Elastic scattering of low-energy electrons from oxygen-covered Si surfaces

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We present results for the elastic scattering of low-energy (4-eV) electrons from Si(100)(2×1) and Si(111)(7×7) surfaces during O_2 adsorption experiments. We observe striking variations in the elastic peak height as a function of surface condition. The peak height for the clean surfaces, which contain metallic surface states, or for surfaces covered with physisorbed O_2 (at 20 K), is more than an order of magnitude larger than that of surfaces that have reacted with oxygen to form Si-O-Si or are slightly contaminated with carbon. These observations are *qualitatively different* from previously reported results for metals.

Low-energy electrons have been extensively used in surface studies. Among the techniques available are low-energy electron diffraction (LEED), high-resolution electron-energy-loss spectroscopy (HREELS), and electron-reflection spectroscopy (ERS). In each technique, the objective is to strike the surface with a beam of low-energy electrons and in some way examine the emergent electrons for changes in their momentum, or energy, which are characteristic of the surface condition. The infrequently used ERS technique deals with specularly scattered elastic electrons and has been used to investigate resonant states,[1,2] adsorbate surface band structures,[3,4] interference effects,[5,6] and surface reflectivity.[7] Systematic changes of the reflectivity with surface condition have very seldom been discussed, however.

In this Rapid Communication we report a variation on the ERS technique, using HREELS to measure the height of the elastic peak in a series of experiments on Si surfaces at $20 \leq T \leq 300$ K during oxygen adsorption. The HREELS technique normally examines the energy distribution of the inelastically scattered electrons (usually in the near specular direction) which have lost energy via various surface-loss mechanisms.[8,9] Information is mostly contained in loss features at energies below the elastic peak. Additional information may be deduced from the shape of the elastic peak; however, although the broadening of the elastic peak has been used to study semiconductor surfaces,[10,11] its magnitude is ignored.[8] In our data the elastic peak height exhibits a strikingly strong and reproducible dependence on the surface condition. When the surface is clean and metallic surface states are present, or when it is covered (at $T < 35$ K) with physisorbed O_2, the elastic peak is quite high. When the surface is slightly contaminated (with carbon), or if a small amount of dissociated oxygen is adsorbed on the clean surface, then the elastic peak height drops by more than a factor of 10. Although a full understanding of our observations requires further theoretical and experimental work, the experimental data alone imply that elastic peak height measurements on semiconductor surfaces can be useful, and information about the surface and adsorption phenomenon can be obtained.

Experiments were carried out in a standard ion-pumped ultrahigh vacuum chamber with a base pressure of 7×10^{-11} Torr. The chamber is equipped with an Auger electron spectrometer, a reverse-view LEED system, a field-emission retarding potential gun for work function measurements,[12] a commercial HREELS instrument with 7-meV resolution,[13] and a variable-temperature ($20 \leq T \leq 450$ K) continuous-flow He cryostat. The silicon samples were highly doped (resistivity < 0.005 Ωcm) n type to avoid carrier freezeout at low temperatures. The surfaces were cleaned *in situ* by direct resistive heating to 850–900 °C. Auger electron spectroscopy of the surface following heating showed no detectable oxygen or carbon contamination, while the observed LEED patterns indicated a (7×7) surface reconstruction for Si(111), and a (2×1) reconstruction for Si(100). Surface cleanliness was confirmed by the absence of any adsorbate-loss peaks in the HREELS spectra. For Si(111) and Si(100), we also observe a metallic band tail, which extends out past 500 meV.[14] Routine examination of the sample by Auger or LEED resulted in carbon contamination of the surface.[15,16] To maintain the highest degree of cleanliness, Auger and/or LEED were not routinely used. Instead, the surface cleanliness was monitored by the characteristic features of HREELS, namely the presence of the metallic band tail and the absence of any adsorbate loss features. Gas exposure was made by filling the experimental chamber with O_2 for prescribed dosages which are given in langmuirs (1 L = 10^{-6} Torr s). Dosage accuracy is estimated at ± 30%. For pressure measurements, we used the ion-pump current so that no hot filaments were present during the experiments.

A selection of HREELS traces from an experiment at 20 K on clean Si(100)(2×1) is shown in Fig. 1. The experiment consists of two parts: exposure of the sample to a sequence of O_2 doses at 20 K, and then the heating of the oxygen-covered sample to 250 K. The amplitude of each trace is referenced to trace *a* and is given by the indicated magnification factor. Trace *a* is the loss spectrum for the clean surface showing a two-dimensional metallic loss tail. The next trace, *b*, shows the collapse of the metallic-loss tail with the smallest oxygen exposure (0.025 L). The nonmetallic-loss tail terminates at ≈ 200 meV. Trace *b* also indicates the appearance of the vibrational modes at 91 meV (Si-O-Si symmetric stretch) and 136 meV (Si-O-Si asymmetric stretch),[16,17] along with a sur-
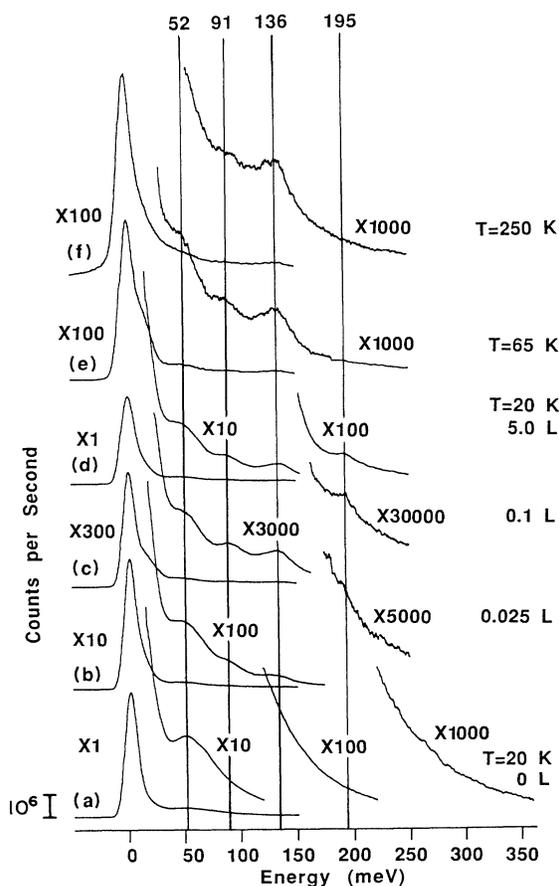

FIG. 1. High-resolution electron-energy-loss spectra are shown for different sample conditions: a, clean Si(100) surface at 20 K; b–d after 0.025, 0.1, and 5 L of oxygen exposure at 20 K, respectively; and e,f after warming the surface to 65 and 250 K, respectively. The observed loss peaks are 52 meV (surface phonon), 91 and 136 meV (Si-O-Si vibrational modes), and 195 meV (O-O vibrational mode of physisorbed oxygen). The spectra were all taken with the same incident electron energy (4 eV) and current, and their amplitudes are referenced to spectrum a for the clean surface.

face phonon at 52 meV.[18] The initial appearance of the 195-meV physisorbed O_2 bond[19] occurs at 0.1 L. Trace d shows the loss spectrum after 5.0 L of exposure. As the oxygen-covered sample is warmed (trace e), the 195-meV-loss peak disappears above ≈ 35 K, indicating the evaporation of the physisorbed O_2. Simultaneous with the disappearance of the 195-meV-loss peak from the energy-loss spectrum, the ion-pump current recorded a pressure spike due to oxygen evaporating from the sample and cryostat. Trace f shows the Si-O-Si vibrational-loss peaks after warming to 250 K.

The observed losses described above are consistent with previously reported HREELS data for O/Si(100) at higher temperatures.[16] Our new observation is the dramatic dependence of the elastic peak height on surface condition, as shown in Fig. 2. The data illustrate the following points: (1) The clean surface gives a relatively large elastic peak height, approaching that of a clean and flat single-crystal metal sample. Coincident with this
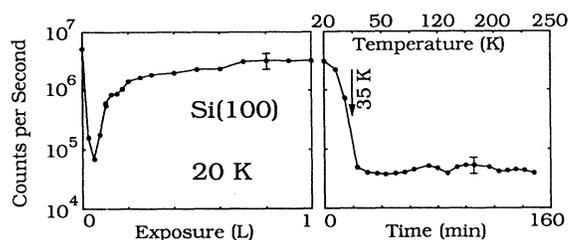

FIG. 2. HREELS elastic peak height data are presented for Si(100)(2×1) as a function of exposure to oxygen at 20 K (left-hand side) and subsequent annealing (right-hand side). The incident electron beam energy is 4 eV. In the annealing experiment, the temperature of the oxygen covered surface was raised monotonically but not linearly with time. The data are plotted here as a function of time, and the recorded temperatures are indicated on the top axis.

large elastic peak height we observe evidence of surface metallic states in the Si(100) HREELS-loss spectrum. (2) Upon exposure to a small amount of oxygen, the elastic peak height drops by about a factor of 100 and the chemisorbed-oxygen loss features appear. (3) With exposure to more oxygen, the elastic peak height increases. Coincident with this recovery is the appearance of the physisorbed O_2 loss peak. (4) As the surface is warmed past the O_2 condensation temperature (≈ 35 K), the O_2 loss feature disappears, and the elastic peak height once again drops drastically. (5) We have repeated the experiment of Fig. 2 using higher energies for the incident electron beam. The results are qualitatively similar to those shown in Fig. 2, but the variations of the elastic peak height are smaller. The results in Fig. 2 suggest that the large elastic peak heights correlate with the clean metallic surface and the presence of physisorbed O_2.

We have observed similar, although smaller, variations of the elastic peak height for the metallic Si(111)(7×7) and the semiconducting Si(110)(2×1) surface.[20] The results for Si(111) are shown in Fig. 3(a). On Si(111), we performed the following additional experiments. First, we repeated the experiment of Fig. 3(a), with exposures conducted at $T = 78$ K. The results are shown in Fig. 3(b). Similar to the low-temperature data of Fig. 3(a), the elastic peak height starts at a high value for the clean surface and drops by a factor of 10 upon exposure to O_2. Unlike the 20-K experiment, however, the elastic peak height does not recover with increasing exposures. Nor do we observe the 195-meV-loss peak due to physisorbed O_2. Upon warming the surface, the elastic peak height remains nearly constant. Second, we repeated the experiment of Fig. 3(a) on a Si(111)(7×7) surface which was slightly contaminated with carbon. The results, shown in Fig. 3(c), indicate that the elastic peak height is initially small but rises by a factor of 10 after exposure to O_2. These experiments again suggest the correlation of the large elastic peak height with clean surface and with physisorbed molecular oxygen.

To begin the discussion, we first note that in the few instances where variations in HREELS elastic peak height have been noted in the literature, explanations based on either order-disorder transitions[21] or temperature-dependent effects[10,11] have been advanced. We have exam-
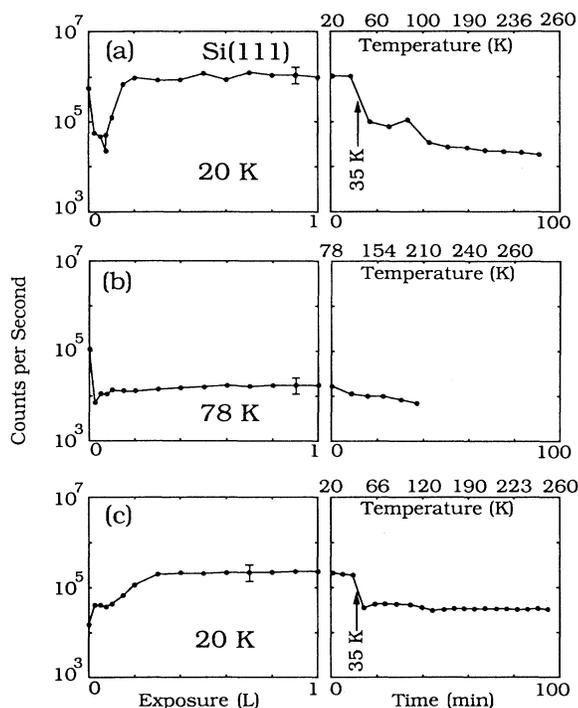
FIG. 3. HREELS elastic peak height data are presented for Si(111)(7×7). The results shown in (a) and (b) are for clean Si(111), while the data in (c) are for a Si(111) surface which is slightly contaminated with carbon. The incident electron-beam energy is 4 eV.

ined the Si(111) surface with LEED during our experiments. The sharp (7×7) pattern observed for a clean surface becomes increasingly diffuse with cumulative O_2 exposures. At no point does the apparent diffuseness abate. If we compare the elastic peak height changes due to O_2 exposure at 20 and 78 K with the LEED patterns under the same conditions, we note that the drop in the high initial elastic peak height is not synchronized with surface disordering. Furthermore, the large rebound of the elastic peak height at 20 K does not have any corresponding LEED features. Nor does the sharp decrease in elastic peak height at ≈ 35 K. Similar observations were made for Si(100)(2×1). For these reasons we do not believe that an order-disorder transition, or a series of transitions, is responsible for the elastic peak height changes.

As for the temperature-dependent effects, Persson and Demuth have reported variations in the full width at half maximum (FWHM) of the HREELS quasielastic peak.[10] For clean Si(111)(7×7), they observed a twofold increase in the FWHM as the sample is warmed from 15 to 300 K. In our measurements, we do not observe any measurable changes in the FWHM as a function of oxygen exposure at 20 K. We do observe a roughly twofold increase in the FWHM as the surface is warmed to 300 K, similar to the results of Ref. 10. Persson and Demuth explain their data based on a small-angle scattering theory. It is not clear, however, how small-angle scattering can explain the dramatic elastic peak height variations that we observe at a fixed temperature or in a very narrow temperature range: such scattering would widen the FWHM, an effect

which we do not observe.

Finally, the variations in elastic peak height do not appear to be due to changes in the work function either. We have measured the work function for Si(111) (Ref. 12) and Si(100) (Ref. 22) under the experimental conditions of Fig. 2. The work function increases *monotonically* with oxygen exposure at 20 K and saturates at ≈ 1 L, and does not change (within the experimental accuracy) as the sample is warmed through the O_2 condensation temperature (≈ 35 K).[12,22]

We propose a qualitative explanation for our data based on the quantum reflection of the incident electrons at the surface potential barrier (SPB).[2,6] In our experiments, the electrons approach the SPB with an energy 4 eV above the vacuum level. At the SPB, as the electrons transit the (work function) potential step, a fraction of their wavefunction amplitude is reflected specularly. We believe that it is the structure of the SPB which determines the specular reflectivity of the surface and is responsible for our observations. The SPB of a real surface is not perfectly flat (in a plane parallel to the surface) on an atomic scale. Rather, it conformally follows the position of atoms and charges on the surface and, therefore, reflects the surface roughness and disorder. On the other hand, since the electrostatic fields from all the charges on the surface make up the SPB, the smoothness of the SPB is also determined by the characteristics of the surface charges. For instance, *dipole* charges on the surface produce long-range electric fields which extend tens of angstroms into the vacuum. Because of the long-range nature of these dipole fields, the effect of the surface roughness on the SPB is minimized. The electrostatic fields generated by multipole charge distributions, however, have a range of only a few angstroms and can maximize the effect of surface roughness on the SPB. Therefore, when few or no dipoles are present on the surface, through the SPB, the reflectivity becomes very sensitive to surface roughness.

A tentative and qualitative explanation for our data is the following. In our measurements, we observe large elastic peaks for the clean metallic surfaces of Si(100) and Si(111). With O_2 exposure at 20 K, the chemisorbed atoms eliminate the metallic-surface states,[20] roughen the SPB, and therefore reduce the height of the elastic peak as more electrons scatter elastically in nonspecular directions. Additional O_2 exposure produces physisorbed molecular oxygen on the surface, as indicated by the 195-meV-loss peak observed in the HREELS traces (Fig. 1). Coincident with the presence of the molecular oxygen, the surface reflectivity increases. The normal-to-the-surface dipoles of physisorbed O_2 appear to be smoothing the SPB and increasing the reflectivity.[23]

In summary, using a HREELS instrument, we have observed striking variations in the elastic peak height of electrons specularly reflected from Si surfaces, and have established a correlation between these changes and the presence or absence of metallic surface states and physisorbed O_2 on the surface. Although the physical mechanism for these changes is not clearly understood, our results demonstrate the potential usefulness of HREELS elastic peak height measurements in studies of semiconductor surfaces and adsorption phenomena.

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[23] We note that this explanation is consistent with our observation that the changes in reflectivity are smaller for larger values of incident electron energy.