Atomic and Electronic-Band Structures of Anomalous Carbon Dimers on 3*C*-SiC(001)-$c(2 \times 2)$

H. W. Yeom,[1,*] M. Shimomura,[2] J. Kitamura,[3] S. Hara,[3] K. Tono,[4] I. Matsuda,[4] B. S. Mun,[5] W. A. R. Huff,[6] S. Kono,[2] T. Ohta,[4] S. Yoshida,[3] H. Okushi,[3] K. Kajimura,[3] and C. S. Fadley[5]

[1]*Research Center for Spectrochemistry, the University of Tokyo, Tokyo 113, Japan*

[2]*Research Institute for Scientific Measurements, Tohoku University, Sendai 980-77, Japan*

[3]*Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan*

[4]*Department of Chemistry, the University of Tokyo, Tokyo 113, Japan*

[5]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720 and Department of Physics, University of California at Davis, Davis, California 95616*

[6]*KLA-Tencor, Milpitas, California 95035*

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The atomic structure of the $c(2 \times 2)$ reconstruction of the *C*-terminated 3*C*-SiC(001) surface was unambiguously determined by scanning tunneling microscopy and surface-core-level-resolved photoelectron diffraction studies. This surface is found to uniquely and uniformly consist of anomalous bridge-bonded C dimers with a C-C bond length of 1.22 Å. Furthermore, an extensive angle-resolved photoemission study clearly identifies two occupied π state bands due to the surface-normal and -parallel π orbitals of the *triple-bonded* C dimers. This provides an electronic explanation of the stability of this unique surface reconstruction.

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SiC has attracted much recent interest due to its potential for novel device applications [1] as well as due to its unique surface properties, most popularly cubic 3*C*-SiC(001) [2] and hexagonal 6*H*(4*H*)-SiC(111) [3] surfaces. The partially ionic character of SiC provides an interesting variety of complex reconstructions and local bond configurations on its surfaces. It has been known that the 3*C*-SiC(001) surface exhibits three major surface phases [2]: the *C*-terminated $c(2 \times 2)$ surface, the Si-terminated 2×1 [or $c(4 \times 2)$] surface, and the Si-rich 3×2 surface. Peculiar surface properties have been reported such as a metal-insulator transition for the Si-terminated surfaces [4] and a zero-dimensional fluctuation [5] and quantum wires for the Si-rich surface [6]. However, further detailed discussion on such surface properties is mainly prohibited by the lack of consensus on the structures of these surfaces [2,7,8].

As for the *C*-terminated $c(2 \times 2)$ surface, the possibility of a very unusual *bridge-bonded* dimer (BD) structure has been discussed [Fig. 1(a)] [9–19], which is unprecedented among the known reconstructions of semiconductor surfaces. This was first introduced by a low-energy electron diffraction (LEED) study for the $c(2 \times 2)$ surface prepared by Si sublimation [9] against the earlier model of conventional dimers [the staggered dimer (SD) model, Fig. 1(b)] [10]. In contrast to this LEED study suggesting a "double-bonded" BD, a recent x-ray absorption study favored a *triple-bonded* BD [9] structure for a $c(2 \times 2)$ surface prepared by C_2H_4 flux [11]. Some of the theoretical calculations, contradictorily, suggested a 2×1 conventional dimer structure as the energetically favored ground state [12–15], and others, the SD $c(2 \times 2)$ structure [16,17]. Furthermore, in the major *ab initio* calculations [12,13,18] the total energy differences between the SD and BD $c(2 \times 2)$ structures were trivially small, which leads to the prediction of the coexistence of different surface structures or the subtle dependence of surface structures on the preparation methods [12].

In this Letter, we provide unambiguous answers to the questions of (i) the uniqueness, (ii) the quantitative details of the surface structure, and (iii) the bond configuration of the 3*C*-SiC(001)-$c(2 \times 2)$ surface. Scanning tunneling microscopy (STM) studies for the $c(2 \times 2)$ surface

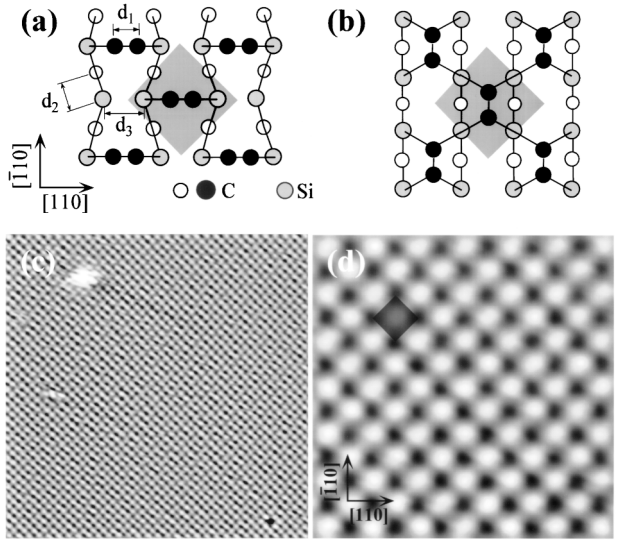

FIG. 1. The two structure models of 3*C*-SiC(001)-$c(2 \times 2)$: (a) The bridge dimer and (b) the staggered dimer model. Filled-state STM images of the 3*C*-SiC(001)-$c(2 \times 2)$ surface: (c) a wide scan (195 × 195 Å) at a sample bias of −2.95 V and (d) a close-up (40 × 40 Å) scan at −2.95 V. These images were smoothed by averaging over 5×5 pixels. A $c(2 \times 2)$ unit cell is depicted by hatched diamonds.

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prepared in different ways establish the uniqueness and uniformity of the surface structure, whose quantitative details are revealed by photoelectron diffraction (PED). The angle-resolved photoelectron spectroscopy (ARPES) study clearly identifies two occupied π-bond surface states. All these results consistently confirm the triple-bonded BD structure and its electronic configuration.

STM, PED, and ARPES investigations were performed in three different locations. Details of the ultrahigh-vacuum STM system used were described before [20]. A surface-core-level-resolved C 1s PED experiment was carried out on the beam line BL 9.3.2 of the Advanced Light Source [21]. Valence-band ARPES measurements were performed on the beam line BL-7B of the Photon Factory [22]. Well-ordered single-domain 3C-SiC(001)-$c(2 \times 2)$ surfaces were prepared by annealing 3C-SiC(001) films at $\sim$1180 °C (Si sublimation) *in situ* for the PED and ARPES experiments [8,20,23]. In the STM study, the methods of Si sublimation and C_2H_2/C_2H_4 exposure [2,9] were compared.

Figures 1(c) and 1(d) show high-resolution filled-state STM topography of the $c(2 \times 2)$ surface obtained by C_2H_4 exposure. These images, which are to our knowledge the first successful real-space imaging of this surface, clearly show one oval-shaped protrusion in each $c(2 \times 2)$ unit cell, which are slightly elongated along the [110] azimuth (the C dimer bond axis of the BD model). These protrusions (and their characteristic bias dependence [24]) appear uniformly over the whole surface. Extensive STM imagings of the surfaces prepared by C_2H_2 exposure or by Si sublimation showed no essential difference. The only noticeable difference was the density of defect structures (clusterlike defects appear as very bright in Fig. 1(c) or stripe defects not shown here): the number of defects is reduced significantly as shown in this figure by an optimal C_2H_4 treatment [24]. This result apparently denies any substantial coexistence of different $c(2 \times 2)$ or 2×1 surface reconstructions suggested by theories [12–18]. However, due to the dramatic bias dependence of the STM images and its mismatch with the presently available calculations [12], the STM image alone cannot point out the correct $c(2 \times 2)$ structure.

Further structural information can be achieved by resolving out C 1s photoemission from the surface C atoms. The previous studies [2,23] have shown that the C 1s level is composed of two main components originating from the bulk C and the topmost C layers (B and S, respectively, in Fig. 2). The energy shift between B and S is as large as 1.1 eV [2,23] indicating a large deviation of the electronic and structural environment of surface C atoms from those of bulk. However, the fact that both SD and BD models have only single surface C sites prevents them from being distinguished through the C 1s spectra. In order to obtain *quantitative* information on the surface structure, the PED from the surface C 1s component (S) was investigated [25]. As shown in Figs. 2(a) and 2(b), S shows a large intensity modulation

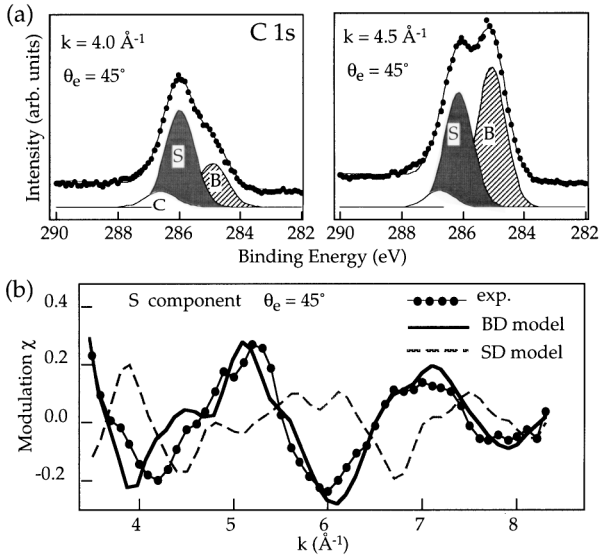

FIG. 2. (a) C 1s spectra of 3C-SiC(001)-$c(2 \times 2)$ with decompositions taken along the [110] azimuth at an emission angle (θ_e) of 45° for the two different kinetic energies ($hk^2/4\pi m_e$ where $k = 4.0$ and 4.5 Å^{-1}). S and B denote the surface and bulk components, respectively [23]. The spectra were normalized by the photon flux on the sample. (b) Intensity modulation of the S component as a function of the photoelectron wave vector (k). This is given in the χ function: $\chi = (I - I_0)/I_0$, where I is the photoelectron intensity and I_0 is its smooth background. The overall modulation thus amounts to $\sim$40% ($\pm$0.2 in χ) of the background intensity. The dots with a thin solid line represent the experimental data and the thick solid (dashed) line is the optimized result of theoretical simulations for the BD (SD) model.

when its kinetic energy ($hk^2/4\pi m$) is varied. This modulation, due mainly to the scattering of photoelectrons by the near-surface atoms, is measured in detail by scanning the photon energy at an emission angle of 45° along the [110] azimuth [25]. The photoelectron intensity modulation, after subtracting a smooth background (so-called the χ function) [25], is shown in Fig. 2(c) for photon energies of $\sim$330–552 eV ($k = \sim$3.5–8.4 Å^{-1}). The χ function was theoretically simulated including the multiple scattering of photoelectrons fully [26] with more-than-200-atom clusters of the two structure models. The optimized results of simulations through the R-factor analyses [25] are compared to the experimental result in Fig. 2(c). As evident in this comparison, the SD model can be ruled out due to the apparent disagreement with the experiment. In sharp contrast, the BD model gives an excellent agreement with a convincingly low R factor of 0.11. The large difference in the simulations for SD and BD models can easily be understood: only the BD model has the direct backscatter (second layer Si atoms) at the 45° emission angle along [110]. This result provides *an independent and unambiguous evidence for the BD structure.* The optimized bond lengths for the BD model [see Fig. 1(a)] are 1.22 $\pm$ 0.05 Å for the C-C bond (d_1), 1.84 $\pm$ 0.02 Å

for the C-Si bond between the top and the second layer (d_2), and 2.70 ± 0.1 Å for the Si-Si bond (d_3). *The C-C bond length determined corresponds to that of the triple-bonded C_2H_2 molecule* and agrees well with the theoretical calculations for the BD model [12–14,18,19]. This suggests the triple bonding of C dimers [13,19], which will further be corroborated below. A similar PED pattern was also measured along the normal emission, and it was analyzed consistently but with larger uncertainties in determining the structural parameters due to the smaller modulation of S along the normal emission.

We have, then, extensively measured the valence-band ARPES spectra in order to directly determine the bond configuration of the surface C dimers. At first the normal emission spectra (not shown here) at various photon energies revealed six different nondispersing spectral features at ~2.2–10 eV below the Fermi level (E_F) in addition to dispersing bulk-related peaks. A comparison to similar spectra of the Si-rich 3×2 [8] and Si-terminated 2×1 surface evidences that these spectral features (denoted as S_1–S_6) are inherent to the $c(2 \times 2)$ surface. Figure 3 shows the detailed dispersion curves of S_1–S_6 taken by angle-scanned ARPES. While S_1 and S_6 states are located within the bulk band gap as surface states, the others overlap with the bulk bands as surface resonances. The invariance of their dispersions for different photon energies confirms their surface origin.

The experimental dispersion curves of S_1–S_6 are compared with the theoretical calculations based on the SD and BD models [13]. The SD model yields a strongly dispersing surface state (P_5') within the band gap [13] in sharp contrast to the experiment observing a flat band S_1 near the bulk valence-band maximum (VBM). On the other hand, the theory for the BD model predicts two nearly degenerated surface states (P) at the $\bar{S}$ point of the surface Brillouin zone near the top of VBM. They come from the hybridization of the C-C dimer bond (a σ state) and the second layer Si dangling bonds [13]. We can easily assign the neighboring surface states S_1 and S_2 to the P states. The energy splitting between these states seems to be underestimated in the theory. From the comparison of the highest-occupied states within the band gap between the theory and the experiment, it is already clear that the SD model is denied in consistent with the PED result. The theory for the BD model [13] further predicts two π surface states due to surface parallel (π_2, mainly p_x) and perpendicular (π_1, mainly p_z) dangling bonds of triple-bonded dimers. Close to the calculated binding energies, we found two characteristically dispersing surface states S_3 and S_4, which can tentatively be assigned to the π surface states. Note that the surface state dispersions within the bulk band region were not fully traced in theory. Finally the two higher binding energy states S_5 and S_6 are assigned as due to the two back-bond orbitals of C dimers. The theory gives the binding energy of one back-bond surface state as ~7.3 eV [13] in qualitative agreement with that of S_5. These six surface states complete the picture of surface bonds/orbitals of the BD model.

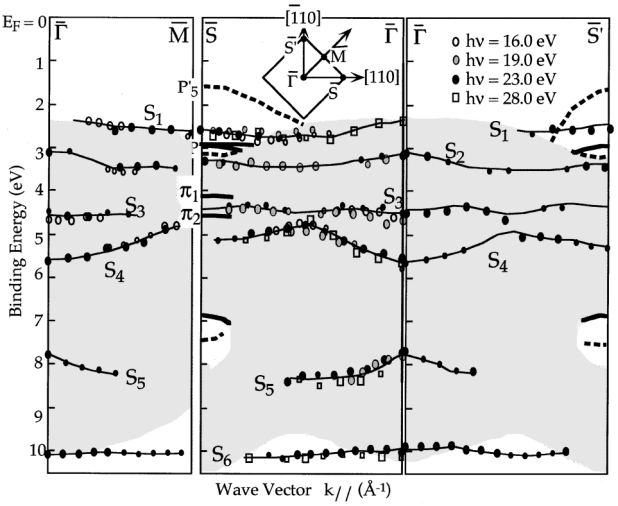

FIG. 3. Dispersion curves for the surface states of $3C$-SiC(001)-$c(2 \times 2)$. The $c(2 \times 2)$ surface Brillouin zone is shown as an inset. The symbols (large and small ones for relatively strong and weak spectral features, respectively) guided by solid lines are experimental data for S_1–S_6 taken from ARPES measurements with various photon energies ($h\nu$). The dashed lines (thick solid lines) are the calculated surface-state dispersions of the SD (BD) structure [13]. The hatched area corresponds to the bulk bands projected onto the 1×1 surface Brillouin zone.

The most important surface states in the above assignment are the two π states, which directly evidence the triple-bond dimer configuration. One can recognize the definite symmetry properties of these two characteristic surface states. At first the π_z state must have the most strong p_z character among the above surface states. In Fig. 4(a), we show the polarization dependence (s and p polarization) of the ARPES spectra. S_4 is enhanced predominantly for the p polarization indicating its strong p_z character. This clearly confirms S_4 as the π_z state. On the other hand, the π_x state should possess a unique odd symmetry property with respect to the mirror reflection about the [110] azimuth (about the C-C dimer axis). In Fig. 4(b), S_3 is shown to enhance significantly for the odd symmetry-sensitive geometry $A_{\pm}$ [27], while other surface states are depressed, verifying S_3 as the π_x state. In general, a surface state of p_z orbitals disperses towards lower energies from $\bar{\Gamma}$ [28], which is in agreement with the dispersion of S_4. Although the theory expects two π states at qualitatively consistent binding energies, the π_z (π_1) state was shown to have less binding energy than π_x (π_2) in contrast to the experiment.

Through the combined experimental information given above, we have unambiguously shown that *the $c(2 \times 2)$ surface has a unique surface reconstruction of the triple-bonded C dimers in a bridge configuration.* This type of surface reconstruction with triple-bonded dimers has never been recognized and seems to violate the general trend of minimization of the number of unsaturated dangling bonds. The unsaturated dangling bonds of C

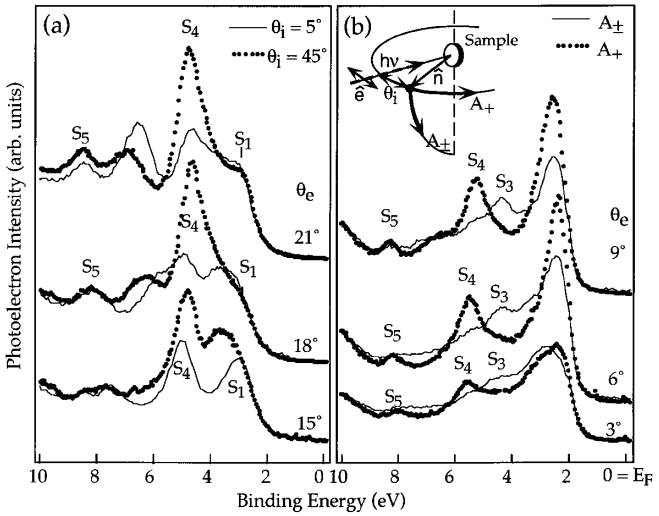

FIG. 4. (a) ARPES spectra for $3C$-SiC(001)-$c(2 \times 2)$ taken along the [110] azimuth at photon incident angles (θ_i) of 5° (lines) and 45° (dots), which roughly correspond to the s and p polarization, respectively. (b) ARPES spectra taken along the [110] mirror-symmetric azimuth at the two different measurement geometries (inset) denoted $A_\pm$ (lines) and A_- (dots), where the odd and even symmetry states are preferentially excited, respectively, due to the selection rules [27]. $\hat{n}$ and $\hat{e}$ in the inset are the surface normal and the light polarization, respectively.

dimers, instead, form unusually strong π bondings (S_3 and S_4), which have a higher binding energy than the σ bond (S_1 or S_2). Compared to the π surface states of the double-bonded C (Si) dimers of the diamond(001) [Si(001)] surface, the π states of SiC(001)-$c(2 \times 2)$ have significantly higher binding energy. This may explain the stability of the triple-bonded structure, that is, *the reconstruction is governed by the strong molecularlike C-C multiple bonding, especially by the extraordinary π bondings.* It can also be noticed that the theory significantly underestimates the binding energy of the π_z state. This can be the reason that the theory failed to uniquely predict the ground state as the triple-bonded BD structure [12,13].

Although the previous LEED study indicated the BD structure at least for the $c(2 \times 2)$ surface prepared by Si sublimation, the reported dimer length of 1.31 Å suggested a double-bond configuration [9]. This is clearly denied by the present study. Since PED picks up only the local structure information around a selected emitter, in this case a C dimer atom, the present result would not depend on the surface defects mentioned above in contrast to LEED analyses [9,19]. For the C_2H_2 exposed surface, a recent x-ray absorption study suggested a triple-bonded BD structure [11], although no direct information on the atomic structure nor on the occupied electronic states was provided. Given the present PED and ARPES results for the surface prepared by Si sublimation, the x-ray absorption result is consistent with our STM observation of a unique and uniform surface reconstruction over differently prepared surfaces.

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*Corresponding author.
TEL/FAX: +81-298-64-5584
Electronic address: yeom@sr.t.u-tokyo.ac.jp

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