ANGLE-RESOLVED PHOTOEMISSION STUDIES OF THE
3C–SiC(001)(2 × 1) SURFACE

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We have investigated the electronic structure of the single-domain 3C–SiC(001)(2 × 1) using angle-resolved photoemission and synchrotron radiation. Two different surface-state bands are clearly identified within the bulk bandgap. The upper band has a binding energy of 1.4 eV at the center of the surface Brillouin zone (SBZ) and shows a weak dispersion of 0.3 eV in the Γ–J direction, but is non-dispersive in the perpendicular direction. It has a polarization dependence suggesting a \( p_z \) character, as expected for a Si dangling-bond state. The second band is located at 2.4 eV binding energy and is non-dispersive. The weak or nonexistent dispersions suggest very localized electronic states at the surface and show poor agreement with calculated dispersions for the proposed models for the 2 × 1 and c(4 × 2) reconstructions.

1. Introduction

SiC surfaces have in recent years attracted an increasing interest in surface-science and solid-state research. Of the many SiC polytypes and surfaces, the cubic 3C–SiC(001) surface is one of the most interesting. Several surface reconstructions have been observed on this surface, depending on stoichiometry and surface preparation: carbon-terminated c(2 × 2), Si-terminated 2 × 1 and c(4 × 2), and Si-rich 3 × 2 surfaces. However, the detailed structures of these surface reconstructions are still under debate. Very few experimental reports are available on the surface electronic structure of the 2 × 1 surface, although the expected similarity of this reconstruction to the c(4 × 2) surface should give a promising insight into the reconstruction behavior of these surfaces.

Early low-energy electron diffraction (LEED) and Auger-electron spectroscopy (AES) studies of the 2 × 1 and c(4 × 2) reconstructions by Kaplan indicated that the surfaces were terminated with a full Si monolayer. It was suggested that the surface structures were similar to the corresponding reconstructions on the Si(001) and Ge(001) surfaces. It is well known that on those surfaces, the 2 × 1 and c(4 × 2) reconstructions consist of rows of asymmetric (buckled) Si or Ge dimers, respectively. Several subsequent studies supported or assumed this structure also for the 2 × 1 and c(4 × 2) reconstructions on SiC(001). Hara et al. confirmed the 1 ML Si termination of c(4 × 2) and 2 × 1 using medium-energy ion scattering (MEIS). Shek found a stable c(4 × 2) structure where the LEED pattern showed weak additional spots, denoted c(4 × 2)*. Additionally, the 2 × 1 surface was described as a defective c(4 × 2)* structure with incomplete Si coverage.

In contrast, recent \textit{ab initio} theoretical calculations have consistently found a very weak or no...
dimerization and buckling for a 1 ML Si coverage (below called the 1 ML $2 \times 1$ dimer model). In the calculated electronic structure, the topmost filled band displayed a significant dispersion of almost 1 eV in the $\Gamma - J'$ direction. On the other hand, recent angle-resolved photoemission (ARUPS) results from the $2 \times 1$ surface found dispersionless surface states, in clear disagreement with the calculated surface-state dispersions.

Recent theoretical studies\cite{12, 13} have tried to resolve these obvious discrepancies between experiment and theory. Lu et al.\cite{13} suggested a new model with an additional 0.5 ML Si on the top Si monolayer. This extra 0.5 ML of Si adatoms is arranged into a missing-row asymmetric-dimer (MRAD) $c(4 \times 2)$ reconstruction.

We present here a detailed high-resolution angle-resolved photoemission investigation of the 3C-SiC(001) $(2 \times 1)$ surface, employing synchrotron radiation. Comparing to theoretical results, our results are in disagreement with the calculated band structures for the 1 ML $2 \times 1$ dimer model.\cite{8, 9} Based on the expected similarity between the $2 \times 1$ and $c(4 \times 2)$ reconstructions, we have also compared our results to calculations for the latter. For the recently proposed MRAD model we find a somewhat better agreement, in particular in the $\Gamma - J$ direction.

2. Experiment

High-resolution photoemission measurements were performed on the spherical grating beamline (BL-33) at the MAX-Lab synchrotron radiation facility in Lund, Sweden.\cite{14} The beamline is equipped with an angle-resolved photoelectron spectrometer (ARUPS-10, VG Microtech). At the photon energies used in this experiment (14–40 eV) the total energy resolution was chosen to be 150 meV and the analyzer acceptance angle was set to $\pm 2^\circ$. The base pressure in the analysis chamber system was $7.0 \times 10^{-11}$ mbar. For all spectra we used the measured Fermi-level position of a tantalum foil as the energy reference, $E_F = 0$.

The samples were 3C-SiC(001) films $\sim 3$ $\mu$m thick grown by chemical-vapor deposition on a mis-oriented Si(001) substrate and unintentionally n-doped by nitrogen impurities in the CVD process.\cite{16} Before insertion into UHV, the samples were rinsed with hydrofluoric acid. Then, in vacuo, the samples were outgassed at about 600°C and cleaned by resistive heating at 900°C. We determined the surface structure with LEED. A single domain $3 \times 2$ diffraction pattern was visible after these preparation steps. This Si-rich surface was then transformed into the single domain $(2 \times 1)$ reconstruction by annealing at 1050°C. For further cleaning, the samples were heated to 1050°C in a Si flux.

If not specified differently the ARUPS spectra shown below are taken in the following geometry (called $A_\pm$). In this geometry the incidence angle of the light ($\theta_i$) is 45° and photoelectrons are collected in the plane defined by the surface normal and the direction of the incident light. The vector $A$ of the incoming linearly polarized synchrotron radiation lies parallel to the plane of emission. For the identification of the symmetries of the surface state wave functions the $A_\pm$ geometry was additionally used. In this case the incidence angle is $\theta_i = 15^\circ$ and the emission plane is kept perpendicular to the plane mentioned above. Thus the $A$ vector has a dominant component perpendicular to the emission plane in the $A_\pm$ geometry.

3. Results and Discussion

Figure 1 shows a collection of ARUPS spectra from the single domain 3C-SiC(001) $(2 \times 1)$ surface, recorded with $h\nu = 21.2$ eV for different emission angles along the $[110]$ direction, i.e. the $\Gamma - J'$ direction in the SBZ of the 3C-SiC(001) $(2 \times 1)$. At an energy of $-1.4$ eV a peak denoted $S_1$ is observed. It shows practically no noticeable dispersion as a function of the emission angle. At about $-2.4$ eV another dispersionless feature, named $S_2$, is seen as a weak shoulder for emission angles between 15° and 54°. For other angles the appearance of $S_2$ is strongly suppressed by other features dispersing upwards from lower energies. In order to investigate the surface or bulk origin of the spectral features, normal emission ARUPS spectra were also recorded for various photon energies (not shown here). Thereby $S_1$ was identified as a surface state due to its constant energy position for different photon energies. $S_1$ lies, as expected for a surface state, completely in the bulk bandgap, since the position of the valence band maximum (VBM) at $\Gamma$ was found to be at 1.7 eV below the Fermi level position. To investigate the nature of the state $S_2$ we also recorded a series of
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Fig. 1. ARUPS spectra from the single-domain 3C-SiC(001)(2 x 1) surface taken with linearly polarized synchrotron radiation (h\nu = 21.2 eV) along the [110] direction, i.e. the \Gamma - J' direction in the SBZ of the 3C-SiC(001)(2 x 1). The peak positions of the surface states S_1 and the bulk features are indicated with tick marks.

spectra with a photon energy of 17 eV (not shown here). Since S_2 is found at the same binding energy for both photon energies, we attribute S_2 to a surface band. Our comparison to a recent ARUPS study of the 3 x 2 surface\textsuperscript{17} shows that all other features at lower binding energies in Fig. 1 can be attributed to bulk transitions.

Detailed ARUPS spectra taken with 21.2 eV photon energy in the plane of the 2 x 1 surface containing the [110] azimuth, which corresponds to the \Gamma - J direction in the SBZ, are presented in Fig. 2. The surface state S_1 mentioned above is observed at most emission angles showing maximum intensity at negative angles. In comparison to the \Gamma - J' direction, S_1 here shows a clearer dispersion. It disperses within a range of about 0.3 eV. The band S_2 is not detectable in this direction. As before, the bulk bands are dominant features in the spectra. At emission angles > 6° a characteristic bulk band B_1 moves steeply to higher binding energies with decreased intensity until it fades away at 24°. Another bulk band, denoted B_{u1}, appears for higher emission angles showing a very similar dispersion, but displaced by a k-vector of \sim 1 \text{ Å}^{-1}. This is about the same as the smallest reciprocal lattice vector of the surface in this direction (1.02 \text{ Å}^{-1}) and the B_{u1} band is therefore interpreted as surface Umklapp scattering of the B_1 band. In a recent ARUPS study of the 3 x 2 surface of 3C-SiC(001) a similar surface Umklapp scattering of the same bulk band was reported.\textsuperscript{17} In that case the scattering reciprocal lattice vector was 0.68 \text{ Å}^{-1}, corresponding to the \times 3 periodicity.

We have investigated the polarization dependence of the surface state S_1 in normal emission, as well as in off-normal emission in the two emission
planes containing the $\Gamma - J'$ and the $\Gamma - J$ azimuths using the two different measurement geometries $A_+$ and $A_{\pm}$, as explained above. Figure 3 shows ARUPS spectra taken for the $A_{\pm}$ (dots) and $A_+$ (lines) geometries along the $\Gamma - J'$ direction for a photon energy of $h\nu = 21.2$ eV. The two lowermost spectra were recorded in normal emission for $A_+$ and $A_{\pm}$, respectively. In that case (i.e. $\theta_e = 0^\circ$), the only difference between the spectra is the incidence angle, with $\theta_i = 45^\circ$ for $A_+$ and $\theta_i = 15^\circ$ for $A_{\pm}$. As can be seen, the intensity of the $S_1$ peak is dramatically decreased in the $A_{\pm}$ spectrum. This indicates a strong $p_z$ character of the $S_1$ state, which is expected for a Si dangling-bond state pointing out from the surface. This is well known from earlier ARUPS studies of, for example, the Si(001) and Si(111) surfaces.\(^{18}\)

The emission planes containing the $\Gamma - J'$ and the $\Gamma - J$ azimuths are mirror planes in the bulk crystal structure and possibly also in the surface structure. The comparison of off-normal spectra recorded in these planes with both geometries gives information about the symmetry properties of the electronic states. For states with their $k$-vectors in a mirror plane of the crystal, their symmetry can be either even or odd with respect to the mirror plane. With the $A_+$ geometry only electrons from even states would be emitted, whereas with the $A_{\pm}$ geometry emission from states with odd symmetry would dominate. In the off-normal spectra in Fig. 3, along the $\Gamma - J'$ and the $\Gamma - J$ directions, it can be seen that also here $S_1$ appears with much smaller intensities in the $A_{\pm}$ geometry than in the $A_+$ geometry. From these results, we expect that $S_1$ has even symmetry with respect to both emission planes, assuming that these planes are mirror planes in the surface structure. In the case of no mirror symmetry in the surface geometry, the polarization dependence of $S_1$ in any case suggests a $p_z$ character of the state, as discussed above. This is consistent with assigning $S_1$ to a dangling-bond type state.

Our detailed ARUPS measurements of a single domain $2 \times 1$ surface have led to the identification of two surface state bands, $S_1$ and $S_2$, within the bulk bandgap at 1.4–1.7 eV and 2.4 eV below the Fermi level, respectively. Photoemission from surface states on the $2 \times 1$ surface has been observed before in angle-integrated soft X-ray photoemission experiments\(^6,19\) and recently in ARUPS experiments.\(^{11}\) In the latter work by Hüsken et al.\(^{11}\) two surface states were found, denoted A and B, which are located at 0.85 eV and 1.5–2 eV below the Fermi level. These features look similar to our $S_1$ and $S_2$ states, although the binding energies are about 0.6 eV lower. Comparing the dispersions of the surface states, their surface state A showed no dispersion, in contrast to our $S_1$ band in the $\Gamma - J$ direction. On the other hand a weak dispersion was reported for the B state, corresponding to our nondispersive $S_2$ state. However, there is a significant energy spread in their plotted dispersions.

Finally, we note that our ARUPS results and the above related earlier photoemission results all find a semiconducting surface electronic structure for the
3C–SiC(001)(2 × 1) surface. In a recent STM and photoemission study\textsuperscript{20} of the 3C–SiC(001)\textit{c}(4 × 2) surface, a phase transition from \textit{c}(4 × 2) to 2 × 1 upon annealing was observed, accompanied by a change to a metallic character in the electronic structure. This can most likely be explained by a thermal disorder and an increased thermal broadening of the spectral features, leading to a finite density of states at the Fermi level. Therefore, those results\textsuperscript{20} are not necessarily in conflict with our results. In contrast, recent high-resolution electron-energy loss (HREELS) and angle-integrated photoemission experiments\textsuperscript{21} report a metallic 2 × 1 surface also at room temperature, clearly contrary to our results.

Figure 4 shows a comparison of our measured dispersions of the surface states $S_1$ and $S_2$, to the calculated electronic band structure of Sabisch \textit{et al.} for the 1 ML 2 × 1 model\textsuperscript{9} and the one of Lu \textit{et al.}\textsuperscript{13} for the \textit{c}(4 × 2) MRAD model. For the experimental points, wave vectors from outside the first SBZ have been backfolded. A semiconducting surface was found for the 1 ML 2 × 1 model, and within the bulk bandgap two occupied surface bands, $\pi$ and $\pi^*$, originating from bonding and antibonding combinations of the dangling bonds, are predicted. However, along the high-symmetry lines $\Gamma - J$ and $\Gamma - J'$ in the SBZ, only the topmost $\pi^*$ band is observable in the calculated band structure, as plotted in Fig. 4. As can be seen, the agreement between the experimental $S_1$ dispersion and the theoretical $\pi^*$ band is quite poor.

A theoretical band corresponding to the $S_2$ band was not found along these lines in the SBZ, but we note that the bonding $\pi$ band appears at a similar energy to the $S_2$ band along the lines $J - K - J'$.

As seen in Fig. 4, the dispersion of $S_1$ shows noticeably better agreement with the theoretical result of the MRAD model than with the 1 ML 2 × 1 dimer model. Along the $\Gamma - J$ line both the dispersion and the energy position of the $S_1$ band are well reproduced by the theoretical $D_{\text{up}}$ band. Along the $\Gamma - J'$ direction the difference between experimental and theoretical data is still significant, although smaller than for the 1 ML 2 × 1 dimer model. Assuming that the 2 × 1 surface can be described as...
a disordered c(4 × 2) structure, as in the previous reports,7,22 one may speculate that the dispersion of S1 is reduced because of defects disturbing the order of the surface. ARUPS measurements on the 3C–SiC(001)c(4 × 2) surface is needed to clarify this point.

We did not find any evidence of the predicted second surface band of the MRAD model. Finally, we note that although the MRAD model is in better agreement with our ARUPS data than the 1 ML 2 × 1 dimer model, there are still significant arguments against it; for example, quantitative measurements with MEIS3 found only one monolayer of Si on the c(4 × 2) surface, not 1.5 ML as in the MRAD model.

A second recent model for the c(4 × 2) surface is the AUDD model by Soukiassian et al.,22 based on STM experiments. This model consists of dimer rows as in the 2 × 1 dimer model, but neighboring dimers are displaced vertically up and down, respectively, leading to a c(4 × 2) periodicity. In the calculations by Lu et al.13 it was found that the energy of the AUDD model was higher but very close to the energy of the 1 ML 2 × 1 dimer model. Lu et al. also calculated the electronic structure (although not published) for the AUDD model and found that it was essentially identical to the 1 ML 2 × 1 dimer model.13,23 Thus the electronic structure of the AUDD model from these calculations is also in disagreement with our results.

4. Conclusions

In summary, the electronic structure of the single-domain 3C–SiC(001)(2 × 1) surface has been studied using polarization-dependent angle-resolved photoemission, employing synchrotron radiation. Two occupied surface-state bands were found at binding energies of 1.4 eV and 2.4 eV, lying completely and partially, respectively, in the bulk bandgap. The upper band is dispersionless in the \( \Gamma - J' \) direction, but displays a clear downward dispersion of 0.3 eV in the \( \Gamma - \bar{J} \) direction. The polarization dependence of the upper band indicates a strong \( p_z \) character, as expected for a Si dangling-bond-type state, and we consequently interpret this state as derived from dangling bonds of the top Si layer.

Our results are in poor agreement with the calculated surface band structures for a 1 ML 2 × 1 dimer model, which show a weak or no dimerization of the top Si monolayer and a large dispersion of the topmost filled surface band in \( \Gamma - J' \) direction. Considering the expected strong similarity between the \( 2 \times 1 \) reconstruction and the c(4 × 2) reconstruction, we have also compared our results to theoretical surface band structures for the c(4 × 2) reconstruction. We find an equally bad agreement for the AUDD model, but a somewhat better agreement for the MRAD model.

References


23. W. Lu, private communication. The calculated bandstructure of the AUDD model was essentially identical to the 1 ML 2 × 1 model.