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Relationship between Atomic Structure and Electronic Properties of (111) Surfaces of Silicon*

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The effect of annealing on electronic properties of vacuum-cleaved surfaces of Si is investigated by means of photoelectron and secondary-electron emission. It is found that annealing results in a change in the surface structure, which in turn influences the electronic properties of the surface, such as the work function, ionization energy, electron affinity, position of the Fermi level in the band gap, and spectrum of surface states.

Low-energy electron diffraction (LEED) studies[1] have shown that the arrangement of atoms on the (111) surface of Si represents three different structures that depend on the thermal history: The freshly cleaved surface has a 2×1 superstructure; annealing at moderate temperatures produces a surface mesh of the same size as the projection of the bulk unit cell; and heating to 800°C results in a 7×7 superstructure. The positions of the surface atoms in these structures are not yet known, but the existence of structural changes has been verified by numerous workers.

Measurement of electronic properties, and in particular of the spectrum of surface states, has been done mostly on the freshly cleaved (111) surface. Allen and Gobeli[2] have first shown the existence of surface states by establishing the pinning of the Fermi level in the band gap at the surface. These measurements were later extended to lower temperatures.[3] Recently, Eden,[4] Eastman and Grobman,[5] and Wagner and Spicer[6] have obtained direct evidence from photoemission by excitation of electrons from the surface states of the freshly cleaved surface. Field emission from surface states on differently oriented surfaces has been reported by Lewis and Fischer.[7] Allen and Gobeli[8] have shown that annealing changes the photoemission from the (111) surface of Si. No correlation between the electronic properties and the different structures of this surface has been investigated to date. This paper presents the results of a systematic study of such a correlation.

Clean surfaces were first exposed by cleavage *in situ*; their structure was later changed by several anneals at increasing temperatures. After each heat treatment, the samples were allowed to cool and the structure was monitored by LEED and electronic properties were measured by photoelectron and secondary-emission spectroscopy at room temperature.

All measurements were performed in an ion-pumped stainless-steel vacuum system at pressures better than 3×10^{-11} Torr. A rotatable sample holder was equipped with a metallic emitter for Fermi-level determinations and experimental calibration.[9] Si crystals were cut in an L shape in cross section, exposing the (111) surfaces. This shape proved to give most satisfactory cleavages.[10] The results from four cleavages were exactly reproducible and agreed with those previously reported.[2,3]

We used 1-Ω-cm n-type crystals which were degassed by electron bombardment for more than 2 h at temperatures around 1300°K. This enabled us to maintain the very low pressures while annealing the samples (8×10^{-11} Torr at 1100°K). Evaporation of cathode material onto the surface was avoided by proper positioning of the filament.

Figure 1 shows the changes of the work function φ as one anneals the cleaved crystal to successively higher temperatures. The dashed line in the same figure represents the position of the Fermi level in the band gap at the surface, $(E_F - E_v)_s$, for different annealing temperatures. It is in reasonable agreement with surface-conductivity measurements.[11] Both quantities plotted in Fig. 1 are obtained[12] from the shifts of the low- and high-energy ends of the energy distributions of photoelectrons shown in Fig. 2. The ionization potential ξ can be determined from the two quantities shown in Fig. 1 by the relation $\xi = \varphi + (E_F - E_v)_s$.

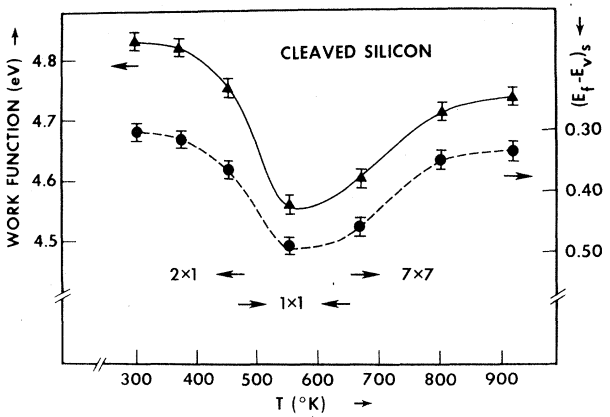

FIG. 1. Work function (solid line) and the position of the Fermi level with respect to the top of the valence band (dashed line), plotted for different annealing temperatures. Also shown are the representative LEED patterns for each region of anneal.

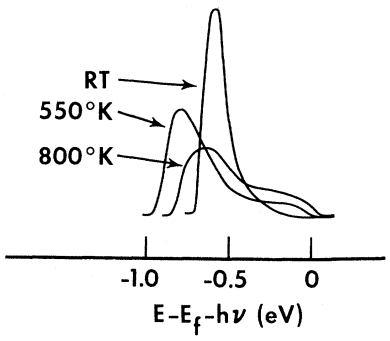

FIG. 2. Normalized energy distributions of photoemitted electrons with $h\nu = 5.53$ eV from Si after cleavage and anneal at two different temperatures.

The freshly cleaved surface has the highest work function (4.83 eV) which does not change if the sample is left at room terperature for a few hours. Its LEED pattern, as expected, contains the half-order spots characterizing the 2×1 superstructure. We usually observe the simultaneous occurrence of domains with the 2×1 structures in two or all three possible orientations on an area of the size of the electron beam (≃ 1 mm).

Heating the cleaved surface to 370°K for 15 min lowers the work function at room temperature by about 15 mV. Prolonged heating at the same temperature does not produce any further changes. The 2×1 LEED pattern is retained for anneals at 450°K, although the work function first decreases by 20 mV for a 5-min anneal, and then assumes a final value of 4.76 eV when annealed for 15 min. Annealing at the same temperature for an additional 45 min does not produce any further changes.

LEED indicates a transformation to the well-known 1×1 structure when the samples are annealed at 550°K. This change in structure occurs within less than 50°K. At this point, the silicon surfaces have their lowest work function, i.e., $\Phi = 4.56$ eV. Annealing at higher temperatures causes the gradual appearance of the fractional order spots of the 7×7 structure. Primary beam voltages less than 100 V already show a 7×7 pattern for heat treatments at 670°K for 15 min. Heating to 800°K produces a very clear pattern, also at higher electron energies. Figure 1 shows the associated change in the work function. In agreement with Mönch,[13] we observed that the onset temperature for the 7×7 structure depends on the pressure in the vacuum chamber (at $p = 1\times10^{-9}$ Torr, we have to anneal the surfaces at 1000°K to obtain the 7×7 pattern); however, no influence of the higher pressure (10^{-9} Torr) could be found in the formation of the 1×1 structure. These observations can be interpreted as a proof that the 7×7 structure is an intrinsic property of the clean Si surfaces[13] and that the contaminants are more strongly bound to "1×1" surfaces than to "2×1," i.e., the "1×1" surface is more reactive than the "2×1."

We observe that the change in the band bending is the same as the change in the work function for temperature regions between 300 and 450°K and between 550 and 900°K, indicating that the electron affinity and ionization potential are insensitive to annealing.

The photoemission results obtained at $h\nu = 5.53$ eV are illustrated in Fig. 2. The abscissa shows the initial energies of emitted electrons with respect to the Fermi level. The distributions from freshly cleaved surfaces do not give clear evidence for surface states at this photon energy, but their shape is not inconsistent with a contribution from surface states as reported by Eastman and Grobman.[5] The energy distributions we observed from freshly cleaved surfaces agree with those of Allen and Gobeli,[2] those of Callcott,[14] and those of Fischer,[3] and disagree with those of Wagner and Spicer[6] in that we do not observe a hump at the high-energy end of the distributions for the freshly cleaved surfaces. In this sense, our results are consistent with those obtained by Eastman and Grobman[5] at the higher photon energy. Therefore, we do not agree with Wagner and Spicer's comment that the disagreement between their data and Eastman and Grobman's could be explained by the bad cleavage of samples by the latter authors.

Leaving the sample in good vacuum, $p \simeq 3\times10^{-11}$

Torr, for 3 h does not have any any effect on the shape of the energy distributions; neither the work function nor the band bending changes with time, an occurrence that was interpreted in terms of low sticking probability by Allen and Gobeli.[2]

After annealing at 550°K and higher temperatures, we observe, at the high-energy end of the distributions (Fig. 2), the emission of electrons due to excitation of a band of surface states extending to or beyond the Fermi level. This occurrence was observed on four different surfaces; the results were perfectly reproducible. Auger spectra did not reveal the presence of impurities. It is interesting to notice the similarity between these distributions from annealed surfaces and the distributions obtained by Wagner and Spicer from one of their cleavages (Fig. 2 of Ref. 6). Because of the limited range of photon energies ($h\nu < 6.5$ eV), we cannot make an estimate of the density of surface states.

We analyzed secondary-electron spectra from a cleaved and annealed surface, with emphasis on the characteristic losses within 20 V of the primary beam. Figure 3 shows second derivatives of energy distributions of the secondary electrons. The abscissa represents the amount of energy loss with respect to the primary energy of incident electrons. We prefer to concentrate on the second derivative of the energy distributions, $d^2N(E)/dE^2$, because its maxima occur at the same energy as the structure in $N(E)$, where the curvature is maximum. We observe that all Si surfaces show a bulk plasma peak at 16.9 eV, in agreement with Raether[14]; its position does not change with surface treatments. We observe another peak at 11.6 eV below the primary energy. It lies at the right energy for a surface plasmon, e.g., $\omega_s \simeq 16.9/\sqrt{2} = 11.6$ eV, and its intensity depends on the surface structure: We observe it only with the two surfaces exhibiting superstructure, i.e., 2×1 and 7×7 LEED patterns (Fig. 3). We feel that we have insufficient evidence to decide unequivocally on a particular energy-loss mechanism.

A peak corresponding to an energy loss of 6 eV is clearly visible in the energy distributions and their derivatives (Fig. 3) for all surface structures. We do not understand its origin, but the fact that it is observed immediately after cleavage at 3×10^{-11} Torr indicates that it is an intrinsic property of silicon and that it is not due to an adsorbate.

We have also investigated the spectrum of secondary electrons over their entire energy range.

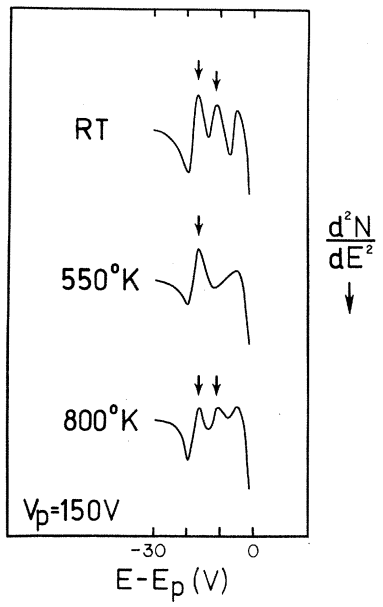

FIG. 3. Second derivatives of the energy distributions of secondary electrons showing the bulk- and surface-plasmon excitations for a cleaved and annealed (111) Si surface. The peak at 11.6 eV cannot be detected for the primitive surface showing a 1×1 LEED pattern.

No further changes were observed. In particular, the silicon Auger peak remained unchanged, and no Auger peaks due to impurities appeared.

We have observed that the structural rearrangements and resulting changes in the electronic properties of the (111) surface described above do not represent two-dimensional phase transitions. We have searched for but have not found definite transition temperatures, and all changes are irreversible.

In conclusion, we have observed that some of the electronic properties of cleaved (111) silicon surfaces, i.e., work function, position of the Fermi level in the band gap, spectrum of surface states as well as the cross section for surface-plasmon excitations, are related to the arrangement of surface atoms and its changes due to annealing. The electron affinity and the ionization potential are unaffected by the structural transformations.

Quite obviously, an interpretation of these findings must await a quantitative theory of solid surfaces. These data are presented in the hope of offering some guidance in the elaboration of such a theory.

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α Transfer to ^{44}Ti by the (^{6}Li, d) Reaction

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The reaction ^{40}Ca(^{6}Li, d) has been studied at $E(^6\text{Li}) = 32$ MeV. Clearly structured angular distributions, with maximum cross sections of the same order of magnitude as those reported for the reaction ^{40}Ca(^{16}O, ^{12}C), are obtained. They are well described by α-transfer distorted-wave Born-approximation calculations.

The (^{6}Li, d) reaction, though rather extensively applied to the study of light nuclei,[1] has scarcely been used[2,3] for target nuclei with $A \geq 40$. Its cross section was believed to be very small in this mass region, and the (^{16}O, ^{12}C) reaction has been mainly used instead for α-transfer studies.[4,5] Increased interest in such studies has been prompted by the experimental results of the (^{16}O, ^{12}C) reaction on Ca and Ni isotopes and by the interpretation of these results in terms of quartet structures.[5]

In spite of its reported weakness, the (^{6}Li, d) reaction exhibits important advantages over the (^{16}O, ^{12}C) reaction which make it highly desirable to extend (^{6}Li, d) measurements to heavier nuclei. (i) Better energy resolution can be obtained because of the smaller energy loss of Li ions in the target. (ii) More clearly structured and hence more conclusive angular distributions are expected at energies easily obtained with tandem accelerators (Coulomb-barrier heights, $E_{\text{lab}} \approx 15$ MeV for Li+Ca and 40 MeV for O+Ca). (iii) The strongly developed α-d cluster structure[6] of ^{6}Li favors α transfer and justifies, at least as a first attempt, the utilization of an α-stripping distorted-wave Born approximation (DWBA) (which can be performed in zero-range approximation because of the s state of mutual α-d cluster motion). The parentage for $^{16}\text{O} \rightarrow \alpha + {}^{12}\text{C}$(g.s.) is weak,[7-9] and the comparably strong $^{16}\text{O} \rightarrow \alpha + {}^{12}\text{C}$(4.4 MeV) component impairs[10,11] the usefulness of the (^{16}O, ^{12}C) reaction for studies of α-particle transfer.

In the present study for the first time angular distributions for the reaction ^{40}Ca(^{6}Li, d)^{44}Ti are presented and discussed. This reaction is of special interest, ^{44}Ti with four nucleons outside a doubly closed shell being the fp-shell analog of ^{20}Ne, for which well-developed features of the α-like correlations are found.

The experiment was concurrently begun at Argonne[12] and at Rochester, and was finished at