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Hydrogen-induced 3×1 phase of the Si-rich $3C$ -SiC(001) surface

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A single-domain 3×1 phase induced by hydrogen adsorption on a Si-rich $3C$ -SiC(001) 3×2 surface is investigated by photoemission using synchrotron radiation. Three surface components of the Si $2p$ core level are identified for the 3×1 -H phase, which resemble those of the 3×2 surface. A H-Si bonding state is observed by angle-resolved valence-band photoemission. These results are consistent with the recent assignments of the Si $2p$ surface components and the valence band spectra of the 3×2 surface, based on the 3×2 structure model with $\frac{2}{3}$ ML Si addimers. A straightforward 3×1 -H structure model is introduced featuring Si dimer-bond breaking and dangling-bond saturation.

Recently there has been considerable interest in the surface structures of cubic (mostly $3C$ polytype) and hexagonal ($6H$ or $4H$) SiC crystals.^{1,2} Such interests are not only due to the technological importance of SiC thin films for advanced device applications,³ but also due to the unique surface properties of this partly ionic IV-IV compound semiconductor. Indeed, a variety of intriguing surface properties have been reported, such as a Mott-insulating ground state,⁴ an exotic carbon bonding,^{5,6} a metal-insulator transition,⁷ a cellular fluctuation of unit cells,⁸ and Si or C one-dimensional chains.^{9,10}

In spite of vigorous investigations performed so far, the atomic structures of the reconstructions of SiC surfaces are still not clear, especially for the Si-rich and Si-terminated $3C$ -SiC(001) surfaces.^{1,2} In particular, the Si-rich $3C$ -SiC(001) 3×2 surface structure¹¹⁻¹⁷ is currently under significant debate with three contradicting structure models of different Si coverages and even different unit-cell orientations. The so-called Dayan-Hara (DH) model has $\frac{2}{3}$ ML of Si addimers with a 3×2 orientation on top of the Si termination layer (see Fig. 1).^{1,11} Another model, the so called Yan-Semond (YS) model, has a 2×3 unit cell with $\frac{1}{3}$ ML of Si addimers on the Si termination layer.^{1,12} While the YS model was recently supported by an STM study,¹² we reported that only the DH model can explain the Si $2p$ surface components observed,¹³ and further, the surface-state band structure is consistently interpreted within the DH model.¹⁴ Very recently, three independent *ab initio* calculations have considered the energetics of these two models, including the modifications of the DH model from symmetric to asymmetric dimers, only to give contradictory results.¹⁵⁻¹⁷ One of these calculations by Lu *et al.* even proposed a new model as

the most stable structure, which has a 3×2 unit cell but with an additional $\frac{1}{3}$ ML of Si dimers on top of the DH model, resulting in the double Si adlayers with a total coverage of 1 ML.¹⁷

In this Rapid Communication, we report on a detailed

FIG. 1. LEED patterns for (a) the clean single-domain $3C$ -SiC(001) 3×2 surface, and (b) the 3×1 -H surface. The surface unit cells are depicted by white lines. Schematic illustration of (c) the $3C$ -SiC(001) 3×2 (Refs. 1, 8, 11, 13, 14) and (d) 3×1 -H surface structure models. Only the surface Si layers are shown. The surface unit cell is depicted by solid lines and the surface Si atoms with different local registries are indicated with different symbols. The previous atomic assignments of the Si $2p$ surface components, S1, S2, and S3, of the 3×2 surface (Ref. 13) is also given in (c). See text for explanation.

experimental study of the 3×1 surface induced by hydrogen adsorption onto the $3C\text{-SiC}(001)3 \times 2$ surface, which provides a crucial criterion to differentiate the above structure models proposed. The LEED investigation of a single-domain surface confirms the orientation of the 3×2 and $3 \times 1\text{-H}$ reconstructions, which makes the YS model impossible and the new model by Lu *et al.* unfavorable. Instead, valence band and Si $2p$ core-level spectra measured for the $3 \times 1\text{-H}$ surface are consistent with the DH model and our previous photoemission studies for the 3×2 surface.^{13,14}

The experimental setup for angle-resolved photoelectron spectroscopy (ARPES) and Si $2p$ core-level measurements are the same as reported before.^{13,14} The total energy resolution was set to ~ 150 meV and ~ 80 meV at the photon energies of $h\nu = 21.2$ eV and 110–140 eV, respectively, for the valence band and Si $2p$ measurements at room temperature. A well-ordered single-domain $3C\text{-SiC}(001)3 \times 2$ surface was prepared as reported before by high-temperature annealing *in vacuo* [Fig. 1(a)].^{11,13,14} Hydrogen adsorption was performed by exposing a fresh 3×2 surface at room temperature to H_2 gas activated by a hot W filament.

During the exposure of the clean Si-rich 3×2 surface to hydrogen, the intensity of the streaky $\frac{1}{2}$ -order superspots gradually decreases and a clear 3×1 LEED pattern is observed at exposures of 400–500 L. Figures 1(a) and 1(b) show the LEED patterns for the *single-domain* 3×2 and *single-domain* $3 \times 1\text{-H}$ phases, respectively. By also observing the LEED pattern of the Si-terminated *single-domain* 2×1 surface, it is unambiguous that the $\times 3$ axes of the 3×2 and 3×1 surfaces are parallel to the $\times 2$ axis of the 2×1 phase [(the $[110]$ bulk crystallographic direction, see Fig. 1(c)]. Further H exposure gradually also destroys the $\times 3$ superspots to finally result in a 1×1 pattern. No trace of oxygen has been detected even after the formation of the 3×1 and 1×1 phases. The 3×2 phase recovers from either the 1×1 or 3×1 phase by H desorption induced by annealing at 900–1000 °C. The quality of the regenerated 3×2 surface is checked by LEED and photoemission spectra and no sign of surface degradation is found. This indicates that *the surface Si coverage is conserved during the formation of the 3×1 and 1×1 phases through H adsorption and desorption.* It is also implied that the H-induced surface reconstruction does not involve a significant rearrangement of the surface Si atoms. This will be further verified by the Si $2p$ photoemission results discussed below.

From the confirmed orientation of the 3×2 unit cell, we can clearly exclude the YS model, which has a “ 2×3 ” unit cell rotated by 90° compared to the actual LEED pattern observed.^{1,12} It should also be noted that the periodicity of the YS model and even the new model of Lu *et al.* cannot be changed into 3×1 in any simple way, since they have only a single Si addimer in each 2×3 or 3×2 unit cell. That is, *simply the LEED observation of the single-domain 3×2 and $3 \times 1\text{-H}$ phases rules out the YS model and does not favor the new model by Lu *et al.** In contrast, the DH model trivially leads to the 3×1 periodicity by breaking the dimer bonds of all Si addimers. The straightforward structure model for the $3 \times 1\text{-H}$ phase based on the DH model is illustrated in Fig. 1(d). In this model, all dangling bonds of the Si surface layers (both the addimer layer and the termination

FIG. 2. Si $2p$ photoemission spectra for the $3C\text{-SiC}(001)3 \times 2$ (upper) and $3 \times 1\text{-H}$ (lower) surfaces taken at photon energies ($h\nu$) of 130 and 118 eV. The electron emission angle from the surface normal (θ_e) is zero or 60° . For the spectrum of the clean 3×2 surface, a decomposition into spin-orbit doublets is given (Ref. 13) with the Si $2p_{3/2}$ peak positions indicated by vertical lines for the four major components, B, S1, S2, and S3.

layer) are occupied by the H adatoms, and all Si addimer bonds are broken. This model will be further supported by spectroscopic information below.

Figure 2 shows Si $2p$ core-level spectra of the $3 \times 1\text{-H}$ surface: the spectrum taken at a photon energy ($h\nu$) of 130 eV and an emission angle (θ_e) of 60° is the most surface-sensitive one and that observed at $h\nu = 118$ eV and $\theta_e = 0^\circ$ is far less surface sensitive with a considerably larger probing depth.¹³ For comparison, a similar surface-sensitive spectrum for the 3×2 surface is shown with the decomposition into three distinctive surface components and the bulk component B. The S1, S2, and S3 surface components were assigned to the second layer Si atoms, which do not bond to the addimers, Si addimers of the topmost layer, and the second layer Si atoms bonded to addimers, respectively [see Fig. 1(c)].¹³ The origin of D was not clear, but it was proposed to be extrinsic to the 3×2 reconstruction.¹³ In the figure, the spectrum for the 3×2 surface is shifted to a lower binding energy by 0.27 eV in order to compensate for the band bending shift due to hydrogenation.¹⁴

A quick look at the Si $2p$ lineshape of the $3 \times 1\text{-H}$ surface reveals the existence of certain surface-related features at lower binding energy than the bulk component B. That is, the lower binding energy shoulders of the Si $2p$ spectra have enhanced intensities under more surface-sensitive conditions. The Si $2p$ line shape of the $3 \times 1\text{-H}$ surface were then quantitatively analyzed by a standard curve-fitting procedure described before.¹³ The decomposition with spin-orbit doublets of Voigt line shape is given in Fig. 3. The most important choice in this analysis concerns the number of constituting

FIG. 3. Decompositions of three Si $2p$ photoelectron spectra for the $3C\text{-SiC}(001)3 \times 1\text{-H}$ surface shown in Fig. 2. Each surface component ($S1'$, $S2'$, and $S3'$) is indicated with different hatching.

components and a wide variety of different sets of components were tried. Nevertheless, only the decomposition with four components beside B yields reasonable fits as shown in the figure. The resulting components are labeled $S1'$, $S2'$, $S3'$, and D' , following the apparent similarity to the 3×2 surface. It is evident that at least $S1'$, $S2'$, $S3'$ have surface origin due to their enhanced intensity under the surface-sensitive conditions. The final results of the fitting gave almost perfect fits to the experimental line shape with the same line widths for the $S1'$, $S2'$, and $S3'$ components: the Gaussian full width is 0.52 ± 0.01 eV for $S1'$ – $S3'$ and 0.68 ± 0.01 eV for B .¹³ The peak positions of $S1'$, $S2'$, $S3'$, and D' are shifted from the bulk component B [so-called surface core level shifts (SCLS)] by 0.37, 0.80, 1.21, and 1.67 eV, respectively. These SCLS values are reliably determined within ± 0.03 eV among independent fits of several different spectra.

The SCLS's of the $S1'$, $S2'$, $S3'$, and D' components are very well correlated to those of $S1$ (0.58 eV), $S2$ (0.92 eV), $S3$ (1.27 eV) and D (1.70 eV) on the 3×2 surface,¹³ indicating that these components have similar origins. Since the uncertainty in determining these relative shifts is about 0.05 eV when conservatively estimated, only the $S1$ and $S2$ components exhibit obvious shifts by 0.21 and 0.12 eV, respectively, upon forming the $3 \times 1\text{-H}$ surface. Furthermore, the relative intensities of these components are changed only marginally (less than 6% of the total integrated intensity) between the 3×2 and $3 \times 1\text{-H}$ surfaces. Therefore, it is very reasonable to conclude that the $S1$ – $S3$ and the correspond-

ing $S1'$ – $S3'$ components represent Si surface atoms of similar origins. It can also be deduced that the 3×2 and $3 \times 1\text{-H}$ surfaces have qualitatively similar surface structures, which is already implied by the reversible 3×1 – 3×2 phase transformation.

It is noteworthy that only the $S1$ and $S2$ components show nontrivial energy shifts after hydrogen adsorption, in contrast to $S3$. This suggests that mainly the surface Si atoms represented by $S1$ and $S2$ are affected directly by hydrogen adsorption. From the DH model and our previous assignments of $S1$ – $S3$ [Ref. 13] [see Fig. 1(c)], we conclude that the two types of surface Si dangling bonds at the first and second Si layers are terminated by the hydrogen adsorbates. Then the obvious structure model with broken Si dimers (to make a 3×1 periodicity from 3×2) is that shown in Fig. 1(d). Since the hydrogen adsorbates take charge from the Si surface atoms, the increased binding energies of $S1$ and $S2$ induced by hydrogen adsorption are chemically consistent. Within this model, the second-layer Si atoms represented by $S3$ have no direct bonding with hydrogen. This naturally explains the negligible change in the $S3$ SCLS by hydrogen adsorption. One may expect that $S2$ (representing the Si addimer atoms) should have a larger shift than $S1$ in contrast to the present result, since the addimer atoms bond to two hydrogen atoms. This is, however, not obvious since the dimer bonds are broken by hydrogen adsorbates and this bond breaking leads to additional redistribution of charge beyond the chemical bonding with hydrogen. Further support for our $3 \times 1\text{-H}$ model can be obtained by the following ARPES results for the valence bands.

Recently, four very distinct surface states were identified for the 3×2 surface, which were assigned as due to the eight dangling bond electrons within a surface unit cell of the DH model.¹⁴ Since the present $3 \times 1\text{-H}$ model has all dangling bonds saturated, all dangling-bond surface states of the 3×2 surface are expected to vanish by hydrogenation. Figure 4 shows a comparison of typical ARPES spectra taken at photon energies of 17.0 and 21.2 eV for the 3×2 and $3 \times 1\text{-H}$ surfaces. Indeed, the four surface states S_1 – S_4 of the 3×2 surface completely vanish on the 3×1 surface, as expected from the structure model of Fig. 1(d). The completion of the 3×1 phase in LEED coincides with the complete quenching of the four surface states. One may assume a structure model with only monohydride species on the $3 \times 1\text{-H}$ surface. In that case, the topmost surface atoms should have new dangling bonds created by breaking the dimer bonds, which is in contradiction to the experimental observation. That is, it is apparent that the structure given in Fig. 1(d) is the most reasonable choice for the $3 \times 1\text{-H}$ surface compatible with our LEED, Si $2p$ and ARPES results.

In addition to the quenching of the surface states, we observed a broad feature S_H for the $3 \times 1\text{-H}$ surface at 6.5–6.8 eV. This feature shows no significant dispersion and no photon-energy dependence of its energy. By comparing with hydrogenated Si surfaces,¹⁸ S_H is identified as a surface resonance due to the Si-H bonding states. Although there is no available theoretical calculation for the hydrogen adsorption on the 3×2 surface, a semiempirical calculation showed that monohydride species on the Si-terminated $\text{SiC}(001)2 \times 1$ surface has a Si-H bonding state at 4–6 eV below the bulk valence band maximum (VBM).¹⁹ The theory also pointed

FIG. 4. Comparison between the angle-resolved valence band photoelectron spectra taken at $h\nu=21.2$ and 17.0 eV for the $3C\text{-SiC}(001)3\times 2$ (solid lines) and $3\times 1\text{-H}$ (dots) surfaces. The major bulk (b_1) and surface-state ($S_1\text{--}S_4$) peaks are indicated for the 3×2 surface as reported before (Ref. 14). The spectra for the two surfaces are aligned by the position of the carefully determined valence band maximum (Ref. 14) in order to compensate the band bending shift. The H-induced resonance state S_H is indicated by shadowing.

out that while the Si-H bonding state of the $\text{Si}(001)2\times 1\text{-H}$ surface has a very sharp peak in the density of states, that on $\text{SiC}(001)2\times 1\text{-H}$ has a very broad density of states. Otherwise, the hydrogen adsorption on the $\text{Si}(001)2\times 1$ and $\text{SiC}(001)2\times 1$ surfaces are rather similar in both chemical and structural aspects.¹⁹ This result is in good agreement with the present observation of S_H surface resonance at $4.6\text{--}4.9$ eV below the VBM with a very broad shape (the VBM is located at ~ 1.9 eV below E_F).¹⁴ One complication here for the 3×2 surface is the coexistence of the monohydride and

dihydride species, and the presence of the double Si surface layers. Regardless of such a complication on the $3\times 1\text{-H}$ surface, the consistency between the theoretical results for the $\text{SiC}(001)2\times 1\text{-H}$ surface and the present experiments for the $3\times 1\text{-H}$ surface is remarkable.

Through LEED and photoemission studies of atomic hydrogen adsorption on the Si-rich $3C\text{-SiC}(001)3\times 2$ surface, we have provided further experimental support for the DH model of the 3×2 reconstruction with $\frac{2}{3}$ ML Si addimers. It should be stressed that the YS model¹² is out of any serious consideration due to its wrong 2×3 orientation. Also, the new model by Lu *et al.*¹⁷ turned out to be unfavorable since it cannot easily be converted to the $3\times 1\text{-H}$ phase. While the recent *ab initio* calculation by Pizzagalli *et al.* favored the YS model over the DH model through total energy consideration,¹⁶ the calculation by Gutierrez *et al.* favored the DH model for the Si-rich condition of the surface.¹⁵ Further, the calculation by Lu *et al.* indicated that a modified version of the DH model can be more stable than the YS model over a wide chemical potential region.¹⁷ While our previous and present photoemission results are consistently interpreted in terms of symmetric Si addimers as in the original DH model, all recent theoretical results suggested that the buckling of Si dimers yields lower energy configurations.^{15–17} We recently reported that the buckling (a lower symmetry 3×2 surface structure) occurs only on the defect-free 3×2 surface.⁸ The defect-free 3×2 surface is accessible only through Si evaporation and the present 3×2 and $3\times 1\text{-H}$ surfaces prepared through high-temperature annealing always exhibit missing dimer defects.⁸ We, thus, suggest that the missing dimer defects inhibit the buckling of the Si addimers through, most probably, the change of the surface stress. On the Si-terminated $\text{SiC}(001)$ surface, the importance of the surface stress has been indicated and the generation of missing dimer defects was shown to induce a phase transformation.²⁰ Theoretical considerations of the effect of missing dimer defects on the surface structure are promising in the understanding of the present discrepancy between the theoretical results and our photoemission studies.¹⁷

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