RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 5 15 AUGUST 1989-I

Degenerate doping and conduction-band properties of Si studied by synchrotron photoemission of Sb/Si(001)

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(Received 9 May 1989)

Photoemission of the Sb-covered Si(001) surface showed that the Fermi-level position crosses the conduction-band minimum of Si for Sb coverages approaching a one-monolayer saturation limit. Momentum-resolved photoemission of the Sb-saturated Si(001) surface revealed the existence of an occupied initial state located near the conduction-band minimum. The metallic character of the surface is shown to be indicative of degenerate doping in the near-surface region.

The degenerate doping of semiconductor surfaces and fabrication of δ-function doped interfaces are topics of high-current interest among various fundamental and device-oriented research groups. The ability to prepare a surface or interface with sharp doping characteristics is extremely important and molecular-beam-epitaxy (MBE) prepared δ-function doping layers which exhibit quantum confinement of charge have been previously studied.[1,2] In this paper, we present the results of a momentum-resolved synchrotron photoemission study of the Sb-terminated Si(001) surface. The results indicate that under certain sample preparation conditions the surface Fermi level moves just above the conduction-band minimum (CBM) of Si and a distinct emission occurs within a narrow energy and momentum window defined by the conduction-band structure of Si. The angle-resolved photoemission techniques of "$k_\perp$ and $k_\parallel$ scans" are employed to measure the CBM position of Si in k space; this is the first time that a full determination of the wave vector $\mathbf{k}$ is carried out for the conduction-band minimum of a semiconductor. The measurement itself provides an interesting demonstration of the utility and applicability of the photoemission techniques. The discovery of the occupancy of the CBM further demonstrates that the Sb termination prepared by conventional MBE techniques will degenerately dope (n^{2+} type) the near-surface region of Si(001), revealing a host of unusual electronic properties and a variety of potential applications in semiconductor-surface and thin-film research.

The experiments were carried out with synchrotron radiation dispersed by a 6-m toroidal-grating monochromator on the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin-Madison at Stoughton, Wisconsin. A small hemispherical analyzer having a full acceptance angle of 3° was used for the momentum-resolved experiments and a large hemispherical analyzer was used for angle-integrated core-level measurements. The overall instrumental resolution was 0.1–0.2 eV. The photoemission system possessed MBE capabilities. The n-type Si(001) samples having a resistivity of 10 Ω cm were cleaned by heating to about 1100°C for 10 s. The Sb overlayers were prepared by evaporation with a rate of 1–10 monolayers (ML) per min. In this paper 1 ML of Sb is defined as 6.8×10^{14} atoms/cm^2, which is the site density for an unreconstructed Si(001) surface. The sample temperature during evaporation was maintained between 320 and 370°C, and typical, Sb exposures ranged from 30 to 50 ML. Upon exposure to the Sb beam, the sticking coefficient was found to approach zero once the surface coverage approached the saturation limit of approximately 1 ML.[3–5] After the Sb exposures, the surface was further annealed for 1 min at the same temperature, and allowed to cool to room temperature before the measurements.

The normal-emission spectra for the Sb-saturated surface in the valence-band region are shown in Fig. 1 for various photon energies. A spectrum for the clean surface (the bottom spectrum) is also included for comparison. The binding energy is referred to the Fermi level determined by observing the Fermi edge of a polycrystalline gold foil in electrical contact with the sample. The dispersive features labeled A and B can be identified as direct transitions from bulk Si valence bands.[5,6] The existence of transitions A and B, as well as other bulk band transitions observed in a related study of the Sb-terminated Si(001) surface, indicates a good bulk Si crystal order beneath the Sb.[5] In Fig. 1, spectral regions which are uncertain due to Sb 4d core-level emission excited by stray second-order light from the monochromator are replaced by arbitrary smooth dotted curves. The clean-surface spectrum in Fig. 1 exhibits a surface-state peak at a 0.7-eV binding energy, which originates from the dangling bonds.[7] At Sb saturation, this state is no longer present; this observation is consistent with recent core-level spectroscopy and scanning tunneling microscopy findings which showed that the dangling bonds are saturated by Sb adsorption.[5] The most striking feature in Fig. 1 for the Sb-covered surface is the distinct sharp peak located just below the Fermi level, indicative of the presence of a metallic state, followed by a gap with no emission. The onset of emission below the gap is at 1.21 ± 0.05-eV binding energy with respect to the Fermi level for each spectrum shown in Fig. 1 obtained from the Sb-saturated surface. This must then be the position of the valence-band maximum (VBM), and a dashed line labeled E_v is shown in Fig. 1 to indicate this position for the

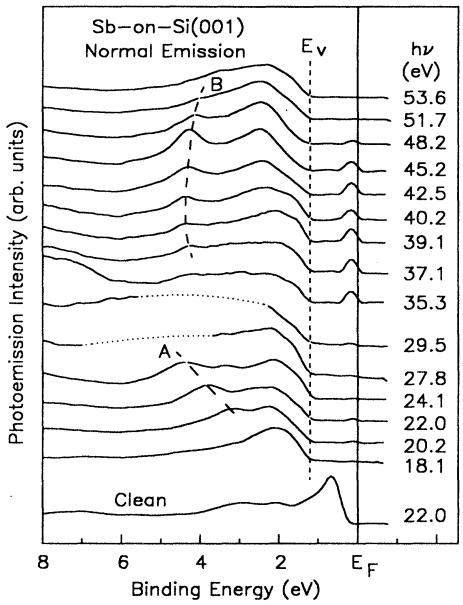

FIG. 1. Normal-emission spectra of the Sb-saturated Si(001) system for various photon energies. Also included is a clean Si(001)-(2×1) spectrum at the bottom. The binding energy is referred to the Fermi level E_F and the valence-band maximum for the Sb-saturated surface is labeled E_V. Uncertain regions due to the Sb 4*d* core levels appearing in second order are replaced by arbitrary smooth dotted curves.

Sb-saturated case. As a confirmation, the Fermi-level position relative to the band gap as a function of Sb coverage has also been determined by measuring changes in the bulk Si 2*p* core-level binding energy (data not shown here). An adsorbate-induced change in the Fermi-level position due to band bending is equal to the induced change in the core-level binding energy relative to the Fermi level.[8] The Fermi level, initially at 0.58 eV above the VBM for the clean surface,[9] gradually moves upward and reaches 1.21 ± 0.12 eV above the VBM at saturation. This value, although not as accurate, is consistent with that deduced from the valence-band measurement discussed above. Since the Si band gap is 1.12 eV, it is evident from these measurements that the Fermi level resides in the conduction band for saturation coverages, and the peak just below the Fermi level in Fig. 1 is right at the CBM within the uncertainty.

The metallic state was observed only after the Fermi level was pushed up slightly above the CBM, which only occurred at saturation coverages. This behavior, as well as its extreme insensitivity to residual-gas contamination, tends to indicate that it is not a surface state of the usual kind. The most straightforward interpretation is degenerate doping of the near-surface region, resulting in a significant population of conduction electrons near the CBM (the $\Delta_1^{\min}$ point in *k* space); these electrons give rise to the sharp peak in Fig. 1. To verify this assertion, we have determined the wave vector **k** of these electrons, which should be at $\Delta_1^{\min}$ according to our model. For all photon energies used, a slight departure from the normal-emission direction (~3°) caused the peak to disappear, meaning that the wave-vector component parallel to the surface is zero. Figure 2 illustrates this by showing the sudden evanescence of the metallic state for small angular deviations θ from the normal direction with $\mathbf{k}_\parallel \| [110]$ and $h\nu = 37.1$ eV. A small dispersion of the metallic state position towards the Fermi level for increasing θ is observed just before its disappearance; this is consistent with the sign of the transverse effective mass of Si at the CBM. Since the observed angular spread of the metallic state is about the same as the acceptance angle of the analyzer, it is impossible to determine accurately this effective mass from the present data.

To determine $k_\perp$, the wave-vector component perpendicular to the surface for the metallic state, we use the well-established technique of "$\mathbf{k}_\perp$ scan" by plotting the intensity of this peak as a function of the photon energy.[10] Since the relevant final band is well approximated by a broadened free-electron dispersion, the photon energy used can be directly converted to the final electron wave vector k_f by the formula

$$E_i + h\nu = \hbar^2 k_f^2/2m - U , \qquad (1)$$

where E_i (the CBM state energy) and U (the inner potential) are both referred to the VBM.[10] The results are shown in the lower panel of Fig. 3 with U taken to be 5.6 eV (see below). This value of U is consistent with that (~5 eV) determined previously.[6,11] The results in Fig. 3 show a strong resonance centered about $k_f = 3k_{\Gamma X}$ in the extended-zone scheme ($k_{\Gamma X} = 2\pi/a = 1.16$ Å^{-1} is the distance between the Γ and X points in the Brillouin zone; a is the lattice constant). The small dip near the peak of the resonance suggests the presence of two nearby peaks. Shown in the upper panel of Fig. 3 are the dispersion

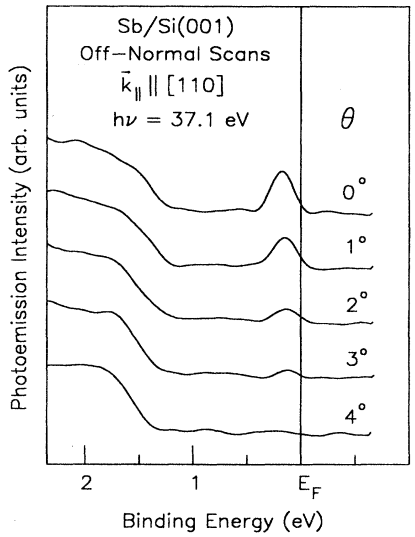

FIG. 2. Spectra of the Sb-saturated Si(001) system for small angular deviations θ from the normal direction. The photon energy is $h\nu = 37.1$ eV and the direction of the component of the momenta parallel to the surface is along [110]. The binding energy is referred to the Fermi level E_F.

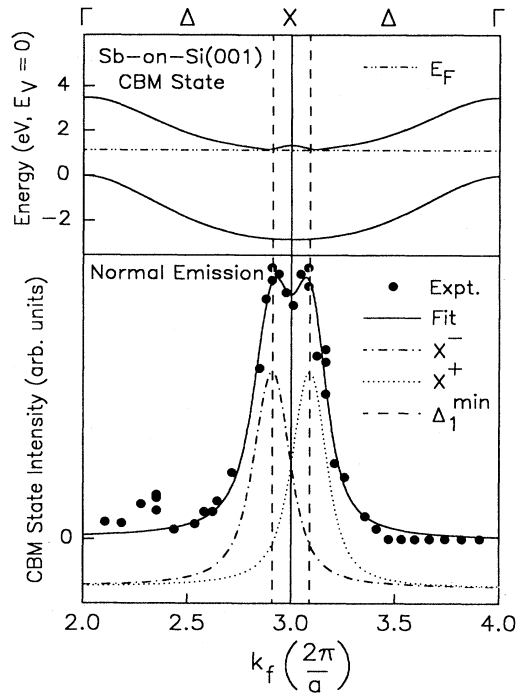

FIG. 3. The lower panel shows the CBM-state intensity as a function of k_f (measured in units of $2\pi/a$) which is determined from Eq. (1). The data (dots), the fit to the data (solid curve), the individual X^- and X^+ components (dash-dotted and dotted curves), and the resulting Δ_1^{min} positions (dashed vertical lines) are indicated. The data uncertainty is dominated by the limited experimental precision in intensity measurement, which is less than about 10% near the peak and follows from the degree of data scattering. The upper panel shows the highest valence band and the lowest conduction band along the Δ line (from Ref. 12) with the initial energy referred to the VBM at E_V. The Sb-induced Fermi-level position (E_F) is indicated.

curves for the highest valence band and the lowest conduction band of Si taken from the calculation of Chelikowsky and Cohen,[12] presented in the repeated-zone scheme. The two nearby resonance peaks, indicated by the vertical dashed lines, correspond very well with the CBM, which is located very near, but not at the X critical point. This is strong evidence that our interpretation is correct. In another study, Eastman *et al.*,[13] using a constant photon energy of 21 eV and an off-normal emission geometry, have shown that an As-implanted Si(111)-(1×1) surface may exhibit a metallic emission due to an initial-state occupation at the CBM. However, the electron momentum is uncertain in this study since the final-state band dispersion is unknown for this photon energy.[10]

Within the direct-transition model, the position and linewidth of the resonance are determined by the value of k_i, the initial electron wave vector, and broadening effects, respectively.[10] The solid curve describing the data in Fig. 3 is a least-squares fit based on this model. The model function is a superposition of two Voigt functions (convolution of a Gaussian and a Lorentzian) as indicated near the bottom of Fig. 3, each separated from the X critical point by an adjustable amount. The inner potential was also made adjustable in the fit; the final value was 5.6 eV (see above). From the fit, the centers of the two Voigt line shapes occur at $k_i = (3 \pm 0.09)k_{\Gamma X}$, meaning that the CBM, or the Δ_1^{min} point, is separated from the Brillouin-zone center Γ by $0.91k_{\Gamma X}$. This is very close to Chelikowsky and Cohen's theoretical result of $0.89k_{\Gamma X}$,[12] and differs somewhat from Feher's result of $0.85k_{\Gamma X}$ deduced from a model fit to the electron-spin-resonance data.[14] The Lorentzian width of the Voigt functions represents the final-state electron lifetime broadening; from the fit, a value of 4.3 eV is obtained which translates into a 6.2-Å mean free path. This value is consistent with the mean free path in Si obtained from core-level spectroscopy.[8] The Gaussian width represents the distortion and smearing of the free-electron final-state character; the fit gives a value of 3.4 eV which is close to the expected values based on the typical order of pseudopotential form factors (~3 eV).[10,12] Thus, all of the essential features of the resonance behavior are nicely explained.

By comparing the integrated intensity of the CBM state over its narrow cone of emission to the integrated intensity of the valence-band region summed over all angles due to the four valence electrons per Si atom, we estimate a carrier concentration of 10^{19}–10^{20} electrons/cm^3 in the conduction band within the photoemission probing depth of ~6 Å. This is close to the expected doping concentration necessary to raise the Fermi level into the conduction band.[15] Since the spatial confinement of the donor electronic charge is on the order of the Sb-donor radius of 20 Å,[16] which is greater than the photoemission probing depth, a dense Sb doping profile near the surface is sufficient to cause the degenerate-doping conditions observed here.

In conclusion, this experiment shows the following: (i) Under conventional MBE conditions, the Si(100) surface can be degenerately doped by saturation coverage of Sb. This discovery allows us to probe the conduction-band properties with photoemission, and should serve as a stimulus for further related research into interfacial systems of group III and V materials on Si and Ge. Even though degenerate doping can also be achieved through ion implantation,[13] this method tends to degrade the electrical, electronic, and crystalline characteristics of the material. In addition, the control of the spatial distribution of the dopant atoms is much less precise. For these reasons (as well as cost consideration), MBE techniques are much more preferred for the purpose of materials preparation and synthesis. (ii) The combination of $k_\perp$ and $k_\parallel$ photoemission scans yields a full determination of the k-space location of the conduction-band minimum of Si. This represents a new level of achievement in the application of angle-resolved photoemission spectroscopy.

This material is based upon the work supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76ER01198. Some of the personnel and equipment support was also derived from grants from the U.S. National Science Foundation (Grants No. DMR-8352083 and No. DMR-8614234), the IBM T.J. Watson Research Center (Yorktown

Heights, NY), and the E.I. du Pont de Nemours and Company (Wilmington, DE). The Synchrotron Radiation Center of the University of Wisconsin-Madison is supported by the U.S. National Science Foundation under Contract No. DMR-8020164. We acknowledge the use of the central facilities of the Materials Research Laboratory of the University of Illinois, which is supported by the U.S. Department of Energy, Division of Materials Sciences, under Contract No. DE-AC02-76ER01198, and the U.S. National Science Foundation under Contract No. DMR-8316981.

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[15]The Fermi-level position as a function of the donor concentration can be calculated from charge-neutrality conditions and Fermi statistics; see, for example, S. M. Sze, *Physics of Semiconductor Devices,* 2nd ed. (Wiley, New York, 1981), pp. 16–27. We assume the donor-level binding energy to be described by a Mott-transition behavior in which all the donors are ionized after a critical concentration of 1.7×10^{18} cm^{-3} (see Ref. 16). For donor densities $10^{19} < N_D < 10^{20}$ cm^{-3}, the Fermi level is above the CBM by $0 < E_F - E_C < 0.1$ eV. In Ref. 1 a donor density of $\sim10^{20}$ cm^{-3} is demonstrated to cause metallic conductivity from Hall measurements.

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