Fermi-Level Pinning and Surface-State Band Structure of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Ag Surface

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The surface-state band structure and symmetry properties of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Ag surface have been studied with polarization-dependent, angle-resolved photoemission. In contradiction to the prevailing picture of this surface, we find an intrinsic, dispersive surface-state band in the bulk band gap. The minimum of this band is located 0.1 eV above the valence-band maximum (E_V), and the observed partial occupation of the band determines the Fermi-level position (0.2 eV above E_V) on this surface.

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The atomic and electronic structure of the Si(111)-($\sqrt{3}\times\sqrt{3}$)R30°-Ag surface ($\sqrt{3}$-Ag for short) has been the subject of numerous studies in recent years.[1,2] Despite the wealth of obtained information, the details of the reconstruction are still controversial. Recent contributions to this debate include conflicting scanning tunneling microscopy (STM) studies,[3,4] photoemission core-level studies,[5] and ion channeling,[6] ion scattering,[7] and surface x-ray diffraction studies.[8,9]

In the present work, we have studied the surface-state band structure of the $\sqrt{3}$-Ag surface with polarization-dependent angle-resolved photoelectron spectroscopy (ARPES). By the systematic use of linearly polarized synchrotron light and highly n-doped samples, new important information about the surface electronic structure has been obtained. We show in this paper that the Fermi level (E_F) on the $\sqrt{3}$-Ag surface is pinned close to the valence-band maximum (E_V) by the minimum of a dispersive surface-state band. This result disproves the idea of an inherently charged $\sqrt{3}$-Ag surface unit cell, which has been proposed as an explanation for the pinning of E_F.[5] Our results also resolve the main differences between earlier ARPES studies[10-12] of the surface band structure on this surfaces.

The ARPES experiments were performed in a VG ADES 400 spectrometer with polarized synchrotron radiation from the DORIS II storage ring at Hamburger Synchrotronstrahlungslabor (HASYLAB), DESY.[13] The base pressure of the ultrahigh-vacuum (UHV) system was $\sim 2\times10^{-10}$ Torr. Spectra were recorded with photon energies in the range 17–23 eV, with a total energy resolution of 0.17–0.22 eV and an angular resolution of $\pm2°$. The Fermi-level (E_F) position was determined by photoemission from the metallic (Ta) sample holder.

The sample was an n^+-doped, mirror-polished Si single crystal ($\rho = 4$–6 mΩ cm, As-doped). Before insertion into the vacuum chamber it was precleaned using an etching procedure.[14] In UHV it was cleaned by stepwise resistive heating up to $\sim 900\,°\mathrm{C}$. After that, a sharp 7×7 low-energy electron diffraction (LEED) pattern was observed and the recorded ARPES spectra showed no sign of contamination.

The $\sqrt{3}$-Ag surface was formed in the following way: Ag atoms were evaporated onto the sample from a tungsten filament at a rate of 0.8 monolayer (ML) per minute. One ML is defined as 7.83×10^{14} atoms/cm^2. The evaporation rate was measured with a quartz microbalance. Just prior to evaporation, the sample was flashed to 900 °C and during the evaporation it was heated to $\sim 500\,°\mathrm{C}$. Approximately 1.2 ML was evaporated, after which a sharp $\sqrt{3}\times\sqrt{3}$ LEED pattern was observed. The sample was subsequently flashed to $\sim 600\,°\mathrm{C}$, without any change in the LEED pattern.

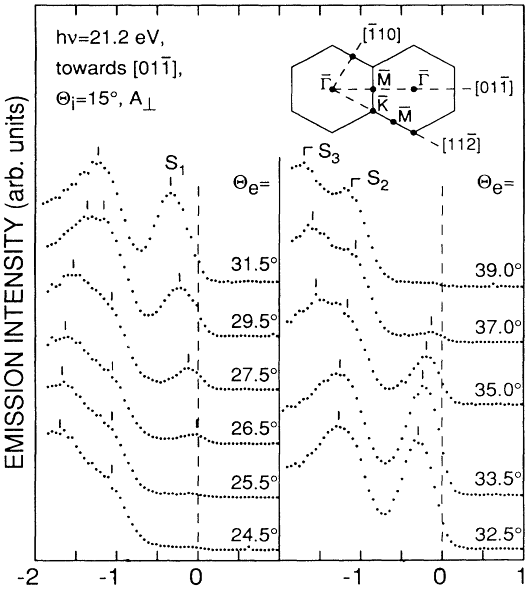

FIG. 1. ARPES spectra recorded with 21.2-eV photon energy in the [01$\bar{1}$] direction with the $A_\perp$ geometry. The emission angles correspond to $\mathbf{k}_\parallel$ points around the $\bar{\Gamma}$ point in the second $\sqrt{3}\times\sqrt{3}$ SBZ (see inset at the top).

In order to explore the polarization dependence of the surface-state emission, ARPES spectra were recorded with four different geometries: With the light incident at an angle of $\Theta_i = 15°$, referred to the surface normal, the electric field vector was either *in* the plane defined by the surface normal and the emission direction, or essentially *perpendicular* to the same plane. These will be referred to as the $A_\parallel$ case and the $A_\perp$ case, respectively. Similarly, for spectra recorded with $\Theta_i = 45°$, the component of the electric field vector parallel to the surface was directed either according to the $A_\parallel$ case or the $A_\perp$ case.

In Fig. 1, spectra recorded in the [01$\bar{1}$] direction with 21.2-eV photon energy and the $A_\perp$ geometry ($\Theta_i = 15°$) are presented. The emission angles correspond to $\mathbf{k}_\parallel$ points around $\bar{\Gamma}$ in the second $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone (SBZ) (see inset in Fig. 1). The dominant feature in the spectra is the surface state, denoted S_1, close to the Fermi level. It disperses steeply around $\bar{\Gamma}$ in the second SBZ, as indicated in Fig. 2. The steep dispersion implies that this is an intrinsic surface-state band, and not a defect state. The S_1 state showed a strong emission with both $\Theta_i = 15°$ and $\Theta_i = 45°$ in the $A_\perp$ geometry, but was practically invisible in the $\Theta_i = 15°$, $A_\parallel$ spectra. The emission from S_1 was also very weak in normal emission (see Fig. 3) and at $\bar{\Gamma}$ in the opposite azimuthal direction, [0$\bar{1}$1]. This may be one reason why this state has not been identified in inverse photoemission studies.[15] An interesting change occurred on the surface during the experiment, involving this state. The minimum of S_1 was gradually shifted from 0.1 eV below E_F for a "new" surface (i.e., just after anneal to 600 °C) to ~0.4 eV below E_F for an "old" surface (more than 18 h later). The initial time dependence of these shifts roughly followed an exponential curve with a time constant of 3 ± 0.5 h. The new surface was restored with an anneal to 600 °C for 15 sec. From recent high-resolution Si-2p core-level photoemission studies of the $\sqrt{3}$-Ag surface,[16] we find a shift in the E_F position of 0.42 eV downwards, from 0.63 eV above E_V for the clean 7×7 surface[17] to 0.21 eV above E_V from the new $\sqrt{3}$-Ag surface. From these data and the observed shift of the valence-band structures in the ARPES spectra, we estimate that the minimum of S_1 is 0.1 eV above E_V for a new surface, and 0.1 eV below E_V for an old surface. Thus, the E_F pinning position changed from 0.2 eV above E_V to ~0.3 eV above E_V. Except for the above-mentioned energy shifts, no differences were observed between corresponding spectra from the new and old surfaces. In order to clearly show the dispersion of S_1, the spectra and dispersions presented here are taken from the old surface.

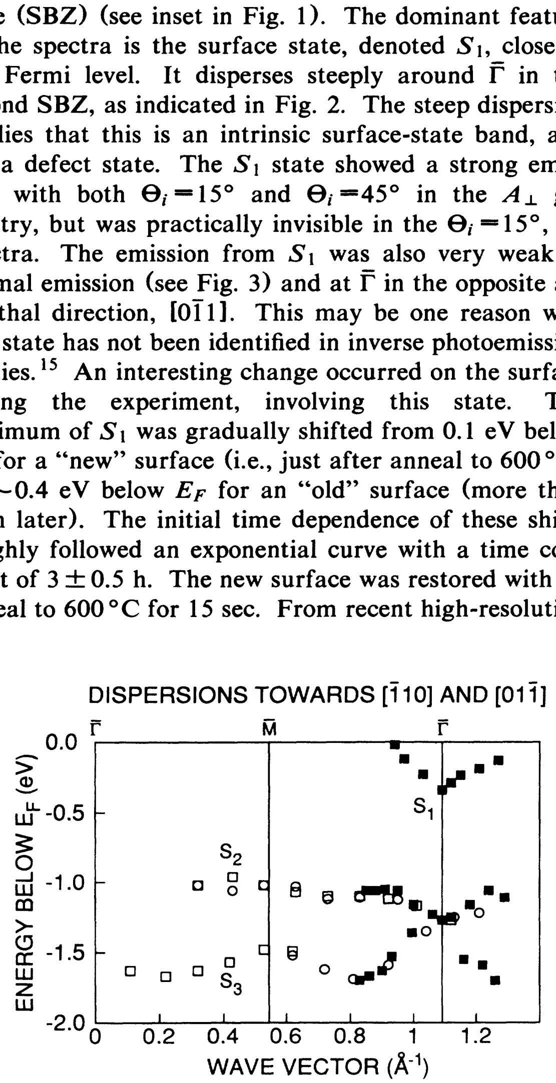

FIG. 2. Dispersions of the S_1, S_2, and S_3 states recorded in the [$\bar{1}$10] direction (open symbols) and the [01$\bar{1}$] direction (filled symbols), corresponding to the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ direction, with 21.2-eV photon energy and the $A_\perp$ geometry. The angles of incidence are $\Theta_i = 15°$ (□■) and $\Theta_i = 45°$ (○).

Kono *et al.*,[5] using core-level photoemission, have recently studied the pinning of the Fermi level on the $\sqrt{3}$-Ag surface. They found a shift of 0.48–0.50 eV compared to the clean 7×7 surface, indicating a E_F position very close to E_V. In order to explain the resulting band bending, they proposed that the $\sqrt{3}$-Ag layer is negatively charged with at least one electron per unit cell. A consequence of this assumption is that the E_F position would have to be located slightly *below* E_V. The results of the present study rule out this proposal. The E_F pinning position does not reach E_V and the existence of the S_1 state unambiguously explains the pinning position. As shown below, the amount of charge accumulated in this band can also fully explain the observed band bending.

By assuming an isotropic dispersion around $\bar{\Gamma}$, we can estimate the area in the $\sqrt{3}\times\sqrt{3}$ SBZ where the S_1 band

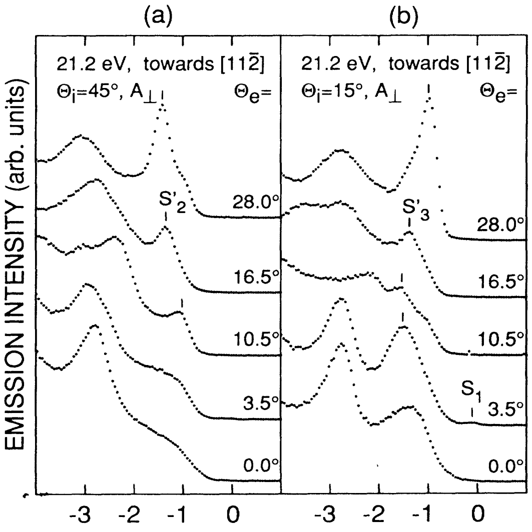

FIG. 3. ARPES spectra recorded on the $\sqrt{3}$-Ag surface in the [11$\bar{2}$] direction with 21.2-eV photon energy and the $A_\perp$ geometry. (a) $\Theta_i = 45°$; (b) $\Theta_i = 15°$.

is filled, and thereby the degree of filling of the band. For a new surface $(2.5\pm0.5)\%$ of the band is filled, which corresponds to a charge of $\sim1.3\times10^{13}$ electrons/cm^2. This value is precisely the charge needed to balance the space charge in the depletion layer for a band bending of ~1.0 eV on these highly n-doped samples, which indicates that the band bending and doping is the only cause for the partial filling of the band. This implies that the surface-state band structure is inherently semiconducting. However, the S_1 band minimum, located 0.1 eV above E_V, is below the bulk Fermi-level position, relative to E_V, for most doping concentrations (both n and p) and will therefore, in general, have a finite occupation, which determines the Fermi-level position. For the old surface, a filling of $(10\pm3)\%$ of the band is estimated. This is far too much to be explained by the band bending and bulk doping only. It is also significantly less than the 50% filling expected for an inherently metallic, homogeneous, and defect-free surface. This extra filling of the S_1 band indicates a gradual formation of extrinsic donor-type defect states on the surface. One possible source for the extra charge is excess, loosely bonded Ag atoms on the surface. It has been proposed earlier that a dilute Ag adatom layer is formed upon further Ag deposition, after the completion of the $\sqrt{3}\times\sqrt{3}$ structure.[5,18] These atoms may be captured at surface defects or, alternatively, at adsorption sites in the surface reconstruction. However, chemical reactions on the surface involving residual gases in the UHV system cannot be excluded as an explanation to the extra filling of the S_1 state.

Two other surface states or resonances, denoted S_2 and S_3, are also seen in Fig. 1. The dispersions of these states in the $[\bar{1}10]$ and $[01\bar{1}]$ directions are also presented in Fig. 2. These states showed the strongest emission in the $\langle11\bar{2}\rangle$ directions. A collection of spectra, recorded in the $[11\bar{2}]$ direction with 21.2-eV photon energy, is shown in Fig. 3. In the spectra in Fig. 3(a), which were recorded with $\Theta_i=45°$ ($A_\perp$), only the S_2' state is seen, dispersing downwards from -1.1 eV at low emission angles to a minimum of -1.5 eV at higher angles. Similarly, in the spectra in Fig. 3(b), which were recorded with near-normal incidence ($\Theta_i=15°$) in the $A_\perp$ geometry, only the S_3' state is observed. It disperses first downwards to a minimum at -1.7 eV and then upwards to a maximum at -1.0 eV.

The dispersion curves of these states are shown in Fig. 4. We observe that the dispersions of the S_2' and S_3' states follow the symmetry of the $\sqrt{3}\times\sqrt{3}$ SBZ and that they *cross* each other at $\bar{K}$. (In this azimuthal direction, we label the bands according to their symmetries, with primed symbols.) It is directly clear that the two states have different symmetry and that the reconstruction has a mirror plane containing the surface normal and the $[11\bar{2}]$ direction. The selective excitation of S_2' and S_3' by $\Theta_i=45°$ and $\Theta_i=15°$, respectively, together with the mirror-plane selection rules,[19] allows us to determine the initial-state symmetries. S_2' is excited by the z component of the electric field vector, which is even under reflection in the mirror plane, and must therefore have even symmetry. Similarly, S_3' is excited by an odd component of the electric field vector and must therefore be odd. In spectra recorded in the $[11\bar{2}]$ direction with the $A_\parallel$ geometry ($\Theta_i=15°$), which also excites even states, the S_2' emission is strongly diminished. Thus the emission from the S_2' state is highly dependent on the z component of the electric field vector, indicating a strong p_z character for this state.

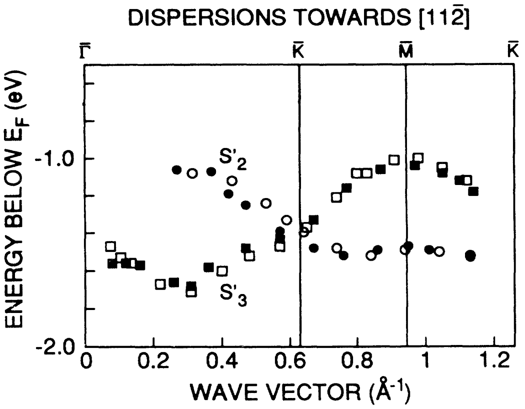

FIG. 4. Dispersions of the S_2' and S_3' states recorded in the $[11\bar{2}]$ direction ($\bar{\Gamma}$-$\bar{K}$-$\bar{M}$) with the $A_\perp$ geometry. For $\Theta_i=45°$, data recorded with 21.2 eV (●) and 23 eV (○) are shown. For $\Theta_i=15°$, data recorded with 17 eV (□) and 21.2 eV (■) are included.

The results presented above explain the conflicting results obtained in previous ARPES measurements of the surface-state dispersions. In the study of Hansson, Bachrach, Bauer, and Chiaradia,[10] linearly polarized synchrotron light was used, with $\Theta_i=45°$. Thus, only the S_2' state was observed in the $[11\bar{2}]$ direction. In the study of Yokotsuka, Kono, Suzuki, and Sagawa,[12] an unpolarized light source was used, with $\Theta_i=45°$. Therefore, the S_2' and S_3' states were observed in the same spectra in the $[11\bar{2}]$ direction and the crossing of the dispersion curves could not be resolved.[20] In the $[\bar{1}10]$ direction, our dispersions for the S_2 and S_3 states are very similar to the ones presented by Yokotsuka *et al.*[12]

The electronic structure of the $\sqrt{3}$-Ag surface has also been studied with STM, by van Loenen, Demuth, Tromp, and Hamers.[3] In STM images taken with -1.0-V sample bias (corresponding to tunneling from filled states in the surface), a honeycomb pattern of protrusions is seen. It is very likely that the filled states giving the honeycomb patterns are the S_2,S_2' and S_3,S_3' states described in the present study. The charge densities of the odd and even states are expected to reflect their symmetries, having nodes in, or "bands" of charge across, the mirror planes, respectively. The STM images[3] are entirely consistent with a superposition of contributions from these two states. However, a significant difference is the absence of the S_1 state close to the Fermi level in the STM study. The protrusions in the STM images were attributed to a top layer of Si atoms.[3] It is worth noting that the strong emission and apparent p_z character of the S_2' state is characteristic for a Si dangling-bond orbital, with its dominating Si $3p_z$ content, but is not expected for a Ag $5s$ orbital. The suggested model also consisted of a buried Ag monolayer arranged into trimers. The 1-ML-Ag stoichiometry was motivated by the observed semiconducting nature of the $\sqrt{3}$-Ag surface,[3,12] which leads to an even number of valence electrons per unit cell. In Ref. 5, an Ag honeycomb model with $\frac{2}{3}$-ML Ag atoms was suggested, based on the proposed charging of the surface, which breaks the valence charge conservation and indicates an odd number of valence electrons. However, as shown in the present study, the conservation of valence charge holds and the two-dimensional surface band structure is inherently semiconducting. Thus our data favor models with an even number of valence electrons.

In summary, we have shown that the Fermi-level position on the Si(111)-$(\sqrt{3}\times\sqrt{3})R30°$-Ag surface is determined by the partial occupation of a dispersive surface-state band. The minimum of this band is initially positioned $\sim$0.1 eV above E_V, with an occupation that is fully accounted for by the band bending and the bulk doping only. This implies that the surface band structure is inherently semiconducting. This result, together with the p_z character of one of the filled surface-state bands, favors a model of the $\sqrt{3}$-Ag surface with an even number of electrons per unit cell and Si atoms on top.

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