Optical Anisotropy of the $SiC_{(001)}$-(3×2) Surface: Evidence for the Two-Adlayer Asymmetric-Dimer Model

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The structure of the (3 × 2) reconstruction of β-SiC(001) surface has been identified by comparing reflectance anisotropy spectra calculated from *first principles* with recent measurements. Only the calculations for the two-adlayer asymmetric-dimer model agree with experiment. The two prominent peaks at 3.6 and 5.0 eV found experimentally are assigned to electronic transitions between surface and bulklike electronic states. A further pronounced anisotropy at 2.0 eV, due to transitions between surface states, is predicted.

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Much attention has recently been focused on the properties of SiC growth planes, driven by the technological interest in SiC as a material for high-power, high-voltage, and high-temperature electronic devices. Moreover, a variety of intriguing surface properties have been reported. The β-SiC(001) surface, exhibiting three major surface phases, $c(2 \times 2)$, (2×1), and (3×2), serves as a prototype in that respect. It has been intensively investigated by both experiment [1–16] and theory [17–22]. Of particular importance are Si-rich conditions, because of the high Si vapor pressure in most methods of growth. In a Si-rich environment, the formation of a (3 × 2) reconstruction has been observed by numerous workers, but its atomic structure remains highly controversial. It is known that this reconstruction results from Si adsorption on the Si-terminated SiC(001) surface, but only the ratio of the Si coverages $\Theta_{(3\times2)}/\Theta_{(2\times1)} = 1.3$, is known experimentally [1]. No exact data are available. Furthermore, the outcome of scanning tunneling microscopy (STM) experiments is inconclusive. Semond *et al.* [2] used an alternate dimer-row model (ADRM), due to Yan *et al.* [18], to explain their STM images. Hara and coworkers [3], on the other hand, interpreted similar images as supportive of the double dimer-row model (DDRM), which was suggested by Dayan [4]. A further structure, the single dimer-row model (SDRM), was proposed on the basis of medium energy ion scattering experiments [5]. Yeom and coworkers [6–9] explained their photoemission and hydrogen adsorption experiments using the DDRM. Clearly, the current experiments have not convincingly determined the geometry of the Si-rich SiC(001)-(3 × 2) surface.

The theoretical situation is no less contradictory. Total energy calculations by three theoretical groups arrived at different conclusions, due mainly to the small differences in the total energies between the competing models. Using a self-consistent-charge density-functional tight-binding approach, Gutierrez *et al.* [19] found the DDRM to be stable for Si-rich surfaces and the ADRM to be stabilized for C-rich conditions. Pizzagalli *et al.* [20] found the ADRM to be stable irrespective of the surface chemical potentials. In Ref. [21], on the other hand, the two-adlayer asymmetric-dimer model (TAADM), a structure not considered previously, was found to have the lowest formation energy of all investigated models in the whole thermodynamically allowed range of the Si chemical potential.

Alternative methods of surface characterization are thus needed to determine the structure of the (3 × 2) reconstruction. In particular, reflectance anisotropy/difference spectroscopy (RAS/RDS) is an extremely sensitive and versatile tool to characterize surface structures in various environments [23–26]. Recently, Rossow and coworkers [16] measured the RAS of the β-SiC(001) surface. However, since the line shapes of RAS provide only indirect information, structural identification requires comparisons with either similar spectra for surfaces with known structures or with calculations. In this Letter we present the results of accurate, *first principles* calculations of the RAS spectra of the four structural models discussed above and show that only the TAADM is consistent with the measured data. In fact, the agreement between the experimental and the theoretical results is remarkably close in the entire measured range, which provides an unambiguous confirmation of TAADM and leads to the identification of the major spectral features with specific surface configurations.

Our calculations are based on density-functional theory (DFT) [27] in the local density approximation (LDA). Nonlocal, norm-conserving pseudopotentials in the separable form [28] are used to mimic the electron-ion interaction. The electronic structure calculations are performed with the real space multigrid method [29]. The spacing of the finest mesh used to determine the electron wave functions and charge density is 0.19 Å, corresponding to an energy cutoff of 37.4 Ryd in plane-wave calculations. We model the surface by periodic super cells, consisting of asymmetric slabs of ten SiC layers and vacuum regions of the same thickness. The dangling bonds at the bottom layer are saturated by hydrogen atoms. Six special **k** points in the irreducible part of the surface Brillouin

zone (SBZ) are used to sample the charge density for the calculation of the structurally relaxed ground state of the surface. Based on the self-consistently obtained electronic structure, we obtain the reflectance anisotropy $\Delta R/R$ in the independent-particle approximation, according to the scheme devised by Manghi *et al.* [25]. The calculations of the dielectric function include all conduction bands up to 13 eV from the top of the valence bands and 96 uniformly distributed **k** points. To avoid spurious contributions to the RAS from the bottom surface we use a linear cutoff function [30]. Because of the well-known insufficiency of DFT-LDA to describe excitation energies, our calculations underestimate the SiC bulk band gap by 1.1 eV. Therefore, in order to compare the calculated spectra to the experimental data, we apply a scissors operator and shift the excitation energies accordingly [26]. Further details of the calculations are analogous to those in Ref. [24].

Figure 1 shows the geometries of the four models for the SiC(001)-(3 × 2) surface. Their atomic and electronic details have been discussed previously [21]. In short, the TAADM is characterized by six adatoms per surface unit cell. They adsorb on the surface as two adlayers. The four adatoms in the lower adlayer bond to the Si-terminated substrate and form symmetric dimers. In the top adlayer, two adatoms form an asymmetric dimer. In the DDRM, there are four adatoms per unit cell. They form two asymmetric dimers, which can be arranged in at least four different configurations that are energetically nearly degenerate and have very similar electronic properties [21]. We focus in the following on the structure shown in Fig. 1(b). The SDRM and the ADRM feature two adatoms per unit cell that form an asymmetric dimer. The difference between these two models is the dimer arrangement: the SDRM is a (3 × 2) reconstruction and the ADRM is a (2 × 3) reconstruction.

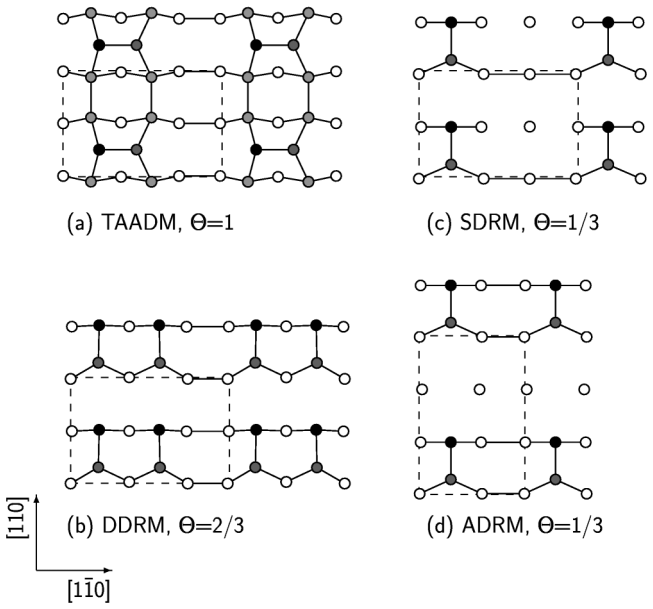

FIG. 1. Top view of (3 × 2) reconstruction models: (a) two-adlayer asymmetric-dimer model; (b) double dimer-row model; (c) single dimer-row model; and (d) alternate dimer-row model. Open circles represent substrate-surface Si atoms, and shaded and solid circles represent Si adatoms. The substrate carbon atoms, which are below the substrate-surface Si atoms, are not shown in these top views. A (3 × 2) unit cell for each model is given by dashed lines. The coverage Θ gives the number of Si monolayers on top of the Si-terminated substrate.

Figure 2 shows the calculated RAS spectra for the four models discussed above in comparison with the measured data [16]. Two peaks *A* and *B*, at 3.6 eV and at 5.0 eV, respectively, were found experimentally. They are separated by a dip at about 4.2 eV. No negative anisotropies were observed in the whole energy region considered. The energetic positions of the measured RAS features are in excellent agreement with the calculated spectrum of the TAADM. Our calculated anisotropy peaks *A* and *B* are at 3.5 and 5.0 eV, respectively. They are separated by a minimum at 4.3 eV. The slight differences between the positions of the measured and the calculated peaks may be due to different quasiparticle shifts experienced by the electronic states localized at the surface and within the bulk [24]. In the low energy region, we predict another peak *C* at 2.0 eV. This peak could not be resolved experimentally, due to interference effects. Overall, the calculated anisotropy signal is slightly larger than measured. Such

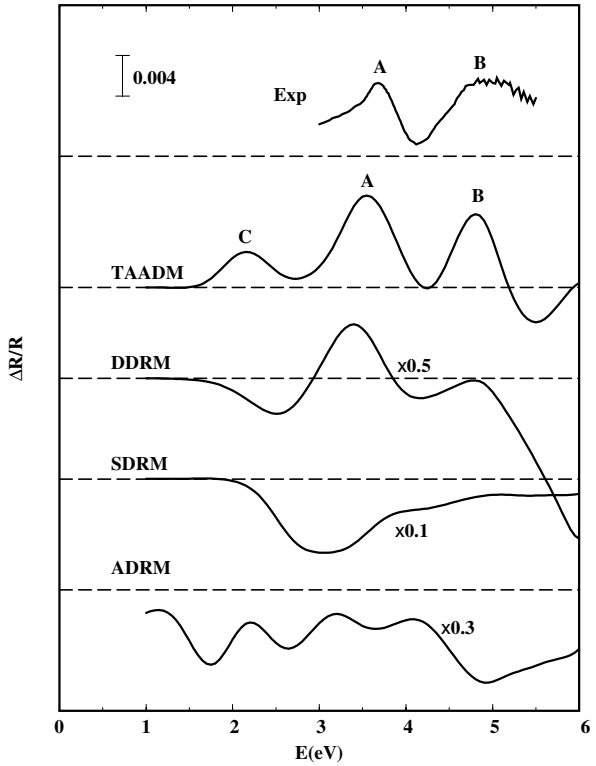

FIG. 2. RAS spectra $\Delta R/R = 2(R_{[110]} - R_{[1\bar{1}0]})/(R_{[110]} + R_{[1\bar{1}0]})$ for the SiC(001)-(3 × 2) surface. The experimental values have been taken from Ref. 16; the calculations refer to the models shown in Fig. 1. Zero values are indicated by dashed lines.

an overestimation is typical [24] and is usually related to temperature effects and sample imperfections, neglected in our study.

The RAS features calculated for the three remaining surface models clearly do not agree with experiment. For the DDRM, the peak A is at 3.5 eV, but no anisotropies show up in the energy region of the measured peak B, at 5.0 eV. Furthermore, negative signals appear below 3.0 eV and above 3.9 eV. This is not observed in experiment. For the SDRM and the ADRM, we obtain negative anisotropies in the complete energy range, which contradicts the experimental findings. In addition, the calculated line shape is very different from the measured one.

One should point out that the large and broad dip around 3.0 eV in the calculated RAS for the SDRM is very similar to the experimental findings for the nominal (2×1) surface [16]. Unfortunately, the geometry of the apparent (2×1) structure is not clear; it may be a disordered $c(4 \times 2)$ surface or a $c(4 \times 2)$ reconstruction with a high defect density. Nevertheless, the similarity between the 3 eV feature in the calculated RAS spectra for the SDRM and the measured data for the (2×1) surface indicates the occurrence of some similar structural elements, i.e., asymmetric and well-separated Si dimers on top of the Si-terminated substrate.

The optical anisotropy results are not the only ones that favor the TAADM. Table I summarizes the abilities of the four structural models of the SiC(001)-(3×2) surface to account for the available LEED, STM, photoemission, RAS, and H adsorption results. It is clear from the Table that the TAADM is the best candidate for explaining all the experiments, which probed both the atomic and the electronic structure of this surface. However, in order to explain the observed phase transition from (3×2) to (3×1) upon H adsorption [9], the desorption of Si adatoms has to be assumed. The experimental ratio of Si coverage $\Theta_{(3\times2)}/\Theta_{(2\times1)} = 1.3$ cannot disprove any model since the exact coverage of the (2×1) reconstruction is not known from either experiment or theory. A detailed discussion of coverage issues is given in Refs. [21,31].

We now turn to the origin of the RAS features of the TAADM. From the similarity of the measured RAS line shapes of β-SiC(001) and GaAs(001)$c(4 \times 4)$, Rossow *et al.* [16] concluded that the SiC(001)-(3×2) surface is characterized by Si dimers. They also suggested that the main RAS features must be related to the adatom-induced surface states. This is confirmed by our calculations, where we separate the contributions to the RAS in terms of transitions between different electronic states. The results are shown in Fig. 3. The peak C is related to transitions between two surface states: the occupied dangling-bond state D_b and the unoccupied dangling-bond state D_a. (For details of the electronic structure of the TAADM we refer the reader to Ref. [21].) Peak A is mainly due to the transitions between the occupied dangling-bond state and unoccupied bulklike conduction bands. These transitions contribute also somewhat to the peak B. However, the main contributions to B arise from electronic transitions between occupied bulklike states and the unoccupied dangling bond D_a. Finally, the anisotropy minimum at 4.3 eV is related to transitions between unoccupied bulk states and the backbonds $S1$ and $S2$ in the lower adlayer.

Our findings provide an intuitive understanding of the major spectral features. In agreement with earlier results on Si(001) surfaces [32,33] we observe that both intradimer and interdimer transitions have to be taken into account to explain the RAS. When interactions between the dimers are weak, the dimer direction determines the RAS. Dimers oriented along the $[110]/[1\bar{1}0]$ direction give rise to negative/positive optical anisotropies. This agrees with the expectation of larger polarizabilities along the bond direction.

TABLE I. The ability of the structural models in Fig. 1 to account for the experimental findings on the SiC(001)-(3×2) surface. The $+$, $-$, and $\circ$ symbols indicate existing, missing, and possible agreement with experiment.

	TAADM	ADRM	SDRM	DDRM
LEED symmetry [15]	+	−	+	+
STM [2,3]	+	+	−	∘
Photoemission [8,21]	+	∘	∘	−
RAS [16]	+	−	−	−
H adsorption [9]	∘	∘	+	+

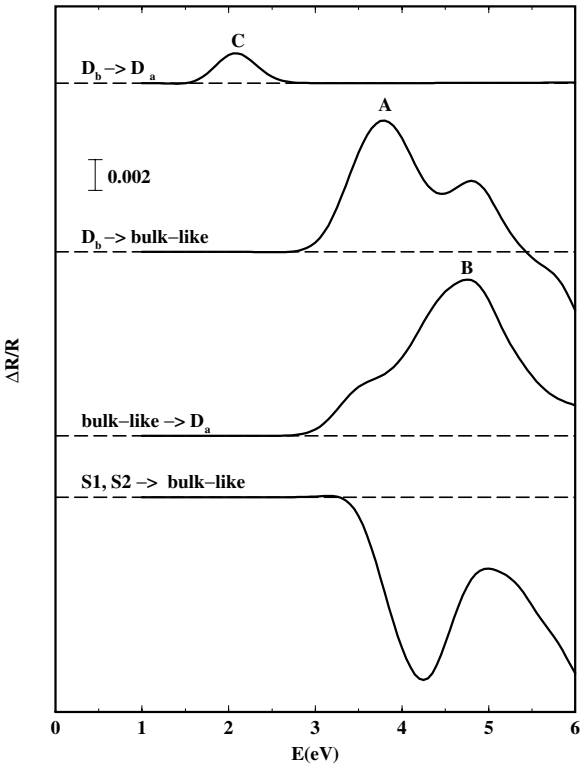

FIG. 3. Contributions of transitions between surface and bulklike states to the RAS features of the TAADM (see text). Zero values are indicated by dashed lines.

Therefore, the RAS for the SDRM and ADRM is negative throughout the considered energy window, while it is positive for the TAADM. The small dimer-dimer separation in the DDRM, however, is responsible for the occurrence of both negative and positive anisotropy features.

In summary, the RAS of the β-SiC(001) (3×2) surface has been calculated from *first principles* for different surface models. The results for the two-adlayer asymmetric-dimer model (TAADM) are the only ones that agree with the experimental data. In conjunction with the previous experimental and theoretical findings, the TAADM appears thus to be the only correct model for the β-SiC(001)-(3×2) surface. Its spectrum is characterized by three positive peaks related to ad-dimer induced surface states. The dip at 4.2 eV is related to backbonds in the second adlayer. Our results are consistent with a simple picture relating prominent RAS features to the spatial orientation and arrangement of surface dimers.

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[1] T. Yoshinobu, I. Izumikawa, H. Mitsui, T. Fuyuki, and H. Matsunami, Appl. Phys. Lett. **59**, 2844 (1991).
[2] F. Semond, P. Soukiassian, A. Mayne, G. Dujardin, L. Douillard, and C. Jaussaud, Phys. Rev. Lett. **77**, 2013 (1996).
[3] 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).
[4] M. Dayan, J. Vac. Sci. Technol. A **4**, 38 (1986).
[5] S. Hara, S. Misawa, S. Yoshida, and Y. Aoyagi, Phys. Rev. B **50**, 4548 (1994).
[6] H. W. Yeom, M. Shimomura, J. Kitamura, S. Hara, K. Tono, I. Matsuda, B. S. Mun, W. A. R. Huff, S. Kono, T. Ohta, S. Yoshida, H. Okushi, K. Kajimura, and C. S. Fadley, Phys. Rev. Lett. **83**, 1640 (1999).
[7] H. W. Yeom, Y.-C. Chao, S. Terada, S. Hara, S. Yoshida, and R. I. G. Uhrberg, Phys. Rev. B **56**, R15 525 (1997).
[8] H. W. Yeom, Y.-C. Chao, I. Matsuda, S. Hara, S. Yoshia, and R. I. G. Uhrberg, Phys. Rev. B **58**, 10 540 (1998).
[9] H. W. Yeom, I. Matsuda, Y.-C. Chao, S. Hara, S. Yoshida, and R. I. G. Uhrberg, Phys. Rev. B **61**, R2417 (2000).
[10] V. M. Bermudez, Phys. Status Solidi (b) **202**, 447 (1997), and references therein.
[11] F. Widulle, T. Ruf, O. Buresch, A. Debernardi, and M. Cardona, Phys. Rev. Lett. **82**, 3089 (1999).
[12] P. Soukiassian, F. Semond, A. Mayne, and G. Dujardin, Phys. Rev. Lett. **79**, 2498 (1997).
[13] V. Yu. Aristov, L. Douillard, O. Fauchoux, and P. Soukiassian, Phys. Rev. Lett. **79**, 3700 (1997).
[14] P. Soukiassian, F. Semond, L. Douillard, A. Mayne, G. Dujardin, L. Pizzagalli, and C. Joachim, Phys. Rev. Lett. **78**, 907 (1997).
[15] R. Kaplan, Surf. Sci. **215**, 11 (1989).
[16] U. Rossow, K. Lindner, M. Lübbe, D. E. Aspnes, and D. R. T. Zahn, J. Vac. Sci. Technol. B **16**, 2355 (1998).
[17] J. Pollmann, P. Krüger, and M. Sabisch, Phys. Status Solidi (b) **202**, 421 (1997), and references therein.
[18] H. Yan, A. P. Smith, and H. Jónsson, Surf. Sci. **330**, 265 (1995).
[19] R. Gutierrez, H. Haugk, J. Elsner, G. Jungnickel, M. Elstner, A. Sieck, Th. Frauenheim, and D. Porezag, Phys. Rev. B **60**, 1771 (1999).
[20] L. Pizzagalli, A. Catellani, G. Galli, F. Gygi, and A. Baratoff, Phys. Rev. B **60**, 5129 (1999).
[21] W. Lu, P. Krüger, and J. Pollmann, Phys. Rev. B **60**, 2495 (1999).
[22] G. Galli, A. Catellani, and F. Gygi, Phys. Rev. Lett. **83**, 2006 (1999).
[23] D. E. Aspnes and A. A. Studna, Phys. Rev. Lett. **54**, 1956 (1985).
[24] W. G. Schmidt, F. Bechstedt, and J. Bernholc, J. Vac. Sci. Technol. B **18**, 2215 (2000).
[25] F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, Phys. Rev. B **41**, 9935 (1990).
[26] R. Del Sole and R. Girlanda, Phys. Rev. B **48**, 11 789 (1993).
[27] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[28] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[29] E. L. Briggs, D. J. Sullivan, and J. Bernholc, Phys. Rev. B **52**, 5471 (1995); **54**, 14 362 (1996).
[30] A. I. Shkrebtii, N. Esser, W. Richter, W. G. Schmidt, F. Bechstedt, B. O. Fimland, A. Kley, and R. Del Sole, Phys. Rev. Lett. **81**, 721 (1998).
[31] W. Lu, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **81**, 2292 (1998).
[32] L. Kipp, D. K. Biegelsen, J. E. Northrup, L.-E. Swartz, and R. D. Bringans, Phys. Rev. Lett. **76**, 2810 (1996).
[33] C. Kress, A. I. Shkrebtii, and R. Del Sole, Surf. Sci. **377**, 398 (1997).