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Electron-spectroscopic studies of the early stages of the oxidation of Si

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Photoelectron spectroscopy (PES) and Auger electron spectroscopy have been used to study the early stages of the oxidation of the cleaved silicon (111) surface. The Si-2*p* core level as well as valence emission were studied with PES, using monochromatized synchrotron radiation at a photon energy which allows maximum surface sensitivity. In the initial adsorption stage (i.e., when the surface states are removed from the band gap), oxygen can be adsorbed either molecularly or atomically. The molecularly chemisorbed oxygen was characterized by a zero shift of the Si-2*p* core level, while the atomic state was associated with a 2.0-eV shift. Both types of chemisorption led to a removal of the filled surface states from the band gap. A third chemisorbed state, characterized by a 2.6-eV shift of the Si-2*p* core level, was observed in the adsorption stage beyond monolayer coverage. A broad 3.3-eV chemically shifted peak was attributed to Si atoms bonded to three oxygen atoms with smaller contributions from other states (i.e., SiO_2 and Si atoms bonded to one or two oxygen atoms). Finally, the formation of SiO_2 can be unambiguously identified by a 3.8-eV shifted peak. After an SiO_2 layer ~ 12 Å thick had formed, asymmetric emission on the low-binding-energy side of the SiO_2 shifted peak revealed that approximately two layers of silicon atoms in the SiO_2–Si interface were bonded to less than four oxygen atoms.

I. INTRODUCTION

The Si–SiO_2 interface is the most important oxide-semiconductor interface being used at this time by the semiconductor industry. Therefore, this interface has been the subject of many studies. Most studies have been empirical or semiempirical, directly concerned with device fabrication; however, in recent years, there has been an increasing attempt to understand the bonding electronic structure at the interface and the oxidation process. These problems can be studied by observing the interface at different stages of oxide growth: (a) adsorption of oxygen onto the surface, (b) the growth of the initial oxide layers, (c) the study of relatively thin oxides (<500 Å), (d) the interface after a thick oxide (≥500 Å) has formed, such as the oxide layers used in devices. In this study, Auger electron spectroscopy (AES) and photoelectron spectra (PES) of the Si-2*p* core level and valence band have been used to study the adsorption of oxygen and the initial formation of an oxide layer on the cleved Si (111) surface. The use of these tools gives us the ability to study the adsorption and oxidation on a molecular level.

In the past, there have been numerous studies of the bonding of oxygen to Si on the surface, the oxidation process, and the electronic structure of the Si–SiO_2 interface. Law[1] and Green *et al.*,[2] using gas volumetry, observed a fast oxygen-adsorption process which saturated rapidly and was followed by a much slower sorption process. Green *et al.*[2] proposed that the fast-adsorption stage saturated with a monolayer of atomic oxygen and that, in the slower sorption process, oxygen atoms formed a bridge between two silicon atoms (this involved breaking of Si–Si bonds and drastic rearrangements of bonds). Green and Liberman[3] later proposed that molecular oxygen formed a bridge between two surface Si atoms without dissociation of the oxygen molecule as in the previous model of the Si surface at the saturation of the fast-adsorption process. These two models of Green *et al.*[2,3] of the bonding at the saturation of the fast-adsorption process (i.e., whether oxygen is adsorbed in a nondissociated molecular state or an atomic state) have been, in various versions, a major controversy. This question, whether oxygen is adsorbed in a molecular or atomic state, is most basic and important for the understanding of the adsorption process of oxygen on silicon.

With the more widespread use of electron spectroscopy to study surfaces [i.e., AES, (electron-loss spectroscopy) ELS, and PES], it was possible to study the fast-adsorption stage in greater detail than previously possible. In the early studies of the sticking coefficient, different experimenters observed initial sticking coefficients which could vary over four orders of magnitude with different surface preparation. Ibach *et al.*[4] studied the adsorption of oxygen on the cleaved (2 × 1 reconstructed) surface and found the sticking coefficient to vary greatly with step density. From the results of AES, (high-resolution electron-loss spectroscopy) HRELS, and optical-ellipsometry studies, Ibach *et al.*[4] proposed that, in the fast-adsorption stage, the molecular oxygen was nondissociatively adsorbed and that the slow-sorption process was another process entirely. Meyer and

Vrakking[5] disagreed with the model of Ibach *et al.* and proposed, as they had stated earlier, that the adsorption is a single-step process with oxygen occupying a bridge site. In other studies, Ibach *et al.*,[6] ultraviolet-photoemission spectroscopy using (UPS) and ELS, observed four additional energy levels, which he related to the adsorption of molecular oxygen, further supporting the model of Ibach *et al.*[4] However, Ludeke and Koma,[7] using ELS to study the adsorption of oxygen on the annealed Si surface, proposed that the oxygen would dissociate on the Si surface. Rowe *et al.*[8] disputed the model of Ludeke and Koma and presented XPS and HRELS results supporting the adsorption of O_2 onto the surface without dissociation. Goddard *et al.*[9] recently compared the bonding energy of the atomic versus molecular adsorption and found the molecular adsorption to be favored.

The initial formation of a thin oxide layer on the Si surface has been the subject of much controversy. If the Si–SiO_2 interface is atomically abrupt, this would result in a very different electronic property than an interface which is compositionally graded over ~30 Å. Thus, it is extremely important to understand the bonding (i.e., abrupt or graded) at the Si–SiO_2 interface. Hill *et al.*,[10] Raider and Flitsch,[11] Hollinger *et al.*,[12] and Carriere *et al.*,[13] using XPS, have observed the Si-2*p* shifted peak to shift from ~3.2 to ~4.3 eV upon going from the thin oxide layer ~10 Å to thicker oxide layers. These results have caused considerable discussion about the composition and structure of the SiO_2–Si interface region. Raider and Flitsch[11] have proposed that a layer of SiO_x ($1 \leq x \leq 2$) approximately 30 Å thick exists between Si and SiO_2. Hollinger *et al.*[12] disagree with Raider's model and propose that no layer of SiO_x exists, but the shift of the SiO_2 shifted peak can be explained by a shift of the Fermi level and extra atomic relaxation. These two models are in complete disagreement and will be discussed later in this work. In a study of thin thermally grown oxide layers, Hill *et al.*,[10] using angular XPS, have observed an asymmetry of the Si-2*p* shifted peak which they attribute to the presence of silicon atoms at the interface bonded to less than four oxygen atoms.

The kinetics of the growth of thick oxide layers have been the subject of many studies by Deal *et al.*[14] and others.[15,16] These studies have shown that the growth rate of SiO_2 oxide layer is controlled for substrates which are not too heavily doped by the reaction at the interface for thin oxide layers, and by diffusion of oxygen for thick oxide layers. In the study here, the oxide layers studies are grown in the interface limited reaction. The growth studies of oxide layers by Deal and co-workers[14] have shown that an activation energy of 2.0 eV exists although little is known of its origin. Therefore, it has been assumed that this was the energy to break Si–Si bonds (2.0 eV is the Pauling bond energy of Si).[17]

Various works indicate the importance of the presence of activated oxygen, i.e., oxygen in a state other than the molecular ground state. Studies by Strukov *et al.*[18] have shown that the presence of an activated Pt or Pd catalyst 0.1 to 1.2 mm from a Si crystal can drastically increase the growth rate of the oxide. Furthermore, Abe *et al.*[19] have shown that oxide layers grow more rapidly when the oxygen has been passed through a microwave discharge. In studies of the adsorption of oxygen on Si, Ibach *et al.*[4] observed that the presence of a hot filament ionization gauge stimulates the adsorption process, and Iback and co-workers also noted that the presence of the ionization gauge or high-surface-step densities on the cleaved Si surface increased the sticking coefficient significantly. In this context, it should be noted that in the work on the adsorption of oxygen on cleaved GaAs, Pianetta *et al.*[20] observed that the rate of adsorption was increased by approximately six orders of magnitude when an ionization gauge was on during the oxygen exposure. It was suggested[20] that this increase in the adsorption rate is the result of molecular oxygen being excited into the singlet state which may adsorb or disassociate on the surface more easily than molecular oxygen in the ground state. These results indicate that the state of the oxygen may be a very important factor to the growth of oxide layers. Therefore, the state of the oxygen will be carefully considered in this study of the oxidation of Si.

In this study, the adsorption and early stages of the oxidation of Si have been studied with AES and photoemission from the Si-2*p* core level. The present work suggests that, depending on experimental conditions, oxygen is adsorbed in either a molecular or an atomic state and these states are characterized by no shift of the Si 2*p* and a 2.0 eV shift, respectively. Furthermore, chemically shifted peaks of 2.6 and 3.3 eV indicate that there is an interface region (~2 layers thick) with Si atoms bonded to two and three oxygen atoms, respectively, prior to the formation of SiO_2. Thus, the Si–SiO_2 interface is very abrupt.

In Sec. II, the experimental procedures used in this study will be described. This will be followed by a presentation of the results of the PES and AES studies. After the results are presented (Sec. III), the discussion section (Sec. IV) will follow and is divided into three smaller sections: A. the fast-adsorption process, B. the slow-sorption process, and C. the SiO_2–Si interface.

II. EXPERIMENTAL

A. General

Atomically clean surfaces were produced by cleaving Si samples in UHV at a base pressure of less than or equal to 5×10^{-11} Torr. In this study, degenerate *n*-type Si was used. Unless otherwise specified, the pressure was measured with a cold cathode Redhead gauge. In the oxygen exposures 99.998% pure oxygen was leaked into the UHV system with a high-precision variable-leak valve. The ion pump was valved off from the chamber during the oxygen exposures. Three exposure procedures (the notations EP1, EP2, and EP3 will be used throughout the rest of this paper) were employed in this study as shown in Table I. EP1 and EP2 are similar in that a cold cathode gauge was used to measure the pressure; but, EP1 starts with an initial exposure to 10^{-8} Torr for 100 sec and requires three additional exposures to reach an exposure of 10^3-L O_2 (1 langmuir $= 10^{-6}$ Torr sec), while EP2 starts with an exposure of 10^3-L O_2. On the other hand, to stimulate the growth of an oxide layer, an ionization gauge was used in procedure EP3 to create excited oxygen.

B. Photoelectron spectra

The photoelectron spectra were measured with a PHI double-pass cylindrical mirror analyzer (CMA) in a system described by Pianetta[21] elsewhere. The source of radiation in these experiments was the Stanford Synchrotron Radiation Laboratory. For photon energies of <32 eV, the monochromatized radiation was produced by the monochromator described by Rehn *et al.*[22] A monochromator, described by Brown *et al.*,[23] was used to produce monochromatic radiation at photon energies above 32 eV. The combined resolution of the CMA and the monochromator are listed in Table II for the photon energies in interest in this work. The width of core levels is determined by their intrinsic width, the resolution of the monochromator and CMA, but the location of the core-level binding energy is determined by the reproducibility of the monochromator and the accuracy of the electronics. Thus, an accuracy of ±0.1 eV can be claimed for the energy positions of core levels.

C. AES

The AES spectra were measured in a Varian high-resolution scanning Auger system. After ex-

TABLE I. Exposure procedures (1 L $= 10^{-6}$ Torr sec).

	Exposure number	Exposure	Pressure and time
EP1	1	1-L O_2	(10^{-8} Torr for 100 sec)
	2	9-L O_2	(10^{-8} Torr for 900 sec)
	3	90-L O_2	(10^{-7} Torr for 900 sec)
	4	900-L O_2	(10^{-6} Torr for 900 sec)
	5	9 000-L O_2	(10^{-5} Torr for 900 sec)
EP2	1	1 000-L O_2	(10^{-6} Torr for 1000 sec)
	2	9 000-L O_2	(10^{-5} Torr for 900 sec)
		90 000-L O_2	(10^{-4} Torr for 900 sec)
		900 000-L O_2	(10^{-3} Torr for 900 sec)
EP3	1	10^6-L O_2	(10^{-3} Torr for 1000 sec)
	2	10^6-L O_2	(10^{-3} Torr for 1000 sec)
	3	2×10^6-L O_2	(2×10^{-3} Torr for 1000 sec)
	4	4×10^6-L O_2	(4×10^{-3} Torr for 1000 sec)
	5	4×10^6-L O_2	(4×10^{-3} Torr for 1000 sec)

	Vacuum gauges used	
Exposure procedure	Pressure range	Gauge
EP1 and EP2	10^{-11}–10^{-5} Torr	Redhead
	10^{-5}–10^{-1} Torr	mTorr or cold cathode
	10^{-1}–10^{1} Torr	Thermocouple
	10^{2}–10^{3} Torr	Mechanical
EP3	10^{-11}–5×10^{-3}	Nude ionization

TABLE II. Combined resolution of the monochromator and CMA.

$h\nu$ (eV)	Combined resolution (eV)
21	0.17
32	0.32
130	0.34
150	0.38
200	0.5
240	0.65

posure to oxygen, the system was pumped to below 7×10^{-10} Torr before the electron gun filament was turned on. The electron beam (4.5 keV with a beam current of 1 μA) was scanned over an area of 100×100 μm^2. Since exposure of a surface to *e* beam has been found to affect the amount of oxygen adsorbed in subsequent exposures, the sample was moved to a new position after each exposure. To determine the surface coverage, the Si(*LVV*), O(*KLL*), and Si(*KLL*) were measured after each oxygen exposure on at least three different positions on the Si surface (none of which had been exposed to *e* beam previously) for each exposure. Additional information was obtained from the shape of the Si(*LVV*) as it changed with coverage.

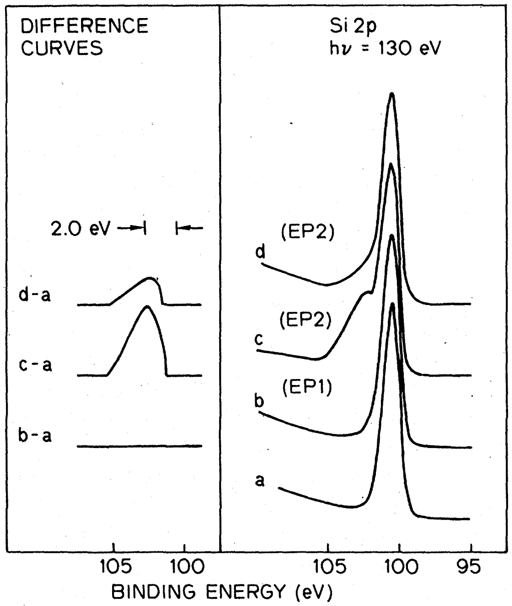

FIG. 1. Si-2*p* core-level shifts of the adsorbed states in the fast-adsorption process. These are (a) the clean surface, (b) the surface exposed to 10^3-L O_2 by EP1, (c) and (d) surfaces exposed to 10^3-L O_2 by EP2.

III. RESULTS

A. The Si-2*p* core level

The Si 2*p* of the clean surface is shown in Fig. 1, Curve a. Upon exposure to a total of 10^3-L O_2 by EP1, the Si 2*p* (Fig. 1, Curve b) did not exhibit any change as seen by the emission from the core level and the difference curve (despite the fact that the surface states disappear, as seen in Fig. 5). This adsorption stage will be referred to as State 1 below. In contrast to this, by exposing the surface to 10^3-L O_2 by EP2, a 2.0-eV shifted peak (state 2) was observed as seen in Fig. 1, Curve c, and the associated difference curve. This provides evidence for two different kinds of adsorbed states in the fast adsorption stage, as mentioned elsewhere.[24] The magnitude of the 2.0 eV shifted peak, observed after 10^3-L O_2, was dependent on the cleavage quality of the Si surface, as is evidenced from Curve d in Fig. 1, which shows the results from a different cleave than that in Curve c. It is thus possible that varying amounts of the two suggested states may exist simultaneously on a cleaved surface.

With increased oxygen exposure beyond 10^3-L O_2, a broadening of the Si-2*p* shifted peak occurs to high-binding energy suggesting the presence of at least two bonding states. For a sample exposed by EP1 to 10^3-L O_2 and then to 10^{12}-L O_2, a peak shifted by 2.6 eV (state 3) is the dominant shifted peak as seen in Fig. 2(g). The growth of this 2.6 eV shifted peak and the onset for an additional peak shifted by ~3.3 eV is more easily distin-

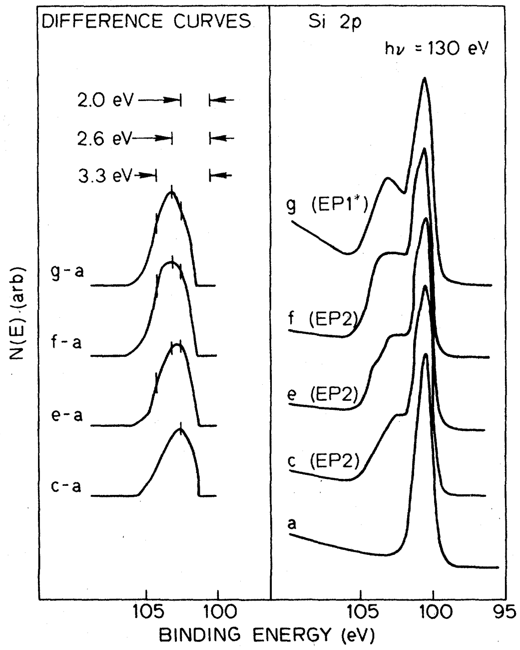

FIG. 2. Si-2*p* core-level shifts of the states in the slow-sorption process. The curves are (a) the clean-surface, the surfaces exposed by EP2 to (c) 10^3-L O_2, (e) 10^6-L O_2, and (f) 10^9-L O_2, while (g) was exposed to 10^3-L O_2 by EP1 and then to 10^{12}-L O_2.

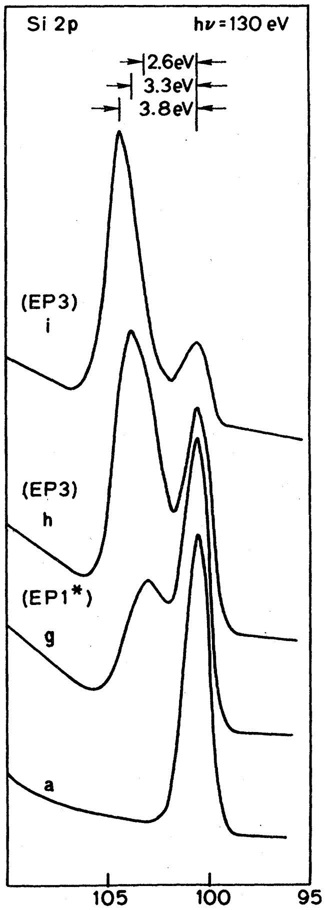

FIG. 3. Si-2*p* core-level shifts of the early oxide formation. The curves are (a) the clean surface, (g) was exposed to 10^3-L O_2 by EP1 and then to 10^{12}-L O_2, (h) was exposed to 4×10^6-L O_2 by EP3, and (i) was the surface in h exposed to an additional 4×10^6-L O_2.

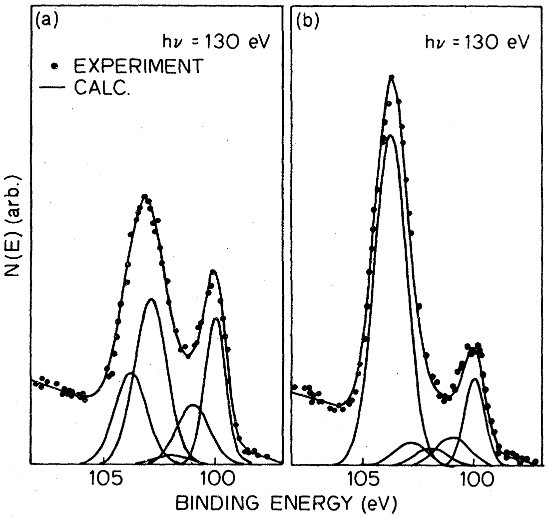

FIG. 4. Si-2*p* core levels and the calculated Gaussian fit of (a) Curve h from Fig. 3 and (b) curve i from Fig. 3. The individual Gaussian peaks of the fit are plotted below the curves.

guished by comparing the corresponding difference spectra shown in Fig. 2. Therefore, the slow-adsorption process (exposures above 10^3 L) results in the creation of: (a) the 2.0 eV shifted state (state 2), if it is not already present, (b) the state with a 2.6 eV shift (state 3) of the Si-2*p* core level, and possibly (c) another state with a 3.3 eV shift of the Si-2*p* core level.

Since, after exposure to 10^{12}-L O_2 of unexcited oxygen, no evidence was observed for the formation of SiO_2, a sample which had been exposed by EP2 to 10^9-L O_2 was exposed to oxygen with the ionization gauge on (i.e., EP3). After a 4×10^6-L O_2 exposure by EP3, the Si-2*p* shifted peak was shifted by 3.3 eV as shown in Fig. 3, Curve h. The shifted 2*p* core level is very broad and has a full width at half maximum (FWHM) of 2.3 eV, suggesting the presence of multiple states. After another exposure to 4×10^6-L O_2 by EP8, the Si-2*p* shifted peak was shifted by 3.8 eV as shown in Fig. 3, Curve i. In contrast to the FWHM peak width of 2.3 eV observed in Curve h, the FWHM is 1.7 eV for the state produced by the additional exposure. Since the shifted 2*p* peak is very broad, it is possible that it is composed of more than one shifted Si 2*p*. For comparison purposes 1.0, 2.0, 2.9, and 3.8-eV Gaussian-shifted peaks were added to form the 2.3 FWHM peak shown in Curve h. The results are given in Fig. 4(a). Even if this fit is not unique, it demonstrates that it is conceivable that the 3.3-eV shifted peak comprises approximately three different chemical states. As will be discussed in more detail later, these states are assigned to SiO_2, Si bonded to three oxygen atoms, and Si bonded to two oxygen atoms. Similarly, the Si-2*p* core level curve of the thicker oxide layer, Fig. 3, Curve i, was fit to Gaussians, as shown in Fig. 4(b). The SiO_2 (i.e., 3.8 eV) shifted state is dominant with smaller contributions from intermediate states (i.e., peaks shifted by 2.9, 3.0, and 1.0 eV) and the unshifted bulk Si. Again, this will be discussed later in more detail. All assignments made here between detailed atomic configurations and Si-2*p* core-level shifts must be considered tentative but offer one possible explanation to the large width of the shifted Si-2*p* peaks.

B. The valence-band structure

In this section, each energy distribution curve of valence-band spectra will be assigned the same notations as those of the corresponding Si-2*p* emission after the same oxygen exposure. The emission spectra from the surface states in the band

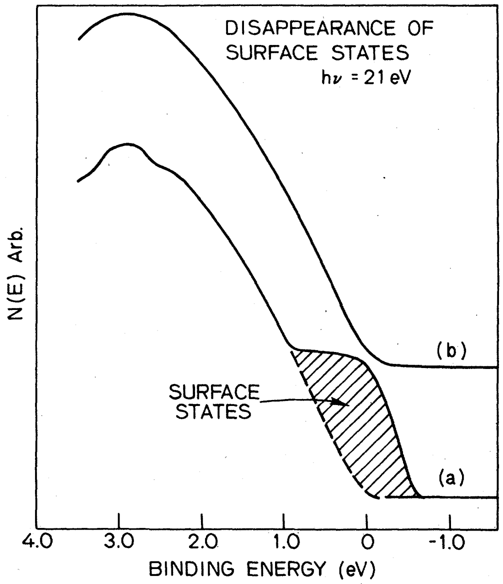

FIG. 5. Surface states of the clean surface (a) are removed by exposure to 10^3-L O_2 by EP1 or EP2 (b).

gap, first established by Wagner and Spicer[25] and Eastman and Goodman,[26] are shown in Fig. 5(a). After exposure of this surface to 10^3-L O_2 by either EP1 or EP2, the emission from these surface states was removed as shown in Fig. 5, Curve b.

Figure 6 shows the valence structure at $h\nu = 32$ eV and difference spectra between the oxygen exposed and the clean surface for three different chemisorbed states of oxygen. The valence-band maximum of Si has been chosen as the zero of energy. A broad increase in emission is observed in the spectra between −4 and −9 eV in all three cases. However, state 2 (the 2.0-eV shifted state) has a sharp increase in emission (Fig. 6, Curve c−a), which state 1 (no shift of the Si 2*p*) does not have (Fig. 6, Curve b−a). In state 3 (the 2.6-eV shifted state), the entire peak between −5 and −9 eV is much larger (Fig. 6, Curve g−a) than state 1 or state 2. Furthermore, in going from state 1 to 2 to 3, additional emission increases at −13 eV as is shown in the difference curves of Fig. 6. By comparing the difference spectra with the emission from the valence band of heavily oxidized Si (with Si 2*p* shown in Fig. 3, Curve i), Fig. 6, Curve i, it is seen that the additional structure observed is in some cases reasonably close in energy to the valence structure of SiO_2. Note, however, that the small features of the difference spectra may be an artifact of subtracting the clean spectrum.

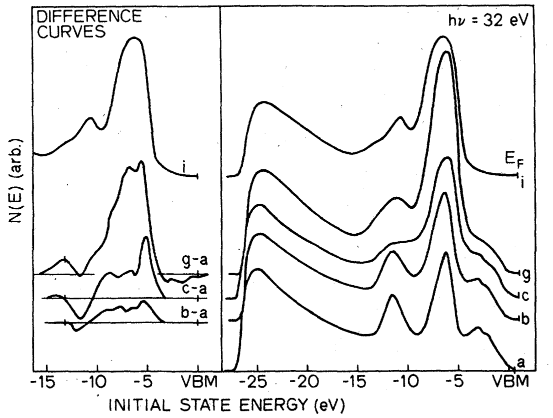

FIG. 6. Valence spectra of the three states of oxygen on silicon. These valence spectra correspond to (a) the clean surface, (b) the Si 2*p* seen in Fig. 1, Curve b, (c) the Si 2*p* seen in Fig. 1, Curve c, (b) the Si 2*p* seen in Fig. 2, Curve g, and (i) the Si 2*p* seen in Fig. 3, Curve i.

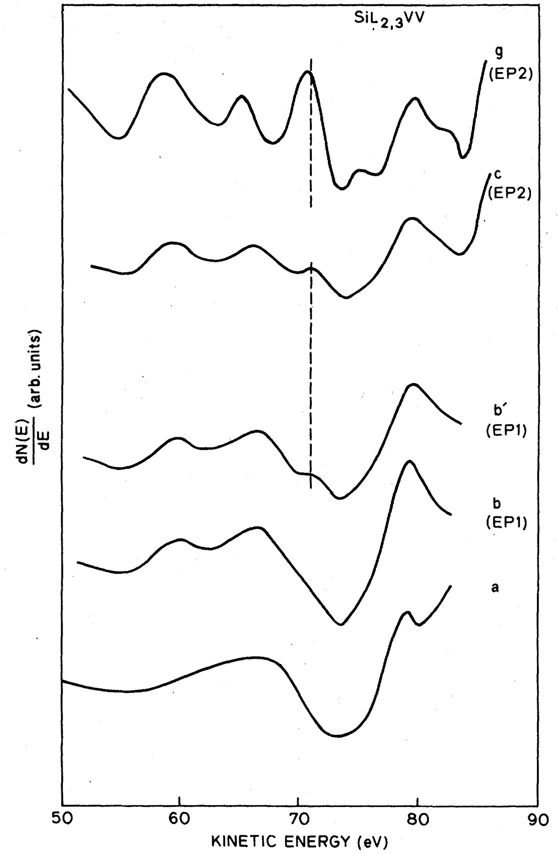

FIG. 7. Si (*LVV*) spectrum for the three states of oxygen on silicon. The spectra are (a) the clean surface, (b) the surface exposed to 10^3-L O_2 by EP1 (state 1), (b′) the surface in b exposed to *e* beam for approximately ten minutes, (c) a surface exposed to 10^3-L O_2 by EP2 (state 2), (g) a surface exposed to 10^{12}-L O_2 by EP2 (state 3). Note only the lower-energy part of the Si (*LVV*) is shown.

In contrast to this, distinct differences were observed in the Auger Si(*LVV*) spectra of the three sorbed states as seen in Fig. 7. Upon adsorption of oxygen, all three states exhibit additional structure around 60 eV; however, for state 2, there is additional structure at 71 eV not existing for state 1, as seen in Fig. 7, Curves c and b, respectively. However, exposing state 1 to an *e* beam for approximately ten minutes converted it to state 2 as is seen in Fig. 7(*b*′). Although state 3 and state 2 exhibit the same general features in the Si(*LVV*), Fig. 7, Curves g and c, respectively, the features of the Si(*LVV*) of state 3 are much sharper and may have shifted slightly to lower energy (<1 eV).

C. AES measurements of the oxygen coverage

Auger electron spectroscopy was used to estimate the oxygen coverage on the Si surface. Although the relative coverages obtained from the ratio of the O(*KLL*) to Si(*KLL*) and the O(*KLL*) to Si(*LVV*) in the exposure range of 10^3- to 10^{10}-L O_2 were in general agreement, diffraction effects of the Si(*KLL*) electrons were found to cause a greater deviation of the O(*KLL*) to Si(*KLL*) ratio than the O(*KLL*) to Si(*LVV*). The Si(*KLL*) peak-to-peak (p-p) height varied (as much as 40%) with sample position as a result of the strong angular (diffraction) effects. This observation is in agreement with the results on thin Si oxide layers obtained by Chang,[27] who found that the Si(*KLL*) p-p height (measured by a CMA) was decreased by a factor of 2 by rotating the sample five to ten degrees from the CMA normal, whereas the O(*KLL*) p-p height was not changed by this rotation. Because of these diffraction effects for the Si(*KLL*), the O(*KLL*) to Si(*LVV*) ratio will be shown as a function of exposure. The Si(*LVV*) was found to decrease by a factor of 1.5 after exposing the cleaved surface to a total exposure of 10^3-L O_2. Then, the Si(*LVV*) p-p height remains approximately constant for exposures of 10^3- to 10^{12}-L O_2.

The O(*KLL*) to Si(*LVV*) p-p height ratio for EP1 and EP2 are shown in Figs. 8(a) and 8(b), respectively. In each case, two samples were simultaneously exposed to the oxygen. Some scattering can be seen in the data for the two different cleaves, but the overall reproducibility is good. The samples exposed by EP2 at 10^3-L O_2 and above [curve 8(b)] have a larger coverage than those given the same exposure of EP1 [curve 8(a)]. However, in both cases, the surface states had disappeared after an exposure of 10^3-L O_2 (compare Fig. 5). In the exposure range of 10^3 to 10^{12} L, Curves a and b have slightly different slopes of 0.047 and 0.035, respectively. For comparison of the final coverage at 10^{12}-L O_2, a sample was cleaved at atmospheric pressure of oxygen and then exposed to a total of 10^{12}-L O_2 (Fig. 8, point c). As is seen from the figure, this sample has approximately the same coverage as that obtained by EP2 at 10^{12}-L O_2. Therefore, the initial exposures at 10^{-6} Torr (EP2) does not result in a markedly different final coverage than one done at much higher pressures. On the other hand, the initial exposure at 10^{-8} Torr (i.e., EP1) results in a lower-oxygen coverage over the entire range of exposures.

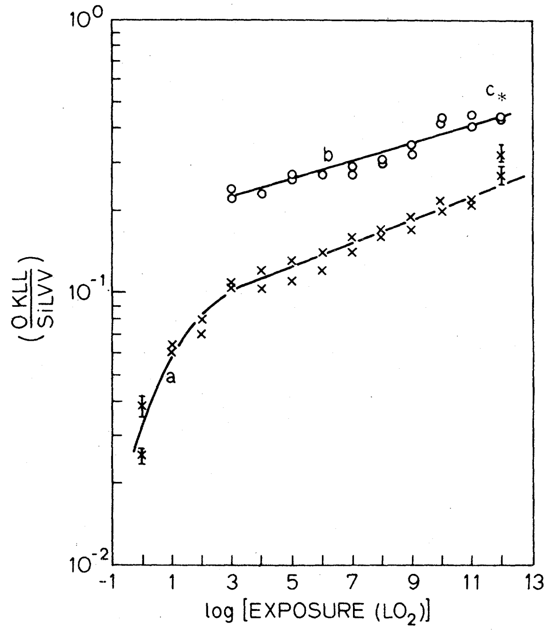

FIG. 8. Oxygen coverage vs exposure. The uptake curves correspond to (a) two samples exposed by EP1 and (b) two samples exposed by EP2. Point c was obtained by cleaving the sample in atmospheric pressure of oxygen and then exposing it to 10^{12}-L O_2.

IV. DISCUSSION

Our results for oxygen chemisorption on Si(111) can be summarized as follows. Two different states were found for the fast adsorption stage, i.e., exposures up to 10^3 L. The first state (state 1) had no shift of the Si-2*p* core level, while the Si-2*p* of state 2 was shifted by 2.0 eV. As the oxygen exposures were increased into the slow-sorption stage, an additional state shifted by 2.6 eV (state 3) and a possible shift of 3.3 eV of the Si 2*p* were observed, indicating the possibility that additional oxygen atoms are bonding to the surface silicon atoms. When the Si surface was exposed to excited oxygen, a 3.8 eV shift of the Si 2*p* indicated the formation of SiO_2. These different adsorption states will be discussed in detail below.

A. The fast-adsorption process

From the AES studies, it is seen that the adsorption consists of a fast-adsorption stage followed by a much slower sorption process (Fig. 8). It was shown that EP1, i.e., initial exposures at 10^{-8} Torr, resulted in a lower coverage of oxygen over the entire exposure range than samples exposed by EP2. The difference in oxygen uptake for the two procedures has not previously been reported, but the results of Joyce and Neave[28] show that lower exposure pressures resulted in lower coverages at saturation of the fast-adsorption procedure. In the gas volumetry studies of Boonstra,[29] it was reported that, at the saturation of the fast-adsorption stage, one oxygen had been adsorbed per surface silicon atom; however, these studies were done at much higher pressure (i.e., 10^{-2}–10 Torr). Therefore, caution has to be taken to equate saturation of the fast-adsorption state with the completion of a monolayer coverage for our studies done at lower pressure.

Since no measurable shift is observed in our work for the Si-$2p$ core level of state 1, we would tentatively assign this state to molecular oxygen adsorbed onto the surface and state 2 to be atomic oxygen (Fig. 9).

In our AES study of the shape of the Si(LVV) Auger structure, the surface exposed by EP2 has structure at 71 eV which the sample exposed by EP1 did not exhibit. Allowing the surface exposed by EP1 to remain in the e beam for approximately ten minutes resulted in the same structure at 71 eV, Fig. 7, Curve b′, as in the surface exposed by EP2. This indicates the conversion of state 1 to state 2 upon extended exposure to an e beam. In this context, it should be mentioned that Rowe *et al.*[8] deduced from the vibrational structure in low-energy-loss spectroscopy and from x-ray photoemission that oxygen was adsorbed molecularly onto the surface for low exposures, less than or equal to 10^3 L.

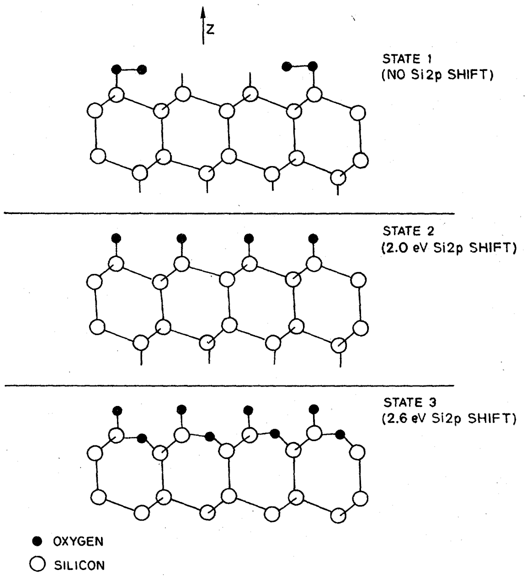

FIG. 9. Simple model of the three states of oxygen on silicon, with the z axis being the surface normal.

In the study of the valence-difference spectra, it is interesting to note the similarities observed between states 1 and 2 (Fig. 6, Curves b–a and c–a). The major portion of the increased emission occurs at approximately −5 eV and is close to the major states in SiO_2 emission associated with emission from the nonbonding oxygen orbitals.[30] The emission from the bonding orbitals usually has a lower cross section and is thus very weak. It is possible that the energies of the bonding levels may differ for state 1 and state 2, but the weak emission would make it difficult to locate accurately the positions of these peaks. Furthermore, in a theoretical study by Goddard *et al.*,[9] the nonbonding-energy levels associated with molecular or atomic oxygen were predicted to be very close in energy, possibly explaining the similarity of the valence spectra.

The lower oxygen coverage for molecular oxygen (Fig. 8a) on the cleaved Si(111) surface appears to be a problem; however, a tentative explanation can be given. If we assume that at ~10^3-L O_2 the atomic oxygen is bonded to all of the surface silicon atoms (i.e., monolayer), then the surface covered with molecular oxygen has ~50% of a monolayer of oxygen; however, if each molecule of oxygen is bonded to only one Si, then ~25% of the surface Si atoms are bonded to oxygen. If the oxygen molecule forms a covalent bond with a surface Si atom, the surface around this adsorbed molecule may rearrange itself to lower its energy and become more nonreactive. This could result in the neutralization of several surface atoms without resulting in a complete coverage of the surface Si atoms with oxygen molecules. Since the [2 × 1 Si(111)] surface is strongly reconstructed, the adsorption of a "covalently" bonded O_2 may affect the local arrangement of Si atoms, removing the surface reactivity. Needless to say, this suggestion is very speculative.

Although the exact reason for obtaining states 1 and 2 by different exposure procedures is not yet established, several important observations can be made. First of all, the major difference between obtaining state 1 as opposed to state 2 appears to be the lower-initial-exposure pressure. At 10^{-8} Torr, each surface silicon atom is struck by an oxygen molecule approximately every hundred seconds, while at 10^{-6} Torr this occurs approximately every second. Therefore, if a relaxation of the surface, taking between 1 and 100 seconds, occurs upon the adsorption of the molecular oxygen, then exposing at a lower pressure would allow the relaxation to occur before another oxygen molecule strikes that site. It is also possible that the details of the surface of the cleaved sample may affect the amounts of states 1 and 2 on the surface. If the steps on the surface are important in the adsorption as suggested by Ibach *et al.*,[4] then it may be possible that the relative occurrence of states 1 and 2 (Curves c and d in Fig. 1) may be dependent upon the step density.

B. The slow-sorption process

Upon increasing the oxygen exposure beyond 10^{-3}-L O_2, the oxygen coverage increased very slowly, in agreement with previous studies.[28,29] We propose that the 2.6 eV shift of the Si-$2p$ core level is the result of breaking at least one bond between the surface Si atoms and the bulk Si atoms and the subsequent bonding of an oxygen atom to these Si atoms. This results in a Si with two oxygen neighbors. The 3.3 eV shift, then, is believed to be the result of one surface Si atom being bonded to three oxygen atoms (two of the O atoms being bonded to other Si atoms).

In the past, ligand shifts have been used to calculate chemical shifts of bulk components. Although some of the basic concepts of ligand shifts may be applicable to a surface, as discussed by Pianetta *et al.*,[31] the bonds which occur at a surface may not be equivalent. If we consider the model of Lindberg and Hedman,[32] the total core-level shift (for a level such as the Si $2p$) can be expressed by Eq. (1)

$$\Delta E_B = \sum_{j=1}^{N} \Delta E(j)\,, \qquad (1)$$

where $\Delta E(j)$ is the shift associated with a given ligand and N is the number of nearest neighbors of the atom in question. It must be remembered that, in bulk SiO_2, the Si atoms are all bonded to four oxygen atoms and the oxygen atoms are each bonded to two silicon atoms. On the other hand, if one atomic oxygen atom is adsorbed onto a single Si surface atom, the oxygen atom must receive more charge transfer from the single silicon atom than if it were in SiO_2 and receiving charge from two Si atoms. Therefore, this oxygen atom cannot be considered to be equivalent to the other oxygen ligands which will be bonded to two silicon atoms. To get an estimate of the ligand shift associated with the first adsorbed oxygen atom onto the silicon, it is assumed that each oxygen atom gets half of its charge from each silicon to which it is bonded in SiO_2. Then, each oxygen atom in SiO_2 causes a shift of $\frac{3.8}{4}$ eV to each silicon atom to which it is bonded. Therefore, if one oxygen were bonded to only one silicon, the charge transferred to the oxygen would result in a ligand shift of $2\times\frac{3.8}{4}$ eV ≈ 1.9 eV. This is close to the 2.0-eV shift observed for the state 2.

When the second oxygen is bonded to the surface silicon atom, it is also bonded to another silicon (i.e., next layer Si) as shown in Fig. 9. Thus, the two oxygen ligands bonded to the surface silicon are not equivalent. However, with the same simplified assumptions as above, the three equivalent bonds will give rise to an additional shift of $\frac{1.9}{3}$ ≈ 0.6–0.7 eV. The second oxygen atom would then extract additional charge from the next layer to compensate the amount that it could not get from the surface silicon atom. The total shift on the surface silicon atom by ligand theory is thus $2+0.6\approx 2.6$ eV, which is the observed value. Although these calculations of surface ligand shifts are very simple, the agreement is remarkable. We therefore propose that the ligand concept is applicable and that the 2.0 and 2.6 eV shifts may arise from the bonding geometries shown in Fig. 9.

The slopes from the oxygen uptake data of EP1 and EP2 (Fig. 8) in the slow-adsorption process are less than those from the data of Boonstra.[29] In the study of Boonstra,[29] clean silicon surfaces were produced by powdering crystalline silicon, decomposing SiH_4 onto quartz wool, and thermal etching of crystalline Si. From his raw data, log-log plots of the coverage versus time yielded slopes of 0.81 (powdered Si), 0.058 (decomposed SiH_4), and 0.043 (thermally etched) for the three preparation techniques. The slopes of the data in Fig. 8 are 0.047 and 0.035 for Curves a and b, respectively. Since the surface prepared by thermal etching may be more closely related to the cleaved surface of our studies than the powder or the decomposed SiH_4, the agreement between the thermally etched sample and our cleaved sample seems reasonable. The surfaces prepared by the other techniques may result in more surface defects which can explain the more rapid incorporation of oxygen.

C. The SiO_2-Si interface

Two important questions related to the Si–SiO_2 system are the abruptness of the interface and the Si–O bonding configuration at the interface. The discussions in the previous sections have shown that, based on the multiplicity of the Si-$2p$ shifted peaks, the Si–O bonding may be very complex. In this section, we want to combine the results of ligand shift analysis with information on the electron escape depth to gain further insight into the different chemical states present at the interface and its abruptness. A detailed description of how the electron escape depth can be used to extract this kind of information is given in the Appendix.

We will first treat the case where a hot filament ionization gauge was used at the oxygen exposure and where we had the first evidence for formation of SiO_2 (3.3-eV shifted peak, Fig. 3, Curve h). The ratio of this broad shifted peak to that of the unshifted Si is 2.0:1 (from the measured areas). If we assume that the electron escape length is 4 Å (as is discussed in the Appendix), then a layer-by-layer calculation of the surface-to-bulk ratio would result in the values given in Table III for the number of surface layers shown. A comparison of the values of shifted to unshifted Si-2p core level to the calculated (layer) values shows that ~2–3 layers of Si core levels are chemically shifted. If each Si atom in the entire surface Si layer were bonded to four oxygen atoms, then each Si atom in the next layer back would be bonded to three oxygen atoms; however, it cannot be assumed that the oxidation proceeds in a purely layered manner. Thus, it is likely that there would also be some bonding of oxygen to the third layer, resulting in several shifted states which would be different from those associated with the surface layer. If it is assumed that the chemical shifts of the second and third layers of Si atoms are those given by bulk ligand shift theory (since the oxygen atoms are bonded to two Si atoms), then a Si atom of one of these layers bonded to n oxygen atoms would have a chemical shift of $\sim\frac{1}{4}n \times 3.8$ eV. Thus, Si atoms in these layers bonded to one, two, or three atoms would have shifts of 0.95, 1.9, or 2.9 eV, respectively. It was exactly these arguments which motivated us to try to fit the Gaussian peaks described earlier and shown in Fig. 4(a). Based on this analysis, we would suggest that the 3.3-eV shifted peak is probably composed of Si bonded to four oxygen atoms (i.e., SiO_2) and Si bonded to three oxygen atoms as well as one and two. Hollinger *et al.*[12] offers an alternative explanation and assume that all Si-2p shifts in the early oxidation of Si are associated with the formation of SiO_2 with the Fermi-level shifts or extra atomic relaxation accounting for the shifts to lower binding energy with thinner oxide layers. However, the distinct chemical shifts observed in the early chemisorption and oxidation stages in our work are very suggestive of different chemical states. The model proposed by Hollinger *et al.*[12] may have, in our opinion, more validity for the gradual shift of the Si-2p level ($3.5 \rightarrow 4.2$ eV) towards higher binding energy observed for thicker oxides.

TABLE III. Calculated ratio of shifted Si 2p to unshifted Si 2p for an escape depth of 4 Å.

Number of layers	Calculated ratio: shifted Si 2p to Si 2p unshifted
1	0.43:1
2	1.19:1
3	2.12:1
4	3.8:1

The core-level shifts may provide information on the crucial issue whether the interface is ideally abrupt or compositionally graded. Raider and Flitsch[11] support the graded interface model, while Hollinger *et al.*[12] support the ideally abrupt model. As has been discussed above, our study suggests that other chemical states exist when SiO_2 was first formed (the 3.3-eV shifted peak) but that these states exist only over one to two atomic layers. After a thicker oxide is formed (3.8-eV shifted peak, Curve i of Fig. 3) for which the model calculations presented in the Appendix give a SiO_2 layer thickness of 10–12 Å, our results again show that other chemically shifted states are present to a small extent. These may be at the interface, as shown in Fig. 4(b). The ratio of these shifted states to that of the unshifted Si 2p is 1.2 which is the same as that of the ~2 interface layers to the bulk (see Table III). This indicates that the transition from SiO_2 to Si occurs over approximately two layers. These results indicate an abrupt interface width of <4 Å consistent with the results from internal photoemission experiments.[33] These results are also in agreement with the conclusions of Hollinger *et al.*[12] and also with the work of Johannessen *et al.*[34] and Helms *et al.*[35] who found the transition from Si to SiO_2 to occur within one to two layers at any point along the interface.

V. SUMMARY

In the fast-adsorption stage (exposures below 10^3 L) of oxygen on cleaved Si(111), two distinct adsorbed states of oxygen were observed, one proposed to be associated with Si bonded to molecular oxygen and the other with Si bonded to atomic oxygen. As the surface was exposed to larger amounts of oxygen, the oxygen was found to break the bond between the surface Si atom and the Si atom in the next layer back, and then bonded to these two Si atoms. Silicon dioxide was formed with a very abrupt (one to two atomic layers) interface between Si and SiO_2.

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APPENDIX: THE ELECTRON ESCAPE DEPTH OF SILICON

When studying photoemission, AES, or other electron spectroscopies of surfaces, the electron mean-free path (λ) determines the probing depth of the experimental technique. The mean-free path (λ) is a strong function of the electron kinetic energy and typically has a minimum in the energy region 30–200 eV.[36] In this study, two types of Si-oxygen layers were studied to determine the escape depth (mean-free path) and the minimum of λ. The first type of layer was oxygen adsorbed onto the cleaved Si(111) surface by successive exposures to 10^9-L O_2, resulting in a Si-2*p* core shifted peak similar to that observed in Fig. 2, Curve f (i.e., a 2.0, 2.6, and possibly a 3.3 eV shifted Si-2*p* peak). The second was a layer of SiO_2 ~10 Å thick on the surface, resulting in a Si 2*p* shifted by 3.8 eV. By studying the ratio of the areas of the Si-2*p* unshifted peak to the Si-2*p* shifted peak as a function of photon energy, it was possible to determine the kinetic energy at which the minimum electron escape occurs. As seen in Fig. 10, the minimum of the ratio for Curve a (the adsorbed layer) or Curve b (the thicker oxide layer) occurs in the kinetic-energy range of 30–40 above E_F. The uncertainty of the amount of the shifted Si 2*p* for the adsorbed layer increases with photon energy because the peak becomes wider as the combined resolution of the CMA and monochromator becomes wider. Thus, only the SiO_2 layer will be used to calculate quantitative values of the escape depth versus kinetic energy.

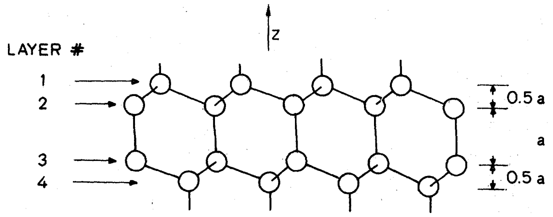

FIG. 11. Cross-sectional view of the layer separation beneath the (111) surface of Si. Note, *a* is the interatomic distance and the *z* axis is the surface normal.

Since the optical absorption coefficient (α) of silicon is ~1×10^5 to 1.5×10^5 cm^{-1} for photon energies 100–160 eV (although it does change with *hν*) as shown by Brown and co-worker,[37] the value of $1/\alpha$ is large (1000 Å) compared to the escape depth of the electrons (<20 Å for kinetic energies

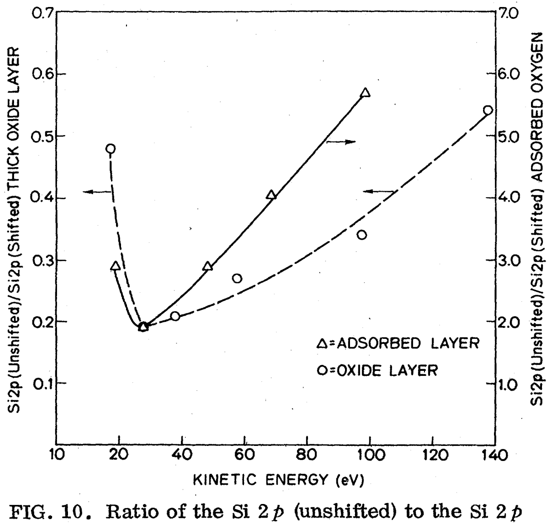

FIG. 10. Ratio of the Si 2*p* (unshifted) to the Si 2*p* (shifted) vs electron kinetic energy for an adsorbed-oxygen layer and a thick oxide layer.

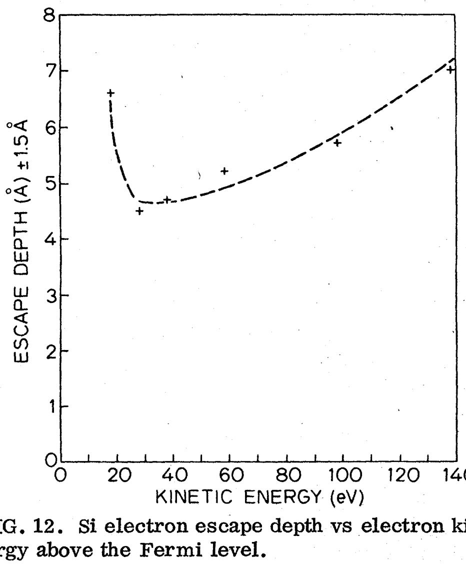

FIG. 12. Si electron escape depth vs electron kinetic energy above the Fermi level.

of this study). Thus, the intensity of radiation at each Si atom in the first ~100 Å of Si can be assumed to be constant.

An idealized cross-sectional view of a Si(111) surface is shown in Fig. 11. The surface layer 1 is separated from the next layer back (layer 2) by $0.5a$ (where a is the interatomic spacing). Layer 2 is separated from layer 3 by a, as is shown in Fig. 11. Thus, this periodicity continues through the Si. If each layer of atoms emits an intensity I_0 toward the surface, then the intensity of electrons (I) of a given layer arriving at the surface layer will be

$$I = I_0 \exp(-d/\lambda)\,, \tag{A1}$$

where d is the distance of that layer from the surface. Since the core electrons are tightly bound, it is assumed that on average they originate from the plane of each layer. Since the spacing of the layers is known, it will be possible to calculate the ratio: intensity (surface)/intensity (bulk). For emission perpendicular to the surface, this is simply

$$\left(e^{-0.5/\lambda} + \sum_{n=1}^{\infty} \left(e^{-1.5na/\lambda} + e^{-(1.5n+0.5)a/\lambda}\right)\right)^{-1}. \tag{A2}$$

If layer 2 is bonded to oxygen as well as layer 1, then the ratio of shifted to unshifted is

$$(1 + e^{-0.5/\lambda}) \Big/ \left(\sum_{n=1}^{\infty} e^{-1.5na/\lambda} + e^{-(1.5n+0.5)a/\lambda}\right)^{-1}. \tag{A3}$$

The ratio of Si $2p$ (shifted) to Si $2p$ (unshifted) for the sample exposed to 10^3-L O_2 by EP2 (Fig. 1, Curve c) was found to be 4. Assuming the surface layer is covered with oxygen, the electron escape depth at this energy was calculated to be 4.5 Å. The escape depths of the other kinetic energies were then calculated and are shown in Fig. 12. The escape depth at a kinetic energy of 140 eV is 7 Å, in agreement with the values reported by Raider and Flitsch.[11] The curve in Fig. 12 should give a good quantitative indication of the electron escape depth versus kinetic energy.

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