Surface states on Si(111)$\sqrt{3}\times\sqrt{3}$-In: Experiment and theory

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Angle-resolved photoemission has been used to study the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface. Two occupied dangling-bond-derived surface-state bands have been found. The experimental results are compared with dispersions from pseudopotential calculations for the energy-minimized geometries of two different adatom configurations of the surface. The measured dispersions as well as the observed momentum distributions are found to be in good agreement with the calculations.

The problem of understanding the geometric and electronic configuration of reconstructed semiconductor surfaces with metal overlayers has for a long time attracted considerable interest.[1-6] Several models have been proposed for the different surfaces, but until recently no theoretical studies enabling detailed comparison of experimental and calculated electronic structures had been carried out.[7]

In this paper we present experimentally determined surface-state bands for the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface, with approximately $\frac{1}{3}$ of a monolayer of indium, and compare this with calculated electronic structures for energy-minimized geometries of indium adatoms on Si(111).

There are two likely possibilities for an indium induced Si(111)$\sqrt{3}\times\sqrt{3}$ reconstruction using $\frac{1}{3}$ monolayer of In. The In atoms can rest in either the threefold symmetric hollow sites (H_3), or in the threefold symmetric sites above a second-layer Si atom (T_4). Total-energy calculations have been carried out for both geometries using the pseudopotential method and the local-density approximation. Analogous calculations have been reported for the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface.[8] For indium it is found that the T_4 geometry is preferred by 0.2 eV/adatom. For the T_4 geometry, the equilibrium Si-In distances are 4.97 a.u. between the In and the three surface Si atoms and 4.89 a.u. between the In and the second-layer atom directly below. For the H_3 site the calculated distance is 4.95 a.u. from the In to the three surface Si atoms. These distances are slightly larger than those corresponding to the Al-covered surface; this probably reflects the larger covalent radius of In. The dispersions calculated for both geometries are similar to each other and to the corresponding dispersions on the Al-covered surface.[8] This is in accordance with the fact that the surface states are mainly derived from Si dangling bonds which hybridize with p_x and p_y orbitals on the adatoms. This interaction causes an energy lowering for those dangling-bond states with wave vectors in the outer parts of the 1×1 Brillouin zone; it is these states which form the two occupied bands of surface states.

In the angle-resolved photoemission experiment a VG ADES 400 UHV spectrometer was used, with a base pressure of 5×10^{-11} Torr. Unpolarized light from a resonance lamp was used ($\hbar\omega=16.8$, 21.2 eV), with a total-energy resolution (for 21.2 eV), of ~0.15 eV and angular resolution $\pm2°$. The sample was a Si(111) single crystal of p type ($\rho\sim10$ Ωcm). Initially a clean Si(111)7×7 surface was produced by resistive heating of the crystal to 1150 °C followed by a slow cooling to room temperature (~20 min). Evaporation of 0.5 ML of indium (as monitored by a quartz oscillator), onto the surface, followed by a heat treatment with temperatures up to 575 °C, produced the following sequence of reconstructions: 4×1 (3 domain), $\sqrt{31}\times\sqrt{31}$, and finally $\sqrt{3}\times\sqrt{3}$.[9] For the Si(111)$\sqrt{3}\times\sqrt{3}$-In surfaces used in the photoemission experiments clear $\sqrt{3}\times\sqrt{3}$ low-energy electron diffraction (LEED) patterns were observed with a very low background and with no indications of other superstructure spots.

In Fig. 1 spectra recorded along the $[10\bar{1}]$ direction are shown ($\hbar\omega=21.2$ eV). The geometries of the 1×1 and the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zones (SBZ's) are indicated in Fig. 2 together with the three main directions $[10\bar{1}]$, $[2\bar{1}\bar{1}]$, and $[11\bar{2}]$ probed in the photoemission experiment. Several surface-related structures are present in the spectra: A_1, A_3, A_3', A_3'', and A_3''', as well as several bulk-related peaks.

From several photoemission studies,[4,10,11] it is well established that the Si(111)7×7 surface exhibits three surface-state peaks at ~-0.2 eV, ~-0.8 eV, and ~-1.8 eV relative to the Fermi level (here denoted by S_1, S_2, and S_3, respectively). On the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface one prominent surface-state peak A_3 is observed with a dispersion similar to the S_3 surface-state dispersion[4] on the Si(111)7×7 surface. The A_3 surface-state peak is present at all emission angles, and has an overall dispersion of 0.55 eV. For the two adatom models discussed here the dangling bonds on the free Si surface with wave vectors near the edges of the 1×1 SBZ couple favorably to the adatom electrons and give rise to two occupied states below the valence-band maximum.[8] On the other hand, dangling bonds with wave vectors near the center of the 1×1 SBZ give rise to unoccupied states in the projected band gap. Consequently, the photoemission intensity from the occupied states should be high in the outer region of the 1×1 SBZ, i.e., in the secondary $\sqrt{3}\times\sqrt{3}$ SBZ's. Himpsel *et al.*[10] have observed resembling emission patterns for the annealed surfaces of both Ge(111)2×8 and Si(111)7×7 suggesting a common local bonding geometry for these surfaces.

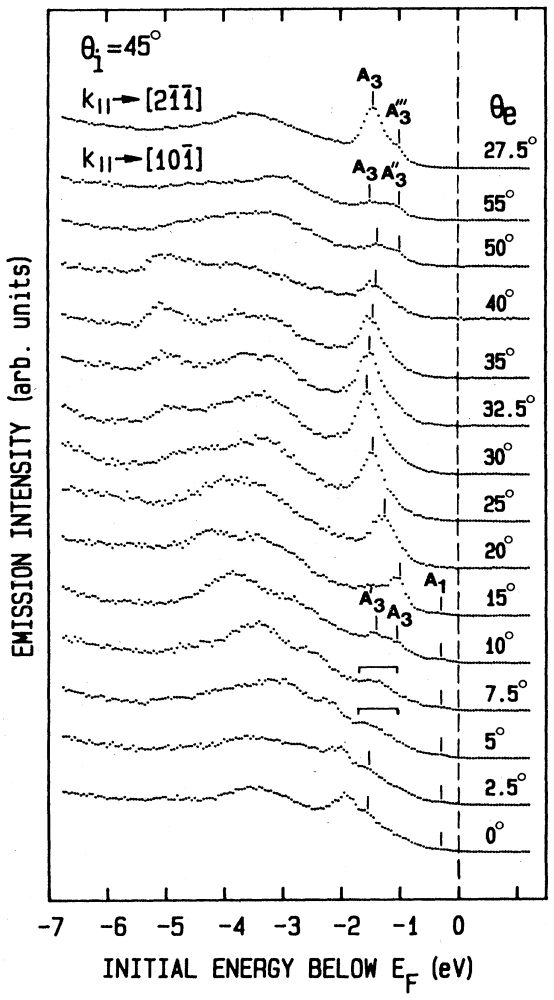

FIG. 1. Photoemission spectra for various angles of emission θ_e, at photon energy $\hbar\omega = 21.2$ eV, along the [10$\bar{1}$] and [2$\bar{1}\bar{1}$] directions. The A_3 structures corresponding to the two-adatom surface-state bands are indicated.

In Fig. 1 the emission from the A_3 state is weak within the primary $\sqrt{3}\times\sqrt{3}$ SBZ ($\theta_e < 15°$), but increases rapidly while entering the second $\sqrt{3}\times\sqrt{3}$ SBZ and crossing the 1×1 zone boundary. In Fig. 2 initial energy dispersions $E_i(\mathbf{k}_\parallel)$ are plotted for the various surface peaks (strong peaks are marked with filled symbols and weak structures with open symbols). The dispersion of the A_3 peak along the [10$\bar{1}$] direction reveals two different $E_i(\bar{M}')$ values for $k_\parallel \sim 0.55$ Å^{-1} and $k_\parallel \sim 1.64$ Å^{-1}, corresponding to the two occupied bands for the $\sqrt{3}\times\sqrt{3}$ reconstructed surface. For emission angles 5°–7.5° the surface contribution is broader and contains a double structure (A_3, A_3') within the marks (see Fig. 1), corresponding to the two different bands. A double structure is also present at high emission angles ($\theta_e \sim 50°$), A_3 and A_3'', corresponding to the two bands at the second $\bar{M}'$ point.

For the [2$\bar{1}\bar{1}$] azimuth (Fig. 2), the main surface contribution A_3 has an intensity pattern similar to the one in the [10$\bar{1}$] azimuth, with strong emission outside the primary $\sqrt{3}\times\sqrt{3}$ SBZ. At the $\bar{M}'$ point along the [2$\bar{1}\bar{1}$] direction ($k_\parallel \sim 0.95$ Å^{-1}), where the separation of the two bands is at a maximum, the second band can be seen as an additional weak structure (A_3,A_3''') (see Fig. 1 topmost spectra). For the [11$\bar{2}$] direction the surface structures have an emission pattern identical to that in the [2$\bar{1}\bar{1}$] direction except for the (A_3''') structure, which does not appear in the spectra. This difference is natural since the [2$\bar{1}\bar{1}$] plane does not have mirror symmetry.

In Fig. 2 the bands calculated for the T_4 and H_3 models of the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface are drawn with full and dash-dotted lines, respectively, where the theoretical model predicts strong emission. From the bands that are folded from the outer region of the 1×1 SBZ into the $\sqrt{3}\times\sqrt{3}$ SBZ (dashed and dotted lines), low emission is expected. From the comparison of theory with experiment in Fig. 2 it is clear that for the [10$\bar{1}$] and [2$\bar{1}\bar{1}$] directions the visibility of the surface peaks is in accordance with the models. Similar good agreement is obtained for the [11$\bar{2}$] direction. For the $\bar{\Gamma}$–$\bar{K}'$ region two weak structures close to each other are predicted, while in the experiment only one structure is observed. It is possible that one of these bands is too weak to be observed, but more probably the bands are too close to be resolved.

Comparing the calculated dispersions from the two different models H_3 and T_4 there is a qualitative agreement with experiment in both cases. Quantitatively the H_3 model gives a broader bandwidth (0.55 eV), in better agreement with the observed value 0.55 eV, while in the T_4 model the energies of the bands are lower, in good agreement with experiment. Since the level of agreement with experiment is similar for the H_3 and T_4 models it is not possible from our photoemission data to select a preferred geometry.

In photoemission spectra the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface exhibits a very weak structure A_1 close to the Fermi level ($E_i \sim -0.25$ eV). This state is visible at emission angles $\lesssim 15°$ in all the directions probed (see Fig. 1). The corresponding A_1 structure was also observed for the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface.[4] However, this structure is not predicted by the calculations for the adatom reconstructed surfaces. It is possible that this minor structure corresponds to some feature of the 7×7 surface that remains as a defect on the $\sqrt{3}\times\sqrt{3}$-In surface.

As mentioned before, the adatom induced states on the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface are derived from p_z orbitals on the Si surface atom coupling to orbitals of p_x and p_y character on the In adatom. A similar situation is at hand for a 2×2 Si-adatom model[12] for the Si(111)7×7 surface. The dependence on the angle of light incidence is very strong for the A_3 surface state and similar to the dependence of the S_3 state on the 7×7 surface. When the angle of incidence is altered from $\theta_i = 45°$ to $\theta_i = 0°$, thereby reducing the component of the electric field perpendicular to the surface, the emission intensity is very much reduced. The In-reconstructed surface was also tested for sensitivity to O_2 and H_2 gas exposure. The A_3 surface state was found to be far less sensitive than the S_3 state; it thus seems that the In atoms stabilize the surface against the gas molecules. The observed surface structures A_1 and A_3 are situated in the band gap ($E_F - E_V \sim 0.5$ eV) for the whole 1×1 SBZ except close to the $\bar{\Gamma}$ points where the A_3 state is within the projected bulk band structure.[4]

To summarize, we report two measured surface-state bands of the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface that are found to be very similar to those calculated for the T_4 and H_3 adatom

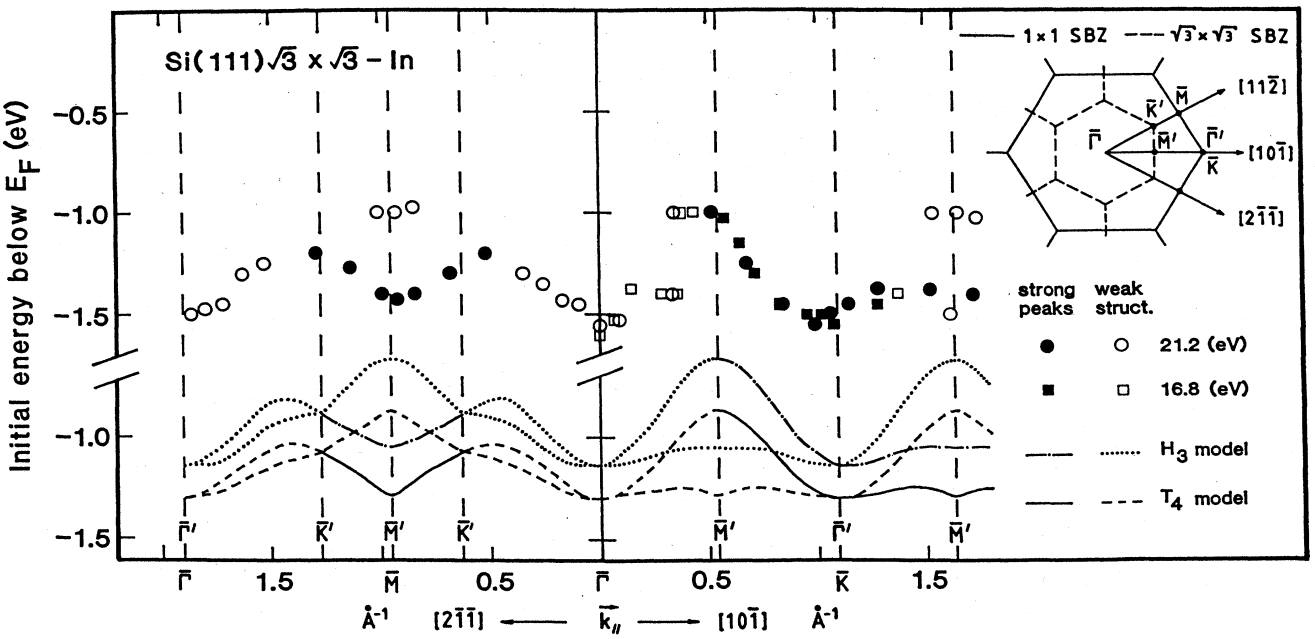

FIG. 2. Experimental surface-state plots, $E_i(\mathbf{k}_{\parallel})$, and calculated surface-state bands for the T_4 and H_3 models. $E_F - E_V \sim 0.5$ eV. The geometry of the 1×1 and $\sqrt{3}\times\sqrt{3}$ SBZ's and the directions investigated are shown in the insert.

models. The photoemission measurements are also in agreement with the predicted momentum distribution for the adatom-induced surface states. More structures associated with the $\sqrt{3}\times\sqrt{3}$ periodicity are present: A_3, A_3', A_3'', and A_3''' in spectra for the In-reconstructed surface than for the Al-reconstructed surface,[4] probably due to a more efficient scattering from the larger In atoms. The experimental dispersions for the strong surface peaks on the Al- and In-adatom surfaces have very similar shapes, the major difference being an upward shift of 0.4 eV for the dispersion of the In-adatom surface.

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