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Photoemission study of the surface states that pin the Fermi level at Si(100)2×1 surfaces

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Clean Si(100) surfaces of a heavily *n*-doped crystal have been studied with angle-resolved photoemission. A new surface state is observed at the Fermi level, only appearing close to the $\bar{\Gamma}$ and $\bar{J}'$ points in the 2×1 surface Brillouin zone. Because of the localization in momentum space it is concluded that the observed states are spatially extended and not related to localized defects. The emission at the Fermi level is assigned to the dispersion minima of an unoccupied surface-state band responsible for the pinning of the Fermi level at Si(100)2×1 surfaces.

Because of its technological interest, the clean Si(100) surface has been studied with many experimental techniques and several structural models have been suggested to account for the observed surface reconstructions.[1] In spite of these efforts the atomic and electronic structures of the Si(100) surface have not yet been established unambiguously.

The most frequently observed reconstruction of the clean Si(100) surface is the two-domain 2×1 reconstruction.[2] However, some low-energy electron diffraction (LEED) studies have indicated a $c(4\times2)$ reconstruction,[3] while He-atom diffraction experiments have shown the presence of 2×1, 2×2, and $c(4\times2)$ domains on the surface.[4] In a very recent scanning tunneling microscopy (STM) study[5] it has been shown that, on an atomic scale, the surface reconstruction is essentially 2×1 with a large amount of defects, including small regions with local 2×2 and $c(4\times2)$ order.

The electronic structure of Si(100)2×1 surfaces has been studied with angle-resolved ultraviolet photoelectron spectroscopy (ARUPS).[6-8] The ARUPS measurements agree on the existence of two filled surface-state bands, one band that disperses downwards along the [010] azimuthal direction and one nondispersing band close to the $\bar{J}'$ point along this direction. Evidence for the existence of an empty band of surface states has been obtained with surface photovoltage spectroscopy,[9] differential reflectivity measurements,[10] inverse photoemission spectroscopy,[11] and electron-energy-loss spectroscopy (EELS).[12] In the differential reflectivity[10] and EELS[12] experiments, transitions with a threshold of ~0.4 eV between the bulk valence band and an empty surface-state band have been observed. The EELS study indicated a direct transition at the $\bar{\Gamma}$ point in the surface Brillouin zone (SBZ), while the transition observed in the differential reflectivity study was interpreted as an indirect transition. This suggests the existence of an empty surface-state band with two minima, one of which is at $\bar{\Gamma}$. Since the difference in energy between the Fermi level E_F and the valence-band maximum E_V has been shown to be ~0.4 eV,[13] this empty band could be responsible for the pinning of the Fermi level at Si(100)2×1 surfaces.

In recent ARUPS studies using highly *n*-doped crystals,[14,15] it has been shown that it is possible to populate the states pinning the Fermi level enough to make a direct observation in photoemission possible. Previous ARUPS studies on Si(100)2×1 were performed using samples with low doping levels, and no states at the Fermi level were observed.[6,7] In this paper we present an ARUPS study on clean, highly *n*-doped Si(100) crystals. The surface states responsible for the pinning of the Fermi level have been observed around the $\bar{\Gamma}$ and $\bar{J}'$ points in the 2×1 SBZ.

Angle-resolved photoemission spectra were recorded in an ultrahigh-vacuum chamber at a pressure of less than 5×10^{-11} Torr. Monochromatized 10.2-eV radiation from a hydrogen discharge lamp was used. The estimated combined energy resolution as determined by the analyzer voltages and the monochromator slit widths was ~60 meV, except for the spectra in Fig. 1 for which it was ~100 meV. The position of the Fermi level was determined to an accuracy of ±25 meV by photoemission from the metallic sample holder. The angle of incidence of the light θ_i and the emission angle θ_e are defined according to the inset of Fig. 1. The angular resolution of the analyzer was $\pm2^0$. The sample was a heavily *n*-doped, mirror-polished Si(100) single crystal ($\rho\sim6$ mΩ cm, $N_D\sim1\times10^{19}$ Sb atoms/cm^3 Wacker Chemitronic) with a size of 8×17×0.3 mm^3. The surface normal was off by less than 0.1° from the [100] direction. Before insertion into the vacuum chamber, the sample was degreased and etched according to the procedure by Ishizaka, Nakagawa, and Shiraki.[16] In ultrahigh vacuum it was thoroughly outgassed at ~500 °C and then annealed at ~850 °C for 10 min. This cleaning procedure has been shown to give well-ordered surfaces with negligible contamination.[16]

The emission observed at the Fermi level was found to be very contamination sensitive. In one hour the emission intensity decreased by ~50%, but by flashing the sample to ~600 °C the contaminant could be removed. During the photoemission experiment this was done every 30 min. Apart from restoring the intensity of the peak at E_F, this treatment had no observable effect on the photoemission spectra. After recording a series of spectra the surface was studied with LEED. A sharp two-domain 2×1 diffraction pattern with low background was always observed. After every LEED study the sample was flashed to ~800 °C before new spectra were recorded.

For highly *n*-doped Si(100) samples the band bending is ~0.7 eV, assuming a value of 0.4 eV for E_F-E_V.[13] At the doping level used in the present experiment this corresponds to an estimated surface charge of ~0.014 electrons per surface atom,[17] which is slightly more than the amount that could be detected clearly on Ge(111)2×1 (Ref. 14) and on Si(111)2×1.[15] At the temperature needed for cleaning

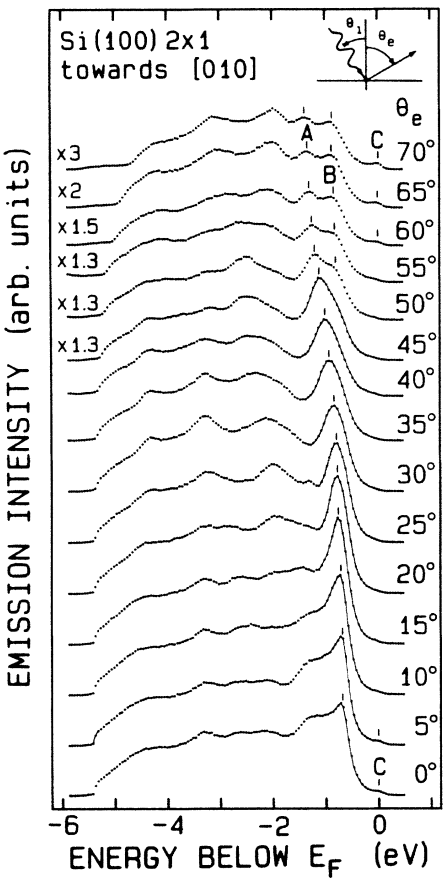

FIG. 1. Photoemission spectra recorded with 10.2-eV photon energy for various angles of emission along the [010] azimuthal direction. The angle of incidence is $\theta_i = 45°$ except for $\theta_e = 45°$ and 50° for which $\theta_i = 55°$.

the Si(100) surface it is possible that the rate of desorption of the Sb dopant atoms is higher than the rate of diffusion to the surface. If this is the case the surface layer will become partly depleted of dopant atoms, resulting in a lower value for the surface charge.

Figure 1 shows photoemission spectra recorded for various angles of emission θ_e in the [010] azimuthal direction. This geometry eliminates complications due to the existence of two different 2×1 domains since along the [010] azimuth equivalent $\mathbf{k}_\parallel$ points in the two domains are probed [see Fig. 2(c)]. The structures A and B are due to emission from previously reported occupied surface states.[6-8] In addition to these structures, a weak structure C can be observed at the Fermi level for emission angles around 0° and 70°. For emission angles between 15° and 55° there is negligible intensity at E_F.

In Figs. 2(a) and 2(b) photoemission spectra recorded with high energy resolution are shown. For emission angles $\theta_e = 0°$ and $\theta_e = 75°$ the state C is probed at the $\bar{\Gamma}$ and $\bar{J}'$ point in the 2×1 SBZ, respectively. In Fig. 2(d) spectra recorded for angles of emission along the [011] azimuthal direction are shown. For $\theta_e = 45°$ the structure C at E_F can be observed. This geometry corresponds to probing the state C in a $\bar{\Gamma}$ point in one 2×1 domain and in a $\bar{J}'$ point in the other 2×1 domain.

Figure 3 shows the measured initial-energy dispersions $E_i(\mathbf{k}_\parallel)$ for the three surface states A, B, and C along the [010] azimuthal direction. The measured dispersions for states A and B are nearly the same as found in the earlier study by Uhrberg, Hansson, Nicholls, and Flodström.[7] The total dispersion for state A is 0.7 eV in both experiments, while the experiments by Himpsel and Eastman[6] and by Koke *et al.*[8] gave a dispersion of 0.5 eV. It has been suggested that peak B originates from surface state A and that

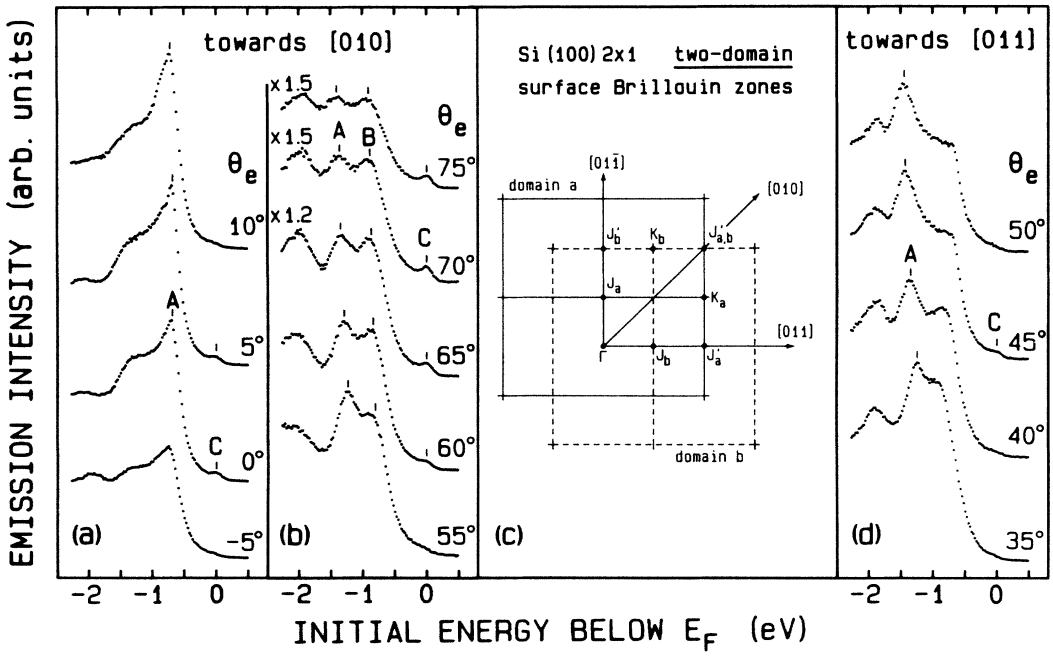

FIG. 2. (a) and (b) Photoemission spectra recorded for various emission angles along the [010] azimuthal direction. $\theta_i = 45°$. (c) Superposed surface Brillouin zones of the two different 2×1 domains in the repeated zone scheme. (d) Photoemission spectra recorded for various emission angles along the [011] azimuthal direction. $\theta_i = 45°$ for $\theta_e = 35°$, 40°, and $\theta_i = 55°$ for $\theta_e = 45°$, 50°.

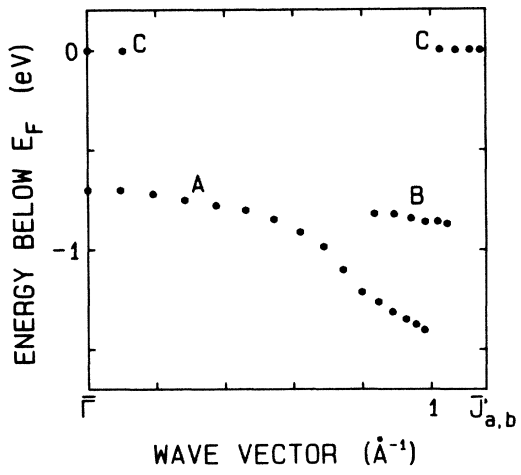

FIG. 3. Initial-state energy dispersions for the surface states *A*, *B*, and *C* along the [010] azimuthal direction.

it, through Umklapp processes, merely reflects a 2×2 periodicity on parts of the surface. However, the present study shows clearly that peak *B* is too low in energy (~ 0.15 eV) for such an explanation to be valid.

In Fig. 4 the dependence of the emission intensities from surface states *A*, *B*, and *C* on the angle of incidence of the light is shown. When θ_i is changed to 0° the intensities are strongly reduced, demonstrating the p_z character of surface states *A*, *B*, and *C*.

Spectra were also recorded from a surface obtained by argon-ion sputtering (10 min, 5 μA/cm^2, 500 eV) and annealing (800 °C, 5 min) in order to study the dependence of the emission intensity from state *C* on sample preparation. Although the LEED diffraction spots were slightly streaked, indicating some disorder of the surface, the peak *C* was still observable, but with a slightly lower intensity. Also the filled surface states *A* and *B* were somewhat less pronounced on the sputter-cleaned surface.

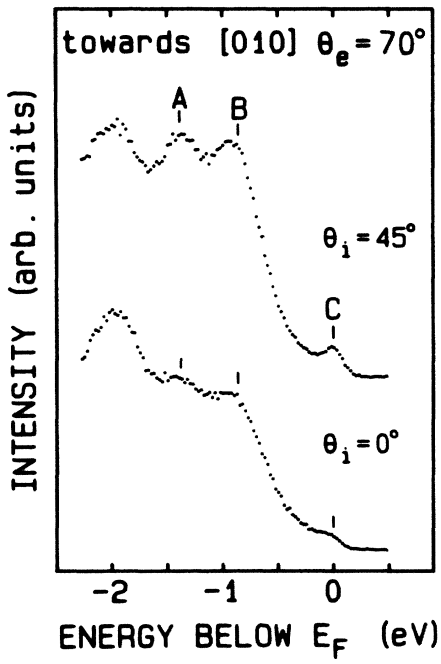

FIG. 4. Dependence of the surface-state emission intensities on the angle of incidence.

The peak position of the state *C* is at E_F, indicating that this state is responsible for the pinning of the Fermi level at Si(100)2×1 surfaces. The state *C* could, in principle, be due to defects on the surface which, however, due to the localization in momentum space cannot be strongly localized in real space. Since the structure *C* is observed only at high-symmetry points in the 2×1 SBZ, and no correlation between defects and surface periodicity has been observed in the STM experiment,[5] we conclude that structure *C* is due to emission from the minima of an almost empty dispersing surface-state band. The disorder of the Si(100)2×1 surface seen in the STM study does not exclude the existence of such a dispersing empty band since, in spite of this disorder, there exists a dispersing filled band. The localization in *k* space of structure *C*, together with the fact that the filled surface-state band does not change with doping, excludes the possibility that this structure is due to dopant atoms at the surface.

Theoretical calculations of surface-state bands have been performed for different symmetric and asymmetric dimer models,[1] but no calculations exist so far for a model involving buckled as well as nonbuckled dimers and missing dimers. Such a model would be in accordance with the results from the STM measurement[5] and might give an explanation for the existence of two filled surface states and for the observed two minima in the almost empty surface-state band.

In differential reflectivity[10] and EELS[12] measurements on Si(100)2×1 surfaces, transitions from the bulk valence band into an empty surface-state band have been observed, the threshold energy being ~ 0.4 eV. In the EELS experiment the transition was interpreted as a direct transition at $\bar{\Gamma}$ in the SBZ, indicating that the minimum of the empty surface-state band is located at this point. In differential reflectivity the transition was instead interpreted as an indirect transition, locating the minimum of the empty band in another point in the SBZ. Together with the value of 0.4 eV for $E_F - E_V$,[13] the present ARUPS observation at $\bar{\Gamma}$ and $\bar{J}'$ of the states that pin the Fermi level shows that both interpretations can be correct.

Recently, Kevan and Stoffel[18] have reported ARUPS measurements on lightly *n*-doped Ge(100)2×1 surface showing the existence of a metallic surface state at the $\bar{\Gamma}$ point in the SBZ. From the narrow $\mathbf{k}_\parallel$ range for which this state was observable ($\Delta k \sim 0.09$ Å^{-1}, full width at half maximum) it was concluded that the metallic state was related to defects with an estimated real-space extent of 10–12 Å. Using an expression derived for minimum-uncertainty wave functions, we instead find a *lower limit* of ~ 30 Å (Ref. 19) for the real-space extent of the surface states. Since the localization was reported to be isotropic in the $\mathbf{k}_\parallel$ plane, the surface state is thus extended over *at least* 50 atoms. In view of these arguments, we suggest that the peak observed at E_F on Ge(100)2×1 is not due to emission from localized defects, but to emission from the bottom of an almost empty dispersing surface-state band pinning the Fermi level. This explanation could account for the observation that the $\mathbf{k}_\parallel$ range for which the emission is observed

increases with temperature, since a temperature increase will lead to an increased population of the almost empty band.

To summarize, a new surface state at the Fermi level is observed on the clean Si(100)2×1 surfaces of a heavily *n*-doped crystal. Since the state is observed only at the $\bar{\Gamma}$ and the $\bar{J}'$ points in the 2×1 surface Brillouin zone, we conclude that the Si(100)2×1 surface has an almost empty surface-state band with minima at these points.

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