Electronic transitions of oxygen adsorbed on clean silicon (111) and (100) surfaces

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Second-derivative energy-loss spectra of 100-eV electrons reflected from silicon (100) and (111) surfaces have been studied with increasing oxygen coverages. Two different binding states are found. The first state which occurs up to monolayer coverage is characterized by electron transitions at 3.5, 5, 7, and 11 eV. After electron irradiation, annealing, or high exposures, oxygen goes into an SiO_2-type binding state. The spectrum of a completely oxidized surface agrees with the second derivative of the loss function $-Im(1/\epsilon)$ calculated from optical data. An interpretation of the spectra on the basis of dielectric-scattering theory also explains the shifts in peak positions below monolayer coverage.

I. INTRODUCTION

A detailed understanding of adsorption processes on surfaces in terms of chemical-bonding mechanisms requires a knowledge of the electronic energy levels of surface and adsorbate. Several techniques such as ion-neutralization spectroscopy (INS),[1] photoemission spectroscopy,[2,3] and field-emission spectroscopy[4] have been used for this purpose. Recently Steinrisser and Sickafus[5] and Küppers[6] have shown that electron-energy-loss spectroscopy may also be used as a tool to study molecular-orbital energies of adsorbates. Previous energy-loss measurements were performed with primary electron energies of 50–200 eV in standard four-grid-type low-energy-electron-diffraction systems. This technique can be further improved by using the cylindrical-mirror energy analyzer and taking the second derivative of the loss spectra.[7]

In energy-loss spectroscopy (ELS), initial occupied states as well as final empty states are involved. Therefore an assignment of an observed transition to certain occupied energy levels of either adsorbate or substrate might be difficult unless additional information is available. The interpretation of ELS is further impaired by the incomplete understanding of the inelastic-scattering mechanism at energies $E_0 = 50$–200 eV. At high electron energies the inelastic-scattering intensities of transmitted and reflected electrons are proportional to the loss function,

$$-Im(1/\epsilon) = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2) \qquad (1)$$

and

$$-Im \, 1/(\epsilon + 1) = \epsilon_2 / [(\epsilon_1 + 1)^2 + \epsilon_2^2] \qquad (2)$$

for "bulk" and "surface" losses, respectively, and thus are determined by the complex dielectric constant $\epsilon(0, \omega)$ of the material.[8-10] In this "dielectric-scattering theory" peaks in the loss function may be considerably shifted compared to the

quantum energies of the transitions involved.[11] The magnitude of the shift depends on the transition energy with respect to the collective excitations as well as on the oscillator strength.

In this paper ELS results using low-energy electrons are presented for silicon surfaces with increasing coverages of oxygen. A shift and splitting of the surface-plasmon peak with oxygen coverage is observed up to monolayer coverage. The measured second-derivative loss spectrum of SiO_2 is practically identical to the second derivative of the loss function calculated from optical data. It is further demonstrated that oxygen in the first adsorption state yields a loss spectrum qualitatively different from SiO_2.

II. EXPERIMENTAL DETAILS

The vacuum system used consisted of an ion-pumped stainless-steel chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. A single-pass PHI 10-234G Auger analyzer with an integral coaxial electron gun was used as an electron spectrometer. The primary beam had an angle of incidence normal to the surface while the inelastic intensity was analyzed at $\theta = 42° \pm 6°$ integrated over all azimuthal angles. The second derivative of the loss spectra was obtained by modulating the deflection voltage and observing the second harmonic with a peak-to-peak modulation voltage of 0.8 V. The energy resolution ΔE of the analyzer is (in principle) proportional to the pass energy of the electrons but is also affected by the focus-spot diameter of the electron beam and by residual magnetic fields. A primary electron energy of 100 eV was used as a good compromise considering resolution, noise, and sensitivity to both surface and bulk transitions. The energy resolution as measured by the full width at half-maximum of the second derivative of the elastic peak was then 0.7 eV. The average time required for scanning a loss spectrum was ~ 5 min. By using the analyzer in the conven-
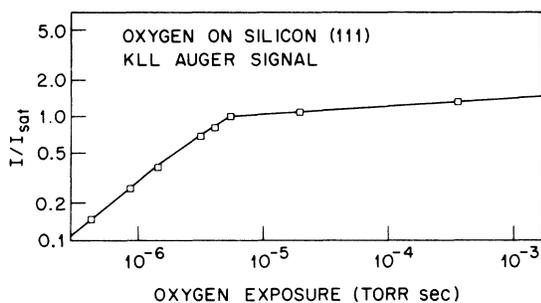
FIG. 1. Normalized Auger-signal intensity vs oxygen exposure. The slope of the curve at low exposures is smaller than unity indicating an inhomogeneous surface roughness. The additional oxygen uptake at higher exposures is due to the electron irradiation.

tional mode, Auger analysis could be carried out on the same surface.

The silicon samples were cut from As-doped material (5×10^{17} cm^{-3}), polished, and oxidized. The samples were cleaned by argon bombardment and annealing to 1100 K. They exhibited a clear 7×7 and 2×1 LEED pattern for the (111) and (100) surfaces, respectively. The samples were considered as being "clean" when the Auger signals of contaminants, especially carbon, were smaller than 2×10^{-3} of the silicon 91-eV signal. Oxygen was leaked into the system by means of a silver tube. The amount of oxygen was controlled by a leak valve.

III. EXPERIMENTAL RESULTS

Since the sticking coefficient of oxygen on silicon is severely influenced by the roughness of the surfaces[12] the coverage had to be determined after each exposure by observing the oxygen-Auger-signal intensity. A typical Auger-signal intensity versus exposure plot is given in Fig. 1. The saturation coverage is believed to correspond to one oxygen atom per silicon surface atom[13] and is referred to in this paper as monolayer coverage ($\theta = 1$). Neither the slope of the exposure plot below saturation nor the initial sticking coefficient were entirely reproducible. Electron micrographs as well as visual inspection showed considerable surface roughness on the sputtered and annealed samples. It is therefore assumed that the variation of initial sticking coefficient and its dependence on coverage is due to inhomogeneous surface roughness.[12] With the above preparation techniques our initial sticking coefficients were in closer agreement with the values obtained by Rovida et al.[14] than with Joyce and Neave.[15]

As already reported for the cleaved silicon surfaces,[12] a true saturation of the oxygen signal is obtained only when the Auger signal is determined

at a fresh surface area that has *not* been previously electron irradiated, or when sufficiently low beam currents (≈ 1 μA) are used. Partially-oxygen-covered surfaces, which have been irradiated by electrons, are capable of an additional oxygen uptake corresponding to a total coverage ~1.5 monolayers even at moderate exposures (10^{-2} Torr sec). No additional uptake is observed when only the clean surface has been exposed to the electron beam.

The second derivatives of the energy-loss spectra of the Si(111) surface are shown in Fig. 2. On the clean ordered surface seven peaks are observed (2.0, 3.5, 5.0, 7.4, 10.6, 14.5, and 17.3 eV). The peaks labeled E are bulk interband transitions, S corresponds to transitions from occupied surface states,[16] and $\hbar\omega_s$ and $\hbar\omega_p$ are surface and bulk plasmons, respectively. During oxygen adsorption the intensities of S_1 and S_3 decrease, while the intensity of S_2 seems to increase. In order to understand this behavior the same experiments were carried out for the (100) surface and the results are shown in Fig. 3. Instead of the S_2 and S_3 peaks only weak shoulders are present in the spectra of the (100) surface. At a monolayer coverage of oxygen, a strong peak
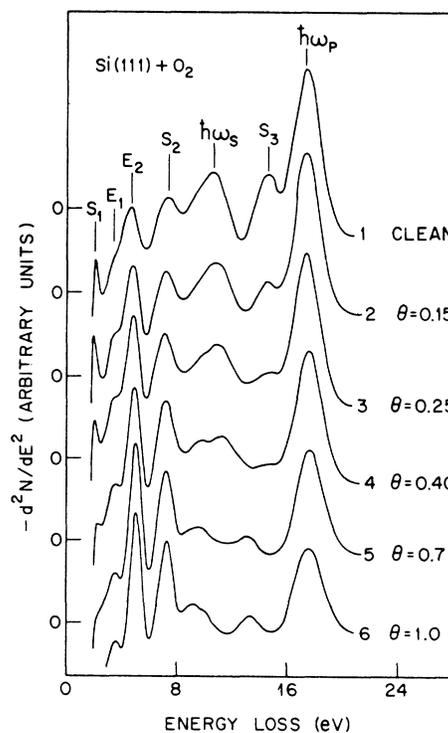

FIG. 2. Negative second derivative of the loss spectrum of a clean silicon (111)7 $\times$7 surface (curve 1) and spectra of increasing coverage with oxygen. Primary energy is 100 eV.
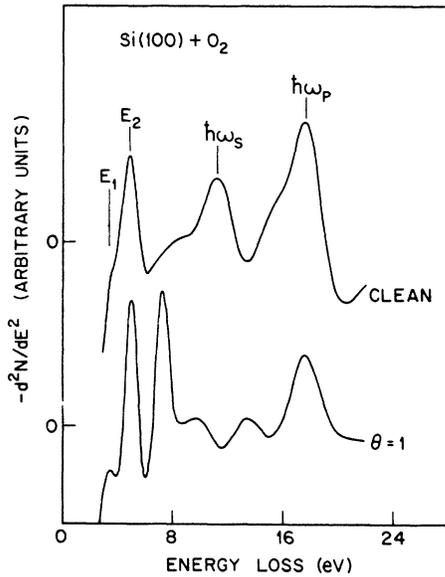
FIG. 3. Negative second derivatives of the loss spectra for the silicon (100)2 ×1 surface. For monolayer coverage the spectra of the (111) and (100) surface agree within the limits of reproducibility.

at 7.2 eV is seen just as on the (111) surface.

At approximately one-fourth of a monolayer coverage of oxygen the surface-plasmon loss peak splits into two loss peaks (Fig. 2) which shift apart with increasing coverage. This splitting (see Fig. 4) was reproducible in several experiments and was found to be independent of the primary electron energy between 40 and 100 eV within experimental error.

The loss spectra of surfaces covered with more than a monolayer of oxygen are distinctively different from spectra of oxygen obtained for lower
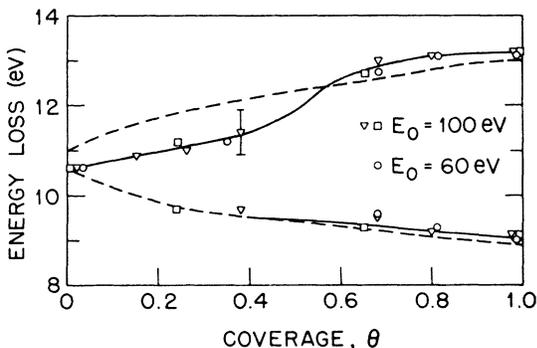

FIG. 4. Splitting of the surface-plasmon peak with coverage. The dotted line is the calculated splitting from a dielectric model (see text).

coverages. These results are shown in Fig. 5. Curves 1–4 were obtained by repeated cycles of electron irradiation and oxygen exposures. Curves 5 and 6 correspond to 5-min sputtering in 5×10^{-6} Torr of oxygen at 750 K and 2-min heating in 2×10^{-1} Torr of oxygen at 1250 K respectively. With increasing coverage, the 9-eV loss peak splits again and a strong peak at 10.7 eV develops. Depending on the amount of electron irradiation applied before monolayer coverage is reached this splitting is sometimes also observed for coverages below monolayer. The same result can be obtained by annealing the partially-oxygen-covered surface. Annealing for 10 min at 800 K converts the loss spectrum of a partially covered surface, e.g., curve 5 in Fig. 2 to a spectrum like that observed at higher coverages (curve 2 in Fig. 5). In addition, peaks at 12.5, ~21, and ~25 eV arise and the 13.2-eV transition is shifted to ~14.5 eV. The oxidation of silicon can also be studied by observing the LVV Auger transitions[15,17] (see Fig. 5). Curve 4 in Fig. 5 corresponds still to a partially oxidized surface, since the silicon E_2 interband transition as well as the 91-eV Auger peak characteristic of unoxidized silicon are still present. Both disappear for the completely oxidized surface (curve 5) and no further changes in the loss spectrum with heavier oxidation are observed.
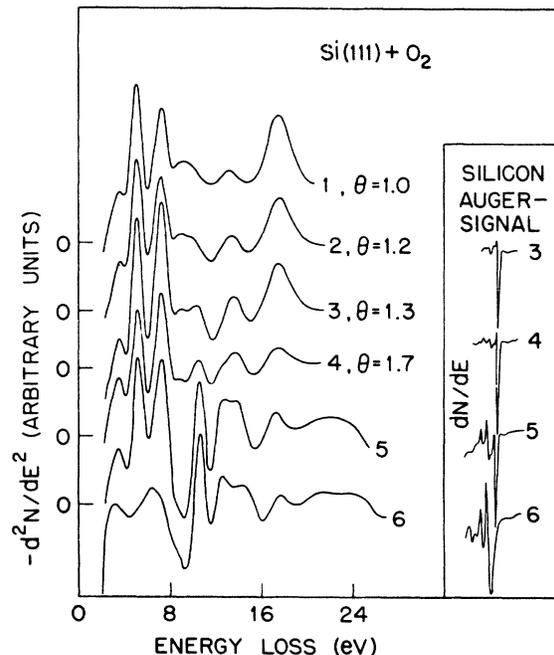

FIG. 5. Negative second derivatives of loss spectra for higher coverages. The continuous growth of an oxide layer is reflected by the loss spectra as well as by the silicon Auger signals.

IV. DISCUSSION OF OXYGEN ADSORPTION

By observing the vibrational frequencies of ad-sorbed oxygen between $\theta = 0.02$ and $\theta = 1$, Ibach et al.[12] were able to show that oxygen adsorbs in a single state. From the number of vibrational frequencies it has been concluded that this state is quasimolecular and a peroxide model[18] has been proposed. This model is also satisfying from the chemical point of view. The silicon-oxygen single bond length is about 1.60 Å. On both the (111) and (100) surfaces the silicon atoms are 3.84 Å apart, which makes a single-oxygen-atom bridge configuration unlikely. For the formation of a silicon-oxygen bridge bond con-necting nearest-neighbor silicon atoms as in SiO_2, the silicon-silicon bond has to be broken which would require some additional activation energy. The proposition that oxygen adsorbed at room temperature is in a different state than it is in SiO_2 is strongly supported by the very different loss spectra shown in Fig. 2 and Fig. 5.

The over-all loss spectrum of the oxygen-cov-ered (111) and (100) surfaces are essentially identical at $\theta \approx 1$. It is therefore concluded that the electronic states at a monolayer coverage are similar for the (100) and the (111) surfaces and that the 7.2-eV peak corresponds to an oxygen transition for the (111) surface as well. Since this transition happens to occur at the same energy as the S_2 surface-state transition, an apparent intensity increase during adsorption is simulated. Sharp loss peaks at 3.5 and 5.0 eV are observed for monolayer coverage. It is not clear from the experimental data whether electrons of the silicon-oxygen surface layer are involved in these transi-tions. Since they occur at the same energy as the bulk E_1 and E_2 transitions, they could be of bulk origin as well.

Above monolayer coverage the spectrum de-velops continuously into the SiO_2 spectrum (see Fig. 5). Significant changes in the Auger spectrum are seen only in curves 5 and 6. This can be ex-plained by assuming that on the average more than one of the silicon bonds have to be replaced by an Si–O–Si bond to produce significant changes in the Auger spectrum. From the loss spectra in Fig. 5 it seems most likely that some of the oxygen in curves 1–4 is in the same bonding state as in SiO_2 and that the changes from curves 2–6 indicate quantitative differences in the occupation numbers of the two states observed rather than qualitatively different bonding states for each curve.

V. DIELECTRIC INTERPRETATION OF ENERGY-LOSS DATA

In high-energy-electron transmission spectros-copy good agreement has been found between the loss spectra and the loss function [Eq. (1)] cal-culated from optical data.[8,9,11] It would there-fore be interesting to see whether this holds also for lower electron energies and the scattering geometry employed here.

The optical properties of noncrystalline SiO and SiO_2 films have been studied by Philipp.[19] In Fig. 6 (a) his data for the optical reflectance are replotted. The peak positions in the reflec-tance for SiO_2 resemble closely the position of the loss peaks [Fig. 6(b)]. This give us confidence to make a more detailed comparison with the optical loss function $-$ Im $1/\epsilon_{opt}$ obtained from the dielectric functions ϵ_1 and ϵ_2 that Philipp had calculated from a Kramers-Kronig analysis of the reflectance. The negative second derivative of this optical loss function is shown in Fig. 6(b). Over the entire energy range, ϵ_1 of SiO_2 is posi-tive and different from either 0 or -1. There-fore, the derivatives of the surface and bulk loss functions show peaks at approximately the same positions with only minor changes in relative in-tensities. Therefore, the surface loss is not plotted in Fig. 6(b). Considering the extraordi-
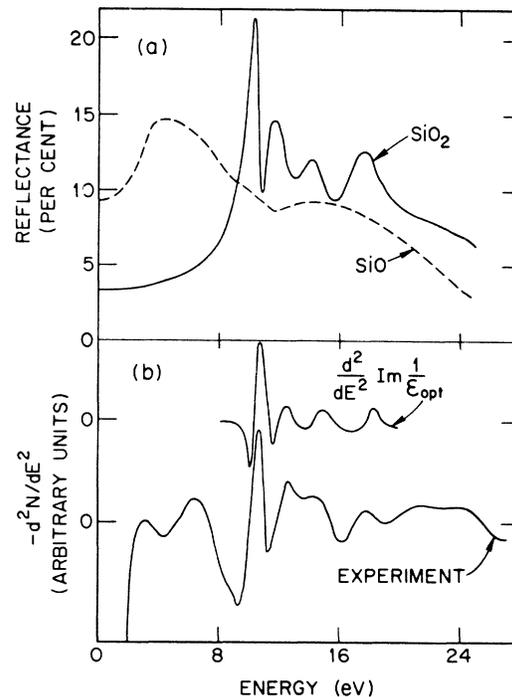

FIG. 6. (a) Optical reflectance of SiO and SiO_2 films after Philipp (Ref. 18). (b) The second derivative of the energy-loss spectrum for SiO_2 (curve 6 in Fig. 5) is com-pared to the second derivative of the loss function, cal-culated from optical data given by Philipp (Ref. 18). The agreement strongly suggests an interpretation of the loss spectrum based on the dielectric-scattering theory.

nary sensitivity of the second derivative to small changes in the dielectric functions, the agreement in Fig. 6(b) is as good as can reasonably be expected. It is noteworthy that in the case of SiO_2 surfaces, as in the case of silicon surfaces covered with a monolayer of oxygen, the loss spectrum is observed not to vary with incident energy in the range 50–200 eV. The calculated optical-loss-function curve shows no structure below 8 eV; however, a comparison with the reflectance of SiO [Fig. 6(a)] indicates that the experimentally observed structures at ~3.5 and 7 eV might be a contribution of silicon atoms still in a less oxidized (SiO) state.

A direct comparison between optical properties and the observed loss spectra is not possible for the adsorbed oxygen below monolayer coverage since the optical constants of this system are not known. The most remarkable effect in the loss spectra in Fig. 2 and Fig. 4 is the "splitting" of the surface-plasmon peak and the energy shift with increasing coverage. Since the vibrational frequencies of adsorbed oxygen do not shift (less than 4%) with increasing coverage,[12] it is difficult to interpret the shifts in the electronic energy losses as actual shifts in the electronic levels of several electron volts. Furthermore, it would be difficult to understand why this shift is observed only for the transition close to the surface-plasmon energy. In the following, a model calculation based on the dielectric-scattering theory is presented that describes the observed energy shifts. We have adopted our model from the textbook of Geiger[11] where it has been used to explain the shifts in observed bulk-plasmon frequencies and bulk-interband transitions compared to calculated values.

For a surface excitation, the incident 100-eV electron probes a region roughly $\sim 1/k_c \approx 6$ Å deep into the solid.[10] This is approximately the extent of the wave functions of surface electrons localized in bonds. On this scale no sharp breaks in the optical properties should occur. Increasing coverage with oxygen would then correspond to an increase in oscillator strength of oxygen-associated transitions averaged over the surface area. The average oscillator strength per unit surface area is proportional to the coverage θ, if the oscillator strength per adsorbed atom is constant with increasing coverage. This assumption is reasonable, since the high values of the vibrational frequencies and their small shift with coverage[12] indicate a strong localized silicon-oxygen bond. Such a model can give a reasonable account for the splitting in Fig. 4. In the energy range under discussion the dielectric constant of silicon is approximately represented by a free-electron gas,

$$\epsilon_1^{Si} = 1 - \omega_p^2/\omega^2 , \qquad (3)$$

where $\hbar\omega_p = 15$ eV. An oxygen transition may be described by

$$\epsilon^0 = A\omega_0^2 \, \theta / (\omega_0^2 - \omega^2 - i\omega\Gamma) , \qquad (4)$$

where A, ω_0, and Γ are the oscillator-strength parameter, transition frequency, and broadening parameter, respectively, of an oxygen transition. In Fig. 7 real and imaginary parts of $\epsilon(\omega)$ $= \epsilon^{Si} + \epsilon^0$ are drawn for $A = 0.3$, $\theta = 1$, $\Gamma = 1$ eV, and $\hbar\omega_0 = 11$ eV. The surface-loss function is calculated as well. By varying θ one obtains the calculated curve in Fig. 4. The agreement is satisfactory considering the simplicity of the model which treats only the oxygen transition at ~11 eV. A certain amount of arbitrariness is involved in choosing $\hbar\omega_0$. It is obvious however, that $\hbar\omega_0$ cannot be very much larger, since then a larger splitting would be observed for lower coverages. Also the oscillator frequency cannot be smaller than the surface-plasmon frequency since in that case the upper branch would be the shifted surface plasmon and the lower branch would be the oxygen transition. This does not agree with the development of the peaks at higher coverages. Once $\hbar\omega_0$ is chosen to be 11 eV, the oscillator-strength parameter $A = 0.3$ is obtained from the total splitting at monolayer coverage. The damping parameter Γ has no significant effect on the dispersion
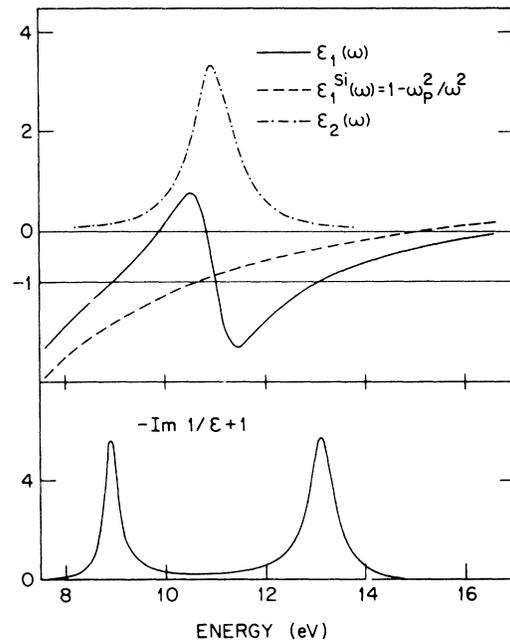

FIG. 7. Dielectric and surface-loss functions of a free-electron gas [Eq. (3)] with an additional single oscillator [Eq. (4)]. The parameters are fitted to represent the silicon surface with a coverage of a monolayer oxygen.

in Fig. 4. We conclude that the observed shifts in frequencies are indeed explained by the dielectric-scattering model.

Similar shifts have been observed earlier and have been explained by assuming the adsorbed layer would contribute a different[21,22] frequency-independent dielectric constant. An easy way to find the eigensolutions for an overlayer system with a frequency-dependent dielectric function has been described by Schmüser.[23] In both frequency-dependent and frequency-independent cases, however, the solution depends on a parameter $\vec{K} \cdot \vec{L}$ with $\vec{K}$ being the wave vector parallel to the surface and $\vec{L}$ the thickness of the layer. This dispersion is often referred to as "coupling dispersion." By choosing a reasonable set of parameters it can be shown that this coupling-dispersion model does not apply to the silicon-oxygen system. It would predict a considerable shift in frequencies with varying primary energy, which is not observed.

VI. CONCLUSIONS

Oxygen adsorbed on silicon surfaces at room temperature does not immediately oxidize the surface layer to form SiO_2-type bonding. Instead oxygen adsorbs in a well-defined molecular state characterized by certain vibrational frequencies[12] and electron transitions at approximately 3.5, 5.0, 7.2, and 11 eV. These losses have not been resolved in an earlier experiment carried out by Wei[24] who interpreted his data in terms of screened surface plasmons. No significant differences were found between oxygen transitions on (111) and (100) surfaces. The silicon is oxidized to SiO_2 either by exposure to considerably higher doses of oxygen or by converting the adsorbed oxygen into SiO_2 by electron irradiation. The same results are obtained by annealing a surface covered with less than a monolayer of oxygen. These findings are not easy to explain within the model of an immediate oxidation of silicon recently proposed by Meyer and Vrakking.[25]

Electron-energy-loss spectra can at least partly be interpreted in terms of dielectric theory (which at present is incomplete) even for electron energies as low as 50 eV and for adsorbed overlayers. This is not in agreement with the discussion of Steinrisser[5] and Küppers.[6] Steinrisser and Sickafus[26] did not consider a dielectric-scattering

mechanism in discussing their data. Küppers assumes that at low electron energies the dielectric losses are replaced by losses due to exchange interactions.[27] As Küppers himself points out, however, the data could be interpreted as well by a dielectric model. The energies of loss peaks do *not* depend on incident energy in the range $50 < E_0 < 200$ eV. A layer model of the dielectric function of an adsorbate-substrate system as discussed by Levine[22] therefore does not apply in this case. Instead of well-defined layers, the incident electron probes an inhomogeneous or spatially-dependent dielectric function in the above ELS experiments. An important consequence of the dielectric model is that loss-peak positions are not exactly equal to the energy differences between occupied and unoccupied energy levels responsible for the peaks. However, if loss peaks can be resolved at low coverage and studied as a function of surface-averaged oscillator strength by using a technique like the second-derivative spectroscopy employed here, then it is possible to determine the actual transition energies by using a model dielectric function as discussed in Sec. IV. This does not hold for loss spectra of clean surfaces since the oscillator strength of surface losses cannot easily be varied. Shifts between observed peaks and transition energies are usually small, especially when the transition energy is far away from clean surfaces. Thus ELS is capable of detecting surface states and provides a very sensitive tool to study adsorption and surface reactions. Since the final states for the observed transitions are not known, any detailed model for the energies of the occupied bonding states would be purely speculative. It is, however, possible to correlate these measurements with photoemission spectroscopy. Such measurements are in progress and will be reported at a later time.

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