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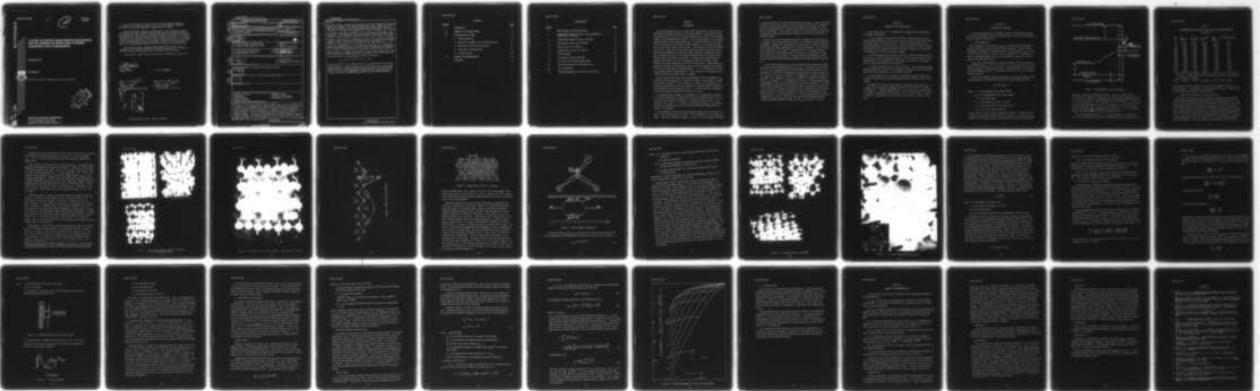
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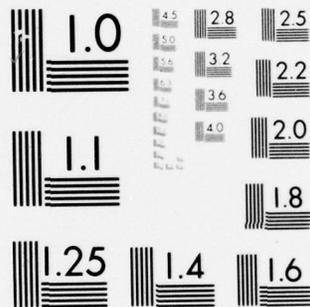


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A STUDY OF SILICON OXIDE GROWTH MECHANISMS FOR THE PURPOSE OF IDENTIFYING HARDNESS ASSURANCE TOTAL DOSE SCREENS

February 1977

Final Report



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AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base, NM 87117

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ture was searched, analyses were performed, and special wooden ball molecular models were studied. The current model of oxide layer growth and the relations of such growth to total dose susceptibility were gleaned from the literature. This model was extended by the study as follows: Q_{SS} is caused by an oxygen atom which is bonded to three interface silicon atoms. This produces an interface donor state whose energy is above the silicon conduction band. N_{SS}^+ is primarily caused by a Si-O-Si bond in which the oxygen has been removed leaving a stretched Si-Si bond. This produces two interface states; a donor level near the valence band and an acceptor level near the conduction band. N_r near the band edges has the same cause as N_{SS} . The oxygen is removed from the Si-O-Si bond by direct action of the radiation and by the attractive action of the positively charged ions which produce Q_r . Q_r is a result of the holes which are produced by the ionizing radiation being trapped on silicon excess centers. Silicon excess centers are centers where one oxygen is bonded to three silicon atoms in the bulk of the SiO_2 . The excess centers are distributed according to the form

$$A_{Si} = K(e^{-\alpha x} - e^{\alpha(x-2t)}) / (1 + e^{-2\alpha t})$$

The susceptibility to Q_r is proportional to Q_{SS} measured after oxidation, before annealing. Internal electric fields are important in oxide growth processes and the growth can be influenced by anything which alters the field. Finally, the extended model was examined for suggested hardness assurance screens and suggested experiments to confirm the extensions.

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SECTION I
INTRODUCTION

The problem addressed by this report stems from efforts to harden silicon semiconductor devices to surface or total dose effects. Two surface effects are produced by the action of ionizing radiation on the silicon dioxide layers common to silicon semiconductor devices. One of these effects is the apparent accumulation of positive space charge (Q_r). The second effect is the production of electrically active defect centers located at the interface between the silicon and the silicon dioxide layer. These centers are called interface states (N_r). During the last few years, empirical efforts have been made to minimize these effects by varying the growth parameters (temperature, thickness, oxidizing gas, etc.) of the silicon dioxide layer or by adding impurities (aluminum, chromium) to the layer. Processes exist today which will produce oxide layers on silicon semiconductor devices with these surface effects sufficiently suppressed to satisfy military needs. There remains the problem of assuring that the devices produced by these processes on a production line are indeed hard to surface effects, i.e., an unintentional variation in processing has not reduced hardness. Thus, some sort of acceptance test, called a hardness assurance screen, is needed.

Work in the past has shown that surface effects could be annealed out of the oxide layer by baking (e.g., 300°C for 24 hours). One successful screening procedure consists of first irradiating a device, thus determining its radiation susceptibility, and then annealing the induced effects (reference 1). This procedure is very involved and costly. A simple electrical measurement involving no special ambient would be much less costly.

Two approaches are possible. One approach is to experimentally measure all measurable properties, determine the radiation susceptibility by a radiation test, then look for correlations. The second approach (which is the subject of this report) is to examine the most detailed model of the responsible basic mechanisms to see if any correlations between measureables and hardness are suggested.

The procedure of examining the most detailed model available normally will yield no new insights unless the model is first extended to include some new ideas. Then, such a model may suggest a screen, and it may suggest variations

in processing which will produce harder device oxide layers. Here, we extended the model by including the electric field present during growth, so that the currently accepted models of thermal oxide growth were expanded to include anodic oxide growth. Also, molecular models of the silicon lattice were used to study the oxidation process atom by atom and to explore the structure of interface states.

There are two surface properties which can be measured by simple electrical methods. One, the surface state charge, Q_{SS} (normally given in electronic charges/cm²), produces the same effects in the silicon as a sheet of electrostatic charge and seems unaffected by any surface potentials. Two, the interface state density, N_{SS} (given in states/cm²/eV), is a spectrum of energy levels located in the forbidden gap of silicon which can trap and/or recombine electron and hole carriers. The post-irradiation properties Q_r and N_r are the radiation induced properties detected by the same methods as Q_{SS} and N_{SS} .

In the following sections, the insight obtained from extending the model are used to develop hypotheses about Q_{SS} and N_{SS} . We propose that the rate that silicon is stripped off the silicon lattice during oxide growth is proportional to a function of temperature and oxygen partial pressure times Q_{SS} . For increases in rate due to increases in temperature or electric field, Q_{SS} decreases. For increases in rate due to increases in oxidation nucleation sites, Q_{SS} increases. It is hypothesized that N_{SS} is a direct measure of the oxygen chemical activity at the silicon-silicon dioxide interface. We relate the radiation susceptibility of the oxide layer to the amount of excess silicon in the oxide. The amount of excess silicon is determined by the balance between the rate of silicon introduction and the rate of oxidation of the extra silicon, i.e., the oxygen activity. Thus, we propose that a function of temperature, Q_{SS} and N_{SS} , may prove to be the desired hardness assurance screen and that variations of either Q_{SS} and N_{SS} are cause for concern.

SECTION II
SUMMARY OF THE PRESENT MODEL

In March 1967, Deal, et al. (reference 2) suggested the following model for thermal oxide growth:

a. At the oxygen-silicon dioxide interface, oxygen enters the SiO_2 increasing the stoichiometric proportion of oxygen in the SiO_2 above the normal two oxygen atoms for each silicon atom. The excess oxygen cannot be uniformly distributed on an atomic scale but must be located in discrete centers. The structure of the centers can be an interstitial oxygen or a single dangling oxygen bond, called a non-bridging oxygen.

b. At the silicon-silicon dioxide interface, silicon interacts with silicon dioxide to form silicon excess centers. A silicon excess center can be an oxygen vacancy, a single dangling silicon bond, or an oxygen atom bonded to three silicon atoms instead of the normal two.

c. The above centers diffuse into the bulk SiO_2 . Since the excess oxygen center diffuses more rapidly than the excess silicon center, the two recombine near the silicon interface, i.e., within 100 to 200 Å.

d. After growth, the oxide contains oxygen excess centers except for a region 100 to 200 Å from the silicon interface which contains silicon excess centers.

This model could explain the production of positive space charge (Q_p). It is known that this charge is trapped within 200 Å of the silicon interface (reference 2). A commonly proposed model is that this positive space charge is trapped in the excess silicon centers, item b. of Deal's model. There is no generally accepted model of what causes the increase in interface states (N_p).

SECTION III
EXTENSIONS OF THE MODEL

In this section the model is extended to explain additional data about Q_{SS} , the electro-chemical nature of the oxide film, and the lattice structure of the silicon at the interface.

1. Surface Charge Q_{SS}

Deal (reference 2) proposed that Q_{SS} was a volume charge distributed in the 100 to 200 Å of oxide next to the silicon interface. However, Powell (reference 3) performed an experiment which is best explained if Q_{SS} is within 20 Å of the interface. If this is true, Q_{SS} cannot be a volume charge. Powell's experiment suggests that Q_{SS} is an interface state and is not located on the same centers as Q_r .

If Q_{SS} were a volume charge, it would be trapped on the same centers as the radiation charge Q_r . Thus, the size of Q_{SS} would depend directly on the number of centers as would the size of Q_r . There would then be a direct correlation between Q_{SS} and Q_r . A correlation as direct as this has not been generally observed.

If Q_{SS} were a volume charge and distributed on the excess centers, then because positively charged excess centers are unfilled electron states,

$$Q_{SS} \cong (1-f)\bar{N}_{es} \cdot \Delta X \quad (1)$$

where ΔX is the thickness of the layer (100 Å)

\bar{N}_{es} is the average density of excess centers

f is the Fermi factor

$(1-f)$ is approximately $\exp [(E_i - E_f)/kT]$

E_i is the energy level of the excess center

E_f is the Fermi level of electrons

In the silicon, at oxide growing temperatures (1000°C), the Fermi level E_f must be in the center of the gap as shown in figure 1. In going from the silicon to the silicon dioxide, the electrostatic potential must change by

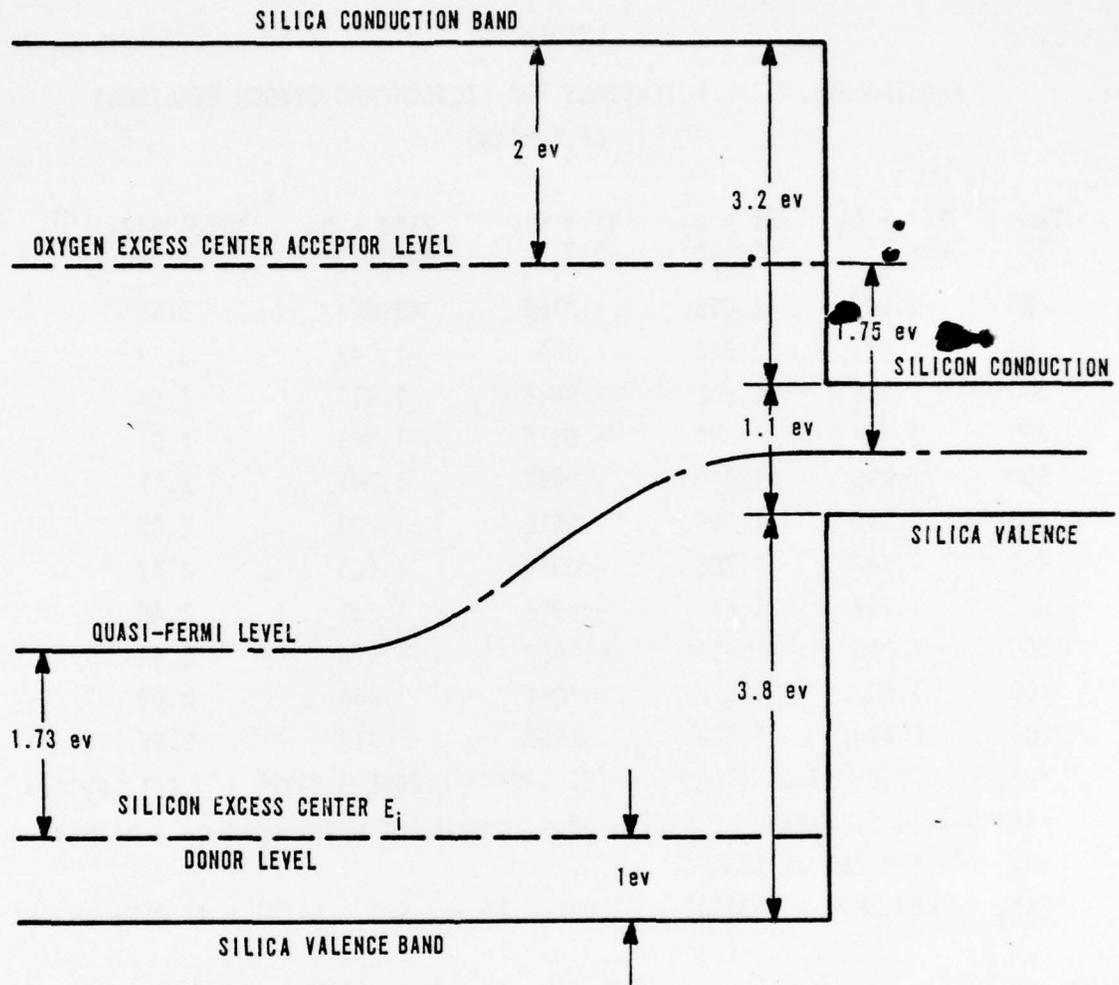


Figure 1. Band Diagram of Si-SiO₂ Interface.

the amount of the electrochemical potential, 1.616 V at 1000°C (table 1). The value of E_i is about 1 eV above the SiO₂ valence band (reference 4) which is in turn 3.8 eV below the valence band of silicon (reference 3). Then $(1-f) = 8 \times 10^{-8}$ and using $Q_{ss} = 10^{11}$ charges/cm², $N_{es} = 1.2 \times 10^{24}$, which is about 10² times the atomic density and is quite impossible. Temperature corrections to take the above room temperature energy levels to 1000°C are about 5 percent (reference 5), which would not change the result.

Thus, the hypothesis that Q_{ss} is a volume charge and is distributed in the 100 to 200 Å band near the silicon interface as proposed by Deal does not

Table 1.

ELECTROMECHANICAL POTENTIALS FOR SILICON AND OXYGEN REACTIONS
 ΔF_t (volts)

Temp °C	2Si + O ₂ →2SiO*	Si + O ₂ →SiO ₂ **	Si + SiO ₂ →SiO	2SiO + O ₂ →SiO ₂	$K_{(E_{SiO}-E_{SiO_2})/kT}$
25	-2.043	-2.058	+0.0153	-2.074	0.55
65	2.031	2.040	+0.0091	-2.049	0.73
300	1.956	1.932	-.0246	1.917	1.64
400	1.924	1.886	-.0376	1.848	1.91
500	1.890	1.840	-.0497	1.791	2.11
600	1.846	1.795	-.0612	1.734	2.25
800	1.787	1.705	-.0819	1.623	2.42
900	1.752	1.661	-.0912	1.569	2.46
1000	1.716	1.616	-.1000	1.516	2.49
1100	1.686	1.572	-.1081	1.464	2.49
1200	1.644	1.529	-.1157	1.413	2.49

* $\Delta F_t = -97709. + 3.84 T \log T + (.16E-3)T^2 - (.295E + 5)T^{-1} + w.45T$, Bulletin 542, U.S. Bureau of Mines, 1954, corrected using heat of sublimation of $-.76,619$ cal at 1880°C .

** $\Delta F_t = -203,380. - .43T \ln T - (1.06E-3)T^2 + (.98E + 5)T^{-1} + 47.01T$.

fit the data and can be rejected in favor of the hypothesis that Q_{ss} is an interface state. This extension of the model says that Q_{ss} is a donor state with an energy level above the conduction band.

2. Constraints Imposed by the Lattice Structure

The silicon crystal lattice is by definition a regular structure with short and long range order and with certain separations between atoms. Obviously, this structure must impose limitations on the structure of the interface between the silicon lattice and the amorphous silicon dioxide surface layer. The purpose of this section is to theoretically explore, using wooden ball molecular models, possible surface structures and the attendant implications. The study is restricted to considering only structures involving silicon and oxygen atoms. With this restriction, only three bonding configurations are probable. First, the oxygen can have one bond with the silicon

lattice and either one or none with the amorphous SiO_2 . Second, the oxygen can have two bonds with the silicon lattice. The third configuration consists of triply coordinated oxygen with three bonds to three different silicon atoms.

In the following discussion, two bonding structures will be defined. Standard quantum mechanical considerations of the way the energy levels of these structures must split will qualify them as candidates for the structure of the defects which cause Q_{SS} , the fixed interface charge resulting from oxidation, and N_{SS} , the interface state density following oxidation. To find experimental confirmation that these structures are indeed Q_{SS} and N_{SS} , the implications of the hypothesis are explored. By studying the way they are created, N_{SS} is related to oxygen activity during oxide growth and Q_{SS} to the rate of oxidation. By assuming that stoichiometrically excess silicon introduced during growth is the cause of the hole traps which produce flat band shift, a complex formula predicting effective hole trap density as a function of Q_{SS} , N_{SS} , temperature, and oxide thickness is derived. The formula is not inconsistent with known experimental data, and it suggests new experiments.

When oxygen forms a single bond with the silicon lattice, it would normally have a second bond with the amorphous SiO_2 . However, attempts to attach SiO_2 tetrahedra to the silicon lattice yielded a negative result. Basically, the lattice constraints of the crystal forms of silica are so different from silicon that order cannot be transferred across the interface. This situation is shown in figure 2, which actually, is very unreal. The $\langle 111 \rangle$ surface is shown bonded to silica tetrahedra. In silica the Si-O-Si bond is from 3 to 3.1 Å long. The $\langle 111 \rangle$ surface (see figure 3) has silicon atoms, with one dangling bond per atom, in equilateral triangles 3.84 Å on side, i.e., in figure 1, the silica tetrahedra wouldn't be tetrahedra. If order is not transferred across the interface, then there must be frequent defects. The knowledge that the oxide reduces 10^{15} dangling bonds of the cleaved lattice to between 10^{10} and 10^{11} interface states (reference 2) indicates that such single bonds are uncommon.

The possibility of oxygen making a single bond (nonbridging oxygen) with the surface cannot be discarded on theoretical grounds. However, such a bond would produce an interface acceptor level near or below the valence band. These have not been observed.



Figure 2. Unsuccessful Attempt to Place Silica Tetrahedra on the Silicon $\langle 111 \rangle$ Plane.

Considering the single bond cases results in the conclusion that, bridging bonds between the lattice and the oxide cannot exist in any great number (i.e., $> 10^{10} - 10^{11}/\text{cm}^2$, nonbridging oxygen would produce an unobserved energy level).

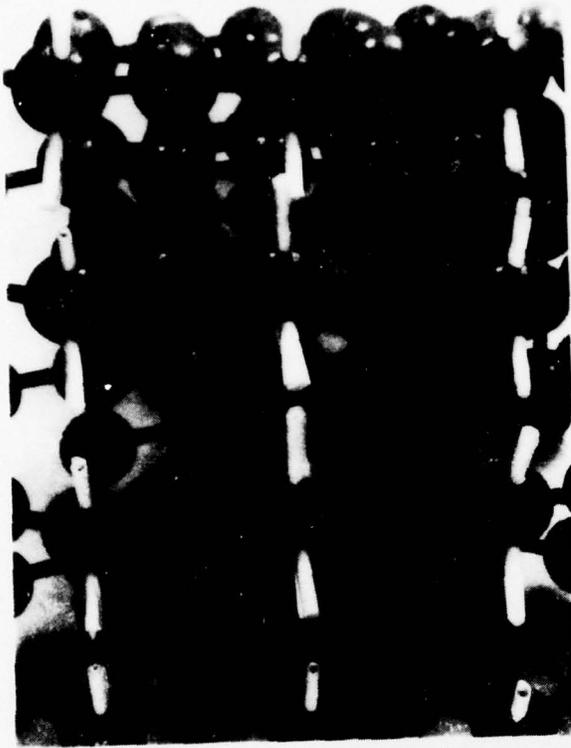
Next, consider the double lattice to oxygen bond case. Here oxygen forms bonds with two different Si atoms in the lattice. In figure 3, the available Si bonds are shown for the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ planes. Surprising is the fact that the broken bond density, σ , is the largest for $\langle 100 \rangle$. This is the reverse of the occurrence of Q_{SS} , the surface charge density, and N_{SS} , the interface state density. Figure 4 shows the simple way that oxygen atoms can be double bonded to the silicon lattice in the $\langle 100 \rangle$ case. Because of the way the wooden balls were drilled, figure 4 shows a Si-O-Si bond angle. Silicon atoms in the Si-O-Si bonds of figure 3 are 3.84 Å apart. This bond is 3 to 3.1 Å in silica. Accordingly, this bond is probably straight, as it is in β - quartz.

In the $\langle 110 \rangle$ and $\langle 111 \rangle$ cases, the Si-O-Si bonds can be made in more than one way. The ways are illustrated in figure 5 $\langle 110 \rangle$ and figure 6 $\langle 111 \rangle$. As can be seen in figure 3, the atoms of the $\langle 110 \rangle$ surface are in chains as shown in figure 5. These chains are separated by 5.43 Å centerline to centerline. The atoms in different chains are at least 4.5 Å apart. Thus, the passivation* of the chains can proceed independently of each other. In figure 5, locations for the passivating oxygen location atoms are numbered. To passivate the chain, only every other oxygen location on each side of the chain is filled; i.e., all the 1's or all the 4's and all the 3's or all the 2's. Clearly, this is a more complicated passivation structure and defects are more probable than in the $\langle 100 \rangle$ case.

From figure 3, it can be seen that the surface atoms on the $\langle 111 \rangle$ surface have an equilateral triangle pattern as represented by the small circles in figure 6. In figure 6, the possible oxygen sites are large circles. Only a sixth of the circles actually have oxygen atoms in them when the surface is fully passivated. In figure 6, six oxygen sites about one atom have been numbered. Other sites have numbers with a line over them, e.g., $\bar{3}$. The

*The Si-O-Si bond has the ionization energies of silica, i.e., very far above and below the band gap of silicon. Because the electrons in this bond are accordingly made inactive, the making of these bonds is called passivation.

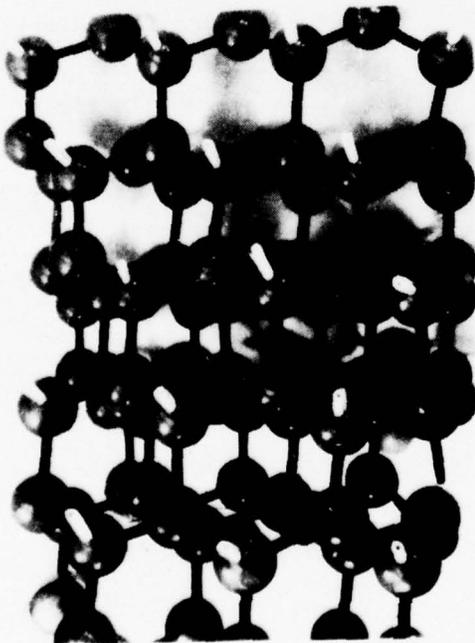
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$$\langle 100 \rangle \sigma = 1.36 \times 10^{15} \text{ cm}^{-2}$$



$$\langle 110 \rangle \sigma = .959 \times 10^{15} \text{ cm}^{-2}$$



$$\langle 111 \rangle \sigma = .27 \times 10^{15} \text{ cm}^{-2}$$

Figure 3. Broken Bond Patterns of the Si Interface, σ is the Broken Bond Density.

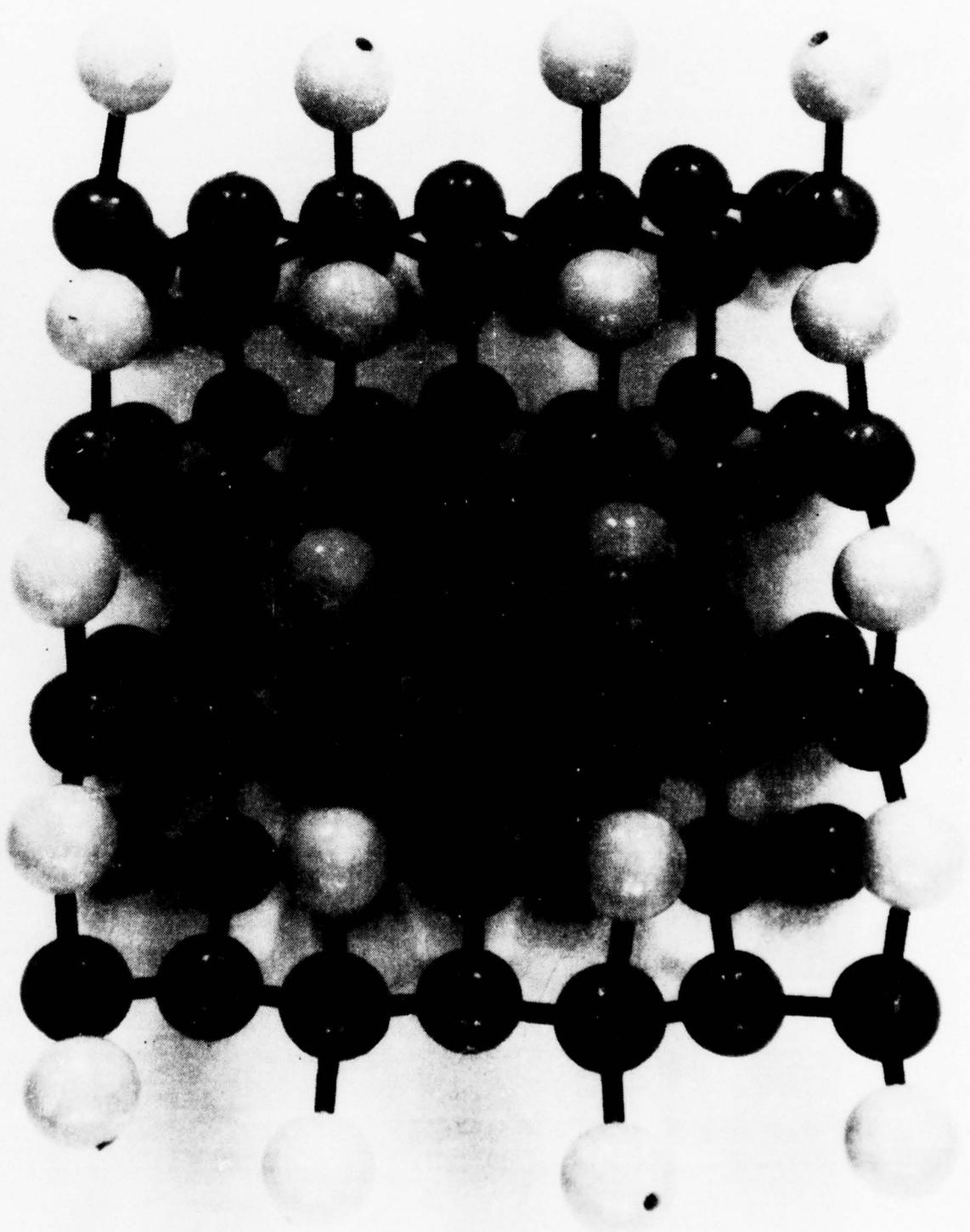


Figure 4. Passivation of the $\langle 100 \rangle$ Interface. White Balls are Oxygen.

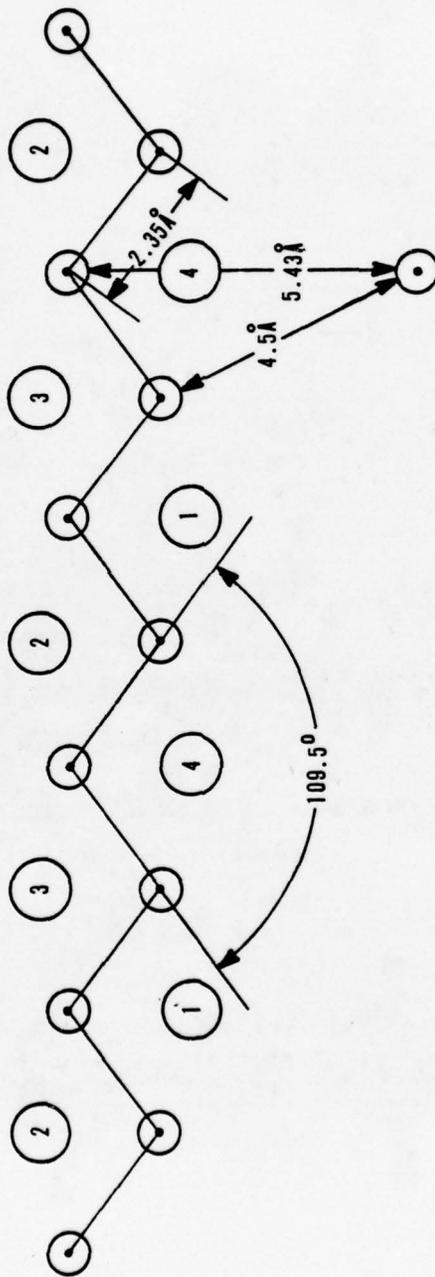


Figure 5. Chain on the $\langle 110 \rangle$ Surface.

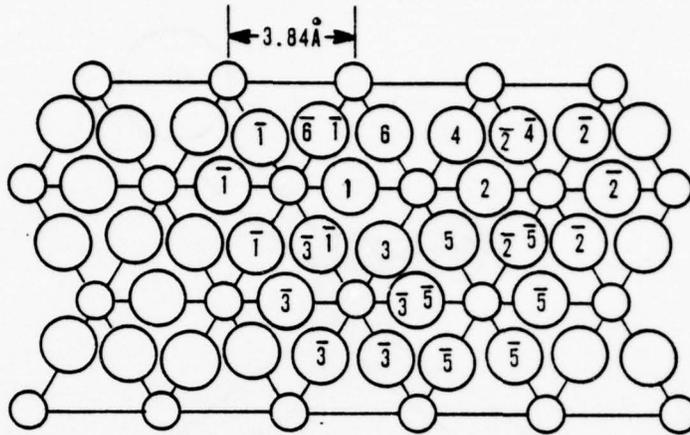


Figure 6. Oxygen Sites on the $\langle 111 \rangle$ Surface.

overlined numbers mean that if there is an oxygen atom in the numbered site, there cannot be one in this site and vice versa. Clearly, this $\langle 111 \rangle$ face has a still more complicated passivation structure than the $\langle 110 \rangle$ face and defects would be still more probable.

The above discussion shows the way that the dangling, energetically unfavorable, broken bonds of a perfectly cleaved silicon surface can be passivated with stable Si-O-Si double bonds. Because no surface is perfectly cleaved and because entropy forbids a perfectly orderly passivation of such surfaces, there will be defects in this order. Such a defect is a pair of dangling bonds with no oxygen atom. Specifically, one of the oxygens in figure 4 could be removed leaving two unpassivated bonds. A similar situation occurs in bulk silicon. In figure 7 the SiA center (reference 7) is shown. The SiA center is a defect in the bulk caused by a substitutional oxygen. The levels in this center are produced by the stretched Si-Si bond. Because the silicon atoms are further apart, the splitting between the bonding (valence band) and the anti-bonding (conduction band) is less. Thus, two levels are created in the forbidden gap. Similar levels would be produced by such a stretched bond on the surface. The above yields a model for observed states near the band edges (references 4, 5, and 6). Also, as shown in figure 7 (ψ_A) the energy level of a single dangling bond which is now unsplit, would be in the center of the band gap. For the remainder of this report, let N_{SS} denote the levels near the band edges only.

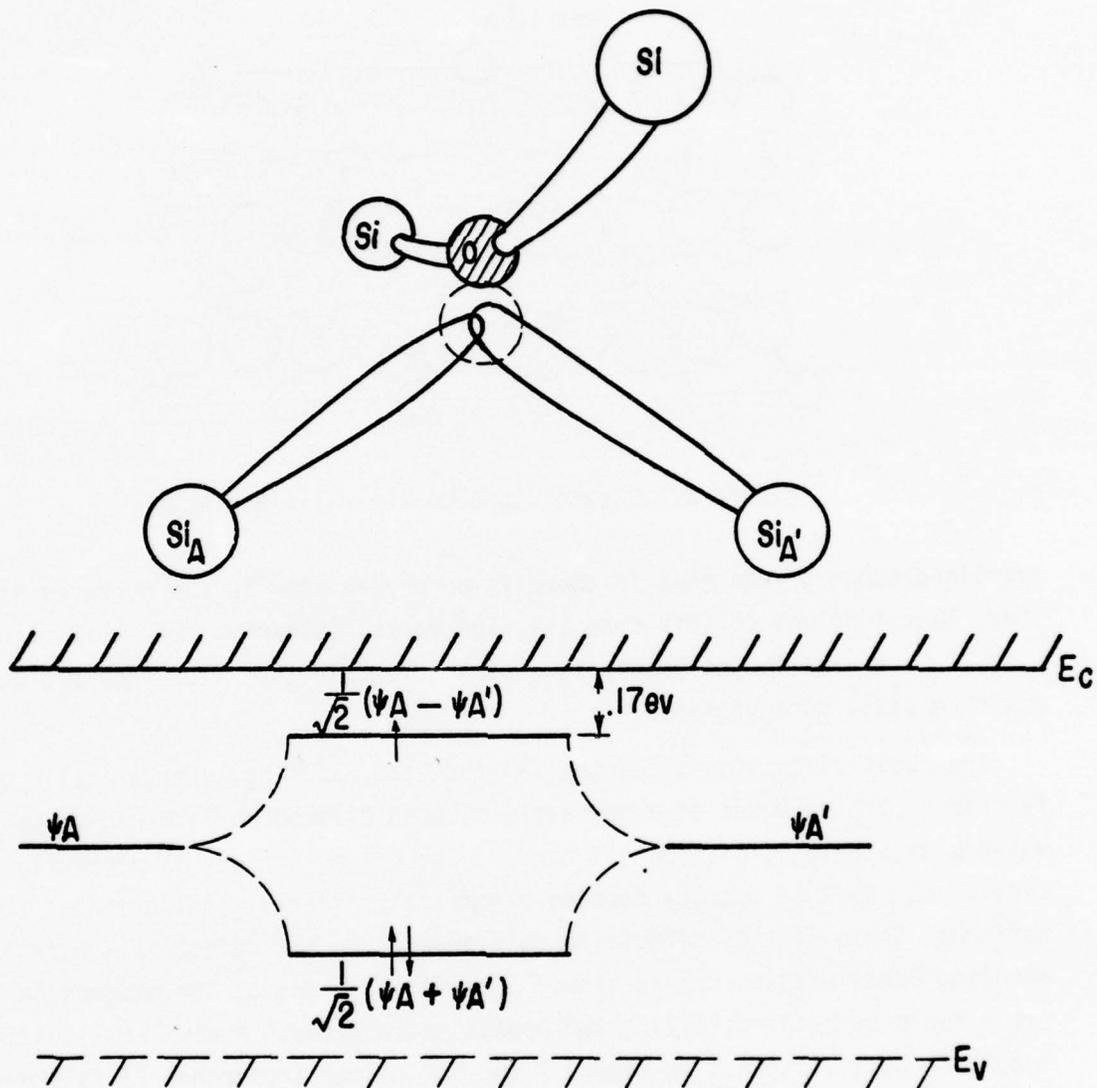


Figure 7. The SiA Center (reference 7).

The number of these states (N_{ss}) which are not passivated by an oxygen atom will be determined as thermodynamically required by the law of mass action, i.e.,

$$N_{ss} A_o = F(T)e^{-E_s/kT} \quad (2)$$

where A_0 is the oxygen activity (= oxygen atom concentration at the silicon interface)

T is absolute temperature

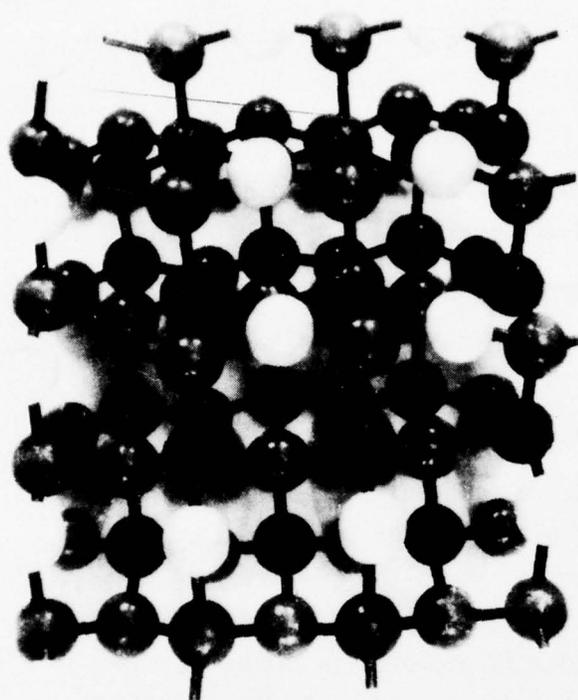
$F(T)$ is some varying function of temperature and has a radically different value for different Si lattice planes

E_s is the activation energy for separating the oxygen from the pair of dangling bonds

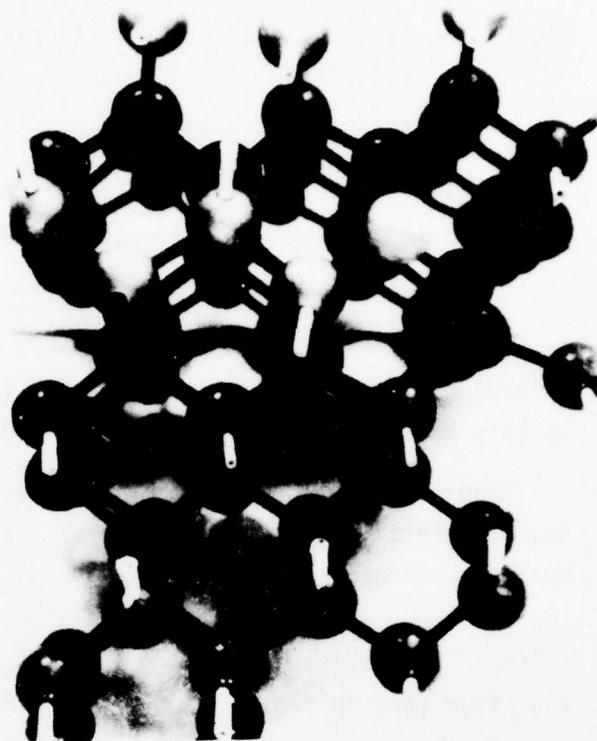
Accordingly, a lack of oxygen near the interface produces N_{ss} , and N_{ss} is inversely proportional to oxygen partial pressure.

Conditions which permit triply bonded oxygen can be found by exploring the way the silicon surface oxidizes. Each plane must be penetrated by removing a silicon atom. Then succeeding atoms in the plane are removed, spreading in circular waves, peeling the plane away like the leaves of a magazine in a fire. The nature of this exposed plane edge is explored in figure 8. In the $\langle 100 \rangle$ case in figure 8, notice the three exposed bonds. In the oxidizing process the oxygen atoms take the position of the silicon atoms to which they are bonded. The displaced silicon atoms enter the oxide and the starting structure is repeated. Thus, the plane is progressively stripped off. In the $\langle 110 \rangle$ case, planes are stripped off by nipping off the end of the chain (figure 6). The process of stripping in each case produces a local region much more oxygen deficient than other areas of the interface. Imperfect passivation is likely and pairs of unpassivated bonds do not have time to diffuse to adjacent sites. Centers of the type shown in figure 9 are likely to occur. Figure 8 shows how this center occurs in each of the cases. The center has two silicon atoms with their broken bonds well screened by the oxygen. The third silicon has its fourth bond partially screened by the same oxygen. This situation, studied in SiO_2 glass by Weyl (reference 8) results in a center with a very loosely bound electron where a net positive charge is energetically favorable. At the interface such a structure with a positive charge and the neutralizing electron orbiting in the silicon conduction band could be the source of the positive fixed charge Q_{ss} . The resulting level would be above the conduction band edge where the Fermi level would never reach it, thus a fixed charge.

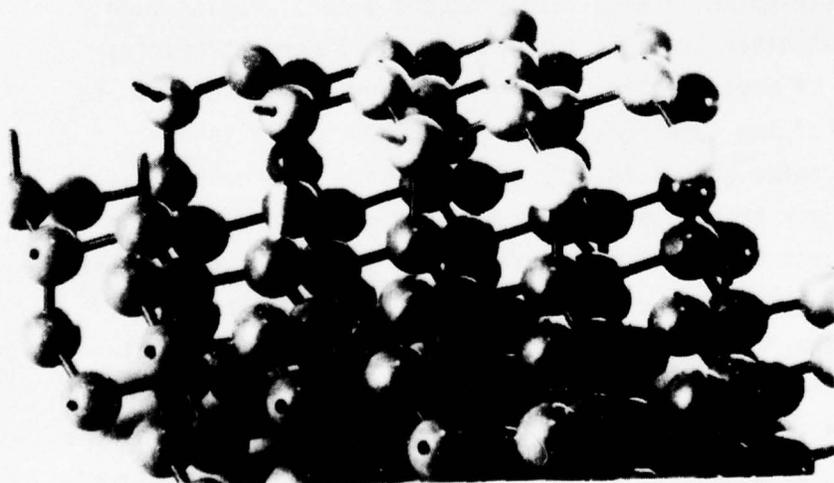
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<110>



<111>

Figure 8. The Exposed Crystal Plane Edge.

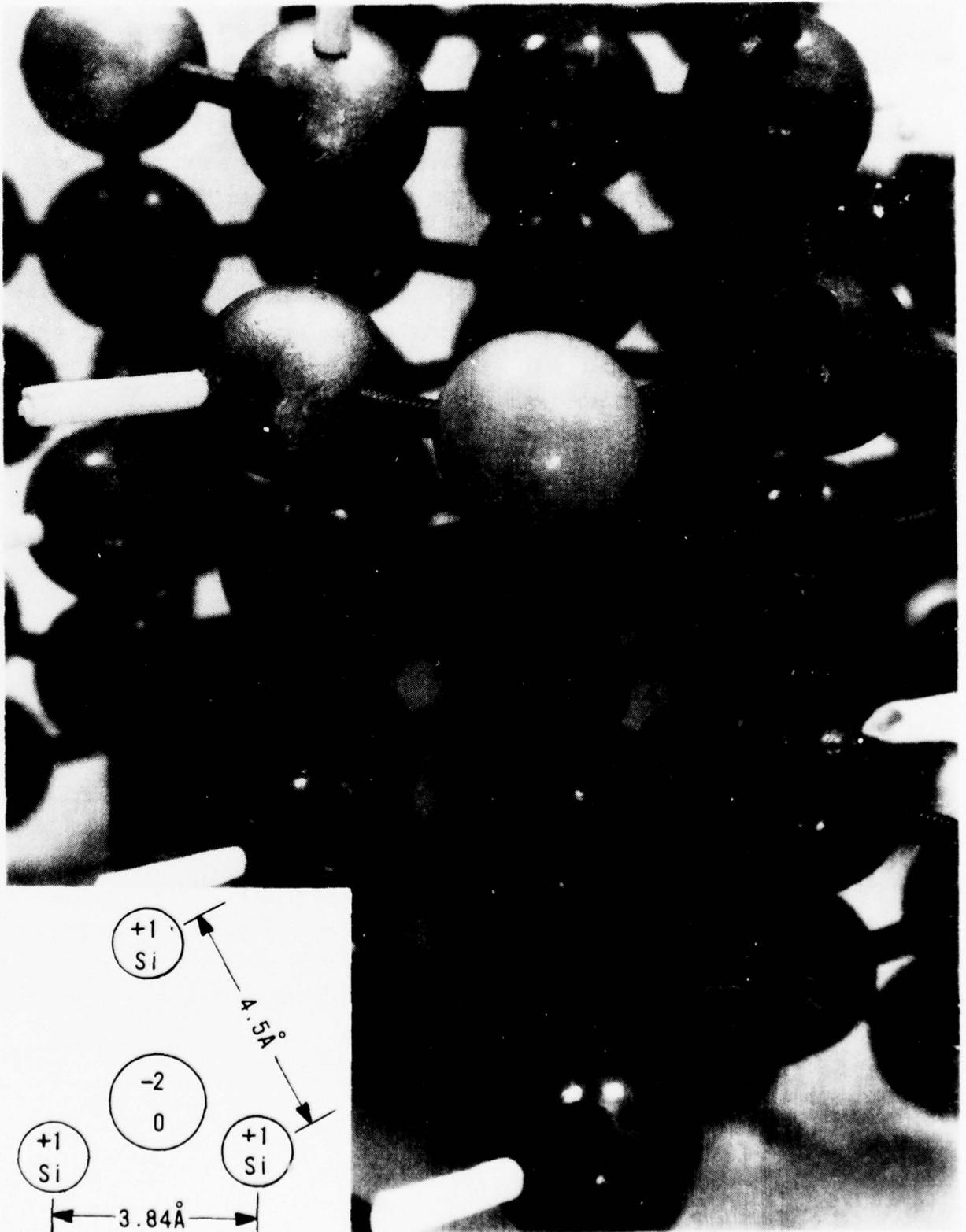


Figure 9. The Triply Coordinated Oxygen Center.

Next, consider the way successive planes of silicon are removed. Given the assumption that the silicon oxidizes more readily at the plane edges than on the surface of the plane, the condition discussed above results in a model of oxide growth. The oxidation of each successive plane must begin with the puncture of the plane surface. The plane is then quickly oxidized off, uncovering the next plane. A puncture can occur just as readily on a plane which is already punctured as one which is not. If this puncturing is a random process, then the probability of a puncture must be proportional to the exposed area. This situation can be visualized as rain falling in a pool of water; the rain drops are the punctures and the expanding wavelets are the oxidizing edges. The analogy is not perfect, in that in the pool of water, two wavelets flowing together do not disappear. However, it illustrates that there are two important independent parameters, the rate of punctures and the wave velocity of the oxidizing edge. Each must obey the Arrhenius form,

$$R = N\nu e^{-E_a/kT} \quad (3)$$

where N is the number of available sites

ν is the vibration frequency $\sim 10^{13} \text{ sec}^{-1}$

kT is the thermal energy

E_a is an activation energy which can be modified by electric fields

The structure shown in figures 8 and 9 requires that Q_{SS} be proportional to the total of all oxidizing edge arc lengths remaining after cooling. Then Q_{SS} increases with puncture rate and decreases with oxidizing wave velocity. It is known that Q_{SS} decreases with temperature (reference 2). This effect can be produced if the activation energy of the wave velocity is greater than the activation energy of the puncture rate. Observe that each puncture (which oxidizes one silicon atom) sets off a wave which oxidizes many silicon atoms. Thus, most of the silicon atoms come from the wave front. Since the total wave front arc length is proportional to Q_{SS} , then from equation (2), the rate that silicon atoms enter the oxide is

$$R = R_0 Q_{SS} \exp(-E_{SS}/kT) \quad (4)$$

where R_0 is a function of temperature equal to Nv/Q_{SS}

E_{SS} is the activation energy for the wave front.

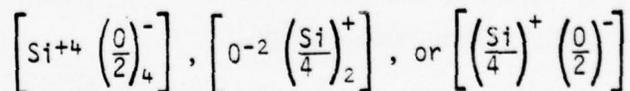
There is no reason to believe that the ratio of N to Q_{SS} does not vary with temperature so R_0 contains temperature components from N/Q_{SS} and v . R_0 will also contain A_0 as a factor, as shown in the next section (3).

Thus the lattice produces at the edge of a plane a region where three bonds must be made with oxygen rather than the energetically more favorable two. This produces a model relating Q_{SS} to growth rate.

3. The Electric Field at the Interface

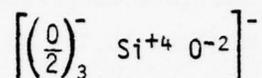
In 1962 Jorgensen (reference 9) showed the electrolytic nature of the SiO_2/Si system by making a reversible $Pt/SiO_2/Si$ electrolytic cell. Hot, very pure SiO_2 must then be an electrolyte, i.e., be ionized. Here, the possible nature of the ions in SiO_2 will be explored, as well as the effects of the electrolytic nature has on the growth of the oxide film. This will introduce the presence of an electric field in the oxide. In the following discussion, the possible forms of the ions will be explored and then the possible electric fields will be investigated. The viewpoint of Weyl (reference 8) and his notation will be used.

Weyl approached the bonding of silica from a starting point of completely ionized atoms, Si^{+4} and O^{-2} . The outer electrons on the oxygen are loosely bound, and when brought close to the Si^{+4} , they assume more tightly bound states which screen the positive charge in the silicon. Weyl regarded the covalent bond from an electrical screening viewpoint and indicated this bond and the coordination by writing the bonded ions adjacent to each other, i.e.,

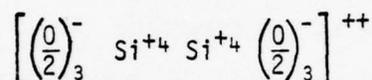


When the bonds an atom is making are only partially indicated, only half or a quarter of the atom is shown.

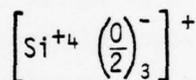
If pure SiO_2 is an electrolyte, then SiO_2 must divide into ions somewhat like water divides into hydrogen and hydroxyl ions. There are two possibilities for the negative ion; interstitial O^{-2} ions and the non-bridging oxygen bond.



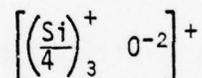
There are three possibilities for the positive ion: an oxygen vacancy



a dangling silicon bond

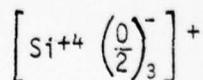


or "trily coordinated oxygen"



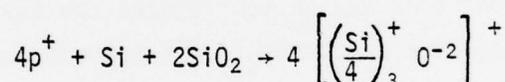
Energetically, the triply coordinated oxygen is more favorable because it results in better screening, i.e., the charges are more diffuse (each Si would be left with only one third of an unscreened positive charge). In the case of the dangling silicon bond, there is one extra positive electronic charge. The oxygen vacancy requires two positive charges side by side and its existence obviously requires too much energy.

Diffusion or motion of the non-bridging oxygen is achieved by breaking a bond of an adjacent oxygen and making a bond with the previously unbonded oxygen. Diffusion of the triply coordinated oxygen requires that one of the silicons break its triply coordinated bond, briefly forming a dangling bond,

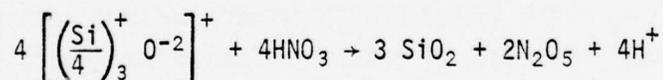


The silicon then passes through the center of the triangle made by the three oxygens and makes a triply coordinated bond on the other side by bonding to a formerly doubly coordinated oxygen. In the case of excess oxygen ion diffusion, the extra energy required to form the ion can be transferred along with the non-bridging character. Diffusion of triply coordinated oxygen requires enough energy to form a dangling silicon bond. Thus, we would expect from the above that oxygen ions would diffuse more readily than silicon, which is the observed case (reference 10).

Oxide films can be grown in three different ways: (1) thermal, in an oxidizing atmosphere; (2) anodic, anodize in special liquid electrolytes (e.g., tetrahydrofurfuryl alcohol solutions); (3) plasma, anodize using an oxygen plasma as the electrolyte. During anodic growth, silicon moves to the electrolyte SiO_2 interface. It is also known that either light or another (doping) source of holes is required at the Si-SiO_2 interface. Thus, anodic growth consists of a half cell reaction

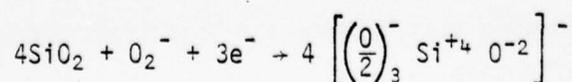


and the transport of the silicon excess centers to the SiO_2 -electrolyte interface, e.g., in a concentrated nitric acid solution where oxidation is completed by



The H^+ ions then proceed to the other electrode in the nitric acid to complete the circuit.

In the case of plasma anodization, activation energy to create oxygen excess centers at the SiO_2 plasma interface is available from the bombarding oxygen ions.



These centers are transported toward the Si-SiO₂ interface by diffusion and the electric field. The excess silicon ions are transported by the electric field toward the SiO₂ plasma interface. The two types of centers can combine in the bulk of the SiO₂.

A thermal oxide could proceed by a process similar to plasma. However, despite Jorgensen's experiment, thermal oxidation must proceed mostly by uncharged oxygen excess centers for the following reasons.

(a) There is no external circuit to carry the electrons from the silicon interface to the oxygen interface.

(b) Grove (reference 10) indicates that there are 5×10^{16} O₂/cc. If these were all uniformly distributed charged oxygen excess centers, i.e., (1×10^{17}) charges, then integrating Poisson's equation, the charge density in a 1000 Å thick film would result in a potential of 4.5 volts.

(c) It is known that in thermal oxidation, the oxygen diffuses toward the silicon interface rather than the silicon toward the oxygen interface. In thermal oxides, the negative electrode is not present, however, the positive electrode is present. Accordingly, positive silicon excess centers can be created and drawn into the oxide if the necessary field is present. Once the excess center is in the oxide, a hole can quantum mechanically tunnel back to the silicon, leaving an uncharged center behind. Thus, thermal oxide could proceed by the process of introducing excess silicon centers into the first 100 Å of the silicon dioxide, where excess oxygen centers combine with them to form stoichiometric SiO₂. The rate of excess silicon center introduction would depend on the field.

In anodic and plasma oxidation, there is an applied electric field present. According to Jorgensen's experiment (references 9 and 11), there is a chemical EMF present during the growth of thermal oxides. In table 1, these electrochemical potentials for various reactions are recorded. The possibility that the electric field present during oxidation could have an important influence on the resulting oxide is discussed in the following paragraphs.

Consider the formula that Cabrera and Mott (reference 12) give for the rate of oxidation of metals

$$dx/dt = NV v \exp [-(W+U)/kT] \sinh [qaE/kT] \quad (5)$$

where: V is the volume per metal atom in the oxide

$$\approx 1/(2.3 \times 10^{22})\text{cm}^3,$$

n is the number of sites per cm^2 on the interface from which a metal atom can be extracted (figure 10),

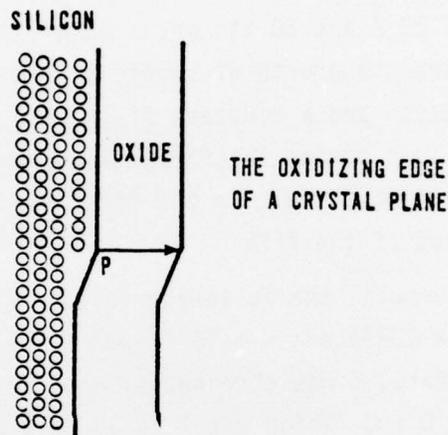
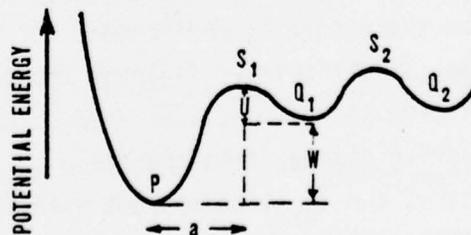


Figure 10. The Oxidizing Edge of the Crystal Plane.

ν is the vibrational frequency of the metal atom $\sim 10^{12} - 10^{13} \text{ sec}^{-1}$,
 W and U are the activation energies of ion creation and diffusion of the metal ion as shown in figure 11,



THE ION POTENTIAL

Figure 11. The Ion Potential.

q is the electronic charge,

kT is the thermal energy,

E is the electric field, and

a is the distance shown in figure 11.

The formula can be applied to SiO_2 growth data. First, from Wegener (reference 13), 8 Å of thermal oxide takes 5 min at 850°C and 15 min at 800°C (also at 850°C, 15 min gives 23 Å and 30 min gives 43 Å). Second, Schmidt (reference 14) reports room temperature growth of anodic oxide with a growth rate of 25 Å/min at a constant 7 mA/cm² and a constant field of 0.26 V/Å or 3.8 Å/V. However, there is a 30 V jump during the first minute which corresponds to an unknown thickness, indicating a field in the first few angstroms greater than the 0.26 V/Å in the rest of the film.

To evaluate this formula, the following values were assigned: $N = Q_{\text{SS}} = 10^{10} \text{ cm}^{-2}$; $V = 1/(2.3 \times 10^{22}) \text{ cm}^3$; $\nu = 10^{13} \text{ sec}^{-1}$; implying $NV\nu = 2.6 \times 10^{10} \text{ Å/min}$. For Wegener's data, E was obtained by dividing the value from table 1 by 6 Å and solving for $W + U$, which was 2.36 eV (6 Å was chosen because the rate was nearly linear from 8 Å, thus some thickness less than 8 Å was needed). For Schmidt's data, the above $W + U$ (i.e., 2.36 eV) was used to solve for E , which was 3.4 V/Å (30 volts across 8.8 Å gives 3.4 V/Å). Consistent results are then obtained with the above formula if the available voltage is expressed across the first 6 to 9 Å.

The above analysis is based on the idea that there is a high field in the first 6 to 9 Å. This field (0.23 to 3.4 V/Å) has not been detected after oxidation. Since it corresponds to 10^{13} to 10^{15} negative charges per cm², it would have been seen if it was present. Consequently, either it anneals when the wafer is removed from the oxidizing environment, or it is not there. In the case of thermal oxide, an alternative field is possible. If each Q_{SS} site is assumed to have a positive charge, and also, opposite it in the oxide, there is an opposing negative charge, then the field to pull the silicon into the oxide is only present at the Q_{SS} site and not everywhere, and the formula in equation (5) would still apply. This nonuniform field would still be affected by externally applied fields so the above possibilities can still be explored experimentally.

In the discussion, the form that ions might take in SiO_2 has been explored, as well as the electric fields that might be present. It was concluded that the nonbridging oxygen and the triply coordinated oxygen were the most likely form of the ions and that a field produced by separate individual dipoles is the most likely in thermal oxides.

4. Final Model of Oxide Growth

The idea of a nonuniform charge sheet leads to modification of the Cabrera and Mott model. Given Q_{SS} with a positive charge, then a nearby negative charge could pull this ion away from the interface. Where do the negative charges come from? Williams (reference 15) has observed at room temperature electron trapping centers 2 eV or more below the SiO_2 conduction band. Williams (reference 15) also gives 4.25 eV as the energy difference between the silicon valence band and the silicon dioxide conduction band. The Fermi level in the silicon must be at the intrinsic point at thermal oxide growing temperatures (i.e., $E_F - E_{\text{valence}} = 0.55$ eV). Then the above trapping centers are ~ 1.7 eV above the Fermi level as shown in figure 1. Thus, given these traps are within quantum mechanical tunneling distance, they will be filled by electrons from the silicon with an activation energy of ~ 1.7 eV. If these traps are assumed to be oxygen excess centers, a complete model of the oxidation process is obtained.

Thermal Oxides

Oxygen is absorbed at the oxygen SiO_2 interface forming neutral oxygen excess centers. The neutral oxygen excess centers diffuse to the silicon interface where they are charged negatively. Then they are drawn toward a Q_{SS} center until the force between the oxygen and the positive Q_{SS} center is large enough to pull a silicon atom out of the silicon.

Examination of figures 8 and 9 will show that this involves breaking two Si-Si bonds. The excess oxygen center can satisfy only one of these bonds. The second bond becomes an excess silicon center. The excess silicon center diffuses into the oxide until it meets and combines with another oxygen excess center to make stoichiometric SiO_2 . The oxidation rate is given by

$$\frac{dx}{dt} = Q_{SS} R A_0 V_{ve}^{-\left(E_0 - E_F\right)/kT} \quad (6)$$

where A_o is the oxygen excess center activity

= the excess center concentration given as 10^{17}cm^{-3} by Grove (reference 10) for dry oxygen 10^{19} for steam

R is a reaction rate constant

= $R_o e^{-E_R/kT}$ where E_R is the activation energy for the Q_{SS} negative oxygen center reaction

$E_o - E_F$ is the energy difference required to charge the oxygen center
 = 1.7 eV

Grove (reference 10) has shown that the activation energy for this reaction is 2 eV; as shown earlier, the decreasing of Q_{SS} with temperature adds a requirements for an additional 0.3 eV; then E_R must be about 0.55 eV, half the silicon band gap. It is interesting to note that 10^{17} centers/cm² is one center per 210 Å cube. Thus for films less than 210 Å the basic solubility must change, probably increase, causing an increase in A_o and causing the initial rapid growth described in Grove (reference 10).

Plasma and Platinum Electrode Oxide

The growth of plasma oxides and the platinum electrode oxides of Jorgensen (references 9 and 11) differs from the growth of thermal oxides in that the oxygen excess centers are charged at the plasma or platinum interface and diffuse or can be driven through the oxide film as ions. At the silicon interface, the negatively charged excess oxygen ion draws a silicon from the Q_{SS} complex, the same as in thermal oxides. The combination produces a silicon excess center which can be easily charged positive by quantum mechanical tunnelling of a hole from the silicon. The silicon excess ion is then drawn toward the plasma or platinum interface. As the silicon excess ions move, they help to electrically neutralize the space charge of the oxygen excess ions and may frequently combine with oxygen ions to form stoichiometric SiO_2 . The creation of new oxide in the middle of the film should create a film which is both denser and more highly stressed (easily etched) than thermal oxides.

Anodic Oxides

In the case of anodic oxides, the silicon must be drawn from the Q_{SS} complexes by the applied electric field. Here the above formula from Cabrera and Mott applies. The positive silicon excess ions proceed rapidly to the

electrolyte interface producing negligible space charge to modify the applied field. At the electrolyte interface, the silicon excess centers are oxidized to stoichiometric SiO_2 .

In each of the above methods of oxide film growth, silicon centers are left behind when the growth process stops. We would expect the plasma/platinum oxides to leave behind a generally ionized and stressed film. Anodic oxides might be very excellent unless some neutral excess silicon centers are created and left near the silicon interface.

In thermal oxides, a residue of dissolved oxygen and excess silicon is left. The excess silicon is next to the silicon interface penetrating into the oxide with a decreasing exponential, the solution for lossy diffusion.

$$D_{\text{Si}} \nabla^2 A_{\text{Si}} - \langle \sigma v \rangle A_0 A_{\text{Si}} = 0$$

$$A_{\text{Si}} = B e^{-\alpha x} + c e^{+\alpha x} \quad (7)$$

where $\alpha = \sqrt{\langle \sigma v \rangle A_0 / D_{\text{Si}}}$

D_{Si} is the diffusion constant for excess silicon centers

A_{Si} is the excess silicon center activity (concentration)

D_{Si} contains an activation energy $E_{D_{\text{Si}}}$

$\langle \sigma v \rangle$ is the capture constant of oxygen excess centers for silicon excess centers

A_0 is the oxygen excess center concentration $\propto 1/N_{\text{SS}}$

B and c are constants to be determined by boundary conditions

The boundary conditions are

1. At $x = 0$ the flux of centers as determined by Fick's equation must be equal to twice the rate that Si atoms enter the oxide, i.e.,

$$J_{\text{Si}} = \left(-D_{\text{Si}} \nabla A_{\text{Si}} \right)_{x=0} = \frac{1}{V} \frac{dx}{dt} = D_{\text{Si}} \alpha \left(B e^{-\alpha x} - c e^{+\alpha x} \right) \quad (8)$$

2. At $x = t$, the thickness of the oxide, the presence of an oxygen atmosphere will oxidize any remaining excess Si centers thus

$$Be^{-\alpha x} + ce^{+\alpha x} = 0 \quad (9)$$

With the above boundary conditions, the solution for A_{Si} is

$$A_{Si} = K \left(e^{-\alpha x} - e^{\alpha(x-2t)} \right) / \left(1 + e^{-2\alpha t} \right) \quad (10)$$

where $K = J_{Si} / D_{Si} \alpha$

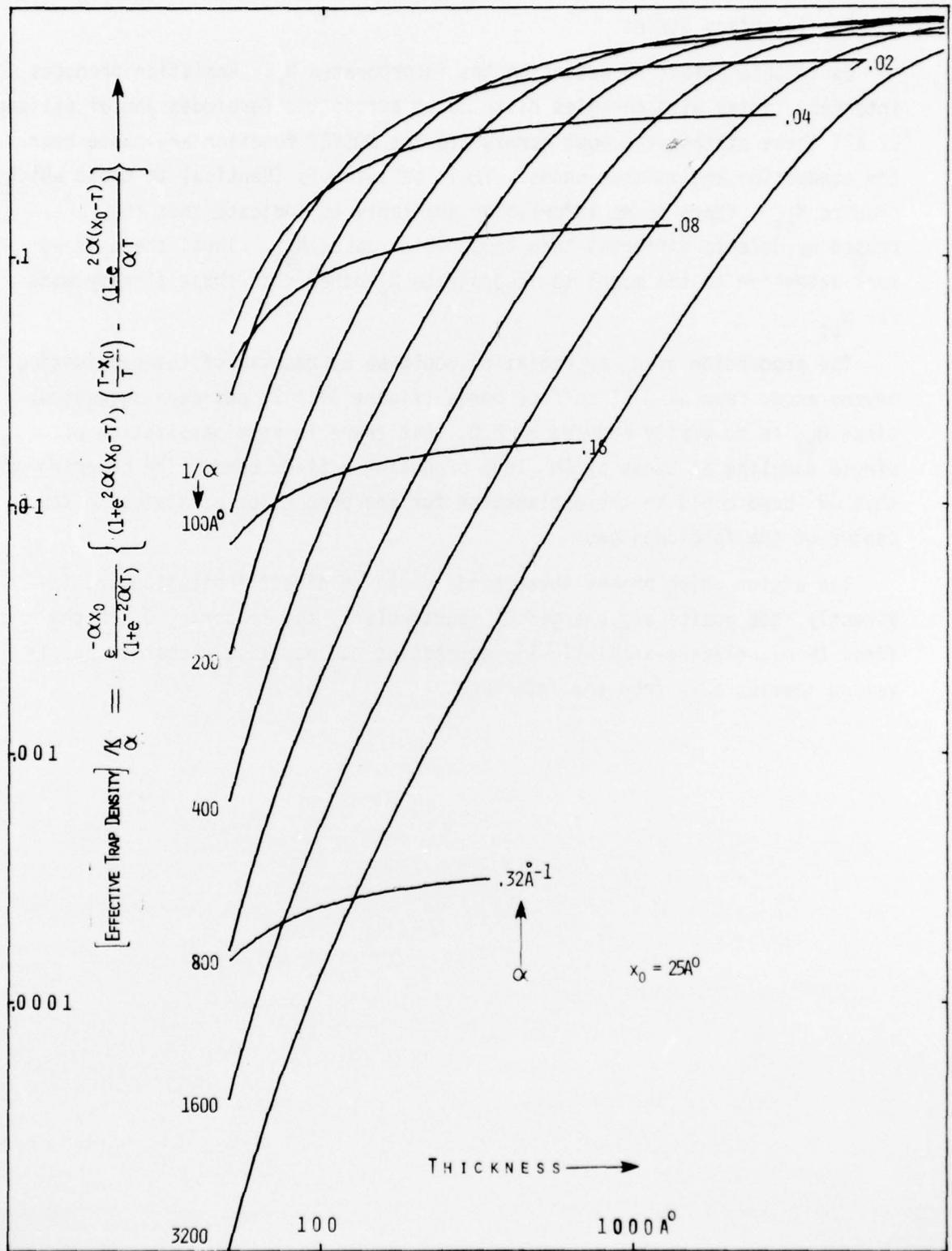
Next consider the worst case radiation susceptibility problem, i.e., all the silicon excess centers have been charged positively except the first 25 Å, (x_0), from which the charge can escape by QM tunnelling (reference 16). The amount of charge induced at the silicon interface and at the silicon dioxide metal interface is equal to the charge in the trap and is divided $\frac{t-x}{t}$ to the Si interface and $\frac{x}{t}$ to the metal interface. Thus, the charge induced in the silicon is

$$\begin{aligned} Q &= \int_{x_0}^t \left(\frac{t-x}{x} \right) A_{Si} dx \\ &= \frac{K}{\alpha} \frac{e^{-\alpha x_0}}{(1+e^{-2\alpha t})} \left\{ \left(1+e^{2\alpha(x_0-t)} \right) \left(\frac{t-x_0}{t} \right) - \frac{(1-e^{2\alpha(x_0-t)})}{\alpha t} \right\} \quad (11) \end{aligned}$$

Using equation (6)

$$\frac{K}{\alpha} = \frac{Q_{ss} R_0 v e^{-(2.3 \text{ eV})/kT}}{\langle \sigma v \rangle} \quad (12)$$

The value of $\alpha Q/k$ is plotted in figure 12 for $x_0 = 25 \text{ \AA}$ and $1/\alpha = 12.5, 25, 50, 100, 200, 400, 800,$ and 1600 \AA . It is known that the positive charge after radiation is within 200 \AA so α must be 50 to 200 \AA . Notice that at $t = 1000 \text{ \AA}$ a variation of α between 50 and 400 \AA makes little difference. Thus, the variation of hardness with oxygen partial pressure must be looked at at a different thickness.



5. Interface States

Up to this point, no extension has incorporated N_r . Radiation produces interface states with energies distributed across the forbidden gap of silicon. Of all these states, the most harmful to the MOSFET function are those near the conduction and valence bands. Their behavior is identical to those which produce N_{SS} . There is no information available to indicate that they are caused by defects different than those which cause N_{SS} . Thus, there is no real extension to the model to incorporate N_r other than those already made for N_{SS} .

The production of N_r by radiation could be by removal of the passivating oxygen atoms from Si-O-Si surface bonds (figure 3). It has been suggested, since N_{SS} is so easily reduced by H_2O , that there is some passivation of single dangling Si bonds by OH^- ions producing a Si-OH bond. The breaking of this OH^- bond could be the explanation for the production of states in the center of the forbidden gap.

The action which breaks these bonds could be direct ionization or, indirectly, the positively charged Q_r (particularly the temporary Q_r in the first 25 Å), electro-statistically attracting the negatively charged passivating species away from the interface.

SECTION IV
SUMMARY AND RECOMMENDATIONS

In the preceding discussions, the model has been changed and extended in the following ways:

(a) Q_{SS} is caused by an oxygen atom which is bonded to three interface silicon atoms. This produces an interface donor state whose energy is above the silicon conduction band.

(b) N_{SS} is primarily caused by a Si-O-Si bond in which the oxygen has been removed leaving a stretched Si-Si bond. This produces two interface states, a donor level near the valence band and an acceptor level near the conduction band.

(c) N_r near the band edges has the same cause as N_{SS} . The oxygen is removed from the Si-O-Si bond by direct action of the radiation and by the attractive action of the positively charged ions which produce Q_r .

(d) Q_r is the result of the holes which are produced by the ionizing radiation, being trapped on silicon excess centers.

(e) Silicon excess centers are centers where one oxygen is bonded to three silicon atoms in the bulk of the SiO_2 . The excess centers are distributed according to the form $A_{Si} = k(e^{-\alpha x} - e^{\alpha(x-2t)}) / (1 + e^{-2\alpha t})$.

(f) The susceptibility to Q_r is proportional to Q_{SS} measured after oxidation, before annealing.

(g) Internal electric fields are important in oxide growth processes, and the growth can be influenced by anything which alters the field.

The above are not an established part of the model but working hypotheses. It is unnecessary to perform experiments to establish each of the extensions. Better, use these hypotheses to analyze current processing practice and to predict methods which would produce hardened oxides. The test of these methods gives both experimental confirmation and a hardening process modification.

Experiment #1

Aubuchon (reference 17) reported that electron beam evaporation of aluminum produces softer oxides than crucible aluminum. This effect was blamed on ionization of the oxide by x-rays and stray electrons. Others have reported

that this is not true. Moreover, the effect is not annealed by the 500°C aluminum sinter. whereas other researchers have observed that the irradiate and anneal process, if anything, improves hardness (references 1 and 4). However, if there was irradiation in the electron beam process and that radiation did charge the excess silicon centers positive, then the positive ions could be moved deeper (e.g., from the 0 to 25 Å region to the 25 Å to 200Å region) in the oxide by an anodizing field (e.g., applied by collecting stray electrons). Thus, depending on the particular apparatus, there may or may not be an effect, which would explain the controversy. The experiment then involves putting contacts on the wafer during electron beam aluminum ionization and applying both anodic and cathodic fields. If the cathodic potential produces harder devices (by pushing excess silicon centers from the 25 Å to 200 Å region into the 0 to 25 Å region), then the ionic nature of the centers is confirmed and a new hard process is available.

Experiment #2

An extension of the above is to apply anodic or cathodic fields during high level irradiation (10^6 rads/min) at different temperatures to control diffusion rates and the rate of thermal release of trapped charge. This could result in a modification of the sintering process.

Experiment #3

The concentration of oxygen in SiO_2 during oxidation is 5×10^{16} atoms/cc whereas water reaches a level of 3×10^{19} (reference 10). Q_{ss} and N_{ss} are both much smaller in steam oxides than dry oxides. Thus, steam oxides should be much harder, which is not observed. The answer could lie with the exponential in equations (6) and (12). If the activation energy for charging the excess oxygen center is changed, Q is changed. This could be caused by a variation in the field. Water does have a different ∇F_t (table 1) which means a different field. Goetzberger (reference 18) reports that fields can be applied through steam during oxide growth but not dry oxygen, and such fields alter Q_{ss} . The experiment is then to repeat Goetzberger's experiment evaluating radiation susceptibility. If the results prove important, a laser or microwave energizer can be added to ionize the oxidizing gas, thus permitting the application of a field through dry oxygen.

Experiment #4

The previous experiments are based on changing the location of the excess silicon centers by ionizing the centers and driving them about with electrostatic fields. This cannot be done with impunity, for experiments with anodic growth (references 13 and 19) have shown that such fields can induce further growth and the introduction of additional centers. Thus the final experiment is to further explore the properties of anodic growth. First, at what fields does growth begin? One, perform anodic growth of very thin 0 to 25 Å films, continuously measuring thickness versus time and voltage to explore the observed 30 V initial jump in applied voltage. Two, induce anionic growth in hard oxide films as a function of temperature. These two experiments determine if there is a charge sheet in anionic growth. Second, how many centers does anodic growth introduce? Irradiate the above films to measure Q_r .

Experiment #5

This is both an experiment and reanalysis of old experiments. The task is to gather all susceptibility data available and compare equations (6) and (9) to look for a correlation.

Experiment #6

Evaluate the susceptibility of 400 Å or less oxides grown in different reduced partial pressures of oxygen. Also evaluate at 2000 Å in reduced and increased partial pressure. This experiment should use etch back or some other means of locating the charge centroid.

The above experiments and tasks are then recommended to verify or reject the model extensions and to investigate possibilities for hardened processes and hardness assurance screens.

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