

## Novel Pathway to the Growth of Diamond on Cubic $\beta$ -SiC(001)

K. Kong,<sup>1</sup> M. Han,<sup>2</sup> H. W. Yeom,<sup>3</sup> Y. Miyamoto,<sup>4</sup> O. Sugino,<sup>4</sup> T. Sasaki,<sup>5</sup> T. Ohno,<sup>5</sup> and B. D. Yu<sup>2</sup>

<sup>1</sup>*IQUIPS, University of Seoul, 90 Jeonnong-dong, Dongdaemun-gu, Seoul 130-743, Korea*

<sup>2</sup>*Department of Physics, University of Seoul, 90 Jeonnong-dong, Dongdaemun-gu, Seoul 130-743, Korea*

<sup>3</sup>*ASSRC & Institute of Physics and Applied Physics, Yonsei University, 134 Shinchon, Seoul 120-749, Korea*

<sup>4</sup>*Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305-8501, Japan*

<sup>5</sup>*National Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan*

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By carrying out first-principles calculations on diamond-forming processes, we predict a method for the heteroepitaxial growth of diamond on cubic  $\beta$ -SiC(001). In the method, we used two processes: (i) the preformation of an  $sp^3$ -like surface configuration of  $\beta$ -SiC(001) by the adsorption of group-V surfactants; (ii) the successive growth of diamond by the segregation of the surfactants onto a surface and the desorption of surface hydrogen. Analyzing the segregation energies, we found that the atomic size effect plays a crucial role in the surfactant-mediated growth of diamond on  $\beta$ -SiC(001).

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The quest for methods to grow thin films of diamond on a nondiamond substrate has attracted great interest due to its enormous potential for technological applications, such as hard coatings, bearing surfaces, heat sinks, and microelectronic devices [1–9]. Thin films of diamond are typically grown as a thermodynamically metastable phase using a low pressure technique. For the growth of the diamond crystals, the presence of atomic hydrogen helping  $sp^3$  hybridization of carbon atoms has been considered essential [1–3], though it partly hinders the growth due to the poor reactivity of the H-terminated surface. Some studies reported that diamond could be synthesized at low pressure in a hydrogen-free environment [4–6]. The growth mechanism of diamond in those cases, however, remains poorly understood, largely because of the lack of a detailed knowledge of the diamond-forming atomic process and structural properties at the growth front. This is one of the major obstacles to further development in diamond science and technology.

Here we studied the atomic processes for the growth of diamond on a single crystalline  $\beta$ -SiC substrate in a hydrogen-free environment. Silicon carbide has been widely used as one of the probable substrate materials for the wide-band-gap semiconductors. Actually, the cubic phase of a wide-band-gap semiconductor GaN for blue-light emitting diode devices and blue lasers has been grown on SiC [10]. Compared to silicon often used as a substrate for diamond heteroepitaxy [7,8], silicon carbide seems to be more reasonable [11] because the lattice mismatch between diamond and  $\beta$ -SiC,  $\delta = 22\%$ , is much smaller than that between diamond and silicon,  $\delta = 52\%$ . Furthermore, it also offers the advantage of a higher melting temperature. When growing diamond on  $\beta$ -SiC, a C-terminated  $\beta$ -SiC surface with a (001) crystallographic orientation is naturally chosen as the substrate. It has been known that the C-terminated  $\beta$ -SiC surface exhibits a  $c(2 \times 2)$  structure consisting of unique  $sp$ -bonded (triply bonded) carbon dimers at bridge sites [see Fig. 1(a)], not

of conventional  $sp^3$ -bonded dimers at diamondlike lattice sites [12–15]. As a result, subsequent incoming carbon adatoms suffer from difficulties in growing pseudomorphic diamond (001) overlayers on  $\beta$ -SiC(001).

With the aim of overcoming such a surface-structure problem and finding out promising atomic processes for the diamond growth on  $\beta$ -SiC, we examined possible atomic configurations during the growth of diamond on the C-rich  $\beta$ -SiC(001) surface. By employing first-principles simulations, we found that the growth of diamond on  $\beta$ -SiC(001) can be achieved by using a hydrogen-free, surfactant-based growth technique [16]. In the technique, surfactants of a group-V element, instead of hydrogen, help the preformation of  $sp^3$  hybridization of carbon atoms at diamond lattice sites, removing the unfavorable  $sp$ -bonded surface configuration against the epitaxial growth of diamond. Subsequently, incorporation of carbon into the  $\beta$ -SiC(001) substrate proceeds by the segregation of the surfactants

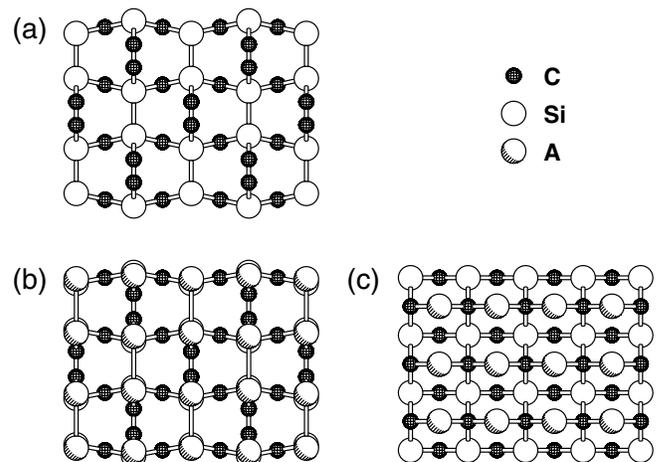


FIG. 1. Top views of the various surface-structure models: (a) the  $sp$ -bonded model for “clean”  $c(2 \times 2)$   $\beta$ -SiC(001), (b) the bridge-dimer model, and (c) the  $sp^3$ -like bond model for group-V-covered  $\beta$ -SiC(001).

onto the growth front and the desorption of surface hydrogen atoms. This approach will allow us to grow a high quality of diamond on SiC which has not been possible using conventional growth techniques, thereby opening a wider range of potential applications of thin diamond films.

All calculations were carried out using the density-functional theory (DFT) [17], norm-conserving, fully separable pseudopotentials [18], and a plane-wave basis with a cutoff energy of 40 Ry as implemented in the FHI96MD code [19]. Most calculations were done with the local-density approximation (LDA) of the exchange-correlation functional [20], but the main results were checked using the generalized-gradient approximation (GGA) [21]. To simulate the diamond growth process on  $\beta$ -SiC(001), we used a repeating slab structure consisting of one surfactant layer, one carbon adatom layer, and five SiC layers with a 7.3 Å vacuum region. The bottom of the slab was terminated by hydrogen atoms. For the  $\beta$ -SiC slab, we used a theoretical lattice constant  $a_0 = 4.32$  Å (4.37 Å) of bulk SiC in the LDA (GGA) calculations. We relaxed all atoms in the slab except for the bottom-most Si, C, and H atoms. Geometry optimization was terminated when the remaining forces were smaller than 0.05 eV/Å. We also performed test calculations using a more extensive set of parameters, for example, a slab of seven SiC layers and a 50-Ry cutoff energy. These tests suggest that the values in the total energy difference presented here are accurate to  $\pm 0.05$  eV/dimer, which is sufficient for the purpose of our study.

For the heteroepitaxial growth of diamond on cubic  $\beta$ -SiC, we first investigated surface structures of cubic  $\beta$ -SiC(001) related to surface adatom species, using a  $2 \times 2$  surface unit cell and 16  $\mathbf{k}$  points in the surface Brillouin zone (SBZ) of the  $2 \times 2$  unit cell. Experiments [12–14] and first-principles calculations [15] revealed the  $sp$ -bonded  $c(2 \times 2)$  reconstruction as the most stable surface structure of clean C-terminated  $\beta$ -SiC(001) [see Fig. 1(a)]. Our DFT calculations agreed well with the previous *ab initio* result [15]: In the LDA, the  $p(2 \times 1)$  model was 0.16 eV/dimer lower than the  $sp$ -bonded dimer model; in the GGA, the energy ordering of the  $sp$ -bonded and  $p(2 \times 1)$  dimer models was reversed, the  $sp$ -bonded dimer model being lower in energy by 0.10 eV/dimer. Subsequently, the  $\beta$ -SiC(001) surface of  $sp$ -bonded carbon dimers was exposed to group-V atoms  $A$  ( $A = \text{Sb, As, P}$ ). Figures 1(b) and 1(c) display the results at 1 monolayer (ML) coverage of group-V atoms. There are two stable configurations: the  $c(2 \times 2)$  bridge-dimer configuration in which the subsurface carbon dimer bonds are kept [see Fig. 1(b)] and the  $sp^3$ -like bond configuration in which the carbon atoms reside at diamondlike lattice sites [see Fig. 1(c)]. It is noted that in the bridge-dimer configuration the subsurface carbon dimer distance is considerably elongated, e.g., in the case of antimony, from 1.23 to 1.69 Å. This result suggests the weakening of the carbon dimer bond due to the C-A interactions.

As a result, the bridge-dimer structure becomes metastable. Actually, we found that for 1 ML of antimony the LDA (GGA) energy of the  $sp^3$ -like bond configuration is 0.91 (0.59) eV/dimer lower than that of the bridge-dimer configuration. The calculated surface energies also showed that the  $sp^3$ -like structure is a stable surface phase in the wide range of the Sb chemical potential. Furthermore, this new approach provides a way of forming an  $sp^3$ -like carbon structure on a “large” surface area, in contrast to the previous result of local  $sp^3$ -carbon-line formation on C-terminated SiC(001) [22]. *The preliminary growth condition of the  $sp^3$ -like bond configuration for the heteroepitaxy of diamond was thus attained.*

We now look at the growth process of diamond on  $\beta$ -SiC. The growth of diamond might be achieved by using a surfactant-mediated growth reaction, where incoming C atoms are effectively incorporated into a substrate by exchanging sites with surfactants. In searching for such a suitable surfactant, we have performed total-energy calculations for a number of atomic configurations during the growth process. Here we used a  $2 \times 1$  surface unit cell and 32  $\mathbf{k}$  points in the SBZ of the  $2 \times 1$  unit cell. The main results were confirmed by using a larger  $2 \times 2$  unit cell. The initial configuration for the surfactant-mediated growth was taken to be a surfactant-covered  $\beta$ -SiC(001) surface, that is,  $A/\text{SiC}(001)$  [ $A = \text{Sb, As, P}$ ]. As a result of the exposure of  $A/\text{SiC}(001)$  to molecular hydrocarbon species, a H-terminated structure of  $\text{H}/\text{C}/\text{A}/\text{SiC}(001)$  is expected to be formed [see Fig. 2(a)]. Subsequently, the site exchange between C and surfactant  $A$  [ $\text{H}/\text{C}/\text{A}/\text{SiC}(001) \rightarrow \text{H}/\text{A}/\text{C}/\text{SiC}(001) + \Delta E_1$ ] would take place, as shown in Figs. 2(a) and 2(b). The resulting site-exchange (segregation) energies ( $\Delta E_1$ ) are listed in Table I. For antimony it is positive, indicating that Sb would act as a good surfactant for the diamond heteroepitaxy. For phosphorus and arsenic, however, the exchange energy is negative, and thus continued growth of diamond using a surfactant is energetically very unfavorable.

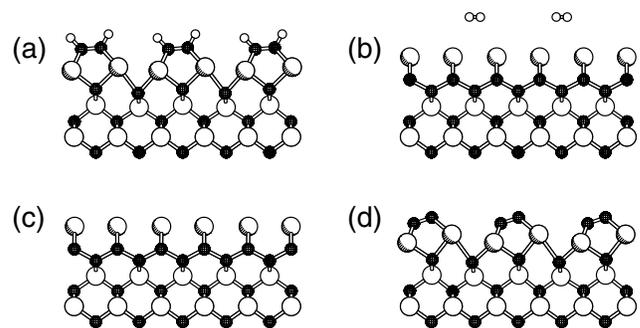


FIG. 2. Segregation reactions for the surfactant-mediated growth of diamond on  $\beta$ -SiC(001): exchange reaction I [(a)  $\rightarrow$  (b)] and exchange reaction II [(c)  $\rightarrow$  (d)]. In (b) surface H atoms exist in the form of stable  $\text{H}_2$  molecules. These  $\text{H}_2$  molecules are readily desorbed from the surface surfactant atoms, leading to the configuration (c). Here small open spheres represent H atoms.

TABLE I. LDA energies for the surface segregation of surfactants during the growth of diamond on  $\beta$ -SiC(001) (the GGA results are in parentheses). In the exchange reaction I [ $\text{H/C/A/SiC}(001) \rightarrow \text{H/A/C/SiC}(001) + \Delta E_{\text{I}}$ ], surface C atoms exchange sites with subsurface surfactant (A) atoms. Subsequently, surface H atoms desorb from the A surface atoms. Under conditions when there is no surface hydrogen, the surfactant-covered structure is stabilized through the unfavorable ( $\Delta E_{\text{II}} > 0$ ) exchange reaction II [ $\text{A/C/SiC}(001) \rightarrow \text{C/A/SiC}(001) - \Delta E_{\text{II}}$ ].

	Atomic radius ( $\text{\AA}$ )	Segregation energy ( $\text{eV}/2 \times 1$ )			
		$\Delta E_{\text{I}}$	(GGA)	$\Delta E_{\text{II}}$	(GGA)
Sb	1.36	0.76	(0.85)	2.98	(2.78)
As	1.18	-0.89	(-0.66)	2.12	(1.82)
P	1.10	-2.77	(-2.64)	0.22	(-0.01)

After the C atoms exchange sites with the subsurface surfactant atoms, the surface H atoms form stable  $\text{H}_2$  molecules and then readily desorb from the surfactant atoms due to the very weak  $\text{A-H}_2$  bonds compared to the C-H bonds: For instance, in the case of antimony, the  $\text{H}_2$  molecule is located 2.81  $\text{\AA}$  above the surface layer, and its LDA desorption energy is only 0.08 eV (the GGA value is 0.01 eV). The resulting atomic configuration is back to the surfactant-covered configuration  $\text{A/C/SiC}(001)$  that is very stable [see Figs. 2(c) and 2(d)]. The energy differences are listed in Table I. For Sb, the segregation energy ( $\Delta E_{\text{II}}$ ) in the exchange reaction II [ $\text{A/C/SiC}(001) \rightarrow \text{C/A/SiC}(001) - \Delta E_{\text{II}}$ ] is positive and very large.

The above results clearly indicate that Sb *not only helps the  $sp^3$  hybridization of carbon atoms but also acts as a good surfactant that enhances the diamond growth on  $\beta$ -SiC.* Our calculations of more carbon layers on SiC also showed that the continued segregation of surfactants onto the growth front is energetically favorable. In spite of the rather larger lattice mismatch of 22% between diamond and  $\beta$ -SiC, the present surfactant growth technique could possibly allow us to increase the critical thickness of 2D/3D growth transition and give rise to a better quality of diamond films, because the exchange process of surfactants enhances carbon incorporation by reducing the surface diffusion of incoming carbon atoms [23]. This behavior is in contrast with the very rough morphology of the hillock in the diamond-on-silicon interface [7].

For the surfactant-mediated growth of diamond, the key attribute of the surfactant is its high ability to segregate onto the growth front during the growth. Our calculations showed that the segregation energy increases as the atomic size of the surfactant increases (see Table I). Considering the very similar chemical nature of the group-V elements, this allows us to represent the crucial role of the atomic-size effect in the segregation of the surfactant.

Since the incorporation of a large atom typically influences the surface stress, the above explanation suggests the possibility that the surface stress plays a role in the segregation. In order to quantify such a role, we systematically

analyzed the segregation reaction for a strained Sb/SiC slab that was made by changing the SiC lattice constant. The results are shown in Fig. 3. When the system is under compressive strain, we found that the segregation energies increase for both exchange reactions. In contrast, for a stretched system the segregation energies decrease. The variation of the segregation energy (the energy difference between the subsurface- and surface-surfactant systems) can be understood in terms of the different strain effect of the surfactant at subsurface and surface sites: As the lattice constant was varied, the total energy showed a larger variation for the subsurface-surfactant system compared to the surface-surfactant one.

Furthermore, the above result will lead to the atomic-size dependence of the surface stress. Consistently, our stress calculations for the Sb, As, and P systems showed a significant change in the stress of the subsurface-surfactant system with respect to the atomic size. We have indeed found that the atomic-size effect (or the surface strain effect) plays the key role for the surfactant-mediated growth of diamond on  $\beta$ -SiC. These findings also well explain the surfactant behavior of large size atoms in the homoepitaxial growth of GaN [24] and diamond [9,25], and in the heteroepitaxial growth of GaN on GaAs with a large lattice mismatch of 20% [10] whose physical mechanism has remained unexplained so far.

In summary, by performing first-principles calculations, we examined promising atomic processes and the physical mechanism for the growth of diamond films on  $\beta$ -SiC in a hydrogen-free, surfactant environment. The exposure of an  $sp$ -bonded  $c(2 \times 2)$  C-rich  $\beta$ -SiC(001) surface to group-V (Sb, As, P) adatoms was here used to make the reconstructed surface of an  $sp^3$ -like configuration. In the

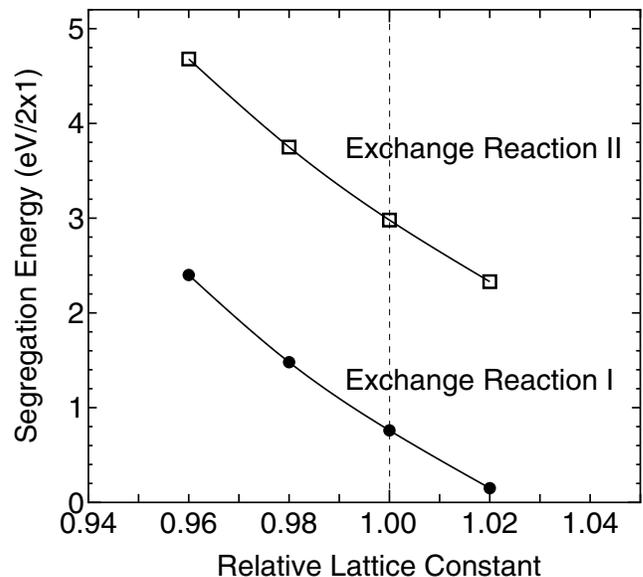


FIG. 3. Segregation energies in the LDA for a strained Sb/SiC(001) film as a function of the relative surface lattice constant.

process, the group-V surfactants instead of “excess” hydrogen help the formation of  $sp^3$ -bonded diamond. Among the isoelectronic group-V atoms atomic species of a larger size such as Sb acts as a better surfactant for the heteroepitaxial growth of diamond on  $\beta$ -SiC. This result suggests the role of surfactant size in the surfactant-mediated growth.

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