

Photoemission study of the effect of bulk doping and oxygen exposure on silicon surface states*

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The energy distribution of electrons photoemitted from the surface of ultrahigh-vacuum-cleaved silicon has been studied as a function of bulk doping and controlled oxygen exposure. The high sensitivity of surface states to oxygen has been utilized to observe the saturation of dangling bonds, identify the formation of the first monolayer of oxide, and to monitor the growth of the first few silicon dioxide layers. Comparison is made with the electron-spin-resonance signal.

Recently we have reported the observation,¹ using ultraviolet-photoemission and ultrahigh-vacuum techniques, of a band of surface states containing about one electron per surface atom on the cleaved (111) face of silicon.² Eastman and Grobman³ have independently reported this, as well as similar surface bands on Ge and GaAs. The key point of these papers is that surface states, which arise from unsatisfied bonds, are highly sensitive to surface contamination. In this paper we extend this work to consider the changes that occur with controlled oxygen exposure on silicon crystals of various dopings. Varying the doping aids the separation of bulk and surface states and demonstrates the consistency of the surface-state picture with the band-pinning model of Allen and Gobel.⁴ It also allows some estimate to be made of the spatial localization of the surface states. We then follow the changes which occur at the Si surface during the formation of the first monolayer of oxide through the growth of about 15 Å of silicon dioxide.

We have studied crystals with three different dopings, as indicated in Table I. The energy distributions in Fig. 1(a) were taken from these samples within 1 h of cleave at a pressure of 2×10^{-11} Torr or less. Each curve is referenced to the Fermi energy using an interchangeable copper photoemitter.¹ As the doping is changed, the structure in these curves undergoes three different types of relative energy shift.

(i) The peak at the high-energy (right-hand) side due to electrons in surface states^{1,3} is about 0.2 eV higher in energy for the p^{**} Si relative to the n^{**} Si. In order to understand the factors which control the location of this structure, consider a simplified "chemical model." Each broken bond on the cleaved surface gives rise to two surface-associated states, one of which must be filled for a neutral surface. On an n -type semiconductor a few of the normally empty states will be filled, causing a net negative surface charge which is compensated by ionized donors in the band-bending region. The Fermi energy E_F will then go through

the surface states slightly above the neutral level E_N , as is indicated in Fig. 1(b). The situation is reversed for p -type doping. Since a few of the normally filled states are empty, E_F falls below E_N , causing a small upward displacement of the surface-state peak, as observed.

This effect called "pinning" was first observed on the cleaved-silicon surface by Allen and Gobel,⁴ who made contact-potential and photoemissive-yield measurements over a complete range of dopings. They also observed a 0.2-eV relative displacement of the surface position of the valence-band maximum for extreme dopings.

(ii) Displacements in the low-energy (left-hand) side of the energy distributions [Fig. 1(a)] correspond to a 0.1-eV difference in work function. In order to be consistent with the surface position of the bands, the electron affinity χ must be lower by about 0.1 eV on the p^{**} silicon as compared to the n^- and n^{**} . Allen and Gobel⁴ also found that this conclusion was necessary to explain their data.

(iii) The n^{**} and p^{**} crystals were chosen degenerately doped in order to keep the band-bending region as short as possible compared to the electron-electron scattering length. In practice, these lengths are roughly comparable (12 Å), and we observe the bulk structure shifted by about 0.2 eV toward its surface position in both crystals.¹ Thus the bulk structure [central peaks, Fig. 1(a)] is displaced by 0.7 eV instead of the band-gap value of 1.1 eV. The bands in the lightly doped n^- crystal bend over a relatively long distance (10^4 Å), and all structure appears in its surface position.

TABLE I. Crystal data.

Type	Resistivity	Dopant	Concentration
n^{**}	0.001 Ω cm	arsenic	$N_D = 10^{20}$ cm ⁻³
n^-	25 Ω cm	phosphorus	$N_D = 2 \times 10^{14}$ cm ⁻³
p^{**}	0.0014 Ω cm	boron	$N_A = 10^{20}$ cm ⁻³

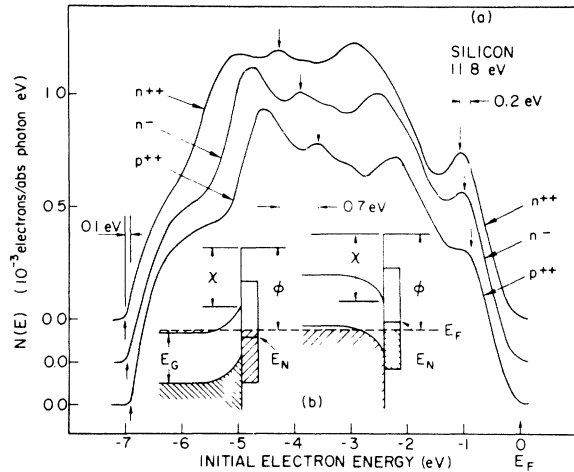


FIG. 1. (a) Energy-distribution curves for n^{++} , n^- , and p^{++} silicon, taken with a photon energy of 11.8 eV, are shown referenced to the Fermi energy E_F . The high-energy (right-hand) peak is due to electrons in surface states. The pinning effect causes a 0.2-eV relative displacement of this peak and a 0.1-eV shift in the work-function (left) edge. The bulk structure is displaced by only 0.7 eV, instead of the 1.1-eV gap, indicating that electrons are escaping from the band-bending region. (b) The pinning effect of a high density of surface states is illustrated for n^{++} and p^{++} semiconductors. The surface states would have no net charge if E_F went through the neutral level E_N . On the n^{++} semiconductor the bands bend upward until equilibrium is established. When this occurs E_F is greater than E_N , filling more surface states, thus causing a net negative surface charge which is compensated by ionized donors in the bulk band-bending region. The situation is reversed in the p^{++} case. E_N falls above E_F , thus displacing the surface-state peak and the surface position of the bands upward in energy.

The energy distribution of the electrons in surface states is best observed on the n^{++} Si at the highest photon energy, 11.8 eV, since here the bulk structure overlaps the surface structure the least.¹ Below about 8 eV, the surface and bulk structures coincide on n^- and p^{++} Si.

In view of the above observations, it appears that a band-bending model with surface states is adequate to explain our data. This statement has two implications. First, that we can talk about band bending over distances as short as 30 Å implies that doping atoms are sufficiently screened to give the appearance of a uniform charged background, and that a bulk band-structure picture is viable over distances within a few unit cells of the silicon surface. Second, the fact that the surface-state peak is not displaced toward the bulk position of the bands suggests that the surface states must be localized within the first few atomic layers of the surface.

In Fig. 1 of Ref. 1 on n^{++} silicon, we divided the

surface-state structure into a peak *A* and a shoulder *B*. Our present interpretation is that the break in slope between *A* and *B* is simply the upper edge of strong emission from the surface position of the valence band. This is particularly evident for photon energies of 8.6 eV or less, where emission from the upper valence band is strongest.⁵ At 11.8-eV photon energy, emission from the upper valence band is weak, obscuring this feature in our present data. The break in slope can also be found on n^- silicon, but it is more difficult to identify particularly at the higher photon energies,³ since the apparent position of the valence-band emission is closer to E_F . On p^{++} silicon, some bulk valence-band emission always extends up to E_F and there is no break in slope.

The cleaved surface of each crystal was exposed to oxygen at room temperature, beginning about one day after cleave. Due to the low base pressures, no significant surface contamination had taken place. The two major changes which occur in the energy distribution on oxidation are illustrated in Fig. 2(a) for the n^- crystal.

(i) The high-energy (right-hand) surface-state peak decreases in amplitude, being at least 90% removed by an exposure of 10^3 L ($L = \text{langmuir}$

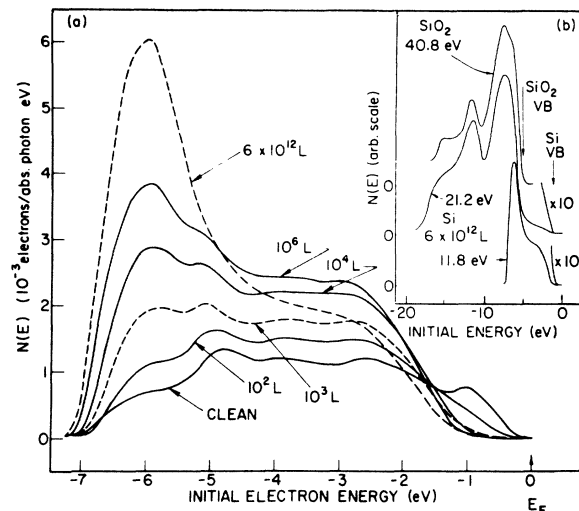


FIG. 2. (a) Oxygen exposure causes the surface-electron (right-hand) peak to reduce to a small residual level, coinciding with the growth of a peak (left-hand side) due to the formation of the SiO_2 valence band. These changes have taken place after a 10^3 -L exposure, at which time the first monolayer of oxide has formed. The oxide peak increases in amplitude with more exposure as the layer grows thicker. (b) After an exposure of 6×10^{12} L the LiF window isolating the ultrahigh vacuum from the monochromator is removed. The similarity of our data (11.8 and 21.2 eV) with those of DiStefano and Eastman (Ref. 6) (40.8 eV) shows that we have indeed formed a thin layer of SiO_2 .

= 10^{-6} Torr sec). This indicates that the dangling bonds exposed by the cleave are chemically combining with the oxygen, removing these electrons to lower energies.^{1,3}

(ii) A large new peak grows at the low-energy (left-hand) side of the energy distribution. This structure, which is well formed by 10^3 -L exposure, continues to grow with increasing exposure. After an exposure of 6×10^{12} L, the LiF window isolating the ultrahigh vacuum from the monochromator vacuum was removed and the sample was studied with 21.2-eV light. In Fig. 2(b) comparison is made with data taken by DiStefano and Eastman⁶ on thermally grown SiO_2 . From the similarity of these structures we conclude that we have formed a thin layer of SiO_2 . The 11.8-eV curve is included to show that the new peak which we observe in Fig. 2(a) represents the upper valence electrons of SiO_2 .

The coincidence of the removal of the surface states and the formation of the oxide valence band at an exposure of 10^3 L indicates that this is the exposure required to form the first monolayer of oxide. A saturation at 10^3 L in the oxygen absorption on cleaved silicon can also be found in the ellipsometry measurements of Archer and Gobeli⁷ and the recent Auger data of Ibach *et al.*⁸ For larger exposures the increase in amplitude of the oxide structure simply means that the oxide layer is growing thicker. At 6×10^{12} L we can compare with data of Lukes⁹ and estimate that the oxide is about 15 Å thick (approximately ten SiO_2 molecules deep).

The surface position of the valence-band maximum relative to the Fermi energy E_F following various oxygen exposures is plotted in Fig. 3(a). The curve for n^- Si is obtained by plotting the relative energy of a peak in the bulk structure, since the bulk structure appears in its surface position. Comparing this to the work-function change yields changes in the effective electron affinity [Fig. 3(b)]. The work-function changes on n^{++} and p^{++} Si are corrected for this in order to obtain the valence-band maximum and then are plotted in Fig. 3(a). This construction gives relative changes only. The absolute position of the n^- curve is obtained from the edge of strong valence-band emission at 7.6 eV just after cleave. The absolute top of the valence band could be as much as 0.1 eV closer to E_F .

Note that band-bending changes stop at about 10^3 L. This implies that the oxide-silicon interface-state density, which determines the final band bending, is fixed as soon as the first monolayer of oxide is formed. As the oxide grows thicker the interface simply moves deeper into the silicon with little additional change. The effective electron affinity, however, peaks at 10^3 L and then decreases, indicating that it is a function of oxide-layer thickness.

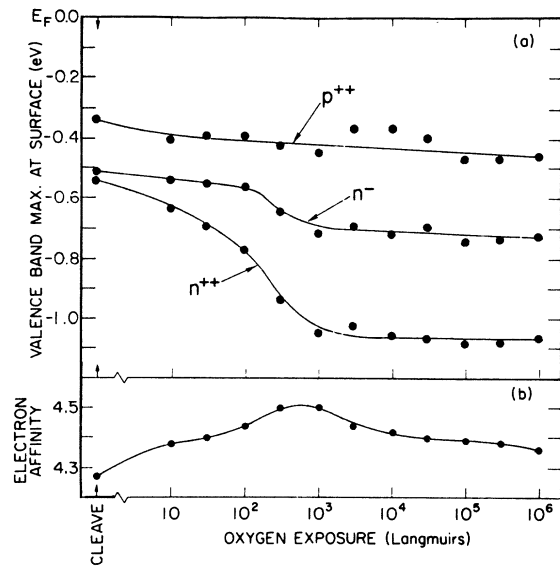


FIG. 3. (a) Surface position of the valence-band maximum relative to the Fermi energy E_F plotted vs oxygen exposure. Note that band-bending changes cease at about 10^3 -L exposure, indicating the formation of the oxide-silicon interface. The n^- curve is obtained by following the relative energy of a bulk structure peak. The n^{++} and p^{++} curves are obtained by correcting work-function changes for changes in the effective electron affinity. (b) The effective electron affinity χ is obtained by comparing changes in the work function with changes in the location of a bulk peak on n^- silicon. This gives the location of the silicon bands relative to the vacuum level.

As the oxide layer forms the surface states change to interface states. The energy distribution of these is difficult to measure due to the low residual level of emission; however, some important properties can be inferred from Fig. 3(a).

(a) Since the Fermi energy on the lightly doped n^- Si goes through the neutral level of the surface or interface states, we conclude from the downward shift of the n^- Si valence band that the neutral level falls about 0.2 eV higher in the gap of the oxidized silicon.

(b) The relative surface position of the bands on n^{++} and p^{++} Si separates from 0.2 eV after cleave to 0.6 eV after 10^6 -L oxidation. This reduction of the "pinning" effect is due to the lower density of residual interface states.

(c) After oxidation the residual band bending is largest on the p^{++} silicon, indicating that the interface-state density is largest near the valence-band side of the gap.

(d) The bands did not completely straighten on the n^{++} silicon as they did for one case of vacuum contamination.¹ This indicates that the interface-state density is dependent on the species of reacting gas.

The silicon-dioxide valence-band maximum can be located by extrapolating the edge of the oxide peak in Fig. 2(a). We find that after 10^6 -L oxidation the relative position of the silicon and oxide valence-band maxima differs by 4.5 eV independent of the doping; that is, the oxide band structure moves up and down with the silicon band bending. Adding this value to the position of the oxide conduction band, 4.2 eV, obtained from internal photoemission,¹⁰ we obtain 8.7 eV for the silicon-dioxide band gap. This value agrees with the silicon-dioxide photoconduction threshold obtained by DiStefano and Eastman.¹¹

To illustrate one important aspect of this work, let us compare our results with those obtained

from spin-resonance studies.¹² We have shown that electrons in silicon surface states are highly sensitive to oxygen and are almost completely removed by an exposure of 10^3 L. In contrast, the surface-related spin-resonance signal remains unchanged up to a 10^6 -L exposure and then sharpens with exposures up to 10^9 L.¹² These results show that photoemission and spin resonance are looking at two different things.¹³ Similar spin-resonance signals have been seen in amorphous¹⁴ and ion-implanted¹⁵ Si and used as a method for determining the density of "dangling bonds." This interpretation is now open to question.

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