Adatom electronic structure of the Si(111)7×7 surface

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With the technique of k-resolved inverse photoemission a pronounced dispersing surface state is observed for the Si(111)7×7 surface, 0.5 eV above the Fermi level. This state bears strong similarities with the empty adatom states observed on Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces, and originates from the 12 adatoms in the 7×7 surface cell observed with scanning-tunneling microscopy. Reinterpretation of recent band-structure calculations identify the origin of all major surface states observed.

Considerable progress has been made lately towards the understanding of the geometric and electronic structure of the Si(111)7×7 surface. With experimental techniques such as transmission-electron diffraction[1] (TED) and scanning tunneling microscopy[2] (STM) a geometric structure has been derived for this surface described by a dimer-adatom-stacking fault (DAS) model. The various surface states observed with angle-resolved photoemission spectroscopy[3,4] (ARUPS) and k-resolved inverse photoemission[5,6] (KRIPES) were recently resolved in real space in a spectroscopic STM study.[7] In all, there are now three occupied and three unoccupied surface states observed with these different methods, with the addition of a possible metallic state at the Fermi level. However, many questions remain to be answered concerning the geometric and electronic structure of the Si(111)7×7 surface.

In this paper we present KRIPES measurements of the unoccupied electronic structure of the Si(111)7×7 surface, and the different surface states are related to the local atomic configurations within the 7×7 unit cell. The details of the KRIPES experiment and preparation of the samples have been described previously.[6,8,9] The outgoing photons were filtered with a Geiger-Müller–type detector, and the total-energy resolution (electrons and photons) was $\Delta E \approx 0.35$ eV. The Si(111)7×7 surfaces were prepared by direct resistive heating of the samples (p-doped, $\rho = 0.03\ \Omega$ cm) up to 1000 °C.

In Fig. 1 inverse-photoemission spectra are shown for the $\bar{\Gamma}$-$\bar{K}$ direction in the (1×1) surface Brillouin zone (SBZ). A pronounced surface state U_1 is present at an energy 0.55 eV above the Fermi level for normal incidence ($\theta = 0°$) of the electrons, corresponding to the $\bar{\Gamma}$ point of the (1×1) SBZ. The observation of this surface state, as well as the bulk structure A, have been presented previously[5,6] but only for normal incidence of the electrons. In the $\bar{\Gamma}$–$\bar{K}$ as well as the $\bar{\Gamma}$–$\bar{M}$ direction the surface state U_1 disperses towards the Fermi level with decreasing intensity for increasing angles of incidence. After that a minimum in energy position and intensity is reached at $\theta = 25°$; the peak disperses upwards again with increasing intensity. At angles corresponding to the (1×1) SBZ border a maximum energy position and intensity is reached. The angle between the electron gun and the photon detector is fixed in the experiment, and only the sample is rotated for the different incidence angles. At the incidence angle $\theta = 30°$ mainly photons emitted in the normal direction are detected, and the minimum in intensity at this angle, as well as the in-

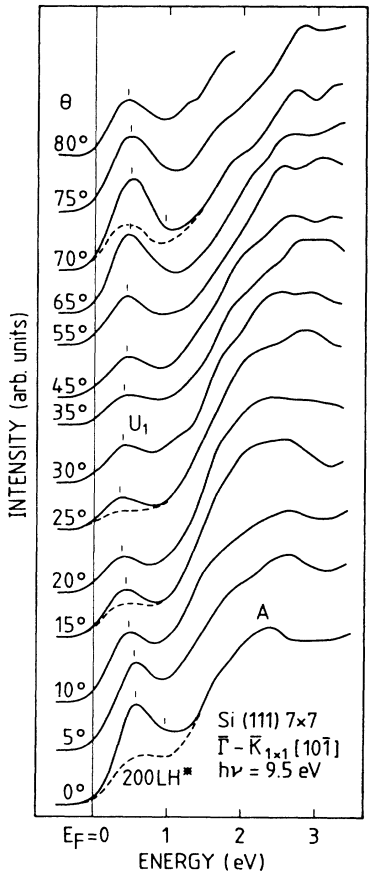

FIG. 1. Inverse photoemission spectra for various angles of incidence along the $\bar{\Gamma}$–$\bar{K}_{1\times1}$ direction. The dispersive surface state U_1 is strongly reduced for a hydrogen contamination (dashed line).

creasing intensity for higher and lower angles, could be due to a p_z character of the state. As previously observed[5,6] a weak tail at the Fermi level is also present in the spectra.

After an exposure of 200 langmuirs (1 L$=1\times10^{-6}$ Torr sec) of hydrogen excited by a hot filament, the surface-state intensity is strongly reduced (dashed line in Fig. 1), whereas the bulk state A is unaffected. The full width at half maximum (FWHM) value of the structure U_1 is larger than 0.5 eV, i.e., larger than the resolution of the spectrometer ($\Delta E \approx 0.35$ eV). It is possible then that a second structure is present within the peak. The difference spectra though reveal only one symmetric structure with the exception of a weak asymmetry at the angles for which the intensity is the highest (see tic marks at right side of U_1 for $\theta=0°$, $\theta=70°$ in Fig. 1). Instead, the strong umklapp scattering of the (7×7) surface is most probably responsible for the broad width of the structure U_1 (such a broad peak is not observed for the unoccupied adatom states on the Si(111)($\sqrt{3}\times\sqrt{3}$)-Al, -Ga, -In surfaces[9]). A 7×7 LEED (low-energy electron diffraction) pattern could still be observed after the contamination although now with a higher background.

In Fig. 2 the surface state dispersion $E(k)$ of the unoccupied state U_1 is shown (filled symbols) together with the dispersions of the occupied surface states found with ARUPS: S_1, S_2, S_3 [crosses, $h\nu=21.2$ eV (Ref. 10)]. The experimental surface-state dispersions are also compared with the calculated surface-state bands (Σ_1,Σ_3) of a Si(111)$\sqrt{3}\times\sqrt{3}$-Si adatom surface.[11]

Two further unoccupied surface states have been observed in STM measurements,[7] at approximately 1.3 eV above the Fermi level. These states are within the bulk bands and more difficult to separate out with the available resolution, and no evidence for their existence is found in the present study.

In the spectroscopic STM study of the Si(111)7×7 surface[7] several occupied and unoccupied surface states were localized within the (7×7) surface cell with a new current-imaging method, and the results were interpreted in terms of the DAS (dimer-adatom-stacking fault) model;[1] see Fig. 3(a). In Fig. 3(b) a schematic drawing of the positions of the different components of this model is shown. Groupwise, the adatoms with equivalent positions are marked A, A′, B, and B′, respectively, and group wise equivalent rest atoms are marked C and C′. The equivalent corner vacancies are marked D and the dimers are positioned along the full drawn lines. The left half of the model is the part with the stacking fault.

In an effort to describe the origin of the surface electronic structure of the Si(111)7×7 surface a calculation was recently performed for a Si(111)$\sqrt{3}\times\sqrt{3}$-Si surface.[11] For such a surface no rest atoms of type C and C′ exist and so only adatom surface states are the result of the calculation. On the ($\sqrt{3}\times\sqrt{3}$)-Si surface the adatoms can sit in threefold-symmetric sites, either above

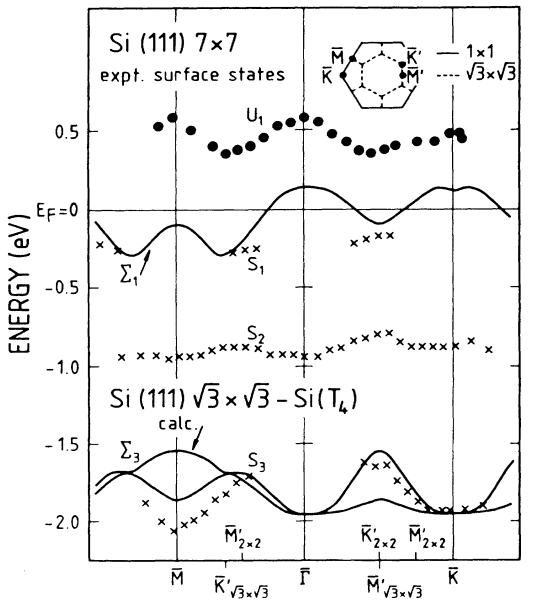

FIG. 2. Experimental dispersion plots for the empty surface state U_1 and the filled surface states S_1, S_2, S_3 obtained with ARUPS (Ref. 10). Also shown are the calculated surface-state bands for a Si(111)$\sqrt{3}\times\sqrt{3}$-Si surface (Σ_1,Σ_3) (Ref. 11).

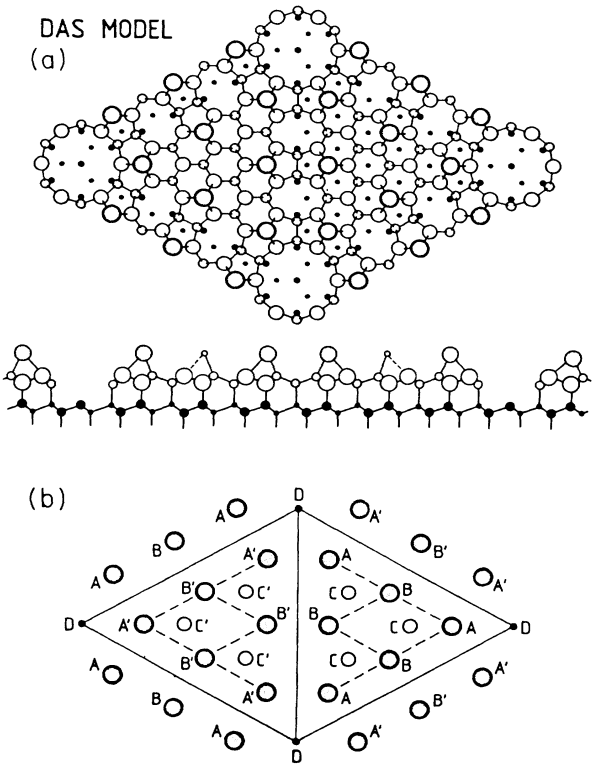

FIG. 3. (a) The DAS model of Takayanagi *et al.* (Ref. 1) top and side view. The larger shaded circles correspond to adatoms. The stacking sequence in the surface layers is faulted in the left half of the unit cell. (b) Positions of the different components of the DAS model: adatoms A, A′, B, B′; rest atoms C, C′; corner hole atoms D. The dimers are positioned along the full drawn lines. A quasi-(2×2) ordering is indicated with dashed lines.

the second-layer Si atoms (T_4) or above the fourth-layer atoms (H_3). Anologously to previous calculations on the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces[9] it was found that the total energy for the T_4 geometry is 0.64 eV/adatom lower than for the H_3 geometry (the DAS model has twelve adatoms in T_4 sites within every 7×7 unit cell). The resulting band structure of the ($\sqrt{3}\times\sqrt{3}$)-Si surface (see Fig. 2) is very similar to those of the ($\sqrt{3}\times\sqrt{3}$)-Al, -Ga, and -In surfaces. For the ($\sqrt{3}\times\sqrt{3}$)-Si surface three bands are found of which the uppermost is half filled, as compared to the ($\sqrt{3}\times\sqrt{3}$)-Al, -Ga, and -In surfaces where this band is completely empty. In the comparison with ARUPS data of the Si(111)7×7 surface[11] it was concluded that the two lower bands correspond to the S_3 surface state and the upper half filled band to the metallic state S_1. In a preliminary calculation[11] of a (2×2) unit cell, including one adatom and one rest atom [see Fig. 3(b)], the origin of a band at the energy of the S_2 surface state (≈ 0.85 eV) could be attributed to the rest-atom dangling bonds. [Recently a semiempirical tight-binding–based energy-minimization calculation was performed for the DAS model of the Si(111)7×7 surface.[12] Several of the surface states found in that study could be related to the surface states observed experimentally while others have not been verified by experiment.]

In the spectroscopic STM study[7] the unoccupied state U_1 is found to be uniformly distributed on the twelve adatoms in the (7×7) surface unit cell (A, A′, B, B′) with a symmetric appearance of the conductance in the two halves. In contrast, the state around the Fermi level is found to have a clear asymmetric appearance of the two halves for both positive and negative biases. Also the conductance to or from the different groups of adatoms (A, A′, B, and B′) were different for this state.

The dispersive behavior of the state U_1, found in the present study, and its uniform distribution in spectroscopic STM is indicative of a periodical state originating from the local-bonding arrangement with overlap to the neighboring states. This behavior would correspond well to the case of adatom p_z orbitals coupling to underlaying dangling bonds, which is actually the origin of the calculated Σ_1 band in Fig. 2. The experimentally found S_1 state, on the other hand, has a flat dispersion as observed with ARUPS, typical of localized atomiclike states, with little or no overlap to neighboring states of identical character. In ARUPS the S_1 state at -0.25 eV (Refs. 4 and 10) is visible over the whole (1×1) SBZ for a photon energy $h\nu = 10.2$ eV and the intensity has a maximum at half way to the SBZ border. For $h\nu = 21.2$ eV (Ref. 10) the intensity behavior is the same except that the state is not visible in the outer parts of the SBZ. Although the intensity maximum of the S_1 state is at 0.25 eV below the Fermi level, metallic tails are observed with ARUPS (Refs. 4 and 10) and KRIPES (Refs. 5 and 6) and a wide state is observed on both sides of the Fermi level with STM.[7] All these observations indicate the existence of several states or a mixture of states in a broad set of bands positioned on both sides of the Fermi level.

From the calculation of the Si(111)$\sqrt{3}\times\sqrt{3}$-Si surface[11] it was proposed that the dispersing Σ_1 band corresponds to the S_1 state. The Σ_1 band has a large bandwidth and the agreement with the flat S_1 state is far from good. Instead we note that the shape of the dispersing U_1 state is very similar to the calculated Σ_1 band. The U_1 and Σ_1 state have also a behavior similar to the empty adatom states, calculated and observed experimentally for the ($\sqrt{3}\times\sqrt{3}$)-Al, -Ga, and -In adatom surfaces.[9] We suggest therefore that U_1 is instead the uppermost adatom state that corresponds to the Σ_1 band. Taking into account the large bandwidth calculated for the Σ_1 band (0.5 eV) and that bandgaps are usually underestimated in the local-density calculations, the agreement is much better with the U_1 state than with the S_1 state. In the calculations of the bands for the metal overlayers[9] the T_4 model gave bandwidths of the empty bands in good agreement with the measured values. In the present case the bandwidth calculated for Σ_1 is very close to that of U_1. It should be noted naturally that the measured dispersion of U_1 does not have the symmetry of a ($\sqrt{3}\times\sqrt{3}$) SBZ but most probably that of a (1×1). [Neither does U_1 have a (2×2) symmetry as different M′ values are observed, see Fig. 2].

In counting the available number of electrons according to the DAS model, 12 adatoms, 6 rest atoms, and one corner atom will each contribute one electron. Of the 19 electrons available twelve will fill the rest atom states and two the corner-atom states (these have the lowest energy). From the present measurements it is argued that the U_1 state, corresponding to the Σ_1 state, is completely empty, and most probably will the five remaining electrons instead occupy states of lower energy, that will pin the Fermi level. Naturally, these remaining electrons must still be associated with the twelve adatoms since the rest atoms and the corner atom have fully occupied bands. The four groups of adatoms A, A′, B, and B′ of the DAS model all have different geometric surroundings and the atoms within one group are far away from each other. It is possible therefore that electrons on each group of adatoms give rise to flat-type subands and that these have small differences in energy. This idea is supported by the spectroscopic STM study[7] where all four groups showed different conductance at given voltages on both sides of the Fermi level. No intrinsic Fermi-level states exist on the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces and it can be assumed that for the Si(111)7×7 surface the Fermi level states are related to the particular geometry of the whole unit cell, and not to the local bonding of the adatoms. It can be noted also that in a recent ARUPS study of the Si(111)$\sqrt{3}\times\sqrt{3}$-Sn surface,[13] where the Sn atoms have the same number of valence electrons as Si, an occupied or partly occupied dispersing Fermi level state was observed. The dispersion of this state is similar to the empty bands of the Al, Ga, and In adatom surfaces.

In order to explain the energy position of the S_1 surface state (-0.25 eV), as well as the finite intensity at the Fermi level observed in ARUPS and KRIPES and the large width of this state observed in spectroscopic STM,

the presence of several bands with small differences in energy is assumed. It is possible then that at room temperature several of these states are only partly occupied due to the small energy differences between them. In photoemission and electron energy loss (EELS) measurements,[14] clear differences in the behavior of these states can be observed between samples at room temperature and at 20 K. It can be noted further that in a combined ARUPS and KRIPES study of the Si(111)7×7-Ge and Si(111)5×5-Ge surfaces[10] large quantitative differences were observed in the dispersions, as compared to the Si(111)7×7 surface, for the states corresponding to S_3 and U_1 while the behavior of S_1 was practically the same for all surfaces. Since these surfaces have different composition in the surface layers and different geometric structure[10] we can expect differences in the states involved in the bonding between adatoms and the second-layer atoms. This indicates further that the S_1 state is not strongly involved in the bonding between the adatoms and the second layer Si atoms, but is more atomic-like.

To summarize, with k-resolved inverse photoemission a pronounced dispersing surface state is observed ≈ 0.5 eV above the Fermi level. This state is attributed to adatom p_z orbitals involved in the coupling to second-layer Si atoms. Another set of adatom states positioned around the Fermi level is more local in nature and is not strongly involved in the bonding of the adatoms to the second-layer atoms, but are related to the geometry of the whole 7×7 unit cell.

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