

Electronic structure of the ideally H-terminated Si(111)-(1×1) surface

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(Received 31 January 2000)*

The valence-band electronic structure of the model system H/Si(111)-(1×1) is measured along the main high-symmetry directions using polarization-dependent angle-resolved photoemission. This allows us to definitively identify the energy dispersion relations of the surface features. In particular, we determine the orbital symmetry of the main surface states related to the topmost Si bonds. Contrary to previous reports, we identify a remarkably sharp surface resonance (less than 260 meV wide), highly localized around the \bar{K} point at 4.3 eV from the valence-band maximum. The results of these measurements are corroborated by theoretical calculations within a tight-binding approach.

Although the electronic properties of silicon surfaces have been studied over past decades,^{1,2} interest has recently been revived by the advent of artificially produced H-terminated surfaces with a high degree of homogeneity. Typically, Si surfaces exhibit a wide variety of reconstructions, originated by the tendency to saturate the dangling bonds resulting from the abrupt surface termination. Much effort has been devoted to finding mechanisms that neutralize this tendency.³ The development of both a wet chemical treatment⁴ and an atomic hydrogen-based method⁵ has allowed the preparation of a highly stable, unreconstructed, very flat, and nearly-defect-free Si(111) termination. This is interesting not only to separate reconstruction effects from those coming just from the lack of periodicity perpendicular to the surface, but also for the interpretation of the reaction processes related with the widely expanded Si-based technology.

As a consequence of the high quality of this hydrogenated surface, remarkably sharp features have recently been measured by angle-resolved photoemission spectroscopy (ARPES), with exceptionally small linewidth of electronic and vibrational states.^{5,6} Moreover, when regarding the projection onto the surface of the bulk electronic states, there does not appear any additional surface state within the gap.^{6–9} These characteristics make this system especially suitable as a basis for molecular-beam-epitaxy growth and have favored its common usage as a substrate with adsorbates of very different nature, from C₆₀ to metallic films and inorganic molecules.¹⁰

Although the conduction and valence bands of the H/Si(111)-(1×1) system have been extensively studied,^{5–9,11–13} there are still basic controversies related to the valence-band properties. Occupied states exist within the bulk forbidden pockets along the high-symmetry lines of the reciprocal lattice. Most of them are located around \bar{K} , making this point especially important in the study of the surface. Up to now, only two pure surface states (SS) called (*a*) and (*a'*) have been reported at \bar{K} , at 3.8 eV and 4.8 eV from the valence-band maximum (E_V), respectively (see Fig. 1 and Fig. 2). From theoretical investigations^{11,12} it seems clear that each state can be associated to a different bond symmetry of the topmost Si atoms. However, there does not exist any experimental evidence of their actual orbital symmetry, which would serve to identify their nature as H-Si or Si-Si states. Another SS labeled (*b'*), resulting from the hybridization of the H(1*s*) and Si(3*s*) orbitals,¹¹ has been found at 8.9 eV at \bar{K} . In a recent photoemission study,⁹ it was suggested that this SS disperses within the bulk pocket around $\bar{\Gamma}$, contrary to any previous analysis.^{5–8,12}

In this work we present a combined experimental and theoretical study in order to conclusively determine the number and origin of the electronic states associated to the H/Si(111)-(1×1) surface. State-of-the-art polarization-dependent ARPES has been used to investigate in detail both the localization at the surface and the energy dispersion of the electronic states. A careful analysis of the valence band

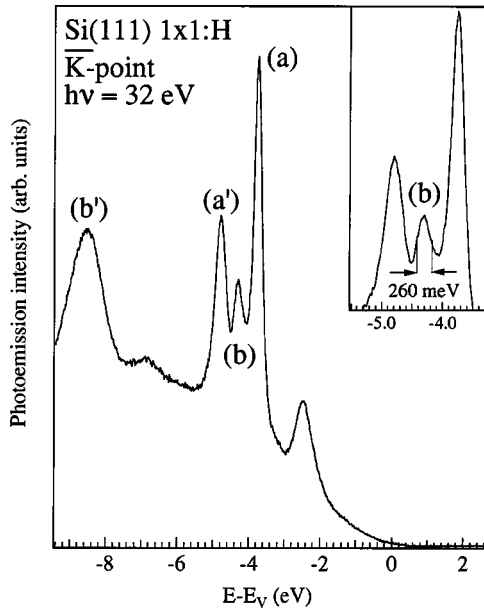


FIG. 1. Photoemission spectra measured around the \bar{K} point using $\theta_i=45^\circ$ and $h\nu=32$ eV. Those features that can be assigned to SS or SR have been labeled.

shows that, besides the above-mentioned SS (a) and (a'), a very sharp surface resonance (SR) not previously reported is found at the \bar{K} point between (a) and (a'). The existence of (b) is supported theoretically using slab models wide enough to resolve SR from bulk states. Finally, the state (b'), although being a SS at \bar{K} , mixes with the bulk band along the adjacent bulk band edges. In addition, we have probed the orbital character of the valence-band states, using two main different polarization geometries which lead to the unequivocal

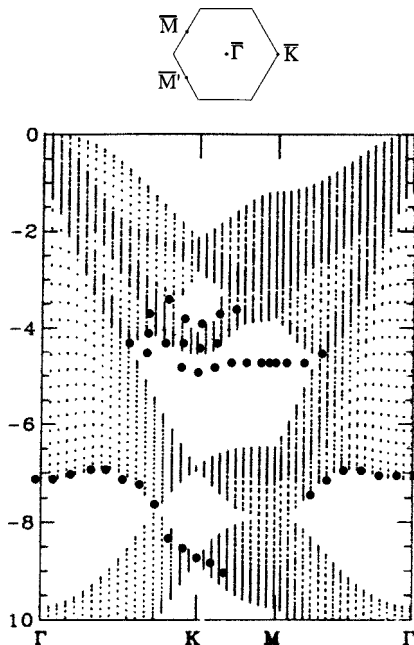


FIG. 2. Valence-band structure along some high-symmetry directions. The experimental SS and SR are marked by small circles and plotted onto the theoretical bulk band projection. As a reference, we show a scheme of the surface reciprocal-lattice unit cell.

identification of (a') as a H-Si bond state and (a) as a Si-Si backbond state.

All measurements presented here have been performed using synchrotron radiation from the SU6 beamline of the Super-Aco storage ring at the Spanish-French station of the LURE. The ultrahigh-vacuum chamber was equipped with an angle-resolving hemispherical analyzer and a high-precision manipulator allowing to cover the whole emission solid angle. The final energy and angular resolutions were 60 meV and 1° , respectively. Four different samples were prepared *ex situ* using a wet chemical treatment that results in a passivated H/Si(111) surface;⁴ afterwards, each sample was introduced in the measurement chamber following a fast differential pumping process. The quality of the surface was systematically checked in each experiment by identifying the intrinsic states (a) and (a') at \bar{K} . In Fig. 1 we show a typical spectra obtained using a photon energy $h\nu=32$ eV for an angle of incidence $\theta_i=45^\circ$; notice the presence of the well-resolved peak (b) between (a) and (a'). The sharpness of these peaks (260 meV wide) evidences the good resolution achieved during the experiment and the excellent surface quality of the sample. Although ≤ 300 meV wide SS have been observed in optimized conditions, such a sharp feature has never been reported for a SR in a semiconductor. The difference between SS and SR comes from their degree of localization in the surface: while SS appear within gaps of the projected bulk band, the SR are degenerate with bulk states; this makes SR more probable to be conserved at interfaces or in the presence of new adsorbates, as they are states directly related to the electronic structure of the substrate.¹⁴

In order to study the dispersion of the detected electronic states, the valence band was mapped along the high-symmetry lines $\bar{\Gamma}\bar{K}$, $\bar{\Gamma}\bar{M}$, and $\bar{K}\bar{M}$, for $h\nu=32$ eV and $\theta_i=45^\circ$. In Fig. 2 we plot our experimental surface features onto the theoretical projection of the bulk bands. All SS and SR contribute at \bar{K} . The SS (a) and (a') were detected at 3.76 and 4.80 eV from E_V , respectively. While (a) appears around \bar{K} , (a') extends along the $\bar{\Gamma}\bar{K}\bar{M}$ and $\bar{\Gamma}\bar{M}$ directions. The state (b') was identified as a SS at 8.56 eV at \bar{K} , and it exhibited some dispersion along the $\bar{\Gamma}\bar{K}$ bulk band edge. A broad peak measured around 9 eV at \bar{M} , dispersing towards both $\bar{\Gamma}$ and \bar{K} , could also be identified as the bulk band edge dispersion assigned here to (b'). In fact, a similar peak has been measured at the (7×1) -H/Si(111), (7×7) Si(111), and $(\sqrt{3}\times\sqrt{3})$ -Al/Si(111) surfaces,¹⁵ where it was identified as a contribution from the *sp* bulk band.

Finally, the sharp SR (b) was clearly identified at 4.30 eV, highly localized around the \bar{K} point. It was measured for all samples, and was also observed at several \bar{K} points of the first Brillouin zone. Even though (b) falls within the bulk band projection, both the remarkable narrowness of the peak and its presence when changing the experimental setup to enhance the surface sensitivity are hints of a non-negligible surface contribution. The energy and momentum conservation rules in a photoemission experiment force bulk states to disperse with the component of the momentum normal to the surface (\vec{k}_\perp); at the surface, the lack of periodicity along the

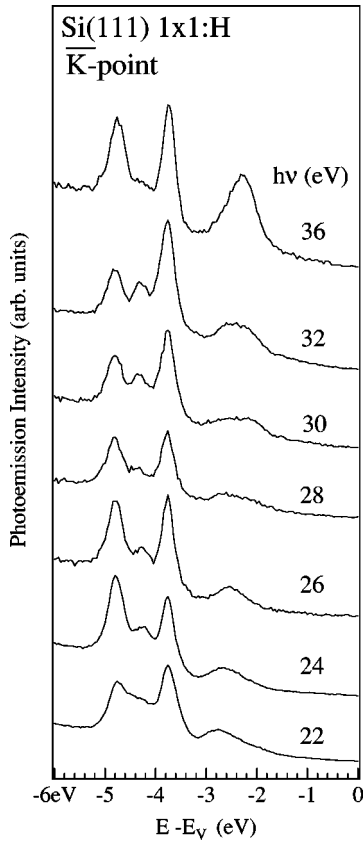


FIG. 3. Same as Fig. 1, varying the incident photon energy.

normal makes the SS dispersion independent of \vec{k}_\perp . To analyze the evolution of (b) with \vec{k}_\perp , we performed measurements varying $h\nu$ from 22 to 36 eV (see Fig. 3). The spectra showed a very strong \vec{k}_\perp dependence of the intensity of the peak on the photon energy due to cross-section effects, with maxima for energies between 24 and 32 eV. This helps to understand why this narrow SR has not been observed previously: in spite of the good energy resolution of the former measurements,⁵⁻⁷ they were obtained using $h\nu$ in a range around either 17 or 21 eV. We observed an energy dispersion of the state (b) with \vec{k}_\perp of less than 0.25 eV in the total photon energy range investigated, which was not correlated to the variation of \vec{k}_\perp . This small and uncorrelated dispersion is in contrast to that exhibited by direct bulk transitions previously identified in the same energy region.¹⁵

In spite of these clear experimental hints, the delicate distinction between bulk transitions and SR requires a theoretical support able to discern the actual origin of the states. We performed a calculation of the electronic structure of H/Si(111)-(1×1) based on a slab model of the surface. In previous works,^{11,13} slabs of at most 12 Si layers were used. This implies that SR extending more than five to six layers inside the bulk could not be distinguished from bulk states. Using the tight-binding (TB) approach parametrized by Pandey in Ref. 12, we have studied larger slabs containing up to 72 Si layers (not shown). With increasing size, the weight of the true bulk states on these two layers decreases strongly due to wave-function normalization. On the contrary, we verify that an eminent SR state located at 4.4 eV below E_V conserves a constant weight on the topmost layers, evidenc-

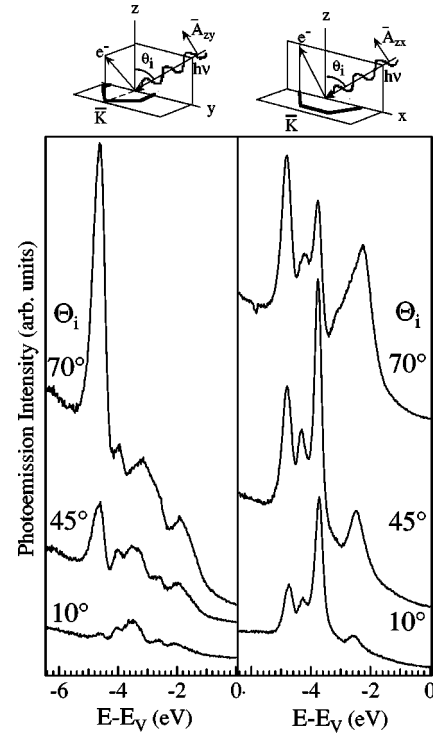


FIG. 4. Photoemission spectra taken around the \bar{K} point using 32-eV photons. The experimental setup is depicted at the upper part of the figure. The right panel shows the spectra obtained placing the polarization vector \vec{A} parallel to the emission plane at three different θ_i : 10°, 45°, and 70°. The left panel corresponds to measurements with \vec{A} contained in a plane perpendicular to the emission one.

ing its surface related character. This state, which we identify to (b), has mainly a p_x - p_y symmetry analog to that of the surrounding bulk states, therefore allowing resonance. In the 12-layer slab case, the two SR located on each side of the slab strongly overlap, inducing a large splitting of the associated level. However, for slabs containing 24 layers or more, this splitting is negligible, indicating that the SR-related wave function is well localized within the topmost 12 Si layers.

Concerning the SS (a) and (a'), the rapid evolution of the DOS to a bulk distribution indicates that they are very localized in the topmost Si atoms. This joint to the high directionality of the Si bonds favors the ability to discriminate the contributions from the H-Si bonds and the Si-Si backbonds. In order to do this, we have profited from the linear polarization of the synchrotron light. The cross section of the photoemission process is proportional to the matrix element of the $\vec{A}\vec{\nabla}$ operator between the initial and final electronic states, \vec{A} being the polarization vector of the incident photons. This matrix element must conserve the symmetry properties of the surface. For electrons emitted within a mirror plane of the surface, this means that parity must be conserved. The orientation of \vec{A} with respect to this plane can then be used to select initial states with a well defined parity, as the final state is always even under reflection from the plane. If \vec{A} is directed perpendicular to the plane (see the upper part of Fig. 4), it becomes odd under reflection, and only odd states will contribute to the measured photoelectron

intensity. Similarly, even states are selected using \vec{A} contained in the emission plane.

In the present experiments two different configurations have been used. As we were interested in the states at the \bar{K} point, we were forced to work with an emission plane intersecting the surface perpendicularly at the $\bar{\Gamma}\bar{K}$ direction. This is not a true mirror plane if we take into account the bulk projection, the $\bar{\Gamma}\bar{M}$ and $\bar{\Gamma}\bar{M}'$ directions not being equivalent; however, neglecting multiple scattering effects, a $H(1s)$ - $Si(3p_z)$ σ state will be even under reflection about any plane normal to the surface. On the contrary, backbond states do not present a well-defined parity with respect to our current emission plane, which can be used to distinguish them from the H-Si bonding type. For each selected configuration, θ_i was varied to 10° , 45° , and 70° . In this way, we were tuning the weight of the components of \vec{A} either along the normal to the surface (A_z , maximum for $\theta_i=70^\circ$) or contained in the surface plane ($A_{x(y)}$ for the $A_{\parallel(\perp)}$ configuration, maximum for $\theta_i=10^\circ$). The measured spectra are depicted in Fig. 4. When placing \vec{A} normal to the emission plane (left panel of the figure), even states do not contribute, that is, we cannot detect p_z states. This is almost the situation for $\theta_i=10^\circ$, where (a') cannot be resolved; this evidences the $H(1s)$ - $Si(3p_z)$ origin of this state. Furthermore, from the derivatives contained in the $\vec{A}\vec{\nabla}$ operator, the main contribution to the photoemission current coming from a p_z (p_{xy}) orbital proceeds along the z (xy) direction. Under the present conditions, this means that the p_z contribution will be enhanced for maximum A_z , which is the case of (a'). On the other hand, increasing the components of \vec{A} within the surface plane, we are increasing the intensity of (a), which relates this state to the backbond direction.

Relying on the TB description, only the $sp\sigma$ parameter accounting for the $H(1s)$ - $Si(3p_z)$ coupling is nonzero, while neighboring $H(1s)$ and $Si(3p_{x,y})$ cannot couple by symmetry. This indicates within a standard orbital hybridization picture that mixed $H(1s)$ - $Si(3p_z)$ states should be located at lower energy as compared to $H(1s)$ - $Si(3p_x)$ ones. This is in

agreement with the present experimental results, and also with the analysis performed by Pandey in Ref. 12 indicating states at ~ -5 eV with weight on the Si backbonds. Such results, however, were based on a Brillouin-zone integrated DOS study, and no details of the origin of such states were derived theoretically. Analyzing further the charge-density distribution of the surface states at \bar{K} provided in Refs. 11 and 13, we note that indeed (a) has a strong weight on the first-layer Si backbond, while (a') has a nearly zero weight between the first and second Si layers.¹⁶ This confirms as well the present experimental findings.

In summary, we have studied the valence band of the $H/Si(111)-(1\times 1)$ system. At the \bar{K} point, our results, contrary to previous reports, evidence the existence of an extremely sharp SR (b), located at 4.3 eV below E_V , in addition to the two well-known SS. This assignment is unambiguously supported by theoretical calculations using large slabs. This new surface feature is degenerate with $Si(111)-(1\times 1)$ bulk states, which makes it highly probable to be conserved at interfaces or in the presence of new adsorbates on silicon. From the experimental point of view, the precisions required to resolve (b), together with its high localization at \bar{K} , make it a more reliable reference for the sample quality than the SS (a) and (a'). These two SS exhibit a distinct orbital symmetry, which allows us to identify (a) as a Si-Si backbond state and (a') as a H-Si state. Finally, the state (b') located at 8.56 eV at \bar{K} is found to disperse following the adjacent bulk band edges along the $\bar{\Gamma}\bar{K}\bar{M}$ and $\bar{\Gamma}\bar{M}$ directions.

This work was financed by DGES (Spain) (Grant No. PB-97-1199) and the Large Scale Facilities program of the European Union assigned to LURE. X.B. acknowledges many discussions with Professor S.G. Louie, and is indebted to the French Commissariat à l'Énergie Atomique (CEA) for providing computer time (Cray-C94, CENG, Grenoble). S.G. acknowledges financial support from the Spanish Ministerio de Educación y Cultura.

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¹⁶For the state (a'), these *ab initio* calculations show a strong bulk component centered between the third and fourth Si layers. However, such calculations predict (a') to be located within the small band of bulk states present between the two pockets containing the true SS (a) and (a'). One has therefore to be cautious when analyzing the charge-density distribution of (a') provided by such calculations, as the bulk component of this state may well be related to a spurious resonant character introduced by these theoretical methods.