



ELSEVIER

Surface Science 516 (2002) L529–L534



www.elsevier.com/locate/susc

Surface Science Letters

# Structural and electronic properties of the Si-rich 6H-SiC(0001) surface

J.R. Ahn<sup>1</sup>, S.S. Lee, N.D. Kim, C.G. Hwang, J.H. Min, J.W. Chung<sup>\*</sup>

Physics Department, Basic Science Research Institute, Pohang University of Science and Technology, San 31 Hyoja Dong, Pohang 790-784, South Korea

Received 12 February 2002; accepted for publication 10 July 2002

## Abstract

We have investigated structural and electronic properties of the Si-rich 6H-SiC(0001)- $3 \times 3$  surface and the clean  $\sqrt{3} \times \sqrt{3}R30^\circ$  surface with high resolution electron-energy-loss spectroscopy. We find that the  $3 \times 3$  and the  $\sqrt{3} \times \sqrt{3}R30^\circ$  surfaces prepared at 980 °C are 2D Mott–Hubbard insulators primarily by evaluating the effective on-site Coulomb repulsion energy ( $U^*$ ) energy directly from our electron-energy-loss spectroscopy data. We find that a criterion of  $U^* \gg t^*$  ( $t^*$ : intersite hopping energy) is well satisfied for these surfaces thus confirming the typical nature of a Mott–Hubbard insulator.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Electron energy loss spectroscopy (EELS); Low energy electron diffraction (LEED); Surface electronic phenomena (work function, surface potential, surface states, etc.); Silicon carbide; Insulating surfaces

The SiC crystal is a promising material both for industrial applications and academic reasons [1–11]. As a device material it has characteristics far superior compared to that of Si-based materials for the production of high-temperature, high-power, and high-speed devices, mainly due to its stability at high temperature (<1000 °C) and its high thermal conductivity, exceeding that of copper.

The SiC crystal exists essentially in two different forms either a cubic (C) or a hexagonal (H)

structure [1] due to different stacking sequences of the Si–C layers. This produces several SiC polytypes such as 3C-SiC, 6H-SiC, 4H-SiC, and 2H-SiC, of which the crystalline surfaces have revealed various interesting properties. For instance, a bridge-bonded C dimer, unexpected on a reconstructed surface, was found on the 3C-SiC(001)- $c(2 \times 2)$  surface [2]. A mechanism of metallization accompanying a reversible surface transition at an elevated temperature was proposed for the surface transition from a semiconducting  $c(4 \times 2)$  surface to a metallic  $2 \times 1$  surface on the  $\beta$ -SiC(001) surface [3].

The most significant property, however, is the Mott–Hubbard nature of the insulating 6H-SiC(0001)- $\sqrt{3} \times \sqrt{3}R30^\circ$  ( $\sqrt{3}$  for brevity) and the

<sup>\*</sup> Corresponding author. Fax: +82-54-279-3099.

E-mail address: [jwc@postech.ac.kr](mailto:jwc@postech.ac.kr) (J.W. Chung).

URL: <http://www.postech.ac.kr/phys/snpl/>.

<sup>1</sup> Also at Physics Department and Atomic-Scale Science Research Center, Yonsei University, Korea.

Si-rich  $3 \times 3$  surfaces [6,8–12] which is in strong contradiction to the metallic surfaces predicted by recent theoretical calculations [4]. Although numerous earlier studies both experimental [6,9,10,12] and theoretical [4,5,8,11] have suggested that these surfaces are Mott–Hubbard insulators with the on-site Coulomb repulsion energy (or Hubbard energy)  $U$  of about 1.0 and 2.0 eV for the  $\sqrt{3}$  and the  $3 \times 3$  surface, respectively, no direct measurement of the Hubbard gaps have been made. Here we present such measurements of the Hubbard gaps of these Mott–Hubbard insulators by directly measuring  $U$  as an interband transition between split Hubbard bands with a high-resolution electron-energy-loss spectrometer (HREELS). We thus not only confirm the nature of Mott–Hubbard insulators of these surfaces but also eliminate the relatively large uncertainty ( $\sim 0.5$  eV) in estimating  $U$  (especially for the  $3 \times 3$  surface) in previous studies [6,8–12].

In order to probe the structural as well as electronic properties of the clean and the Si-rich 6H-SiC(0001) surfaces, we have utilized a variety of surface diagnostic tools including high-spatial-resolution low-energy-electron diffraction (HR-LEED), high-energy-resolution electron-energy-loss spectroscopy, and photoemission spectroscopy (PES). The HRLEED was a spot-profile-analysis LEED (Leybold SPA-LEED) with a nominal transfer width of 1200 Å installed in the HREELS chamber (Leybold ELS-22). The optimum energy resolution of the HREELS optics was 3 meV with a half acceptance angle of  $2^\circ$ . The base pressure of the HREELS chamber has been maintained below  $3 \times 10^{-11}$  Torr throughout the measurements. Electrons inelastically scattered (for HREELS) produced by incident beams of electrons or at an angle  $\theta_i$ . We have used a n-type 6H-SiC(0001) sample purchased from the Cree Research Co. We have prepared a clean Si-rich  $3 \times 3$  surface by in-situ depositing Si atoms evaporated from a Si(111) surface facing the sample surface in parallel at a distance about 5 cm apart from the sample. We have kept the SiC substrate at 850 °C during the deposition of Si atoms as prescribed earlier [9]. The  $3 \times 3$  surface thus prepared was found to transform into a clean  $\sqrt{3}$  surface when annealed at 980 °C as described below. All the measure-

ments were made with the sample at room temperature.

As shown in Fig. 1, we first consider the progressive change in surface structure as a function of annealing time ( $t_a$ ) at 980 °C. We find that the  $3 \times 3$  surface transforms first into a  $1 \times 1$  surface briefly and then into the  $\sqrt{3}$  surface. In order to quantify the structural change, we monitored integrated intensity of a characteristic fractional order LEED spot of the surface structures. The structural change is essentially due to the desorption of Si adatoms by annealing the surface at high temperature. The  $1 \times 1$  surface is believed to be a disordered surface undetected in previous scanning tunneling microscopy (STM) work [14]. It becomes ordered as more Si atoms desorbed with extended annealing. Note that there is an optimum annealing time ( $\sim 35$  min) for the best development of the  $\sqrt{3}$  surface indicating a condition for an equilibrium state.

The atomic arrangement of the  $\sqrt{3}$  surface has been determined by Coati et al., using a grazing-incidence X-ray diffraction [15], which is repro-

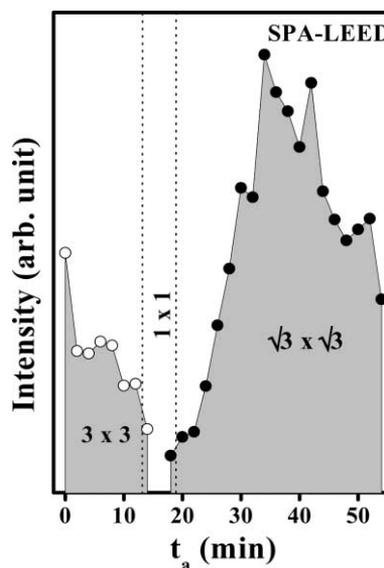


Fig. 1. Evolution of the integrated intensity of the fractional-order LEED spots from the  $3 \times 3$  (open circles) and the  $\sqrt{3}$  (filled circles) as a function of annealing time ( $t_a$ ) at 980 °C. The  $3 \times 3$  surface is seen to disappear completely briefly before the  $\sqrt{3}$  surface shows up.

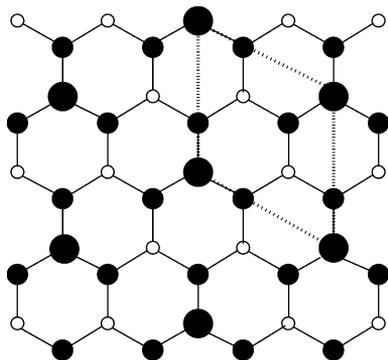


Fig. 2. The atomic arrangement of the  $\sqrt{3}$  surface where filled and open circles denote Si and C atoms, respectively. Note that each Si adatom (larger filled circles) locates at the  $T_4$  sites bonded with three underlying Si atoms in the top-adlayer. The dotted box is a unit cell of the  $\sqrt{3}$  surface.

duced in Fig. 2. There exists essentially two distinct kinds of Si atoms on this surface; the Si adatoms occupying the  $T_4$  sites on the Si-terminated top SiC bilayer and the Si atoms in the top adlayer bonded to the adatoms. One finds that a Si adatom saturates three dangling bond orbitals of the neighboring Si top layer atoms and produces a  $p_z$ -like dangling bond orbital. This structure, therefore, is predicted to produce a half-filled metallic dangling-bond band within one-electron local-density approximation in sharp contradiction to previous experimental observations of an insulating surface [6,8–12]. This has motivated a large number of recent studies as similarly done for other interacting electron systems [16–20]. This topic is discussed further in the following section.

Meanwhile the atomic structure of the Si-rich  $3 \times 3$  surface has been investigated by Starke et al. by using STM, LEED holography, and density functional theory [21]. They proposed a so-called twist model consisting of a Si tetramer on a twisted Si adlayer with cloverlike rings, which turned out to be favored energetically over the other models [22,23]. This model reproduced schematically in Fig. 3 shows several different types of Si atoms; The Si adatom, Si trimers, Si atoms in the Si adlayer, and Si atoms in the SiC bilayer underneath the topmost adlayer. A Si tetrahedral adatom cluster consists of a Si adatom and a Si trimer. Note that the Si adlayer is distorted remarkably

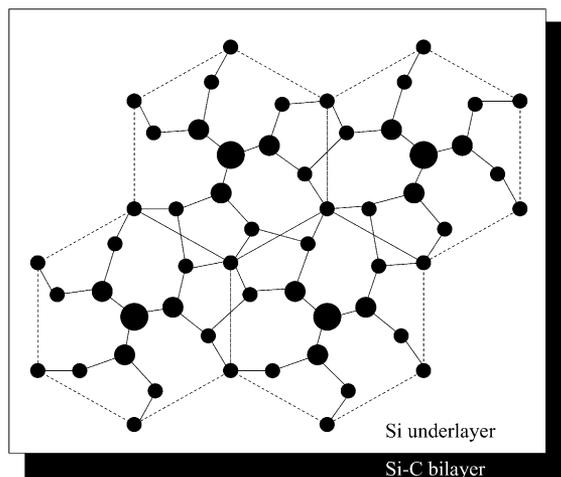


Fig. 3. The atomic arrangement of the  $3 \times 3$  surface consisted essentially of the Si adatoms (larger circles), the Si trimers (mid-sized circles), and remaining Si atoms (small circles) in the top-adlayer. These Si atoms form the Si underlayer (open rectangular background) above the SiC bilayer (filled rectangular background). Note that the Si atoms (small circles) in the outermost Si underlayer are significantly distorted from their sites in the  $1 \times 1$  structure.

when the Si tetramers are formed producing six Si atoms displaced towards the two undistorted Si atoms (see Fig. 3 in Ref. [21]).

Having characterized the structural changes, we now discuss the electronic properties of these surfaces. As shown earlier in previous studies, including angle-resolved photoemission, inverse photoemission [8–10,12,13], and theoretical calculations [4,8,11], the  $3 \times 3$  and the  $\sqrt{3}$  surfaces have well-defined filled and empty surface states considered as lower and upper Hubbard bands from which  $U$  of about 1.0 and 2.0 eV have been estimated, respectively. The precise values of  $U$ , however, have not been directly confirmed experimentally, for example, by measuring the band gaps from the inter-Hubbard band transitions, which is the issue discussed in this work. In HREELS, one can determine the effective on-site Coulomb repulsion energy  $U^*$  directly from the measured loss energy of a loss peak resulting from an inter-Hubbard band transition of a Mott–Hubbard insulator [16]. Fig. 4A shows the changes of loss features in our HREELS spectra as the

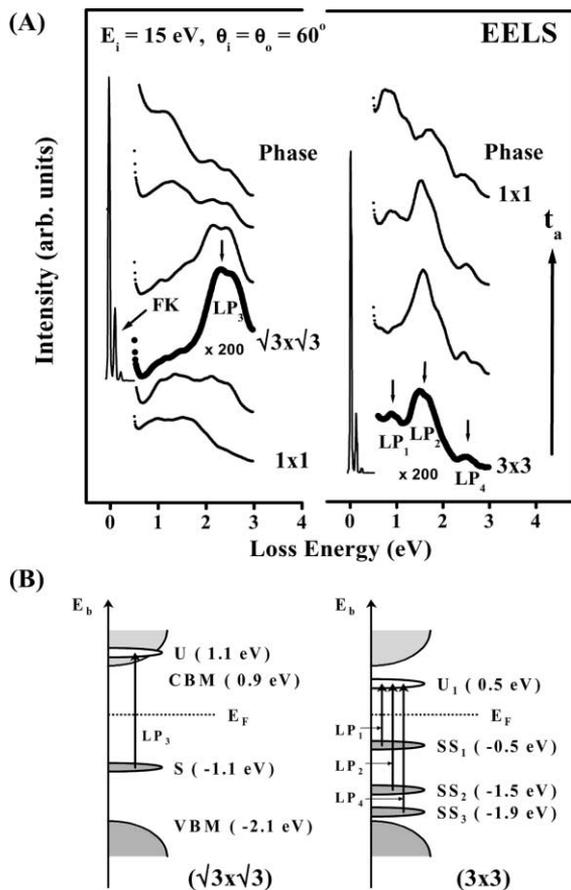


Fig. 4. (A) Evolution of HREELS spectra as a function of annealing time  $t_a$  at 980 °C. For the  $3 \times 3$  surface (bottom right), three characteristic loss peaks (marked with downward arrows),  $LP_1$ ,  $LP_2$ , and  $LP_4$  are seen while a strong peak  $LP_3$  is found for the  $\sqrt{3}$  surface. Note that phonon peaks denoted as FK dominate near the elastic peak. The vertical arrow denotes the time evolution. (B) Schematic band diagram to identify the loss peaks ( $LP_1$ – $LP_4$ ).

initial  $3 \times 3$  surface (bottom right) transforms into a  $1 \times 1$ , and then into the  $\sqrt{3}$  surface (mid left) eventually with increasing  $t_a$ . The tail of the elastic peak in Fig. 4A is dominated by the Fuchs–Kliener (FK) phonon peaks of bulk SiC [24]. From the two thick spectra in Fig. 4A for the  $3 \times 3$  and the  $\sqrt{3}$  surfaces, one finds that the  $3 \times 3$  surface is characterized by the three unique loss peaks centered at 0.9 eV ( $LP_1$ ), 1.5 eV ( $LP_2$ ), and 2.5 eV ( $LP_4$ ) whereas the  $\sqrt{3}$  surface is dominated by a

strong loss peak centered at 2.3 eV ( $LP_3$ ). Notice that the  $LP_2$  dominates in intensity over the other peaks ( $LP_1$  and  $LP_4$ ) for the  $3 \times 3$  surface. Careful inspection shows that these loss peaks consist of two narrowly spaced peaks of which the separation ( $0.2 \leq \Delta E \leq 0.4$  eV) varies slightly with increasing  $t_a$ . Previous spin-polarized band calculation predicts such a splitting due to a ferromagnetic alignment at zero temperature [11]. Intrinsic defects found on the SiC surfaces may also cause such splitting by creating another band slightly shifted ( $\sim 0.2$  eV) from a surface band as observed in recent study [25].

Now we discuss the origin of these loss peaks largely by considering the surface electronic bands determined in previous studies [8–12]. Johansson et al. showed that there are three filled surface bands with binding energies of  $-0.5$  eV ( $SS_1$ ),  $-1.5$  eV ( $SS_2$ ), and  $-1.9$  eV ( $SS_3$ ) below Fermi energy and one empty band at  $+0.5$  eV ( $U_1$ ) above Fermi energy for the  $3 \times 3$  surface as schematically drawn in Fig. 4B (right) [12]. These surface bands are found to be quite flat with bandwidth less than 0.1 eV except the  $SS_2$ , which is found at  $-1.2$  eV at the Brillouin zone center (see Fig. 4 in Ref. [12]). From the energies of these bands, we ascribe  $LP_1$  ( $LP_2$ ) to the interband transition between the filled  $SS_1$  ( $SS_2$ ) band and the empty  $U_1$  band.  $LP_4$  may then be an interband transition between the  $SS_3$  and  $U_1$  bands. Such an identification makes sense when considering the relative intensities of the peaks in previous PES spectra [12], i.e., the peaks associated with  $LP_1$  (or  $LP_4$ ) are much weaker than those associated with  $LP_2$ . Other possible interband transitions such as from the three surface bands to the bulk conduction band and from the bulk valence band to the unoccupied Hubbard band are thought to form the background intensity. By identifying  $LP_1$  as an inter-Hubbard band transition, we obtain effective on-site Coulomb energy (or a Hubbard gap)  $U^* = 0.9$  eV for the  $3 \times 3$  surface. When a similar argument is applied to the  $\sqrt{3}$  surface, we identify  $LP_3$  peak as a Hubbard gap between the lowest filled surface band ( $-1.0$  eV) and the lowest empty band ( $+1.0$  eV) of the surface [8–10,13] (left in Fig. 4B) thus producing  $U^* = 2.3$  eV from its loss energy. Our values of  $U^*$  for both the  $3 \times 3$  and  $\sqrt{3}$  surfaces are

in good accordance with previous measurements of PES [8–10,12] and of scanning tunneling spectroscopy studies [6,25].

It is now well recognized that the  $3 \times 3$  and  $\sqrt{3}$  surfaces are Mott–Hubbard type insulators by numerous previous studies both experimentally [6,9,10,12] and theoretically [4,5,8,11]. The insulating property is explained by the strong  $U^*$  compared to the effective intersite hopping energy  $t^*$ , which splits a metallic band near the Fermi level into a completely filled lower Hubbard band and a completely empty upper Hubbard band with a Hubbard gap  $U^*$ . The metallic bands commonly expected on both surfaces stem from the half-filled dangling bonds of the Si adatoms. We obtain the effective Hubbard energy  $U^* = 0.9$  eV for the  $3 \times 3$  surface and 2.3 eV for the  $\sqrt{3}$  surface directly from the loss energies representing the inter-Hubbard band transitions in Fig. 4. We now examine if  $U^*/t^* \gg 1$  for these surface [26]. The bandwidths of the lower band and upper Hubbard bands have been measured to be about 0.2 and 0.34 eV [8,9]. We may estimate  $t^*$  from the relation  $t^* = BW/2z$  ( $z$  is a coordination number, 3 and 4 for a Si adatom of the  $3 \times 3$  and the  $\sqrt{3}$  surfaces, respectively). The value  $t^* \leq 0.043$  that we obtain satisfies the criterion  $U^*/t^* \gg 1$  for a Mott–Hubbard insulator very well. The enhanced  $U^*$  for the  $\sqrt{3}$  surface compared to that of the  $3 \times 3$  surface may be understood in terms of the reduced dielectric constant  $\sim 6.5$  of the SiC sample compared to  $\sim 12$  of the Si sample due to the presence of the Si buffer layers in the  $3 \times 3$  surface.

In conclusion, we find that the  $3 \times 3$  surface obtained by depositing Si atoms on a 6H-SiC(0001) surface at 850 °C transforms into a  $\sqrt{3}$  surface when annealed at 980 °C. By identifying the characteristic loss features in our HREELS spectra, we find that the  $3 \times 3$  and the  $\sqrt{3}$  surfaces are 2D Mott–Hubbard insulators as proposed previously. We observe the inter-Hubbard band transitions of these surfaces, and we determine the effective on-site Hubbard repulsion energy  $U^* = 0.9$  and 2.3 eV for the  $3 \times 3$  and the  $\sqrt{3}$  surfaces, respectively from their loss energies of the characteristic loss peaks. We further show that a criterion  $U^*/t^* \gg 1$  for a Mott–Hubbard insulator is well satisfied for these surfaces.

## Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-99-015-DP0134).

## References

- [1] C.H. Park, B.H. Cheong, K.H. Lee, K.J. Chang, Phys. Rev. B 49 (1994) 4485 and references therein.
- [2] H.W. Yeom et al., Phys. Rev. Lett. 83 (1999) 1640.
- [3] V.Yu. Aristov, L. Douillard, O. Fauchoux, P. Soukissian, Phys. Rev. Lett. 79 (1997) 3700.
- [4] J.E. Northrup, J. Neugebauer, Phys. Rev. B 57 (1998) R4230.
- [5] V.I. Anisimov, A.E. Bedin, M.A. Korotin, G. Santoro, S. Scandolo, E. Tosatti, Phys. Rev. B 61 (2000) 1752; G. Santoro, S. Scandolo, E. Tosatti, Surf. Sci. 454 (2000) 534.
- [6] V. Ramachandran, R.M. Feenstra, Phys. Rev. Lett. 82 (1999) 1000.
- [7] G. Santoro, S. Scandolo, E. Tosatti, Phys. Rev. B 59 (1999) 1891; S. Scandolo, F. Ancilotto, G.L. Chiarotti, G. Santoro, S. Serra, E. Tosatti, Surf. Sci. 402 (1998) 808.
- [8] J. Furthmüller, F. Bechstedt, H. Hüsken, B. Schröter, W. Richter, Phys. Rev. B 58 (1998) 13712.
- [9] J.-M. Themlin, I. Forbeaux, V. Langlais, H. Belkhir, J.-M. Debever, Europhys. Lett. 39 (1997) 61.
- [10] L.I. Johansson, F. Owman, P. Martensson, C. Persson, U. Lindefelt, Phys. Rev. B 53 (1996) 13803.
- [11] M. Rohlfing, J. Pollmann, Phys. Rev. Lett. 84 (2000) 135.
- [12] L.S.O. Johansson, L. Duda, M. Laurenzis, M. Kriefewrith, B. Reihl, Surf. Sci. 445 (2000) 109.
- [13] C. Benesch, M. Fartmann, H. Mertz, Phys. Rev. B 64 (2001) 205314.
- [14] L. Li, I.S.T. Tong, Surf. Sci. 351 (1996) 141.
- [15] A. Coati, M. Sauvage-simkin, Y. Garreau, R. Pinchaux, T. Argunova, K. Aid, Phys. Rev. B 59 (1999) 12224.
- [16] J.R. Ahn, S.S. Lee, N.D. Kim, J.H. Min, C.G. Hwang, J.W. Chung, Phys. Rev. Lett. 84 (8) (2000) 1748.
- [17] J.M. Carpinelli et al., Nature (London) 383 (1996) 398.
- [18] H.H. Weitering et al., Phys. Rev. Lett. 78 (1997) 1331.
- [19] K.-D. Lee, J. Chung, Phys. Rev. B 57 (3) (1998) R2053.
- [20] K.D. Lee, J.R. Ahn, J.W. Chung, Appl. Phys. A (Rap. Commun.) 68 (1999) 115.
- [21] J. Schardt, J. Bernhardt, U. Starke, K. Heinz, Phys. Rev. B 62 (2000) 10335; U. Starke, J. Schardt, J. Bernhardt, M. Franke, K. Reuter, H. Wedler, K. Heinz, J. Furthmüller, P. Käckell, F. Bechstedt, Phys. Rev. Lett. 80 (1998) 758.
- [22] R. Kaplan, Surf. Sci. 215 (1989) 111.

- [23] M.A. Kulakov, G. Henn, B. Bullemer, *Surf. Sci.* 346 (1996) 49.
- [24] J.W. Liu, F.Q. Xie, Q.Z. Zhang, K.H. Wu, X.C. Ma, E.G. Wang, W.X., Liu, *Thin Solid Films* 375 (2000) 77.
- [25] V.A. Gasparov, M. Riehl-Chudoba, B. Schröter, Wo. Richter, *Europhys. Lett.* 51 (2000) 527.
- [26] N.F. Mott, *Metal-Insulator Transitions*, second ed., Taylor and Francis, New York, 1990.