

Oxide Growth on Etched Silicon in Air at Room Temperature

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ABSTRACT

Oxide growth on etched silicon wafers at room temperature was studied as a function of etching procedure, wafer orientation, dopant concentration, and exposure to ultraviolet light. An impurity film was rapidly deposited on the silicon surface after etching with hydrofluoric acid. Impurity adsorption was distinguished from oxide growth by x-ray photoelectron spectroscopy (ESCA). The impurity film greatly reduced the initial oxide growth rate when compared with oxide growth on a cleaved silicon surface. The thickness of oxide films formed on etched surfaces was determined and compared using ESCA and ellipsometry.

The interaction of silicon with oxygen on atomically clean silicon surfaces has been described (1). The silicon surface for these studies is generally prepared in ultra-high vacuum at elevated temperatures. A related problem of practical importance in semiconductor processing is the growth of oxide films at room temperature on etched silicon single-crystal substrates (2-4). Ellipsometric measurements of film growth have been used to describe oxide growth kinetics on silicon after an initial film is rapidly formed (2, 4). Changes in ultra-thin film thickness were determined from ellipsometric data by employing the index of refraction of silicon dioxide and treating the films as oxides. These films were not characterized although Archer (2) noted that an impurity layer, which could be removed with organic solvents, was present in addition to an oxide film after exposure to air for 24 hr. Recent Auger studies of etched silicon surfaces also indicated the presence of both carbon and oxygen (5-8). The present work describes the growth rate of an oxide at room temperature for a silicon surface prepared by etching in HF and covered with adsorbates.

X-ray photoelectron spectroscopy, or ESCA (electron spectroscopy for chemical analysis), is used here to complement ellipsometric measurements of ultra-thin film formation on etched silicon surfaces. ESCA is particularly well suited as a technique for examination of oxide films $\leq 100\text{\AA}$ thick and can provide analytical and bonding data in terms of photoemitted electron line intensities and binding energies. The basis of the ESCA technique is the excitation of the electronic structure of an atom by x-rays and the analysis of the kinetic energies of the photoemitted electrons. The mean free paths of the monoenergetic, inelastically scattered photoelectrons are $< 30\text{\AA}$ in the 1 keV energy range. Contributions to a photoelectron line intensity decrease exponentially with distance from the film surface. Photoelectrons excited from core levels are mainly atomic in character but are subject to shifts in binding energy caused by the chemical environment of the atoms. By comparing ESCA and ellipsometric data, the films formed on etched silicon at room temperature are characterized and those factors which affect oxide growth are determined.

Experimental

Sample preparation.—Silicon dioxide films, 2000 $\text{\AA}$ thick, were grown in dry oxygen at 1050°C on chem-mech polished silicon wafers. The substrates used were $\langle 100 \rangle$, p-type, 2 ohm-cm, although $\langle 111 \rangle$ orientations, n-type silicon and different resistivity wafers were also examined. The 2000 $\text{\AA}$ films were generally etched at 25°C for 30 sec in freshly prepared HF diluted with an equal volume of deionized water. A variety of etching procedures were used in attempts to

reduce transfer of contaminants to the silicon surface and for comparisons with reported results. Pendant HF was removed either by rinsing in deionized water for about 10 min until the water resistivity reached 16 megohm-cm or by drying with nitrogen gas without solvent rinsing or by other procedures described below.

Film growth on etched silicon was allowed to occur in air in clean hoods in our oxidation laboratory. The temperature and relative humidity in this area remained at $25^\circ \pm 2^\circ\text{C}$ and 30-50%, respectively.

Impurities were adsorbed on sample surfaces either during processing or during exposure to the laboratory environment. Attempts were made to remove the adsorbed contaminants by rinsing in solvents or by heating at different temperatures in nitrogen gas. Oxidants in the nitrogen gas caused some modification of the oxides. Heating with quartz-iodine lamps in vacuum (10^{-7} Torr) reduced the level of surface contamination without modifying the oxides.

Oxide growth rates were determined using groups of wafers exposed to similar environments from which samples were randomly selected for examination by ellipsometry and ESCA. Etched wafers were stored either in metal containers, in plastic containers, or in deionized water. They were either exposed to room fluorescent lighting, 2537 $\text{\AA}$ ultraviolet light (Mineralight, UltraViolet Products, Inc.), or were kept in the dark. Unless explicitly stated, wafers were exposed to air in the dark or in red filtered light. Etched wafers were split into halves and comparisons were made on the same wafer in studies of the effect of light on film growth rates. Cleaved samples were formed by fracturing 2 ohm-cm, p-silicon slugs, essentially along the $\langle 111 \rangle$ plane, either in air, deionized water, or deionized water containing 1% isopropanol.

Ellipsometry.—The thicknesses of films formed on silicon substrates were determined using a Rudolf ellipsometer. All data points were measured in two zones with the quarter-wave plate at 45.00° , at a wavelength of 5461 $\text{\AA}$ and with an angle of incidence of 70.00° . For ultra-thin films on silicon substrates, the thicknesses were evaluated using the measured value of Δ and by assuming an index of refraction (n) of 1.47. A change in the imaginary part of the silicon refractive index [0.028 (9, 10)] affects the Δ value and, therefore, the ellipsometric film thickness value for a very thin oxide film; the real part of the index (4.076) will almost exclusively shift the Ψ value and not alter film thickness (11). An alternate value of 0.042 (12) has been assigned to the imaginary part of the silicon refractive index. Use of this value would decrease measured film thicknesses about 1.5 $\text{\AA}$.

Changes in ellipsometric measurements upon exposure of freshly prepared surfaces to air at 25°C in a darkened room indicated that film formation was occurring. The rate of impurity film growth on a 24 $\text{\AA}$

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Key words: native oxide, x-ray photoelectron spectroscopy (ESCA), ellipsometry, oxidation.

silicon dioxide film was about 0.05Å/min (assuming $n = 1.47$) during the first hour, followed by a much slower subsequent growth. Impurity film growth on freshly etched silicon, which rapidly formed about 7Å of film prior to the first ellipsometric measurement, was about 0.03Å/min during the first hour of exposure to air. Ellipsometer measurements were therefore made within 3 min after the surfaces were prepared.

ESCA.—ESCA has previously been described by Siegbahn *et al.* (13). An AEI photoelectron spectrometer with a magnesium anode in the x-ray source ($K\alpha_{12}$ radiation = 1253.6 eV) was employed in this work. About 10 to 20 min were required for preparing and mounting a sample of appropriate size and for evacuating the spectrometer sample chamber. Spectral data were obtained at a pressure of $<10^{-6}$ Torr from samples 0.2×0.5 in. A broad kinetic energy scan (1300 eV) of the sample was first obtained at 2 eV/sec. The kinetic energies of the photoelectron lines of interest were then scanned at a rate of 0.02 eV/sec. All data were referenced to the Au $4f^{7/2}$ line at 83.8 eV (14). The electron binding energies were determined to ± 0.1 eV by subtracting the kinetic energies of the emitted photoelectrons and a spectrometer correction from the energy of the incident x-rays; i.e.

$$E_b = E_{x\text{-ray}} - E_{\text{kinetic}} - E_{\text{spectrometer correction}}$$

The silicon dioxide binding energy data were corrected for a shift of +0.3 eV which was presumably due to charging (15). The magnitude of this shift was found to be independent of oxide thickness in the thickness range under consideration.

Estimates of the thickness of oxide films formed in air at room temperature were made from comparisons of photoelectron line intensities with intensity data extrapolations of O 1s and Si 2p photoelectron lines in silicon dioxide films oxidized at 850°C (16). The detection limit for an element decreases with film but is about 0.1 monolayer at the film surface. Therefore, trace impurities which might be observed in Auger and backscattering spectra after etching silicon are not detected by ESCA.

The carbon line, C 1s, was monitored on all samples examined. Wagner (17) has reported that the specific intensities of the O 1s and C 1s photoelectron lines are in the ratio of about 2:1. The number of carbon atoms in a given volume of amorphous carbon film is about twice the number of oxygen atoms in a similar volume of silicon dioxide film. A 10Å thick carbon impurity film, assumed to be amorphous carbon, contains $9.0\text{--}10.5 \times 10^{15}$ carbon atoms/cm³ whereas a 10Å thick silicon dioxide film contains about 4.5×10^{15} oxygen atoms/cm³. A carbon impurity film was therefore considered to be equal in thickness to an oxygen film with the same photoelectron line intensity.

Comparison of ellipsometric and ESCA measurements.—Reference oxide thicknesses were obtained from ellipsometric measurements of silicon dioxide films formed at 850°C by oxidation with 1% oxygen in nitrogen. The precision of these ellipsometric measurements is $<\pm 1\text{Å}$.

Changes in ellipsometric data of oxides or etched silicon exposed to atmospheric pressure occur rapidly relative to changes in the ESCA spectra obtained in vacuum. Therefore, ellipsometric measurements of film thickness were made immediately after sample preparation and were followed with ESCA measurements on the same wafer. Discrepancies can exist with respect to the thickness of films and oxides formed on etched silicon at room temperature. These may be related to desorption of volatile surface contaminants in the ESCA vacuum chamber which contribute to the film thickness measured by ellipsometry and/or adsorption of organic impurities in the ESCA spectrometer.

Both techniques provide average measurements of macroscopic sample areas. Discontinuities in ultra-

thin oxide films formed a room temperature in the presence of surface contaminants generally cannot be discerned using these techniques. The consistency and reproducibility of the ESCA and ellipsometric data obtained, however, permit conclusions to be reached concerning oxide growth at room temperature, despite the small differences in measured film thicknesses.

Results and Discussion

Freshly etched silicon wafers.—Typical ESCA spectra of the elements observed on a thermally grown silicon dioxide film are shown in Fig. 1a and are compared in Fig. 1b with elements observed in the spectrum of a freshly etched 2 ohm-cm $<100>$ silicon wafer. The spectra indicate the presence of oxygen (O 1s), carbon (C 1s), and silicon (Si 2p) photoelectron lines with binding energies of 532.5, 284.3, and 99.3 eV, respectively. An additional Si 2p line found at 103.7 eV, which corresponds to silicon in the silicon dioxide film (Fig. 1a), is not detected in the etched silicon spectrum (Fig. 1b).

The contaminants always found in ESCA spectra of etched silicon surfaces are carbon and oxygen. Fluorine is present in the ESCA spectrum only if a sample is etched and dried without a deionized water rinse. No detectable difference in the ellipsometric film thickness 7–8Å is observed when the etched sample is immediately dried or first rinsed in deionized water for 10–15 min.

The O 1s and Si 2p oxide line intensities on etched silicon (Fig. 1b) indicate that the film thickness of 7.4Å measured by ellipsometry does not correspond to an oxide film thickness. By extrapolation from thermally grown silicon dioxide data to be described elsewhere (16), the O 1s line intensity in Fig. 1b corresponds to an oxide film $<2\text{Å}$ thick or $<10^{15}$ oxygen atoms/cm². This oxygen line may either be due to oxygen bound to silicon or is associated with oxygen in species adsorbed or incorporated in impurities on the etched surface. Little can be deduced from the oxygen binding energy since no significant O 1s shift is observed for the weak, broad line shown in Fig. 1b from the O 1s line in Fig. 1a.

Significant differences in the concentration of oxygen present on freshly etched silicon surfaces have been observed. Chang (8) has estimated, from Auger spectral line intensities, that $2\text{--}5 \times 10^{15}$ oxygen atoms/

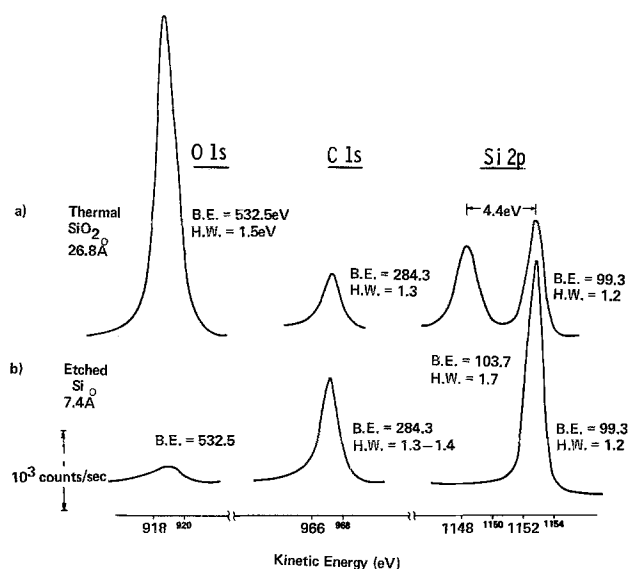


Fig. 1. Binding energies and relative line intensities for O 1s, C 1s, and Si 2p ESCA photoelectron lines (a) from silicon dioxide film grown at 850°C and (b) from a freshly etched silicon surface. Film thicknesses are determined by ellipsometry.

cm² are present on his etched, unheated silicon samples which is more oxygen than we observe with ESCA. Charig and Skinner (5) have published an Auger spectrum of unheated, cleaned silicon which appears nearly free of oxygen. We have repeated the etching procedure used by Charig and Skinner but no change was found in the result shown in Fig. 1b for the ESCA oxygen line intensity.

Carbon contamination on the etched silicon surface.—Carbon was always identified on all ESCA spectra. Particular attention was therefore given in an attempt to determine its source and its influence on the room temperature oxidation of etched silicon wafers.

Carbonaceous contaminants may be chemisorbed on our etched silicon samples, together with more volatile impurities, prior to insertion into the ESCA spectrometer. These contaminants contribute to the ellipsometric film thickness. Henderson (7) has observed that etching silicon with HF enhances carbon contamination and has suggested that the carbon impurity is co-deposited within the oxide phase during the etching step. Alternately, organic impurities may be exchanged with adsorbed HF at the etched silicon surface during the deionized water rinse. Other workers (8) have observed carbon contamination on etched silicon, even in oil-free vacuum systems, which suggests that a part of the carbon film may be transferred to the etched silicon samples prior to insertion into the ESCA spectrometer. In addition, carbon contamination may be attributed partly to oil backstreaming from the spectrometer vacuum pumps.

In order to reduce carbon contamination prior to insertion into the ESCA vacuum system, the silicon was etched in distilled HF solution, in distilled diluted (1:10) HF solution, in HF solution pretreated with crushed silicon to getter carbon (18), and in gaseous HF. The etched samples were either rinsed for 10 to 15 min in deionized water and then dried, immediately spun dry in a nitrogen ambient, immersed into distilled acetone to remove HF (2), or immediately rinsed in a carbon tetrachloride solution saturated with iodine. Very little change from samples etched in nondistilled HF, rinsed in deionized water, and dried in nitrogen gas was detected in most of the ESCA spectra. A small decrease in the carbon line intensity was observed when using the distilled acetone rinse. A decrease in ellipsometric thickness was also noted after rinsing in acetone (7.7-6.8Å) which is consistent with Archer's observations (2). Iodine was detected on the sample rinsed in carbon tetrachloride saturated with iodine in addition to the normally observed oxygen and carbon line intensities. The silicon bonding energy was unaffected by this rinse, but the oxygen line was shifted to a lower binding energy (532.0 eV) and the carbon was shifted to a higher binding energy (285.5 eV). The ellipsometric thicknesses of these films ranged from 30 to 40Å.

The ellipsometric film thicknesses of etched silicon were generally not changed by the different etching procedures used. It is not known whether these treatments had any effect on the carbon contamination present at the surface. Part of the nonvolatile carbon contamination on an oxide surface appears to originate from inside the spectrometer after the ellipsometric measurement is made. Transferring the sample in and out of the roughing pump insertion lock section of the spectrometer increases the ellipsometric film thickness. In addition, the sample is contaminated with carbon while in the ESCA vacuum chamber. On an etched silicon sample, an estimated carbon film thickness of 4.5-5.5Å (about $4-6 \times 10^{15}$ carbon atoms/cm²) is initially present, which increases to about 7Å after several hours in the ESCA vacuum chamber. Chang (8) has observed less carbon ($2-20 \times 10^{14}$ carbon atoms/cm²) in Auger spectra of etched, unheated silicon samples. Less carbon remains adsorbed under vacuum once an oxide surface is formed than on freshly etched silicon surface. After insertion into the ESCA spec-

trometer, a carbon film on an oxide surface is estimated at be 2-3Å thick initially and increases to about 5Å after 15 hr. The initial carbon film thickness can be reduced to about 1Å by minimizing the sample time in the roughing pump section of the insertion lock and by direct insertion into the ESCA vacuum chamber. A decrease of only about 1Å in carbon impurity level is detected by direct insertion of an etched silicon sample into the ESCA vacuum chamber. The additional carbon adsorbed during insertion into the spectrometer completely masked any improvements which may have been achieved by purification of the etchant or modifications of the etching procedure.

Oxidation and film growth on etched silicon surfaces.—Film growth on etched silicon wafers in air at 25°C exposed to room light was monitored both by ESCA and ellipsometry. Changes in the spectrum of the Si 2p line in the oxide with time are shown in Fig. 2 together with the corresponding ellipsometric changes in film thickness. The baseline of the silicon spectra is the spectrum of a freshly etched silicon surface. For comparison, the Si 2p line from a thermal oxide spectrum is shown in Fig. 2. The magnitudes of the shifts in the oxide binding energies from that of the silicon substrate binding energy, designated by δ , are given in Fig. 2. These shifts in binding energy will be discussed in a subsequent paper (19). The data for the increases in film thickness (ellipsometry) as a function of time on an etched silicon surface are summarized in Fig. 3 together with the estimated oxide thicknesses (ESCA). The initial oxide growth process as determined from ESCA spectra extrapolates back to the origin and has an oxide thickness dependency proportional to the logarithm of the oxidation time. Upon increasing the exposure time of the etched silicon surface to air, the intensity of the Si 2p oxide line is

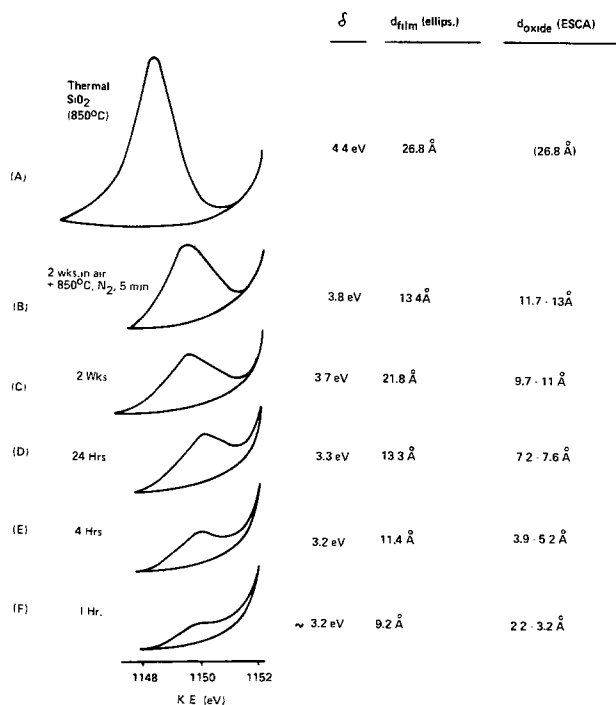


Fig. 2. Changes in the Si 2p oxide ESCA line as a function of exposure time to air at room temperature (samples C through E). The baselines correspond to the spectrum from a freshly etched silicon surface. Spectrum B is sample C exposed for 2 weeks to air followed by an anneal in nitrogen at 850°C for 5 min. Spectrum A is a silicon dioxide film 27Å thick grown in oxygen at 850°C. The difference in binding energies between the maxima of the Si 2p substrate and oxide lines are represented by δ values. The range in oxide thickness is based on estimates using both the Si 2p and O 1s line intensities.

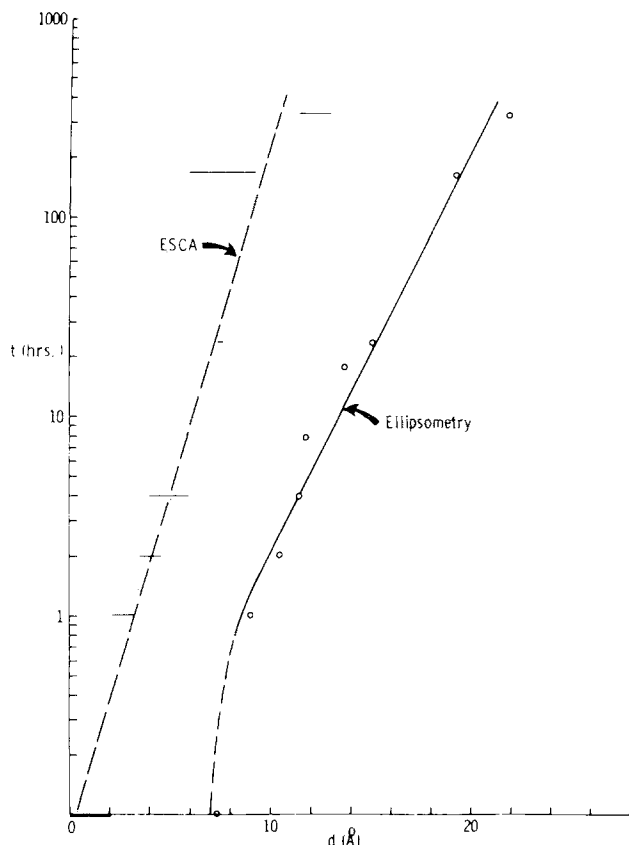


Fig. 3. Ellipsometric and ESCA thickness data plotted as a function of the logarithm of the time of exposure of etched samples to air at room temperature.

increased and its binding energy is shifted toward that of thermally grown oxide films. After exposure to air for 2 weeks, both the binding energy and the line intensity were still significantly different from that of the thermal oxide. After a 1 year exposure to air at room temperature, negligible additional change in the oxide binding energy or line intensity was observed. From this data and the cleavage experiments described below, an equilibrium oxide film thickness for oxide growth at room temperature in air is estimated to be $<14\text{\AA}$. This value is considerably lower than previous indications which were based on ellipsometric measurements (2,4).

Oxide growth and impurity adsorption occur simultaneously on etched silicon wafers during exposure to air at room temperature. The difference between an ellipsometric film thickness and estimated film thickness (ESCA) is often too large to be accounted for by nonstoichiometry or densification of the oxide film. Volatile contaminants are presumably adsorbed from air and desorbed in vacuum and contribute to increase the ellipsometric film thickness relative to the estimated ESCA film thickness.

Heating an oxide to 850°C for 5 min in nitrogen at 1 atm pressure was found to remove the adsorbed species from the oxide surface. Milder conditions were sought to remove the adsorbed contaminants from oxide surfaces formed in air at 25°C . Samples were rinsed in various solvents or heated to 200°C in nitrogen for 5 min. Although some scatter is observed, the results given in Table I are characteristic of the changes in ellipsometric film thickness found on different quarters of the same wafer as a function of sample treatment. Solvent rinses (aqueous, organic) reduce the film thickness. An additional decrease is observed by heating at 200°C . However, a significant additional decrease in adsorbed contaminants is obtained by heating the sample at 850°C . It has been reported (8) that a temperature of $>800^\circ\text{C}$ is required to remove the carbon adsorbed on silicon.

Table I. Effect of solvent rinses and heating on ellipsometric film thickness of films formed on etched silicon

	Etched Si, $\text{\AA}$	SiO_2 (thermal), $\text{\AA}$
t_0	7.2	27
Air; R.T.	18 (5 weeks)	33 (4 months)
Solvent rinse	17	30
200°C , N_2 , 5 min	16	—
850°C , N_2 , 5 min	12	27
	(ESCA: $d_{\text{oxide}} = 12$)	(ESCA: $d_{\text{SiO}_2} = 27$)

Closer agreement is obtained between ESCA and ellipsometry with regard to oxide thickness after heating the exposed etched samples at 850°C in nitrogen. For example, when the etched sample left in air for 5 weeks is heated at 850°C in nitrogen at 1 atm pressure for 5 min, a decrease in ellipsometric thickness from 18 to $12\text{\AA}$ is observed. A second example, shown in Fig. 2, indicates that the oxide film thickness (ESCA) increased due to oxygen impurities in the nitrogen gas stream (1-5 ppm) from 10 to $12\text{\AA}$ and a small increase in the silicon binding energy of 0.1 eV was detected. Negligible changes in the ESCA spectra were observed for exposed samples after heating at 850°C in vacuum for 15-20 min. The observed difference in binding energies between silicon dioxide and oxides formed in air at 25°C is not related to densification of the oxide film, since similar binding energies are not obtained even after heating at 850°C .

Oxidation of cleaved silicon surfaces.—Silicon single crystals cleaved in air form oxide films more rapidly than do etched silicon wafers. For example, the thinnest oxide film observed on a cleaved silicon surface was 5-7 $\text{\AA}$ thick after 5-10 min exposure to air. This thickness was estimated from ESCA spectra taken 15-20 min after cleaving the sample. If exposure to air is increased about 10 min, the estimated oxide film thickness is 10-12 $\text{\AA}$. For comparison, etched silicon wafers with either $\langle 100 \rangle$ or $\langle 111 \rangle$ orientations possess oxide films only 2-3 $\text{\AA}$ after 1 hr exposure to air. After 3 and 24 hr of exposure of the cleaved sample to air, the estimated oxide thickness is 11-13 $\text{\AA}$. Each of the cleaved samples exposed to air and then examined by ESCA contained carbon contamination on the silicon surface similar in thickness to carbon on etched oxide surfaces.

Cleavage of the silicon crystal either in deionized water or in deionized water containing an intentionally added organic impurity both significantly reduce the rate of oxidation on the clean surface even in the absence of HF. For example, a sample cleaved in deionized water containing 1% isopropanol, dried, and then examined by ESCA about 5-10 min after cleavage possessed an oxide film 1-2 $\text{\AA}$ thick. The cleaved silicon oxidation results are summarized in Table II.

As is shown by the cleavage experiments, an oxide can readily grow on a clean silicon surface in air at room temperature. Etching in HF results either in HF or other impurities to be adsorbed on the silicon surface and reduce the rate of oxide growth. The adsorbed impurities provide a barrier to the initial oxidation of the etched silicon surfaces. Deionized water,

Table II. Oxide growth on cleaved silicon samples

Cleavage ambient	Exposure time (to ambient)	d_{ox} (estimated), $\text{\AA}$
Air	5-10 min	5-7
Air	20 min	10-12
Air	3 hr	11 $\pm$ 2
Air	24 hr	11-13
DI H_2O	5-10 min*	3-4
1% isopropanol in DI H_2O	5-10 min*	1-2

* A 0.5-1 min exposure to aqueous media (to simulate HF etch step) followed by drying, mounting the sample on a holder, and insertion into the spectrometer.
Temperature: 24°C .

which contains organic impurities in the ppm range, reduces the rate of oxide growth on cleaved samples with respect to air. Roikh *et al.* (20) have shown that water vapor in air increases the rate of oxidation of silicon at room temperature when compared with dry air. It is the presence of impurities on the sample surface or in the deionized water which limits the oxide growth rate on silicon rather than the reactivity of water with silicon at room temperature. Isopropanol (1%) in the deionized water further reduces, but does not eliminate, oxide growth.

Factors affecting oxide growth rates on etched silicon.—Oxide growth rates on etched silicon wafers at room temperature were examined by ellipsometry and ESCA as a function of wafer orientation, dopant type and concentration, exposure to ultraviolet light, and storage in deionized water. Typical ellipsometric data are shown in Fig. 4 for growth rates in air on p-type silicon surfaces. Ellipsometric results indicate that a freshly etched $\langle 111 \rangle$ oriented wafer surface possesses $\leq 5\text{\AA}$ of film. The ESCA spectra of these surfaces are identical and indicate the presence of $\leq 2\text{\AA}$ of oxide. The C 1s line intensities on $\langle 111 \rangle$ and $\langle 100 \rangle$ etched silicon surfaces are equal. After exposure to air in the dark (in a metal container), both ellipsometry and ESCA indicate that an oxide is forming somewhat more rapidly on the $\langle 111 \rangle$ surface than on the $\langle 100 \rangle$ surface. This initial difference in oxidation rate may be related to the difference in thickness of the impurity film adsorbed on the silicon surfaces in air.

The dopant concentration in the silicon substrate affects the oxidation of an etched silicon surface (21). Similar ellipsometric and ESCA results were obtained for growth on p-type (boron) and n-type (phosphorus) silicon wafers as a function of dopant concentration. Lightly doped ($\sim 5 \times 10^{14}/\text{cm}^3$) silicon wafers appear to exhibit the same film growth rate as do the 2 ohm-cm ($\sim 5 \times 10^{15}/\text{cm}^3$) wafers. However, heavily doped 10^{-3} ohm-cm silicon wafers with about 10^{20} dopant atoms/ cm^3 oxidize more readily than the 2 ohm-cm wafers. For example, freshly etched 10^{-3} ohm-cm wafers possess an ellipsometrically measured film 8.5–10Å thick and an estimated (ESCA) initial oxide thickness of 2–4Å. In contrast to the results of Ritter *et al.* (22) which indicated that an anomalously thick oxide layer formed in air on etched, p-type 10^{-2} ohm-cm silicon, p-type 10^{-2} ohm-cm

($10^{19}/\text{cm}^3$) silicon wafers exhibit an intermediate growth rate between that of 2 and 10^{-3} ohm-cm silicon. The rate of subsequent oxide growth in air is more rapid on the heavily doped silicon and is indicated by both ellipsometry and ESCA. It is suspected that differences in impurity adsorption on highly doped silicon surfaces and changes in the reactivity of the heavily doped silicon both contribute as causes for the enhanced oxidation.

Immersion of freshly etched silicon wafers into non-agitated, deionized water at room temperature generally reduced the rate of oxide growth when compared with growth in air. As previously indicated, oxidation of cleaved surfaces also occurs less readily in deionized water than in air. In a static system, the growth of an oxide film on an etched silicon wafer often proceeded at a normal rate only after an induction period. This induction period was occasionally observed for etched wafers immersed in deionized water or for rinsed wafers contained in a closed plastic container. For example, no changes in ellipsometric film thickness from the t_0 measurement were observed for a period of 6–10 hr for samples contained in a closed container. Once oxide growth was initiated, subsequent oxidation within the container occurred at a normal rate. When an etched wafer is rinsed in stirred deionized water, the rate of oxidation is increased. Bubbling nitrogen or oxygen gas through the deionized water also increased the rate of oxidation.

The etched silicon surface is hydrophobic due to the presence of Si-F bonds (23) or adsorbed HF. Covalent organic impurities, present in the deionized water in trace quantities, are preferentially adsorbed on the silicon as the HF goes into solution. These impurities apparently form a barrier film which inhibits aqueous oxidation of the silicon. Water or oxygen permeation into this barrier is enhanced by agitation of the system. Modification of the adsorbed barrier film by coadsorption of water or ionic species from solution can make the surface of the sample appear hydrophilic.

The frequency distribution of laboratory fluorescent lighting extends into the near ultraviolet. Exposure to this light accelerated the oxide growth rate on etched silicon when compared with oxide growth in the dark. The effect of ultraviolet light on oxide growth is shown in Fig. 4 using light with a wavelength of 2537Å. Irradiated films were compared with films grown in the dark after 3 weeks by ellipsometry and ESCA when an oxide has nearly reached its equilibrium thickness in air in the dark. Results in Table III indicate that both the total film and estimated oxide thicknesses are greater after exposure to ultraviolet light than after growth in the dark. The extent to which oxidation is modified by ultraviolet irradiation is much less than is indicated by ellipsometric measurements. The ESCA spectrum indicated that the exposed wafers possessed a significant increase in the thickness of the carbon impurity film on the oxide surface. Multiple carbon lines rather than the single carbon line normally observed suggested that the adsorbed carbon film was modified due to photolysis at the silicon surface. This result suggests that an organic film is present on the silicon surface prior to insertion into the ESCA spectrometer. The presence of ozone or heating of the wafer during exposure were experimen-

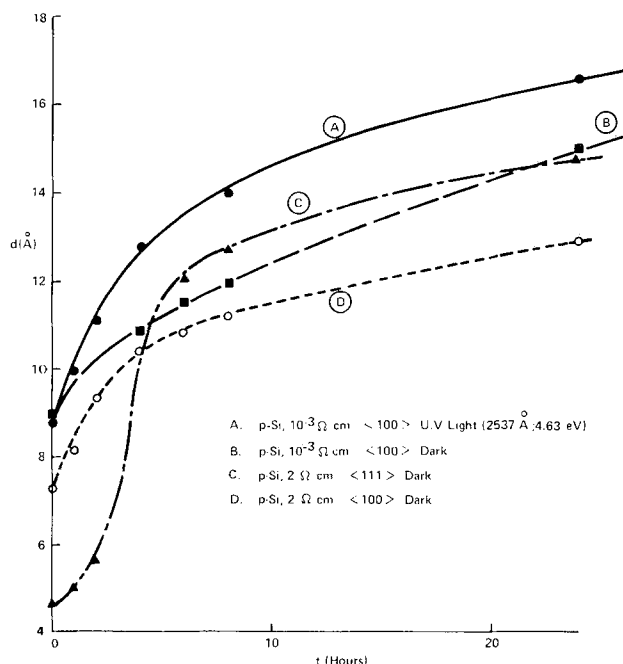


Fig. 4. Film growth rates on etched silicon wafers at room temperature measured by ellipsometry.

Table III. Effect of ultraviolet light on oxide growth in air

Technique	Measurement of	UV (2537Å), Å	Dark, Å
Ellipsometry	Total film thickness	44.5	17.8
ESCA	Estimated oxide thickness	15-16	11

Temperature, 25°C.
Exposure time: 3 weeks.

tally eliminated as possible causes for the increase in oxide thickness.

Cabrera (24) has reported that ultraviolet irradiation enhances the oxidation of aluminum and Oren and Ghandhi (25) have made similar observations for oxidation of silicon at elevated temperatures. However, Fehlner (26) has recently noted that ultraviolet irradiation of silicon under clean, dry conditions does not affect silicon oxidation. It remains to be determined whether our observations of the enhanced oxidation of silicon are related only to irradiation of silicon with ultraviolet light or to irradiation in the presence of impurities.

Summary

Impurities are rapidly adsorbed on moderately doped substrates after etching in HF. The film present on a freshly etched silicon surface and measured by ellipsometry is primarily an impurity film rather than an oxide film. A Si 2p oxide photoelectron line is not detected on a freshly etched silicon surface. The intensity of an oxygen photoelectron line for a substrate etched and then rinsed in deionized water indicates that $<2\text{\AA}$ of oxide is present. A difference in surface behavior is observed between a freshly etched silicon wafer and an oxidized wafer. More carbon is initially adsorbed on an etched surface than on a surface with oxide present. It is likely that <0.1 monolayer of silicon dioxide (detection limit of ESCA) forms on a freshly etched silicon surface rinsed in deionized water and exposed to air and that the oxygen detected in the ESCA spectra is largely from adsorbed oxidized impurities. Oxide film thicknesses on etched silicon surfaces, as well as oxide growth rates, are therefore overestimated by ellipsometry.

The initial oxide growth rates on etched silicon surfaces in air or water at room temperature are lower than on cleaved silicon surfaces. HF etching enhances the rate of impurity adsorption on a silicon surface relative to the rate of surface oxidation. An induction period is sometimes observed during which oxide growth does not occur on etched silicon but it is not observed once oxidation is initiated. The thickness of the impurity layer on etched silicon is decreased after oxidation is initiated and its effect on the rate of subsequent oxidation of silicon is also decreased.

A number of factors affect the rate of oxide growth on etched silicon at room temperature. An increased oxide growth rate is observed if the substrate dopant (n- or p-type) concentration is $\geq 10^{19}/\text{cm}^3$. The oxide growth rate in air is greater on $<111>$ oriented substrates than on $<100>$ surfaces. Ultraviolet light (2537Å) also increases the oxide growth rate in air. However, the major effect of ultraviolet irradiation is to increase the nature and film thickness of the carbon impurities at the silicon surface presumably by a mechanism different from that of adsorption in the dark. The equilibrium oxide thickness in air at room temperature is less than 14Å unless the substrate dopant concentration is greater than $10^{19}/\text{cm}^3$ or the substrate is exposed to u.v. light during oxidation.

Acknowledgments

We are grateful to F. W. Anderson, A. Berman, D. L. Klein, W. A. Pliskin, and B. H. Vromen for many helpful discussions.

Manuscript submitted April 1, 1974; revised manuscript received Oct. 14, 1974. Portions of this paper were presented as Paper 357RNP at the Miami Beach, Florida, Meeting of the Society, Oct. 8-13, 1972.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1975 JOURNAL. All discussions for the December 1975 Discussion Section should be submitted by Aug. 1, 1975.

Publication costs of this article were partially assisted by IBM Corporation.

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