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Angle-resolved ultraviolet-photoelectron-spectroscopy study of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface

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Angle-resolved ultraviolet-photoelectron spectra have been measured for the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface. Two surface-state bands have been found at $E_b = \sim 1.3$–1.9 eV below the Fermi level which disperse in accordance with the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone. It is suggested that a nondispersive surface-state band found at $E_b \approx 0.3$ eV is extrinsic to the $\sqrt{3}\times\sqrt{3}$ surface. The two dispersive bands are in qualitative agreement with those calculated for threefold-hollow adatom models.

The Al submonolayer interface on the Si(111) surface has been drawing much attention lately, due in part to its technological importance.[1] In a pioneering experiment on this subject, Lander and Morrison[2] (LM) observed several phases of surface superstructures as a function of Al coverage and substrate temperature. However, it is only rather recently that the surface electronic structure and geometry of the smallest superstructure of the Al/Si(111) interface, i.e., α-$\sqrt{3}\times\sqrt{3}$ in the notation of LM,[2] has been investigated. Hansson, Bachrach, Bauer, and Chiaradia[3] reported spectra from angle-resolved ultraviolet-photoelectron spectroscopy (ARUPS) of the α-$\sqrt{3}$ surface which turned out to show seemingly a single surface-state (SS) dispersion which did not have the symmetry of the $\sqrt{3}$ surface Brillouin zone (SBZ). Very recently, Uhrberg and co-workers[4] observed two SS bands in their ARUPS spectra for the $\sqrt{3}$ surface, which also turned out to be inconsistent with the $\sqrt{3}$ SBZ.

Northrup[5] has very recently reported first-principles pseudopotential calculations of the total energy and SS dispersions for the $\sqrt{3}$ surface. He has examined two adatom models, H_3 and T_4, H_3 being a model in which adatoms of $\frac{1}{3}$ monolayer of Al are in the threefold-hollow sites, no second layer of Si underneath, and T_4 being a model of adatoms in the threefold-hollow sites above the second layer of Si. From the total-energy calculation and comparison of the calculated SS dispersion with that of Hansson *et al.*,[3] Northrup has proposed that the T_4 model[5] is the correct one.

The SS dispersions as reported by Hansson *et al.*[3] and Uhrberg *et al.*[4] are similar for the dispersing surface state but do not show the expected periodicity of the $\sqrt{3}$ SBZ. In fact, the comparison of the calculated SS dispersion by Northrup[5] with that of Hansson *et al.*[3] depends on an interpretation of the experiment. In this Rapid Communication, we report that a nominal α-$\sqrt{3}$ surface shows three SS bands, two of which show dispersions of ~ 0.3 and 0.6 eV, respectively, with the expected periodicity of the $\sqrt{3}$ SBZ. The other band is nondispersive and it is suggested, from the coverage dependence of ARUPS spectra, that it is not directly related to the $\sqrt{3}$ surface.

The experimental apparatus has been described previously.[6] An electron-energy analyzer was used at energy and angle resolutions of 0.1 eV and $\sim \pm 2°$, respectively. The surface normal of a mirror-polished Si(111) wafer ($0.15\times4\times20$ mm^3, P doped, ~ 10–15 Ω cm) used in the experiment was off by 2.2′ from the ⟨111⟩ orientation. Ar$^+$ bombardment followed by annealing at ~ 900 °C was applied for the *in situ* cleaning of the sample in order to prevent the formation of surface roughness and the diffusion of Al into the substrate. A pyrolytic BN crucible was used for submonolayer depositions of 99.9999% pure Al under a pressure of 4×10^{-10} Torr. Auger electron spectroscopy showed no indication of contaminants before or after the Al depositions. The five phases of the Al/Si(111) submonolayer interface identified by LM (Ref. 2) were confirmed by reflection high-energy electron diffraction (RHEED), i.e., α-7×7 (RHEED spot-intensity profiles are different from those of the clean 7×7), α-$\sqrt{3}\times\sqrt{3}$ (a stable phase), β-7 (which is $\sqrt{7}\times\sqrt{7}^3$), γ-7 (which seems to be an incommensurate phase), and β-$\sqrt{3}\times\sqrt{3}$ (a metastable phase which converts to the γ-7 when heated). The α-$\sqrt{3}$ or $\sqrt{7}$ surface observed in an ARUPS measurement of ~ 30 min was prepared each time by a Al deposition onto the heated (~ 650 °C) substrate, which gave a clearer RHEED pattern.

Figure 1 shows representative ARUPS spectra of the α-$\sqrt{3}$ surface along the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ direction of the SBZ. These spectra and others not shown here have been used to plot the binding energy E_b vs $k_{\parallel}$ as shown in Fig. 2. The E_b-$k_{\parallel}$ diagram is also compared with that for the Si(111)7×7 surface.[7] It can be seen in Figs. 1 and 2 that the three SS bands of the 7×7 surface, i.e., the so-called surface-metallic-edge, dangling-bond, and back-bond SS's,[8] are replaced by new SS bands, S_1, S_2, and S_3, for the $\sqrt{3}$ surface. For $E_b \gtrsim 2$ eV, the E_b-$k_{\parallel}$ diagrams for the $\sqrt{3}$ and 7×7 surfaces appear almost identical to each other indicating the mostly bulk nature of these structures. The S_1 band is nondispersive and located close to the surface-metallic edge of the 7×7 surface. As is discussed later, this S_1 band is likely to originate from the boundary regions of the $\sqrt{3}$ domains. The S_2 and S_3 bands are most clearly seen around the $\bar{M}$ point at the boundary between the first and second SBZ's and are just barely seen at the next $\bar{M}$ point as can be seen in Fig. 1. If their separation were not visible in the spectra, the dispersion of the S_2 and S_3 bands as a whole would give a dispersion which did not show the symmetry of the $\sqrt{3}$ SBZ since the S_2 peak would be stronger at the first $\bar{M}$ point and the S_3 peak would be stronger at the next $\bar{M}$ point. This may be the case for the result of Uhrberg *et al.*[4]

The E_b-$k_{\parallel}$ diagram for the S_1, S_2, and S_3 bands is summarized in Fig. 3(a) both for the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ and $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$ directions. Along the $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$ direction, the separation of the S_2 and S_3 bands is not visible and even at the $\bar{M}$ point, where the separation can be expected from the result for the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ direction, only the S_3 band dominates as shown in Fig.

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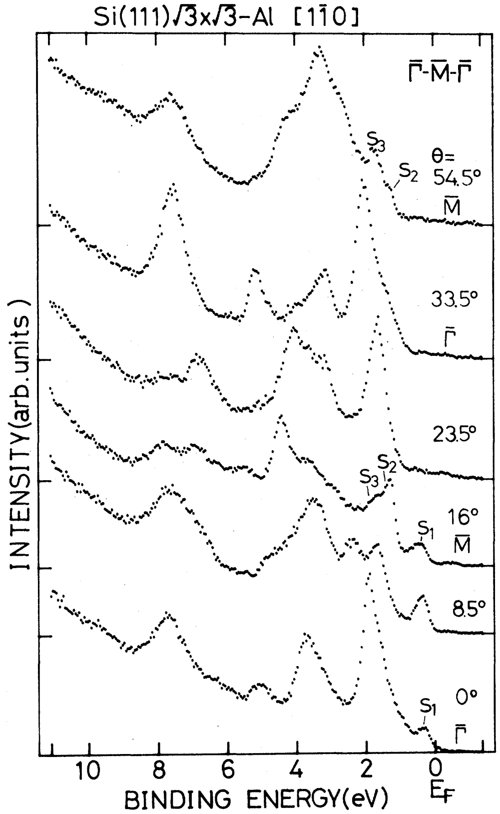

FIG. 1. Representative ARUPS spectra of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al surface. Polar angle θ of electron emission is changed along $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ line of the $\sqrt{3}$ SBZ and incident He I light is at $\theta = 45°$ on the opposite side of electron emission. The Fermi level is determined from that of a Ta holder.

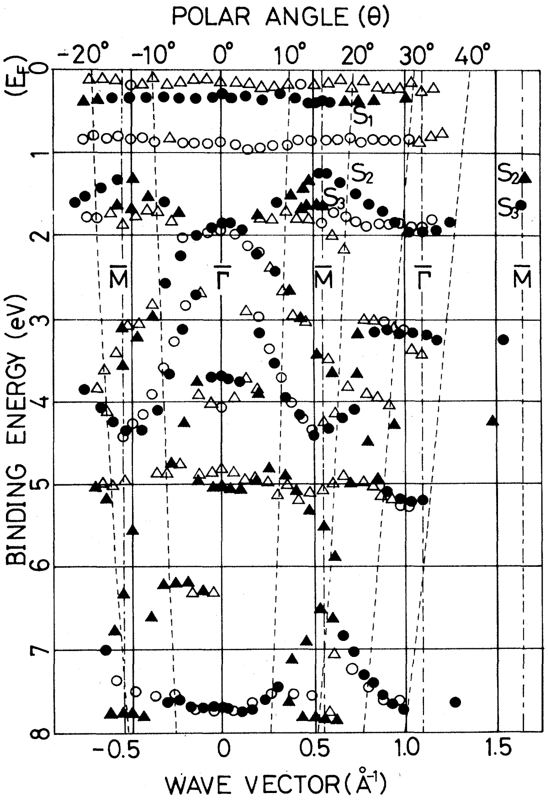

FIG. 2. E_b-$k_{\parallel}$ diagrams for the Si(111)$\sqrt{3}\times\sqrt{3}$-Al (solid symbols) and clean Si(111)7×7 (open symbols) surfaces. Circles are strong or sharp peaks and triangles are weak or broad structures in the actual ARUPS spectra.

3(b). This must be due to a cross-section effect since the directions of electron emission for the two $\bar{M}$ points are different with respect to the surface atom arrangement.

As we compare the present results with those of Hansson *et al.*[3] and Uhrberg *et al.*,[4] we note the following. Hansson *et al.* did not report the presence of the S_1 band and the S_2 and S_3 are not resolved at all. Northrup's interpretation[5] of the result of Hansson *et al.*, however, was in qualitative agreement with the present result. Uhrberg *et al.*[4] reported the presence of the S_1 band but seemed to fail to resolve the S_2 and S_3 bands.

We now turn to the coverage dependence of the SS bands. Figure 4 shows the coverage dependence of the ARUPS spectra for the $\bar{M}$ point along the $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ direction from the clean 7×7 to the α-$\sqrt{3}$, $\sqrt{7}$, and γ-7 surfaces. The periodicities were monitored by RHEED after each ARUPS measurement although absolute-coverage determination was not performed. For the clean 7×7 surface (0 min), we see well-defined surface-metallic-edge, dangling-bond, and back-bond SS's in accordance with previous measurements.[8] As Al is deposited onto this 7×7 surface, the three SS's disappear (6–8 min) and the new SS's, S_1, S_2, and S_3 develop (10–12 min) for the α-$\sqrt{3}$ surface. However, the S_1 peak starts to disappear (14 min) well before the disappearance of the $\sqrt{3}$ RHEED pattern. The S_2 peak, on the other hand, develops with a little shift in binding energy from 16 to 20 min corresponding to the development of the $\sqrt{7}$ surface. The S_3 peak does not show much change after 16 min.

Figure 4, therefore, suggests that the S_2 and S_3 bands have common origins in the $\sqrt{3}$ and $\sqrt{7}$ surfaces and that the S_1 band ceases to exist when the $\sqrt{3}$ structure is almost fully developed, since the full development of the $\sqrt{3}$ surface is most probably reached at the stage just before the appearance of the $\sqrt{7}$ periodicity (14 min). Although unambiguous interpretation is impossible, the S_1 band seems to originate from boundary regions of the $\sqrt{3}$ domains where random arrangement of dangling bonds can be expected. These boundary regions should become narrower as the $\sqrt{3}$ domains become wider, and at the beginning of the $\sqrt{7}$ surface, the surface may be almost completely covered by either $\sqrt{3}$ or $\sqrt{7}$ domains. We, therefore, tentatively state that the S_1 band is extrinsic to the $\sqrt{3}$ surface.

Having established that the S_2 and S_3 bands are the SS bands of the $\sqrt{3}$ surface and that the S_1 band is very likely not associated with the $\sqrt{3}$ surface, we compare the dispersions of the S_2 and S_3 bands with those calculated. Nagayoshi[9] reported self-consistent local pseudopotential calculations of the surface electronic structures for $\frac{1}{3}$ monolayer Si(111)$\sqrt{3}$-Al surfaces using ~12–16 layer slabs. He examined an on-top adatom model and a threefold-hollow adatom model with no second layer of Si underneath without substrate relaxation. As noted earlier, Northrup[5]

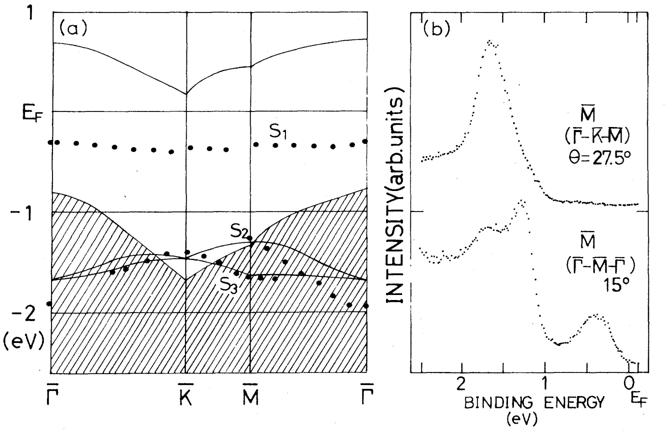

FIG. 3. (a) Summary of the surface-state dispersions for a nominal $\sqrt{3}$ surface (dots) as compared with the calculated ones by Northrup[5] for the T_4 model (solid lines). Shaded areas are the projected bulk bands. (b) Detailed ARUPS spectra at two different $\bar{M}$ points along $\bar{\Gamma}$-$\bar{K}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{M}$-$\bar{\Gamma}$ directions.

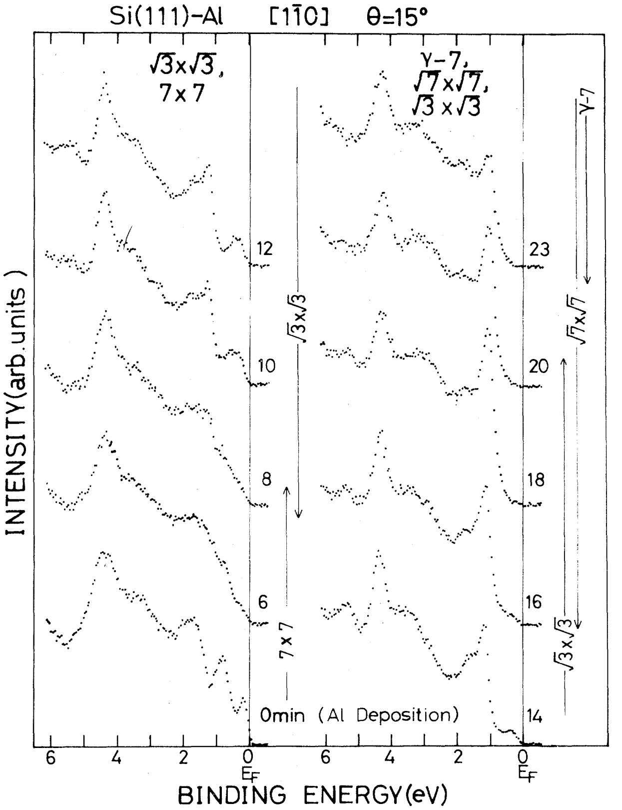

FIG. 4. Coverage dependence of the ARUPS spectra from clean Si(111)7×7 to α-$\sqrt{3}\times\sqrt{3}$-Al, $\sqrt{7}\times\sqrt{7}$-Al, and γ-7-Al surfaces. Al coverage can be assumed roughly proportional to the noted duration of deposition.

has very recently calculated total energies and SS dispersions of the two substrate-relaxed threefold-hollow adatom models, H_3 and T_4. The calculated SS dispersions for the H_3 and T_4 models are qualitatively similar to each other. The SS dispersion by Nagayoshi for his hollow-site model is also similar to those calculated by Northrup for the H_3 and T_4 models. However, Northrup reported the superiority of the T_4 model over the H_3 model from the viewpoint of the total-energy calculation. The calculated SS dispersions for a total-energy-minimized T_4 configuration are compared with the present result in Fig. 3(a). The Fermi level of the calculated bands is assumed to be 0.8 eV above the top of the bulk valence band as was done in Ref. 5. The calculation shows fair agreement with the experiment; in particular, the separation of the S_2 and S_3 bands at the $\bar{M}$ point matches quite well. The calculated dispersions from $\bar{\Gamma}$ to $\bar{M}$, however, appear to be about half of the experiment.

The present result, thus, gives qualitative support to the T_4 model of Northrup. However, since the calculated SS dispersions for the T_4 and H_3 (including Nagayoshi's) models are similar, the present comparison cannot be used for the distinction between the two models. Furthermore, the tested models are so far limited to the adatom models and the agreement between experiment and theory is still qualitative. Therefore, we need further investigations to be convinced of the T_4 model.

We would like to thank Dr. Uhrberg *et al.* for sending us a copy of their work prior to its publication and Dr. H. Nagayoshi and Dr. K. L. I. Kobayashi for their discussions. We are also indebted to Dr. S. Suzuki for experimental support.

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