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# *Ab initio* calculations on etching of graphite and diamond surfaces by atomic hydrogen

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Etching of graphite and hydrogenated diamond C(100) $2\times1$ surfaces by irradiating atomic hydrogen, which is one of the key reactions to promote epitaxial diamond growth by chemical vapor deposition, has been investigated by *ab initio* pseudopotential calculations. We demonstrate the reaction pathways and determine the activation energies for breaking C-C bonds on the surfaces by irradiating hydrogen atoms. The activation energy for C-C bond breaking on graphite is found to be only one-half of that on the hydrogenated diamond surface. This indicates that graphite, which is a typical nondiamond phase unnecessarily generated on the diamond surface during epitaxial growth, can be selectively eliminated by atomic hydrogen, resulting in methane desorption. Our result supports the growth rate enhancement in diamond epitaxy observed in a recent experiment by gas-source molecular beam epitaxy under hydrogen beam irradiation.

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## I. INTRODUCTION

Recently, the behavior of hydrogen atoms and molecules at semiconductor surfaces has attracted the attention of scientists as an important subject in gas-phase semiconductor processes. The role of hydrogen in diamond growth by chemical vapor deposition (CVD) with hydrocarbon gases such as methane is especially important, because not only the growth rate but also the crystallographic quality of grown layers is significantly influenced by the surface reaction of hydrogen.[1–10] For example, to get a diamond layer without graphite and amorphous carbon, it is well known that the hydrocarbon gas should be greatly diluted by hydrogen down to a few volume percent and that atomic hydrogen as well as hydrocarbon radicals are produced by a hot tungsten filament or a microwave and effectively transferred to the diamond-growing surface.[2,5] This means that the atomic hydrogen interacting with the surface during diamond growth is important. Therefore, the interaction of atomic hydrogen with the diamond surface is experimentally investigated by various methods of surface analyses.[3] In spite of progress in rates of film production[1,2,5] and discoveries of new methods of diamond growth,[7,8] very little is currently understood at the atomic level about the chemical processes responsible for diamond growth.

In the experiment of gas-source molecular beam epitaxy (GSMBE) with pure methane, Nishimori *et al.*[7] demonstrated that the epitaxial diamond growth is rate limited by hydrogen desorption; hydrogen atoms on diamond surfaces prevent methane from being adsorbed onto the surface. Furthermore, they have shown that irradiating the diamond surface with an atomic hydrogen beam during GSMBE with pure methane enhanced the growth rate (GR) by about fivefold without the concurrent growth of amorphous carbon.[8] In the GSMBE method, since the gas pressure is of the order of $10^{-6}$–$10^{-4}$ Torr, the gas-phase reaction is negligible and diamond growth is predominantly governed by surface reactions such as methane adsorption and hydrogen desorption. The experimental results of GSMBE prove that GR enhancement of diamond and suppression of growth of nondiamond components are due to the surface reactions of atomic hydrogen. Thus, in the growth of high-quality diamond, atomic hydrogen is known to fulfill important roles including the stabilization of the diamond surface, the production of vacant surface sites, and the preferential etching of graphite[11–14] during the codeposition of graphite and diamond surfaces.

Although Battaile *et al.*[15] have performed the detailed calculations of various chemical reactions involving hydrocarbon complexes and of the surface-orientation-dependent etching effect on CVD growth, and some theoretical studies with empirical calculations have been reported,[16–18] *ab initio* calculations, in particular, focusing on the atomic processes of hydrogenated diamond surfaces are very rare compared with those of hydrogenated silicon surfaces.[19,20]

In our previous studies,[21,22] we have calculated the potential energy curves and the reaction pathways for the Langmuir-Hinshelwood (LH) desorption of hydrogen molecules and for the Eley-Rideal (ER) extraction of a hydrogen atom by irradiating atomic hydrogen from hydrogenated diamond C(100) surfaces (monohydride and dihydride surfaces) by the *ab initio* pseudopotential method. In the LH desorption of hydrogen molecules from C(100) surfaces, we found that the activation energy of 1.45 eV from a dihydride surface is less than that of 4.94 eV from a monohydride surface. This allows us to conclude that the dihydride C(100) surface is less stable than the monohydride surface and that hydrogen desorption occurs mostly from the dihydride sites as defects on the monohydride surface. On the other hand, in the ER extraction of a hydrogen atom from the dihydride C(100) surface, a hydrogen atom is extracted with zero activation energy to form a hydrogen molecule with an irradiating atomic hydrogen. This indicates that the dihydride phase, which is less stable than the monohydride phase, tends to become even more unstable and may disappear under atomic hydrogen beam irradiation. It was also found that a hydrogen atom on the monohydride surface can be extracted with an activation energy of 0.20 eV with the aid of irradiating hydrogen, having a kinetic energy of 0.22 eV. Comparing the low activation energy (0.20 eV) for the ER extraction with that (4.94 eV) for the LH desorption of a hydrogen molecule from the monohydride surface, we demonstrated that H beam irradiation promotes hydrogen removal from the diamond surface, leading to GR enhancement in diamond epitaxy. These numerical results are in good agreement with the experimental observations by GSMBE. In the GSMBE experiment with atomic hydrogen,[8] it was conjectured that irradiating hydrogen atoms eliminates nondiamond phases such as graphite generated on the diamond surface, resulting in the improvement of the crystallographic quality of grown layers. Hydrogen etching of the diamond surface itself is also practically important from the viewpoint of surface processes to get a smooth diamond surface on an atomic scale.[9,23]

The objectives of this study are to reveal the etching processes by atomic hydrogen on graphite and diamond surfaces, and to provide a theoretical interpretation for the difference in the degree of etching between graphite and diamond surfaces. In this paper, we present *ab initio* calculations of the atomic processes for etching of both graphite and diamond surfaces by atomic hydrogen, which are the essential surface reactions of atomic hydrogen in diamond growth by CVD. This paper is organized as follows. In Sec. II, the computational method to determine atomic and electronic structures including the transition states for the etching processes is briefly described. In Sec. III, we present the results and discussion on the hydrogen etching processes on graphite and diamond C(100) surfaces. A summary is given in Sec. IV.

## II. METHOD AND MODEL

Our calculations were performed using the *ab initio* molecular dynamics method[24] within the framework of the density functional theory (DFT).[25,26] The generalized gradient approximation (GGA) by Perdew *et al.*[27] was used for the exchange-correlation potential. In our calculations, total energies and atomic forces were determined self-consistently by employing the preconditioned conjugate gradient method[28] and the efficient density mixing scheme.[29] We employed the norm-conserving pseudopotentials which were formulated by Troullier and Martins[30] and Kobayashi[31] and expanded the electronic wave functions in plane waves up to a kinetic energy of 36 Ry. We chose two $\boldsymbol{k}$ points for the system of the diamond surface and a $\Gamma$ point for the system of graphite in each Brillouin zone. In our calculations of the diamond surface, the substrate was modeled by a repeated slab for diamond C(100), which had six atomic layers with $4\times 2$ atoms per layer (see Fig. 1) and was separated by a vacuum region equivalent to 12 atomic layers. The dangling bonds on the bottom surface of the slab were saturated with hydrogen atoms. Atoms on the top four layers of the slab were relaxed, and those in the remaining two layers were fixed at their bulk positions. In the present calculation, graphite was replaced by a graphene sheet in a unit cell for simplicity. This replacement was not expected to qualitatively influence the etching mechanism. The graphene in the unit cell contained 24 carbon atoms, as shown in Fig. 2. All of the atoms contained in the unit cell were relaxed in this work. The atomic distances on the monohydride C(100) surface obtained in this study differed by less than 1% from those reported by a previous elaborate work with the Vienna *ab initio* simulation package (VASP).[32,33]

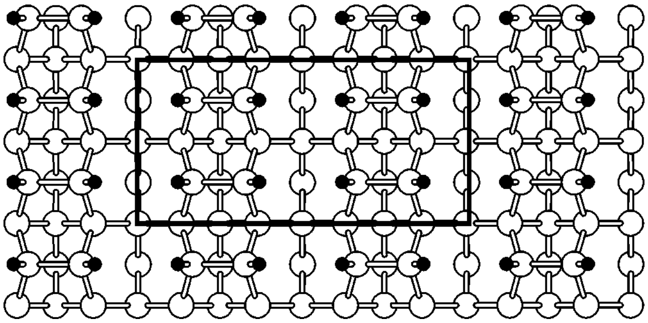

FIG. 1. Top view of the monohydride C(100) $2\times 1$ surface. Open and closed circles denote carbon and hydrogen atoms, respectively. The region surrounded by a solid line is a unit cell used in the present calculations. The unit cell contains six atomic layers with $4\times 2$ atoms per layer.

In this paper, we present the energy diagrams for the reaction processes of hydrogen etching of graphite and diamond surfaces. For the most probable etching process of graphite and diamond, we assumed that a hydrogen atom adsorbs to a carbon atom on the diamond surface or graphene and the C-C back bond of the surface carbon atom is broken, leading to methane evaporation after four hydrogen atoms adsorb to the same carbon atom. We employed a hybrid of two algorithms to efficiently determine the transi-

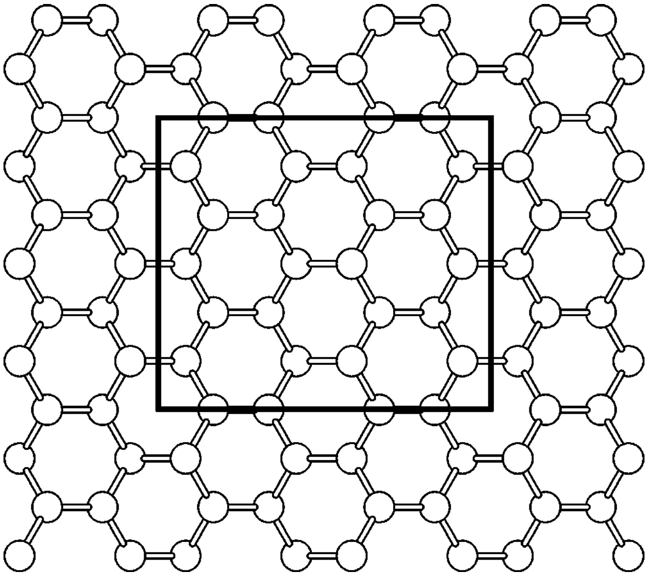

FIG. 2. Top view of graphene. Open circles denotes carbon atoms. The region surrounded by a solid line is an unit cell used in the present calculations.

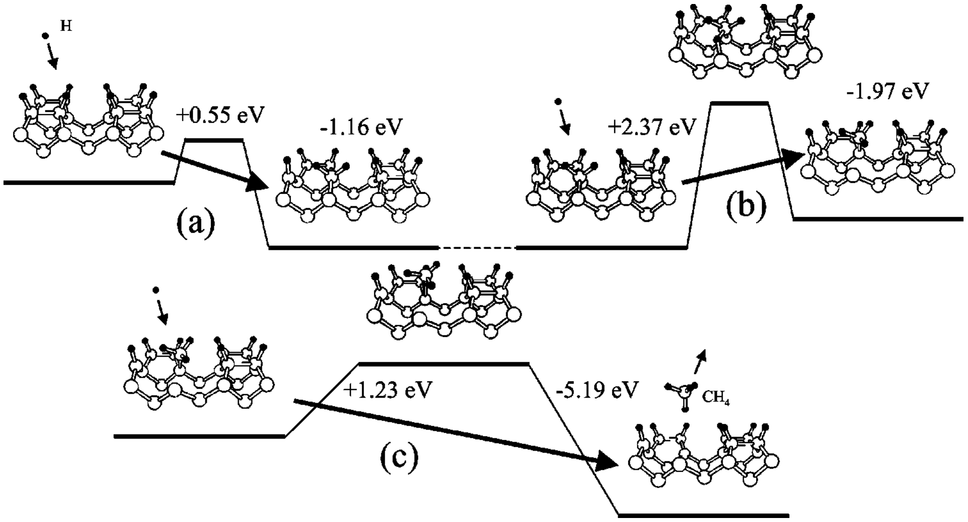

FIG. 3. Energy diagram for hydrogen etching of monohydride diamond surface. Open and closed circles denote carbon and hydrogen atoms, respectively. Hydrogen adsorption proceeds in sequence through processes (a) to (c) with two activation barriers, leading to methane desorption. The number is the energy change in each process.

tion states of C-C bond breaking at the surfaces: First, the steepest descent paths (SDP) algorithm[34] is used to roughly search the saddle point of potential energy surfaces in the atomic configuration space. Second, the force-inversion (FI) technique[35] is used to determine the exact saddle point configuration from the initial conditions obtained with the SDP algorithm.

## III. RESULTS AND DISCUSSION

The energy diagrams calculated for hydrogen etching of diamond and graphene are given in Figs. 3 and 4, respectively. The energy change in each process is given in these diagrams. First, we discuss the hydrogen etching process of the diamond surface using three steps (a), (b) and (c) in Fig. 3. A hydrogen atom is supplied externally to the same carbon atom on the surface in each step. In step (a), atomic hydrogen adsorption leads to the formation of the dihydride structure after the carbon dimer opening with an energy barrier of 0.55 eV. In step (b), the dihydride changes into a trihydride by adsorption of another hydrogen atom with breaking of a C-C back bond of the dihydride. In this process, there is an activation energy barrier (AEB) of 2.37 eV. In step (c), a C-C back bond of the trihydride is broken by atomic hydrogen adsorption, leading to $CH_4$ desorption precursor formation. This process has an AEB of 1.23 eV. Therefore, the etching of a carbon atom on the diamond surface is completed as methane evaporation only if energies sufficient for overcoming the two AEB's are supplied.

Thomas *et al.*[36] have already done similar calculations on a finite cluster of $C_{28}H_{46}$ by a semiempirical [modified neglect of differential overlap (MNDO)] method. They reported AEB's of 2.1 eV for breaking of the dimer bond and 3.3 eV for breaking the back bond. Their values are compared with our values of 0.55 eV in step (a) and 2.37 eV in step (b), respectively. It is physically reasonable that AEB's obtained from the the semiempirical cluster calculations are generally larger than those obtained by first-principles calculations under periodic boundary conditions, because the constraint on the geometrical optimization in the finite cluster unavoidably increases the energy for transition to a different geometry.

We describe the dimer-opening state in step (a) in greater detail. The second hydrogen atom was assumed to hit the dihydride carbon atom in step (b) to evaluate the reaction potentials leading to $CH_4$ desorption. The second hydrogen atom, however, does not always hit the same carbon atom. Rather, it may adsorb to the neighboring monohydride carbon atom, resulting in two dihydride carbon atoms adjacent to each other. It is found in our previous study[22] that the dihydride phase, which is less stable than the monohydride phase, becomes even more unstable by the attack of atomic hydrogen and goes back to the monohydride $2\times1$ phase eventually. That is, the dimer-opening configuration in Fig. 3(a) is possibly transformed to the $2\times1$:H dimer under irradiation of atomic hydrogen unless the trihydride carbon is generated by the following atomic hydrogen, as investigated in the present work. In any case, the dimer-opening state is not stable, which is consistent with the experimental observation by scanning tunneling microscopy (STM).[4]

We have also performed the calculation of thermal desorption of $CH_3$ from the surface after step (b) without the attack of atomic hydrogen. The activation energy for $CH_3$ desorption is found to be 1.34 eV, which is slightly higher than the value of 1.23 eV for $CH_4$ desorption in step (c) in Fig. 3. It should be noted that the present calculation has been performed with two idealizations. One is that the system is at zero temperature and the other is neglect of the H-flux effect. Therefore, $CH_4$ is considered to be an etch product only at a low temperature, which is consistent with experiment.[37] Of course, the primary etch product may change to $CH_3$, depending on the experimental conditions, i.e., the substrate temperature and H-flux intensity, because the two values of the activation energy are very close to each other.

Second, the hydrogen etching process of graphene is considered in Fig. 4. Hydrogen etching of a carbon atom of graphene is composed of four steps (a), (b), (c), and (d), leading to methane desorption and carbon vacancy formation. In step (a), atomic hydrogen adsorption to graphene

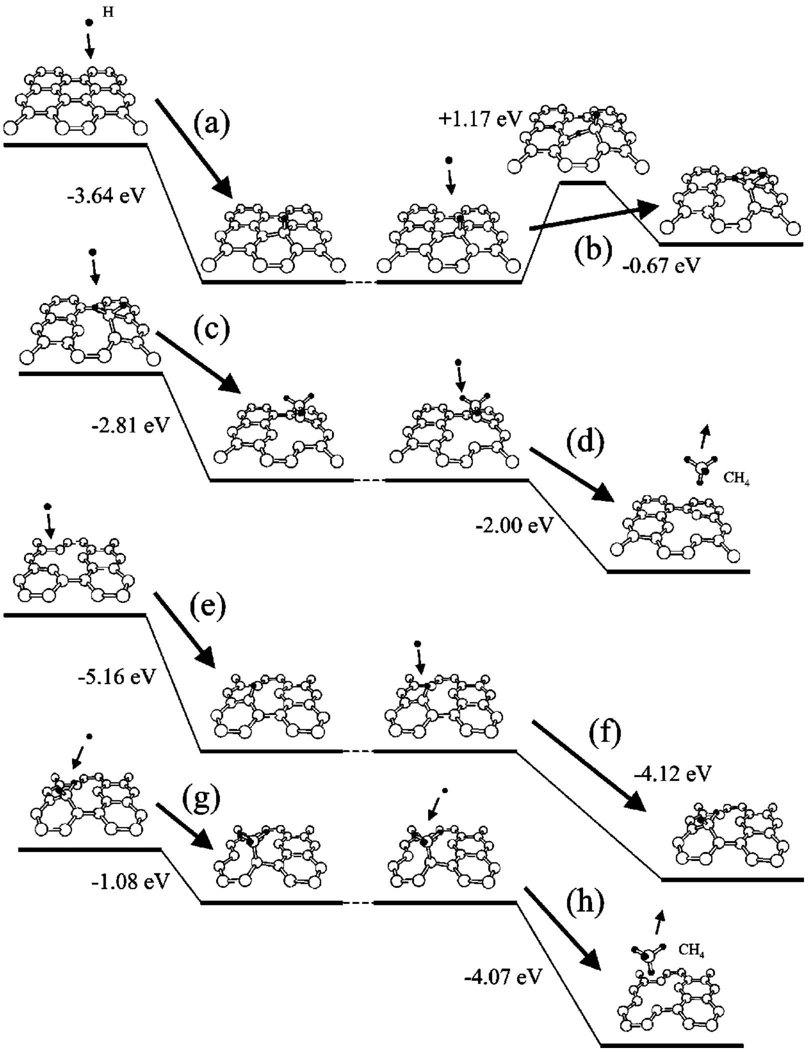

FIG. 4. Energy diagram for hydrogen etching of graphene. Open and closed circles denote carbon and hydrogen atoms, respectively. The number is the energy change in each process. Hydrogen adsorption proceeds in sequence through processes (a) to (d) with an activation barrier, leading to methane desorption. Further, methane desorbs after a sequence of hydrogen adsorption through cascade reactions (e) to (h) with no activation barriers.

leads to monohydride formation without breaking any C-C bonds. The hydrogen-bonded carbon atom sticks out from the graphene plane, so that its electronic structure changes from $sp^2$ to $sp^3$-like orbitals. In this process, there is no AEB and the energy gain of hydrogenation is 3.64 eV. Upon further hydrogenation in step (b), a C-C back bond of the monohydride is broken to produce a dihydride species. For the C-C bond breaking, the AEB reaches 1.17 eV. In the case of the diamond surface, there is no AEB to change the monohydride into the dihydride, as shown in step (a) of Fig. 3. This is because the C-C dimer bond opening on the C(100) surface can occur more easily than C-C back bond breaking. In fact, when the C-C back bond is broken on the C(100) surface, AEB's of 2.37 eV and 1.23 eV appear in steps (b) and (c) of Fig. 3 for the trihydride and the CH$_4$ desorption precursor, respectively. In contrast with hydrogenation of the C(100) surface to produce a trihydride, the dihydride in graphene can be hydrogenated to a trihydride with no AEB while a C-C back bond is broken. Furthermore, in step (d) of Fig. 4, for CH$_4$ desorption precursor formation with C-C back bond breaking, the trihydride can be also hydrogenated with no AEB. Thus, the AEB in the hydrogen etching of graphene exists only in the process of dihydride formation. It is noted that the AEB of 1.17 eV for graphene is about one-half of that of 2.37 eV for diamond.

The reason for the difference in the AEB between diamond and graphene comes from the bonding nature of the hydrogenated carbon atom ($C_H$) and another carbon atom on the surface ($C_S$). For diamond, both $C_H$ and $C_S$ in steps (a) and (b) of Fig. 3 have the $sp^3$ orbital, so that they are stably bound to each other. On the other hand, $C_H$ and $C_S$ have $sp^3$ and $sp^2$ orbitals, respectively, for graphene in steps (a), (b), and (c) in Fig. 4. Namely, the results of dihydride and trihydride formation in Figs. 3 and 4 mean that the C-C back bond with the nature of the $sp^2$ orbital for graphene is more easily broken by atomic hydrogen adsorption than that with the nature of $sp^3$ orbital for diamond. Then, CH$_3$ is rather loosely bound to graphene, because it is already known that bonding of a CH$_3$ ($sp^3$) to a benzene ring ($sp^2$) is weaker than that to another CH$_3$ ($sp^3$).[38] Therefore, a $C_H$ atom is more easily extracted from graphene with no AEB, as shown in step (d) of Fig. 4, than from the diamond surface with an AEB of 1.23 eV, as shown in step (c) of Fig. 3.

More importantly, further etching processes for graphene have no AEB's in steps (e), (f), (g), and (h) of Fig. 4. In both steps (e) and (f) for monohydride and dihydride formation, respectively, there are no AEB's, while dihydride formation in step (b) has an AEB of 1.17 eV. The difference is ascribed to the C-C back bond breaking. In step (f), an impinging hydrogen atom can produce a dihydride with no C-C back bond breaking because the monohydride produced in step (e) has a dangling bond due to $CH_4$ desorption in step (d). The C-C back bond breaking occurs in steps (g) and (h) in a manner similar to steps (c) and (d). Therefore, we conclude that carbon atoms near vacancies of graphene are easily etched without any activation energies. Once a vacancy in graphene is generated, many carbon atoms around that vacancy would be evaporated by hydrogen atoms in sequence, as clearly seen in steps (e) to (h). Therefore, carbon atoms at the edge of holes generated by $CH_4$ desorption would be easily etched without any activation energies, resulting in a large hole after sequential etching. This result also indicates that the edge plane of graphite is more readily etched than the basal plane, supporting the experimental observation by Balooch and Olander.[13] In contrast, sequential carbon desorption hardly occurs around the vacancy on the diamond surface, because breaking a C-C back bond with the nature of an $sp^3$ orbital requires finite activation energies to extract a carbon atom.

Lastly, we describe how sensitively the electronic states of graphene are influenced by atomic hydrogen adsorption. For the calculation of hydrogen adsorption on graphene, electronic level densities corresponding to the Fermi level are shown in Fig. 5(b) [same as step (a) in Fig. 4] compared with that for the hydrogen-free surface in Fig. 5(a). The contours in Figs. 5(a) and 5(b) are drawn under the same conditions. Closed and open circles represent carbon atoms and a hydrogen atom, respectively. In Fig. 5(b), the $\pi$ electron density around the adsorbed hydrogen disappears and changes into $\sigma$ ($sp^3$) bonding with a low energy. As mentioned above, $C_H$ with the $sp^3$ orbital is loosely bound to $C_S$ with the $sp^2$ orbital. Thus, the considerable change in the electronic states of the hydrogen-adsorbed carbon is the main reason why graphene is more easily etched by a hydrogen atom than diamond. Therefore, the present results enable us to conclude that irradiation of atomic hydrogen etches graphite selectively at much higher rates than the diamond surface,[11] in agreement with the experiments showing that the concurrent growth of amorphous carbon and graphite can be suppressed under hydrogen beam irradiation while the GR of diamond is appreciably increased.[8]

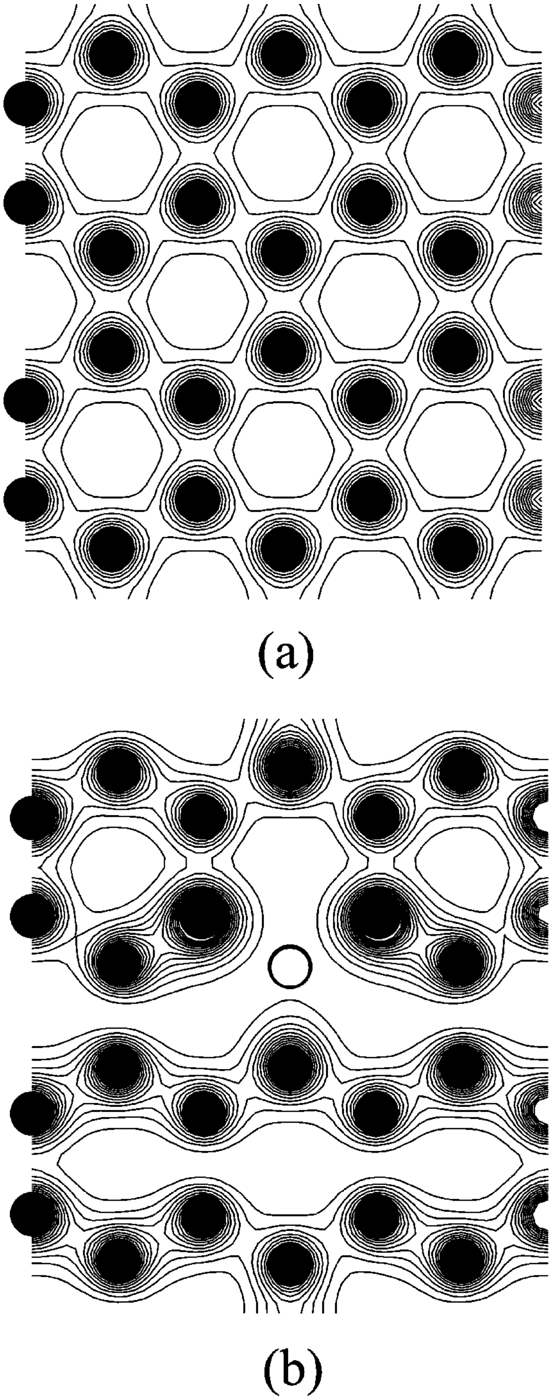

FIG. 5. $\pi$ orbital densities of graphene (a) without and (b) with a hydrogen atom. Closed circles and an open circle refer to carbon atoms and a hydrogenated carbon atom, respectively. The contour spacing is $0.02a_B^{-3}$, where $a_B$ is the Bohr radius.

## IV. CONCLUSION

The energetics of the possible hydrogen etching reactions occurring on hydrogenated diamond and graphite surfaces were investigated using *ab initio* calculations in order to elucidate the essential processes of hydrogen etching. In the etching of the hydrogenated diamond surface, breaking a C-C back bond is accompanied with an activation energy barrier, the values of which are 2.37 eV and 1.23 eV in the steps for the formation of the trihydride and the $CH_4$ desorption precursor, respectively. In the etching of graphite, there is an activation energy barrier of 1.17 eV only in the stage of dihydride formation. We found that hydrogen adsorption markedly modifies the local electronic states of graphene from $sp^2$ to $sp^3$ bonding, making it easy to break a C-C bond in the graphene sheet. Furthermore, it is clarified that carbon atoms are extracted one after another by irradiating hydrogen with no activation energy from graphene, because carbon atoms around the vacancy have dangling bonds and are loosely bonded to other carbon atoms due to the change in the electronic states.

From these results, we conclude that atomic hydrogen etches graphite selectively at much higher rates than the diamond surface. Thus, our *ab initio* study provides theoretical interpretations to the experimental observation that irradiation of atomic hydrogen promotes epitaxial diamond growth without concurrent growth of graphite and amorphous carbon. Finally, it is noted that surface migration,[39] which has not been taken into account in the present study, possibly affects the etching reaction. This will be considered in future studies.

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[1] C.J. Chu, R.H. Huge, J.L. Margrave, and M.P. D'Evelyn, Appl. Phys. Lett. **61**, 1393 (1992).

[2] S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, Jpn. J. Appl. Phys., Part 2 **21**, L183 (1982).

[3] H. Kawarada, Surf. Sci. Rep. **26**, 205 (1996).

[4] H. Kawarada, H. Sasaki, and A. Sato, Phys. Rev. B **52**, 11 351 (1995).

[5] B.D. Thoms, J.N. Russell, Jr., P.E. Pehrsson, and J.E. Butler, J. Chem. Phys. **100**, 8425 (1994).

[6] B.D. Thoms, P.E. Pehrsson, and J.E. Butler, J. Appl. Phys. **75**, 1804 (1994).

[7] T. Nishimori, H. Sakamoto, Y. Takakuwa, and S. Kono, J. Vac. Sci. Technol. A **13**, 2781 (1995).

[8] T. Nishimori, H. Sakamoto, Y. Takakuwa, and S. Kono, Diamond Relat. Mater. **6**, 463 (1997).

[9] K. Hayashi, S. Yamanaka, H. Okushi, and K. Kajimura, Diamond Relat. Mater. **5**, 1002 (1996).

[10] C.-L. Cheng, H.-C. Chang, J.-C. Lin, and K.-J. Song, Phys. Rev. Lett. **78**, 3713 (1997).

[11] C.M. Donnelly, R.W. McCullough, and J. Geddes, Diamond Relat. Mater. **6**, 787 (1997).

[12] Y. Gogotsi, T. Kraft, K.G. Nickel, and M.E. Zvanut, Diamond Relat. Mater. **6**, 1459 (1998).

[13] M. Balooch and D.R. Olander, J. Chem. Phys. **63**, 4772 (1975).

[14] W.L. Hsu and R.A. Causey, J. Vac. Sci. Technol. A **5**, 2768 (1987).

[15] C.C. Battaile, D.J. Srolovitz, I.I. Oleinik, D.G. Pettifor, A.P. Sutton, S.J. Harris, and J.E. Butler, J. Chem. Phys. **111**, 4291 (1999).

[16] D. Huang and M. Frenklach, J. Phys. Chem. **96**, 1868 (1992).

[17] B.J. Garrison, E.J. Dawnkaski, D. Srivastava, and D.W. Brenner, Science **255**, 835 (1992).

[18] S.J. Harris and D.G. Goodwin, J. Phys. Chem. **97**, 23 (1993).

[19] E. Pehlke and M. Sheffler, Phys. Rev. Lett. **74**, 952 (1995).

[20] P. Kratzer, B. Hammer, and J.K. Nørskov, Phys. Rev. B **51**, 13 432 (1995).

[21] C. Kanai, K. Watanabe, and Y. Takakuwa, Jpn. J. Appl. Phys., Part 2 **38**, L783 (1999).

[22] C. Kanai, K. Watanabe, and Y. Takakuwa, Appl. Surf. Sci. **159-160**, 599 (2000).

[23] R.E. Rawles, S.F. Komarov, R. Gat, W.G. Morris, J.B. Hudson, and M.P. D'Evelyn, Diamond Relat. Mater. **6**, 791 (1997).

[24] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).

[26] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[27] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[28] D.M. Bylander, L. Kleinman, and S. Lee, Phys. Rev. B **42**, 1394 (1990).

[29] D.D. Johnson, Phys. Rev. B **38**, 12 807 (1988).

[30] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1193 (1991).

[31] K. Kobayashi, Comput. Mater. Sci. **14**, 72 (1997).

[32] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **53**, 7334 (1996).

[33] G. Kresse and J. Hafner, Phys. Rev. B **54**, 11 169 (1996).

[34] A. Ulitsky and R. Elber, J. Chem. Phys. **92**, 1510 (1990).

[35] Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki, Phys. Rev. B **54**, 14 994 (1996).

[36] R.E. Thomas, R.A. Russer, R.J. Markunas, D. Huang, and M. Frenklach, J. Chem. Vap. Deposition **1**, 6 (1992).

[37] J.S. Foord, K.P. Loh, and R.B. Jackman, Surf. Sci. **399**, 1 (1998).

[38] See, e.g., *CRC Handbook of Chemistry and Physics*, edited by D.R. Lide (CRC Press, Washington, D. C., 1994).

[39] M. Frenklach and S. Skokov, J. Phys. Chem. B **101**, 3025 (1997).