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Surface states of the 3C-SiC(001)-$c(4\times2)$ surface studied using angle-resolved photoemission

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We provide a detailed experimental investigation of the electronic band structure of the 3C-SiC(001)-$c(4\times2)$ surface using angle-resolved photoemission and synchrotron radiation. A prominent surface state was identified at -1.5 eV and referred to the Fermi level, showing a downwards dispersion by about 0.2 eV. Two other surface states were found at the energies -0.95 eV and -2.5 eV. The electronic structure is semiconducting and very similar to the one for the 2×1 reconstruction, proving the close relationship between the $c(4\times2)$ and the 2×1 structures. Comparison to theoretical band structure calculations gives no satisfactory agreeement, leaving the question about the structure of the $c(4\times2)$ and the 2×1 reconstructions still open.

SiC surfaces have recently attracted a lot of interest due to both fundamental physics reasons and exciting technological applications. Of the many SiC polytypes and surfaces, the cubic 3C-SiC(001) surface is one of the most well studied. Reconstructions of 3×2, 2×1, $c(4\times2)$, $c(2\times2)$, and 1×1 have been reported depending on the actual growth and surface preparation conditions.[1] However, the detailed structures of these surfaces are still being discussed, especially the $c(4\times2)$ and 3×2 reconstructions. Until now, the $c(4\times2)$ reconstruction has been investigated by low-energy electron diffraction (LEED),[2–4] Auger electron spectroscopy (AES),[2] scanning tunneling microscopy (STM),[5,6] medium-energy ion scattering (MEIS),[7] core level spectroscopy,[3,4] and *ab initio* calculations.[8,9] There is conflicting evidence both from experiment and theory concerning the main features, as well as quantitative details of the reconstruction.

Recently, two models have been proposed for the 3C-SiC(001)-$c(4\times2)$ surface. Based on their STM results, Soukiassian *et al.*[5] suggested a model where the one monolayer (ML) Si-terminated surface is arranged into rows of symmetric dimers displaced alternately up and down, giving a $c(4\times2)$ periodicity (the AUDD model). In contrast, recent theoretical studies from Lu, Krüger, and Pollmann[8] favor another model with a 1.5 ML Si termination. The extra 0.5 ML of Si adatoms is arranged into asymmetric dimers in a $c(4\times2)$ periodicity (the missing-row asymmetric dimer model, MRAD). In addition, the question of the correspondence between the 2×1 and the $c(4\times2)$ reconstruction is still an ongoing discussion. Shek[4] and Soukiassian *et al.*[5] reported that the 2×1 surface observed at room temperature (RT) can be attributed to a defective $c(4\times2)$ surface. A closely related issue is the observed[6] reversible $c(4\times2)$–2×1 phase transition upon annealing a $c(4\times2)$-reconstructed surface, which was claimed to be accompanied by a semiconducting-metallic change of the surface electronic structure.

In the present paper, we report results of a detailed angle-resolved photoemission study of the 3C-SiC(001)-$c(4\times2)$ surface. Using synchrotron radiation, we have measured the occupied part of the surface band structure. Our results are compared to the available theoretical band structure calculations for the $c(4\times2)$ surface, without finding any satisfactory agreement. The measured surface electronic structure is very similar to the electronic structure of the recently investigated 2×1 surface,[10] strongly supporting the idea that the 2×1 surface reconstruction is a degraded $c(4\times2)$ surface.

The photoemission study was performed at beamline 33 at the MAX-lab synchrotron radiation facility in Lund, Sweden,[11] where a spherical grating monochromator produces usable light in the range 14–200 eV. The electrons were analyzed by a hemispherical analyzer (Vacuum Generators, ARUPS 10). At the photon energies used in this experiment (14–35 eV) the total energy resolution (analyzer and monochromator) was chosen to be <100 meV. The acceptance angle of the analyzer was set to $\pm2°$. Photoelectrons were collected in the plane defined by the surface normal and the direction of the incident light. For all spectra presented here the incidence angle of the light (Θ_i) was set to 45°. The emission angle of the detected electrons was varied by rotation of the analyzer. In this geometry the polarization vector of the incoming linearly polarized synchrotron radiation lies parallel to the plane of emission.

We used n-doped 3C-SiC(001) films (~3 μm thick) grown by chemical-vapor deposition on a misoriented Si(001) substrate.[12] The samples were chemically etched by hydrofluoric acid before they were inserted into the vacuum system. After extensive outgassing at 600 °C and cleaning by resistive heating for a few minutes at 1050 °C single domain 3×2 diffraction patterns were visible with LEED. The $c(4\times2)$ reconstruction was then achieved with high quality and reproducibility by the so-called atomic layer epitaxy technique (ALE).[13] First a 5×2 LEED pattern was obtained

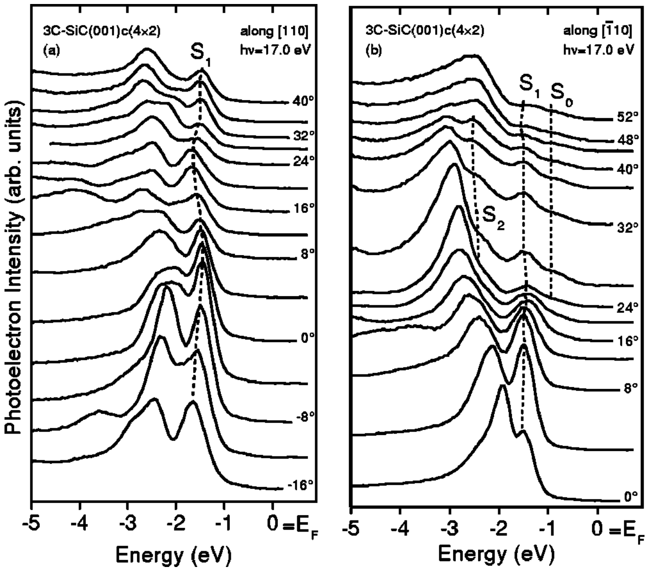

FIG. 1. (a) ARUPS spectra recorded from the single domain 3C-SiC(001)-$c(4\times2)$ surface with linearly polarized synchrotron radiation ($h\nu=17$ eV) along the [110] direction. (b) Same as (a) except that the azimuth is the [$\bar{1}10$] direction.

by either annealing the 3×2 surface at 1050 °C, or from a $c(4\times2)$ or 2×1 reconstruction by heating the sample to 1100 °C in a Si flux for some minutes. In the next step, a $c(2\times2)$ surface was formed by exposing the samples to a C_2H_4 gas dose of 1000 Langmuirs during simultaneous heating of the surface at 1050 °C. After that, a further Si evaporation step during annealing at 1050 °C led to a $c(4\times2)$ surface reconstruction. Leaving the surface in UHV for several hours resulted in the gradual disappearance of the $c(4\times2)$ spots in the LEED pattern, so that only the 2×1 spots were left. For this reason we carefully checked the surface with LEED directly before and after taking spectra. Spectra were only taken from samples that showed sharp single domain $c(4\times2)$ diffraction patterns.

Figure 1(a) shows spectra recorded with a photon energy of 17 eV along the [110] direction, which correspond to the $\bar{\Gamma}$–$\bar{X}$ direction of the surface Brillouin zone (SBZ). All spectra are referenced to the Fermi level position (E_F) which was determined from a clean Ta surface. The most dominant feature is the state labeled S_1. It shows a small but noticeable dispersion, its energy position changes from -1.45 eV at normal emission ($\Theta_e=0°$) and at 40° to -1.65 eV at $-16°$ and at $+20°$. In order to investigate the surface or bulk origin of the spectral features, spectra were also recorded with different photon energies in normal emission mode (not shown). Thereby, S_1 was identified as a surface state due to its constant binding energy for all photon energies. From the analysis of the normal emission spectra, we also estimated the position of the valence-band maximum (VBM) to be at -1.95 eV. A logical consequence is that S_1 lies in the bulk band gap, as expected for a surface state. In addition, the S_1 peak is highly sensitive to contamination of the surface. The other features in Fig. 1(a) can be attributed to emission from bulk states in agreement with an earlier photoemission study of the 3C-SiC(001)3×2 surface.[14]

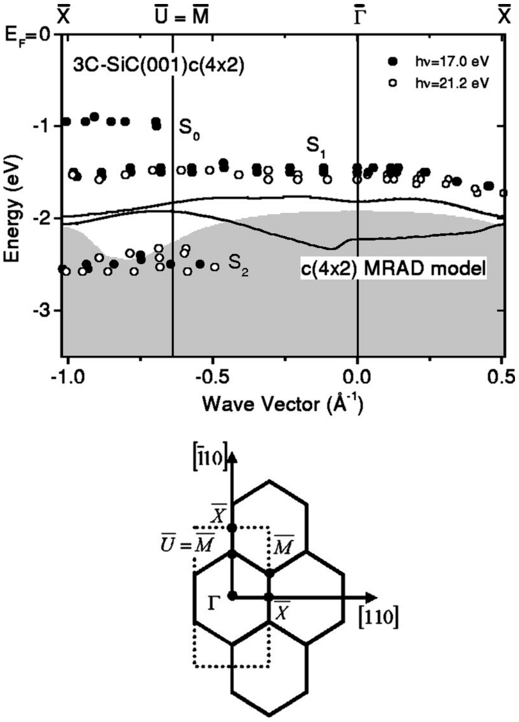

FIG. 2. The measured dispersions for the single domain 3C-SiC(001)-$c(4\times2)$ surface. Closed circles correspond to features in the 17 eV spectra shown in Fig. 1 and in Fig. 2. Open circles correspond to features taken from spectra obtained at $h\nu=21.2$ eV (not shown). The gray area is the bulk valence band (Ref. 8) projected onto the $c(4\times2)$ surface. The broken lines are the theoretical surface bands for the MRAD model by Lu *et al.* (Ref. 8). In addition, the surface Brillouin zone (SBZ) for the 3C-SiC(001)-$c(4\times2)$ surface (solid lines) and the 2×1 surface (dashed lines) is shown.

Figure 1(b) shows ARUPS spectra taken along the perpendicular [$\bar{1}10$] direction using a photon energy of 17 eV. Peak positions are marked with dotted lines. The surface state S_1 is observed also in this direction. It dominates at lower emission angles while it loses intensity at higher angles. It shows nearly no noticeable dispersion by varying the emission angle. Another strong dispersive spectral feature, lying in the energy range 2–3 eV below E_F, can be attributed to bulk emission. At emission angles between 20° and 40°, a weak but discernible feature S_2 develops at an energy of -2.55 eV showing no dispersion. At nearly the same emission angles, another weak shoulder S_0 appears at an energy of -0.95 eV below the Fermi level position. Although the small intensity of S_0 makes it difficult to determine its exact binding energy, it seems to have no dispersion as a function of emission angles. Due to its energy position in the bulk band gap, we assign S_0 to a surface state. For further investigations of the surface features, similar spectra were recorded along the [110] and [$\bar{1}10$] directions with a photon energy of 21.2 eV (not shown). Whereas we found the band S_2 as a weak shoulder at the same energy position, the state S_0 was not detectable for $h\nu=21.2$ eV.

Investigations of the polarization dependence of the surface-state emission showed that the S_1 emission intensity was highly dependent on the z component of the photon polarization vector (data not shown). This is an indication for a strong p_z character of the S_1 state, as expected for a Si dangling-bond state.

The experimentally observed dispersions of all three surface states of the single domain 3C-SiC(001)-$c(4\times2)$ surface are plotted in Fig. 2. Data points outside of the first SBZ have been backfolded into the first SBZ. Both surface states S_0 and S_1 are clearly located within the bulk band gap above the VBM as explained above. Emission from the bands S_0 and S_2 was only detectable in the $\overline{U}-\overline{X}$ region of the SBZ, whereas S_1 was observed in all parts of the SBZ that were probed. The surface state S_1 shows no dispersion in the $\overline{\Gamma}-\overline{U}-\overline{X}$ direction but a weak downwards dispersion for wave vectors along the $\overline{\Gamma}-\overline{X}$ line of about 0.2 eV. As can be seen, the S_2 band is mostly located within the bulk band, close to the valence band edge. There is a slight spread in the measured energies for this feature, which is caused by the weak signal from this state and the corresponding difficulty in determining the energy positions. S_2 shows maximum intensity for both photon energies when it is close to the bulk band edge, which is a further indication that S_2 can be assigned to a surface state or resonance.

So far only one theoretical surface band structure calculation of the $c(4\times2)$ surface is available, for the MRAD model, proposed by Lu, Krüger, and Pollmann.[8] In this model, half a monolayer of Si atoms are adsorbed on a Si-terminated surface and are arranged into buckled dimers in a staggered pattern, giving a $c(4\times2)$ periodicity. The 1.5 ML Si coverage is contrary to earlier quantitative measurements[7] of the surface composition that found a 1 ML Si coverage, but the idea of Si adatoms on top of the 1-ML Si-terminated surface is, on the other hand, supported by Si $2p$ core-level photoemission results.[3,4] As expected, Ref. 8 predicts a semiconducting surface for the MRAD model. For comparison to our data we have plotted the calculated dispersions of the two topmost filled dangling-bond bands of the MRAD model in Fig. 2. As can be seen, along the $\overline{\Gamma}-\overline{X}$ line the dispersion of the S_1 state is well reproduced by the topmost theoretical band (denoted D_{up} in Ref. 8). There is only a small energy shift of about 0.3 eV visible. Along the $\overline{\Gamma}-\overline{U}-\overline{X}$ direction, the difference between S_1 and the topmost theoretical band is more pronounced. The calculated band disperses slightly downwards towards the $\overline{X}$ point, whereas the experimental band S_1 shows a practically dispersionless course. The observed polarization dependence of S_1, indicating a p_z character, is consistent with the orbital character of the theoretical D_{up} band, which originates from the dangling bonds of the dimer up atoms in the MRAD model. Theoretical bands corresponding to the S_0 and S_2 bands are not found along the $\overline{\Gamma}-\overline{U}-\overline{X}$ line in Ref. 8. We also did not find any evidence of the predicted second surface band of the MRAD model. Thus, it is clear that although the S_1 band fits reasonably well to the theoretical D_{up} band, there are significant deviations between the calculated band dispersions of the theoretical MRAD model and our photoemission data for the 3C-SiC(001)-$c(4\times2)$ surface.

A second model for the $c(4\times2)$ surface is the recently proposed AUDD model by Soukiassian *et al.*[5] In this model, the surface is terminated with 1 ML Si. The Si atoms are arranged into dimers with neighboring dimers being displaced vertically alternately up and down. Recent theoretical calculations[9] give some support for this model, especially in conjunction with the expected similarity of the $c(4\times2)$ reconstruction to the 2×1 surface. Unfortunately, no calculated band structure of the AUDD model has been published. We note that Lu *et al.*[15] found in their calculations (although not published) that the electronic structure of the AUDD model is essentially identical to the 1-ML 2×1 dimer model[16] (and has considerably higher energy than the MRAD model). This is reasonable, since the AUDD model basically can be obtained through a small modification of the 1-ML 2×1 dimer model.[9] We therefore compared the theoretical band dispersions of the 1-ML 2×1 dimer model from Ref. 16 to our experimental data by mapping it into the $c(4\times2)$ SBZ (not shown). Thereby a worse agreement was found than for the MRAD model. This would suggest that the AUDD model is also inconsistent with our results, however, for a quantitative analysis a calculated band structure for the AUDD model is necessary.

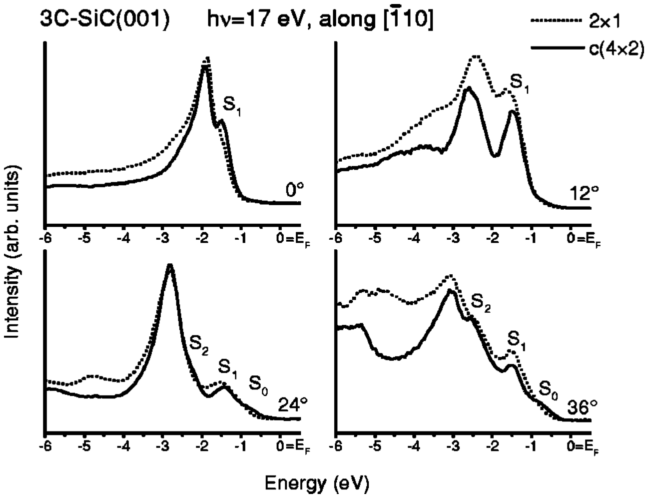

FIG. 3. Comparison of spectra obtained from a single domain 3C-SiC(001)-$c(4\times2)$ and a 2×1 surface along the $[\bar{1}10]$ azimuth. The spectra taken from the 2×1 surface are shifted by 0.15 eV in order to compensate for a different Fermi level position on the two surfaces. All spectra are normalized to the background intensity above E_{F}.

More details of the reconstruction mechanisms of the 3C-SiC(001) surface can be found directly by comparison of the electronic structures of the 2×1 and the $c(4\times2)$ surface. We have recently made extensive ARUPS measurements on the 2×1-reconstructed surface.[10] In Fig. 3, spectra taken from the 2×1 and the $c(4\times2)$ surface, respectively, are compared. The spectra recorded from the 2×1 surface were shifted by 0.15 eV in order to account for a slightly different Fermi level pinning position. As can be seen in the figure, the spectra from the two surfaces are very similar. In particular, the surface states S_1 and S_2 appear at the same energy positions on both surfaces. However, the emission from S_1 and S_2 is generally higher and the peaks appear sharper on the $c(4\times2)$ than on the 2×1 surface. This observation can be explained by defects on the 2×1 surface leading to a higher disorder on the surface. A comparison of the plotted band structure of Fig. 3 to the corresponding band structure from the 2×1 surface[10] confirms the close similarity of the two surfaces: the dispersions of the S_1 and S_2 states are practically identical.[17] These results confirm the assumptions of previous studies,[4,5] namely, that the 3C-SiC(001)2×1 reconstruction is essentially a defective or disordered $c(4\times2)$ structure. The main difference in the spectra from the two reconstructions is the existence of the surface state S_0 on the $c(4\times2)$ surface, and its absence on the 2×1 surface. This indicates that S_0 is a characteristic feature of the $c(4\times2)$ surface. The fact that it appears in the bandgap at the edge of the SBZ on the more well-ordered $c(4\times2)$ surface confirms this conclusion and excludes an interpretation of S_0 as a defect state.

The close relationship between the $c(4\times2)$ and the 2×1 structures is further emphasized by the recently observed[6] reversible $c(4\times2)$–2×1 phase transition upon annealing the $c(4\times2)$ surface. This phase transition was observed by LEED also in this work. However, whereas the 2×1 reconstruction at room temperature appears to be induced by adsorbates and defects, the high-temperature 2×1 structure seems to be a thermally disordered $c(4\times2)$ surface, similar to the $c(4\times2)$–2×1 phase transitions on the Si(001) and Ge(001) surfaces. The phase transition on 3C-SiC(001) was accompanied by an apparent semiconducting-metallic change of the surface electronic structure, as measured by scanning tunneling spectroscopy (STS).[6] In contrast, both the $c(4\times2)$ and the 2×1 surfaces at RT are clearly semiconducting, as measured here and in Ref. 10, with the highest occupied state lying about 1 eV below the Fermi level. Actually, from electron-counting arguments a metallic surface is not expected for any stable structural model of the clean 3C-SiC(001) surface. The observed weak tendency to metallicity in Ref. 6 at elevated temperatures can be more easily explained by thermal broadening of the electronic states, without invoking a true metallic state.

Finally, we note that the close relationship between the $c(4\times2)$ and the 2×1 structures described above is consistent with both the AUDD model and, to a lesser extent, with the MRAD model. Catellani *et al.*[9] reported that the AUDD model may be stabilized by a tensile stress in the surface structure. Relaxation of the stress, e.g., by defects or adsorbates, would then stabilize a weakly dimerized 2×1 surface. The $c(4\times2)$–2×1 phase transition at elevated temperatures is also easily explained by the AUDD model. The MRAD model can be reduced to a 2×1 periodicity by breaking the dimer bonds, which is energetically unfavorable.

In conclusion, we present an experimental investigation of the electronic band structure of the 3C-SiC(001)-$c(4\times2)$ surface reconstruction. The surface displays three occupied surface state bands and is semiconducting. Our results show a close relationship between the $c(4\times2)$ surface and the 2×1 surface reconstructions. Comparison of the experimental surface band structure to theoretical results shows that the question about the detailed structures of the $c(4\times2)$ and 2×1 reconstructions is still unsolved.

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[1] *Silicon Carbide: A Review of Fundamental Questions and Applications to Current Device Technology*, edited by W. J. Choyke, H. Matsunami, and G. Pensl (Akademie Verlag GmbH, Berlin, 1997).

[2] R. Kaplan, Surf. Sci. **215**, 111 (1989).

[3] M.L. Shek, Surf. Sci. **349**, 317 (1996).

[4] M.L. Shek, K.E. Miyano, Q.-Y. Dong, T.A. Callcott, and D.L. Ederer, J. Vac. Sci. Technol. A **12**, 1079 (1994).

[5] P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli, and C. Joachim, Phys. Rev. Lett. **78**, 907 (1997).

[6] V.Y. Aristov, L. Douillard, O. Fauchoux, and P. Soukiassian, Phys. Rev. Lett. **79**, 3700 (1997).

[7] S. Hara, W.F.J. Slijkerman, J.F. van der Veen, I. Ohdomari, S. Misawa, E. Sakuma, and S. Yoshida, Surf. Sci. **231**, L196 (1990).

[8] W. Lu, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **81**, 2292 (1998).

[9] A. Catellani, G. Galli, F. Gygi, and F. Pellacini, Phys. Rev. B **57**, 12 255 (1998).

[10] L. Duda, L.S.O. Johansson, B. Reihl, H.W. Yeom, S. Hara, and S. Yoshida, Surf. Sci. **439**, 199 (1999).

[11] B.N. Jensen, S.M. Butorin, T. Kaurila, R. Nyholm, and L.I. Johansson, Nucl. Instrum. Methods Phys. Res. A **394**, 243 (1997).

[12] S. Hara, S. Misawa, S. Yoshida, and Y. Aoyagi, Phys. Rev. B **50**, 4548 (1994).

[13] S. Hara, J. Kitamura, H. Okushi, K. Kajimura, and S. Yoshida (unpublished).

[14] H.W. Yeom, Y.-C. Chao, I. Matsuda, S. Hara, S. Yoshida, and R.I.G. Uhrberg, Phys. Rev. B **58**, 10 540 (1998).

[15] W. Lu, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **82**, 3722 (1999).

[16] M. Sabisch, P. Krüger, A. Mazur, M. Rohlfing, and J. Pollmann, Phys. Rev. B **53**, 13 121 (1996).

[17] In Ref. 10, the dispersion of the S_1 band was found to be 0.3 eV, i.e., 0.1 eV more than in the present work. This can be explained by the statistical spread in the energy position of S_1 in the previous work.