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Occupied and unoccupied surface states on the Si(111)$\sqrt{3}\times\sqrt{3}$:B surface

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The Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface has been studied with **k**-resolved inverse photoemission and angle-resolved photoemission. In the unoccupied region of the band structure, one strongly dispersing surface state is observed and in the occupied region, three surface states are observed. The unoccupied surface state is identified as an empty dangling-bond state and two of the occupied surface states are identified as backbond states of the adatom. The third occupied surface state, not observed on any other Si(111)$\sqrt{3}\times\sqrt{3}$:group-III surfaces, is found to be connected with boron bonded beneath the surface top layer. The experimentally observed energy dispersions are compared with published band-structure calculations.

INTRODUCTION

It is well established that $\frac{1}{3}$ of a monolayer deposition of the group-III elements In, Ga, and Al onto a Si(111) surface can lead to a $\sqrt{3}\times\sqrt{3}$ reconstruction.[1-7] By comparison between calculated and measured surface-state dispersions it has been possible to determine the geometric structure of the surfaces, and it is shown that the three different group-III atoms occupy the T_4 adatom position [see Fig. 1(a)], directly above a second-layer Si atom.[2-6] The lightest of the group-III elements, the B atom, distinguishes itself from the other elements by its ability to diffuse from the bulk of a Si sample towards the surface and when the concentration of B is high enough at the Si(111) surface a rearrangement of the 7×7 reconstruction to the $\sqrt{3}\times\sqrt{3}$ reconstruction can occur.[8-12]

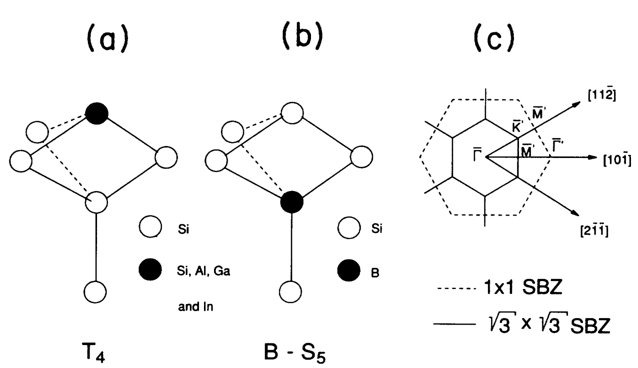

FIG. 1. (a) The T_4 adatom model with Si in the adatom position. (b) The B-S_5 adatom model where B is placed in a fivefold coordinated site directly under a Si adatom. (c) The $\sqrt{3}\times\sqrt{3}$ SBZ relative to the 1×1 SBZ.

Scanning tunneling microscopy (STM) measurements report that the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° structure is composed of Si adatoms on a Si double layer and that this configuration is stabilized by a high concentration of B in near-surface layers.[9,10] Total energy calculations of the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface predict that the B atom occupies the B-S_5 positioned [see Fig. 1(b)] in the second layer with a Si atom directly above it in the T_4 adatom position.[9-11]

In this work we present results from angle-resolved photoemission spectroscopy (ARPES) and **k**-resolved inverse photoemission spectroscopy (KRIPES) measurements on a Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface.

The surface reconstruction was obtained by annealing a heavily B-doped Si(111) wafer and was identified with low-energy electron diffraction (LEED). In contrast to ordinary bulk doped crystals, the samples used in the present study were doped by an implantation procedure, yielding a high B concentration ($\geq 10^{20}$ cm^{-3}) in the top 500 Å. Measurements were performed along the [10$\bar{1}$], [11$\bar{2}$], and [2$\bar{1}\bar{1}$] symmetry directions. In the occupied region, two dispersing surface states with different intensity to $k_{\parallel}$ relation and one surface state observable only around the $\bar{\Gamma}'$ point in the second surface Brillouin zone (SBZ) were found. In the unoccupied region one strongly dispersing surface state was identified. All surface states showed a dispersion with the periodicity of the $\sqrt{3}\times\sqrt{3}$ SBZ. A previously reported dispersion of an unoccupied surface state shows a maximum in energy position at the $\bar{\Gamma}$ point[11] whereas a local minimum is observed in the data presented here. The measured data are compared with calculated dispersions for the geometries Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° with a Si in the T_4 position and Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° with the B atom in the B-S_5 geometry.

EXPERIMENT

In the KRIPES experiment the surface is irradiated with a collimated beam of electrons from an electron gun, rotatable relative to the surface (with an angle resolution of ±1.5° resulting in an uncertainty in momentum parallel to the surface of $\Delta k_{\parallel} < 0.1$ Å^{-1}). The emitted photons are collected by an elliptically shaped mirror and focused into a Geiger-Müller counter tube that filters and detects photons of energy $h\nu = 9.5$ eV. The sample and mirror are mounted vertically and are held in fixed positions relative to each other, while the angle of incidence of the electrons is changed by rotating the electron gun in the horizontal plane via a goniometer. The combined energy resolution of the spectrometer, determined from the width of the Fermi level onset of a tantalum foil, is $\Delta E = 0.35$ eV.

The ARPES experiments were performed with two different setups. In one setup, unpolarized light from a He resonance lamp (21.2 eV) was used. The emitted electrons were energy analyzed by a 180° hemispheric analyzer with a total energy and angle resolution of ≤ 0.16 eV and ±2°. Measurements were also carried out using polarized synchrotron radiation (photon energies 15 and 21.2 eV) at MAXLAB synchrotron light source, Lund, Sweden. In the latter experiment the electrons were also energy analyzed with a 180° hemispherical analyzer and a total energy and angle resolution of 0.20 eV (15 eV), 0.18 eV (21.2 eV), and ±2°, respectively, were used. Identification and azimuthal alignment of the surface were performed with LEED. In both the KRIPES and the ARPES studies the energy scale was referenced to the Fermi level of a tantalum foil, which was in electrical contact with the sample. The base pressure in all three vacuum chambers was $\leq 2 \times 10^{-10}$ Torr. In the experiment using polarized synchrotron radiation, the electric field vector was always parallel to the probed crystal direction.

The sample was implanted with B ions of 90 keV energy to a coverage of 5×10^{15} cm^{-2}. The sample was then oxidized in air. In ultrahigh vacuum the samples were thoroughly outgassed at 600 °C, and heated to 1050 °C in 1-min cycles. The sample temperature was measured with an infrared pyrometer. After 10 min of annealing a sharp $\sqrt{3} \times \sqrt{3}$ LEED pattern had formed.

EXPERIMENTAL RESULTS

Inverse photoemission

Inverse photoemission spectra for the Si(111)$\sqrt{3} \times \sqrt{3}$:BR30° surface are displayed for the $\bar{\Gamma}$-$\bar{M}'$ direction in Fig. 2 and for the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction in Fig. 3. The geometry of the $\sqrt{3} \times \sqrt{3}$ SBZ relative to the 1×1 SBZ is shown in Fig. 1(c). A dispersing state labeled U is identified at 1.15 eV above the Fermi level at the $\bar{\Gamma}$ point. The total bandwidth of this state is 0.65 eV. The intensity of the U peak relative to the bulk related features was for short annealing times found to be proportional to the total time of heating. After ~10 min of annealing time no further improvement was observed in the quality of the U state. A decrease in intensity of the U peak relative to the bulk related structure was observed when the Si(111)$\sqrt{3} \times \sqrt{3}$:BR30° surface was exposed overnight to rest gases of the vacuum chamber. The energy position of the peak U is in Fig. 4 plotted as a function of $k_{\parallel}$, together with the projected bulk band.[13] It is commonly known that the band gaps in band-structure calculations have a tendency to become too small.[14] Optical measurements on Si show an indirect band gap of 1.11 eV. Si has a conduction-band minimum along the Γ-X direction in the bulk Brillouin zone, which corresponds to the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction in the $\sqrt{3} \times \sqrt{3}$ SBZ when projected onto the Si(111) surface. The valence-band maximum is located at the Γ point. To compensate for the differences between measurements and calculations, the valence-band maximum and the conduction-band minimum of the projected bulk band structure from Ref. 13 have in Fig. 4 been separated to give a 1.11-eV band gap. This gives an energy difference at the $\bar{\Gamma}$ point, between the projected valence-band maxima and the conduction-band minima, of 2.1 eV which is close to the value 2.4±0.15 eV observed in KRIPES measurements

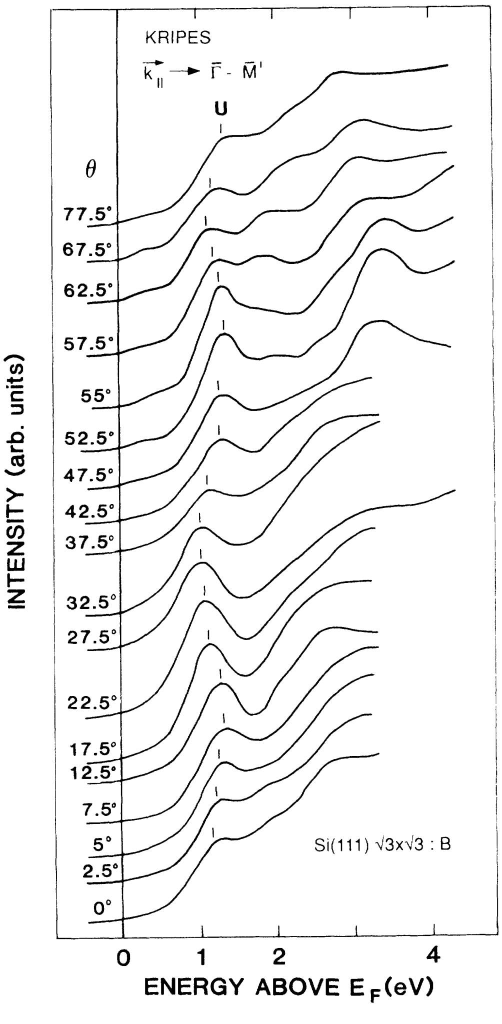

FIG. 2. KRIPES spectra along the $\bar{\Gamma}$-$\bar{M}'$ azimuth. Tick marks denote the dispersing surface-state emission U.

on the Si(111)2×1 surface.[14] The value of the valence-band maximum $E_{\rm VBM}$ relative to the Fermi level used in Fig. 4 is -0.5 eV.[12]

In the $\bar{\Gamma}$-$\bar{M}'$ direction the U state shows a symmetric dispersion around polar angles 27.5°–32.5°, that is, around the $\bar{M}'$ point in the $\sqrt{3}\times\sqrt{3}$ SBZ, with maxima in energy position of 1.35 eV at 12.5° and 52.5°. Local minima in energy position of 1.15 eV are observed at polar angles 0° and 62.5° corresponding to the $\bar{\Gamma}$ and $\bar{\Gamma}'$ point, respectively. In the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction the U state reaches a maximum in energy position of 1.4 eV at polar angle 7.5° and a minimum of 0.75 eV at an angle of 32.5° corresponding to the $\bar{K}'$ point in the $\sqrt{3}\times\sqrt{3}$ SBZ. For higher angles of incidence a second maximum exists for polar angle between 47.5° and 52.5° corresponding to the region around the $\bar{M}'$ point. In Fig. 4 the dispersion of U overlaps with the projected bulk at the $\sqrt{3}\times\sqrt{3}$ zone border in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction. Accordingly in Fig. 3, spectra where the U state overlaps with the bulk bands, display a lower peak intensity than those where the U state is located in the band gap.

It can be seen in Fig. 4 that the U band is mainly positioned in the band gap of the projected bulk bands. Taking also into account that this state is not observed on the Si(111)7×7 surface[15] and its sensitivity to contamination, it can be concluded that the U state is a surface state. The measured dispersion of the U peak in Fig. 4 is compared with calculated dispersions of the surfaces Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° with B in the B-S_5 position[11] and Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° with the Si atoms in the T_4 geometry.[16]

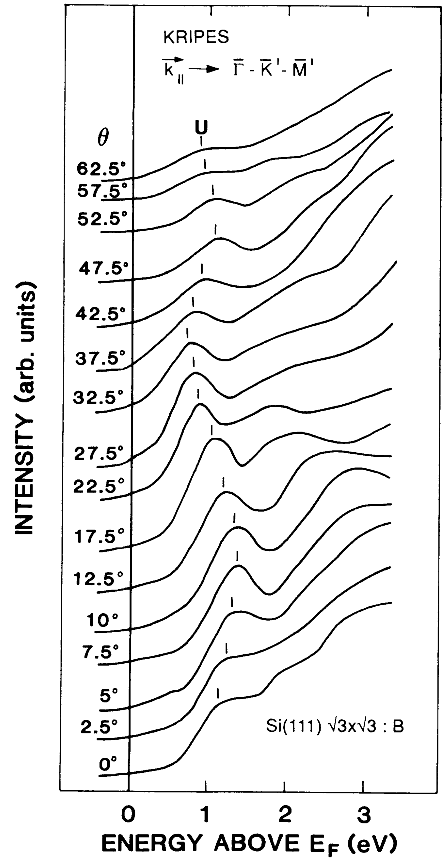

FIG. 3. KRIPES spectra along the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ azimuth. Tick marks denote the dispersing surface-state emission U.

It can be seen in Fig. 4 that the energy positions of the M' point in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction and the $\bar{\Gamma}$-$\bar{M}'$ direction are the same. This indicates the existence of only one surface state in the unoccupied region.

In the KRIPES measurement on the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface performed by Kaxiras *et al.*[11] a surface-state dispersion is reported within the first $\sqrt{3}\times\sqrt{3}$ zone with a maximum in energy position of ~1.3 eV above the Fermi level at the $\bar{\Gamma}$ point (see Fig. 4). It is reported that this surface state is dispersing towards lower-energy positions on both sides of the $\bar{\Gamma}$ point to an energy position ~1 eV at the $\bar{M}'$ point in the $\bar{\Gamma}$-$\bar{M}'$ direction and to ~0.8 eV at the $\bar{K}'$ point in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction.

A comparison between the dispersion observed in Ref. 11 and the one presented here indicates a different energy position for the $\bar{\Gamma}$ point [1.3 eV (Ref. 11) versus 1.15 eV]

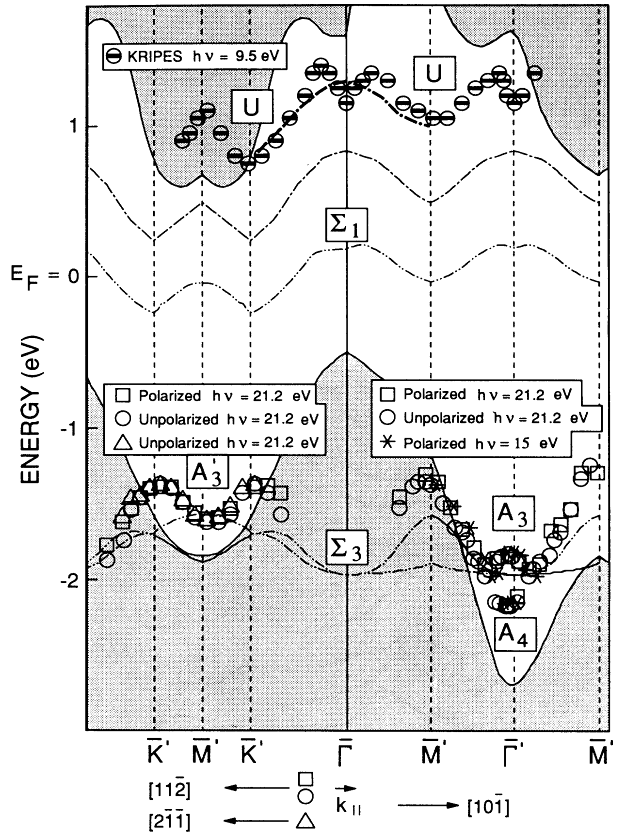

FIG. 4. Plot of the surface-state dispersion for the directions $\bar{\Gamma}$-$\bar{M}'$ and the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$. Included in the figure are calculated surface-state dispersions for the reconstructions Si(111)$\sqrt{3}\times\sqrt{}$:BR30° (Ref. 11) (------) and Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° (Ref. 15) (··–··–··–). The dispersion labeled –·–·– is measured by Kaxiras *et al.* (Ref. 11). The shaded areas represent the projected bulk ($E_F-E_{\rm VBM}=0.5$ eV) (Ref. 14).

while similar energy positions are found for the $\bar{M}'$ and $\bar{K}'$ points. In Ref. 11 the reported dispersion has a maximum at the $\bar{\Gamma}$ point whereas our measurements show a local minimum. These discrepancies could be an effect of different experimental setups but also of different sample preparation. In the measurement by Kaxiras *et al.*[11] the sample was a bulk doped Si wafer whereas in the present study a sample prepared by implantation of B into the surface region is used. The STM investigation by Bedrossian *et al.* on the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface[10] has shown that a sputter implantation of B into the surface region gives a surface which has a lower number of defects than if it is prepared from a bulk doped crystal.

Angle-resolved photoemission

In Fig. 5 spectra recorded along the $\bar{\Gamma}$-$\bar{M}'$ ([10$\bar{1}$]) and the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ ([2$\bar{1}\bar{1}$]) directions with synchrotron radiation are shown ($h\nu$=21.2 eV). The directions $\bar{\Gamma}$-$\bar{M}'$ ([10$\bar{1}$]) and $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$, along the two bulk inequivalent directions [11$\bar{2}$] and [2$\bar{1}\bar{1}$], were also studied using unpolarized He resonance light ($h\nu$=21.2 eV) and the direction $\bar{\Gamma}$-$\bar{M}'$ ([10$\bar{1}$]) was studied with synchrotron radiation ($h\nu$=15 eV). Several surface related structures labeled A_1, A_3, A'_3, and A_4 are present in the spectra as well as several bulk related peaks. The binding energies of the A_3, A'_3, and A_4 peaks are plotted in Fig. 4 as a function of $k_{\parallel}$ for the directions $\bar{\Gamma}$-$\bar{M}'$ and $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$. The measured data in Fig. 4 are compared to calculated surface-state dispersions for the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface with Si in the T_4 geometry.

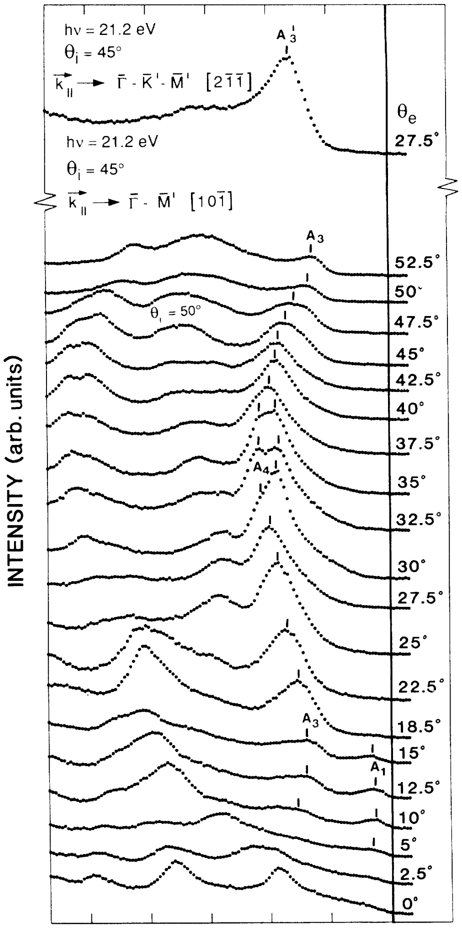

FIG. 5. Photoemission spectra for various angles of emission θ_e, at photon energy $h\nu$=21.2 eV, along the [10$\bar{1}$] and the [2$\bar{1}\bar{1}$] directions. Tick marks denote the identified surface-state peaks A_1, A_3, A'_3, and A_4.

The intensity of the A_3 state is weak within the first $\sqrt{3}\times\sqrt{3}$ SBZ ($\theta_e \leq 15°$) in the probed symmetry directions but increases for the second SBZ. In the $\bar{\Gamma}$-$\bar{M}'$ direction the intensity has a maximum at θ_e=32.5° corresponding to the $\bar{\Gamma}'$ point and in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction a maximum in intensity is observed at θ_e=27.5° corresponding to the $\bar{M}'$ point. Spectra from measurements with polarized and unpolarized light show the same intensity behavior for the A_3 and A'_3 peaks. In the data for the unpolarized case, the peak A_4 is weaker in intensity relative to the A_3 peak, than in the polarized case. The dispersion of two states was the same in both experiments. The very weak structure A_1 is visible close to the Fermi level at emission angles ≤15°, i.e., only within the first SBZ, shows no dispersion, and resembles the S_1 peak observed on the Si(111)7×7 reconstruction.[17] The intensities of this peak were found to be dependent on the annealing time and in the experiment with unpolarized light it was found that after $\frac{1}{2}$ hour of annealing the intensity of the peak was nearly zero. The intensity of the A_3, A'_3, and A_4 peaks was on the contrary found to be independent of annealing time. In STM measurement[9,10] on the Si(111):B surface a state near the Fermi energy in both the occupied and unoccupied region was found over "bright" atoms. The bright atoms are identified as Si adatoms in the T_4 geometry (see Fig. 1). On the other hand, STM spectroscopy over dark atoms, identified as Si atoms with a B atom in the B_5 position, showed no density of states in the vicinity of the Fermi level. The A_1 feature, which shows no dispersion and is found to be dependent on annealing time, is therefore interpreted as a defect state of the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface arising from areas with Si adatoms in the T_4 geometry.

By being positioned in the band gap of the projected bulk the bands A_3, A'_3, and A_4 are surface states. The dispersions along the $\bar{\Gamma}$-$\bar{M}'$ direction in Fig. 4 have different energy values at the $\bar{M}'$ point $E(\bar{M}')$= −1.3 eV ($k_{\parallel}$=0.55 and 1.16 Å^{-1}) than in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction $E(\bar{M}')$= −1.6 eV ($k_{\parallel}$=0.94 Å^{-1}). The full width at half maximum of the peaks is 0.4 and 0.7 eV, respectively. The onset of the A_3 and A'_3 peaks relative to the Fermi level is the same in the spectra, −1.1 eV for the three $\bar{M}'$ points. This indicates that A_3 and A'_3 contain two occupied bands with different intensity to $k_{\parallel}$ relation. In Fig. 6, spectra recorded with unpolarized light at the $\bar{\Gamma}'$ (θ_e=27.5°) point in the $\bar{\Gamma}$-$\bar{M}'$ direction of a clean surface, and one exposed to 250 L H_2 (1 L= 10^{-6} Torr s) in the presence of a hot filament, are shown. The exposure led to a band bending of 0.3 eV towards lower binding energies measured with reference to the observed bulk

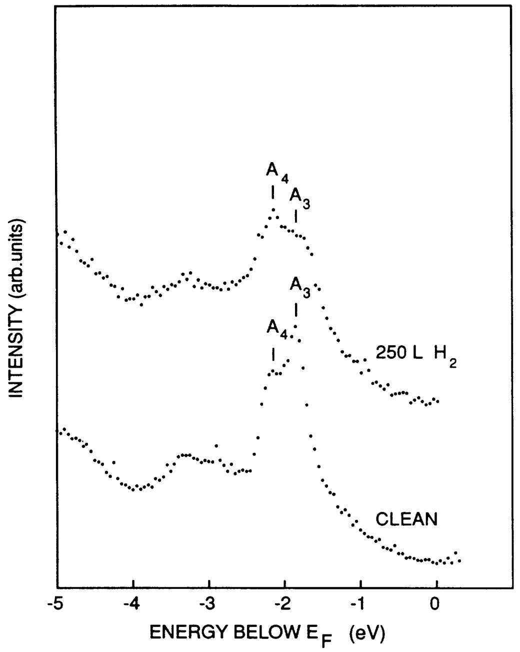

FIG. 6. ARUPS spectra of a clean and a H contaminated $\sqrt{3}$:B surface in the $\overline{\Gamma}$-$\overline{M}'$ direction at $\theta_e = 27.5°$, corresponding to the $\overline{M}'$ point.

features. In the figure the energy scale is referenced to the bulk features of the clean surface.

It has been shown that a saturation exposure of hydrogen on the Si(111)7×7 surface leads to a formation of silicon monohydride and the erasure of the three surface states at 0.2, 0.8, and 1.7 eV.[18] A comparison between the spectra obtained, at an emission angle off 30° in the Γ-$\overline{M}'$ direction, from the clean Si(111)7×7 (Refs. 7 and 17) surface and the Si(111) monohydride surface,[18] displays in the monohydride case no observable bulk band structure, in the energy region down to 5 eV below the Fermi level. In the present study the exposure of 250 L of H_2 to the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface had no effect on the bulk related structure and only a minor effect on the A_4 state whereas the intensity of the A_3 structure was partially attenuated. Based on the distinction of the bulk feature of the hydrogen exposed Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface, in comparison to the washed out bulk feature of the Si(111)7×7 monohydride surface and that the A_3 surface state was only partially attenuated after the 250 L H_2 exposure it can be assumed that the coverage on the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface was in the submonolayer region. The decrease in intensity of the A_3 peak reflects that this structure is connected to the bounding of the adatom to the first-layer atoms in a manner similar to that observed for the Si(111)$\sqrt{3}\times\sqrt{3}$:AlR30°, Ga, and In surfaces. The A_4 peak, which is situated in the band gap, is not affected by the hydrogen exposure, and could correspond to the specific binding configuration below the surface caused by the position of the B atom in the B-S_5 geometry.

DISCUSSION

From first-principles pseudopotential total energy and electronic-structure calculations of the surfaces Si(111)$\sqrt{3}\times\sqrt{3}$:AlR30°, Ga, In, and Si,[2,3,6,16] where the adatoms are positioned in the T_4 position, one surface state is identified in the unoccupied region and two in the occupied region. The surface states in the unoccupied and occupied regions are related to the empty dangling-bond and backbond states of the adatom. In general, the shapes of the calculated surface-state bands of the four surfaces resemble each other but they differ in bandwidth and absolute energy position. The calculated surface state of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° in Fig. 4 can therefore exemplify the surface-state band structures of the other three surfaces, with the exception that the Σ_1 band, which is half filled on the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface, is empty on the Si(111)$\sqrt{3}\times\sqrt{3}$:group-III surfaces. For the systems Si(111)$\sqrt{3}\times\sqrt{3}$:AlR30°, Ga, and In, one surface state in the conduction band and two surface states in the valence band have been experimentally identified in close agreement with calculations.[3,5,6] The dispersion of the unoccupied surface state observed with KRIPES on the Si(111)$\sqrt{3}\times\sqrt{3}$:AlR30°, Ga, and In show a maximum in energy position at the $\overline{\Gamma}$ point which is slightly different from the Σ_1 band.

It has not yet been possible to produce a Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface but information about the band structure on this surface can be gained from studies of the adatoms of the Si(111)7×7 surface. On the Si(111)7×7 surfaces three surface states S_1, S_2, and S_3 are identified below the Fermi level and one surface state U_1 is found in the unoccupied region.[17,15] The S_3 and the U_1 states showed dispersions similar to the calculated Σ_3 and Σ_1 bands of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface. It is suggested that the Σ_1 state is empty and corresponds to the U_1 state and that the S_3 band corresponds to the backbond state Σ_3.

Total energy calculations of different adatom geometries of the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface[9,10] show that a configuration with the B atom in the S-B_5 position is energetically the most favorable. In the B-S_5 configuration the Si atom in the adatom position forms three bonds to its nearest Si neighbors in the first layer and donates one electron to the B atom directly below it. As a result, the dangling bond of the adatom becomes unoccupied.

A comparison between the calculated dispersion of the empty dangling-bond state of the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface[11] and the U state, in Fig. 4, reveals similar bandwidths (0.6 and 0.65 eV, respectively), but different shapes around the $\overline{\Gamma}$ and $\overline{\Gamma}'$ points. Around those two points the calculated dispersion shows a maximum in energy position whereas the U state shows a minimum. The U state and the Σ_1 band show different bandwidths (0.44 and 0.65 eV, respectively).

The origin of the local minima in the dispersion of U observed at the $\overline{\Gamma}$ and $\overline{\Gamma}'$ points, but not observed for the other Si(111)$\sqrt{3}\times\sqrt{3}$ systems, is not fully understood. In the S-B_5 model the adatom donates one electron to the second-layer B atom and it can be argued that the minima observed in the dispersion of the U band at the $\bar{\Gamma}$ and $\bar{\Gamma}'$ points are effects of surface relaxation, correlated to the charge transfer.

The calculated dispersion of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface,[16] in the occupied region, is proposed to have an intensity maximum at the border of the 1×1 SBZ that is at the $\bar{M}'$ point in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction and at the $\bar{\Gamma}'$ point in the $\bar{\Gamma}$-$\bar{M}'$ direction. Strong intensity of the Σ_3 is indicated with a solid line in Fig. 4. The experimentally observed dispersions of the Si(111)$\sqrt{3}\times\sqrt{3}$-Al, Ga, and In systems follows, in general, the shape and intensity behavior of the calculated dispersions. The dispersion of the surface state A_3' of the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface (Fig. 4) in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ direction resembles quite well the Σ_3 band of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface. The different energy values for the $\bar{M}'$ points in the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ and the $\bar{\Gamma}$-$\bar{M}'$ directions indicate, as mentioned above, that A_3 and A_3' contain two occupied bands with different intensity to $k_\parallel$ relation. The A_3 band in the $\bar{\Gamma}$-$\bar{M}'$ direction does not follow the intensity profile of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface, however. This can be an effect of the different periodicity in the two top layers of the S-B_5 model as compared to the T_4 model. In a surface where a B atom has occupied every Si-B_5 position the periodicity of both the adatom and the second layer is $\sqrt{3}\times\sqrt{3}$, whereas when the group-III atoms occupy the T_4 position only the adatoms have the $\sqrt{3}\times\sqrt{3}$ periodicity. The A_4 structure, which is only detected around the $\bar{\Gamma}'$ point, is clearly positioned in the band gap of the projected bulk and must therefore originate from the surface. The existence of a state similar to the A_4 has not been reported for any of the surfaces Si(111)$\sqrt{3}\times\sqrt{3}$:AlR30°, Ga, In, or the Si(111)7×7.

After exposing the surface to 250 L H_2 in the presence of a hot filament the peak A_3 decreases in intensity whereas the peak A_4 is unaffected. The structure A_3 which shows a dispersion similar to the Σ_3 band of the Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° surface is suggested to originate from the backbond of the Si atom in the T_4 position, i.e., a Si adatom in the position directly above a second-layer atom.

For the Si(111)$\sqrt{3}\times\sqrt{3}$:group-III systems studied so far, the Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° is the only one where the metal atom is likely to be positioned below the top layer. The Si(111)$\sqrt{3}\times\sqrt{3}$:BR30° surface is the only surface for which the filled surface states are found to be separated at the $\bar{\Gamma}'$ point. It is therefore suggested that the A_4 state, observed only at the $\bar{\Gamma}'$ point, in this case originates from the bonds between the B atom in the S-B_5 position and the surrounding Si atoms. The position of these bonds, below the surface, could explain the behavior of the A_4 structure during the hydrogen exposure.

SUMMARY

In summary, with **k**-resolved inverse photoemission one dispersing surface state is observed at 1.15 eV above the Fermi level at the $\bar{\Gamma}$ point with a total bandwidth of 0.65 eV. In the occupied region, two overlapping surface states A_3 and A_3' corresponding to the backbond between the adatom and the first-layer Si atoms, are observed. One surface state A_4 found only in the vicinity of the $\bar{\Gamma}'$ point is associated with the bonding between the B atom in the S-B_5 position and the surrounding Si atoms.

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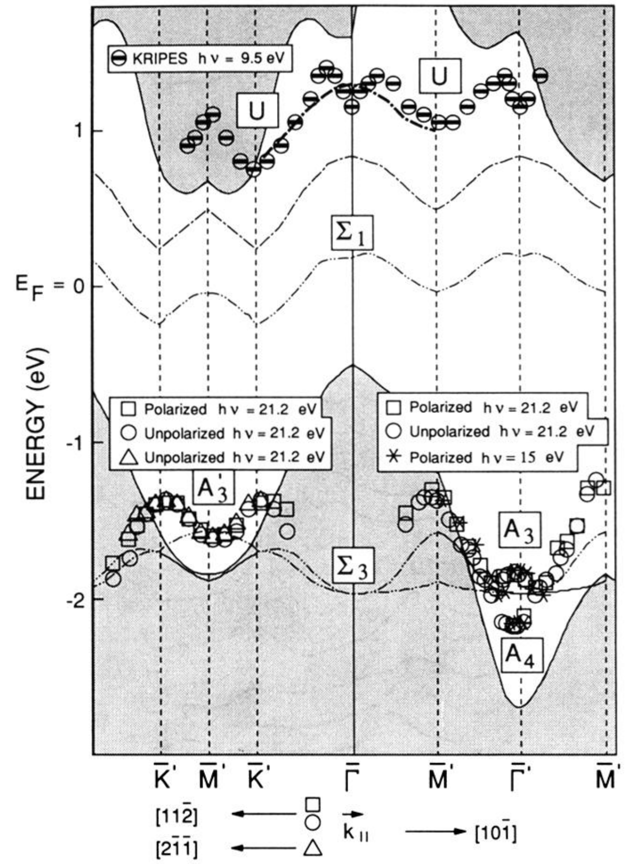

FIG. 4. Plot of the surface-state dispersion for the directions $\bar{\Gamma}$-$\bar{M}'$ and the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$. Included in the figure are calculated surface-state dispersions for the reconstructions Si(111)$\sqrt{3}\times\sqrt{}$:BR30° (Ref. 11) (------) and Si(111)$\sqrt{3}\times\sqrt{3}$:SiR30° (Ref. 15) (··–··–··–). The dispersion labeled –·–·–· is measured by Kaxiras *et al.* (Ref. 11). The shaded areas represent the projected bulk ($E_F - E_{\mathrm{VBM}} = 0.5$ eV) (Ref. 14).