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Monitoring the surface oxidation process with an energy-tunable monoenergetic positron beam

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Monoenergetic positrons with incident energies of less than 25 eV were employed as a nondestructive surface and near-surface sensitive probe. Positron reflectivity and the positronium emission were measured as a function of incident energy for various oxygen coverages ranging from submonolayer to 3500 Å of SiO_2 on Si. The characteristics of these spectra change systematically with oxidation and are in good agreement with the known development of the surface electronic structure. Different oxidation stages are identified.

The oxidation of a semiconductor surface has long been studied for its technological importance in making metal-oxide-semiconductor (MOS) devices. In the present study, a Si(111) surface was chosen to demonstrate the use of slow positron beams as a surface sensitive probe. Information about the near-surface electronic structure can be deduced by measuring the positron reflectivity and the production of positronium (e^--e^+ bound state) as a function of e^+ incident energy.

When a low-energy positron $L(\geq 0.5$ eV) is injected into a solid, it loses energy through electronic excitations which depend mainly on the band-structure properties of the solid. At the low-energy stage of thermalization in a material with filled valence bands, electronic excitations are no longer possible. In a perfect lattice phonon creation then becomes the dominant way to lose energy, giving a much lower energy-loss rate as evidenced by the emission of nonthermalized positrons in wide-band-gap insulators.[1-4] When positrons enter the solid below the minimum excitation energy, an increase in the reflectivity and energy spread (ΔE) is observed. The minimum particle-hole electronic excitation energy is mainly determined by the direct band gap but also depends on the final-state coupling between the excited electron, hole, and positron. The energy for forming an exciton is ≈ 1 eV lower than the gap. Since the dielectric constants are relatively large in Si, compared to insulators, the screening processes reduce the final-state interaction considerably and the excitations are expected to be similar to the band-gap energies. This is often observed for excitonic excitations in semiconductors and is expected to be the case for bulk positronium (Ps). The formation of Ps in the bulk Si is through the virtual excitation of a valence electron into a conduction band and is not expected to be stable in Si at room temperature. At present no experimental results have demonstrated the existence of Ps in bulk Si between 10 and 300 K. However, in the SiO_2 overlayer it will form. In creating a stable Ps, there exists an optimum energy range of e^+, $E_{\min} < E < E_{\max}$, called the Ore gap.[5] Here, E is the e^+ energy; $E_{\min}$ is the minimum energy required to extract an electron to form Ps; and $E_{\max}$ is the maximum energy that a positron can have so that the created Ps does not have a kinetic energy exceeding the Ps binding energy in the system, thereby causing ionization.

For Si, the oxidation process has two stages.[6-8] The first stage is the initial chemisorption process which produces several intermediate oxidized states ranging from Si^{1+} to Si^{3+}. At higher coverage of about 11 Å (Refs. 7 and 8), the second stage is where the SiO_2-like compound begins to form and the chemisorption states decrease. For the first time, the process was studied by using an energy-tunable e^+ beam. Our measurements are consistent with the picture of two-stage oxidation processes and the onset of SiO_2 formation can be clearly identified.

The experiments were performed in a ultrahigh vacuum (UHV) chamber. The Si(111) p-type samples studied had a low boron-doping concentration of $\approx 6.4 \times 10^{14}$ cm^{-3}. The surface of the samples was cleaned by the standard procedures.[7] Auger electron spectroscopy showed small traces of carbon but no oxygen. A sharp (7×7) surface reconstruction low-energy electron-diffraction (LEED) pattern was clearly observed. The oxidation process was done by similar procedures as described in Ref. 6. The oxygen coverage was determined by the attenuation of the Si (LVV) Auger signal.[9] A magnetically guided monoenergetic positron beam was utilized in this work with a measured e^+ energy resolution, full width at half maximum (FWHM) ≤ 0.5 eV. Some spectra were taken with an improved e^+ energy resolution, FWHM ≈ 100 meV, and showed identical features with more resolution. A detailed description of the beam is provided elsewhere in the literature.[10] The positron incident energy was changed by biasing the sample voltage. The positrons were detected by detecting the annihilation gamma rays using a gamma-ray Ge detector mounted behind the sample. In the annihilation spectra the data were separated into two energy regions: one the total T and the other the photopeak P centered around 511 keV (m_0c^2). The total T is the sum of 3γ and 2γ events of the e^--e^+ annihilation. P is defined by a window around annihilation photopeak (511 keV) which detects mainly 2γ events. Three-fourths of vacuum Ps decays by three photons which is seen in the total and essentially not in the peak region.

The total and photopeak[11] were used to determine Ps fraction formed at the surface. Ps is formed as a positron leaves the surface and picks up an electron. If Ps exists in the bulk it is not detectable in the present experiment as the Ps will annihilate with a nearby electron (pick-off process)[12] and not with the correlated bound electron. The fraction of positrons R, which are reflected from the sample, are removed by an $\mathbf{E}\times\mathbf{B}$ filter in the source region and are therefore not detected and do not contribute to T. Therefore, $R = 1 - T'$, where T' is the total normalized to the incident e^+ intensity. All of the data were taken with 90% transmission grids in front of the sample grounded to avoid the energy broadening from the reemitted positrons returned by the retarding fields.

It is worth emphasizing that the Ps fraction deduced from the standard total and peak measurements is the fraction among detected annihilations which do not include the e^+ or Ps escaped from the detector region. To calculate the absolute fraction of the Ps formation, $F_{\text{Ps}}(\text{abs})$, certain assumptions about the escaped particles must be made. If one assumes that the undetected counts arise only from the escaped positrons and all the emitted Ps are detected with the same efficiency as the direct annihilation, then $F_{\text{Ps}}(\text{abs}) = F_{\text{Ps}}(\text{meas.})T'$. We have examined the validity of this assumption and estimated that the error is within 10% of the absolute value. A detailed analysis of the subject is provided by Shut, van Veen, Nielsen, and Lynn.[13]

At various oxygen coverages on the Si(111)(7×7) surface, the positron reflectivity and the measured Ps fraction as a function of incident energy are shown in Figs. 1 and 2, respectively. The absolute Ps fraction, calculated with the assumptions described above, is presented in Fig. 3. All the data were taken at room temperature. The clean surface data are shown in Fig. 1(a) where two reflection peaks were observed as indicated by the arrows, one at ≈ 2.5 eV and the other at ≈ 8.8 eV. The latter peak has a broad distribution which spans from 4.9 to 10.2 eV. At the present time we associate with the threshold energy for the surface plasmon excitation,[14,15] ≈ 10 eV, and this is in rough agreement with other experimental results, for example, electron energy-loss spectroscopy.[16] For the e^+ with energy below ≈ 10 eV, the plasmon excitation is no longer energetically accessible. On the other hand, as the incident energy decreases further, the particle-hole becomes the dominant energy-loss mechanism. It is this factor that possibly lowers the reflectivity at ≈ 4.9 eV. The possibility for the specular Bragg reflection[17] was considered to be unlikely in this region.

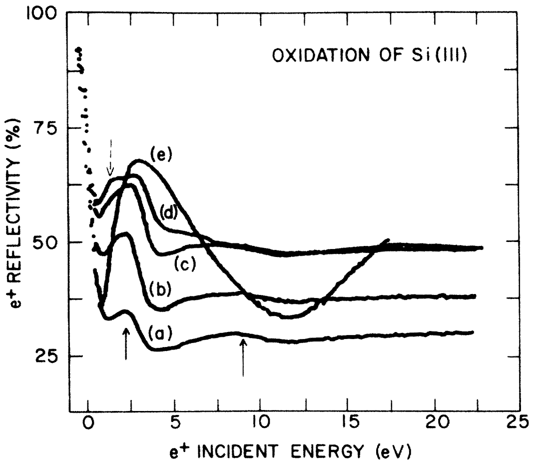

FIG. 1. At various oxygen coverages (a) clean Si(111)(7×7), (b) 2.5 Å overlayer, (c) 5.4 Å overlayer, (d) 14 Å overlayer, and (e) 3500 Å SiO_2, the e^+ reflection spectra have shown the noticeable changes in overall reflectivity and the transformation towards the SiO_2-like spectrum.

The first peak which starts at 3.5 eV extends to ≈ 2.5 eV. Figure 1(a) is interpreted as the minimum energy for the electronic excitation to the gap between filled valence bands and empty conduction bands. However, to predict

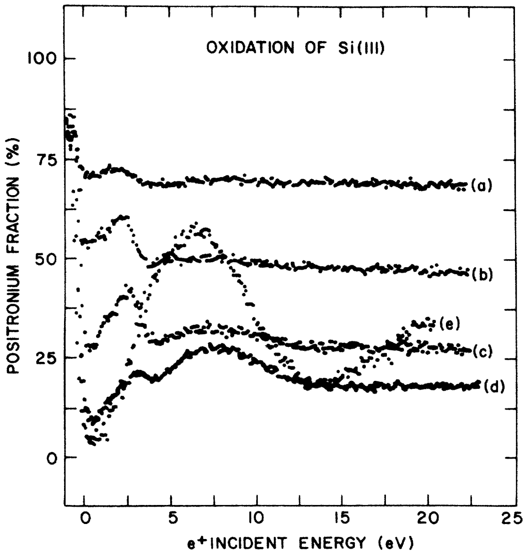

FIG. 2. The relative Ps fraction at the same coverage as denoted in Fig. 1. These data represent the Ps fraction. The peaks at ≈ 2.5 eV are unnormalized largely due to the reduced total detectable annihilations, i.e., the enhanced reflectivity.

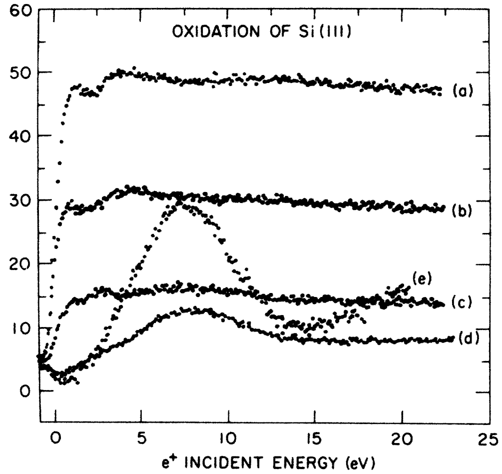

FIG. 3. Absolute positronium fraction, $F_{Ps}(\text{abs})$, normalized to the intensity of the incident beam, representing the Ps formation probability as a positron interacts with the solid. The normalization is done by the approximation: $F_{Ps}(\text{abs}) = (1-R)\times F_{Ps}$ (measured by $3\gamma/2\gamma$ technique), where R is the reflectivity shown in Fig. 1. The oxygen coverages are the same as in previous figures.

this minimum energy of the interband transition by a positron, proper consideration of the dielectric response of the Si to e^+ should be included, as has been done in electron energy-loss spectroscopy.[16] Our value of 3.5 eV is in agreement with that of the minimum bulk excitation by electrons.[16] An increase of the reflectivity could also occur at an energy just below the E_{min} for Ps formation. A rough estimation of the Ps binding energy in Si is ≈ 40 meV suggesting that bulk Ps is not stable at room temperature. Indeed, our present experimental data do not show a bulk Ps signal in Si (see Fig. 3). Lack of Ps inside Si probably is the reason why a similar minimum excitation energy was found for both e^- and e^+. The drop of the reflectivity at nearly zero incident energy is very likely produced by the trapping of positrons in the image-induced surface state.[18] Positrons of very low incident energy only need to experience small energy loss to make escape impossible, due to the positive work function.[3]

Figure 3 shows the absolute Ps spectra again with the same coverages of oxygen. The energy required to remove an electron from Si is 5.12 eV (Ref. 19) and is less than the energy gain from forming Ps (6.8 eV). The Ps formed with a thermalized positrons at the surface escapes into the vacuum with a maximum energy of 1.7 eV. The Ps formation cross section seems to be relatively constant in the energy range of positrons returning to the Si surface. The peak in Fig. 2 is associated with the reflection peak at the same energies (Fig. 3) and should not be interpreted as the increase of the Ps formation cross section. Figure 2 demonstrates how the measured Ps fraction couples to the e^+ reflectivity.

In Figs. 1 and 3 curves (a), (b), and (c) show noticeable effects with oxygen adsorption which increases the overall e^+ reflectivity and decreases the Ps fraction. The decrease in Ps fraction is attributed to the stronger binding of the electrons in the presence of oxygen, possibly due to the saturation of the dangling bonds. The decrease in the branching ratio for Ps, as the oxygen coverage increases, is found to add both to the direct annihilation and the reflectivity. The situation is different for the case of oxygen on Al(111) where an increase of the Ps fraction was observed upon oxygen adsorption; e.g., 15 L (L = langmuir, 1 L = 10^{-6} Torr sec) oxygen (≈ 0.15 monolayer) on aluminum surfaces increased the Ps fraction by $\approx 25\%$.[20] This behavior was explained by a reduction in e^+ binding to the image-induced potential well on the surface thus lowering the activation energy for thermally desorbed Ps. The reflection peak thresholds at 3.5 eV in Figs. 1(a), 1(b), and 1(c) do not seem to change with increasing oxygen coverage, suggesting that the near-surface region still retains the electronic properties of pure Si, in agreement with results by other techniques.[7,8,16]

An intermediate stage of oxidation is exemplified in the case of 14-Å oxygen coverage, curves (d) in Figs. 1 and 3, which shows signs of both silicon and silicon dioxide features. Curves (e) represent the case of thermally grown SiO_2 of 3500 Å thickness on a Si(110) crystal. The reflectivity for pure SiO_2 in Fig. 1 shows a conspicuous peak, which is characteristic of a wide-band-gap material. The position and shape of the peak in the reflectivity curves are mainly determined by three factors: the SiO_2 band gap, 8.9 eV,[21] the final-state interaction of the interband transition, and the positron work function. The valley at low energy is associated with surface trapping as previously mentioned. In contrast with the case for the rare-gas solids,[2] the distinctive thresholds for exciton and Ps formation are not observed here. It is assumed that for SiO_2 phonon broadening is much more severe, especially by optical phonons [≈ 50 meV (Ref. 22)] which do not exist in rare-gas solids.

The Ore gap for Ps formed in SiO_2 was estimated using the band gap, 8.9 eV,[19] the Ps binding energy, 4.8 eV,[23] and the positron work function, 0.2 eV.[24] The resultant E_{max} 8.7 eV is in agreement with the experimental results shown in Fig. 3(e) where at energies above ≈ 8 eV, the Ps signal is clearly reduced. However, the estimated E_{min}, ≈ 3.9 eV does not agree with the experimental data. Instead, the data show that the E_{min} for Ps formation is at near-zero energy. We suggest that this discrepancy could be associated with the existence of the partially filled electron surface states located ≈ 1.5 eV below the conduction band[25,26] and possibly negatively charged surface defects which can easily donate an electron to Ps. The Ps formed by the surface-state electrons is energetically allowed, but the rate is limited by the total density of electrons available.

It is also worth noting that at a coverage of 5 Å oxygen on Si(111) a small low-energy peak, shown by the dotted line in Fig. 1(d), begins to develop. It is clearly resolved in curve (d) but eventually disappears at higher coverage. Similar study of the Ge(100) oxidation processes is in agreement with our present interpretation for Si. However, the development of the low-energy peak is more obvious in the oxidation of Ge(100) and will be discussed in a more detailed publication.

In conclusion, we have shown that both positron reflectivity and Ps formation from Si are sensitive to oxidation. The evolution from the chemisorption of oxygen to the formation of a SiO_2-like compound was clearly observed by measuring both the e^+ reflectivity and Ps formation probability versus e^+ incident energy. Spectral features were associated with changes of the near-surface electronic structure. Our measurements also suggest that the band gap affects both the e^+ thermalization and Ps formation, and can be utilized in some cases to nondestructively detect a near-surface chemical reaction.

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