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Si-rich SiC(111)/(0001) 3×3 and $\sqrt{3}\times\sqrt{3}$ surfaces: A Mott-Hubbard picture

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The electronic structures of Si-rich reconstructions of SiC surfaces oriented parallel to the *c* axis are studied by means of first-principles calculations and angle-resolved photoemission spectroscopy (ARUPS). Independent of the reconstruction model, but in particular for the most favorable Si adtetramer-adlayer and T_4-site Si adatom models, the density-functional theory gives rise to half-filled pronounced dangling bond bands within the fundamental gap clearly indicating metallic surfaces. In contrast to theory, ARUPS observes only fully occupied surface-state bands but no density of states at the Fermi energy. The explanation of the discrepancies within a Mott-Hubbard picture allows a reliable description of the details of the surface band structure.
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Silicon carbide (SiC), as a semiconductor with wide energy gap, is an interesting material for microelectronic and optoelectronic applications. It crystallizes in various crystal structures, e.g., the zinc-blende polytype 3C and hexagonal polytypes *n*H with *n* Si-C bilayers in the unit cell. The [111] direction is the natural growth direction in the cubic case. It corresponds to [0001] for hexagonal crystals. Independent of the polytype the basic reconstructions of the corresponding Si-rich surfaces are $\sqrt{3}\times\sqrt{3}$ and 3×3.[1–3]

The structure of not too Si-rich 6H-SiC(0001) and 3C-SiC(111) surfaces with $\sqrt{3}\times\sqrt{3}$ translational symmetry is now generally identified by total-energy (TE) calculations[4–6] and scanning-tunneling microscopy[7] (STM) as a T_4-site Si adatom at the uppermost bulklike Si layer. For the corresponding reconstructions on the (111) and (0001) surfaces the low-energy electron diffraction (LEED) patterns[3] as well as the total energies and geometries[6] were found to be essentially identical, indicating that the surface reconstructions of the cubic and hexagonal polytypes are the same. There are only weak indications from other experiments[8] that a second metastable $\sqrt{3}\times\sqrt{3}$ surface structure may exist which can be explained by a vacancy model. The 3×3 reconstruction of the very Si-rich surfaces has been discussed within various models: a dimer-adatom-stacking-fault (DAS) arrangement[1,7,8] and as a modification of the DAS structure a single-adatom model.[9] Very recently TE calculations[10] and their combination with LEED, LEED holography, and STM experiment[11] found the 3×3 reconstruction to be related to a Si adatom cluster on top of a polymerized triple-dangling-bond Si adlayer independent of the 6H or 3C polytype.

The electronic structure of the 6H-SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface has been studied by angle-resolved photoemission spectroscopy,[12] **k**-vector-resolved inverse photoemission spectroscopy,[13] and spectroscopic STM.[7,14] No density of states is found at the Fermi level. However, this is in contrast to the band-structure calculations in the framework of the density-functional theory (DFT) and local-density approximation (LDA).[4,5] The question arises if this discrepancy is related to structural or many-body effects. From their ion-scattering studies and, respectively, core-level photoemission measurements Li *et al.*[8] and Johansson *et al.*[12] suggested Si adlayer structures different from the adatom model. On the other hand, such a discrepancy may be also traced back to effects of the strong electron correlation not included within the DFT-LDA.[4]

We have studied the energetical stability of a vast number of adsorption geometries of Si-rich SiC(111) surfaces with $\sqrt{3}\times\sqrt{3}$ and 3×3 translational symmetry and varying Si stoichiometry. The surface bands resulting for the most favorable structures within the DFT-LDA are compared with band structures mapped within ARUPS studies of 3C-SiC(111), 6H-SiC(0001), and 4H-SiC(0001) surfaces for both translational symmetries. The bands and their dispersion are compared and explained in terms of adatom interactions and strong electron correlation.

The calculations are performed within the framework of density-functional theory in the local-density approximation. Explicitly we use the Vienna *ab initio* simulation package described elsewhere.[15,16] Ultrasoft pseudopotentials are used for carbon, silicon, and hydrogen, which allow us to reduce the cutoff in the plane-wave expansion to 13.2 Ry. The surfaces are modeled by repeated slabs with 3×3 or $\sqrt{3}\times\sqrt{3}$ lateral unit cells. Each slab consists of six Si-C bilayers and a vacuum region of the same thickness. The dangling bonds at the lower C-terminated half of the slab are saturated by hydrogen in order to avoid spurious interactions or electron transfers. Additional Si adatoms are allowed to cover the Si-terminated slab side. We use 8 (4) **k** points to sample one half of the Brillouin zone (BZ) of the $\sqrt{3}\times\sqrt{3}$ (3×3) surface. Cubic stacking has been assumed along the (111) direction in each slab. We have shown[6,17] that the actual stacking is of minor influence on the surface geometry and energetics. However, discussing the electronic structure we have to take into account that the fundamental energy gap of 6H-SiC is about 1 eV larger than that of 3C-SiC. On the other hand, in any case we have to introduce a scissors op-

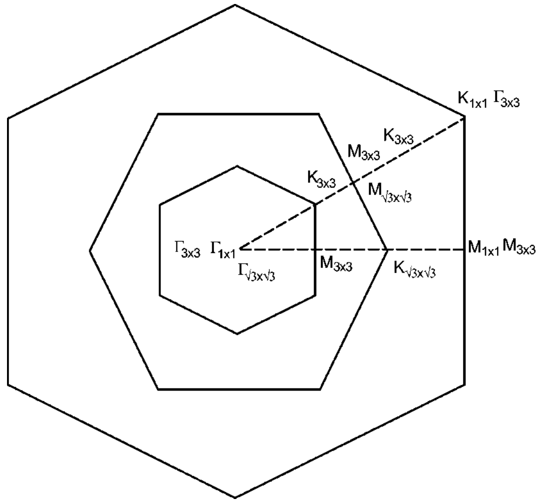

FIG. 1. Brillouin zones for 3×3, $\sqrt{3}\times\sqrt{3}$, and 1×1 reconstructions. The directions of measurements and few high-symmetry points are indicated.

erator to widen the energy gap due to the well-known gap underestimate within the DFT-LDA.

The samples we use are (111)-oriented cubic SiC films grown on a 6H-SiC(0001) substrate by means of solid-source molecular-beam epitaxy.[2] In few cases we have also directly investigated Si-terminated 6H-SiC(0001) and 4H-SiC(0001) substrates. Natural oxide is removed in the preparation chamber by heating the sample in a Si flux at 900 °C. Depending on the heating time and the silicon supply, the $\sqrt{3}\times\sqrt{3}$, 1×1, and 3×3 reconstructions of the Si-rich faces could be observed and changed reversibly. Stoichiometry and symmetry of the surfaces are controlled using LEED, STM, and Auger as well as x-ray photoemission spectroscopy. The dispersion of the occupied energy bands near the top of the valence bands is studied by rotating the sample around an axis perpendicular to the direction of the analyzer (SPECS EA200). The incident direction of the radiation source is kept fixed to the analyzer direction. The ARUPS measurements are performed along a direction in **k** space which includes the ΓK, KM, and ΓM directions via implicit BZ folding (cf. Fig. 1). UV-light excitation with three different photon energies 16.9 eV (NeI), 21.2 eV (HeI), and 40.8 eV (HeII) is used. The acceptance angle of the analyzer is $\pm 2°$.

The ground state of the surfaces is evaluated by means of total-energy optimizations. All atomic coordinates in the upper slab half are relaxed until the Hellmann-Feynman forces vanish. Four different models suggested by various authors[8–11] have been used as initial configuration of the total-energy optimization in the 3×3 case. This number has been vastly increased for the $\sqrt{3}\times\sqrt{3}$ translational symmetry.[6,17] Under very Si-rich preparation conditions it is found that the 3×3 translational symmetry is represented by a Si tetramer on a twisted Si adlayer with cloverlike rings on top of the Si-terminated face.[10,11] Under less Si-rich preparation conditions a $\sqrt{3}\times\sqrt{3}$ structure is favored. There is consensus that this structure is formed by a T_4 adatom on top of the uppermost bulklike Si layer.[4–6] The DFT-LDA band structures resulting for the two reconstructions are plotted in Fig. 2. In both cases of reconstructions a well-pronounced dangling-bond-related band is observed in the upper part of the projected fundamental gap of 3C-SiC. According to the electron-counting rule this band pins the Fermi level. It is half filled since there is only one dangling bond per surface unit cell. The bands are mostly related to Si *s*-like orbitals localized at the adatoms. Therefore, they exhibit an extremely small dispersion in agreement with the adatom distances $D=9.19$ or 5.31 Å. The bandwidths amount to 0.13 and 0.40 eV. They approximately differ by a factor of 3 in agreement with the variation of the hopping constant according to $1/D^2$.[18] The band maximum is located at the K (Γ) point, whereas the band minimum occurs at the Γ (K) point in the case of the 3×3 ($\sqrt{3}\times\sqrt{3}$) phase. For the smaller reconstruction $\sqrt{3}\times\sqrt{3}$ these findings and the bandwidth are in agreement with other DFT-LDA calculations.[4,5] Only the absolute position of the dangling-bond band is slightly higher with respect to the valence-band maximum (VBM) due to the 6H substrate considered there.

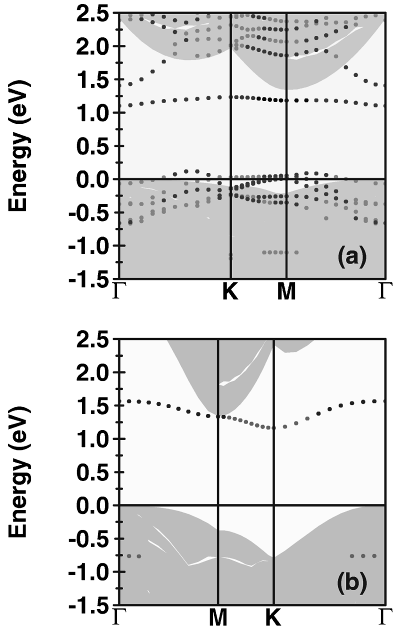

FIG. 2. Electronic structures of the 3×3 (a) and $\sqrt{3}\times\sqrt{3}$ (b) reconstructed 3C-SiC(111) surfaces within DFT-LDA. The projected bulk band structures are shown as shaded regions, whereas dotted lines represent bands of surface bound states. The strength of the dots indicates the degree of localization at the surface. The valence-band maximum is taken as energy zero.

The surface band dispersions near the VBM as derived from ARUPS are plotted in Fig. 3 along the same high-symmetry directions as in the case of the theoretical band structures. For both surface reconstructions occupied surface-state bands are observed in the fundamental gap above the VBM but below the surface Fermi-level position, which is identified to be pinned 1.95 eV (2.15 eV) above the VBM in the case of the 3×3 ($\sqrt{3}\times\sqrt{3}$) structure independent of the underlying polytype. That means that both surfaces are semiconducting in contrast to the results of the DFT-LDA calculations. In the $\sqrt{3}\times\sqrt{3}$ case this observation agrees with other band-mapping investigations.[12,13] On the other hand, the highest occupied surface bands behave in a similar way as the calculated dangling bond bands. The dispersion is weak. The bandwidths amount only to less than

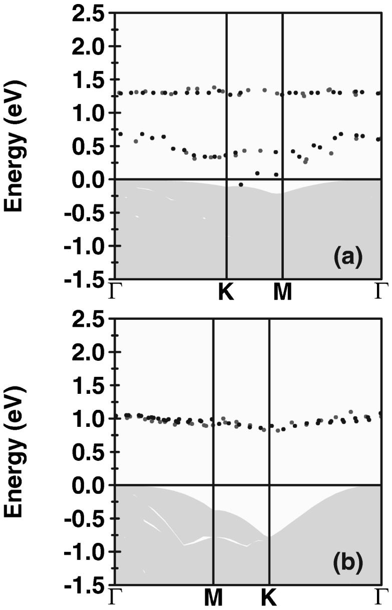

FIG. 3. Experimental surface state band dispersions of the 3 $\times 3$ (a) and $\sqrt{3}\times\sqrt{3}$ (b) structure. The black (gray) dots refer to photon energies of 16.9 eV (21.2 eV), i.e., NeI (HeI). As a guideline for the eyes we also show the theoretical projected bulk valence-band structure (shaded regions). The theoretical and the measured valence-band edge dispersions agree within experimental uncertainties.

0.1 eV (3×3) or 0.2–0.25 eV ($\sqrt{3}\times\sqrt{3}$). The band maxima and minima occur in the $\sqrt{3}\times\sqrt{3}$ case at the same positions as calculated. The uncertainties in the measurements do not allow such an identification in the 3×3 case.

Moreover, for the 3×3 structure measured a second and a third surface band occur slightly above the projected bulk valence bands. The lower one agrees with the theory which finds bands with pronounced surface character more or less degenerate with the topmost bulk valence bands [cf. Fig. 2(a)]. The surface character is especially enhanced for **k** vectors along KM, i.e., along the zone boundary. We trace the states forming the lower band back to bonding combinations of Si orbitals belonging to two atoms in the twisted adlayer or in the adcluster. The band observed experimentally slightly above the VBM cannot be explained in terms of the band structure calculated for 3×3 surface within the adcluster/adlayer model.[11] In the light of the STM studies of this face[19,20] one explanation could be related to surface defects. Among them there are apparently missing adatoms or/and adclusters and regions with additional silicon. Moreover, careful LEED studies[21] of the heat-induced transition between 3×3 and $\sqrt{3}\times\sqrt{3}$ indicate the coexistence of several translational symmetries, e.g., 3×3, 2×2, and $\sqrt{3}\times\sqrt{3}$. To illustrate the idea that other surface structures may be responsible for additional bands of surface bound states we show the band structure for the second energetically rather favorable model suggested by Kulakov *et al.*[9] on the base of a dimer-adatom-stacking-fault model known from Si(111) (Ref. 4) in Fig. 4. The corner holes appearing in this structure which can be viewed as defects (vacancies) in the first Si adlayers induce additional bands in the fundamental gap below and above the position of the half-filled dangling-bond band (about 1 eV above the VBM) associated with the top atom of the adatom cluster. However, the positions of the band maxima and minima do not agree with the experimental findings. Hence, with Fig. 4 we can only demonstrate that defects and defect-induced variations of the surface 3×3 reconstruction may introduce additional surface bands, but we cannot identify the true nature of the second strongly dispersive band occurring above the VBM. A crude scan through the band structures of few other possible defect structures (missing top atom, C antisites in the first Si adlayer) showed that many other structures may possess additional surface bands with considerable dispersion.

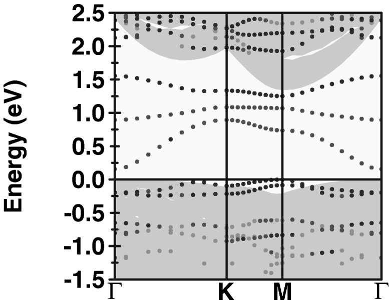

FIG. 4. Band structure of the SiC(111)3×3 surface for the single-adatom model of Kulakov *et al.* (Ref. 9). The same notations as in Fig. 2 are used.

The question arises whether the opposite electronic-structure results of DFT-LDA and ARUPS with respect to the band occupation and hence the metallic or nonmetallic surface character contradict the surface reconstruction models, a Si tetramer on a twisted Si adlayer (3×3) or a T_4-site Si adatom ($\sqrt{3}\times\sqrt{3}$), which have been verified by various experimental and total-energy studies. In the case of the 3×3 and $\sqrt{3}\times\sqrt{3}$ surface translational symmetries of group-IV materials one always cuts an odd number of bonds within one unit cell. Because of the four valence electrons per atom all bonding states should be completely filled with electrons, whereas more or less noninteracting dangling bonds should be occupied with one electron. As a consequence the DFT-LDA band structures (cf. Fig. 2) reflect the metallic behavior of the surface. The contrast to the experimental findings suggests effects of strong electron correlation beyond the scope of the one-electron theory, at least that within DFT-LDA. Spin effects which could be treated within the local spin-density approximation may be excluded. A magnetic exchange splitting of about 2 eV, which has been observed as the gap between filled and empty dangling-bond bands in the $\sqrt{3}\times\sqrt{3}$ case,[13] would be too large. On the other hand, the extremely small bandwidths of the measured surface bands indicate strong correlation effects on the electronic structure in the sense of the Hubbard model.[22] Recently, Northrup and Neugebauer demonstrated for the case of a $\sqrt{3}\times\sqrt{3}$ surface that a Mott-Hubbard insulating ground state may be a realistic scenario.[23] In light of their findings it is a realistic assumption that also the 3×3 surface can be expected to undergo a Mott-Hubbard metal-insulator transition.

In order to include strong correlation effects on electrons in dangling-bond states localized at the top Si atoms of the adclusters (3×3) or T_4-site Si adatoms ($\sqrt{3}\times\sqrt{3}$) we consider a one-band Hubbard Hamiltonian

$$H=t\sum_{i\neq j,\sigma} c_{i\sigma}^{+}c_{j\sigma}+U\sum_{i} c_{i\uparrow}^{+}c_{i\uparrow}c_{i\downarrow}^{+}c_{i\downarrow}, \qquad (1)$$

where the i and j sums run over the various Si dangling orbitals and σ describes the spin orientation. The hopping term with the parameter t indicates that only nearest neighbors are taken into account. The t parameters should be smaller than 0.1 eV for the characteristic distances. With an effective Coulomb integral of 7.64 eV and a surface screening constant of SiC of about 3.85, an effective interaction parameter of roughly $U\approx2$ eV may be estimated empirically.[18] It is also possible to estimate the effective interaction parameter U by means of total-energy differences between different occupations (charge states) of the dangling-bond band within the framework of DFT-LDA calculations. It holds $U=E(+)+E(-)-2E(0)$ with $E(+)$, $E(-)$, and $E(0)$ representing the ground-state energies of a positively charged, negatively charged, and neutral supercell, respectively. The charges have to be localized at the dangling bond giving rise to the surface band of interest. From our calculations we estimate a value $U\approx2.1$ eV ($U\approx1.0$ eV) for the $\sqrt{3}\times\sqrt{3}$ (3×3) surface. However, the calculation of total energies of charged supercells suffers strongly from spurious electrostatic interactions between the supercells. Hence, the values given above represent still a rather crude estimate. The corresponding errors might be as large as ±0.5 eV. In comparison with pure Si surfaces[18,24] the value for U is slightly enlarged in the case of the $\sqrt{3}\times\sqrt{3}$ surface as a consequence of the smaller dielectric constant. For the more-Si-rich 3×3 surface the value of U approaches more closely that of pure Si as a consequence of the rather large Si coverage of this structure. Without electron correlation the resulting dangling-bond band dispersion $\varepsilon(\mathbf{k})$ is given by $\varepsilon(\mathbf{k})=2t[1+2\cos(\pi s)]$ along ΓM or $=2t\{2\cos[(2\pi/3)s]+\cos[(4\pi/3)s]\}$ along the ΓK line ($0\leqslant s\leqslant1$) in the corresponding surface BZ. A fit to the dispersion of the dangling-bond band calculated within DFT-LDA yields a hopping parameter $t=0.014$ eV ($t=0.05$ eV) for the 3×3 ($\sqrt{3}\times\sqrt{3}$) structure.

With electron correlation the single-particle problem belonging to the Hamiltonian (1) cannot be solved exactly. However, in the atomic limit $t\ll U$ and a nearly equal distribution of the electrons in the dangling bonds over the spin states, the band with dispersion $\varepsilon(\mathbf{k})$ known from the uncorrelated limit splits into two bands with approximate dispersion relations $\frac{1}{2}\varepsilon(\mathbf{k})$ and $\frac{1}{2}\varepsilon(\mathbf{k})+U$ with the same spectral strength. The surfaces undergo a Mott transition from a metallic into an insulating stage.[25] Both Si-rich surface reconstructions represent a Mott-Hubbard insulator. The gap between the two bands is defined by the electron correlation energy U. For the $\sqrt{3}\times\sqrt{3}$ surface Themlin *et al.*[13] have aligned their **k**-resolved inverse photoemission data to the occupied band found by former ARUPS studies[12] in an energetical distance of about 2.3 eV. A possible uncertainty of the alignment of about 0.2–0.3 eV may be assumed. The resulting value $U\approx2-2.5$ eV for the $\sqrt{3}\times\sqrt{3}$ surface is in good agreement with our estimate. Northrup and Neugebauer estimated a theoretical value of about 1.6 eV.[23] Corresponding experimental data for the 3×3 structure are not available. Another argument for the validity of the strong correlation picture is the conservation of the dispersion in the empty and filled correlation bands and the reduction of the dispersion of the measured bands by about a factor 2 in comparison to the DFT-LDA result. ARUPS measurements find 0.2–0.25 eV (here) and 0.2 eV,[12] whereas the width of the unoccupied band of about 0.35 eV (Ref. 13) seems to be slightly larger in the $\sqrt{3}\times\sqrt{3}$ case. On the other hand, for the 3×3 surface theory finds a measurable dispersion of 0.13 eV, the ARUPS value is smaller than the experimental uncertainties, i.e., smaller than 0.1 eV.

In conclusion, we have calculated the electronic structure of the Si-rich SiC(111)3×3 and $\sqrt{3}\times\sqrt{3}$ surfaces by means of the DFT-LDA improved by the effects of strong electron correlation. The corresponding filled surface-state bands have been measured using ARUPS for SiC substrates of various polytypes. A puzzle remains on the yet unidentified nature of a third surface band in the fundamental gap in the case of the 3×3 structure. The details of the considered bands of filled surface bound states and the principal findings of insulating surface structures may be explained within the Mott-Hubbard picture. The Hubbard constant U should be of the order of 2 eV (1 eV) for the case of a $\sqrt{3}\times\sqrt{3}$ (3×3) structure.

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