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Unoccupied surface states revealing the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In adatom geometries

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k-resolved inverse-photoemission spectroscopy has been used to determine the empty surface-state band structures of Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces. The results are compared with first-principles pseudopotential total-energy and electronic-structure calculations for energy-minimized geometries of the filled- (T_4) and the hollow- (H_3) site adatom models. Good agreement between experiment and theory for the unoccupied surface-state band structures is found for the T_4 model, which also has the lowest total energy.

For more than 20 years, the interface formation of semiconductor surfaces with the simple metals Al, Ga, and In has been the object of many studies concerning the geometric and electronic structure.[1-7] Amongst the ordered-metal-overlayer systems observed, the most well known is the Si(111)$(\sqrt{3}\times\sqrt{3})R\pm 30°$ reconstruction [from now on denoted as Si(111)$\sqrt{3}\times\sqrt{3}$] which occurs at $\frac{1}{3}$-monolayer coverages of the metals. Several models have been suggested for this reconstruction,[1,3,4] but only recently have detailed total-energy and band-structure calculations[4,5,7] been carried out for different geometries.

In several angle-resolved ultraviolet-photoemission spectroscopy (ARUPS) studies, the occupied surface-state band structures of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces have been measured[3,6-10] and compared with band structures calculated[7-10] for the two most likely geometries. In these two geometries, the metal adatom is placed in either the filled site above the second-Si-layer atoms (T_4) or in the hollow site above the fourth-Si-layer atoms (H_3). It has not been possible, however, to obtain conclusive experimental evidence for either geometry, since the experimental band structures were found to be in equally good agreement with the occupied surface-state bands calculated[4,5,7] for the two different models.

In this paper, we present k-resolved inverse-photoemission spectroscopy (KRIPES) measurements of the empty surface-state bands of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces. These results, together with the occupied surface-state bands determined experimentally,[7-10] allow us to compare the complete experimental band structure with pseudopotential calculations for the energy-minimized T_4 and H_3 adatom geometries. Our studies show that important knowledge of surfaces can be gained when both the occupied and unoccupied parts of the experimental band structure are known. Also, the present study illustrates that first-principles calculations can be applied to interface systems with resulting band structures in good agreement with experiments.

Details of the inverse-photoemission experiment have been presented elsewhere.[11-13] The Geiger-Müller-type photon detector was equipped either with a CaF_2 or a SrF_2 window. With the former, photons of energy 9.7 eV were filtered with a total-energy resolution (electrons and photons) of 0.7 eV, whereas with the latter, photons of energy 9.5 eV were filtered and a total-energy resolution of 0.35 eV obtained.[14] The electrons impinging on the surface at polar angle θ were produced by a custom-built electron gun[12] with a measured beam divergence of 3° resulting in a $k_\parallel$ resolution of $\Delta k_\parallel < 0.1$ Å^{-1}. The Si(111) 7×7 substrate surfaces were prepared by direct resistive heating of the Si sample ($11\times5\times0.4$ mm^3, p doped, $\rho\sim0.03$ Ωcm) up to 1000°C. The ordered metal overlayers were produced by evaporation of ultrapure metals, with the sample at room temperature, followed by careful annealing. The base pressure in the ultrahigh-vacuum (UHV) system was 5×10^{-11} Torr, and remained below 3×10^{-10} Torr during evaporation and annealing.

Inverse-photoemission spectra of the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface are shown in Fig. 1 for the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction of the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone (SBZ). The geometry of the $\sqrt{3}\times\sqrt{3}$ SBZ relative to the 1×1 SBZ and the different directions probed in the experiments are shown in the inset of Fig. 1. For the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface, a very pronounced surface-state peak (S) is present at a different energy from that for the surface state of the clean Si(111) 7×7 surface (0.5 eV).[13,15] For polar angles close to normal incidence, corresponding to $k_\parallel$ values at the SBZ center, the intensity is the strongest. With increasing θ, the In-induced state disperses towards the Fermi level, and its intensity is lowered. The state reaches a minimum-energy position at $\theta=30°$ and moves slightly upwards again. Similar behavior of the dispersion and intensity distribution is observed for the $\bar{\Gamma}$-$\bar{M}'$ direction (not shown). Structures A and B were previously identified as bulk features[13,16] and will not be further discussed here.

The geometries of the two adatom models T_4 and H_3 are shown in Fig. 2. The metal adatoms 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).[4,7] Total-energy calculations were previously carried out for the two geometries of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, and -In surfaces,[4,7] and in this paper for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ga surface, using the pseudopotential method and the local-density approximation. In all three cases, it was

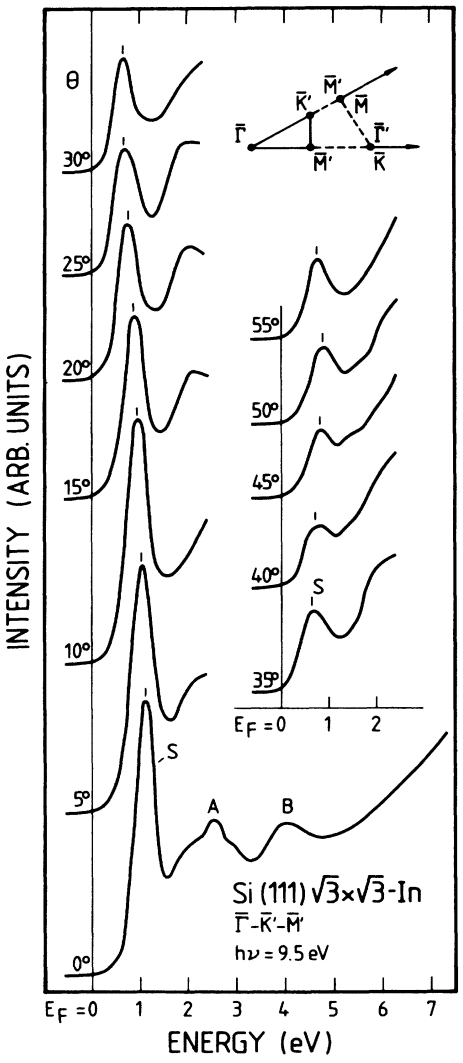

FIG. 1. Inverse-photoemission spectra for various angles of incidence for the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface. The strong peak S corresponds to the adatom-induced state, while A and B are bulk structures (Refs. 13 and 15). The directions probed in the experiments are shown in the inset.

found that the T_4 geometry has the lowest total energy for the energy-minimized geometries. For Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces, the resulting total energy for the T_4 model is 0.3 eV/adatom, 0.38 eV/adatom, and 0.2 eV/adatom lower, respectively, than for the H_3 model.[4,7] The adatom-induced occupied surface states are derived from p_z orbitals on the Si surface atoms coupling to orbitals of p_x and p_y character on the adatom. Dangling bonds with wave vectors near the edges of the 1×1 SBZ couple favorably to the adatom p_x and p_y orbitals, and give rise to two occupied surface-state bands. The adatom p_z orbital couples to dangling bonds with wave vectors near the center of the 1×1 SBZ, giving rise to an unoccupied surface state in the band gap. Therefore, it can be expected that the intensity of the empty surface state, as seen in KRIPES, is strongest close to normal incidence, corresponding to $k_\parallel$ values within the first $\sqrt{3}\times\sqrt{3}$ SBZ. This is indeed observed in the present measurements (see Fig. 1), where the surface-state intensity decreases monotonically for increasing angles of incidence. Correspondingly, in the ARUPS experiments the strongest intensity is found at the outer parts of the 1×1 SBZ.[6,7,9,10]

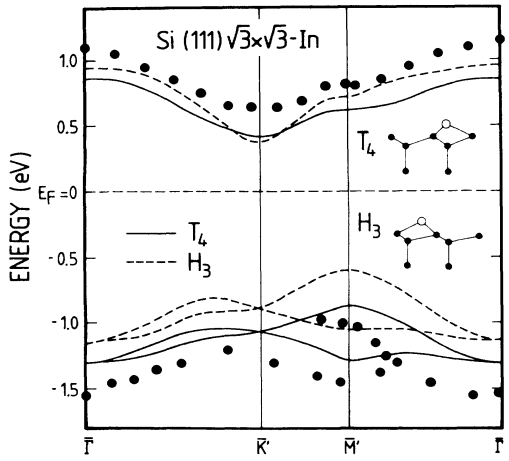

FIG. 2. Comparison between experimental dispersion plots (from Fig. 1 and Ref. 7) and surface-state bands calculated for energy-minimized geometries of the T_4 and H_3 models ($E_F - E_V \approx 0.5$ eV) (Ref. 7).

In Fig. 2, the experimental energy positions of the empty and filled adatom-induced states of the Si(111)$\sqrt{3}\times\sqrt{3}$-In surface are plotted as a function of $k_\parallel$ for the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ and $\bar{\Gamma}$-$\bar{M}'$ directions [$E_F - E_V \approx 0.5$ eV (Ref. 7)]. In this figure, surface-state dispersions $E(k_\parallel)$ are compared with surface-state bands from the pseudopotential calculations[7] for the two energy-minimized geometries (H_3,T_4) of this surface. In comparing the shape of the bands, the empty surface-state band determined experimentally is in better agreement with that of the T_4 model (full line) as the energy difference between them is almost constant along the directions probed. Considering the total bandwidth of the unoccupied bands of the two models, that of the T_4 geometry is slightly smaller, and that of the H_3 slightly larger than the experimental one. The ARUPS data on the filled surface-state bands from a previous study[7] are in good agreement with the bands of both models, since these are very similar.

In Fig. 3, the bands calculated for the energy-minimized geometries of the T_4 and H_3 models of Si(111)$\sqrt{3}\times\sqrt{3}$-Al[4] and -Ga surfaces are shown . The calculated surface-state band structures are compared with the occupied bands obtained in ARUPS studies by Kinoshita, Kono, and Sagawa[9,10] and with the unoccupied bands from the present KRIPES measurements. The KRIPES data of the Al-overlayer surface are shown as empty rings, indicating average values of several measurements, since the $\sqrt{3}\times\sqrt{3}$-Al surface proved quite difficult to prepare, and also was contaminated within only a few hours. It should be noted that in the study by Kinoshita *et al.*[9] on the Al-induced surface, regeneration of the surfaces was made at high temperatures every 20 min, to obtain the best results.

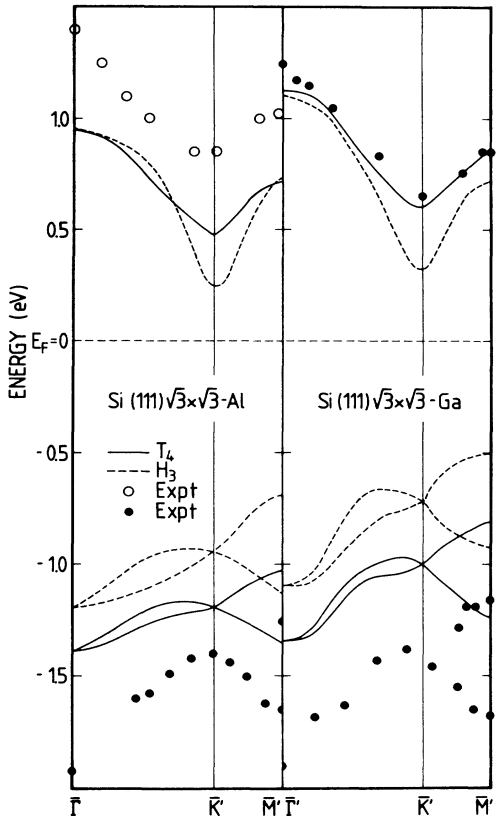

FIG. 3. Comparison between experimental dispersion plots and surface-state bands calculated for the T_4 and H_3 models. The occupied surface-state dispersions are from Refs. 9 and 10. $E_F - E_v \approx 0.5$ eV.

Also for the $\sqrt{3}\times\sqrt{3}$-Al surface, the shape of the T_4 band is in better agreement with experiment, and after a rigid shift of 0.3 eV the bands almost overlap each other completely. The measured bandwidth (0.55 eV) of the unoccupied bands favors the T_4 model with 0.48 eV, relative to the H_3 model with 0.70 eV.

For the empty band of the $\sqrt{3}\times\sqrt{3}$-Ga surface obtained experimentally, better agreement in the shape of the dispersion and the bandwidth is again found with the band of the T_4 model (cf. Fig. 3, right panel). The T_4 band can be seen to be almost identical to the experimental one, with bandwidths of 0.53 eV and 0.6 eV, respectively, while the H_3 band is much wider (0.78 eV).

In all cases, the calculated energy splitting between the occupied and unoccupied surface-state bands is larger for the T_4 model; as in this geometry, the substrate deforms so that the dangling-bond orbitals of the silicon atoms point more directly to the adatom, and this is most probably the reason for the lower total energy of the T_4 geometry. Considering the band gaps of the surface-state bands and, in particular, the indirect-minimum gaps in the outer parts of the SBZ (cf. Figs. 2 and 3), the T_4 bands are considerably more separated than the H_3 bands, and closer to experiment. In general, it appears that the bulk and surface-state band gaps are underestimated in local-density calculations, as, e.g., is the case for the Si(111) 2×1 surface with a gap calculated[17] to be 0.25 eV too small. Therefore, we are reluctant to rely heavily on a comparison of the band gaps of the surface-state bands.

As was also observed for the $\sqrt{3}\times\sqrt{3}$-In surface, the calculated *occupied* bands of the T_4 and H_3 models of $\sqrt{3}\times\sqrt{3}$-Al and -Ga surfaces are too similar, hence it is difficult to discriminate the two models by comparison with experiment. From previous ARUPS studies,[7,9,10] the behavior found for the occupied bands of the $\sqrt{3}\times\sqrt{3}$-In, -Al, and -Ga surfaces supports the adatom concept of both the T_4 and H_3 models, where the surface overlayer is completed ideally for $\frac{1}{3}$ monolayers of the metals. The observed intensity distributions with higher photoemission intensity at the outer part of the 1×1 SBZ are also in agreement with both models since a similar bonding mechanism is involved in both cases and similar intensity distributions are expected. The similarity of the calculated *occupied* bands as well as their predicted intensity distributions then resulted in nonconclusive comparisons between experiment and theory,[7,9,10] and the validity of the T_4 model, found to have the lowest total energy of the two models, could not be verified. In contrast, the *unoccupied* bands calculated for the two models are significantly different from each other in shape and bandwidth. The probable adatom geometry of the $\sqrt{3}\times\sqrt{3}$ surfaces as described by the T_4 model is then corroborated by the dispersions of the empty surface-state bands found for all three surfaces in the present KRIPES measurements.

The conclusive picture now obtained on the geometries of group-III metal-adatom systems on Si(111) may lead to an increased understanding of the adatom systems in general. Recently, T_4 and H_3 models have been applied to the Si(111) 7×7 surface,[18] proposed to have 12 Si adatoms per unit cell.[19] For a Si(111)$\sqrt{3}\times\sqrt{3}$-Si surface with the adatoms in a T_4 geometry, the total energy is again found to be much lower than for an H_3 geometry.

In summary, first-principles pseudopotential calculations of T_4 and H_3 geometries of Si(111)$\sqrt{3}\times\sqrt{3}$-Al, -Ga, and -In surfaces show that in all cases the T_4 geometry has the lowest total energy, and is therefore the most probable geometry of these surfaces. The unoccupied surface-state bands calculated for the two models are significantly different from each other, in contrast to the occupied bands, which are very similar in shape and bandwidth. The unoccupied surface-state bands are measured with k-resolved inverse photoemission, and for all surfaces are found to be clearly in better agreement with the bands of the T_4 model.

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[1]J. J. Lander and J. Morrison, Surf. Sci. **2**, 553 (1964).

[2]G. Margaritondo, J. E. Rowe, and S. B. Christman, Phys. Rev. B **14**, 5396 (1976).

[3]G. V. Hansson, R. Z. Bachrach, R. S. Bauer, and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981).

[4]J. E. Northrup, Phys. Rev. Lett. **53**, 683 (1984).

[5]H. Nagayoshi, Solid State Sci. **59**, 167 (1985).

[6]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, P. E. S. Persson, and S. A. Flodström, Phys. Rev. B **31**, 3805 (1985).

[7]J. M. Nicholls, P. Mårtensson, G. V. Hansson, and J. E. Northrup, Phys. Rev. B **32**, 1333 (1985).

[8]G. V. Hansson, J. M. Nicholls, P. Mårtensson, and R. I. G. Uhrberg, Surf. Sci. **168**, 105 (1986).

[9]T. Kinoshita, S. Kono, and T. Sagawa, Phys. Rev. B **32**, 2714 (1985).

[10]T. Kinoshita, S. Kono, and T. Sagawa, Solid State Commun. **56**, 681 (1985).

[11]B. Reihl, Surf. Sci. **162**, 1 (1985).

[12]P. W. Erdman and E. C. Zipf, Rev. Sci. Instrum. **53**, 225 (1982).

[13]J. M. Nicholls, F. Salvan, and B. Reihl, Phys. Rev. B **34**, 2945 (1986).

[14]The values are determined from the 90%–10% width of the Fermi-level onset in inverse-photoemission spectra from polycrystalline Ta, which could be periodically interchanged with the Si samples.

[15]F. J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. **2**, 815 (1984).

[16]D. Straub, L. Ley, and F. J. Himpsel, Phys. Rev. Lett. **54**, 142 (1985).

[17]J. E. Northrup and M. L. Cohen, Phys. Rev. Lett. **49**, 1349 (1982).

[18]J. E. Northrup, Phys. Rev. Lett. **57**, 154 (1986).

[19]K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).