Physical Origin of Hydrogen-Adsorption-Induced Metallization of the SiC Surface: *n*-Type Doping via Formation of Hydrogen Bridge Bond

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We perform first-principles calculations to explore the physical origin of hydrogen-induced semiconductor surface metallization observed in β-SiC(001)-3 × 2 surface. We show that the surface metallization arises from a novel mechanism of *n*-type doping of surface band via formation of hydrogen bridge bonds (i.e., Si-H-Si complex). The hydrogen strengthens the weak Si-Si dimers in the subsurface by forming hydrogen bridge bonds, and donates electron to the surface conduction band.

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SiC has long been recognized as a better electronic material than Si for high-power, high-frequency, and high-temperature applications. Its development, however, has been hindered by the difficulty in growing SiC single crystals. Recent advance made by Nakamura *et al.* [1] in producing ultrahigh-quality SiC wafers is expected to pave the way for future development of SiC-based electronic devices [2]. In addition to single crystal growth, surface treatment and processing is the next important step in electronic device fabrication. These include, for example, surface cleaning, chemical surface passivation, and building surface electronic contact.

In general, an intrinsic semiconductor surface can be metallic due to the presence of dangling bonds, which introduce surface states in the gap. The dangling bonds can be passivated by monovalent atoms such as hydrogen. Therefore, it is commonly believed that hydrogen surface adsorption (passivation) will make a metallic semiconductor surface semiconducting. Surprisingly, a recent experiment by Derycke *et al.* [3] showed for the first time that hydrogen adsorption on β-SiC(001)-3 × 2 surface induces surface metallization (β-SiC is a cubic polymorph of SiC, and is extensively studied because of its potential device application). This finding not only is scientifically interesting but may also have important technological implications, such as on building electronic contacts on chemically passivated surface and interfacing semiconductors electronically with biological systems. Furthermore, they explained the H-adsorption induced SiC surface metallization due to formation of rows of Si dangling bonds induced by H breaking the subsurface Si dimers.

Here, we perform extensive first-principles calculations of structural and electronic properties of β-SiC(001)-3 × 2 surfaces, as a function of H coverage. We confirm the physical phenomenon of H-induced SiC surface metallization observed by Derycke *et al.* [3], but disagree with their explanation of the physical origin of this unusual phenomenon. Our calculations reveal that the metallization is induced by formation of a particular form of H-adsorption structure in the surface region, the Si-H-Si complex, which is much stronger than the original weak Si-Si dimers in the subsurface and more importantly donates one electron (per hydrogen) to the original semiconducting surface conduction band. Therefore, the surface metallization is originated from a *n*-type doping effect; the hydrogen functions effectively as an electronic dopant via formation of the hydrogen bridge (HB) bond pushing up the Fermi level to the bottom of conduction band without changing the overall band structure. It is not energetically favorable for H to break the subsurface Si dimers to metallize the SiC surface by forming dangling bonds, as suggested by Derycke *et al.* [3].

Our calculations are performed by using the density-functional-theory method [4] in the formalism of plane-wave ultrasoft pseudopotential [Vanderbilt scheme [5] and

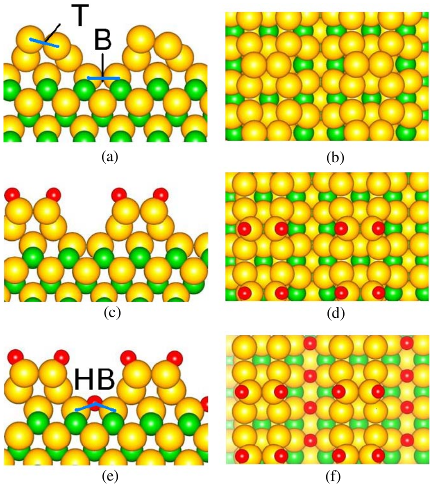

FIG. 1 (color online). Structure of SiC surface with and without H adsorption. (a), (c), and (e) show the side view of the clean surface, the surface with H at top dimer, and the surface with H at both top and bottom dimers, respectively. (b), (d), and (f) show the corresponding top view. Red atoms stand for H atom, green for C, and yellow for Si. *T* and *B* indicate the top and bottom dimers which are active in H adsorption. *HB* indicates the H-bridge bond.

PW-91 exchange-correlation potential [6]] within the generalized gradient approximation (GGA) [7]. The plane-wave cutoff energy is about 440 eV. Integration over the Brillouin zone is done using Monkhorst-Pack scheme [8] with 7×11 k points for atomic structure relaxation and 11×17 k points for electronic structure calculation.

The clean and H-adsorbed SiC surfaces are modeled by supercells of slab, using the theoretically optimized SiC lattice constant of 3.089 Å, which is in good agreement with the experimental value of 3.082 Å. The supercell includes six stoichiometric Si and C atomic layers alternating in the (001) direction, plus two additional Si adlayers on the top surface [9] and a vacuum layer of 6.5 Å. Three bottom C and Si layers are frozen at their bulk positions to simulate the SiC substrate. The dangling bonds of the bottom carbon layer are saturated with hydrogen atoms to eliminate their surface effects. Hydrogen adsorption of different coverage is modeled by adding H atoms on the top surface.

The structure of a 3×2 reconstructed clean β-SiC(001) surface was first optimized, as shown in Figs. 1(a) and 1(b). Our results agree well with the two-adlayer asymmetric-dimer model, proposed as the most stable surface structure by the previous theoretical study [9] and experimental observations [10,11]. The two Si adlayers are under large stress, resulting from the large mismatch between Si and SiC lattices. To partially relax the mismatch stress, the Si adlayers reconstruct forming a long-range 3×2 ordering in which the tilted top Si-Si dimers (T dimers) rest on the slip Si-Si dimers in the second layer [9]. Below the two Si adlayers is the third Si layer, which would have been the surface layer of a bulk-terminated β-SiC(001) surface. The mismatch stress also induces a large distortion in this third Si layer; in particular, it results in the formation of subsurface Si-Si dimers (B dimers) in the third layer at the bottom of the trench between two surface dimer rows [see Fig. 1(a)]. Our calculations give an optimized bond length of B dimer as 2.43 Å, in good agreement with the previous calculation [9].

Next, we determine the surface structures and energies associated with H adsorption. Because the dangling bonds on the surface T dimers make them most reactive toward H, the initial H deposition will bond to the T dimers to saturate the surface dangling bonds. The resulting H adsorption energy is calculated to be -4.27 eV per atom, corresponding to the typical H-Si bond formation energy. The optimized structure is shown in Figs. 1(c) and 1(d). As the dangling bonds being saturated by H, the original tilted (asymmetric) T dimers become flat (symmetric), with the bond length being increased from 2.30 Å to 2.40 Å, while the bond length of the B dimers in the third layer remain unchanged at 2.43 Å.

After all the surface T dimers are saturated by H, further deposited H atoms will likely attack the weakest Si bonds in the system, i.e., the subsurface B dimers in the third layer exposed at the bottom of the trenches which have the longest bond length and endure the stress due to the lattice mismatch. This is indeed confirmed by our calculations. Furthermore, because of the steric interactions, we find that only 1 H atom can possibly bind to the B dimer with energy gain. The corresponding H-adsorption energy is calculated to be -2.51 eV per atom.

The sequence and amount of H adsorption we obtained, i.e., first 2 H atoms on the surface T dimer followed by 1 H atom on the subsurface B dimer, agree with recent experiments by Derycke *et al.* [3]. However, there is an important difference between our optimized H-adsorption structure and the structure they inferred. Specifically, they have suggested that as a single H atom attacks the B dimer, it breaks up the B dimer binding to one of the two Si atoms while creating a dangling bond on the remaining other Si atom. And then, the created dangling bonds were regarded as the physical origin of the observed surface metallization. On the contrary, our calculations indicate that it is not energetically favorable for 1 H atom to break the subsurface B dimer bond forming a single H-Si bond plus a Si dangling bond. Instead, the most favorable structure is to form a unique Si-H-Si complex, as we discuss below.

Our optimized structure is shown in Figs. 1(e) and 1(f). It is interesting to see that the H atom resides exactly at the middle between the two Si atoms that form the original B dimer. The distance between the two Si atoms is increased to 3.06 Å from the original value of 2.43 Å. The resulting distance between H and Si is 1.65 Å. In order to further verify this structure, we have tried three different initial configurations including (i) putting the H atom closer to the left Si atom of the B dimer in every row at a distance of 1.5 Å; (ii) putting the H atom closer to the left and right Si atom of the B dimer alternately in every other row at a distance of 1.5 Å; (iii) putting the H atom closer to the left and right Si atom alternately as in (ii) and rotating the H-Si bond by about 30° but keeping the distance between neighbor H atoms large enough to prevent them from forming H_2 molecule. In all three cases, the H atom moves to the middle of the two Si atoms upon relaxation, converging to the same final structure. Therefore, we confirm that the structure shown in Figs. 1(e) and 1(f) is the most energy-favorable one.

This unique Si-H-Si three-center structural complex has in fact been identified before as three-center bond [12] or hydrogen bridge (HB) bond [13]. In forming the HB bond by adding a H atom, the original Si-Si bond is weakened, with its interatomic distance increased from 2.43 Å to 3.06 Å, but at the same time two moderate weak H-Si bonds are formed, with a bond length of 1.65 Å slightly longer than the optimal value of 1.48 Å. This gives an overall energy gain of 2.51 eV. In contrast, it is energetically unfavorable for the structure with dangling bond proposed by Derycke *et al.* [3], because it would overall cost energy (about 0.56 eV) to form it. (On average, it costs 2.94 eV to break the Si-Si bond and 2.00 eV for one Si dangling bond, but it only gains 4.38 eV to form 1 H-Si bond.) Thus, both our calculation and physical intuition support the formation of HB bond, but not the structure with Si dangling bond [3].

The above physical picture is further confirmed by charge density plot in the plane of Si-H-Si complex, as shown by the inset of Fig. 2. In accordance with the symmetric complex structural geometry about H atom, the charge density appears symmetric about H atom, too. Thus, it excludes the possibility of a Si-H bond on one side and a Si dangling bond on the other side, as proposed by Derycke *et al.* [3]. There is a slight charge concentration around the H atom, indicating H atom is likely negatively charged (note: H has higher electronegativity than Si). This is very similar to the case of H in the low density region of bulk Si as reported by Van de Walle *et al.* [12], which also showed similar charge distribution around H. There is no noticeable charge density between the two Si atoms, indicating that the strong Si-Si covalent bond is largely broken in the complex.

Since we can discard the presence of Si dangling bonds, the H-adsorption induced SiC surface metallization must have originated from a different physical mechanism. To resolve this puzzle, we have examined the evolution of electronic structure of the β-SiC(001)-3×2 surface as a function of H coverage, focusing on the effect of HB bond on surface band structure. Figure 2(a) shows the band structure of the clean β-SiC(001)-3×2 reconstructed surface [see Figs. 1(a) and 1(b)], which agrees well with previous calculation [9]. The clean surface is semiconducting with an energy gap of 0.75 eV. The two flat bands labeled D_2 and D_1 are, respectively, the lowest unoccupied surface band (state) and the highest occupied surface band, originated from the dangling bond of *T* dimer [9].

Figure 2(b) shows the band structure of the β-SiC(001)-3×2 surface with *T* dimers passivated by H atoms [i.e., the structure shown in Figs. 1(c) and 1(d)]. Note that the D_1 and D_2 bands disappear because the dangling bonds on the *T* dimers are removed. It is well known that because of its large binding energy the Si-H bonding states are well below the Fermi level, and Si-H antibonding states are well above the Fermi level. Furthermore, as expected, the passivation of surface dangling bonds does not cause metallization of the surface, but instead increases the semiconducting surface band gap to about 1.15 eV.

Figure 2(c) shows the band structure of the β-SiC(001)-3×2 surface with H-passivated *T* dimers plus the HB bonds formed by the additional H adsorbed on the *B* dimers. The overall band structure in Fig. 2(c) is similar to that in Fig. 2(b), but the position of the Fermi level is very different in the two cases. Most important, the Fermi level in Fig. 2(b) locates in the gap above the top of the valence band, rendering a semiconducting surface; while the Fermi level in Fig. 2(c) locates above the gap at the bottom of the valence band, rendering a metallic surface. Thus, it is the HB bond formation that has induced surface metallization, which has been experimentally observed by Derycke *et al.* [3].

Figure 2(c) does not exhibit any flat band related to the dangling bonds near the Fermi energy, which is consistent with our optimized HB bond structure without any dangling bond [see Figs. 1(e) and 1(f)]. In fact, the formation of HB bond does not change the overall band dispersions of the original valance and conduction bands substantially, which is consistent with the moderate bonding involved in its formation. Its major effect is to shift the Fermi level upward into the conduction band by adding one more electron to the system. This effect resembles *n*-type doping of semiconductors, causing conducting without changing the original band structure.

The above results clearly reveal that the H-adsorption induced metallization of β-SiC(001)-3×2 semiconductor surface is originated from the formation of a unique Si-H-Si complex structure, the HB bond, which provides effectively an *n*-type surface doping effect with H acting as an electron donor. This is somewhat surprising, because usually H, a ubiquitous monovalent surfactant, acts to passivate existing surface carriers by saturating surface dangling bonds. Its function as an electron dopant in the surface, as we have shown here, is rare. However, H has been reported before as an electron donor in bulk semiconductors. For example, H has been reported to form the HB bonds at the carbon vacancy in bulk 3*C*-SiC acting as a donor center [14,15] and induce an *n*-type doping in $CuInSe_2$ and $CuGaSe_2$ via formation of H complex structures [16].

The physical reason for H in the HB bond to act as an electron donor is the weak bond formed between the H and Si. In other words, the electron in the H does not participate

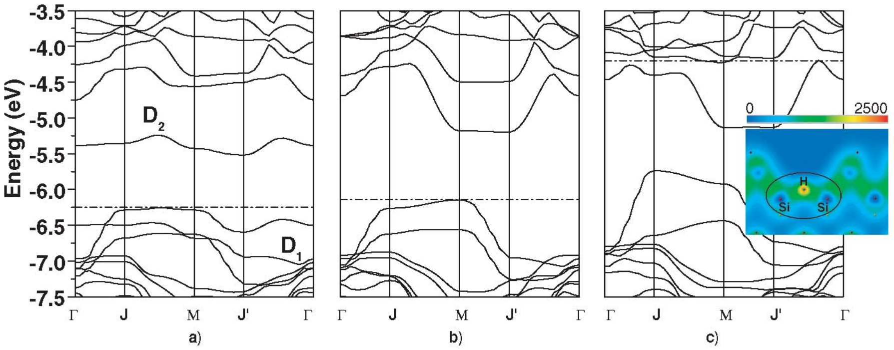

FIG. 2 (color). Band structure of β-SiC(001)-3×2 reconstruction surface with and without H adsorption. (a) Clean surface; (b) only dangling bonds of *T* dimers are saturated by H; (c) dangling bonds of *T* dimers are saturated and H-bridge bonds are formed by H atoms and *B* dimers. The dashed lines denote the Fermi level. The inset shows the charge density in the plane of the H-bridge bond.

in forming a strong covalent bond with Si atoms, but remains as an extra "free" electron. This is reflected by band structure in Fig. 2, in which H shifts the Fermi level upward above the surface conduction band minimum by adding an electron but without changing substantially the overall surface band structure.

The appearance of Si-H-Si complex reveals a specific type of "passivation" process different from normal electric passivation. In some particular geometrical structures with spatial restriction, such as the trench in the surface as discussed in the present work or vacancy in crystals [14,15], the number of H atoms on passivation sites is limited, which prevents the normal electric passivation in the systems. Less H atoms on such sites causes the formation of some complex, leading to some unique metallization behavior.

So far, our calculations have confirmed the observation of H-adsorption induced SiC surface metallization by Derycke *et al.* [3] but disagreed with their explanation. We show that the surface metallization is physically originated from the formation of HB bonds in the subsurface (third layer) rather than the formation of Si dangling bonds. One reason that Derycke *et al.* have proposed the dangling-bond formation is based on the observation of additional H-Si vibration frequencies appearing upon H adsorption in infrared absorption spectroscopy (IRAS) [3]. We have also performed some calculations to determine the effect of HB bond on surface H-Si vibrations, which offers an alternative explanation to their IRAS measurements.

We calculated the vibrational spectrum corresponding to H-Si stretching modes with Hessian matrix derived by finite differences. For structure B (with H atoms adsorbed only on T dimers), the H-Si bond stretching frequencies is calculated to be 2100 cm^{-1} for the symmetric (S) mode and 2095 cm^{-1} for the asymmetric (A) mode, respectively. These agree well with the IRAS spectra showing multiple frequency bands ranging from 2100 cm^{-1} and 2118 cm^{-1} [3] and with the similar vibrations on Si(001) surface by a small blue shift [17].

After H atoms are adsorbed on the B dimers in addition to T dimers [see Figs. 1(e) and 1(f)], we found that the H-Si stretching frequencies on the T dimers are increased to 2150 cm^{-1} (S) and 2046 cm^{-1} (A). These agree well with the IRIS frequency band centered at 2140 cm^{-1} [3]. We note that Derycke *et al.* has assigned the frequency at 2140 cm^{-1} to the H-Si stretching mode with H adsorbed on the subsurface B dimer, as the evidence of dangling-bond formation. In contrast, however, our calculations show that their assignment is likely incorrect; the frequency of 2140 cm^{-1} arises still from the H-Si stretching mode with H adsorbed on the surface T dimer, but only shifted by the presence of the HB bond in the subsurface. The H-Si stretching mode in the HB bond is very soft, at about 1100 cm^{-1}, consistent with its weak H-Si bonding. Thus, it is the HB bond that causes the surface H-Si vibration frequency shift, without the need to incorporate a subsurface H-Si bond and a dangling bond as proposed by Derycke *et al.* [3].

In summary, we have investigated the physical origin of hydrogen-adsorption-induced metallization of β-SiC(001)-3 $\times$ 2 surface by first-principles calculations of H-adsorption structure and energy, surface electronic structure, and H-Si vibration spectra. All the results consistently show that the surface metallization is originated from the formation of a unique Si-H-Si complex structure, the HB bond, in the subsurface. The H in the HB bond acts as an electron donor, donating one electron per H to the surface band and shifting the Fermi energy above the bottom of conduction band. We believe the physical mechanism we discover here might be important in some other semiconductor surfaces.

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Note added.—We just noticed another work addressing the same issue that was published recently [18].

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