_2O rinse, had a final rinse in I_2:MeOH with insertion into a hot diffusion furnace still wet. Circuit substrates given final rinse in HF for 30 sec, then 30 sec DI H_2O, and N_2 blow dry immediately before insertion into vacuum or held under MeOH until ready for insertion. The iodine rinse or being held under methanol gave best results.

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SI-0015b: C-D Lien, et al — *J Appl Phys,* 57,224(1985)

Si, (111) n-type 1.5—2.5 Ω cm resistivity wafers used in study of Pd_2Si. "A" solution used 5 min at RT to oxidize silicon, then HF to strip clean prior to metallization with Pd and annealing for Pd_2Si.

SI-0122: Martin, T I et al — *J Electron Mater,* 13,309(1984)

Si, (100) n-type, 1—4 Ω cm resistivity wafers used for deposition of WSi_2 silicide. Authors used the "RCA" cleaning system followed by an HF dip before tungsten deposition. WSi_2 is tetragonal system.

SI-0173: Schmidt, J et al — *Thin Solid Films,* 110,7(1983)

Si, (100) p-type, 13—17 Ω cm resistivity, and (111) p-type, 4 Ω cm and n-type 4.5 Ω cm resistivity wafers as substrates for the deposition of diamond and borazone followed by aluminum dot evaporation to form capacitive elements for I/V and C/V plot study. Structures were Al/diamond/Si; Al/borazone/Si; and $Al/SiO_2/Si$ — the latter for comparative purposes. Diamond and borazone were deposited by Reactive Pulse Plasma (RPP). Wafer surfaces were cleaned prior to deposition with the following sequence: (1) "RCA" etch clean; (2) HF rinse and (3) DI water rinse. In vacuum, Ar^+ ion sputter clean immediately prior to deposition. Authors say that the high leakage conductance at the dielectric/silicon interface needs further study.

SI-0407: Pande, K P et al — *J Electron Mater,* 13,593(1984)

SI-0406: Martin, T L — *J Electron Mater,* 13,309(1984)

Si, (100) n-type, 1—4 Ω cm resistivity wafers used as substrates for growth of WSi_2 thin films. Clean wafers in the "A" and "B" RCA etch solutions with final clean in $1HF:1H_2O$ and DI H_2O rinse prior to metallization. Tungsten is cubic (bcc), and forms tetragonal WSi_2. (*Note:* Reference to "cubic" means isometric system, normal class, in which the cube, (100) is a crystal form.)

SI-0441: Wu, C S et al — *Thin Solid Films,* 104,175(1983)

Si, (100) p-type, 1—10 Ω cm resistivity wafers used as substrates in a study of ErSi silicide. Wafers cleaned: (1) degrease in solvents; (2) RCA etch clean; (3) HF dip with DI H_2O rinse. Initial evaporation was 500 Å Er with 750 Å poly-Si cover. Band gap measured: RT, 0.68 eV; annealed at 380°C, 0.74 eV; annealed at 500°C, 0.77 eV. Without poly-Si coating, ErSi showed surface pitting at 380°C with pit quantity increase at 400—450°C and best band gap at 0.72 eV.

SI-0102f

ETCH NAME: Landyren's etch

TYPE: Acid, preferential

COMPOSITION:

97% .... HNO_3

3% .... $KMnO_4$

TIME:

TEMP:

ASTM: #140

DISCUSSION:

Si, (111) wafers and other orientations. Solution will develop defects on all orientations. Attacks p-type rapidly, slow attack of n-type. Can be used as a p-n junction delineation etch, and also on germanium.

REF: Turner, D R — *J Electrochem Soc,* 107,810(1960)

SI-0032b: Walker, P — personal application, 1970—1975

Si, (111) n-type, 10—100 Ω cm resistivity wafers as epitaxy SCRs. Used on 2" diameter silicon wafers to develop rotational etch spiral that showed a resistivity increase across spiral toward wafer edges due to loss of growth control during Czochralski (CZ) ingot pulling. Solution also used as a general defect etch on epitaxy silicon, and to etch pattern nickel shim-stock as metallization masks for selective gold deposition on silicon SCRs. Solution used was 10 mg $KMnO_4$:150 ml HNO_3, RT to warm (40°C).

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SI-0036
ETCH NAME: Secco etch
TYPE: Acid, preferential
TIME: 20 min
TEMP: RT
COMPOSITION:
2 .... HF
1 .... 0.15 *M* $K_2Cr_2O_7$
DISCUSSION:

Si, (111) and (100), p-type, 1—10,000 Ω cm resistivity wafers. The 1—300 Ω cm material etches faster. This solution used with ultrasonic agitation 5 min at RT will produce similar results without bubble formation. Silicon wafers were first etch polished in 2HF:3HNO_3:2HAc, RT, 2—3 min with H_2O flush. $Na_2Cr_2O_7$, $(NH_4)_2Cr_2O_7$ or xCrO_3:xHF also can be used. The solution shown is more acidic with less Cr ions than the Sirtl etch.
REF: d'Aragona, F Secco — *J Electrochem Soc,* 119,948(1972)
SI-0263: Banerjee, S K et al — *J Electrochem Soc,* 131,1409(1984)

Poly-Si grown on (100) CZ silicon wafer substrates. Deposits contained large single crystallites with low-angle grain boundaries. Secco etch used to develop grain boundaries and structure.
SI-0270: Robinson, McD et al — *J Electrochem Soc,* 129,2858(1982)

Si, thin film epitaxy layers with low dislocation density were etched in the Secco etch to develop dislocations and slip.
SI-0274: Cerofolini, G F et al — *Thin Solid Films,* 109,137(1983)

Si, (100), n-type, 7—10 Ω cm resistivity wafers used in a study of indium diffusion/segregation with various types of SiO_2 deposition: dry O_2 or steam with time and temperature varied. Secco etch used to etch develop dislocation, segregates, stacking faults.

SI-0037
ETCH NAME: Schimmel etch
TYPE: Acid, preferential
TIME: 30 sec
TEMP: RT
RATE: See below
COMPOSITION:
2 .... HF
2 .... 0.75 *M* CrO_3
1.5 .... H_2O
DISCUSSION:

Si, (111) and (100) wafers used as substrates for silicon epitaxy growth. Wafers were degreased prior to epitaxy: (1) TCE soak, then rinse in MeOH, then EOH; (2) soak in H_2SO_4:H_2O_2, RT for 15 min. After epitaxy deposition, solution shown was used to develop defects and structure in the epitaxy layers.
REF: Archer, V D — *J Electrochem Soc,* 129,2078(1982)
SI-0051: Celler, G K et al — *J Electrochem Soc,* 132,211(1985)

Si, (100) wafers used as substrates for poly-Si deposition studies. Wafers were solvent cleaned and then steam oxidized. The SiO_2 was photolithographically patterned as a mask for selective poly-Si deposition. In vacuum system, HCl vapor at 1050°C was used to oxide clean silicon in the opened windows immediately prior to growth of poly-Si using SiH_4. Wafer surfaces were then capped with SiO_2 using LPCVD. ⟨110⟩ cleaved sections were etched in the Schimmel solution to develop poly-Si defects and structure. The poly-Si showed a columnar grain growth. (*Note:* Columnar growth has been observed in compound semiconductor layers and in silicon dioxide deposited at an angle.)
SI-0294: McFee, J H et al — *J Appl Phys,* 130,214(1983)

Si, (100) wafers used as substrates for MBE growth of silicon layers about 2 μm thick. A dilute Schimmel solution used as a dislocation etch and to step-etch or etch-thru holes in order to study the epitaxy layer and bulk substrate.

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SI-0038a
ETCH NAME: Chrome dislocation etch — TIME: 6 min
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:
"A" 100 g .... CrO_3 "B" x .... HF
200 ml .... H_2O
Mix: 1 "A":1 "B"
DISCUSSION:
Si, (100) and (110) wafers. First, etch polish wafers at RT, 3 min with 3HF:5HNO_3:3HAc and water quench. Mix solution shown when ready to use, and follow etching with a minimum 2 min DI water rinse. Solution used to develop dislocations in the wafers.
REF: Pamphlet — *Monsanto Single Crystal Silicon Evaluation Procedure*, January 1964

SI-0039
ETCH NAME: Sirtl etch — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
1 .... HF
2 .... CrO_3 (33%)
DISCUSSION:
Si, (111) wafers and other orientations. This is the original development of this etch as a dislocation and defect solution on silicon. It has been modified since this time and applied to other semiconductor and metallic compounds. (*Note:* Several chromium compounds have been developed since this etchant appeared in the literature, several for special enhancement of particular types of defects.)
REF: Sirtl, H W — *Z Metallkd*, 52,529(1961)
SI-0224: Tallman, R L et al — *Solid State Electron*, 9,327(1966)
Si, single crystal thin films grown across SiC substrates by a moving-zone deposit technique with directional growth. "Sirtl" etch mixture shown was 200 ml HF:100 g CrO_3:200 ml H_2O.
SI-0149: Hammond, M L — *Solid State Technol*, November 1978, 68
Si, (111) wafers and other orientations used as substrates for growth of silicon epitaxy. Sirtl etch used to develop defects in silicon thin films after epitaxy.
SI-0438: Hu, S M — *J Appl Phys*, 46,1470(1975)
Si, (100) wafers cut 6.4°-off plane toward (110) used in a damage induced etch pits and structure study. Wafers were SiO_2 coated before diamond indented with heating and annealing under various conditions. Sirtl etch used to develop structure referred to as "rosettes". Developed paired parallel lines from indent point in ⟨110⟩ directions. (*Note:* The rosette structure is more often considered a growth rather than etch phenomenon.)

SI-0153a
ETCH NAME: Sirtl etch, modified — TIME: 1—7 min
TYPE: Acid, preferential — TEMP:
COMPOSITION:
"A" 1 g .... CrO_2 "B" 1 ml .... HF
2 ml .... H_2O
Mix "A" and "B" just before use.
DISCUSSION:
Si, (111) wafers. Used as a general dislocation and defect etch and can be used on other orientations.
REF: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7

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SI-0038b
ETCH NAME: Copper dislocation etch — TIME: 4 h
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:

"A"	600 ml .... HF	"B"	1000 ml .... H_2O
	300 ml .... HNO_3		3.54 g .... KBr
	28 g .... $Cu(NO_3)_2.2H_2O$		0.078 g .... $KBrO_3$
			1 drop .... 1 *N* NaOH

Mix: 1 ml "B":5 ml "A":49 ml H_2O when ready to use.
DISCUSSION:

Si, single crystal wafers of different orientations. First, polish wafers in 3HF:5HNO_3:3HAc, RT, 3 min and DI water rinse. The solution shown will develop slip, lineage, dislocations, and grain boundaries. Do not store solution once it is mixed as it is unstable. Continue etching if defects are not distinct after 4 h.
REF: Ibid.

SI-0044
ETCH NAME: Dash etch — TIME: 2—4 h
TYPE: Acid, dislocation — TEMP: RT
COMPOSITION:

1 .... HF
3 .... HNO_3
12 .... CH_3COOH (HAc)

DISCUSSION:

Si, (111) wafers and other orientations, both n- and p-type of different resistivity levels. Solution will develop sharply defined dislocations on (111) and (100) surfaces. May require more than 4 h etching for best development. (*Note:* This was one of the first dislocation solutions developed for silicon and is still used, though others that are faster have largely replaced it.)
REF: Dash, W C — *J Appl Phys,* 1193(1956)
SI-0178: Furuoya, T — *Jpn J Appl Phys,* 1,135(1962)

Si, (111) and (110) wafers cut from CZ grown ingots. First, polish wafers in 1HF:3HNO_3, then copper decorate at 850°C, by 1 h anneal with wafer in contact with a copper plate. Used Dash etch 12 h, RT to develop dislocations.
SI-0179: Iizuka, T & Keruchi, M — *Jpn J Appl Phys,* 2,157(1963)

Si, (111) wafers with high concentration gallium diffusion used in a study of etch patterns. Dash etch used to develop dislocations. Authors say that flat bottom pits are not dislocations, flats are caused by contamination, and pits do not show 180° rotation from positive to negative (111) wafer faces as do dislocations. Gallium concentration was 10^{18}—10^{19}/cm^3 on (111).
SI-0213: Logan, R A & Peters, A J — *J Appl Phys,* 28,1419(1957)

Si, (111) used in a study of etch pit formation as affected by oxygen content in the material. Dash etch used to develop dislocations. Oxygen content varies in CZ pulled ingots relative to seed/ingot rotation or nonrotation. Etch rate decreases with increase of oxygen content. Data was established from study of etch pit size, pit density, and thickness loss of specimens.

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SI-0153b
ETCH NAME: Dash etch, modified
TYPE: Acid, dislocation
TIME: 4 h
TEMP:
COMPOSITION:
1 ml .... HF
3 ml .... HNO_3
10 ml .... CH_3COOH (HAc)
DISCUSSION:
Si, (100), (111), (110) and (112) wafers. Solution develops dislocation pits on all orientations shown. May require additional time for best definition of pits.
REF: Ibid.

SI-0041a
ETCH NAME: Silver glycol etch
TYPE: Acid, preferential
TIME: 10 min
TEMP: RT
RATE: 1 mil/10 min
COMPOSITION:
"A" 10 ml .... HF
400 ml .... HNO_3
10 ml .... *$AgNO_3$

"B" 200 ml .... H_2O
200 ml .... propylene glycol

*1 g/100 ml H_2O

Mix: 1 "A":1 "B" when ready to use.
DISCUSSION:
Si, (111) wafers and other orientation. Solution used as a defect and dislocation etch. Do not store mixed solution in closed containers. Solution was applied by a brush-on technique using a camel hair brush dipped in the etchant, then wiped across specimen surfaces.
REF: Bondi, F J — *Transistor Technology*, Vol. 3, D Van Nostrand, New York, 1958
SI-0042: Stora, G E — *Acta Metall*, 6,65(1958) (in French)
Si, (111) wafers and other orientations. Solution used to develop imperfections in silicon for micrographic study.

SI-0043
ETCH NAME: Sopori etch
TYPE: Acid, preferential
TIME: 1 to 2 min
TEMP: (1) RT (2) 10°C
COMPOSITION:
(1) 36 .... HF
20 .... CH_3COOH (HAc)
1—2 .... HNO_3

(2) 36 .... HF
25 .... HAc
2 .... HNO_3

(3) 3 .... H_2SO_4
1 .... H_2O_2

DISCUSSION:
Si, (111) wafers and other orientations, both p- and n-type; ribbon crystal silicon and poly-Si. Etch solution developed for poly-Si and referred to as an isotropic etch as it will develop pits and structure in all orientation "directions". (*Note:* Isotropic normally means a polish etched surface.). Solution (1) leaves a blue stain due to high HF concentration — remove stain with solution (3), which also was used as a general surface cleaning solution. Solution mixture (2) did not show the blue stain when used at 10°C. The solutions were evaluated against the (1) Dash etch — SI-0044; (2) Sirtl etch — SI-0039; (3) Secco etch — SI-0036; (4) Schimmel etch — SI-0037, and (5) Wright etch — SI-0045.
REF: Sopori, B L — *J Electrochem Soc*, 131,667(1984)

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SI-0038c
ETCH NAME: Dash etch, modified — TIME: 2 h
TYPE: Acid, preferential — TEMP: RT
COMPOSITION:

"A"	1 .... HF	"B"	100 g .... $NaNO_3$
	3 .... HNO_3		1000 ml .... H_2O
	12 .... CH_3COOH (HAc)		

Mix: 60 ml "A":5 drops "B" and stir.
DISCUSSION:
Si, (100) and (110) wafers. This modified etch used to develop dislocations, lineage, and other defects. First, etch polish samples in $3HF:5HNO_3:2HAc$ for 2 min at RT.
REF: Ibid.

SI-0045
ETCH NAME: Wright etch — TIME: 1—5 min or 20 min
TYPE: Acid, dislocation — TEMP:
COMPOSITION:

60 ml .... HF
30 ml .... HNO_3
30 ml .... CrO_3 (g/2 ml H_2O)
*8 g .... $Cu(NO_3)_2.3H_2O$
60 ml .... HAc
60 ml .... H_2O

*Mix in water first. Then add remaining acids.

DISCUSSION:
Si, (100), (111), p- and n-type, 0.2—20 Ω cm resistivity, both CZ and FZ grown wafers used in a study of oxidation defect development. First clean wafers: (1) $1HF:50H_2O$, 30 sec, RT; (2) rinse 5 min in ultrapure water (UPDI): (2) boil 10 min in H_2SO_4 and rinse 5 min in UPDI prior to steam oxidation for 75 min at 1200°C.

Two methods are used for dislocation etching: (1) A single wafer placed flat on beaker bottom. Pour in etch, and hand agitate. Quench any flushing away acid with DI water without exposure of specimen to air. (2) Multiple wafer etch method: place wafers in a Teflon holder in a vertical position. Immerse in etch and hand agitate by swirling holder, and then remove wafers to a beaker of running DI water.

Copper nitrate enhances dislocations. Oxidation produces well-defined stacking faults, dislocations, swirls, and striations. The etchant is superior to both Sirtl and Secco etchants for stacking fault defect definition.
REF: Jenkins, M W — *J Electrochem Soc*, 124,757(1977)
SI-0264a: Werkhoven, C J — *J Electrochem Soc*, 131,1388(1984)

Si, (111), p-type, 7—20 Ω cm resistivity, wafers used as substrates for silicon epitaxy growth. Wright etch used RT, 1 min to develop defects.
SI-0279: Kuroda, E et al — *J Cryst Growth*, 68,613(1984)

Si, (100) wafers. Ingots grown by Czochralski (CZ) method with resistance heating in an argon atmosphere in a study of the effect of temperature oscillations during growth. Wafers were etch polished in $HF:HNO_3$:HAc and then oxidized in dry O_2 at 650°C, 3 h and 1000°C, 16 h. About 50 μm of surfaces were etch removed to observe microdefects; then etched in Wright etch to a depth of 5 μm to measure defect density. Microdefect density was strongly dependent on temperature oscillation amplitude during ingot growth.

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SI-0006a
ETCH NAME: Dash etch, modified
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
3 .... HNO_3
6 .... CH_3COOH (HAc)
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers and other orientations. Solution used to develop dislocation patterns in deformed silicon specimens. Defects were as slip jobs.
REF: Dash, W O — *J Appl Phys*, 29,705(1958)

SI-0173
ETCH NAME: CP4
TYPE: Acid, preferential/polish
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... CH_3COOH (HAc)
0.6 .... Br_2
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers used in cyclotron resonance experiments. Both silicon and germanium were etch polished in this solution. Authors say the solution influences photoconduction efficiency but not scattering frequency. (*Note:* For original CP4 reference, see GE-0065a, as Camp #4 Etch.)
REF: Dexter, R N et al — *Phys Rev*, 104,637(1956)
SI-0047: Rozhkov, V A et al — *Sov Microelectron*, 13,132(1984)
Si, (111), n- and p-type wafers used to fabricate MOS devices. Mechanically polish wafers, then etch polish with CP4. Deposit SiO_2 and then CeO_2 to evaluate this combination of thin film layers for MOS structures.
SI-0048: Walker, P — personal application, 1958
Si, (111) wafers, n-type, 10—20 Ω cm resistivity used in a general reaction study of CP4 on silicon. Evaluations were (1) used at RT as polish etch; (2) used at 60°C as polish etch but difficult to maintain surface planarity due to fast etch reaction; (3) used at temperatures progressively lower below room temperature: 10, 8, 0, and −10°C, were progressively more preferential to surface defects, cracks, and damage, and (4) at RT in an ultrasonic water bath that was frequency variable and developed a concentric ring structure on surface with low center point. Rings appeared to vary with resistivity increase toward wafer edges.
SI-0050: Statz, H et al — *Phys Rev*, 101,1272(1956)
Si, (111) wafers used in a study of surface states on silicon. After etch polish in CP4 at RT, rinse in DI water, then in MeOH, and final rinse in CCl_4.
SI-0051: Bemski, G — *Phys Rev*, 103,567(1956)
Si, (111) wafers used in a study of quenched-in recombination centers in silicon. Etch polish with CP4 at RT, rinse in DI water, then soak in hot HNO_3 and DI water rinse.
SI-0052a: McKenzie, J M & Waugh, J B — *IRE Trans Nuc Sci*, NS-7,195(1960)
Si, (111) wafers used to fabricate particle spectrometers. Etch polish with CP4, then etch mesa structures with 1HF:3HNO_3.
SI-0053: Takaki, R et al — *IRE Trans Nuc Sci*, NS8,64(1961)
Si, (111) wafers, n-type used in fabrication of surface-barrier nuclear detectors. CP4 used as a polish etch at RT.
SI-0054: Ray, R K & Fan, H Y — *Phys Rev*, 121,762(1961)

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Si, (111) wafers used in a study of impurity conduction. CP4 used to etch polish wafers with DI water rinse.

SI-0174: Faust, J W Jr & John, H F — *J Electrochem Soc,* 107,562(1960)

Si, (111) wafers. A comparison of etching and fracture techniques for studying twinning structures in silicon, germanium and III—V compound semiconductors. Study involved three approaches: (1) preferentially etch a lapped surface, and pit characteristics show change with orientation and surface steps due to etch rate variation; (2) chemically polish or electropolish a lapped surface and twins will show as a groove or step and (3) chemically polish or preferentially etch a mechanically polished surface, and twin lines show as grooves. Both germanium and silicon wafers were cleaved by scribing a line on the (111) surface parallel to a ⟨110⟩ direction and then bent to break specimens for cross-section study under microscopic examination.

SI-0175: Stickler, R & Faust, J W Jr — *J Electrochem Technol,* 4,71(1966)

Si, (111) wafers used in the study of a new type defect in silicon related to growth conditions of the ingot. Wafers polished in CP4, RT, 30—60 sec; followed by Sirtl etch to develop defects. Pit was a star-pattern with points in ⟨211⟩ directions. (*Note:* See SI-0039 for Sirtl etch.)

SI-0176a: Deshpande, R Y — *Solid State Electron,* 9,205(1966)

Si, (111), n-type wafers fabricated with heavily diffused p^+ junctions for the observation of double injection and related effects. Etch polished in $1HF:3HNO_3$, DI water rinse, MeOH rinse, TCE rinse, and air dry. Remove oxide with $HF:NH_4F$ solution and end with a flash dip-clean using CP4.

SI-0102e: Ibid.

Si, (111) wafers used in a general etch study of both silicon and germanium. Both CP4 and CP4A (without bromine) were evaluated for cleaning and polishing of surfaces.

SI-0002: Lauriente, M et al — *J Appl Phys,* 35,3061(1964)

Si, (111) epitaxy deposited wafers used in an X-ray analysis of etch pit patterns and faults in the epitaxy layers. Etch 1 sec with CP4 to observe microstructure. Etch 6 sec for micrographic study.

SI-0199: Fowler, A & Levesque, P — *J Appl Phys,* 26,641(1955)

Si, (111) wafers with grown-in transistor n-p-n junctions used in a study of the optical delineation of junction base widths. CP4 used freshly mixed to delineate the emitter junction. Follow with an electrolytic solution of 0.4% KOH using a carbon anode and emitter as the cathode, with power of 10 A/cm^2, 10—45 min to delineate the collector junction.

SI-0200: Davis, W D — *Phys Rev,* 114,1006(1959)

Si, (111) wafers, gold doped and used in a study of lifetime and capture cross section. CP4 used as both a polish and dislocation etch.

SI-0202: Iizuka, T et al — *Jpn J Appl Phys,* 2,442(1963)

Si, (111) wafers used in a dislocation study of large dislocation loops created from nickel and gold plating and diffusion at 1200°C in argon with times ranging from 2 min to 5 h and fast quench to RT. CP4 used as a preferential etch. Hexagonal and circular loops observed with gold; similar with nickel which showed a constant size increase with increase of heat.

SI-0203: Iizuka, M et al — *Jpn J Appl Phys,* 2,309(1963)

Si, (111) wafers, n-type, CZ grown in a study of hexagonal platelets observed in nickel diffused silicon. Specimens nickel plated and diffused 1 h at 1300°C in argon. CP4 used as a preferential etch to develop hexagonal structures that were aligned in ⟨110⟩ directions. Size increased from 10 μm with increased heating. No similar structures were observed with FZ grown silicon. Structure due to oxygen in CZ material?

SI-0122: Goss, A J et al — *Acta Metall,* 4,333(1956)

Si:Ge alloy crystals. CP4 used to develop stria structure on ingots. Silicon fraction of

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single crystal ingots etches more slowly than germanium in CP4. Solution also used to develop edge dislocations.

SI-0242: Blankenship, J L & Borkowski, C J — *IRE Trans Nuc Sci*, NS-7,190(1960)

Si, surface-barrier device. Used CP4 with 10 drops Br_2/50 ml solution. Also varied CP4 reactivity by changing the amount of HAc.

SI-0243: Sheftal, N N et al — *Izvest Akad Nauk SSSR Ser Fiz*, 21,146(1957)

Si, deposited as thin film epitaxy layers. CP4 was a polish etch. Best results were with (110) oriented material.

SI-0254b: Holmes, P J — *Acta Metall*, 7,283(1959)

Si, single crystal hemispheres. Specimens were used in a preferential etch study of type etch pits, patterns, rates, and crystal planes developed. Before preferential etching, use CP4 to etch polish remove lap damage. (*Note:* See GE-0150a-s for both silicon and germanium preferential etches evaluated.)

SI-0102d
ETCH NAME: CP4A — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... CH_3COOH (HAc)
DISCUSSION:

Si, (111) wafers and other orientations. Used as a general polish etch. Reference recommends using CP4 without bromine on both silicon and germanium to improve polish characteristics.

REF: Turner, D R — *J Electrochem Soc*, 107,810(1960)

SI-0011b: Palik, E D et al — *J Electrochem Soc*, 129,2051(1982)

Si, (100) and (111) wafers cut from ingots were directly etched in CP4A, 2 min at RT to remove cutting damage. Follow with two rinses in DI water, then 20 min soak in 1HF:1H_2O. Wafers were prepared with varied n- and p-type doping levels in a study of the etch-stop mechanism of high concentration doped layers using KOH solutions.

SI-0055
ETCH NAME: CP4, variety — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... CH_3COOH (HAc)
x .... $Cu(NO_3)_2$
DISCUSSION:

Si, (111) wafers used in a defect study. Solution develops screw, edge, and spiral dislocations with improved definition over standard CP4 with bromine. Authors suggest spiral pits may be due to impurities such as SiC and SiO_2 as grown-in segregates in ingots.

REF: Christian, S M & Jensen, R V — Am Phys Soc Meet, Pittsburgh, PA, May 15—17, 1956

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SI-0021c
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
1 .... NH_4OH
5 .... H_2O_2
TIME: 60 min
TEMP: 85—92°C
RATE: 0.11 μm/min
DISCUSSION:
Si, (100) wafers used in an anisotropic etch study. Specimens were etched to a depth of 6.6 μm to develop defects and structure.
REF: Ibid.

SI-0056
ETCH NAME: White etch
TYPE: Acid, polish
COMPOSITION:
x .... HF
x .... HNO_3
TIME:
TEMP:
DISCUSSION:
Si, (100) cleaved wafers used in a study of surface energies of crystals. Specimens polished in a "white etch" solution of $HF:HNO_3$. (*Note:* The use of the term "white" is not recommended for a clear, transparent solution.)
REF: Gilman, J J & Johnston, W S — *Dislocations in Crystals*, John Wiley & Sons, New York, 1956

SI-0046b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
3 .... HNO_3
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers used in a deformation study. Specimens polished in this solution prior to deformation and dislocation etching in $1HF:3HNO_3:6HAc$.
REF: Ibid.
SI-0052b: Ibid.
Si, (111) wafers used in fabricating particle detectors. Wafers polish etched in CP4 prior to p-n junction diffusion. Solution shown used to etch form mesas on device surfaces after photo resist masking.
SI-0288: Straumanis, M E et al — *J Appl Phys*, 32,1382(1961)
Si, dislocation free specimens broken into pieces with pliers. Pieces used in a study of lattice perfection. Slivers etched in solution shown to remove breaking damage.

SI-0057
ETCH NAME: White etch
TYPE: Acid, thinning
COMPOSITION:
1 .... HF
4 .... HNO_3
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers, n- and p-type used in a study of the denuded zones near wafer edges. Wafers annealed at 1050°C in $Ar/O_2/N_2$ + 3% HCl for 1, 4, and 16 h. Wafers cleaved in

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the ⟨110⟩ direction. Wright etch (SI-0045) used to develop dislocations. Solution shown used to thin wafers for TEM study.
REF: Wang, P et al — *J Electrochem Soc,* 131,1948(1984)

SI-0201
ETCH NAME: White etch
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HF
4 .... HNO_3
DISCUSSION:
TIME:
TEMP:
ANODE: Si
CATHODE: Pt
POWER:

Si, (111) wafers, n-type, 130 Ω cm resistivity used in a study of oscillatory photocurrent decay. Electropolish included flooding with xenon light through a 2.5 mm slit during etch polish period.
REF: Hoshino, H & Takayama, N — *Jpn J Appl Phys,* 2,438(1963)

SI-0061a
ETCH NAME:
TYPE: Acid, sphere polish
COMPOSITION:
5 ml .... HF
75 ml .... HNO_3
DISCUSSION:
TIME: 10—20 min
TEMP: RT

Si, single crystal spheres $^1/_8$, $^1/_4$, and $^1/_2$" diameter fabricated in a tornado sphere grinder with 600-grit abrasive paper; 1 and $1^1/_2$" diameter spheres were lathe cut. Cylinders of silicon and germanium cut by an ultrasonic impact grinder. Pre-polish spheres in solution shown in a Teflon beaker at about a 30° angle with a hand-swirling motion so that spheres roll but do not tumble. The time shown is for silicon; germanium time is up to 1 h. Maximum load: 10 $^1/_4$" diameter spheres for 80 ml of solution. Spheres used in preferential etch studies of finite crystal form. Both cylinders and spheres used in device fabrication.
REF: Walker, P — personal development, 1957—1961
SI-0289: Klein, D L & D'Stefan, D J — *J Electrochem Soc,* 107,198C(1960)

Si, wafers of different orientations used in an etch rate study with high HNO_3 concentration solutions. Etch rate dependent on fluorine diffusion to silicon surface being etched; otherwise wafer surface is stain oxidized with HNO_3.

SI-0062
ETCH NAME: CP8
TYPE: Acid, defect spray
COMPOSITION:
3 .... HF
5 .... HNO_3
DISCUSSION:
TIME:
TEMP:

Si, (111) wafers. Solution used as a spray to develop metal precipitates in p-n junctions. (*Note:* CP8 is Camp #8 etchant. See Germanium section.)
REF: Goetzberger, A & Shockley, W — *J Appl Phys,* 31,1821(1960)
SI-0290: Camp, P R — *J Electrochem Soc,* 102,1415(1955)
Reference for Camp etchants originally developed for germanium.

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SI-0058
ETCH NAME:
TYPE: Acid, polish
TIME: 4—5 min
TEMP: 20°C
COMPOSITION:
1 .... HF
5 .... HNO_3
DISCUSSION:
Si, (111) wafers used in a study of diffusion control in silicon. Use solution with mechanical agitation to polish prior to diffusion. Authors say there is excellent reproducibility. (*Note:* 20°C is often used with reference to RT etching (22.2°C), but many experimenters say that HF:HNO_3 mixtures used slightly below RT give better results due to their highly exothermic reactivity.)
REF: Frosh, C J & Derick, P — *J Electrochem Soc,* 105,695(1958)

SI-0059
ETCH NAME:
TYPE: Acid, thinning
TIME:
TEMP:
COMPOSITION:
1 .... HF
6 .... HNO_3
DISCUSSION:
Si, (100) wafers, p-type, 2 Ω cm resistivity used in a study of arsenic dislocations induced by As^+ ion implantation. Backside of wafer was etch thinning in this solution for TEM study of dislocation loops developed by arsenic implant.
REF: Davidis, P et al — *J Appl Phys,* 48,3612(1977)

SI-0060
ETCH NAME:
TYPE: Acid, pinhole jet
TIME:
TEMP:
COMPOSITION:
1 .... HF
9 .... HNO_3
DISCUSSION:
Si, (111) wafers used in a study of electron extinction distance in silicon. Solution used to pinhole etch through specimens. Birefringent colors of thin areas around holes used in study.
REF: Frankl, D R — *J Appl Phys,* 35,217(1964)

SI-0063
ETCH NAME:
TYPE: Acid, polish
TIME: 1—3 min
TEMP: RT
COMPOSITION:
3 .... HF
50 .... HNO_3
DISCUSSION:
Si, (111) wafers, n-type, 5—10 Ω cm resistivity used in initial development of diborane, B_2H_6 gas as a diffusion boron doping source for silicon. Solution used to slow polish wafers prior to diffusion.
REF: Walker, P & Crabbs, G — personal development, 1966

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SI-0102c
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
32% .... HF
68% .... HNO_3
TIME:
TEMP:
DISCUSSION:

Si and Ge, (111) wafers and other orientations. Authors say silicon etches about 10× faster than germanium in HF:HNO_3 solutions and light does not affect etch rate when it is rapid. (*Note:* Robbins & Schwartz SI-0126 show 1HF:3HNO_3 as the maximum etch rate mixture.)
REF: Turner, D R — *J Electrochem Soc,* 107,810(1960)

SI-0065
ETCH NAME:
TYPE: Acid, jet thinning
COMPOSITION:
65 .... HF
35 .... HNO_3
TIME: 53 sec
TEMP: RT
RATE: 10 μm/sec
DISCUSSION:

Si, (111) wafers, p-type, 7—21 Ω cm resistivity, 21 mils thick. Solution used to jet-thin wafers for TEM study. Solution flow rate was 12 ml/min and etching was done under a microscope with transmitted white light to control thinning by color of silicon with water added to slow etch rate as color appeared. Three etch factors are important: (1) solution composition, (2) flow rate, and (3) temperature. (*Note:* See SI-0092a-d where KOH solutions are used to etch thin with color defining base widths in transistor fabrication.)
REF: Bulletin: *Micro Etch M-01-006,* A-108, R&G Enterprises, 1983

SI-0066a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
10 .... HNO_3
TIME:
TEMP: RT
RATE: 0.6 mils/min
DISCUSSION:

Si, (111) wafers used in a study of chemical treatment on surface properties. Etch described as a slow etch on silicon.
REF: Buck, T M & McKim, F S — *J Electrochem Soc,* 105,709(1958)
SI-0092b: Walker, P & Waters, W P — personal application, 1958

Si, single crystal spheres and cylinders. Solution used as a slow polish etch. Etch rate without agitation was 0.8 mil/min and with about 10 rpm rotation 1.5 mils/min. Rotation rate varied with solution volume vs. silicon surface area. With sufficient volume, rate was reduced to 0.1 mil/min. Etching was done on 600 grit abrasive formed specimens which, after polishing, were preferentially etched to finite crystal form, and in the fabrication of devices.
SI-0177a: Buck, T M & McKim, F S — U.S. Patent #2,916,407

Si, p-n-p transistors. Solution used as a final junction cleaning etch prior to device encapsulation.

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SI-0177b
ETCH NAME: Hydrogen peroxide, dilute
TYPE: Acid, junction cleaning
COMPOSITION:
x .... H_2O_2
x .... H_2O
TIME:
TEMP:
DISCUSSION:
Si, p-n-p transistors. Solution used as a final junction cleaning etch prior to device encapsulation.
REF: Ibid.

SI-0177c
ETCH NAME:
TYPE: Acid, junction cleaning
COMPOSITION:
x .... HNO_3
x .... H_2O_2
TIME:
TEMP:
DISCUSSION:
Si, p-n-p transistors. Solution used as a final junction cleaning etch prior to device encapsulation.
REF: Ibid.

SI-0181a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
20 .... HNO_3
TIME:
TEMP: RT
RATE: 2 μ/min
DISCUSSION:
Si, (111) wafers, 5—50 Ω cm resistivity, n-type. Used for fabrication of diodes and transistor devices in electrical breakdown studies caused by defect generation in the subsurface from thermal oxidation deposition of SiO_2 thin films. Solution used to slow etch and clean surfaces using 100 ml per 1 to $1^1/_2$" diameter wafer. Etch prior to wafer alloy, diffusion or oxidation. Also used to remove stains produced by HF, boron, and alkalies.
REF: Walker, P & Onidara, O — Phys Failure Conf., Battelle Memorial Institute, Columbus, OH, Spring 1966

SI-0182
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... HF
x .... CrO_3
TIME:
TEMP:
DISCUSSION:
Si, wafers. Wafer sections angle lapped at 5°43′. Solution used to etch develop damage in abraded silicon surfaces.
REF: Pugh, E N & Samuels, L E — *J Electrochem Soc*, 12,1429(1964)

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SI-0063b
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
6 .... HF
50 .... HNO_3
DISCUSSION:
Si, (111) n-type wafers used in a study of B_2H_6 (diborane gas) as a boron, p-type diffusant in silicon. Solution used to etch polish wafers prior to diffusion.
REF: Ibid.

SI-0069
ETCH NAME: Healy junction etch TIME: 10—30 sec
TYPE: Acid, junction etch TEMP: RT
COMPOSITION:
10 ml .... HF
1 drop .... HNO_3, red fuming
DISCUSSION:
Si, (111) n-type wafers used for boron diffusion in fabricating silicon diodes. Solution should be mixed fresh and used within 8 h. If needed, cleave wafer sections ⟨110⟩ to expose junction. Also used on potted, metallographic cross sections, diamond paste polished, then etched to develop junctions and structure. Place a drop of solution across junction, then flush with water, and N_2 dry.
REF: Healy, J — personal communication, 1958

SI-0070
ETCH NAME: 1:1:1 TIME:
TYPE: Acid, step-etch/polish TEMP: 40°C
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) wafers and other orientations used for controlled removal from surfaces in a study of damage depth and crystal perfection. Removal steps were 0.04, 0.06, and 0.1 mm. From X-ray photograph study it was determined that there was no change in the bulk material after 0.04 mm removal. Author says the closer a wafer is cut to a major lattice direction, the more perfect the structure pattern. (*Note:* The term "1:1:1" is not recommended as an etch mixture name. There are many etch solutions of different compositions with such volume ratio.)
REF: Herglotz, H K — *J Electrochem Soc,* 106,600(1959)
SI-0071: Millea, M F & Hall, T C — *Phys Rev Lett,* 1,276(1958)
Si and Ge (111) wafers. Used this solution to polish both materials. Silicon was oxidized at 1000°C with oxygen, 1 h and showed minimum surface conductance.

SI-0072
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
1 .... HF
2 .... HNO_3
2 .... CH_3COOH (HAc)

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DISCUSSION:

Poly-Si rectangular blocks of silicon for use as a susceptor for MOCVD, as silicon has excellent low vapor pressure in the 500—800°C range used in MOCVD processing. First clean material in aqua regia, then cut, mechanically lap, and etch polish in the solution shown. A brass rod and alumina powder were used to drill a thermocouple hole at one end of susceptor.

REF: Blaauw, C et al — *J Vac Sci Technol,* A(2),438(1985)

SI-0073

ETCH NAME: TIME:

TYPE: Acid, removal/polish TEMP: RT

COMPOSITION:

1 .... HF

1 .... HNO_3

50 .... H_2O

DISCUSSION:

Si, (100) wafers, n-type with very shallow diffused junctions on the order of 1—2 μm. Solution used as a slow etch to determine diffusion depth profiles.

REF: Brady, H — personal communication, 1964

SI-0074

ETCH NAME: TIME:

TYPE: Acid, thinning TEMP:

COMPOSITION:

1 .... HF

5 .... HNO_3

1 .... CH_3COOH (HAc)

DISCUSSION:

Si, (111) Dendritic-Web ribbon crystal with a twin zone down ribbon center. Solution shown used to thin silicon ribbon. Follow with Secco etch (SI-0036) to develop defect structure. The (111) surfaces show severe glide planes . . . and growth strain(?)

REF: Cunningham, B et al — *J Electrochem Soc,* 129,1089(1982)

SI-0046b

ETCH NAME: TIME: 3—4 min

TYPE: Acid, dislocation TEMP:

COMPOSITION:

1 .... HF

3 .... HNO_3

1 .... CH_3COOH (HAc)

DISCUSSION:

Si ingot, FZ grown, n-type, 200 Ω cm resistivity. Ingot was subjected to twisting at 900°C before being cut for wafers. The solution shown, without HAc, was used to etch polish sections prior to preferential etching with the solution as shown.

REF: Ibid.

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SI-0076
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:

"A"	1 .... HF	"B"	x .... HF
	5 .... HNO_3		x .... HNO_3
	1 .... CH_3COOH (HAc)		x .... HAc
			x .... Br_2

TIME: 15 min
TEMP: RT

DISCUSSION:

Poly-Si material. This etch system used to develop damage-free polishing on poly-Si surfaces. First, lap on felt pad with 30 μm alumina for 30 min; second, lap with 2 μm diamond paste starting with 5 psi pressure and reducing to 2 psi over a lap period of 2 min — will remove lap damage but not residual stress. Final lap with Nalcog slurry #2250 (colloidal silica). Then etch in the "A" solution; then the "B" solution.
REF: Sopori, B L et al — *J Electrochem Soc*, 128,215(1981)

SI-0077
ETCH NAME:
TYPE: Acid, anisotropic
COMPOSITION:
1 .... HF
50 .... HNO_3
50 .... CH_3COOH (HAc)

TIME:
TEMP:

DISCUSSION:

Poly-Si deposited as silicon-on-insulator (SOI) structure with recrystallization of the silicon using an RF susceptor in the heated Zone Melting Regrowth method (RF-ZMR). The solution shown was used to develop sub-grains and cracks in the silicon recrystallization growth.
REF: Kobayashi, Y et al — *J Appl Phys*, 131,1189(1984)
SI-0297: Bezjian, K A et al — *J Electrochem Soc*, 129,1848(1982)

Poly-Si material. Solution used to develop dislocation arrays and sub-boundaries in this material.

SI-0263b
ETCH NAME:
TYPE: Acid, step-etch
COMPOSITION:
1 .... HF
750 .... HNO_3
250 .... CH_3COOH (HAc)

TIME:
TEMP:
RATE: 300 Å/min

DISCUSSSION:

Poly-Si material. Solution used as a step-etch in studying the morphology of polycrystalline silicon.
REF: Ibid.

SI-0079
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
25 .... HF
100 .... HNO_3
125 .... CH_3COOH (HAc)

TIME:
TEMP:

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DISCUSSION:

Si, wafers of various orientations used as substrates for the study of stacking faults in epitaxy deposits. Use etch shown to polish substrates before epitaxy. To etch thin specimens after epitaxy thin film growth use a Teflon beaker at 45° and rotate at 30 rpm using 5HF:95HNO_3 as etchant. Reduce oxygen content in epitaxy layer to reduce stacking faults.
REF: Finch, R H et al — *J Appl Phys*, 34,404(1963)

SI-0038d
ETCH NAME: TIME: 3 min
TYPE: Acid, polish TEMP: RT
COMPOSITION:

3 .... HF
5 .... HNO_3
3 .... CH_3COOH (HAc)

DISCUSSION:

Si, (111) wafers and other orientations. Solution used to etch polish silicon wafers prior to copper dislocation etching (SI-0038a). Recommend at least $^1/_2$" of solution over specimens during etching with light agitation. Flush away etch with water without exposing etched surfaces to air and follow immediately with dislocation etch.
REF: Ibid.

SI-0080
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:

5 .... HF
8 .... HNO_3
15 .... CH_3COOH (HAc)

DISCUSSION:

Si, (111) wafers used in a study of Ag and Fe ion contamination in commercial acids as they affect surface barrier diodes. Ag acts as a p-type dopant with a 10^{-4} surface concentration acting as recombination center. Fe has almost no effect.
REF: Krebs, B L & Schlacter, R — *J Appl Phys*, 32,1510(1961)

SI-0081
ETCH NAME: TIME:
TYPE: Acid, polish/sizing TEMP:
COMPOSITION:

1 .... HF
1 .... HNO_3
x .... 1% $AgNO_3$

DISCUSSION:

Si, (111) pre-cut bars of material. Solution used to etch thin bars to 75 μm square cross-section and maintain the square cross-section. Bars were used in a deformation and fracture study.
REF: Pearson, G L et al — *Acta Metall*, 5,181(1957)

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SI-0082
ETCH NAME: TIME: 60 sec
TYPE: Acid, polish TEMP: RT
COMPOSITION:
*55—92% .... HF/HNO_3
45—8% .... H_2O
2—0.01% .... $Hg(NO_3)_2$ or $HgCl_2$

*HF/HNO_3: 9:1 to 1:12 ratio by weight

DISCUSSION:
Si, (111) wafers and other orientations. A polish etch for both silicon and germanium. Silicon removal rate from a lapped surface is 13 mg/cm^2 in 1 min. Solution patented by authors referenced.
REF: Faust, J W & Wynne, R H Jr — U.S. Patent #2,705,192, March 29, 1955

SI-0154a
ETCH NAME: Dash, etch, modified TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
1 .... HF
3 .... HNO_3
8 .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) wafers used in a study of crystal perfection. First, mechanical lap on glass plate with 600-grit SiC and use CP4 (120 cm HF:200 cm $3HNO_3$:120 cm HAc:2 cm Br) to remove residual lap damage. Etch in solution shown to develop etch pits.
REF: Grubel, R O Ed — *Metallurgy of Elemental and Compound Semiconductors,* Vol. 12, Interscience, New York, 1961, 469

SI-0154b
ETCH NAME: Dash copper decoration TIME:
TYPE: Metal, diffusion TEMP: 900°C
COMPOSITION:
x .... Cu
DISCUSSION:
Si, (111) wafers used in a study of crystal perfection. See SI-0154a, above. After CP4 etching, wafers were copper diffused to decorate dislocations and studied by transmission infrared microscopy (TIM). X-ray diffraction was used on copper decorated and nondecorated specimens for comparison.
REF: Ibid.

SI-0154b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
3 .... HF
5 .... HNO_3
DISCUSSION:
Si, ingot etched for defects in a study of doping silicon for tunnel diodes. Solution used to develop structure. An alkaline solution of x% $NaOH:H_2O$ was used, 30 min at 80°C following acid etch or was used separately to develop grain boundaries and polycrystalline

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structure. Authors say that the hydroxide solution will work on n-type silicon. (*Note:* Hot to boiling NaOH and KOH solutions are standard for structure etching as light figure orientation solutions, regardless of n- or p-type material.)
REF: Ibid.

SI-0156
ETCH NAME: Arsenic
TYPE: Gas, preferential
COMPOSITION:
x .... As, vapor
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers and whiskers used in fabricating Esaki diodes. During growth or doping of silicon under an overpressure of arsenic vapor, the arsenic attacks silicon surfaces developing a sharply triangular surface etch pit pattern.
REF: Hononyak, N et al — *Metallurgy of Elemental and Compound Semiconductors,* Series Vol. #12, Grubel, R O, Ed, Interscience, New York, 1961, 81

SI-0157a
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
7 .... HNO_3
TIME:
TEMP:
DISCUSSION:
Si, (111) wafers used in a study of screw dislocations perpendicular to the silicon surface. Specimens were chemical polished in the solution shown.
REF: Danil'chuk, L N & Nikitenko, V I —

SI-0157b
ETCH NAME: Copper
TYPE: Metal, decoration
COMPOSITION:
x .... Cu, chips
x .... H_2O
TIME: 1 h
TEMP: 1000°C
DISCUSSION:
Si, (111) wafers. Specimens were copper decorated as shown.
REF: Ibid.

SI-0158
ETCH NAME: Erhard's etch
TYPE: Acid, dislocation
COMPOSITION:
1 .... HF
1 .... CrO_3 (x%)
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers. After copper decoration (SI-0157b) specimens were dislocation etched in the solution shown. (*Note:* See Sirtl etch SI-0019.)
REF: Erhard, S & Adler, A — *Z Metallkd,* 52,529(1961)

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SI-0102b
ETCH NAME: Potassium hydroxide — TIME:
TYPE: Alkali, preferential — TEMP: RT
COMPOSITION:
x .... 1 *N* KOH
DISCUSSION:
Si, (111) wafer and other orientations. Solution used as a preferential etch on silicon. At this concentration it is a very slow etch at room temperature.
REF: Turner, D R — *J Electrochem Soc*, 107,810(1960)

SI-0084
ETCH NAME: Sodium hydroxide — TIME:
TYPE: Alkali, etch-stop — TEMP:
COMPOSITION:
x .... NaOH (x%)
DISCUSSION:
Si, (111) wafers, boron diffused p-type at a 10^{20} cm^3 doping level. Solution acts as an etch-stop against high doping level layers.
REF: Barycka, I et al — *J Electrochem Soc*, 126,345(1979)

SI-0085
ETCH NAME: Potassium hydroxide — TIME:
TYPE: Alkali, etch-stop — TEMP:
COMPOSITION:
x .... 5—20% KOH
DISCUSSION:
Si, (111) wafers, p-type, with a 10^{20} cm^3 boron doping level. Solution acts as an etch-stop with high doping levels.
REF: Price, J B — *J Electrochem Soc*, 120,339(1973)
SI-0886: Palik, E D et al — *J Electrochem Soc*, 129,2051(1982)
Si, (111) and (100) wafers cleaved ⟨110⟩ after diffusion. Both p- and n-type with boron or phosphorus at 10^{14} to 10^{21} cm^3 doping levels. Solution acts as an etch-stop with high doping levels of both types.
SI-0089: Bhgat, J — *Solid State Electron*, 27,441(1984)
Si, (100) wafers, n-type, Sb doped wafers used as substrates for boron implantation followed by boron-doped epitaxy for VMOS transistors. "U" grooves were etched in ⟨110⟩ directions with this solution through photo resist patterned SiO_2 masks.
SI-0090: Suzuki, T et al — *J Electrochem Soc*, 127,1537(1980)
Si, (100) wafers, n-type, 10 Ω cm resistivity. Solution used to etch "V" grooves in ⟨110⟩ directions. Thermal oxide grown 1.7 μm at 1100°C to form a dielectrically isolated (DI) substrate, and followed with evaporation of a poly-Si layer. Lap back poly/Si to expose islands of silicon. Cleave wafers on a ⟨110⟩ bulk plane and Sirtl etch for defects. Due to stress the thin wafers may bow either in a positive or negative direction.

SI-0038a
ETCH NAME: Sodium hydroxide — TIME: 5 min
TYPE: Alkali, preferential — TEMP: Boiling
COMPOSITION:
x .... 10% NaOH
DISCUSSION:
Si, (111) wafers and other orientations; also ingots. On ingots, solution is used to develop poly-Si and twinning zones. For slicing wafers from ingots — initially face-cut ingot —

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then use solution as a light figure orientation etch (etch pits developed) to orient ingot. Recommend twice the volume of solution per ingot volume. Solution can be used on individual wafers or other cut specimens for orientation verification. (*Note:* Concentrations of this level used at RT, warm, hot, and boiling are general cleaning solutions for many semiconductors and metals.)
REF: Ibid.

SI-0088
ETCH NAME: Sodium hydroxide
TYPE: Alkali, preferential
COMPOSITION:
x .... 50% NaOH or KOH
TIME: 12 min
TEMP: 65°C
DISCUSSION:
Si, (111), (100), and (110) wafers and ingots. Used as a light figure orientation etch. The (111) surfaces are etched 6 min; (100) and (110) etched 12 min.
REF: Schwuttke, C H — *J Electrochem Soc,* 106,315(1959)

SI-0091
ETCH NAME: Potassium hydroxide
TYPE: Alkali, preferential
COMPOSITION:
x .... 10—30% KOH
TIME:
TEMP: Hot to boiling
DISCUSSION:
Si, as various cut shaped specimens. Solution referred to as a micro-structure etch and used to produce: "V" grooves, via holes, pits, mesas and specially cut and etch shaped parts. (*Note:* A major review article of uses of silicon as a bulk material other than for its semiconducting properties.)
REF: Peterson, K E — *Proc IEEE,* 70,420(1982)
SI-0021b: Kern, W — *RCA Rev,* 39,278(1978)
Si, (100) wafers used in an anisotropic etch study. A 19% KOH solution was used at 80°C for 120 min. Rate was 0.59 μm/min.

SI-0092a
ETCH NAME: Potassium hydroxide
TYPE: Alkali, sphere
COMPOSITION:
250 ml .... 30% KOH or NaOH
TIME: 15—45 min
TEMP: Boiling
DISCUSSION:
Si, single crystal spheres formed from $^1/_2$, $^1/_4$, and $^1/_8$" cut cubes and ground in a tornado sphere grinder. After initial forming with 600-grit SiC abrasive paper, slow etch polish in 4HF:75HNO_3 (SI-0061). Solution shown used to develop finite crystal form (FCF). Both hydroxides will etch form a tetrahexahedron, (hk0). Faces of the tetrahexahedron are rough but sharply edge defined.
REF: Walker, P — personal development, 1957—1959
SI-0092b: Ibid.
Si, (111) and (100) wafers, n-type, 10—30 Ω cm resistivity used to fabricate aluminum alloy transistors with opposed emitter and collector pits. The original Pennington Pit Method developed in a study of silicon crystallographic structure was used to form pits: a diamond stylus held vertically through a rotatable shaft, top-weighted with variable lead weights with wafer held on an x-y stage below the stylus. Weight and stylus rotation control point-damage depth.
This was the first discrete multiple device fabrication on a wafer (Hughes). Damage

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location was pre-inked on both sides of wafer using a panograph with bottom-plate mirror for opposed side location. Damage points induced by amount of pressure and number of stylus rotations with collector damaged deeper than emitter and etched first, then emitter damaged and both etched to final pit size based on required base width.

Individual dice also used, both triangle and diamond shaped with ⟨111⟩ edge directions for (111) surfaced wafers; square with ⟨110⟩ edge directions for (100) wafers to reduce preferential edge attack during damage pit forming.

Pit shape after 15 min total etch time in boiling solution was hexagonal on (111) with a pit bottom to within 1 μm flatness. Base width between collector/emitter established by transmitted light using standard white light with wafer on a microscope stage. (100) wafer pits were square with a smooth pit bottom and about 1° of bottom curvature.

SI-0092c: Ibid.

Si, as oriented ingots (111), (100) and (110). Ingots were face cut, then etched 10 min in boiling solution to develop light figure orientation etch pits. After mounting ingot on a ceramic block with Dekotinsky cement and placed on an x-y-z holder for face orientation by reflection of light figures in a black box system. Adjust and lock holder for subsequent wafer cutting.

SI-0092d: Ibid.

Si, as oriented pre-cut forms: cube, (100); cube, (110); octahedron, (111) — 8 (111) faces; tetrahedron, (111) — 4 (111) faces; and rhomboid, (111) — 6 (111) faces. Forms used in a study of etched edge facets. Used to pit-damage and etch (111), (100), (110), and (211) surfaces of forms for correlation of convex vs. concave facet development. See the SI-0300-0350 etchant format and series for results on including different chemical additives to the base 30% hydroxide solution in a study of pit shapes and sphere forms.

During these studies it was determined that the KOH solution is slightly more trigonal plane preferential; whereas the NaOH solution is more tetragonal plane preferential on silicon.

SI-0206: Ives, M B & McAustland, D D — *Solid State Electron,* 11,189(1968)

Si, (111) wafers and other orientations. A development study of the slope of etch pit faces.

SI-0208: Garfinkel, R et al — *J Appl Phys,* 35,2321(1964)

Si, (111) wafers used as cleaved triangular dice in a junction resonant structure study. (*Note:* SI-0092b use of both triangle and diamond dice edge cut in fabricating aluminum alloy transistors.)

SI-0092c

ETCH NAME:

TIME: 10—15 min

TYPE: Alkali, preferential/sphere

TEMP: Boiling

COMPOSITION:

250 ml .... KOH/NaOH (30%)

45 g .... I_2

DISCUSSION:

Si, (111) and (100) wafers and spheres (See: SI-0092a); spheres of silicon, germanium, indium phosphide, and gallium arsenide studied. Polish etch spheres before preferential etching to finite crystal form (FCF). Solution shown will preferential etch all materials mentioned to cube, (100) with face surfaces slightly rough, positive curvature, and sharply edge defined. Wafers were used in a correlative pit-damage study (SI-0092b).

Solution can also be used as a light figure orientation etch on germanium ingots, which are not etched in pure hydroxides.

REF: Ibid.

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SI-0093
ETCH NAME: TIME:
TYPE: Alkali, preferential TEMP:
COMPOSITION:
250 g .... KOH
800 ml .... H_2O
200 ml .... isopropyl alcohol (ISO)
DISCUSSION:
Si, as poly-Si thin films. Solution used in a study of crystallite orientation in these films.
REF: Besjian, K A et al — *J Electrochem Soc*, 1129,1848(1982)
SI-0092f: Ibid.
Si, (111), n-type 10—30 Ω cm resistivity wafers. Solution used was 150 ml 30% KOH:100 ml ISO(IPA), boiling, 5—20 min in a damage pit etch study and evaluation of aluminum alloy transistor devices.
SI-0094a: Abu-Zeid, M M — *J Electrochem Soc*, 131,2138(1984)
Si, (100) wafers with evaporated SiO_2 masking used in etch forming mesa structures. Solution used shown as: $xKOH:xH_2O$ propanol. Author says the solution is good for developing (321) oriented facets on the mesa side slopes. (*Note:* This is one of the few examples of this crystallographic face form — isometric (cubic) system, normal class, hexoctahedron, [hkl].)

SI-0095
ETCH NAME: TIME:
TYPE: Alkali, selective TEMP:
COMPOSITION:
x .... KOH
x .... CH_3O_7OH
x .... H_2O
DISCUSSION:
Si, (100) n-type wafer used as substrate. Epitaxy n^+ layer and boron-doped p-type layer followed by a surface oxide. Solution used as a selective etch in a general study of oxidation and silicon surfaces.
REF: Whillen, M & Holsbrink, J — *Solid State Electron*, 26,453(1983)

SI-0092g
ETCH NAME: TIME: 10—20 min
TYPE: Alkali, preferential TEMP: Boiling
COMPOSITION:
125 ml .... 30% KOH
125 ml .... 30% NaOH
DISCUSSION:
Si, (111), (100) wafers n-type 10—30 Ω cm resistivity used in a general study of alkali etching of surfaces and controlled damage-pit development. Surface etch pits and damage etch pits or other structures are similar for KOH or NaOH only; or as the 1:1 mixture shown. All produce a sharply defined hexagonal damage etch pit on (111) and square on (100). These solutions also used to etch thin sections to various depth levels in bulk silicon wafers using this controlled pit in study of bulk defects, tracing movement of defects and establishing one-to-one correspondence of pits and defects between positive and negative wafer surfaces of (111), (100), (110), and (211) orientations.
REF: Ibid.

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SI-0092h
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
250 ml .... 30% KOH
40—60 ml .... Br_2
TIME: 5—15 min
TEMP: Boiling
DISCUSSION:
Si, (100) and (111) wafers, n-type, 10—30 Ω cm resistivity used in a general study of the effect of additives to hydroxide solutions in producing surface pits and controlled damage etch pits. Also used as an ingot light figure orientation etch on both silicon and germanium ingots grown as (111), (100), (110), and (211) orientations. Bromine dissipates rapidly during the first 5 to 10 min of etching.
REF: Ibid.

SI-0092i
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
250 ml .... 30% KOH
100 ml .... ethylene glycol (EG)
TIME: 5—20 min
TEMP: Boiling
DISCUSSION:
Si, (111) and (100) wafers, n-type, 10—30 Ω cm resistivity. Used in a general study of control damaged etch pit structures. Solution produces a truncated triangle etch pit. The three alternating major side slopes contain parallel steps; whereas the three minor plane side slopes are poorly defined with a vertical channel/ridge structure. See SI-0300-0350 etchant formats for a discussion of etch pit progression development.
REF: Ibid.

SI-0096
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, removal
COMPOSITION:
x .... KOH (x%)
TIME:
TEMP:
ANODE:
CATHODE:
POWER:
DISCUSSION:
Si, (111) and (100) wafers, both n- and p-type with low doping levels. Under cathodic etch conditions: etches p-type slowly; n-type not etched, and acting as an etch-stop. Under anodic etch conditions: both p- and n-type act as etch-stops due to passivation of surfaces. Referred to as the etch-stop mechanisms for nucleophilic attack of (111), (100), and (110) orientations. Also referred to as an orientation dependent etch (ODE). Used to selectively develop microstructures such as "V" grooves, pyramids, etc.
REF: Glembocki, O J et al — *J Electrochem Soc*, 132,195(1985)

SI-0097
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, oxidation
COMPOSITION:
x .... 2 *M* KOH
TIME:
TEMP: 20°C
ANODE:
CATHODE:
POWER:
DISCUSSION:
Si, (111) and (100) wafers within +/− 1° of plane, n-type 9—10 Ω cm resistivity used

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in a general study of surface oxidation and etch rates. Oxidation is bias dependent and rates vary with orientation, to include (110) wafers.
REF: Glembocki, O J & Stahlbush, R E — *J Electrochem Soc*, 132,145(1985)
SI-0098: Palik, E D et al — *J Electrochem Soc*, 132,135(1985)

Si, (100) wafers both low concentration and high concentration p- and n-type used in KOH oxidation study. With cathodic etching, n-type is faster than p-type. For heavily doped Si, hold in solution several minutes before applying anodic potential. Cleave wafers and clean with HF prior to KOH oxidation.

SI-0092j
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
250 ml .... 30% KOH
100 ml .... MeOH
TIME: 10—20 min
TEMP: Boiling
DISCUSSION:

Si, (111) and (100) wafers, n-type 10—30 Ω cm resistivity used in a general study of the effect of additives in alkali solutions and etch pit development. Results were similar to those shown under SI-0091j.
REF: Ibid.

SI-0099
ETCH NAME: Potassium hydroxide
TYPE: Molten flux, dislocation
COMPOSITION:
(1) x .... KOH, pellets
(2) 1 .... KOH, pellets
1 .... NaOH, pellets
TIME: 20 min
TEMP: 350°C
DISCUSSION:

Si, (111) wafers and other orientations, as p- and n-type of different doping level concentrations. KOH used as a molten flux to develop dislocations. After etching, quench directly into ethylene glycol. This reduces oxidation of the surface and EG dissolves hydroxides slowly producing less surface damage.
REF: Lessoff, H & Gorman, R — *J Electron Mater*, 14,203(1985)

SI-0195
ETCH NAME: Potassium hydroxide, dil.
TYPE: Electrolytic, junction
COMPOSITION:
x .... 0.4% KOH
TIME: 10—45 min
TEMP: RT
ANODE: Collector, Si
CATHODE: Emitter, Si
POWER: 10 A/cm^2
DISCUSSION:

Si, (111) wafers with diffused n-p-n junctions. Use CP4 to etch delineate emitter junction, then etch with solution shown to develop collector junction.
REF: Fowler, A & Levesque, P — *J Appl Phys*, 26,641(1955)

SI-0100
ETCH NAME:
TYPE: Alkali, preferential/junction
COMPOSITION:
x .... 10% NaOH
x .... 15% $NaNO_3$
x .... H_2O
TIME:
TEMP: 100°C

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DISCUSSION:

Si, (100) n-type wafer with p-type silicon spherical shot melted and alloyed into the base wafer to form p-n junctions. Alloyed sphere produced a recrystallized single crystal pellet about 1 mil deep. Solution shown was used as a macro-etch to develop the p-n junctions. Similar p-n junctions were formed with germanium (GE-0208).

REF: Lesk, I A — *J Electrochem Soc*, 107,534(1960)

SI-0101

ETCH NAME:

TIME:

TYPE: Alkali, junction plate

TEMP: 30 to 70°C

COMPOSITION:

200 g .... KOH
10 g .... $KAu(CN)_2$
800 ml .... H_2O
+ .... IR light

DISCUSSION:

Si, (111) n-type wafers with boron diffused p-n junctions. Very smooth silicon surfaces require longer time for satisfactory plating. Recommend surfaces be prepared with Linde A or 600-grit carborundum. The gold plates out on the more negative side of the junction.

REF: Silverman, S L & Benn, D R — *J Electrochem Soc*, 105,170(1958)

SI-0087

ETCH NAME:

TIME:

TYPE: Acid, junction plate/stain

TEMP: RT

COMPOSITION:

40 ml .... HF
20 ml .... HNO_3
100 ml .... H_2O
2 g .... $AgNO_3$

DISCUSSION:

Si, (111) wafers with n^+/n diffusion. Solution used to delineate the diffused structure. Apply a drop of solution and allow to etch briefly, then DI water rinse and dry. Then etch with $1HNO_3:1H_2O$ and silver will plate out on higher resistivity area.

REF: Berman, I — *J Electrochem Soc*, 107,1002(1962)

SI-0102a

ETCH NAME: Potassium chloride

TIME:

TYPE: Salt, removal

TEMP:

COMPOSITION:

x .... KCl, sat. sol.

DISCUSSION:

Si, (111) wafers. Potassium chloride will etch both silicon and germanium. Solution used as a general removal etch.

REF: Turner, D R — *J Electrochem Soc*, 107,810(1960)

SI-0103

ETCH NAME: Caro's etch

TIME:

TYPE: Acid, cleaning

TEMP:

COMPOSITION:

1 .... H_2SO_4
1 .... H_2O_2

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DISCUSSION:

Si, (111) wafers and other orientations, p- or n-type material with different doping levels used in a device development study. Clean substrate wafers: (1) degrease in TCE; (2) rinse in acetone, then isopropanol; (3) water rinse, before (4) etch cleaning with the solution shown with water quench and N_2 dry. An SiO_2 thin film was deposited, then SnO_2 and an SiO_2 cap.

REF: Hiso, Y-S & Ghandhi, S K — *J Electrochem Soc*, 127,1592(1980)

SI-0104: Pintchovski, F — *J Appl Phys*, 126,1428(1979)

Si, (111) wafers and other orientations. A major study of the thermal characteristics of this solution, including variations of the mixture. Addition of water generates heat. The 1:1 mixture will be a constant boiling solution at 170°C. Addition of sodium phosphate as a stabilizer does not affect the solution. (*Note:* Various Caro solutions are widely used for general cleaning of semiconductor wafers.)

SI-0043b

ETCH NAME: TIME:

TYPE: Acid, cleaning TEMP:

COMPOSITION:

3 .... H_2SO_4

1 .... H_2O_2

DISCUSSION:

Si, poly-Si epitaxy deposited thin films. Solution used as a general cleaning etch. Used to remove the blue stain left on poly-Si after etching in high HF concentration acids solutions.

REF: Sopori, B L — *J Electrochem Soc*, 131,667(1984)

SI-0106: Tsao, K Y & Bostra, K H — *J Electrochem Soc*, 131,2702(1984)

Si, (100) wafers used in a deposition study of tungsten. Wafer surfaces were prepared by depositing an SiO_2 thin film, then poly-Si to act as a deposition mask. After photolithographic patterning, etch pattern openings down to the substrate surface. Solution shown was used to clean the exposed wafer surface at 95°C, then 6 sec 1HF:10H_2O prior to selective deposition of tungsten from a WF_6 source.

SI-0298

ETCH NAME: TIME:

TYPE: Acid, cleaning TEMP:

COMPOSITION:

4 .... H_2SO_4

1 .... H_2O_2

DISCUSSION:

Si, (100) p-type wafers, 1.2—1.8 Ω cm resistivity used as substrates for metallization. Clean in solution shown with final HF dip and water rinse before placing in vacuum. Magnetron sputter Ta_2O_5 from a solid target and use the film for device gate insulation. Anneal 350—450°C for 30 min in a study of the Ta_2O_5/Si interface.

REF: Seki, S et al — *J Electrochem Soc*, 131,2621(1984)

SI-0107

ETCH NAME: TIME: 20 min

TYPE: Acid, cleaning TEMP: RT

COMPOSITION:

5 .... H_2SO_4

1 .... H_2O_2

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DISCUSSION:

Si, (100), n- and p-type wafers, 20 and 25 Ω cm resistivity, respectively. Solution shown used to clean surfaces prior to Ge epitaxy deposit. Follow cleaning with 60 sec in 50% HF before vacuum. Ge growth can vary from single crystal to polycrystalline to amorphous structure with change in overpressure of an arsenic ambient.

REF: Wang, P D et al — *J Vac Sci Technol*, B2,209(1984)

SI-0108a

ETCH NAME: TIME:

TYPE: Acid, cleaning sequence TEMP:

COMPOSITION:

(1)	(2)	(3)
1 .... H_2SO_4	1 .... HNO_3	1 .... HF
1 .... H_2O_2	1 .... HCl	10 .... H_2O

DISCUSSION:

Si, (111) and (100) wafers. The etch cleaning sequence shown was followed by water quenching and N_2 blow dry. Wafers used in a study of pyrogenic steam oxidation. (*Note:* (1) is Caro's etch, normally used hot.)

REF: Lie, L N et al — *J Electrochem Soc*, 129,2828(1982)

SI-0334: Lo, M J T et al — *J Electrochem Soc*, 128,1568(1981)

Si, (111) wafers used in a study of implantation gettering with gold. Clean silicon: (1) BHF clean with ultrasonic to remove native oxide; (2) rinse with DI H_2O; (3) etch clean in aqua regia; (4) rinse with DI H_2O; (5) etch remove 1.5 mils/side in HF:HNO_3:HAc:H_2O, and water rinse. Mechanically polish one side with Lustrox; coat other side with CVD SiO_2 at 380°C. Evaporate 1000 Å Au on polished side and anneal 6 h at 1080°C.

SI-0113

ETCH NAME: Heat TIME: Flash

TYPE: Thermal, cleaning TEMP: 1100°C

COMPOSITION:

x .... heat

DISCUSSION:

Si, (111) n-type wafers 5 Ω cm resistivity used for Si epitaxy with an SiO_2 mask photolithographically opened for He ion implantation. Flash clean silicon wafers in vacuum prior to epitaxy deposition.

REF: Nishigaki, S et al — *Jpn J Appl Phys*, 23,L683(1984)

SI-0114

ETCH NAME: TIME:

TYPE: Alcohol, cleaning sequence TEMP:

COMPOSITION:

(1)	(2)	(3)
x .... TCE	x .... acetone	x .... isopropyl alcohol

DISCUSSION:

Si, (111) n- and p-type wafers cleaned in the sequence shown prior to deposition of Nb_2O_5.

REF: Chen, M-C — *J Electrochem Soc*, 119,887(1972)

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SI-0094b
ETCH NAME: TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... hydrazine
x .... H_2O
x .... isopropyl alcohol
DISCUSSION:
Si, (111) wafers. An SiO_2 thin film mask was deposited and used in developing mesa structures. Solution shown will develop (112) facetted mesa side slopes.
REF: Abu-Zeid, M M — *J Electrochem Soc,* 131,2138(1984)

SI-0094c
ETCH NAME: Ethylenediamine TIME:
TYPE: Amine, preferential TEMP: 85°C
COMPOSITION: RATE: (111) 0.018 μm/min
x .... 55% ethylenediamine (100) 0.5 μm/min
DISCUSSION:
Si, (111) and (100) wafers masked with SiO_2 for forming mesa structures. Solution will develop (212) facets on mesa side slopes.
REF: Ibid.

SI-0116
ETCH NAME: P–ED or EPW TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
x .... $C_6H_4(OH)_2$ pyrocatechol (P)
x .... H_2O
x .... $NH_2(CH_2)_2NH_2$ ethylenediamine (ED)
DISCUSSION:
Si, (100) wafers within +/− 1° of the plane. An SiO_2 photo resist mask was pattern developed in fabrication of silicon for ink jet nozzles. Solution used to form via holes etched through silicon to form an array of hole openings that are then used for ink jet nozzles. After hole etch forming in solution shown, follow with BHF solution to clean holes.
REF: Bassous, E — *IEEE Trans Electron Dev,* ED25,1178(1978)
SI-0117: Bogh, A — *J Electrochem Soc,* 118,401(1971)
Si, (111) wafers with high boron doping levels ($10^{20}/cm^3$) acting as an etch-stop in this solution. Lower doping concentrations etch rapidly.
SI-0118: Cheung, N W — *Rev Sci Instr,* 51,1212(1980)
Si, (111) wafers. See SI-0117 as same discussion applies.

SI-0119
ETCH NAME: EPW TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
17 ml .... ethylenediamine
3 g .... pyrocatechol
8 ml .... H_2O

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DISCUSSION:

Si, (111) and (100), p-type 1—10 Ω cm and n-type wafers. After mixing the solution shown wait about 1 h before use. Solution turns a light yellow color. Wafers used in a study of etch rate vs. boron concentration. Wafers processed as follows: (1) degrease with TCE; (2) rinse in acetone, then MeOH, then H_2O and N_2 dry; (3) clean in BHF, 5 sec ($1HF:5NH_4F$); (4) clean in $4H_2SO_4:1H_2O_2$, 10 min; (5) RCA-1 etch 15 min at 75°C ($1NH_4OH:1H_2O_2:5H_2O$) (6) repeat the BHF etch and follow with H_2O rinse and N_2 dry. After boron diffusion the EPW etch was used to establish etch rates.

REF: Raley, N F — *J Electrochem Soc*, 131,161(1984)

SI-0109

ETCH NAME: TIME:

TYPE: Acid, cleaning TEMP:

COMPOSITION:

x .... 1% HF

x .... NH_4OH

x .... H_2O_2

DISCUSSION:

Si, (100), p-type, 2 Ω cm resistivity, CZ grown wafers used in fabricating NMOS structures. Degrease with TCE, then rinse in acetone. Etch clean with solution shown and follow with 50% HCl. Deposit Si_3O_4 by APCVD or PECVD.

REF: Hezel, R — *J Electrochem Soc*, 131,1675(1984)

SI-0110

ETCH NAME: Carbon TIME:

TYPE: Powder, defect enhancement TEMP:

COMPOSITION:

x .... carbon black

DISCUSSION:

Si, (111) and (100) wafers used in a study of defects. After preferential etching use carbon black to paint-on decorate etched defects for improved definition and recognition under microscope observation.

REF: Comizzoli, R B — *J Electrochem Soc*, 129,667(1982)

SI-0111

ETCH NAME: Methylene chloride TIME:

TYPE: Solvent, cleaning TEMP: RT

COMPOSITION:

x .... CH_2Cl_2

DISCUSSION:

Si, (111) wafers. Use a cotton swab soaked in methylene chloride to clean surfaces prior to silicon epitaxy. Immediately before placing in vacuum soak in HF, 2 min, rinse several times in water and N_2 blow dry.

REF: Nuttall, R S — *J Electrochem Soc*, 116,445(1969)

SI-0121a

ETCH NAME: TIME:

TYPE: Acid, polish/thinning TEMP:

COMPOSITION:

(1) 3 .... HF
5 .... HNO_3
3 .... H_2O

(2) 17 ml .... ED (ethylenediamine)
3 g .... P (pyrocatechol)
8 ml .... H_2O

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DISCUSSION:

Si, (111) wafers and other orientations. Wafers used in a study of etch polish and thinning. First etch used for heavy removal, and final thinning was done the second etch. (*Note:* The first etch is CP4, modified, and without bromine. The second etch is EPD. See SI-0119 or SI-0116.)

REF: Freyer, J — *J Electrochem Soc,* 122,1238(1975)

SI-0121b

ETCH NAME: TIME:

TYPE: Acid, polish/thinning TEMP:

COMPOSITION:

1 .... HF
10 .... HNO_3
+ .... CO_2
+ .... light

DISCUSSION:

Si, (111) wafers. Rotate wafer in solution at 8 rpm. Bubble CO_2 up through etch for both agitation of solution and as an added oxidizer. Flood wafer surface with light during etch period as a photon activator. Used to polish and fine-thin wafers.

REF: Freyer, J — *J Electrochem Soc,* 122,1238(1975)

SI-0034

ETCH NAME: Vogel's etch TIME:

TYPE: Acid, dislocation TEMP:

COMPOSITION:

3 .... HF
5 .... HNO_3
3 .... CH_3COOH (HAc)
2 .... 3% $Hg(NO_3)_2$

DISCUSSION:

Si, (111) and other oriented wafers. Solution used as a general dislocation and defect etch.

REF: Vogel, F L & Lovell, C — *J Appl Phys,* 27,1413(1956)

SI-0124

ETCH NAME: TIME:

TYPE: Acid, polish/thinning TEMP:

COMPOSITION:

95 ml .... HF
900 ml .... HNO_3
14 g .... CH_3COOH (HAc)
+ .... CO_2
+ .... light

DISCUSSION:

Si, (111), (100) wafers used in a study of polishing and thinning. Wafers were floated face down on the surface of the solution. CO_2 is bubbled up through the solution with light flooding the wafer surface during the etch period. See SI-0121a.

REF: Stoller, A I et al — *RCA Rev,* 31,265(1970)

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SI-0125
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: 18°C
COMPOSITION:
50 ml .... HF
50 ml .... CH_3COOH (HAc)
200 mg .... $KMnO_4$
DISCUSSION:
Si, (111), (100), n- and p-type wafers and epitaxy thin film. Solution used to polish wafers. See SI-0102.
REF: Theunissen, M J et al — *J Electrochem Soc*, 137,959(1970)

SI-0126
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:

(1)	(2)	(3)
x .... HF	x .... HF	x .... HF
x .... HNO_3	x .... HNO_3	x .... HNO_3
	x .... HAc	x .... H_2O

DISCUSSION:
Si, (111) wafers and other orientations with n- and p-type resistivity. Initial work was done on individual square dice developing both etch rates and polish characteristics to include dice edge peaking or downward curving using various concentrations of the three etch systems shown. (*Note:* This was one of the first and most extensive studies of these etching systems at the time. Author (Walker) was involved in some of the study development.)
REF: Robbins, H & Schwartz, B — *J Electrochem Soc*, 106,505 & 1020(1959)
SI-0127: Robbins, H & Schwartz, B — *J Electrochem Soc*, 107,108(1960)
SI-0128: Robbins, H & Schwartz, B — *J Electrochem Soc*, 109,37(1962)
SI-0129: Robbins, H & Schwartz, B — *J Electrochem Soc*, 123,1093(1976)
Si, (111) wafers used in an etch rate study as square cut dice. (*Note:* These five articles by Robbins & Schwartz represent some of the most extensive and definitive development work done on silicon with $HF:HNO_3$ +/− HAc/H_2O systems during this period of time, and are still applicable.)
SI-0130: Klein, D L & D'Stefan, D J — *J Electrochem Soc*, 109,47(1962)
Si, (111) wafers and other orientations, n- and p-type. A major etching and polishing study of the $xHF:xHNO_3$ system. Similar to the work of Robbins & Schwartz.
SI-0249: Burgess, T E — *Electrochem Soc Abstr*, 10,145(1961)
Si, wafers of different orientations. Study similar to those of Robbins & Schwartz.
SI-0296: Immirlioa, A A Jr — *Solid State Electron*, 25,1141(1982)
Si, wafers of different orientations. A general study of silicon etching techniques, to include preferential and dislocation etching with the Wright etch SI-0045.

SI-0131
ETCH NAME: TIME:
TYPE: Acid, selective TEMP:
COMPOSITION:
x .... H_3PO_4
x .... HNO_3
DISCUSSION:
Si, (100) p-type, 4—6 Ω cm resistivity wafers used to fabricate MOS capacitors with Ta-Mo gates. MOS structure: $Ta:Mo/SiO_2/Si(100)$. Solution used to etch gates through photo

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resist patterned windows. Hydrogen doped Ta and Mo co-sputtered by RF magnetron in Ar:H_2(20%) on top of an SiO_2 thin film pre-deposited to 400 Å thickness on the substrate at 950°C in dry oxygen.
REF: Ohfusi, S-I & Shiono, N — *J Electrochem Soc,* 132,1689(1985)

SI-0132
ETCH NAME: Sirtl, modified
TYPE: Acid, preferential
COMPOSITION:
1 .... HF
1 .... CrO_3(38%)
TIME:
TEMP:
DISCUSSION:
Si, ingot grown in space and compared to an ingot grown under similar conditions on earth. Sub-grain surface structure and etch pit density were similar. Cut on ⟨110⟩ showed striations to be asymmetric due to temperature field using a mirror heated by a tungsten lamp without rotation during ingot growth in space. Sirtl etch used to develop structure and etch pits.
REF: Eyer, A, Leiste, H & Nitsche, R — *J Cryst Growth,* 71,173(1983)
SI-0133: Arst, M C & Groot, J G — *J Electron Mater,* 13,763(1984)
Si, (100) wafer CZ growth used as substrate for poly-Si growth. After epitaxy, cross section on ⟨110⟩ and polish with c-SiO_2. Use Sirtl etch 30 sec at RT.
SI-0364: Allen, F G et al — *J Appl Phys,* 30,1563(1959)
Si, (111) wafers. A study of surface cleaning by heating in high vacuum.
SI-0365: Law, J T — *J Phys Chem Solids,* 4,91(1958)
Si, (111) wafers. A study of the interaction of oxygen on clean silicon surfaces.
SI-0134: Lu, T C & Bauser, E — *J Cryst Growth,* 71,305(1985)
Si, (111), (110) and (211) wafers with LPE grown epitaxy layers. Specimens cleaved ⟨110⟩ for cross section study of stria called "Valley Trace Type II" that were caused by dopant segregation during growth of epitaxy layers. Sirtl etch was used with illumination with an IR lamp to develop structure. (*Note:* Similar concentric ring resistivity variation on CZ grown wafers, and anomaly segregation in FZ ingots grown for silicon zener devices were observed by author Walker in 1958 (CZ), and 1963 (FZ).)

SI-0132c
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, step-etch
COMPOSITION:
1 .... HF
10 .... H_2O
TIME:
TEMP: 30°C
DISCUSSION:
Si, (100) wafers used as substrates for epitaxy growth and deposition of SiO_2/$TaSi_2$/poly-Si/Si(100). Solution used as a step-etch with a selectivity of SiO_2/$TaSi_2$ shown as 20:1.
REF: Ibid.

SI-0136
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, oxide removal
COMPOSITION:
x .... HF
x .... H_2O
TIME:
TEMP:

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DISCUSSION:

Si, (100) and (111) wafers used in a study of carbon and oxygen contamination. Wafers "as-received" from vendor with one side polished and back-side lightly etched; both sides were polished; Si epitaxy with addition of carbon or oxygen. All study surfaces SiO_2 coated, photo resist applied and window grooves opened in the SiO_2 with an HF etch. Various annealing steps and times. Wright etch, 5 min at RT used to develop defects in etched grooves. Cross-sections ⟨110⟩ with Wright etch show denuded zone under Si epitaxy layer after three-step annealing to be 20 μm deep; epitaxy showed stacking faults, dislocations, and precipitations of carbon and oxygen.

REF: Bailey, W E et al — *J Electrochem Soc,* 132,1721(1985)

SI-0137: McDonald, R & Goetzberger, J A — *J Electrochem Soc,* 109,104(1962)

Si, wafers. Describes the groove etching technique used in SI-0136.

SI-0139

ETCH NAME:

TYPE: Acid, preferential

TIME:

TEMP:

COMPOSITION:

(1) 1 .... HF
1 .... 5 *M* CrO_3

(2) 2 .... HF
1 .... 0.15 *M* CrO_3

(3) 2 .... HF
1 .... 0.75 *M* CrO_3

DISCUSSION:

Si, (111) and (100) wafers used as substrates for silicon MBE thin film epitaxy growth in a study of film defects. Thin films were etched in the solutions shown: (1) "Sirtl" on (111); (2) "Secco" on (100) and (3) "Schimmel" on both (111) and (100). Prior to epitaxy, wafers were (1) detergent scrubbed, (2) DI water rinsed, (3) degreased and N_2 blown dry. No ultrasonic used as it may cause surface damage.

REF: Ota, Y — *J Cryst Growth,* 61,126(1983)

SI-0140

ETCH NAME:

TYPE: Acid, stain

TIME: 10—20 sec

TEMP: RT

COMPOSITION:

1 .... 50 cm^3 HF
4 drops .... HNO_3
4 drops .... HCHO (polyoxymethylene)

DISCUSSION:

Si, (100) wafers used as substrates for superlattice epitaxy growth structures doped with silicon. Wafers cleaved ⟨110⟩ and structure stained with solution shown.

REF: Sakamoto, T — *J Cryst Growth,* 62,704(1983)

SI-0193

ETCH NAME: Argon

TYPE: Ionized gas, thinning

TIME:

TEMP:

COMPOSITION:

x .... Ar^+ ions

GAS FLOW:

PRESSURE:

POWER: 4—6 KeV

DISCUSSION:

Si, (111), (100) and (110) wafers, n-type 0.1—0.7 Ω cm and p-type 0.4—3 Ω cm resistivity. Wafers used in an interface and morphology study of nickel and cobalt silicides. (1) Degrease and clean wafers; (2) CVD deposit 3—5 K Å of SiO_2 and use standard photolithography techniques to open circular windows in oxide; (3) evaporate either nickel

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or cobalt and anneal to form silicides. For TEM evaluation: (1) mechanically polish surfaces, then (2) etch thin by erosion using argon ion bombardment.
REF: Tung, R T & Gibson, J M — *J Vac Sci Technol,* A3,987(1985)

SI-0194
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
105 ml .... HF
745 ml .... HNO_3
75 ml .... HAc
75 ml .... $HClO_4$
TIME: 10 sec
TEMP: RT
RATE: 1700 Å/10 sec
DISCUSSION:
Si, (111) wafers, n-type, used to fabricate diffused p-n-p transistors. Solution used to polish wafers prior to diffusion.
REF: Blaha, R E & Fahrner, W R — *J Electrochem Soc,* 123,515(1976)

SI-0246
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... HF
x .... HNO_3
x .... HAc
+ .... ethylene glycol
TIME:
TEMP:
DISCUSSION:
Si, single crystal wafers. Organic type additives as ethylene glycol, citric, and tartaric acids used as complexing agents with HF:HNO_3:HAc mixtures as dislocation etches on silicon.
REF: Christian, S M & Jensen, R V — *RCA Rep,* LB-1023(1956)

SI-0138
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
3 .... H_2SO_4
1 .... H_2O
TIME:
TEMP:
DISCUSSION:
Si, (111), n-type, 3—5 Ω cm resistivity wafers used as substrates in a study of RF sputtered SiO_2. Clean substrates as follows: (1) degrease with TCE, and acetone rinse; (2) etch in solution shown, and (3) final dip 1HF:10H_2O with DI water rinse.
REF: Lee, N K — *J Appl Phys,* 130,658(1983)

SI-0141
ETCH NAME: Argon
TYPE: Ionized gas, removal
COMPOSITION:
x .... Ar^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER: 10 KeV
DISCUSSION:
Si, wafers of various orientations used in a study of damage introduced by argon ion sputter etching. Damage can be caused by pulsed and CW lasers, E-beam, and ion implan-

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tation (I^2), and varies with gas species and energy levels involved. All can cause surface damage and internal gas trapping. Wafers were furnace annealed prior to and after argon ion sputter etching. Post anneal was done with a Q-switched ruby laser. (*Note:* Damage includes conversion to an amorphous structure which is recrystallized by subsequent laser anneal.)
REF: Lawson, E M — *J Vac Sci Technol,* B1,15(1983)
SI-0207: Davidse, P D — *J Electrochem Soc,* 116,100(1969)

Si, (111) wafers and other orientations. A development study of the use of RF sputter etching as a "universal etch".
SI-0299: Narayan, J et al — *J Vac Sci Technol,* A(2),1303(1984)

Si, (100) wafers cut from ingots grown by the Czochralski (CZ) method. Wafers were etch polished and used in a study of ion implantation (I^2) damage and amorphization. Wafers were Si^+ ion implanted at LHe temperatures (about $-270°C$) at a power level between 100—200 KeV. Wafers were then cleaved ⟨110⟩ and Ar^+ ion thinned for TEM study. The implant induced amorphous layer was 2000 Å deep.

SI-0142
ETCH NAME: TIME: Variable
TYPE: Gas, oxidation TEMP: RT
COMPOSITION:
(1) x .... NO_2 (2) x .... HF (3) x .... H_2O
DISCUSSION:

Si, (111) p-type (B), 10 Ω cm resistivity wafers used in a study of surface films deposited from the three sources shown (1) produced a crystalline film of NH_3SiF_2 (ASF), in part, but all three were mostly amorphous silica, SiO_x with $x = 2$. (*Note:* Water-grown oxide films may be hydrated depending upon method of deposition.)
REF: Heimann, R B — *J Vac Sci Technol,* B1,108(1983)

SI-0143
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, oxide removal TEMP: RT
COMPOSITION:
x .... HF, conc.
DISCUSSION:

Si, (100) n-type, 2—5 Ω cm resistivity wafers used for the evaporation of As_2Te_3. Clean wafers: (1) TCE, agitated, (2) rinse in double distilled water and (3) rinse in acetone. HF rinse immediately before placing wafers in vacuum to remove native oxide. Flash evaporate As_2Te_3 at RT and 5×10^{-6} Torr at 20 Å/sec to 5000 Å thickness.
REF: Krupanidhi, S B et al — *J Appl Phys,* 54,1383(1983)

SI-0144
ETCH NAME: Hydrofluoric acid, dilute TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
x .... 10% HF
DISCUSSION:

Si, (100), p- and n-type wafers, 1—10 Ω cm resistivity used for the evaporation of erbium, Er. Clean substrates: (1) acetone with ultrasonic; (2) EOH rinse; (3) "RCA" etch clean (SI-0031) and (4) DI water rinse. Use final HF rinse immediately prior to placing wafers in vacuum.
REF: Wu, C S et al — *J Electrochem Soc,* 132,918(1985)

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SI-0145
ETCH NAME: Potassium hydroxide
TYPE: Alkali, preferential
COMPOSITION:
x .... 10 *M* KOH
TIME: 10 min
TEMP: 80°C
DISCUSSION:
Si, (111), (100) and (110) wafers and a 1-cm diameter sphere, finished with 600-grit SiC. Etch Time/Temp shown is for sphere etching. Wafers were etched at 62°C for 400 min (?) to form mesas after photo resist patterning. The finite crystal form of the sphere was a tetrahexahedron, (hk0). The study was correlated with mesa side slopes and slow etch planes of the sphere with prediction of type plane that will occur on mesas. (*Note:* Author Walker did similar studies on spheres, mesas, and pits, circa 1957—1958 using boiling KOH, 30 to 40 min [see SI-0092a-c]. The 400 min shown is probably 40 min.)
REF: Weirach, D F — *J Appl Phys,* 46,1478(1975)

SI-0146
ETCH NAME: Potassium hydroxide
TYPE: Electrolytic, oxidation
COMPOSITION:
x .... 2 *M* KOH
TIME:
TEMP: 22°C
ANODE: Si
CATHODE: Si
POWER: Variable
DISCUSSION:
Si, (111) and (100) wafers, p- and n-type of varied resistivity. A major study of anodic and cathodic oxidation of silicon and oxide etch-back.
REF: Palik, E D et al — *J Electrochem Soc,* 132,817(1985)
SI-0273: Orest, J et al — *J Electrochem Soc,* 132,145(1985)
Si, (111) and (100) wafers both p- and n-type, 9—10 Ω cm resistivity. A study of anodic/cathodic oxidation of silicon using KOH.
SI-0097b: Glembocki, O J & Stahlbush, R E — *J Electrochem Soc,* 132,145(1985)
Si, (111) and (100) wafers etched under bias in 2 *M* KOH. Contact was made using an In/Ga amalgam alloy. Etch rates shown for (111), (100), and (110).

SI-0245
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 1 *N* KOH
(+) .... glycerin
(+) .... H_2FSi_6
TIME:
TEMP: Hot
ANODE: Si
CATHODE: Si
POWER:
DISCUSSION:
Si, (111) wafers both p- and n-type. Etching done with switching of anode/cathode. KOH solution used with and without (+) additives shown. P-type wafers will polish; n-type will be pitted.
REF: Turner, D R — *J Electrochem Soc,* 105,402(1958)

SI-0272
ETCH NAME: RIE
TYPE: Ionized gas, selective
COMPOSITION:
x .... 3—10% Cl_2
x .... Ar
TIME:
TEMP:
GAS FLOW: 10—50 cc/min
PRESSURE: 10—100 μm
POWER: 0.16/cm²

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DISCUSSION:

Si, (100) p-type wafers with SiO_2 films. A study of RIE etching with Cl_2/Ar gas mixtures. SiO_2 etch rate was about 5—8 nm/min with Si/SiO_2 ratio rates as high as 20:1. A laser etching technique was used to test SiO_2 thickness in place for adhesion and defect generation.
REF: Pogge, H B et al — *J Electrochem Soc*, 130,1592(1983)

SI-0273
ETCH NAME: RIE
TYPE: Ionized gas, selective
COMPOSITION:
x .... x% O_2
x .... SF_6
TIME: 3 min
TEMP: RT
GAS FLOW: 450 sccm
PRESSURE: 150 mTorr
POWER: 1500 W
DISCUSSION:

Si, (100) n-type 3—6 Ω cm resistivity wafers used as substrates for deposition of SiO_2 and poly-Si in an RIE etch rate study, primarily concerned with poly-Si. Different O_2 plasma gas levels evaluated. Poly-Si/SiO_2 selectivity ratio was above 10:1. Ratio of KTI 1470J photo resist to silicon was about 1:1.
REF: Light, R R W & Bell, H B — *J Electrochem Soc*, 130,1567(1983)
SI-0274: Sakai, Y et al — *J Electrochem Soc*, 131,627(1984)

Si, polycrystalline layers deposited on Si containing an SiO_2 thin film. A study of poly-Si etching in conjunction with aluminum evaporation for VLSI structures. RIE gas composition was SF6:O_2(10%).

SI-0051b
ETCH NAME: Steam
TYPE: Gas, cleaning
COMPOSITION:
x .... H_2O, steam
TIME:
TEMP: >100°C
DISCUSSION:

Si, (100) wafers used as substrates for epitaxy growth of thick and thin poly-Si films grown on SiO_2 films pre-deposited on the substrates. Growth method called Lateral Epitaxy Growth over Oxide (LEGO). After deposition, poly-Si films were thinned using a laser strip heater. All poly-Si films were melted with a halogen lamp furnace. Substrates were cleaned: (1) oxidize in steam; (2) photo resist, patterned with "seed" windows opened; (3) in vacuum use HCl vapor at 1050°C, to remove any native oxide remaining in windows. Epitaxy silicon grown using SiH_4 at 1050°C as poly-Si columnar grains and capped with LPCVD SiO_2. Schimmel etch, RT, 10 sec used as a defect and dislocation etch solution (SI-0037).
REF: Celler, G K et al — *J Electrochem Soc*, 132,211(1985)

SI-0147
ETCH NAME: Sodium hydroxide
TYPE: Alkali, structure
COMPOSITION:
x .... 10 *N* NaOH
TIME: $4^1/_2$ or $2^1/_2$ h
TEMP: 363 K (109°C)
RATE: 120 μm/h (100),
4 μm/h (111)
DISCUSSION:

Si, (100) wafers 100 mm thick, polished on both sides for etch development of pits or via holes. Wafers were photo resist patterned for an open square geometry with nichrome used as the primary mask (its removal rate is much less than that of silicon in this solution). The $2^1/_2$ h etch time was used for single-side pit development; the $4^1/_2$ h — $2^1/_2$ h on either wafer side — used for via holes, and for a controlled pit-bottom or via hole orifice size.
REF: Petit, B et al — *J Electrochem Soc*, 132,982(1985)

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SI-0148
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP: RT
COMPOSITION:
1 .... HF
5 .... HNO_3
1 .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) web-dendritic ribbon crystal silicon specimens used in a study of defects and structure. The solution shown was used to etch thin sections and the Secco etch (SI-0036) was used for defect development. Showed multiple (111) glide planes — due to growth strain(?) — and the usual twinned zone down the center of the ribbon.
REF: Cunningham, B et al — *J Electrochem Soc,* 129,1089(1982)

SI-0149
ETCH NAME: TIME:
TYPE: Halogen, conditioning TEMP:
COMPOSITION:
x .... MeOH
x .... *I_2

*Saturate the solution.

DISCUSSION:
Si, (100) n-type wafers with a p^+ Si epitaxy buffer layer, then a CdSe thin film deposition in structuring a tunnel junction photo anode for solar cells. Prior to CdSe homogeneous chemical vapor deposition (HOMOCVD), (1) HF dip to remove native oxide from p^+/n Si surfaces and (2) quench in solution shown — will produce a p^+ surface with chemisorption of an I_2 film that is stable to about 500°C. Silicon wafer ingots were grown by Horizontal Bridgman (HB) and Liquid Encapsulated Czochralski (LEC) techniques. (*Note:* Author Walker (1964) used an unsaturated solution as a method of complexing silicon surfaces for removal of ionic contamination remaining from acid etch solutions prior to diffusion. Iodine remaining on surface will complex ions and vaporizes at about 100°C leaving a molecularly clean surface for diffusion. See Diamond section for additional use of I_2 to passivate surfaces.)
REF: Pinson, W E — *J Appl Phys Lett,* 40,970(1982)

SI-0076b
ETCH NAME: TIME: 15 min
TYPE: Acid TEMP: RT
COMPOSITION:
1 .... HF
1 .... HNO_3
1 .... HAc
1 .... Br_2
DISCUSSION:
Si, polycrystalline material. The following system was developed to produce damage-free polished surfaces: (1) lap with 30 μm alumina on a felt pad, 30 min for a dull grey surface; (2) polish with 2 μm diamond paste with a starting pressure of 5 psi, reducing to 2 psi over a 2-min period to remove lap damage, but residual stress remains and (3) final

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polish with Nalcog #2250 (colloidal silica slurry). Etch 15 min in 1HF:5HNO_3:1HAc, then in the solution shown.
REF: Sopori, B L et al — *J Electrochem Soc*, 128,215(1981)

SI-0151
ETCH NAME: TIME:
TYPE: Acid, oxidizing TEMP:
COMPOSITION:
x .... 8 *N* H_2CrO_4
DISCUSSION:
Si, wafers. Solution will both oxidize and preferentially etch silicon.
REF: Alpha Products Catalog, 1982

SI-0152
ETCH NAME: Secco etch, modified TIME:
TYPE: Acid, dislocation TEMP: RT
COMPOSITION:
2 .... HF
1 .... 0.005 *M* $K_2Cr_2O_7$
DISCUSSION:
Si, (100) p-type wafers used for ion implantation of arsenic in a study of annealing with E-beam. E-beams were used to grid anneal surfaces after As^+ ion implantation. The implantation produced a 0.1 μm deep amorphous layer. The Secco etch shown was used to develop defects. See SI-0036 for other Secco etchants.
REF: Sun, H T et al — *J Vac Sci Technol*, B(1),827(1985)

SI-0153c
ETCH NAME: Copper etch TIME:
TYPE: Acid, preferential TEMP:
COMPOSITION:
4 ml .... HF
2 ml .... HNO_3
4 ml .... H_2O
0.2 g .... $Cu(NO_3)_2.3H_2O$
DISCUSSION:
Si, (111) wafers and other orientations. Use solution shown as a general dislocation etch.
REF: Ibid.

SI-0153d
ETCH NAME: Copper etch TIME: 2 h
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
"A" 600 ml .... HF "B" x .... H_2O
300 ml .... HNO_3
24 g .... $Cu(NO_3)_2$
2.4 g .... Br_2
Mix: 1 part "A" to 10 parts "B"
DISCUSSION:
Si, (111) wafers. Use ultrasonic agitation of solution during the etch period. This is a general dislocation etch and can be used on other silicon surface orientations.
REF: Ibid.

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SI-0154
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
1 .... HF
3 .... HNO_3
DISCUSSION:
Si, single crystal spheres $^1/_8$" diameter used in determining densitometric and electrical parameters of boron in silicon. Rough spheres fabricated by melt drop-off from glass rods of different density, then tumbled in a "race-track" system on SiC paper. Ground spheres were etch polished in the solution shown and rinsed in DI water. Produces a hydrophobic surface. (*Note:* See SI-0061a-c, SI-0092a-f for additional work on spheres.)
REF: Horn, F H — *Phys Rev*, 97,1521(1955)

SI-0188b
ETCH NAME: TIME:
TYPE: Acid, junction stain TEMP: RT
COMPOSITION:
4 .... HF
2 .... $Cu(NO_3)_2$
DISCUSSION:
Si, (111) wafers with p-n junctions. Solution will plate out on n-type material side first.
REF: Woriskey, P J — *J Appl Phys*, 29,867(1958)

SI-0188c
ETCH NAME: TIME:
TYPE: Acid, junction stain TEMP: RT
COMPOSITION:
50 ml .... x% $Cu(NO_3)_2$
1—2 drops .... HF
\+ .... white light
DISCUSSION:
Si, wafers with p-n junctions. Copper will plate out on the n-type area first.
REF: Ibid.

SI-0189
ETCH NAME: TIME:
TYPE: Acid, junction stain TEMP: RT
COMPOSITION:
x .... HF
x .... 1% HNO_3
DISCUSSION:
Si, p-n junction wafers. Place one drop of solution across junction. The p-type area will turn blackish.
REF: Fuller, C S & Ditzenberger, J A — *J Appl Phys*, 27,544(1956)

SI-0190a
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
1 .... HF
25 .... HNO_3

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DISCUSSION:

Si, (111), (100), (112) and (110) oriented wafers used in a study of surface melt patterns. Polish surfaces with solution shown prior to heat treatment to produce melt patterns. Melt patterns were square on (100); triangles on (111); isosceles triangles on (112) and parallel lines on (110). (*Note:* See SI-0092a-f for similar data.)

REF: Pearson, G L & Treuting, R G — *Acta Crystallogr*, 11,397(1958)

SI-0061b

ETCH NAME: Abrasive cutting — TIME: To 1 h

TYPE: Abrasive, forming — TEMP: RT

COMPOSITION:

x .... SiC, paper

x .... H_2O

x .... glycerin

DISCUSSION:

Si, single crystal spheres, p- and n-type. Use 80-grit SiC for rough forming and 320-grit for final grinding. Use a Buehler polish wheel and four steel tubes to hold material in place. Cubes, $^1/_4$ and $^1/_2$" square, were cut as starting material. Both germanium and silicon spheres formed. See SI-0061a and SI-0066 for polish etches. Spheres were used for finite crystal form etching, and in developing spherical devices.

REF: Walker, P — personal development, 1957—1960

SI-0156

ETCH NAME: Lathe cut — TIME:

TYPE: Lathe, forming — TEMP: RT

COMPOSITION:

x .... oil, coolant

DISCUSSION:

Si, single crystal spheres cut on a lathe using oil as a coolant. Also formed germanium spheres.

REF: Myers, J — personal communication, 1959

SI-0157a

ETCH NAME: Nitrogen — TIME: To 45 min

TYPE: Gas, forming — TEMP: RT

COMPOSITION: — PRESSURE: 2—3 SCFH

x .... N_2, pressure

x .... SiC, paper

DISCUSSION:

Si, single crystal spheres from $^1/_8$ to $^1/_2$" in diameter formed from cut cubes. A "Tornado Sphere Grinder" was designed and fabricated by authors as a circular race-track using glue-back Buehler 600-grit SiC strips for grinding. Cubes are placed in the closed system and rotated by nitrogen gas pressure blowing at 3—5 psi for 20—40 min (silicon). Other materials require different grinding time. Other semiconductors sphere formed: germanium, gallium arsenide, gallium phosphide, gallium antimonide, and indium phosphide. Used spheres in finite crystal form etching studies.

REF: Myers, J & Walker, P — personal development, 1958—1959

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SI-0158
ETCH NAME: Shot Tower — TIME:
TYPE: Drop, forming — TEMP: Hot
COMPOSITION:
x .... hot oil
DISCUSSION:

Si, polycrystalline spheres formed using the Shot-Tower technique: material melt held in a hopper above a cylinder containing a hot oil — liquid droplets of silicon gravity feed down into oil of cylinder forming spheres at cylinder bottom. Method used on Si, Ge, metals, and intermetallic materials. (*Note:* This is the industrial standard method of fabricating ball-bearings and spherical pellets of solder alloy materials.)
REF: Cole, R — personal communication, 1957
SI-0157b: Ibid.

Si, polycrystalline spheres, and special alloy metal mixtures for silicon solders. A Shot-Tower system designed by the authors. The alloys were used in a study of 50 different mixtures as contacts on silicon.

SI-0159
ETCH NAME: — TIME:
TYPE: Acid, light figure — TEMP:
COMPOSITION:
x .... HF
x .... I_2
DISCUSSION:

Si, (111) wafers and other orientations. Solution used as a preferential etch to develop pits which can be used for light figure orientation of wafers or ingots. Germanium light figure etching was done by thermal etching. (*Note:* See SI-0091a-f for hydroxide etchants for both silicon and germanium.)
REF: Wolff, G A et al — J Electrochem Soc Meet, Pittsburgh, PA, Oct 13, 1955

SI-0160
ETCH NAME: — TIME:
TYPE: Acid, planar — TEMP:
COMPOSITION:
20 ml .... HF
150 ml .... HNO_3
50 ml .... CH_3COOH (HAc)
DISCUSSION:

Si, (111) wafers and other orientations. Thin wafers used in a study of thermal stress and plastic deformation. Polish etch in solution shown for a flat, planar surface. After stress, use Sirtl's etch to develop dislocations and other defects (SI-0039).
REF: Merizane, K & Gleim, P S — *J Appl Phys,* 40,4104(1969)
SI-0245: Stolt, L et al — *Solid State Electron,* 26,295(1983)

Si, (100) wafers used in fabricating Shottky Barrier diodes. Etch polish wafer in "planar" etch shown and HF dip just before placing in vacuum. A stainless steel mask was used for pattern definition of evaporation metals.

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SI-0161
ETCH NAME: TIME: 1 min
TYPE: Acid, polish TEMP: RT
COMPOSITION:
15% .... HF
85% .... HNO_3
DISCUSSION:
Si, (111), p-type wafers, 0.1—200 Ω cm resistivity. Used in a study of direct observation of charge storage surface states. Solution used as a surface polish etch.
REF: Harman, C G & Raybold, R L — *J Appl Phys*, 34,380(1963)

SI-0162a
ETCH NAME: TIME:
TYPE: Acid, polish TEMP: RT
COMPOSITION:
25 ml .... HF
100 ml .... HNO_3
125 ml .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) wafers used as substrates for epitaxy growth of silicon. Solution used to polish surfaces prior to epitaxy. After epitaxy silicon substrates were etch removed for study of structure and stacking faults in the epitaxy layer.
REF: Finch, R H et al — *J Appl Phys*, 34,406(1963)

SI-0162b
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP:
COMPOSITION:
5% .... HF
95% .... HNO_3
DISCUSSION:
Si, (111) wafers used as substrates for epitaxy growth of silicon. After deposition, wafers were mounted with epitaxy side down on Teflon discs and etched in a Teflon beaker to remove the bulk silicon substrate. Etching was done with beaker mounted at 45° and rotated at 30 rpm. The epitaxy layer was studied for structure and stacking faults. See SI-0162a.
REF: Ibid.

SI-0163a
ETCH NAME: TIME:
TYPE: Acid, thinning TEMP: RT
COMPOSITION:
(1) 10 .... HF
5 .... HNO_3
14 .... HAc
(2) 1 .... HF
5 .... HNO_3
DISCUSSION:
Si, (111) wafers used in a study of stacking fault energy. Wafers were mechanically polished down to $^2/_{10}$ mm thickness and then a pit was sandblasted at the wafer center. Etch (1) was used as a "rough" removal and polish etch and followed by etch (2) as a final "fine" polish etch. Transmitted light was used to determine the stop-point for etching by color. Transmitted light was brownish-red — sufficiently thin for electron microscope study — at the stop-point. Solutions also developed step angled dislocations in surface. (*Note:*

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See SI-0092a. Transmitted light used to establish aluminum alloy base widths for silicon transistors.)
REF: Aerts, E et al — *J Appl Phys*, 33,3078(1963)

SI-0201b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
1 .... HF
4 .... HNO_3
DISCUSSION:
TIME:
TEMP:
ANODE:
CATHODE: Pt
POWER:

Si, (111) n-type wafers, 130 Ω cm resistivity used in a study of oscillatory photocurrent decay. Etching done with a xenon flash through a 2.5 mm slit during test.
REF: Hoshino, H & Takayama, M — *Jpn J Appl Phys*, 2,438(1963)

SI-0165
ETCH NAME: Camp #2 (Superoxol)
TYPE: Acid, preferential
COMPOSITION:
10 .... HF
10 .... H_2O_2
40 .... H_2O
DISCUSSION:
TIME:
TEMP: RT

Si, (111) n-type wafers and p-doped with ^{60}Co (gamma) used in a study of induced radiation defects in silicon. Alloy contacts were 75 Sn:20 Zn:5 Bi and preferentially etch cleaned in the solution shown, which was called #2 Etch. Samples were annealed in an oil bath under electrical bias. (*Note:* See GE-0065a for original development of etch.)
REF: Saito, H & Hirata, M — *Jpn J Appl Phys*, 2,678(1963)
SI-0067: Dresselhaus, C et al — *Phys Rev*, 98,368(1955)

Si, (111) discs, 3 mm diameter and 0.5 mm thick, used in cyclotron resonance studies. Superoxol used as a preferential and removal etch.

SI-0166
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
5 .... HF
3 .... HNO_3
DISCUSSION:
TIME:
TEMP:

Si, (111) n-type wafers, 50—500 Ω cm resistivity with gold plated contacts as surface barrier diodes. A study of frequency oscillation under intense illumination. The frequency increases with bias and intensity of illumination only under reverse bias conditions. Solution used to etch polish and clean device surfaces.
REF: Yamashita, B et al — *Jpn J Appl Phys*, 2,661(1963)

SI-0112
ETCH NAME: Potassium cyanide
TYPE: Acid, cleaning
COMPOSITION:
x .... 20% KCN
TIME:
TEMP: RT

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DISCUSSION:

Si, (111), p-type (intrinsic) and doped (extrinsic) wafers used in a study of diffusion and solubility of copper in silicon, germanium, and gallium arsenide. Solution used to remove traces of copper prior to and after deposition and diffusion.

REF: Hall, R N & Racette, J H — *J Appl Phys,* 35,379(1964)

SI-0225

ETCH NAME: TIME:

TYPE: Acid, junction TEMP: RT

COMPOSITION:

90 .... HF

10 .... HNO_3

DISCUSSION:

Si, (111) n-type wafers with p-n junctions. Solution was used to delineate the junction. (*Note:* Similar to other "stain" type junction etches.)

REF: Billig, E & Gasson, D B — *J Appl Phys,* 28,1242(1957)

SI-0205: Yeh, T-H & Joshi, M L — *J Electrochem Soc,* 116,73(1969)

Si, (111) wafers and other orientations used in a study of strain compensation in silicon by diffused impurities. No etch shown.

SI-0167

ETCH NAME: TIME:

TYPE: Acid, junction stain TEMP:

COMPOSITION:

1 .... HF(40%)

3 .... HNO_3

10 .... HAc

DISCUSSION:

Si, (111) n-type wafers with diffused p-type layers, sectioned and studied for diffusion depth profile by staining. Stain graded from bright blue at surface down to brown with depth of diffusion. Color represents changes in impurity concentration. Depth of two stains studied varies as the square root of diffusion time as $L = (D.t)^{1/2}$.

REF: Knopp, A N — *Electrochem Technol,* 2,302(1964)

SI-0063c

ETCH NAME: TIME: 1—10 sec

TYPE: Acid, junction stain TEMP: RT

COMPOSITION:

(1) 1 .... HF
20 .... HNO_3

(2) 20 .... HF
1 .... HNO_3

DISCUSSION:

Si, (111) n-type wafers, 15—20 Ω cm resistivity with 1—3 μm depth boron diffusion used in an initial study of boron diffusion in silicon using a diborane, B_2H_6, gas source. After wafers were diffused they were sectioned and angle lapped at 5 and 10° prior to staining. Observation was done with a standard metallurgical microscope with additional side lighting to enhance color definition. Color varied from surface down as brilliant red, blue, yellow, green, and dull brown at depth. Colors used as a measure of diffusion concentration change profiling.

REF: Walker, P & Crabbs, G — personal development, 1965

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SI-0169b
ETCH NAME: Caro's etch, modified — TIME: 10 min
TYPE: Acid, cleaning — TEMP: 110°C
COMPOSITION:
7 .... H_2PO_4
3 .... H_2O_2
DISCUSSION:
Si, (111) p-type wafers used for diffusion of antimony from glass. Solution used to clean surfaces followed by spin rinsing with UPDI (ultra pure DI) water and drying in hot nitrogen. A powdered slurry of antimony glass was spun-on for 10 min at various speeds for different thicknesses and fired at 150 or 400°C in nitrogen for 30 min. Also used 1HF:10H_2O, RT, 1 min for cleaning surfaces (SI-0169a).
REF: Ibid.

SI-0170
ETCH NAME: — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
16 ml .... HF
100 ml .... HNO_3, fuming
44 ml .... HAc
DISCUSSION:
Si, (111) wafers used in a study of ion bombardment cleaning and observed by ion energy electron diffraction. Solution used to polish surfaces prior to ion bombardment. Titanium, germanium, and nickel also studied. (*Note:* The "fuming" concentration not shown . . . white, 70% . . . yellow, 72% . . . red, 74%.)
REF: Farnsworth, H E et al — *J Appl Phys*, 29,1150(1958)

SI-0171
ETCH NAME: — TIME:
TYPE: Acid, preferential — TEMP:
COMPOSITION:
25 .... HCl
75 .... HNO_3
DISCUSSION:
Si, (111) wafers used in a study of light induced plasticity. A Knoop Tukon Hardness Tester was used to indent surfaces with a diamond tool. Solution used to develop structure after indentation. Authors say that surface preparation is dependent upon results observed. Also studied were germanium, indium antimonide, and indium arsenide which were all etched in CP4.
REF: Kuczynski, G C & Hochman, R F — *Phys Rev*, 108,946(1957)

SI-0172
ETCH NAME: SR4 — TIME:
TYPE: Acid, polish — TEMP:
COMPOSITION:
3 .... HF
2 .... HNO_3
1 .... HAc

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DISCUSSION:

Si, (111) wafers used in a study of the variations in surface conductivity of silicon and germanium. Solution used to polish on both materials.

REF: Ioselevich, M L & Fistul', V I — *Sov Phys (Solid State)*, 3,822(1960)

SI-0173a

ETCH NAME:

TYPE: Acid, forming

COMPOSITION:

2 .... HF

15 .... HNO_3

5 .... HAc

TIME: 7—9 min

TEMP: RT

RATE: $^1/_2$ mil/min

DISCUSSION:

Si, (111) n-type wafers, 5—50 Ω cm resistivity with wafer diameters from $^1/_2$ to 2", with closed-tube gallium diffusion depths of 3.5 mils. Solution shown used to etch a well containing pylons in surfaces for n-type epitaxy deposition in fabricating high power SCRs. Well etched into gallium layer for n-p-n structure. Etch produces a highly reflective surface with interlocking etch pits up to 0.5 mil size; well bottom flatness of 0.5 mils; well edge slopes a shallow 25 to 30 mils extending into well; pylon sides preferentially etched with near-hexagonal cross-section. Well depth etched to a controlled depth <3.5 mils in establishing the SCR gate turn-on level.

REF: Walker, P — personal application, 1970

SI-0173b

ETCH NAME:

TYPE: Acid, forming

COMPOSITION:

2 .... HF

3 .... HNO_3

8 .... HAc

TIME: 7—9 min

TEMP: RT

RATE: $^1/_4$ mil/min

DISCUSSION:

Si, (111) n-type wafers, 5—120 Ω cm resistivity with 3.5 mil deep gallium p-type diffusion. A well with pylons etched into surface prior to n-type silicon epitaxy in fabricating high power SCRs $^1/_2$ to 2" in diameter. Pylons were wax ink dotted prior to well etching. This solution gave a well bottom with a shallow pit-and-mound structure, and a dull matte finish. Well edge slope near-vertical; pylon sides vertical with near-circular cross section. Well depth etch to <3.5 mils to establish SCR gate turn-on level. This is an improved well/pylon structure compared to SI-0173a. Ten etch solutions evaluated for improved well shape with the following ratio of constituents shown above: 1:3:3 . . . 1:5:6 . . . 1:5:8 . . . 2:5:8 . . . 2:3:8 . . . 2:3:5 . . . 2:3:4 . . . 2:6:12 and 2:3:6. All well side slopes, pylon side structure, and well bottom planarity measured by cross-sectioning and measuring under a microscope.

REF: Ibid.

SI-0173c

ETCH NAME:

TYPE: Acid, dislocation

COMPOSITION:

2 .... HF

3 .... HNO_3

6 .... HAc

TIME: 2—8 min

TEMP: RT

RATE: $^1/_2$ mil/min

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DISCUSSION:

Si, (111) n-type wafers, 5—120 Ω cm resistivity with a 3.5 mil deep p-type gallium diffusion. Similar to etch shown under SI-0173b. Because of the overall matte finish, dislocations are easily observed. Used to measure dislocation density before and after gallium diffusion. All of the etchants in SI-0173b are dislocation etches to some degree.

REF: Ibid.

SI-0174a

ETCH NAME:

TYPE: Electrolytic, jet polish

COMPOSITION:

x .... 0.2 *N* NaF

5 ml .... HF

100 ml .... H_2O

TIME:

TEMP: RT

ANODE:

CATHODE:

POWER: 3 mA/cm² max

DISCUSSION:

Si, (111) n-type wafers. Orifice of jet was 0.010 diameter and etching was done with light. A discussion of the jet etching of n-type silicon.

REF: Schmidt, P F & Keipler, D A — *J Electrochem Soc*, 106,592(1959)

SI-0174b

ETCH NAME:

TYPE: Electrolytic, jet polish

COMPOSITION:

30 ml .... HF

8.4 g .... NaF/l H_2O

TIME:

TEMP: 70°C

ANODE:

CATHODE:

POWER: 30 mA/cm²

DISCUSSION:

Si, (111) n-type wafers. See SI-0174a for discussion.

REF: Ibid.

SI-0174c

ETCH NAME:

TYPE: Electrolytic, jet polish

COMPOSITION:

40 g .... NH_4F

8 g .... NaF/l H_2O

TIME:

TEMP: RT

ANODE:

CATHODE:

POWER:

DISCUSSION:

Si, (111) n-type wafers. Solution used as a chemical as well as electrolytic etch solution. Authors say that at least a 6 mA/cm² current is needed to reduce SiO_2 passivity effects.

REF: Ibid.

SI-0245b

ETCH NAME: Hydrofluoric acid, dilute

TYPE: Electrolytic, polish

COMPOSITION:

x .... 5% HF

DISCUSSION:

TIME:

TEMP: RT

ANODE: Si

CATHODE: Pt

POWER: 110—850 mA/cm²

Si, (111) wafers used in a study of electropolishing with HF. N-type silicon etches with difficulty, requiring higher current than for p-type and can develop surface pitting. High current is needed to remove SiO_2 layers.

REF: Turner, D R — *J Electrochem Soc*, 105,402(1958)

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SI-0066b
ETCH NAME: Sodium chromate
TYPE: Acid, surface treatment
COMPOSITION:
x .... 1% $Na_2Cr_2O_7$
DISCUSSION:
Si, wafers used in a study of chemical treatments on surface properties of silicon. Solution used to produce a surface with low sulfur content. Soak wafers and allow solution to dry on surfaces.
REF: Ibid.
TIME:
TEMP: RT or 80—90°C

SI-0066c
ETCH NAME: Water
TYPE: Acid, surface treatment
COMPOSITION:
x .... H_2O
DISCUSSION:
Si, wafers used in a study of chemical treatments on surface properties of silicon. After boiling, allow wafers to dry by evaporation.
REF: Ibid.
TIME: 30 min
TEMP: Boiling

SI-0184: Chu, T L & Tallman, R L — *J Electrochem Soc*, 12,1306(1964)
Si, wafers used in a study of water vapor as an etch for silicon as oxidation and removal. Used Sirtl etch at RT, 6—30 sec to develop oxidation-induced defects.

SI-0066d
ETCH NAME: Hydrofluoric acid
TYPE: Acid, surface treatment
COMPOSITION:
x .... HF
DISCUSSION:
Si, wafers used in a study of the chemical treatments on surface properties of silicon. After HF soak, follow with 5-sec rinse in running DI water.
REF: Ibid.
TIME: 5 min
TEMP: RT

SI-0064
ETCH NAME: Gold
TYPE: Metal, junction delineation
COMPOSITION:
10 g .... $KAu(CN)_2$
200 g .... KOH
1000 ml .... H_2O
DISCUSSION:
Si, wafers containing alloyed or diffused junctions. Solution used to chemically plate out gold to differentiate the p-n junction. Authors say that KOH will precipitate at under 5°C. Polished surfaces require longer plating and produce poor adhesion. Surfaces prepared by light lapping with either Linde A or 600-grit carborundum (SiC) are preferred. Use infrared light during plating and gold will plate out on the more negative side of the junction.
REF: Silverman, S L & Benn, D R — *J Electrochem Soc*, 105,170(1958)
TIME:
TEMP: 30—70°C

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SI-0185
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... 1—4% $NH_4F.HF$

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Si, n- and p-type wafers. Development study of electropolishing silicon and n-type germanium.
REF: Klein, D L et al — *Electro Chem Soc Abstr,* 10,72(1961)

SI-0186a
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... KF
x .... KCl
x .... H_2O

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

DISCUSSION:
Si, wafers. Development study of electropolishing silicon and germanium.
REF: El'kin, B I — *Abstr J Metall,* 3 # 4, item 2 (1958)

SI-0187a
ETCH NAME:
TYPE: Acid, junction stain
COMPOSITION:
x .... AgF, sat. sol.
+ .... *HF

TIME:
TEMP:

*1 drop/5 ml of solution.

DISCUSSION:
Si, (111) wafers with p-n junctions. Solution used to etch stain junctions.
REF: Ilies, P A & Coppen, P J — *J Appl Phys,* 29,1514(1958)

SI-0188a
ETCH NAME:
TYPE: Acid, junction stain
COMPOSITION:
x .... HF
+ .... intense light

TIME:
TEMP:

DISCUSSION:
Si, wafers with p-n junctions. Solution turns n-type blackish and p-type is silvery.
REF: Woriskey, P J — *J Appl Phys,* 29,867(1958)

SI-0064
ETCH NAME:
TYPE: Acid, preferential
COMPOSITION:
x .... HF
x .... HNO_3
x .... x% KNO_3

TIME:
TEMP:

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DISCUSSION:

Si, wafers of various orientations. Acid mixtures containing KNO_3 developed spiral terraces.

REF: Matukura, Y & Suzuki, T — *J Phys Soc Jpn*, 12,976(1957)

SI-0041b

ETCH NAME: Hydrofluoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... 24—48% HF

TIME:
TEMP:
ANODE: Si
CATHODE:
POWER: 0.5 A/cm²

DISCUSSION:

Si, wafers. Shown as an electropolish etch for silicon.

REF: Ibid.

SI-0123: Uhiler, A Jr — *Bell Systems Technol J*, 35,333(1956)

Si, specimens. Solution used for electrolytic shaping of specimens. Other electrolytes used for shaping, germanium specimens.

SI-0041c

ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
x .... HF
x .... *alcohol

TIME:
TEMP:
ANODE:
CATHODE:
POWER:

*EOH, MeOH, glycols, or glycerin.

DISCUSSION:

Si, p-type wafers. With the inclusion of alcohols or organic hydroxyls very fine and smooth polished surfaces are achieved. (*Note:* Many authors have pointed out that the use of glycerin or similar agents for viscosity control of etch solutions improves the quality of etched surfaces.)

REF: Ibid.

SI-0016

ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
x .... Linde A alumina
x .... 3—5% CrO_3

TIME:
TEMP:

DISCUSSION:

Si, specimens. A method for metallographic polishing and preparation for studying reactions of thin films on silicon. Place an 0.030 wire in potter with silicon specimen laid on top and pot with plastic. Silicon contained a thin platinum evaporated film 0.1—0.15 μm thickness. After potting, lap on brass metallographic platen with a silk pad at 1150 rpm using the acid/slurry shown above.

REF: Woods, H & Silverman, R — *J Appl Phys*, 38,419(1967)

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SI-0178
ETCH NAME: TIME:
TYPE: Acid, polish + decorate TEMP:
COMPOSITION:
(1) 1 .... HF (2) x .... Cu plate
3 .... HNO_3
DISCUSSION:
Si, (111) and (110) wafers cut from CZ grown ingots. Etch polish wafers with solution shown, then heat on copper plate at 850°C for 1 h to diffuse copper. Use Dash etch for 24 h at RT to develop dislocations. See SI-0044 for Dash etch.
REF: Furuoya, T — *Jpn J Appl Phys,* 1,135(1962)

SI-0180a
ETCH NAME: TIME:
TYPE: Acid, polish TEMP:
COMPOSITION:
4 .... HF
10 .... HNO_3
DISCUSSION:
Si, (111) wafers. Used to fabricate diodes with evaporated aluminum in a study of interfaces. Wafers were etched in solution shown to 150 μm thickness and then quenched in concentrated HNO_3 followed by DI water. Oxidize the surfaces immediately and just before aluminum metallization remove some of the oxide with 1HF:10H_2O. (*Note:* An oxide or oxidized surface will improve aluminum metal adhesion.)
REF: Meade, C A — *Appl Phys Lett,* 9,53(1966)

SI-0180b
ETCH NAME: TIME:
TYPE: Acid, oxide removal TEMP:
COMPOSITION:
1 .... HF
10 .... H_2O
DISCUSSION:
Si, (111) wafers. Solution used to etch remove some deposited silicon dioxide, SiO_2 immediately prior to aluminum metallization on the oxide as Al/SiO_2/Si in a study of interfaces.
REF: Ibid.

SI-0192
ETCH NAME: TIME:
TYPE: Acid, jet polish TEMP:
COMPOSITION:
5 .... HF
15 .... HNO_3
3 .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) and (100) n- and p-type wafers. Surfaces polished with an acid jet using the solution shown.
REF: Unvala, B A et al — *J Electrochem Soc,* 119,318(1972)

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SI-0092k
ETCH NAME: Potassium bromide
TYPE: Halogen, polish/forming
TIME: 10—20 min
TEMP: RT
COMPOSITION:
x .... KBr
DISCUSSION:
Si, (111), n-type, 10—15 Ω cm resistivity wafers used in a general etching study and controlled pit formation. Solution works well for surface cleaning and will produce a small 1—1.5 diameter etch pit in the time shown.
REF: Ibid.

SI-0197a
ETCH NAME:
TYPE: Acid, polish
TIME:
TEMP:
COMPOSITION:
6 .... HF
10 .... HNO_3
9 .... CH_3COOH (HAc)
DISCUSSION:
Si, (111) wafers used in a study of thermal cycle degradation of charge carrier lifetime and resistivity in silicon barrier diodes. Solution used to etch polish wafers.
REF: Walter, F J & Bates, D D — *IRE Trans Nuc Sci*, NS-13,231(1966)

SI-0197b
ETCH NAME:
TYPE: Acid, decoration
TIME:
TEMP:
COMPOSITION:
"A" 600 ml .... HF
300 ml .... HNO_3
2 ml .... Br_2
28 g .... $Cu(NO_3)_2.3H_2O$
"B" x .... H_2O
Mix: 1 "A" to 10 "B" for use.
DISCUSSION:
Si, (111) wafers fabricated as barrier diodes. Solution used as a copper decoration etch.
REF: Ibid.

SI-0092l
ETCH NAME:
TYPE: Alkali, preferential
TIME: To 30 min
TEMP: Boiling
COMPOSITION:
150 ml .... 30% KOH
30 g .... CHI_3
100 ml .... glycerin
DISCUSSION:
Si, (111), p- and n-type wafers used in a controlled damage pit development study. Damage induced with diamond stylus. After 10 min etching, pit diameters were 15 mils for p-type and 25 mils for n-type. Solution is also a preferential etch for germanium.
REF: Ibid.

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SI-0092m
ETCH NAME:
TYPE: Alkali, preferential
TIME: 20—30 min
TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH
30 g .... $FeCl_3$
DISCUSSION:
Si, (100) wafers, n-type, 10—30 Ω cm resistivity used in a controlled damage etch pit study. Damage surface with a diamond stylus. Solution produces sharp, triangle pits with truncated ends in 20 min. p- and n-type size as shown under SI-01921.
REF: Ibid.

SI-0092n
ETCH NAME:
TYPE: Alkali, preferential
TIME: To 30 min
TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH
30 g .... KBr
DISCUSSION:
Si, (111) wafers, p- and n-type. In 30 min, p-type pits were 35 mils in diameter; n-type, 45 mils. Sharp hexagonal shape. See SI-01921.
REF: Ibid.

SI-0209
ETCH NAME: Silver etch
TYPE: Acid, dislocation
TIME:
TEMP:
COMPOSITION:
4 ml .... HF
2 ml .... HNO_3
4 ml .... H_2O
200 mg .... $AgNO_3$
DISCUSSION:
Si, (111) wafers used as substrates for silicon epitaxy deposition and study of stacking faults in epitaxy layers. An interference contrast microscope was used to observe stacking faults before and after etching. Defects showed a 1:1 correspondence. Solution used to develop dislocations.
REF: Dudley, R H — *J Appl Phys,* 35,1360(1964)

SI-0211
ETCH NAME:
TYPE: Acid, oxide removal
TIME:
TEMP:
COMPOSITION:
(1) 2 ml .... HF
3 g .... NaF
96 ml .... H_2O
(2) x .... HF
4 .... H_2O
(3) 1 .... HF
DISCUSSION:
Si, (111) wafers etch cleaned with the sequence shown, primarily to remove native oxide from surfaces. Silicon etch rate was less than 1 Å/min.
REF: Hu, S M & Kerr, D R — *J Electrochem Soc,* 114,414(1967)

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SI-0212
ETCH NAME: TIME:
TYPE: Acid, removal TEMP:
COMPOSITION:
108 ml .... HF
350 g .... NH_4F
1000 ml .... H_2O
DISCUSSION:
Si, (111) wafers used as substrates for epitaxy silicon deposition, both p- and n-type material used in an etch rate study. The etch rate is extremely slow in all cases being less than 0.5 Å/min.
REF: Hoffmeister, W — *Int J Appl Radiat Isot*, 2,139(1969)

SI-0215
ETCH NAME: TIME: To 100 h
TYPE: Thermal, preferential TEMP: 990°C
COMPOSITION:
x .... heat
DISCUSSION:
Si, (111), (100) and (110) wafers used in a study of the work function and sorption properties of silicon. Wafers were thermally etched. The (111) surfaces showed typical triangle pits; (100) typical square pits and the (110) hexagonal pit forms.
REF: Farnsworth, H E & Dillon, J A Jr — *J Appl Phys*, 29,1195(1958)
SI-0216: Farnsworth, H E et al — *Phys Chem Solids*, 8,116(1959)
Si, wafers used in a study of surface structures and work function. Specimens were thermally etched at 1000°C with evaporation of silicon. Above 1000° etching is very rapid.

SI-0217
ETCH NAME: Sodium hydroxide TIME:
TYPE: Alkali, preferential TEMP:
COMPOSITION:
x .... 20% NaOH
DISCUSSION:
Si, (111) wafers used in a study of twinning in silicon. Solution used to develop twinning stria in silicon which was studied by light diffraction.
REF: Hopkins, R L — *J Appl Phys*, 29,1378(1958)

SI-0218
ETCH NAME: Gold TIME:
TYPE: Metal, dislocation TEMP: 1200°C
COMPOSITION:
x .... Au
DISCUSSION:
Si, (111) wafers. After gold diffusion into silicon at 1200°C the wafers were subject to bending stress at 900°C. Alpha-helical loops moved into otherwise dislocation free areas of the wafers.
REF: Dash, W C — *Bull Am Phys Soc*, 5,190(1960)

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SI-0187b
ETCH NAME:
TYPE: Salt, junction
COMPOSITION:
1 .... AgF
10 .... H_2O
+ .... *HF

TIME:
TEMP: 0°C

*1 drop HF/5 ml solution

DISCUSSION:
Si, wafers. Solution used to delineate diffused p-n junctions. The silver plates out on the junction.
REF: Ilies, P A & Coppen, P J — *J Appl Phys*, 29,1514(1958)

SI-0220
ETCH NAME: Oxygen
TYPE: Gas, contamination
COMPOSITION:
x .... O_2

TIME:
TEMP: 900—1150°C

DISCUSSION:
Si, wafers used as substrates for silicon epitaxy as Si/Si. Oxygen in the hydrogen furnace atmosphere and from the quartz tube wall causes stacking faults in the growing epitaxy layer.
REF: Matsuura, Y & Mirura, Y — *Jpn J Appl Phys*, 2,518(1963)

SI-0221a
ETCH NAME: Argon
TYPE: Ionized gas, structure
COMPOSITION:
x .... Ar^+ ions

TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:

DISCUSSION:
Si, wafers. Used an argon laser to etch develop structure on specimen surfaces. Authors refer to the technique as rapid direct writing of surface relief. Also used hot chlorine vapor or hydrochloric acid.
REF: Enrilch, D J et al — *Appl Phys Lett*, 38,1018(1981)

SI-0222
ETCH NAME: BHF
TYPE: Acid, oxide removal
COMPOSITION:
x .... BHF

TIME:
TEMP:

DISCUSSION:
Si, (100), n-type, 3—6 Ω cm resistivity wafers used as substrates to fabricate humidity sensitive capacitors. Degrease, chemically etch silicon and use BHF to remove native oxide. RF sputter in O_2/Ar (5—10% O_2) for a 1 KÅ thick thin film of $BaTiO_3$.
REF: Chen, S N et al — *J Vac Sci Technol*, A3,678(1985)

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SI-0223a
ETCH NAME:
TYPE: Acid, junction
COMPOSITION:
x .... 300 cm^3 HF
+ .... *HNO_3

*1 drop in HF volume shown

TIME:
TEMP:

DISCUSSION:
Si, p-type wafers used in a study of dislocations developed from antimony diffusion into silicon as p-n junctions. Solution shown used as a junction etch. Also used Sirtl etch and anodic oxidation to delineate junctions.
REF: Song, S H & Niimi, T — *Jpn J Appl Phys*, 24,1460(1985)

SI-0221b
ETCH NAME: Chlorine
TYPE: Gas, structure
COMPOSITION:
x .... Cl_2
DISCUSSION:
Si, wafers. Used chlorine gas to etch structure silicon surfaces. See SI-0221a.
REF: Ibid.

TIME:
TEMP: Hot

SI-0224
ETCH NAME: Neutron
TYPE: Particle, damage
COMPOSITION:
x .... neutrons
DISCUSSION:
Si, as 15 mm square cut and oriented cubes (100). After cutting and polishing specimens were subjected to neutron irradiation in a study of directional neutron damage using ultrasonic double refraction measurements.
REF: Trevell, R & Teutonico, L J — *Phys Rev*, 105,1723(1957)

TIME:
TEMP:
DOSE:

SI-0225
ETCH NAME:
TYPE: Electrolytic, polish
COMPOSITION:
1 .... HF
10 .... H_2O
+ .... glycerin
DISCUSSION:
Si, wafers of different orientations used to prepare very flat surfaces by electropolishing. The following reactions were observed: (1) at low speed, with increase of glycerin drip, thicker solutions; (2) less than 10% HF for polishing; (3) light required for n-type, but not for p-type; (4) rotation speed controls bright polish and (5) high current produces pitting on surfaces.
REF: Baker, D & Tillman, J R — *Solid State Electron*, 6,589(1963)

TIME:
TEMP: 30°C
ANODE:
CATHODE: Si
POWER: 10 V
ROTATE: 120 rpm

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SI-0230
ETCH NAME: Hydrofluoric acid, dilute
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... H_2O
TIME:
TEMP: RT
DISCUSSION:
a-Si:H, thin film deposited on an a-SiO_xN_y:H thin film fabricated on the following substrates: UV grade quartz; glass coated with thin film SnO_2; aluminum and stainless steel. All substrates were cleaned as follows: (1) boil in TCE; (2) rinse in warm acetone and (3) boil in isopropanol. All substrates showed good adhesion of deposited films. Final rinse in solution shown prior to deposition of the hydrogenated silicon.
REF: Carasco, F et al — *J Appl Phys*, 57,5306(1985)

SI-0231
ETCH NAME: Hydrogen
TYPE: Ionized gas, defect
COMPOSITION:
x .... H^+ ions
TIME: 15 min
TEMP:
GAS FLOW:
PRESSURE:
POWER: 1 kV
DISCUSSION:
Poly-Si wafers used in a study of the electronic nature of defects and grain boundaries (GB). Part of wafers were masked against ion bombardment. Both laser beam induced current (LBIC) and electron-beam induced current (EBIC) were used in evaluation.
REF: Sastru, O S et al — *J Appl Phys*, 57,5506(1985)

SI-0232
ETCH NAME: Water
TYPE: Acid, film removal
COMPOSITION:
x .... H_2O
TIME:
TEMP:
DISCUSSION:
a-Si, thin film, 300 Å thick. NaCl, (100) substrates were used to develop the following structure: SiO_2/Ni/a-Si/SiO_2/NaCl(100). The composite thin film was removed from the substrate with water by the float-off technique. The film was then annealed and observed for microstructure.
REF: Chen, S N et al — *J Appl Phys*, 57,258(1985)

SI-0174c
ETCH NAME: BHF
TYPE: Acid, preferential/jet
COMPOSITION:
(1) 40 g .... $NH_4F.HF$
8 g .... NaF/l
(2) 40 g .... $NH_4F.HF$
8 g .... NaF/l
x .... $K_3F(CN)_6$
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers used in a defect study. Solution (1) develops flat bottom pits. Solution (2) reduces the size of pits and their quantity.
REF: Schmidt, P F & Keipler, D A — *J Electrochem Soc*, 106,592(1959)

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SI-0174d
ETCH NAME:
TYPE: Electrolytic, defect
COMPOSITION:
5 ml .... HF
x .... 2 *N* NaF
1000 ml .... H_2O
DISCUSSION:

TIME:
TEMP: 60°C
ANODE: Si
CATHODE:
POWER: 3 mA/cm² or 30 mA/cm²

Si, (111) wafers used in a defect study. Use light during etching period. Low power application shown above produced preferential etching; high power level for polish etching.
REF: Ibid.

SI-0233
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
x .... HCl
x .... H_2O_2
x .... H_2O
DISCUSSION:

TIME:
TEMP: Boiling

Si, (111) n-type wafers, 1.63 Ω cm resistivity used as substrates for the deposition of cobalt and growth of $CoSi_2$. Silicon wafers were cleaned as follows: (1) flush with high pressure water; (2) degrease in hot MeOH and water rinse; (3) boil in solution shown and water rinse. Anneal at 750°C in UHV after evaporation of cobalt.
REF: Arnaud, F et al — *J Vac Sci Technol,* B(3),770(1985)

SI-0245
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

TIME:
TEMP: RT

Si, (111) wafer substrates used for epitaxy growth of GaP by fused salt electrolysis. After growth, silicon was etched away in an HF:HNO_3 solution mixture for study of the gallium phosphide thin film. Solution attacks GaP slowly.
REF: Cuomo, J J & Gambino, R J — *J Electrochem Soc,* 117,755(1968)

SI-0234
ETCH NAME: Hydrofluoric acid
TYPE: Acid, passivation
COMPOSITION:
x .... HF, conc.
DISCUSSION:

TIME:
TEMP:

Si, (100) and (111) wafers, both p- or n-type used in a study of passivation of surfaces by fluoridation. Studied active electron sites by surface recombination velocity. Four treatments were used as shown below:

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Step #1	Step #2	Recombination/ velocity
1. CP4 polish	1. HF, dip	1. 4 cm/sec
2. Thermal oxidation	2. HF, dip	2. 4 cm/sec
3. HF remove oxidation	3. HF, dip or soak	3. 40 cm/sec
4. KOH etch silicon	4. HF, dip	4. 300 cm/sec

REF: Weinberger, B R et al — *J Vac Sci Technol,* A(3),887(1985)

SI-0120b
ETCH NAME: Hydrofluoric acid — TIME:
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
x .... HF, conc. (inert atm)
DISCUSSION:
Si, (111) wafers used in a study of selenium adsorption. Silicon wafers were cleaned as follows: (1) Syton mech/polish; (2) rinse in MeOH; (3) degrease in TCE and (4) HF clean in inert atmosphere (no air). Selenium treatment was: (1) soak in 0.5 g Se/cc MeOH; (2) rinse in MeOH and (3) argon blow dry. *Note:* Wafers were cleaved while under the selenium solution. Selenium showed adsorption on the (111) and (220) silicon planes.
REF: Dev, B N et al — *J Vac Sci Technol,* A(1),946(1985)

SI-0236
ETCH NAME: Sulfuric acid, dilute — TIME: 20 min
TYPE: Acid, cleaning — TEMP: RT
COMPOSITION:
5 .... H_2SO_4
1 .... H_2O
DISCUSSION:
Si, (111) p- and n-type, 20 and 25 Ω cm resistivity wafers used as substrates for germanium epitaxy as single crystal, polycrystalline, and amorphous Ge thin films. Silicon wafers cleaned: (1) acetone rinse; (2) MeOH rinse; (3) etch in solution shown; (4) soak in 50% BHF, 60 sec, DI water rinse and N_2 blow dry.
REF: Wang, P D et al — *J Vac Sci Technol,* B(2),206(1984)

SI-0237
ETCH NAME: Nitric acid — TIME:
TYPE: Acid, cleaning — TEMP: Hot
COMPOSITION:
x .... HNO_3
DISCUSSION:
Si, (100) wafers were cleaned: (1) HF; (2) hot HNO_3, and (3) NH_4F:H_2O_2.
REF: Yang, H T & Berry, W S — *J Vac Sci Technol,* B(2),206(1984)

SI-0239
ETCH NAME: — TIME:
TYPE: Acid, photo etch — TEMP:
COMPOSITION:
DISCUSSION:
a-Si:F:H, thin films deposited on Corning 7095 glass as both amorphous, a-, and mi-

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crocrystalline, μc-, structured films in the fabrication of strain gages. The material was photo etched.
REF: Nishida, S et al — *Thin Solid Films,* 112,7(1984)

SI-0240
ETCH NAME: Iodine etch
TYPE: Acid, preferential
TIME: 2 min
TEMP: RT
COMPOSITION:
25 ml .... HF
100 ml .... HNO_3
125 ml .... HAc
2 g .... I_2
DISCUSSION:
Si, (111) wafers, boron doped. Wafers were prepared for boron doping as follows: (1) polish with Linde A; (2) degrease; (3) HF soak, RT, 1 min; (4) etch in iodine solution to remove lap damage. After boron diffusion: (1) rinse in HF, RT, 2 min and then (2) etch 2 min in iodine solution to develop slip patterns in silicon created by boron diffusion.
REF: Queisser, H J — *J Appl Phys,* 32,1776(1961)

SI-0242a
ETCH NAME: Iodine etch
TYPE: Acid, removal
TIME: 1—2 min
TEMP: RT
COMPOSITION:
(1) 1 .... HF
1 .... HNO_3
1.4 .... HAc
0.15% .... I_2
0.24% .... triton (surfactant)
(2) 1 .... iodine etch
4 .... HAc
DISCUSSION:
Si, (111) p- and n-type wafers, 8 Ω cm resistivity. Wafers used in a study of ^{18}F radioactive tracer adsorption. After etching, water rinse or acetone rinse. Also used on germanium in a similar study.
REF: Kern, W — *RCA Rev,* 69,207(1970)

SI-0242b
ETCH NAME: Iodine etch
TYPE: Acid, removal
TIME: (1) 1.7 (2) 30 min
TEMP: RT
COMPOSITION:
(1) 1 .... HF
6 .... HNO_3
3 .... HAc
x .... *NaI
(2) x .... 0.010 *N* NaI

*0.19 mg/100 ml of solution.

DISCUSSION:
Si, (111) wafers used in a radiochemical surface contamination study. Both of these solutions and the iodine etch shown in SI-0242a were all used with ^{131}I radioactive tracer in a study of adsorption of surfaces. Silica, SiO_2, and germanium, Ge, also were studied.
REF: Ibid.

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SI-0243
ETCH NAME: Potassium hydroxide
TYPE: Alkali, selective
TIME: 6 min
TEMP: Boiling
COMPOSITION:
100 g .... KOH
100 ml .... H_2O
DISCUSSION:
Si, (110) wafers with a thermally grown SiO_2 thin film used as an etch mask. Wafers were photolithographically processed with slots opened in the silica mask in bulk ⟨100⟩ directions. Parallel grooves etched to 50 μm depth with 2 μm horizontal etching. Slots were filled with Corning 7070 glass by hot pressing at 750°C before cross sectioning for structure study.
REF: Stoller, A I — *RCA Rev*, 69,271(1970)

SI-0247
ETCH NAME:
TYPE: Electrical, defect
TIME:
TEMP:
COMPOSITION:
x .... *EBIC

*Electron-beam-induced current.

DISCUSSION:
a-Si:H, thin films deposited by RF decomposition of silane on polished stainless steel substrates, then coated with aluminum to form p-i-n devices. Both EBIC and secondary electron image (SEI) with a scanning electron microscope (SEM) used in characterization and defect studies. Pinholes, blisters, and lift-off were observed in films that could be related to either film deposition conditions or defects in the substrate surface. Films are applicable for photovoltaic, solar cell, vidicon, and other electronic devices.
REF: Yacobi, B G et al — *J Electron Mater*, 13,843(1984)

SI-0251
ETCH NAME: Ethylenediamine
TYPE: Acid, selective
TIME:
TEMP: 50°C
COMPOSITION:
x .... ED
DISCUSSION:
Si, (100) wafers. The use of maskless passivation against anisotropic etching to define structure. Both ion implantation and laser annealing used to produce etch-stop mechanisms. The ED solution was used at RT after laser passivation. EDP solutions were also used (ethylenediamine:pyrocatechol). See SI-0094a-d.
See SI-0094a-d.
REF: Day, D J et al — *J Electrochem Soc*, 131,407(1984)

SI-0252
ETCH NAME: Potassium hydroxide
TYPE: Alkali, orientation
TIME: 5—10 min
TEMP: Hot
COMPOSITION:
x .... 5—10% KOH (NaOH)
DISCUSSION:
Si, (111) and (100) wafers and ingots. Ingot growth direction can be established by observing the direction of the hachure miniscus locations on ingot sides . . . 3 on (111); 4

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on (100) ingots. The hachure marks point upward toward the seed ingot end. This can be used to establish a (111)A or ($\overline{1}\overline{1}\overline{1}$)B wafer surface direction. By cleaving a portion of a (100) wafer edge and etching in KOH or NaOH will develop triangle etch pits on the cleaved edge. If triangle points are downward, bulk plane is (011); if upward toward (100) positive wafer surface, with 180° rotation, it is (01$\overline{1}$) which is the preferred orientation for channel and pit etching.
REF: Pennington, P & Walker, P — development work, 1957

SI-0253
ETCH NAME: RIE
TYPE: Ionized gas, selective
COMPOSITION:
x .... ClF_3

TIME: To 10 min
TEMP: RT
GAS FLOW: 20 cm^3/min
PRESSURE: 0.03 Torr
POWER: 70 W
BIAS: 10 V

DISCUSSION:
Si, (100) wafers used in structuring a RAM configuration device with poly-Si and SiO_2. Pure Cl_2 or ClF_3 was evaluated in addition to ClF_3 concentrations of 5, 30, and 80%. Primary etching was on the poly-Si. Etch rate vs. side removal of a pure ClF_3 plasma was linear at 1900 Å/min and 2 μm per side removal in 10 min. The Si:SiO_2 etch ratio reduces with decrease of Cl_2 toward pure ClF_3 — atomic fluorine 42:1. Etch rate is unaffected by ClF_3 concentration for lightly doped p- or n-type single crystals, undoped poly-Si and thermal SiO_2 where SiO_2 is less than 100 Å/min with 0—100% ClF_3. All others etched at an equal rate. There is a wafer quantity mass loading affect as shown on poly-Si etch rate of one wafer at about 3800 Å/min to about 1900 Å/min with six to seven wafers.
REF: Flamm, D L et al — *J Electrochem Soc,* 129,2755(1982)

SI-0254a
ETCH NAME: Hydrogen peroxide
TYPE: Acid, preferential
COMPOSITION:
x .... H_2O_2 (30%), conc.

TIME: 2—4 h
TEMP: RT

DISCUSSION:
Si, single crystal hemispheres. Specimens were used in an etching study to observe etch patterns, type etch pits, etch rates, and crystal planes developed. Before preferential etching, etch polish in CP4 to remove lapping damage. See GE-0150a-s for the 19 different etch solutions evaluated on both silicon and germanium hemispheres.
REF: Holmes, P J — *Acta Metall,* 7,283(1959)

SI-0255
ETCH NAME:
TYPE: Acid, float-off
COMPOSITION:
1 .... HF
5 .... HNO_3

TIME:
TEMP: RT

DISCUSSION:
Si, (100) and (111) wafers used as substrates for CVD growth of single crystal thin films of boron phosphide in a study of thin film morphology, physical properties and semiconducting characteristics. Solution used to etch remove the silicon as a float-off technique for TEM (microscope) and Laue (photograph) study of BP.
REF: Kumashiro, Y et al — *J Cryst Growth,* 70,507(1984)

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SI-0256
ETCH NAME: TIME:
TYPE: Acid, cleaning sequence TEMP:
COMPOSITION:
(1) x .... H_2SO_4 (2) x .... HNO_3
x .... H_2O
DISCUSSION:

Si, (100), n-type, 4—7 Ω cm resistivity wafers used as substrates for CVD growth of a-Si_3N_4:H thin films doped with either boron or phosphorus. Silicon wafers were cleaned as follows: (1) acetone; (2) DI water rinse; (3) clean in solution (1), DI water rinse; (4) clean in solution (2), heavy DI water rinse and N_2 blow dry. Final clean in CVD reactor at 350°C.

REF: Fang, Y K et al — *J Electrochem Soc,* 132,1222(1985)

SI-0257
ETCH NAME: BHF TIME: 2 min
TYPE: Acid, cleaning sequence TEMP: RT
COMPOSITION:
1 .... HF
30 .... NH_4F (40%)
DISCUSSION:

Si, (100) wafers unpassivated surfaces or with SiO_2 or $TaSi_2$ thin films used as substrates for tungsten selective deposition onto silicon photo resist opened circular patterns. All three substrate types were cleaned as follows: (1) clean in BHF; (2) a 10 min rinse in 18 MΩ DI water; (3) spin dry. This leaves about a 20 Å native oxide on the surfaces. Tungsten was deposited from WF_6 between 260 and 400°C and included thermal annealing to form WSi_2 (tetragonal crystal system).

REF: Green, M L & Levy, R A — *J Electrochem Soc,* 132,1243(1985)

SI-0258
ETCH NAME: Hydrochloric acid, vapor TIME:
TYPE: Acid, cleaning TEMP: 1100°C
COMPOSITION:
x .... HCl, vapor
x .... H_2
DISCUSSION:

Si, (110), (112), and (113) wafers for p-p^+ epitaxy. Substrate wafers were 0.007 Ω cm resistivity with epitaxy films 4—6 Ω cm. Substrates were cleaned with HCl vapors in the epitaxy reactor prior to silicon deposition.

REF: Tamura, M & Sugita, Y — *J Appl Phys,* 44,3442(1973)

Si-0173d: Walker, P — personal application, 1971

Si, (111), n-type wafers with resistivity range from 10—150 Ω cm and diameters from $^1/_2$ to 2″ used in the fabrication of SCRs with p-type gallium diffusion and an n^+ silicon epitaxy. Hot HCl vapors used 30 sec at 1000°C as a final cleaning etch in the epitaxy reactor prior to silicon deposition. (*Note:* This is a general and widely used method of final surface cleaning.)

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SI-0260
ETCH NAME:
TYPE: Acid, cleaning sequence
COMPOSITION:
(1) 3 .... H_2SO_4
1 .... H_2O_2
(2) 1 .... HF
10 .... H_2O
TIME: (1) 10 min
(2) 6 sec
TEMP: (1) 95°C (2) RT
DISCUSSION:
Si, (111), p-type wafers used as substrates for tungsten deposition. Silicon wafers were coated with 1000 Å SiO_2, then 4500 Å poly-Si. After acid cleaning wafers were given an Ar^+ ion cleaning prior to tungsten deposition from WF_6 and annealing to WSi_2.
REF: Tsao, K Y & Busta, H H — *J Electrochem Soc*, 131,2702(1984)

SI-0261
ETCH NAME:
TYPE: Acid, cleaning sequence
COMPOSITION:
(1) *RCA procedure
(2) x .... HF, conc.
TIME:
TEMP:

*See SI-0031 for RCA etch.

DISCUSSION:
Si, (111) and (110) wafers used as substrates for reactive pulse plasma deposition of thin film diamond (from carbon) and boron nitride as dielectric coatings.
REF: Szmidt, J et al — *Thin Solid Films*, 110,7(1983)

SI-0262
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... HF, conc.
x .... H_2O
(2) x .... CF_4
x .... O_2
TIME: (1) 2 min
TEMP: RT
DISCUSSION:
Si, (111) p-type wafers, 7—21 Ω cm resistivity as patterned substrates for selective tungsten deposition. Three types of substrates were used: (1) SiO_2/Si; (2) poly-Si/SiO_2/Si and (3) Al/SiO_2/Si. Silicon substrates were initially cleaned by a glow discharge CF_4/O_2 treatment or by immersion in HF, followed by DI water rinse, and spin dry. Tungsten was deposited as a thin film from WF_6 on the entire wafer surface or selectively, to include double tungsten layers separated by thin film SiO_2. Study involved reaction effects of tungsten thin films. The HF treated surfaces gave thin films without erratic surface structure.
REF: Stacy, W T et al — *J Electrochem Soc*, 132,444(1985)

SI-0263c
ETCH NAME:
TYPE: Acid, step-etch
COMPOSITION:
1 .... HF
750 .... HNO_3
250 .... HAc
TIME:
TEMP:
RATE: 300 Å/min

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DISCUSSION:

Poly-Si grown on (100) silicon substrates. Solution used to step-etch the poly-silicon layer. Poly-Si was as (100) crystallites with low angle grain boundaries.

REF: Banerjee, S K et al — *J Electrochem Soc*, 131,1409(1984)

SI-0108c

ETCH NAME: Aqua regia

TYPE: Acid, cleaning

TIME:

TEMP:

COMPOSITION:

3 .... HCl

1 .... HNO_3

DISCUSSION:

Si, (111) and (100) wafers used in a study of high pressure oxidation (800—1000°C and 1—20 atm) using dry oxygen. Wafers were cleaned prior to oxidation: (1) H_2SO_4:H_2O; (2) aqua regia and (3) 1HF:10H_2O and spin dry in nitrogen.

REF: Ibid.

SI-0273

ETCH NAME: RIE

TYPE: Ionized gas, selective

TIME: To 50 min

TEMP:

GAS FLOW:

PRESSURE:

POWER:

COMPOSITION:

x .... CHF_3

x .... O_2

DISCUSSION:

Si, (100) wafers with and without SiO_2 thin surface films used in a study of side wall tapering in RIE etching. Various thicknesses of oxide and photo resist were evaluated in a hex-type reactor. Etch rates were (1) SiO_2: 550 Å/min; (2) silicon: 110 Å/min and (3) photo resist: 170 Å/min. Discusses results relative to ion milling. To obtain vertical etched walls: (1) vertical mask profile; (2) good selectivity between mask and material being etched and (3) mask of sufficient thickness so as to still be present at end of structure forming etching time. (*Note:* In ion milling by these authors and co-workers, using Ar^+ ion milling, etch time was established to remove the photo resist mask in conjunction with pattern etch-thru to substrate. Otherwise, remaining photo resist is severely polymerized and impossible to remove.)

REF: Nagy, A G — *J Electrochem Soc*, 132,689(1985)

SI-0280a

ETCH NAME: Silica

TYPE: Abrasive, polish

TIME:

TEMP: RT

COMPOSITION:

x .... SiO_2, colloidal suspension

DISCUSSION:

Si, (100) wafers and other orientations. Colloidal silica, c-SiO_2, in suspension used to polish surfaces. One method is to wax wafers onto SST or brass circular platens or use a Buehler-type metallographic station: a rotating brass platen with glue-back pellon-type pad saturated with colloidal silica. Surface polish is equivalent to or better than that of diamond paste polishing. Both colloidal silica and alumina are used for polished silicon wafers and other metals and metallic compounds.

REF: Brochure: NALCO, 1983

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SI-0280b
ETCH NAME: Alumina
TYPE: Abrasive, polish
COMPOSITION:
x .... Al_2O_3, colloidal
TIME:
TEMP: RT
DISCUSSION:
Si, (100) wafers and other orientations. Colloidal alumina, as c-Al_2O_3 in suspension used to polish surfaces. See discussion under SI-0280a. (*Note:* Linde A and B alumina are polishing fine powders on the submicron size scale, not colloidal or in permanent liquid suspension. They have been in use for many years as a replacement for diamond paste polishing.)
REF: Ibid.

SI-0285
ETCH NAME: RF plasma
TYPE: Ionized gas, removal
COMPOSITION:
x .... CF_4
x .... O_2 (5%)
TIME:
TEMP: 50 to 70°C
GAS FLOW:
PRESSURE: 0.5 Torr
POWER: 100 W
DISCUSSION:
Si, (100) wafers used as substrates with an SiO_2 thin film were used as substrates for poly-Si growth with various concentrations of boron doping. A tunnel system with an aluminum insert was used in studying accelerated etch rates due to NaOH and KOH residues from AZ- photo resist developer solutions. Etch rate reduces with increase of boron, from 3000 Å/min for undoped to 480 Å/min with 3×10^{21} cm^3 B concentration. Substrates were cleaned by oxidation and stripped with HF. Wafers were dipped 1 min and DI water rinsed in varying pH concentrations of KOH and NaOH and evaluated for plasma etch rates — as dipped, dipped and spun, or dipped and water rinsed. The latter against rinse time. A 10 min water rinse time reduced etch rates from above 5000 Å/min to about 500 Å/min and higher pH values — pH 8 to pH 14 — increased etch rates with similar rates.
REF: Makino, T et al — *J Electrochem Soc,* 128,103(1981)

SI-0092o
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
250 ml .... 30% KOH
100 ml .... glycerin
TIME:
TEMP: Boiling
DISCUSSION:
Si, single crystal spheres and oriented cut forms used in a study of etch planes and rates. The sphere finite crystal form is cube, (100).
REF: Ibid.

SI-0092p
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
250 ml .... 30% KOH
10 ml .... ethylene glycol
TIME:
TEMP: Boiling

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DISCUSSION:
Si, single crystal spheres and oriented cut forms used in an etch structure study. The sphere finite crystal form was cube, (100).
REF: Ibid.

SI-0092q
ETCH NAME: Potassium hydroxide
TYPE: Alkali, preferential
TIME:
TEMP: Boiling
COMPOSITION:
(1) 250 ml .... 30% KOH (2) 250 ml .... 30% NaOH
DISCUSSION:
Si, single crystal spheres and oriented cut forms used in a study of structure. The sphere finite crystal form was tetrahexahedron, (hk0).
REF: Ibid.
SI-0282: Weirach, D F — *J Appl Phys*, 16,1378(1977)
Si, single crystal spheres were etched in 10 *M* KOH, 10 min at 80°C. Finite crystal form was tetrahexahedron, (hk0).

SI-0092r
ETCH NAME: BF3
TYPE: Acid, preferential
TIME:
TEMP: RT
COMPOSITION:
11 g .... $NH_4F.HF$
25 ml .... HNO_3
2 ml .... H_2O
DISCUSSION:
Si, single crystal spheres and cut forms. Finite crystal form of sphere was a cube, (100).
REF: Ibid.

SI-0092s
ETCH NAME:
TYPE: Alkali, preferential
TIME:
TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH
100 ml .... ethylene glycol
DISCUSSION:
Si, as a pre-cut single crystal octahedron, (111) form. The octahedron etched in this solution developed (211) facets on the (111) faces producing a finite crystal form of a trisoctahedron, (hh1).
REF: Ibid.

SI-0092t
ETCH NAME:
TYPE: Alkali, preferential
TIME:
TEMP: Boiling
COMPOSITION:
250 ml .... 30% KOH
100 ml .... MeOH
DISCUSSION:
Si, single crystal spheres and cut crystal forms. Finite crystal form was tetrahexahedron, (hk0).
REF: Ibid.

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SI-0283b
ETCH NAME: RF plasma
TYPE: Ionized gas, removal
COMPOSITION:
(1) x .... SF_6 (2) x .... SF_6
x .... argon

TIME:
TEMP:
GAS FLOW: 50 sccm anode coupled
PRESSURE: 0.23 mbar
POWER: 1000 V ptp

DISCUSSION:
Si, (100) wafers with thermal SiO_2 thin films photolithographically patterned and used in a study of SF_6 RF plasma etching. Best selectivity ratio of Si:SiO_2 was 30:1. Best results were obtained with parallel plate reactor rather than barrel type. Various mixtures of SF_6:Ar and mixtures with up to 50% H_2 evaluated for etch rates and ratio selectivity vs. CF_4:4% O_2. The undiluted SF_6 etch rate was 10 to 15 times greater than the CF_4:4% O_2 plasma. Etch rate of silicon with SF_6 (0 to 25% O_2), cathode coupled, was in the range of 0.5 μm/min; anode coupled about 0.15 μm/min with anode coupled CF_4 (0—25% O_2) slightly under 0.1 μm/min. SF_6:Ar silicon etch rate 0.3 μm/min to 0.5 μm/min, 20—100% SF_6.
REF: Eisele, K M — *J Electrochem Soc*, 128,123(1981)

SI-0286a
ETCH NAME: RF plasma
TYPE: Ionized gas, removal/anisotropic
COMPOSITION:
x .... C_2F_6
x .... O_2 (8%)

TIME:
TEMP: 25—30°C water cooling
GAS FLOW: 200 sccm
PRESSURE: 0.35—0.40 Torr
POWER: 100—550 W

DISCUSSION:
Si, (100) wafers used as substrates with p-doped and undoped poly-Si and SiO_2 thin films, and photo resist were evaluated for etch rates and channel type etch profiles. The gas mixture shown above was anisotropic and gave best results of five mixtures evaluated. RF power was 350 W and pressure 0.35 Torr. Etch rates: (1) P:poly-Si — 800 Å/min; (2) Undoped poly-Si — 350 Å/min; (3) SiO_2 — 60 Å/min and (4) photo resist — 100 Å/min. Selectivity of P:poly-Si to SiO_2 was 13:1.
REF: Adama, A C & Capio, C D — *J Electrochem Soc*, 128,366(1981)

SI-0286b
ETCH NAME: RF plasma
TYPE: Ionized gas, removal/isotropic
COMPOSITION:
1 .... C_2F_6
1 .... CF_3Cl

TIME:
TEMP: 25—30°C
GAS FLOW: 200 sccm
PRESSURE: 0.40 Torr
Power: 550 W

DISCUSSION:
Si, (100) wafers. Etch rates: (1) P:poly-Si — 1590 Å/min; (2) undoped poly-Si — 980 Å/min; (3) SiO_2 — 200 Å/min and (4) photo resist — 570 Å/min. Selectivity of P:poly-Si to SiO_2 was 5:1. See SI-0286a for further discussion.
REF: Ibid.

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SI-0286c
ETCH NAME: RF plasma
TYPE: Ionized gas, removal/isotropic
COMPOSITION:
x .... CF_4
x .... O_2 (8%)
TIME:
TEMP: 25—30°C
GAS FLOW: 200 sccm
PRESSURE: 0.35 Torr
POWER: 100 W
DISCUSSION:
Si, (100) wafers. Etch rates: (1) P:poly-Si — 1150 Å/min; (2) undoped poly-Si — 1050 Å/min; (3) SiO_2 — 120 Å/min and (4) photo resist — 190 Å/min. Selectivity of P:poly-Si to SiO_2 was 10:1. See SI-0286a for further discussion.
REF: Ibid.

SI-0290
ETCH NAME: Alumina
TYPE: Compound, polish
COMPOSITION:
x .... 0.05 μm Al_2O_3 (Linde B)
x .... glycerin
x .... soap (Castille)
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers. Mixture used for polishing material on a Pitch Lap. A mixture of pitch and beeswax is poured and allowed to set on a brass Buehler lap platen. The wax is then cross-scored with "V" groove cuts and the slurry mixture shown dripped onto the lap with wafers held on the lap mounted on disc holders. This polishing method can produce polished surface planarity of $<^1/_4$ wavelength sodium light.
REF: George, D — personal communication, 1959

SI-0291
ETCH NAME: Silica
TYPE: Compound, polish
COMPOSITION:
x .... SiO_2 (sand)
x .... N_2
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers and other orientations. Cutting channels, dicing, and bevelling of wafers done with an S S White abrasive unit. Reference shown used this method to edge bevel high power SCR wafers prior to final etch tuning with $xHF:xHNO_3:xHAc$, and coating exposed n-p-n junction with RTV.
REF: Topas, B et al — personal communication, 1974
SI-0440: Tarn, W H & Walker, P — personal application, 1955—1961
Si, (111) wafers fabricated as aluminum alloy transistors or diffused high power diodes. The S S White dental units used for sand cleaning teeth were converted for dicing silicon wafers with dry sand under nitrogen pressure using a mobile rubberized tube with replaceable metal tips of different orifice shapes. Wafers were wax mounted on steel discs and held on an x-y stage below the stationary system tip. To keep sand dry, the pressurized metal sand holder was wrapped with a heating mantle. Dice was square-cut with a positive side angled slope. This form of sandblast dicing introduces from 2—5 mils damage laterally into the silicon dice. Method used on diffused silicon diodes (Tarn), and transistors (Walker), also on germanium and other compound semiconductors (GaAs, InP, InAs) in development studies of new materials.
SI-0441: Tarn, W H & Walker, P — personal application, 1963—1965

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Si, (111) wafers, with and without silicon epitaxy layers used in fabricating computer diodes. Large sandblast units used for general wafer surface cleaning to remove contamination. See Silicon Dioxide, SiO_2, section for use of bead blast sand units for cleaning vacuum system hardware.

SI-0292
ETCH NAME: Jello
TYPE: Colloid, mask
COMPOSITION:
x .... Jello, lemon
TIME:
TEMP: RT
DISCUSSION:
Si, (111) wafers. Jello used as a patterning mask similar to photo resist lacquers for aluminum evaporation before the advent of resists for Solid State device processing. Jello was painted onto surfaces, allowed to set, hand scribed for patterning, and the aluminum evaporated downward onto wafers from "U" shaped aluminum wire clips hung on tungsten heater coils. Lift-off after evaporation liquefied Jello with water for removal of excess metal. Although the experiment was successful, Jello is temperature-critical to prevent hardening and cracking. Various Jellos were evaluated with lemon giving best results. (*Note*: Other organics, including photo resist lacquers reduced to the colloidal state, would reduce grain size limitations, currently a problem in fine-line definition applications.)
REF: Brumfield, D & Walker, P — personal application, 1958

SI-0293
ETCH NAME: Iodine, vapor
TYPE: Halogen, cleaning
COMPOSITION:
x .... *I_2, sat. sol.
x .... MeOH
TIME:
TEMP:

*Saturate alcohol with iodine.

DISCUSSION:
Si, as p^+-n solar cells. Remove native oxide with HF dip and quench in solution shown. Chemisorption of iodine produces a p^+ surface film that is stable up to 500°C. Addition of a CdSe thin film on silicon structure produces a tunnel photo anode.
REF: Pinson, W E — *J Appl Phys*, 40,970(1982)

SI-0404
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
1 .... HF
5 .... HNO_3
1 .... CH_3COOH (HAc)
TIME:
TEMP:
DISCUSSION:
Si, (100) wafers used in a study of metal decoration defects induced in heat treated wafers from tweezers (Cr, Ni, Fe, and Co contamination). Included dry O_2 oxidation at 1100°C, 30 min. After thinning with solution shown, Secco etch used at RT, 2 min and developed saucer-like etch pits where tweezers gripped wafers. (Secco etch: SI-0036). (*Note:* Similar structures, including drain-marks, observed in GaAs wafers after vertical etching in solutions which produced change in electrical characteristics of FET devices.)
REF: Staxy, W T et al — *J Electrochem Soc*, 129,1128(1982)

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SI-0300
ETCH NAME:
TYPE: Alkali, preferential
COMPOSITION:
387 g .... KOH
250 ml .... H_2O
30 g .... additive

TIME: 10—45 min
TEMP: Boiling

DISCUSSION:

Si, (111), 10—20 Ω cm resistivity, n-type wafers used in a study of etch pits formed by controlled point damaging — concave plane structures vs. convex sphere structure planes. The initial method is called the Pennington Pit Method which is used in goniometer structure study. As further developed in this study for pit depth/size control, a diamond stylus with round shaft was held vertically in a nylon tube, slip-fit for rotation, with lead gram-weights on stylus top — amount of weight and number of stylus rotations in contact with the wafer surface used to establish damage depth, and etch time for final pit depth, which varies with solution mixture for pit shape and size. Shape progression of pit forming goes triangle — subtriangle — hexagon — subhexagon — to a degenerate subtriangle to a roughly circular pit. Progression varies with the additive to the hydroxide solution shown above, and may be triangular to subtriangular, only, triangle to degenerate circular, directly, depending on solution. All of the following additives were evaluated with a base alkali solution of KOH or NaOH +20—30 g of solid chemicals or 25—50 ml of liquid, such as Br_2. Alcohol type additives were 125 ml. Study objective was to develop flat bottom pits for aluminum alloying, and determination of crystallographic planes developed in pit-side slopes vs. solution additive. (100) silicon was evaluated with 30% KOH/NaOH, and with some additives on germanium, (111), (100), (110), and (211) for similar pits, and light figure orientation. Silicon pit shapes established after 20 or 30 min etch time. With the KOH:Br_2 mixture, an additional 100 ml Br_2 added after 20 min. See SI-0092a-s for additional discussion.

Reference no. — additive	Etch time (min) 20	30
SI-0192f — I_2	subtriangle	deg. subtriangle
SI-0300 — S	hexagon	hexagon
SI-0302 — Zn	hexagon	deg. circular
SI-0304 — As_2O_3	hexagon	subhexagon
SI-0301 — $Al(OH)_3$)	subtriangle	subtriangle
SI-0303 — $Ba(OH)_2$	hexagon	deg. subhexagon
SI-0305 — $Ca(OH)_2$	subhexagon	deg. subhexagon
SI-0306 — $Sr(OH)_2.8H_2O$	hexagon	deg. subhexagon
SI-0307 — $AlCl_3.6H_2O$	subtriangle	hexagon
SI-0308 — NH_4Cl	hexagon	deg. subhexagon
SI-0309 — $CaCl_2.2H_2O$	subtriangle	hexagon
SI-0310 — LiCl	hexagon	deg. hexagon
SI-0311 — $NiCl_2.6H_2O$	subtriangle	subtriangle (rough)
SI-0312 — $K_2Cr_2O_7$	subtriangle	subtriangle
SI-0313 — $KClO_3$	subhexagon	deg. subhexagon
SI-0314 — $Mg(NO_3)_2.6H_2O$	subhexagon	subhexagon
SI-0315 — H_3BO_3	hexagon	subhexagon
SI-0316 — HPO_3	hexagon	subhexagon (rough)
SI-0317 — $KHC_8H_4O_4$	hexagon	subhexagon
SI-0318 — $K4Fe(CN)_3.3H_2O$	hexagon	subhexagon

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Reference no. — additive	Etch time (min) 20	30
SI-0198b — KBr	hexagon	deg. subhexagon
SI-0198c — $FeCl_3.4H_2O$	hexagon	subhexagon
SI-0319 — HIO_3	erratic	erratic
SI-0332 — KI	hexagon	subhexagon
SI-0320 — $(NH_4)_2O_4H_4O_6$	triangle	triangle (rough)
SI-0321 — $Al_2(SO_4)_3SO_4.24H_2O$	subtriangle	subtriangle
SI-0198a — CHI_3 + glycerin	hexagon	hexagon
SI-0322 — $3CdSO_4.8H_2O$	triangle	deg. xxxx
SI-0092g — Br_2	triangle	triangle
SI-0092a — 30% KOH/NaOH	hexagon	hexagon
SI-0333 — 1:1 30% KOH:NaOH	hexagon	hexagon
SI-0334 — Bi_2O_3	erratic	erratic (no real pit)
SI-0335 — $ZnCl_3$	erratic	erratic
SI-0336 — $HgBr_2$	erratic	erratic (no real pit)
SI-0337 — Sb_2O_3	erratic	deg. triangle (?)
SI-0338 — $SrBr_2$	erratic	erratic (no real pit)
SI-0339 — $ZrSC_4.7H_2O$	erratic	erratic
SI-0323 — Benzene	circular	circular (both rough)
SI-0324 — Ethyl alcohol	triangle	triangle
SI-0325 — Methyl alcohol	subtriangle	subtriangle
SI-0326 — Ethylene glycol	subtriangle	subtriangle
SI-0327 — Glycerin	subtriangle	subtriangle
	20 min etch	**(111) etch rate**
SI-0329 — 15% K_3CO_3. $^1/_2H_2O$:5 g $Cd(OH)_4$	triangle	0.1 mil/15 min
SI-0330 — 15% Na_2CO_3:5 g $Ce(OH)_4$	triangle	0.1 mil/10 min
SI-0331 — 1 *M* KCN:20 g I_2	triangle	0.1 mil/5 min
SI-0340 — 1 *M* KCN	cleaning, only	
SI-0341 — 30% $K_3CO_3.1$ $^1/_2H_2O$	cleaning, only	

All wafers, dice or single crystal spheres were free etching in the boiling solutions. Square dice, random orientation cut, or edge oriented (111) triangles and diamond shapes also used. (100) silicon, as (100)/(110) edge oriented. Both individual dice and wafers were opposed pit damaged for collector/emitter transistor configuration damage . . . damage and pit-etch the collector first; then damage emitter, and etch both to final size for a specific base width. Transmitted white light with a Richart-Zetopan microscope was used to establish base width by color. Pit bottom planarity to within 0.1 μm on (111) surfaces; a nominal 0.2 μm curve on (100). Oriented dice edges reduced the preferential etch incursion observed in random cut edges. For individual die or wafers, a back-reflecting mirror was used to align opposed pits with the vertical stylus; a similar system used with a panograph for device array pitting of wafers by ink dotting both wafer sides. This was one of the first instances

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of fabricating discrete, individual devices on a wafer (1957), before the advent of photolithography. Silicon aluminum alloy transistors were fabricated with optimum electrical characteristics vs. individual dice with sandblasted pits (which have curved bottoms). Single crystal spheres were etched for finite crystal form in several of the solutions shown to obtain convex planes as against the concave, pit side-slope planes on both silicon and germanium. Walker (referenced below) also fabricated operational diffused spherical radiation detectors and cylindrical lithium-drift germanium radiation detectors, circa 1968, using the above described techniques.

REF: Walker, P & Waters, W P — silicon development, 1956—1959

SI-0342: Waters, W P & Walker, P — Electrochem Soc Meet, Spring 1957

Si, (111) wafers fabricated as aluminum alloy transistors with a controlled pit damage technique and etching with hot alkali solutions. Results showed better electrical characterization due to improved pit bottom planarity.

SI-0400

ETCH NAME: Wright etch — TIME:

TYPE: Acid, preferential — TEMP:

COMPOSITION:

(1) x .... BHF — (2) Wright etch (SI-0045)

DISCUSSION:

Si, (100) p- and n-type substrates for AsH_3 doped poly-Si epitaxy thin films, n-type 0.2—2.0 Ω cm with Si_3N_4 cap. A study of Si_3N_4 gettering effect on silicon. (1) Clean with solution (1), then (2) defect etch with solution (2).

REF: Chen, M C & Silvestri, V J — *J Electrochem Soc,* 129,1294(1982)

SI-0401

ETCH NAME: Hydrofluoric acid — TIME:

TYPE: Electrolytic, decoration — TEMP: RT

COMPOSITION: — ANODE: Si

x .... 5% HF — CATHODE:

POWER: 3 V

DISCUSSION:

Si, as poly-Si films on Si (100) substrates. Solution can be used to decorate defects by a combination of staining with light etching.

REF: Chen, M C et al — *J Electrochem Soc,* 128,389(1981)

SI-0405

ETCH NAME: RIE — TIME:

TYPE: Ionized gas, selective — TEMP:

COMPOSITION: — ANODE:

x .... CF_4 — CATHODE:

x .... H_2 — POWER:

DISCUSSION:

Si, (100) wafers with SiO_2 thin films. This RIE gas mixture used to selectively etch SiO_2.

REF: Mephrath, L & Petrillo, E J — *J Electrochem Soc,* 129,2282(1982)

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SI-0036b
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
2 .... HF
3 .... HNO_3
2 .... CH_3COOH (HAc)
TIME: 2—3 min
TEMP: RT
DISCUSSION:
Si, (100) wafers used in developing the Secco etch (SI-0036a). Solution used to etch polish wafers prior to preferential etching with Secco etch. Material was 1—10 K Ω cm resistivity. The 1—300 Ω cm etched slower in Secco — 20 min below 300 Ω cm; 30—35 min above, for equivalent defect development.
REF: Ibid.

SI-0045b
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
TIME: (1) 20 sec
(2) 10 min
TEMP: RT Boiling

(1) 1 .... HF
50 .... H_2O
(2) x .... H_2SO_4
DISCUSSION:
Si, (111) and (100) wafers, p- and n-type, 0.2—20 Ω cm resistivity, both CZ and FZ grown ingots, used in a study of oxidation defects. Etch clean wafers in solution (1), then solution (2). Water wash after each etch step in UPDI for 5 min with ultrasonic agitation. Use Wright etch (SI-0045a) to develop defects, stacking faults, swirl patterns, and striations caused by oxidation.
REF: Ibid.

SI-0406
ETCH NAME: Sodium hydroxide
TYPE: Alkali, removal
COMPOSITION:
x .... 0.2 *M* NaOH
TIME:
TEMP:
DISCUSSION:
a-Si:H thin films grown on SiO_2, Al_2O_3, and ZrO_2 substrates in a study of surface coating protection against chemical attack. Other materials evaluated were Al, TiN, Ag, and PbS. A collimated light beam was used with aluminum during etching; Ag etched in 1 *M* HNO_3 also with light.
REF: Martin, P J et al — *J Vac Sci Technol*, A2(2),341(1984)

SI-0407
ETCH NAME: Chlorine
TYPE: Gas, preferential
COMPOSITION:
x .... Cl_2 (0.1—0.6%)
x .... He
TIME: 30 min
TEMP: 900—1100°C
RATE: 0.25—2.5 μm/min
DISCUSSION:
Si, (111) wafers used in an etch reaction study. Wafers polished with Lustrox, then cleaned in furnace tube at 1100°C, 30 min in atmosphere of H_2 + 0.1% Pd to remove residual oxide. Switched to Cl_2/He atmosphere mixtures for etching. The 0.2% Cl_2 at 1000—1100°C gave polished surfaces; below 1000°C with higher Cl_2 concentrations gave

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rough surfaces as steps and pits. With an O_2 leak, carbon particles from the susceptor plate deposited on silicon surfaces. Rate control is chemical action, not diffusion. (*Note:* This is an example of using gases in their molecular form for etching, rather than as ionized gases.)
REF: Dismukes, J P & Ulmer, R — *J Electrochem Soc*, 118,634(1971)
SI-0366: Schmidt, P F & Blomgren, H — *J Electrochem Soc*, 106,694(1959)
Si, (111) p-type wafers. A study of potential measurements during jet-etching of both silicon and germanium.
SI-0367: Schmidt, P F & Keiper, D A — *J Electrochem Soc*, 106,592(1959)
Si, (111) n-type wafers. Used in a study of the jet-etching of n-type silicon.
SI-0368: Marks, A — Electrochem Soc Meet, Washington, D.C., 12—16 May 1957
Si, (111) wafers. A description of electrochemical jet-etching of silicon.

SI-0369
ETCH NAME: TIME:
TYPE: Metal, contacts TEMP: RT
COMPOSITION:
x .... Cu, Al, etc.
DISCUSSION:
Si, (111) wafers used in a study of forming metal surface contacts by the dry friction method. Apply a flat silicon surface against a rotating surface of a metal to form a smear-type metal contact area. A rough or disturbed silicon surface made best contacts. The following metals were evaluated: Cu, Al, Ni, Mo, Fe, Sn, Ta, brass, and bronze.
REF: Kirvalidze, I D & Zhukov, V F — *Fiz Tverd Tela*, 1,1583(1959)
SI-0379: Dash, W C — *J Appl Phys*, 29,228(1958)
Si, (111) wafers. A study of the development of distortion layers on silicon surfaces by grinding and mechanical polishing. The mechanical working of a surface does not deform the bulk material other than a small surface fraction — up to about 150 Å deep after a final polish. (*Note:* Damage depth is related to the abrasive particle diameter and physical grain shape of an abrasive, type cutting edge of the grain, abrasive hardness and breakdown characteristics during use, and can be as much as 3 mils in depth of induced damage even after final optical polish. See Silicon Dioxide section with reference to the DeBeye layer.)
SI-0377: Allen, R B et al — *J Appl Phys*, 31,334(1960)
Si, (111) wafers used in a study of oxide layers on the diffusion of phosphorus in silicon. Wafers processed at 1150°C, 2.1 × 10^{15} cm/sec^2 with 1.4 eV power.
SI-0376: Hartke, J L — *J Appl Phys*, 30,1649(1959)
Si, (111) wafers. A study of the effects of oxygen in silicon on the diffusion of phosphorus.
SI-0375: Logan, R A & Peters, A J — *J Appl Phys*, 28,1419(1957)
Si, (111) wafers. A study of the effects of oxygen on etch pit formation in silicon.
SI-0380: Kalnajs, J & Samakula, A — *J Phys Chem Solids*, 6,46(1958)
Si, (111) single crystals. A study of oxygen impurity in silicon.
SI-0360: Czaja, W — *J Appl Phys*, 37,918(1966)
Si, (111) wafers, phosphorus doped for 3 to 4 μm deep junctions used in a study of partial dislocations with observation under SEM. Used an iodine etch, 30 sec to develop slip patterns. Heat treatment in presence of O_2 can cause slip.
SI-0361: Rosenzweig, W — *ISSS Trans Nucl Sci*, NS-12,18(1965)
Si, devices studied for the effects of space radiation.

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SI-0362
ETCH NAME: Ultrasonic
TYPE: Vibration, preferential
COMPOSITION:
x .... Ba_2TiO_3
DISCUSSION:
TIME:
TEMP:
POWER:

Si, specimens of various orientations used in a study of the development of etched figures with ultrasonic vibration. (*Note:* Ultrasonic vibration is widely used for wafers and parts cleaning, and induced damage from a barium titanate transducer element in ultrasonic generators with wafers in acids solutions has been studied.)
REF: Bagdasarov, K S — *Sov Phys-Cryst,* 2,309(1957)
SI-0363: Belyustin, A V — *Sov Phys-Cryst,* 4,569(1959)

Si, and other materials used in a study of face solubility of single crystals. Growth pyramids on surfaces vary with impurity content and stress. As solution concentration decreases upward in a gravitational field crystal faces higher in the solution will show less solubility. Pyramid structures are most stable and will develop on otherwise unstable crystal surfaces.
SI-0383: Dash, W C — *Phys Rev Lett,* 1,400(1953)

Si, (111) wafers and other orientations. Development of prismatic dislocation loops in silicon.
SI-0384: Stephen, W E & Myerhof, W E — Univ Penn Div 14, NDRC #563, 1945, 16

Si, specimens. A study of geometric structure on silicon surfaces.
SI-0385: Vogel, F L & Lovell, C — *J Appl Phys,* 27,1413(1956)

Si, (111) wafers. The development of dislocation etch pits in silicon.
SI-0386: Trakhenberg, A D & Fainstein, S M — *Sov Phys,* 1,335(1959)

Si, (111) wafers. Dislocation development in both silicon and germanium.
SI-0387: Roll, F — *Z Metallkd,* 30,205(1938)

Si, specimens. A study of etching silicon sections.
SI-0388: Hopkins, R L — *J Appl Phys,* 29,1378(1958)

Si, (111) wafers. Appearance of light diffraction striations in silicon.
SI-0378: Wagner, C — *J Appl Phys,* 29,1295(1958)

Si, (111) wafers. A study of surface passivation of silicon during oxidation at elevated temperatures.
SI-0374: Lederhandler, S & Patel, J R — *Phys Rev,* 108,239(1957)

Si, (111) wafers. A study of the behavior of oxygen in plastically deformed silicon.
SI-0373: Hrostowski, H J & Kaiser, R H — *Phys Rev Lett,* 1,199(1958)

Si, (111) wafers. The infrared spectra of heat treatment centers in silicon and different temperature levels. At 450°C, there are 4 band groups, probably SiO_2; at 650°C, these bands disappear; at 1000°C oxygen becomes an acceptor in silicon, and between 300-600°C oxygen acts as a donor in silicon. (*Note:* Float Zone (FZ) (111) oriented ingots of 80,000 Ω cm p-type resistivity showed silica blebs of SiO_4 as segregated agglomerates in wafers.)
SI-0372: Kaiser, W — *Phys Rev,* 105,1751(1957)

Si, (111) wafers. A study of electrical and optical properties of silicon after heat treatment. Oxygen is proportional to the 4th power of concentration in silicon. At 450°C oxygen acts as a donor as SiO_2? and as SiO_4 at 1000°C. After 20 h at 1000°C oxygen is stabilized, and also stabilizes at 1100°C.
SI-0371: Faessler, A & Kramer, H — *Ann Phys (Leipzig) Folge,* 7,263(1959)

Si, (111), wafers. Establishment of the existence of Si, Si_2O, and Si_2O_3 in silicon as oxidation products. Representative as a compound with general formula: SiOR where R = C_2H_5 or $SiO.Si_xO$. (*Note:* Silicon oxides are normally as SiO_x, not Si_xO.)
SI-0170: Rill, D E — *Phys Rev,* 114,1414(1959)

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Si, (111) wafers. Used CP4 to etch material for defects after electron bombardment.
SI-0381: Michel, W & Schmidt, P F — *J Electrochem Soc,* 104,230(1957)

Si, (111) wafers. A study of the anodic oxidation of silicon.
SI-0223b: Ibid.

Si, (111) wafers. Anodic oxidation used as a junction delineation etch for silicon p-n junctions.

SI-0382
ETCH NAME: Heat
TYPE: Thermal, junction forming
COMPOSITION:
x .... heat
TIME:
TEMP:
DISCUSSION:

Si, (111) wafers. A study of the formation of large area p-n junctions in silicon by surface melting. (*Note:* The formation of p-n junctions in n-type silicon by alloying of evaporated or thin sheet aluminum with thermal drive-in on a total wafer surface in fabricating silicon high power diodes or as small aluminum or Al:Si(5%) spherical pellets for the Sphere Alloy Zener process are typical examples of this alloying procedure.)
REF: Billig, E & Gasson, D B — *J Appl Phys,* 28,1242(1957)
SI-0389: Kramer, G — *IEEE Nucl Sci,* NS-13,104(1966)

Si, device fabricated as a fast-neutron dosimeter. Material was Float Zone (FZ) grown (111), 50 Ω cm resistivity with boron and phosphorus doping diffusion. Report on device characteristics and applications.
SI-0390: Imai, T — *Jpn J Appl Phys,* 2,463(1963)

Si, fabricated as a mesa Esaki diode. A study of the effect of uniaxial stress on junctions with varied doping levels. Stress applied was 20 to 200 g. Higher impurity doping levels showed increased stress primarily at p-n junction zones. Both tension and compression stress observed.
SI-0391: Danes, L W — *J Sci Instr,* 35,423(1958)

Si and Gs specimens used in a study of metallic contacts. Shows conductance of different metal lead wires, and use of copper plating on germanium for tinning contacts.

SI-0392
ETCH NAME:
TYPE: Acid, removal
COMPOSITION:
x .... HCl
x .... HNO_3
x .... H_2O
TIME: 100 sec
TEMP: RT
DISCUSSION:

Si, (100) wafers used as substrates for RF sputter of SeGe thin films, 3000 Å thick. After deposition, heat to the 150°C glassification point to homogenize as an amorphous glassy thin film. Plate 100 Å of silver from a silver solution applied in the dark, RT, 3 min, and drive-in with Hg lamp at 200 W. Remove residual silver with solution shown. A study of silver photo-doping of the SeGe films.
REF: Zebutsu, S — *J Appl Phys Lett,* 39,969(1981)

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SI-0393
ETCH NAME:
TYPE: Acid, polish
COMPOSITION:
(1) 10 .... HF
1 .... HNO_3
(2) 1 .... HF
2 .... HNO_3
1 .... HAc
TIME: (1) 30 min
(2) 3 min
TEMP: RT RT

DISCUSSION:

Si and Ge wafers cut from Float Zone (FZ) ingots with 10^4 cm^{-2} grown-in dislocations used in a study of yield point and mobility of dislocations. Both materials were p-type, 200-1000 Ω cm resistivity, and Ge 40 Ω cm. After diamond saw cutting of wafers, mechanically lap with 3 μm, then 1 μm diamond paste. Etch polish germanium in solution (1); silicon in solution (2). Both materials showed slip in the ⟨123⟩ direction. (*Note:* The (321) planes are isometric system, normal class hexoctahedral planes, and not a common slip plane nor a common plane in nature due to high solubility factors of such planes.)
REF: Stevens, D'S & Tiersten, H F et al — *J Appl Phys*, 54,1815(1983)

SI-0394
ETCH NAME:
TYPE: Acid, thinning
COMPOSITION:
5 .... HF
1 .... HNO_3
5 .... HAc
TIME:
TEMP:

DISCUSSION:

Si, (100) wafers used as substrates for LPCVD growth of n-type poly-Si, and substrates coated with Si_3N_4 prior to epitaxy. Solution used to etch thin and removed the substrate for microscope study of deposited films in a form of the float-off technique for TEM observation of thin films.
REF: Hottier, F & Cadoret, R — *J Cryst Growth*, 61,244(1983)

SI-0395
ETCH NAME: Hydrofluoric acid
TYPE: Acid, oxide removal
COMPOSITION:
1 .... HF
20 .... H_2O
TIME:
TEMP: RT

DISCUSSION:

Si, (100) n-type wafers, 10 Ω cm resistivity with P^+ ion implantation. Remove native oxide after I^2 with solution shown, then evaporate Ti and anneal to form TiSi. A study of TiSi growth on ion implanted Si.
REF: Revesz, P et al — *J Appl Phys*, 54,1860(1983)
SI-0396: Suzuki, S & Itoh, T — *J Appl Phys*, 54,1466(1983)

Si, (111) n-type wafers, 100 Ω cm resistivity. Clean wafers by (1) solvent degrease, (2) oxidize in solution shown at 60°C, (3) strip oxide with HF, and (4) rinse in DI water.
SI-0397: Maeda, Y et al — *J Cryst Growth*, 65,331(1983)

Si, grown as poly-Si sheet for use as solar cell material directly as grown. A method developed to reduce cost and time: funnel a hot melt of silicon onto a heated, spinning graphite wheel. Silicon spreads and freezes as a thin sheet 0.1 to 0.5 mm thick. Four 50 mm square sheets can be poured per minute with a grain size of about 3 mm.

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SI-0408
ETCH NAME: RIE
TYPE: Ionized gas, removal
COMPOSITION:
x .... NF_3
x .... O_2
TIME:
TEMP:
ANODE:
CATHODE:
POWER: DC
DISCUSSION:

Si, as poly-Si specimens. Specimens were DC etched in the gas mixture shown in an etch development study of this material.
REF: Honda, T & Brandt, W W — *J Electrochem Soc,* 131,2667(1984)

SI-0407
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) 1 .... NH_4OH
1 .... H_2O_2
5 .... H_2O
(2) x .... H_2SO_4
(3) x .... HF
TIME:
TEMP:
DISCUSSION:

Si, (100) wafers used for MOCVD growth of SiO_2 thin films at 250 to 300°C with plasma enhancement of MOCVD. Wafers were cleaned in the solutions in the order shown prior to MOCVD.
REF: Pandl, K P et al — *J Electron Mater,* 13,593(1984)
SI-0399: Ben-Dor, L et al — *J Electron Mater,* 13,263(1984)

Si, (111) degenerate n-type wafers used for MOCVD growth of ZrO_2 thin films in a study of these film interactions with Si. Clean wafers in $1H_2SO_4$:$1H_2O_2$ with final dip in 1HF:$1H_2O$ prior to MOCVD.

SI-0198
ETCH NAME: RIE
TYPE: Ionized gas, structuring
COMPOSITION:
x .... 0.9 He
x .... 0.1 Cl_2
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:

Si, as poly-Si thin film on silicon wafers. A mesa-like "T" was gas etch structured in a channel by plasma etching. Included the use of hot HCl vapor and Cl_2 gas, alone, for structuring.
REF: Zarowin, C B — *J Electrochem Soc,* 130,1144(1983)
SI-0429: Moore, J B & McCaldin, S C — *J Electrochem Soc,* 124,625(1977)

Si, (111) wafers used for Be evaporation with and without an SiO_2 thin film cover used in a study of Be reactions. Clean Si substrates: (1) TCE degrease, rinse in acetone, then MeOH, then DI H_2O, and (2) 10% HF rinse immediately before Be evaporation. Forms Be_2SiO_4 (with SiO_2 present) and BeO + Si on silicon surface only. Above 400°C an insoluble residue forms (BeO?). Remove excess Be with HCl. (*Note:* See Quartz, Beryllium, and Aluminum Alloys sections for other applications of beryllium on silicon and silicon dioxide.)
SI-0419: Ikuta, K & Ohara, T — *Jpn J Appl Phys,* 23,984(1984)

Si, (100), p-type, 4.4—5.7 Ω cm resistivity wafers used in a study of defects versus argon annealing. Argon used to induce bulk defects and remove surface defects. Wright etch used to step-etch in 5 μm increments for depth profiling.
SI-0418: Sawada, R — *Jpn J Appl Phys,* 23,959(1984)

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Si, (100), p-type, 1—30 Ω cm resistivity wafers cut from Czochralski (CZ) grown ingots used in a damage study. Prepared with and without SiO_2 or SiO_2 thin films added after damaging, and included thermal annealing as an induced and enhanced stress mechanism. Diamond scribe wafer backs with various pressure loads, then bend around a ⟨110⟩ plane direction to neutralize damage induced dislocations. Macroscopic strain disappears with oxidation, but microstrain remains near cut damage even after thermal annealing. Wright etch produced sauce-like etch pits correlated with stacking faults.

SI-0421: Woods, H & Silverman, R — *J Appl Phys*, 38,419(1967)

Si, thin film epitaxy on silicon wafers. Describes metallographic techniques used to study Si/Si reactions.

SI-0422: Jungbluth, D — *J Appl Phys*, 38,133(1967)

Si wafers with double-diffused epitaxy layers. A study of defects generated by diffusion.

SI-0423
ETCH NAME: Implantation
TYPE: I^2, defects
TIME:
TEMP: −195°C
COMPOSITION:
x .... Si^+ ions
DISCUSSION:

Si, (100), n-type 2—6 Ω cm resistivity wafers cut from Czochralski (CZ) grown ingots. Wafers Si^+ ion implanted at LN_2 temperature. Dislocations were up to 4500 Å in depth from surfaces. Surface structure was as a-Si on the immediate surface with a zone of dislocation loops below and then bulk Si. (*Note:* This type damage structure is atypical of implantation damage.)

REF: Marayan, J — *J Appl Phys*, 7,564(1985)

SI-0420: Rudder, R A — *J Vac Sci Technol*, A2(2),326(1984)

Si, (100) wafers and fused quartz blanks used as substrates for deposition of a-Si:H and a-Ge:H thin films. Clean quartz in x% CrO_3:H_2SO_4, RT, 60 sec (QTZ-0009). Both substrates cleaned before deposition: (1) TCE degrease, (2) acetone, then MeOH rinse and DI H_2O rinse. This was a study of hydrogenated thin films. After film growth they were cleaned with HF, RT, 30 sec.

SI-0413
ETCH NAME: BHF
TYPE: Acid, cleaning
TIME:
TEMP: 0°C
COMPOSITION:
134 ml .... HF
452 g .... NH_4F
625 ml .... H_2O
DISCUSSION:

Si thin film epitaxy grown on (100) silicon wafer substrates, then coated with TiN thin film used in a reaction and structure study. Solution used to both remove TiN films and clean poly-Si epitaxy surfaces. See TIN-0003.

REF: Whittmer, N et al — *J Appl Phys*, 54,1423(1983)

SI-0414
ETCH NAME:
TYPE: Acid, cleaning
TIME:
TEMP:
COMPOSITION:

(1)	(2)	(3)
1 .... H_2SO_4	x .... HF	1 .... HF
1 .... H_2O_2		100 .... NH_4F(40%)

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DISCUSSION:

Si, (100), n-type, 5—9 Ω cm resistivity wafers used in developing thin gate dielectrics for MOSFETs using oxide/nitride. Wafers cleaned in solution (1), then (2) prior to SiO_2 deposition at 950°C with 30 min anneal, then 925°C Si_3N_4 deposition with NH_3 for 2 h. BHF solution (3) used to etch nitride and oxide. Nitride etch rate 0.14 nm/sec, increasing with higher nitriding temperatures.

REF: Wong, S S et al — *J Electrochem Soc,* 130,1139(1983)

SI-0428: Turner, D R — *J Electrochem Soc,* 106,786(1959)

Si, (111) wafers used in a study of the electroplating of metal contacts on Si and Ge. See GE-0285.

SI-0415: Kotani, H et al — *J Electrochem Soc,* 130,645(1983)

Si, (100) wafers used as substrates in studying thin film deposits as inter-connects. The following thin films were evaluated: P:SiN, LP:PSG, Al, AlSi, and AlCuSi. CF_4:Ar:O_2 plasma etching used for controlled removal of films at 200°C with 1.7 Pa pressure and 0.5 W/cm² power. Plasma etch rates were (1) Al at 100 Å/min; P:SiN at 70 Å/min; LP:PSG at 60 Å/min. Plasma also used to etch via holes through film/Si. PSG via holes also etched with HF.

SI-0416

ETCH NAME: Pressure — TIME:

TYPE: Pressure, forming — TEMP:

COMPOSITION: — PRESSURE: See discussion

x .... pressure

DISCUSSION:

Si material blanks used in a study of high pressure forms of silicon with change in crystal structure:

Si I: standard temperature and pressure — isometric, cubic . . . ("diamond")
Si II: 10 GPa pressure — B-Si — tetragonal (similar to B-Tin)
Si III: 16 GPa pressure — Theta-Si — hexagonal with one atom/unit cell.
Si IV: unk
Si V: also referenced as Theta-Si
Si VI: 34—36 GPa — Si with unknown and unexpected form — tetragonal?
Si VII: unk
Si VIII: above 39 GPa — hexagonal, close-packed (hcp)

REF: Sharama, S & Sikka, S K — *J Phys Chem Solids,* 46,477(1985)

SI-0417

ETCH NAME: Helium — TIME:

TYPE: Gas, cleaning — TEMP:

COMPOSITION:

x .... He

DISCUSSION:

Si, (111) wafers cleaned with helium "atom impact" prior to epitaxy growth of n-type silicon, 5 Ω cm resistivity, 20 μm thick.

REF: Nishigaki, S et al — *Jpn J Appl Phys,* 23,683(1984)

SI-0425: O'Hara, S — *J Appl Phys,* 35,409(1964)

Si and Ge grown as dendritic ribbon crystal and used in a dislocation study. Sirtl etch used on silicon; CP4 used on germanium with 0.6 ml Br_2/100 ml HNO_3.

SI-00426a: Chu, T L & Gavaler, J R — *Phil Mag,* 10,1064(1964)

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Si, (111) wafers with "vapor grown" thin film silicon. Both Sirtl and Dash etches used in studying stacking faults.

SI-0426b: Ibid.

Si, (111) wafers with "vapor grown" thin film silicon. Both Sirtl and Dash etches used to study stacking faults.

SI-0427: Turner, D R — *J Electrochem Soc,* 106,701(1959)

Si, (111) wafers with p-n junctions. A study of the use of electrochemical displacement plating solutions to delineate junctions.

SI-0430a
ETCH NAME:
TYPE: Acid, cleaning
COMPOSITION:
(1) x .... H_2SO_4
x .... H_2O_2
(2) x .... H_2O_2
(3) x .... HF
TIME:
TEMP:
DISCUSSION:

Si, (100) p-type, 2 Ω cm resistivity wafers used in an evaluation of RIE contamination. Wafers were cleaned in order in the three solutions shown prior to RIE, and in solutions (1) and (2) after RIE. See SI-0430.

REF: Ephrath, L M & Bennett, R S — *J Electrochem Soc,* 129,1822(1982)

SI-0430b
ETCH NAME: RIE
TYPE: Ionized gas, removal
COMPOSITION:
(1) x .... CF_4
(2) x .... CF_4 + O_2
(3) x .... CF_4 + H_2
TIME: 5 min
TEMP:
GAS FLOW:
ANODE:
CATHODE: DC 200 V
PRESSURE: 25 mTorr
POWER: 0.5/cm²
DISCUSSION:

Si, (100) wafers used in a study of RIE contamination. Gases (1) and (2) used for Si, poly-Si, and polycides (WSi_2/Poly-Si). Gases (3) for selective etching of SiO_2 or Si_3N_4 on VLSI chips. Etch rates are in nm/min. Evaluation done with devices structured as MOS capacitors . . . Si oxidized with O_2 at 1000°C for 35 nm thickness and evaporated 35 mil Al dots. Defects in material were under 100/cm².

REF: Ibid.

SI-0435
ETCH NAME: Sulfur
TYPE: Metal, diffusion
COMPOSITION:
x .... S
TIME:
TEMP:
DISCUSSION:

Si, p-type wafers used in a study of n-type sulfur diffusion in silicon. Introduces two donor levels in forbidden band at 0.18 and 0.37 eV. Does not work with n-type silicon. Appears to be a substitutional, interstitial impurity with $^1/_{50}$ the solubility of O_2 in silicon.

REF: Carlson, R O et al — *J Phys Chem Solids,* 8,8183(1959)

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SI-0436
ETCH NAME: Gases
TYPE: Gas, contamination
TIME:
TEMP:
COMPOSITION:
x .... gases
DISCUSSION:
Si, (100) wafers fabricated as VLSI and VHSIC devices. A study of methods of analyzing process gases introducing contamination during the processing of these devices.
REF: Koll, W — *Solid State Technol,* 1984, 220

SI-0437
ETCH NAME: Argon, wet
TYPE: Gas, alteration
TIME: 50 min
TEMP: 800—1300°C
COMPOSITION:
x .... Ar
x .... H_2O, vapor
DISCUSSION:
Si, wafers from p-type Float Zone (FZ) grown ingots with and without grown-in dislocations to 10^6 cm^{-2} concentration. Bars were cut and mechanically lapped with SiC, then cleaned; (1) EOH rinse, (2) TCE degrease, and (3) rinse in double-distilled H_2O. After wet argon treatment, quench to RT in water. Re-mechanically polish and etch in CP4 for dislocations and evaluate photoluminescence. Treatment converts wafers to high resistivity n-type with 7000 Ω cm.
REF: Nakashima, K — *Jpn J Appl Phys,* 23,622(1984)

SI-0440
ETCH NAME:
TYPE: Acid, thinning
TIME:
TEMP: RT
COMPOSITION:
(1) 1 .... HF
3 .... HNO_3
(2) 0.25 g .... I_2
110 ml .... CH_3COOH (HAc)
DISCUSSION:
Si, (100) and (111) wafers both n- and p-type, 3—5 Ω cm resistivity used as substrates in study of nickel silicide. 300 Å Ni evaporation followed by As_4 ion implantation, and N_2 anneal: 400 and 600°C as NiSi; 800°C, $NiSi_2$. To prepare specimens for TEM study, silicon substrate was removed: (1) abrasive lap in KOH; (2) etch in solution (2) and (3) in solution (1) using a wax moat on material surface. Silicide grain size and quantity varied with As flux levels of 10^{15}, 10^{16}, and $10^{19}/cm^2$ . . . as low a-Ni grains; medium grains of Ni_2Si and high Ni_2Si grains, respectively.
REF: Chen, L J & Hou, C Y — *Thin Solid Films,* 104,167(1983)

SI-0439
ETCH NAME: P4A
TYPE: Acid, jet thinning
TIME:
TEMP:
COMPOSITION:
3 .... HF
5 .... HNO_3
3 .... HAc
DISCUSSION:
Si, (100) wafers used in a study of wet oxidation of poly-Si using a deposited structure as poly-Si/SiO_2/Si(100). The poly-Si was phosphorus doped at 950°C, 30 min for 28.3 Ω/

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sq resistivity, then wet oxidized with O_2 bubbled through 95°C H_2O, followed by annealing at 800°C, 30 and 60 min, and 1100°C, 5 min. Some specimens were ⟨110⟩ sectioned with Ar^+ ion thinning, and silicon removed with CP4A by gravity jet etching for film TEM study. The 800°C, 30 min specimens showed single crystal aggregates at grain boundaries and separate grains with loss of poly-Si thickness relative to anneal schedules.
REF: Bravman, J L & Sinclair, R — *Thin Solid Films,* 104,153(1983)

SILICON ALLOYS, SiMx

General: Silicon does not occur in nature as a metallic compound although it is the major mineral former as an oxide or silicate with SiO_2^-, SiO_3^-, SiO_4^-, etc., radicals. The silicate group comprises over 60% of all known natural minerals.

In the processing of silica, one by-product of reduction is known as ferrosilicon, FeSi — a hard, brittle form of iron with 2—10% silicon as an initial "pig". The material is then added to irons and steels, normally, as a 1—3% mixture for hardening. It also is added to aluminum or copper for the same purpose, as well as to other metal alloys.

Technical Application: The most widely used silicon alloy in Solid State processing is aluminum:silicon, AlSi(3—5%) used as a p-type dopant in fabricating silicon alloy devices: diodes, zeners, transistors. It is used as thin sheets, cut pre-forms or spheres — the Sphere Alloy Zener process. When pure aluminum is alloyed into silicon it forms a mixture of silicon needles in an aluminum matrix and, in order to reduce the amount of silicon removed from the substrate in the alloy formation, AlSi pre-mixed material is used. It is a brittle compound in comparison to aluminum. Other alloys, such as silicon:tin, SiSn, are under evaluation as thin film deposits in device structuring.

Silicon and germanium are the two elemental semiconductor materials, are isomorphous, and have been grown as single crystal alloy ingots in the complete range from 0—100% Si or Ge. The oxides and nitrides of silicon are thin film surface coatings with a variety of applications, and covered in individual sections in this book.

Etching: Mixed acids, variable by alloy.

SILICON ALLOY ETCHANTS

Silicon Aluminum: See Aluminum Alloys
Silicon Germanium
Silicon Iron: See Iron Alloys
Silicon Tin

SILICON GERMANIUM ETCHANTS

SIGE-0001
ETCH NAME: CP4 TIME:
TYPE: Acid, preferential TEMP: RT
COMPOSITION:
30 .... HF
50 .... HNO_3
30 .... HAc
0.6 .... Br_2
DISCUSSION:
Si:Ge, single crystal ingots of various compositions and as cut wafers. Silicon does not etch as rapidly in CP4 as does germanium. Developed striation layers in ingots with dislocation etch pits parallel to stria in some of the alloy mixtures.

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REF: Toxen, A M — *Phys Rev*, 122,450(1961)
SIGE-0003: Goss, A J et al — *Acta Metall*, 4,333(1956)

Si:Ge single crystal alloy ingots in a study of composition fluctuations and dislocations. Silicon etches more slowly and produces stria patterns. Solution also developed edge dislocations.

SIGE-0002
ETCH NAME:
TIME:
TYPE: Acid, removal
TEMP:
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

Si, thin film deposition on germanium substrates as mc-SiGe and as an Si_xGe_{1-x} thin film alloy for use as photovoltaic devices. Silicon deposition was by sputter-assisted plasma CVD (SPCVD).
REF: Kohno, K et al — *Jpn J Appl Phys*, 23,L674(1984)

SILICON TIN ETCHANTS

SISN-0001
ETCH NAME:
TIME:
TYPE: Acid, removal
TEMP: RT
COMPOSITION:
x .... HF
x .... HNO_3
DISCUSSION:

SiSn, thin films deposited on (100) silicon wafers used as substrates in fabricating photovoltaic devices. Film growth was by sputter-assisted plasma CVD (SPCVD). Also worked with thin films of SiN and uc-Si_xGe_{1-x}.
REF: Kohno, K et al — *Jpn J Appl Phys*, 23,L674(1984)

PHYSICAL PROPERTIES OF SILICON CARBIDE, SiC

Classification	Carbide
Atomic numbers	14 & 6
Atomic weight	40
Melting point (°C)	2700
Boiling point (°C)	2100 (sublimes)
Density (g/cm^3)	3.21
Oxidation point (°C in air/O_2)	1650
Thermal conductivity (Wm/K) 1000°C	23.7
Mean specific heat (Kg/K) 25—1300°C	795.5
Coefficient of thermal linear expansion ($\times 10^6$ cm/cm/°C) 20—1000°C — SiC	5.2
— 90% SiC:8% SiO_2	4.7
Thermal conductivity (BTU) — 90% SiC:8% SiO_2	109
Flexure strength (psi) — 96.5% SiC:2.5 SiO_2	24,000
Compressive strength (psi) — 96.5% SiC:2.5% SiO_2	150,000
Bond dissociation energy (kJ mol^{-1})	435

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Cohesive energy (kJ mol^{-1})	1183
Atomic mass (mole/g)	40
Young's modulus (Kgf $cm^{-2} \times 10^{-6}$)	4.9
Coefficient of thermal endurance F(cm K $min^{-1/2} \times 10^{-4}$)	1.3
Relative F match	33
Thermal conductivity (W cm^{-1} K^{-1})	1.87
Coefficient of linear expansion ($K^{-1} \times 10^{6}$)	5.0
Specific heat (Jg^{-1} K^{-1})	0.146
Refractive index (n =)	2.654—2.697 (2.4—2.8)
Dielectric constant (e =)	5.8—8.12
Crystal structure (hexagonal — normal) alpha	$(10\bar{1}0)$ prism
(isometric — normal) beta	(100) cube
Color (solid) alpha (natural)	Blue-black
alpha (powder, artificial)	White grey
Cleavage (basal/cubic)	(0001)/(001)

SILICON CARBIDE, SiC

General: Silicon carbide was first grown artificially as carborundum. It was later found as a natural compound and named moissanite, CSi, from an occurrence as small green hexagonal crystals in meteoric iron, such that it may not be considered of terrestrial origin.

It is artificially made by fusing sand and coke (SiO_2 + C) above 4000°F, and is one of the high temperature refractory ceramics with use as refractory brick in furnaces. After initial fusing, it is powdered and pressure bonded using silica or silicon nitride as the bonding medium and, with sufficient temperature and pressure, there is some recrystallization and self-bonding. The material is used for many high temperature heat-resistant, acid resistant and gas impermeable parts, such as hot metal spray nozzles. When molded with graphite, C, it exhibits high wear and corrosion resistance; fabricated as a foam it resembles the natural rock called pumice, SiO_2 of acid magma origin — light weight due to the structure — used as a construction material, and as a pumice stone lapping abrasive. As fibers or whiskers it is added to metals, plastics and glasses as a strengthening agent, and as a thin film spray coating on metal cutting edge surfaces it improves wear and work-life of such blades. It has a low neutron cross section, such that it is stable against radiation and is used in the construction of nuclear power reactors and similar radiation equipment.

Because of its hardness (H = 9+) it has become one of the most widely used lapping and polishing abrasives, replacing the more expensive diamond paste compounds. As an abrasive it is available in various powdered grit-sizes; bonded as a cutting wheel; as sandpaper sheets, strips or belts; and in a variety of bonded, shaped forms as files, cones, cylinders, and so forth.

Technical Application: Grown as a single crystal, silicon carbide is an intrinsic n-type semiconductor. When doped with aluminum it forms a p-n junction diode capable of operating above 600°C, e.g., most semiconductors are rated for maximum 150°C operation.

In Solid State development it is grown by depositing thin carbon films on silicon, followed by thermal heat treatment to form the carbide. Under 500°C as an amorphous thin film, a-SiC or hydrogenated as a-SiC:H, and as single crystal hexagonal alpha-SiC. At greater than 1400°C, as cubic (isometric) beta-SiC. It also has been deposited as an amorphous silicon carbonitride, SiC_xNi_{1-x} thin film. Chemical Vapor Deposition (CVD) is used for growth with a mixture of SiH_4:CCl_4 or other carbon containing compounds and gases such as methane, CH_4, where other than silicon substrates are used.

As grown in any of the structural forms described, it has been used as a substrate for additional epitaxy growth of other semiconductor compounds, or, with metal evaporation, thermal conversion to silicides using the carbide as the silicon source.

It is widely used as a general lapping and polishing abrasive on all Solid State metals

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and metallic compounds, a 600-grit (about 30 μm) finishing being a general "as received" standard on semiconductor wafers. The abrasive form is as sharp slivers, brittle, shiny black in color, with excellent cutting action. The carbide does not wear during use, but will splinter, presenting fresh, sharp edges without reduction of cutting action. As a slurry of abrasive/water/glycerin or as an acid-slurry for improved polishing — it is unattacked by single acids at room temperature.

Though not used to date, it has application as a radiation-hard package material for semiconductors and similar device assemblies. As a thin film coating on graphite, it is in use for epitaxy susceptor plates.

Etching: Very difficult. Molten fluxes; mixed acids or dry chemical etching.

SILICON CARBIDE ETCHANTS

SIC-0001
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HF
x .... H_2O
TIME: 30 sec
TEMP: RT
DISCUSSION:

SiC blanks used as substrates for nickel and palladium evaporation and conversion to silicides. Degrease substrates in acetone, then isopropyl alcohol. Dip in HF solution shown and water rinse prior to metal evaporation. Anneal at 400 to 900°C after metallization in 100°C steps, 30 min for each temperature level. At 400°C, no change; at 500°C, as Pd_3Si; at 700°C, as Pd_3Si and Pd_2Si; and between 800—900°C, as Pd_2Si only. The same pattern was observed when nickel replaced palladium.
REF: Pai, S C et al — *J Appl Phys,* 57,618(1985)

SIC-0002
ETCH NAME: Copper
TYPE: Metal, decoration
COMPOSITION:
x .... Cu
TIME: 12 h
TEMP: 450—500°C
DISCUSSION:

SiC, (0001) blanks. A study of dislocations. Mechanically polish with diamond grit. Degrease in TCE with ultrasonic vibration; then rinse in DI water and N_2 blow dry. Melt copper on surface (alpha-SiC) for 30 sec at 1150°C in H_2 atmosphere, and diffuse copper in argon. Grind off excess copper and re-polish to observe copper decorated dislocations.
REF: Trickett, O A & Griffiths, L B — *J Appl Phys,* 35,3618(1964)

SIC-0003a
ETCH NAME: Argon
TYPE: Ionized gas, step-etch
COMPOSITION:
x .... Ar^+ ions
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:

Beta-SiC, (001) single crystal blanks used in a structure study of the material. First, He^+ ion implant, then Ar^+ ion sputter step-etch to observe depth of helium penetration and defect structure.
REF: Thomas, R L — *Jpn J Appl Phys,* 23,1380(1985)
SIC-0017: Dillon, J A, Jr et al — *J Appl Phys,* 30,675(1959)

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SiC, (0001) wafers used in a study of surface properties. Ar^+ ion clean and anneal. Appears to be more stable than a silicon surface.

SIC-0003b
ETCH NAME: Heat
TYPE: Thermal, clean
COMPOSITION:
x .... heat
TIME: 5 h
TEMP: 800°C
DISCUSSION:

Beta-SiC, (001) single crystal blanks. Mechanically polish for an optical surface. Clean in vacuum at 800°C for 5 h as shown. He^+ ion implant and Ar^+ ion sputter step-etch for material structure study. Density of beta-SiC shown as 3.2 g/cm^3.
REF: Ibid.

SIC-0004
ETCH NAME: Hydrofluoric acid
TYPE: Acid, cleaning
COMPOSITION:
x .... HF
TIME:
TEMP:
DISCUSSION:

SiC, (0001) thin films grown on (100) silicon substrates by sublimation as large area oriented platelets. Clean the grown SiC surfaces with HF and water rinse. Follow with acetone rinse, propanol rinse and wipe dry. To remove residual F^+ ions and O^+ ions, Ar^+ ion sputter clean at 500 eV and temperature anneal.
REF: Bozzo, F et al — *J Electrochem Soc,* 131,1270(1984)
SIC-0005a: Yang, C Y et al — *J Electrochem Soc,* 132,418(1985)

c-SiC:H thin films doped with either boron or phosphorus. Etch rate varies with the carbon source used to grow SiC. Benzene and methane show lowest etch rates. SiC:H rate with benzene is 160 Å/min.
SIC-0006a: Roy, R A — *J Vac Sci Technol,* A(2),312(1984)

a-SiC:H, alpha-SiC and beta-SiC grown by CVD. Alpha-SiC deposited at 500°C is hexagonal. Beta-SiC deposited at 1400°C is cubic. (*Note:* "Cubic" is isometric system, normal class.)
SIC-0007: Primak, W et al — *Phys Rev,* 103,1184(1956)

SiC crystals. Surfaces soaked in HF and then in HCl. Both solutions used hot and specimens soaked for several days followed by water washing. Specimens used in a radiation damage study.
SIC-0010a: Chang, C Y et al — *J Electrochem Soc,* 112,418(1985)

a-SiC:H thin films deposited on (100) silicon and Corning glass 7059 substrates used with "standard cleaning" (?). Also cleaned in BHF and H_3PO_4 at 180°C. Seven different gases for carbon source used with SiH_4(29.5%):H_2 and 1% of B_2H_6 or PH_3 as dopants. After SiC deposition, hold in H_2 at temperature, 10 min. Etching studies done with both acids and dry chemical etching with CF_4:O_2. DC resistivity; dielectric breakdown and refractive indices measured. Also measured pinhole density vs. deposition rates by type gases and dopants.

SIC-0005b
ETCH NAME: BHF
TYPE: Acid, removal
COMPOSITION:
x .... BHF
TIME:
TEMP:

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DISCUSSION:

a-SiC:H thin films deposited on Si (100) substrates and doped with either boron or phosphorus. Etch rates vary with carbon source used to deposit SiC. BHF mixture used not shown.

REF: Ibid.

SIC-0005c

ETCH NAME: Phosphoric acid — TIME:

TYPE: Acid, removal — TEMP: 180°C

COMPOSITION:

x .... H_3PO_4

DISCUSSION:

a-SiC:H thin films deposited on Si (100) substrates and doped with either boron or phosphorus. Etch rates vary with carbon source used to deposit SiC. Solution shown used as a general removal etch.

REF: Ibid.

SIC-0024: Catherine, Y et al — *Thin Solid Films,* 109,145(1983)

a-SiC:H thin films deposited by DC and RF sputtering. Phosphoric acid can be used to remove or pattern. Carbide refractive index, n = 3.6.

SIC-0025

ETCH NAME: — TIME: 30 min

TYPE: Molten flux, polish — TEMP: 500°C

COMPOSITION:

3 .... NaOH, pellets

1 .... Na_2O_2, flakes

DISCUSSION:

SiC platelets. Molten solution used to etch polish surfaces. Authors say specimens are beta-SiC grown with a (111) habit, 10—20 μm thick.

REF: Bartlett, R W & Martin, O W — *J Appl Phys,* 39,2324(1968)

SIC-0006b

ETCH NAME: Aluminum — TIME:

TYPE: Metal, doping — TEMP: 3900°F

COMPOSITION:

x .... Al

DISCUSSION:

SiC, n-type wafers were doped with aluminum at 3900°F to form a p-n junction diode. Device will operate as a diode at 650°C.

REF: Roy, R A — *J Vac Sci Technol,* A(2),312(1984)

SIC-0008

ETCH NAME: — TIME:

TYPE: Acid, removal — TEMP:

COMPOSITION:

2 .... HF

3 .... HNO_3

DISCUSSION:

Beta SiC thin films grown on Si, (100) wafers cut 1 and 6° off the plane, and (111) wafers cut 2 and 4° off-plane. Authors say the silicon wafers were trepanned from larger diameter wafers. With wafers on an SiC coated graphite susceptor in a CVD epitaxy reactor system, etch clean surfaces with hot HCl vapor prior to SiC growth. React silicon with C_3H_4

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before bringing up to SiC reaction temperature. Laue photographs used to study films show overlapping Si and SiC back-reflections. Control remove SiC by black waxing (Apeizon-W) the surface leaving a center opening, then etching with solution shown. This method used to profile carbide thickness.
REF: Liaw, F & Davis, R F — *J Electrochem Soc*, 132,642(1985)

SIC-0009
ETCH NAME: Diboride
TYPE: Gas, doping
TIME:
TEMP: >570°C
COMPOSITION:
x .... B_2H_6
DISCUSSION:
SiC thin films grown on Si (100) wafers; Corning glass 7059 and stainless steel discs as substrates to deposit SiC by CVD. Substrates were held at 250°C and various gas mixtures for SiC growth were used with thickness varied by study requirement. For IR study, 1000 nm and for NR, 200—1500 nm. Some specimens were boron doped with B_2H_6.
REF: Fusimoto, F et al — *Jpn J Appl Phys*, 23,810(1984)

SIC-0010
ETCH NAME: Borax
TYPE: Molten flux, dislocation
TIME:
TEMP: 855°C
COMPOSITION:
(1) x .... Borax
(2) x .... Na_2CO_3
DISCUSSION:
SiC, epitaxy thin films. Both compounds shown were used as molten fluxes to develop dislocation pits in a study of etch pit density.
REF: Brander, R W — *J Electrochem Soc*, 12,881(1964)
SIC-0016: Amelinck, S et al — *J Appl Phys*, 31,1350(1960)
SiC, (111) specimens used in a dislocation study. Used a platinum crucible to contain flux.

SIC-0011a
ETCH NAME:
TYPE: Molten, dislocation
TIME: 2 min
TEMP: 700°C
COMPOSITION:
3 .... NaOH
1 .... Na_2O_2
DISCUSSION:
Alpha-SiC, (0001) wafers used in a defect structure study. As a molten flux will develop dislocations on the (0001) but it is difficult to develop dislocations on prism faces. With specimens in a nickel basket and molten flux at 500°C, 30 min solution will polish surfaces.
REF: Griffiths, L B — *J Phys Chem Solids*, 27,257(1966)

SIC-0011b
ETCH NAME: Chlorine
TYPE: Gas, polish
TIME:
TEMP:
COMPOSITION:
x .... Cl_2

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DISCUSSION:
Alpha-SiC, (0001) wafers used in a defect study. Chlorine gas can be used to etch polish surfaces. To thin for electron microscope study, lap to 0.03—0.05 mm thickness with diamond paste.
REF: Ibid.

SIC-0012a
ETCH NAME: Sirtl etch
TYPE: Acid, polish
COMPOSITION:
2 .... HF
1 .... CrO_3 (33%)
TIME: 5—10 sec
TEMP: RT
DISCUSSION:
SiC, (0001) wafers used as substrates for epitaxy silicon thin film grown. Amount of removal on polished SiC substrates was less than 0.2 μm.
REF: Wolley, E D — *J Appl Phys*, 37,1588(1966)

SIC-0012b
ETCH NAME: Sodium peroxide
TYPE: Molten, dislocation
COMPOSITION:
x .... Na_2O_2
TIME:
TEMP: >400°C
DISCUSSION:
SiC, (0001) wafers used as substrates for epitaxy silicon growth. Solution produces irregular, dendritic structure on (0001)A and triangle pits on $(000\bar{1})$B.
REF: Ibid.
SIC-0015a: Harper, C A — *Handbook of Materials and Processes for Electronics*, McGraw-Hill, New York, 1970, 7
SiC, (111) wafers. Use a molten flux at 350°C for dislocations.

SIC-0013a
ETCH NAME:
TYPE: Molten flux, structure
COMPOSITION:
x .... NaF
x .... K_2CO_3
TIME: 10—60 min
TEMP: 650°C
DISCUSSION:
SiC, thin films vapor deposited on silicon wafers. Solution used as a molten flux to develop microstructure (solution is a eutectic mixture).
REF: Gulden, T D — *J Am Ceram Soc*, 51,425(1968)

SIC-0013b
ETCH NAME:
TYPE: Electrolytic, stain
COMPOSITION:
x .... HF
x .... KF, sat. sol.
TIME:
TEMP:
ANODE: SiC
CATHODE:
POWER:
DISCUSSION:
SiC, thin films vapor deposited on silicon wafers. Solution used to develop microstructure by staining surfaces.
REF: Ibid.

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SIC-0014
ETCH NAME:
TYPE: Molten flux, preferential
COMPOSITION:
90 g .... $NaNO_2$
10 g .... Na_2O_2
TIME: 10 min
TEMP: 500°C
DISCUSSION:
Beta-SiC, (0001) wafers used in a study of stacking faults and dislocations. Solution will develop structure.
REF: Liebmann, W K — *J Electrochem Soc*, 12,885(1964)

SIC-0015b
ETCH NAME: Sodium hydroxide
TYPE: Molten flux, preferential
COMPOSITION:
x .... NaOH, pellets
TIME:
TEMP: 900°C
DISCUSSION:
SiC, (111) wafers. Use as a dislocation etch. Can be used on other orientations.
REF: Ibid.

SIC-0018
ETCH NAME: Hydrofluoric acid
TYPE: Electrolytic, polish
COMPOSITION:
x .... HF, conc.
TIME:
TEMP:
ANODE: SiC
CATHODE:
POWER:
DISCUSSION:
SiC, single crystal specimens used in developing electroless plated contacts on this material. Polish specimens with solution shown.
REF: Raybold, R L — *Rev Sci Instr*, 31,781(1960)

SIC-0019
ETCH NAME:
TYPE: Abrasive, polish
COMPOSITION:
x .... diamond grit
TIME:
TEMP:
DISCUSSION:
SiC, (0001) grown as alpha-II SiC, n-type, about 1 Ω cm resistivity and is a characteristic green color. Grown as a hexagonal pyramid with an (0001) base that can be optically flat. Cut, grind, and polish on copper plates using diamond grit in oil. Form SiO_2 thin film on specimens by oxidizing at 1000°C for 2 h using standard furnace techniques. Remove oxide with HF wash. Specimens used in a study of infrared properties of hexagonal SiC.
REF: Spitzer, W G et al — *Phys Rev*, 113,127(1959)

SIC-0020
ETCH NAME: Hydrogen
TYPE: Gas, polish
COMPOSITION:
x .... H_2, hot
TIME:
TEMP: 1500—1800°C
DISCUSSION:
SiC, (0001) wafers in a horizontal epitaxy-type furnace. Hot hydrogen used to etch

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polish both (0001)Si and (000$\bar{1}$)C surfaces — the silicon face etches approximately twice as fast — up to 4—5 Å/min at the higher temperatures. Method used to obtain planar polished surfaces.
REF: Chu, T L & Campbell, R B — *J Electrochem Soc*, 112,955(1965)

SIC-0010b
ETCH NAME: Phosphoric acid
TYPE: Acid, removal
COMPOSITION:
x .... H_3PO_4
TIME:
TEMP: 180°C
RATE: See discussion
DISCUSSION:
a-SiC:H, thin films deposited on Corning 7059 glass or silicon wafers in a development study of this compound as a passivating dielectric. Seven carbon sources used, plus boron or phosphorus doping. Etch rates, dielectric breakdown and dielectric constant, resistivity, refractive index, and pinhole density measured.
REF: Ibid.

SIC-0010c
ETCH NAME: Copper
TYPE: Metal, pinhole decoration
COMPOSITION:
x .... HAc
TIME:
TEMP:
ANODE: SiC:H
CATHODE: Cu and Si
POWER:
DISCUSSION:
a-SiC:H, thin films as amorphous coatings on glass and silicon wafers. A copper plating system was used to decorate defects and pinholes.
REF: Ibid.

SIC-0010d
ETCH NAME: Dry chemical etch
TYPE: Ionized gas removal
COMPOSITION:
x .... CF_4
x .... O_2
TIME:
TEMP:
GAS FLOW:
PRESSURE:
POWER:
DISCUSSION:
a-SiC:H amorphous thin films grown on glass or silicon wafers using seven different carbon sources and included doping with boron or phosphorus. Etch rate varies with type carbon source and dopant: B-doped rate was 160 Å/min to 980 Å/min. P-doped rate 200 to 400 Å more rapid relative to carbon source.
REF: Ibid.

SIC-0010e
ETCH NAME: BHF
TYPE: Acid, removal
COMPOSITION:
x .... BHF
TIME:
TEMP:
DISCUSSION:
a-SiC:H amorphous thin films 500—3500 Å thick deposited by RF plasma enhanced CVD (PECVD) using seven different carbon sources with either boron or phosphorus doping. Substrates used were Corning 7059 glass or silicon wafers. In general, phosphorus doped films etched more rapidly in BHF solutions.
REF: Ibid.

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SIC-0021
ETCH NAME: TIME:
TYPE: Molten flux, removal TEMP: 650°C
COMPOSITION:
1 .... NaF
2 .... K_2CO_3
DISCUSSION:
SiC, (0001) wafers used in a study of structure and adhesion. The (0001)Si is smoothly polished; the (000$\bar{1}$)C face is rough. Also studied Al_2O_3 and Mn-Zn, Ni-Zn ferrites.
REF: Buckley, D — *J Vac Sci Technol,* A(3),762(1985)

SIN-0023
ETCH NAME: Hydrofluoric acid TIME:
TYPE: Acid, cleaning TEMP:
COMPOSITION:
(1) 1 .... HF
10 .... H_2O
(2) 3 .... HF
5 .... HNO_3
3 .... HAc
DISCUSSION:
Beta-SiC, thin films grown on (100) silicon, p-type, 150 Ω cm resistivity as an oriented (100) film. Deposition used a propane:H_2 atmosphere at 1380—1400°C just below the silicon m.p. of 1414°C. Silicon wafers were cleaned in the solutions shown with DI water rinsing, and applied in the order shown. Did not use HCl:H_2 at 1200°C in epitaxy reactor (a normal pre-cleaning step), as it erodes the SiC coating on the graphite susceptor plate that can affect the characteristic of the SiC films. This was a study of the carbide as a surface coating.
REF: Addaniano, A & Klein, P H — *J Cryst Growth,* 70,291(1984)

PHYSICAL PROPERTIES OF SILICON DIOXIDE, SiO_2

Classification	Oxide
Atomic numbers	14 & 8
Atomic weight	60
Melting point (°C)	600—800 (1400)
Boiling point (°C)	2500 (2350)
Density (g/cm^3)	2.0—2.7 (2.65)
Refractive index (n =)	1.46—1.47
Dielectric constant (e =)	3.5 (3.8)
Mean specific heat (J/kg °C) 25—1000°C	1170
Coefficient of linear thermal expansion ($\times 10^{-6}$ cm/cm/°C) 25—800°C	8.6
Thermal conductivity (W/m °C) 1200°C	2.06
Electrical resistivity (ohm cm) 0°C	1014
Hardness (Mohs — scratch)	7
Crystal structure (hexagonal — rhombohedral)	(10$\bar{1}$0) rhomb (alpha Qtz)
(amorphous) obsidian/glasses	None
(colloidal) silica suspension	None
Color (solid) alpha-quartz	Clear/colors
Cleavage (imperfect)	None
Fracture (solid) — atypical all glassy oxides	Conchoidal

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SILICON DIOXIDE, SiO_2

General: Occurs in nature as the pure compound in the mineral quartz, SiO_2, which has a number of varieties and structural forms: (1) Single crystal: quartz, tridymite, crystobalite — all as low temperature (alpha) or high temperature (beta) structure, and two high-pressure forms associated with meteors: coestite and stisovite, where the tetrahedra structure is a ratio of SiO_2/SiO_4; (2) Colloidal or amorphous structure as opal, $SiO_2.nH_2O$; as silica, SiO_2, exoskeletons of diatom sea-life. As silica with impurities — obsidian, is natural volcanic amorphous glass, often containing carbonaceous matter or other mineral inclusions, viz., "snowflake" obsidian; (3) cryptocrystalline structure that may be colloidal/amorphous, in part, or columnar portions like chalcedony. This category also includes semi-precious stones, the agates, onyx, jaspers, chert, and flint. The latter two are from siliceous diatoms, sponges and other sea-life; (4) phenocrystalline: these varieties are often single crystal with impurities and represent the semi-precious and precious gem stones of quartz — clear rock crystal; amethyst, purple; citrine, yellow; milky quartz, milk-white, and nearly opaque; cat's eye, and several others; (5) massive: these are similar to the cryptocrystalline varieties, such as quartzite, a highly compacted, near-granular massive rock form which may be as a conglomerate mixture of quartz pebbles and fine sand; pseudomorphous quartz is an SiO_2 replacement of other minerals, such as replacing calcite or fluorite, retaining the replaced mineral structure, and includes silicified wood; (6) rock formers: though several of the quartz-type minerals already mentioned, above, occur in extensive beds — notably, flint, chert, and quartzite — there are three other silica minerals that are used by name: pumice or pumice stone, of acidic magma volcanic origin, porous, sand-like, lightweight, and a similar froth variety called tufa, both lightweight building stone or polishing abrasives used in cut, solid form. The best known of the three is sandstone, compacted sand grains often cemented with colloidal iron oxides . . . used as a building stone since antiquity. In addition, probably the best known form of natural silica is sand as loose, spherical particles of quartz produced by the rolling and tumbling action of water. It can be white (sometimes with calcite as atoll beaches in the South Pacific) more often yellow, and the black variety is high in magnetic iron ore (magnetite) as beach sands, or desert sands.

Other than the pure SiO_2 type minerals and rocks, the silicates as a mineral group contain SiO_3^-, SiO_4^- . . . SiO_{12}^- radicals with other metal elements and represent the largest chemical group of natural minerals, perhaps 2000 of the 4000 or more known mineral species. They occur as both single crystals and as primary rock-forming materials: granites, gneisses, slates, clays, micas, etc. Many of these rocks, clays in particular, are the base of the silicate, pottery, and ceramics industries.

Next to oxygen, silicon is the most abundant element in nature and, as some form of silica or silicate, is found in about one quarter of the earth's crust. When the silicates are included with pure silica, possibly 60% of the outer earth is a solid, exterior mantle with the remainder being oxides, carbonates, phosphates, arsenides, borates, and nitrates as well as the native metal elements, such as gold, platinum, silver, sulfur, and others.

Industrially, as used by man, flint and obsidian were some of the first tools and weapons of the Stone Age . . . *Homo sapien sapien* — the "tool maker" . . . is used to differentiate modern man from his prehistoric cousins, the Cro-Magnon, Neanderthal, and hominids. The use of mud and branches (wattle) and clays for construction and utensils probably also should be included as initial mediums, though this use reached its peak during the following Bronze Age. Flint and obsidian are still used as tools and weapons in the more remote areas of the world, today, and were even used in "modern" weapons as late as the 1700s, viz., the flintlock rifle.

Glass, as a manmade product, can be traced back to the Egyptian development of soda-lime glass around 3500 B.C. and that formula is still in use. The development of glass is a separate industry, though it is closely allied with the silicates and ceramic industries of today. Pottery glaze and enamels (silica applied as a thin surface film to harden clay vessels)

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