Fluorine-Based Mechanisms for Atomic-Layer-Epitaxial Growth on Diamond (110)

M. G. Wensell, Z. Zhang, and J. Bernholc
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

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Atomic-layer-epitaxy (ALE) processes for the growth of diamond are evaluated using *ab initio* molecular dynamics. It is shown that the Cl-based ALE cycle on diamond (111) is not advantageous, due to strong steric hindrances. New ALE processes are proposed and shown to be energetically favorable, self-limiting, and sterically unhindered. They exploit the large heat of formation and the small size of the HF molecule and are based on alternating exposure of the diamond (110) surface to hydrocarbons and fluorocarbons. Alternatively, H and F gases can be used in parts of the cycle.

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The discovery of methods to grow thin films of diamond on a variety of substrates with practical growth rates has been viewed as one of the most important technological breakthroughs of the past decade. However, growth of high quality single-crystal films has proven to be a substantial challenge. Even on diamond substrates, the quality of the resulting film is significantly lower than that of natural diamond. On nondiamond substrates, only oriented polycrystalline growth has been achieved to date [1]. These difficulties have largely prevented electronic applications of diamond technology, despite its substantial potential for high speed, high power, and high temperature electronics [2]. The difficulties associated with the growth of diamond can mostly be traced to the competition between the diamond and graphite phases. At the low growth pressures used in thin film growth, graphite is the thermodynamically preferred bulk phase. Therefore, growth of a large area diamond film must be due to kinetic reasons. Growth in the presence of large amounts of hydrogen helps to maintain sp^3 hybridization of C atoms and leads to the formation of diamond coatings and thin films, even on nondiamond substrates. However, the resulting diamond films are not of sufficient quality, due to both the presence of grain boundaries and small graphitic inclusions that do not anneal out despite relatively high growth temperatures.

The quality of growth can be greatly improved if the film grows in a true layer-by-layer mode, in which each layer is fully completed before the next layer starts forming. Atomic layer epitaxy (ALE) is a "digital" growth method that results in a deposition of one or two atomic layers per each growth cycle. The simplest ALE cycle uses two reactant gases chosen in such a way that only a monolayer coverage of each gas is chemisorbed at the growth temperature. The self-limiting nature of ALE leads to uniform growth that does not depend on the geometry of the substrate nor is it sensitive to variations in the growth conditions [3,4]. ALE has been well demonstrated for the growth of II–VI and III–V semiconductor thin films [5,6]. These processes take advantage of the difference in the electronegativity of the two constituents to achieve self-limiting growth. Alternative methods have been proposed for ALE growth of homopolar semiconductors that rely on sequential exposure of precursor gases to the substrate. This results in the alternation of the terminating adatoms [7–12]. Our work has been stimulated by a preliminary report of ALE on the diamond (111) surface by Aleskovski and Drozd [8], based on the use of chlorocarbons and hydrocarbons as precursors. However, to the best of our knowledge, their results have not been repeated by other groups. We have thus set out to investigate this method in mechanistic detail, using *ab initio* molecular dynamics. It was found that the proposed reactions have strong steric hindrances, making them unlikely to proceed at the required rates. However, this analysis has led us to propose a different set of ALE processes based on fluorocarbons and hydrocarbons. On the less crowded (110) surface, our *ab initio* calculations show that the proposed processes are energetically very favorable and sterically unhindered. They may thus lead to a practical ALE process for the growth of diamond films.

The ALE processes described below were investigated by large-scale *ab initio* calculations using the Car-Parrinello method [13], which combines density-functional theory with molecular dynamics. The electrons are described in the local density approximation with wave functions expanded in a plane-wave basis. The ions were described by norm-conserving pseudopotentials generated using either the Hamann procedure [14] (for C and Cl) or the soft-core optimization of Li and Rabii [15] (for H and F) [16]. The plane-wave cutoffs were 35 and 50 Ry, for the Cl- and F-based ALE mechanisms, respectively. The diamond surfaces were modeled as periodically repeated slabs containing 9–11 atomic layers and separated by about 10 Å of vacuum. The large separation was necessary to minimize interactions between slab surfaces. Each layer contained 8 atoms and the bottom layer atoms were held fixed at the perfect lattice positions, while their dangling bonds were passivated with hydrogen. Because of the size of the unit cell, only the Γ point was used for k-space sampling. The total energies of the

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gas species employed in the growth mechanisms were calculated in cubic supercells with a 10 Å cube side.

The halogen-based mechanism proposed by Aleskovski and Drozd [8] involves the successive deposition of CH_4 and CCL_4 onto an initially chlorinated diamond (111) surface. The deposition would lead to evolution of HCl and an energy gain of 0.37 eV per each HCl molecule. However, our *ab initio* calculations show that both the Cl- and CH_3-terminated surfaces are overcrowded, leading to a metallic behavior. The computed energetics is

$$C(111):Cl + CH_4 \longrightarrow C(111):3H + 1\ C\ \text{layer} + HCl + 0.22\ \text{eV}/(\text{surface C}) \tag{1}$$

and

$$C(111):3H + CCl_4 \longrightarrow C(111):Cl + 1\ C\ \text{layer} + 3HCl + 2.61\ \text{eV}/(\text{surface C}). \tag{2}$$

These results can be understood by noting that the covalent radius of Cl is 33% greater than C. Therefore, the density of coverage required to fully terminate the (111) surface leads to a substantial steric repulsion. The (111):3H surface is even more crowded. In order to minimize the steric repulsion we rotated every other methyl group by 60°. Nevertheless, one H atom on each group moved up by 0.5 Å, while the other two H atoms moved downward by 0.2 Å, resulting in a canted structure. We also performed a low-temperature molecular dynamics simulation of the surface and found that it readily becomes disordered. The inherent difficulties in stabilizing the growth surfaces make high quality ALE growth based on Eqs. (1) and (2) unlikely.

However, the above analysis had led us to devise a different class of ALE mechanisms, based on the use of fluorocarbons and utilizing the much more favorable geometry of the (110) surface. Fluorine has the advantage of having a smaller covalent radius than chlorine, which reduces the steric repulsion between halogen adatoms on a diamond surface. In halogenation studies of the diamond (100) and (111) surfaces, fluorine was found to both adsorb more readily and desorb at higher temperatures than chlorine [17]. The (110) surface was chosen because each surface plane in the (110) direction is the same and has only one dangling bond per surface atom. In contrast, in the (111) direction planes having one dangling bond alternate with those having three dangling bonds per atom. The (110) surface thus both is less crowded and results in simpler ALE growth mechanisms than the (111) surface. We propose to use C_2H_4 and/or C_2F_4 as precursor gases. The exposure of F- or H-terminated (110) surfaces to the appropriate precursor gas would lead to the growth of a monolayer of diamond, a release of HF, and a switching of the terminating adatoms from H to F or vice versa. Alternatively, exposure to atomic H, H_2, or F_2 could be used as part of the ALE sequence, resulting in a combination of a growth reaction and a switching reaction. We discuss these reactions in detail below.

The direct analog of reactions (1) and (2) would be an alternative exposure of the (110) surface to C_2H_4 and C_2F_4. Starting from the hydrogenated surface, the reactions are

$$C(110):H + C_2F_4 \longrightarrow C(110):F + 1\ C\ \text{layer} + 2HF + 1.62\ \text{eV}/(\text{surface C}) \tag{3}$$

and

$$C(110):F + C_2H_4 \longrightarrow C(110):H + 1\ C\ \text{layer} + 2HF + 1.94\ \text{eV}/(\text{surface C}). \tag{4}$$

Note that the energies of these reactions were computed from total energies of the completely hydrogenated and fluorinated surfaces. Any steric repulsions between adatoms are thus taken into account. Both surfaces are semiconducting and the energy gains are quite large, which indicates the absence of substantial steric effects, although the 0.32 eV difference in the gain between the two reactions is due to the larger size of the F atom and thus the presence of some repulsion. One should also note that C_2H_4 and C_2F_4 are particularly suitable reactants for the (110) surface, since the existing C-C fragments can add parallel to the surface; see Fig. 1. The sizable energy gains are due to the large heat of formation of HF, which provides the driving force for the reactions (3) and (4). Because of its small size, HF formation and desorption should not be substantially hindered. Since ALE reactions proceed at high substrate temperatures, the reaction barriers are likely to be overcome, and the reactions (3) and (4) are thus excellent candidates for ALE. These factors should further reduce the steric constraints.

The process based on reactions (3) and (4) would lead to the growth of two monolayers per cycle, but in order to corroborate its feasibility for ALE one needs to

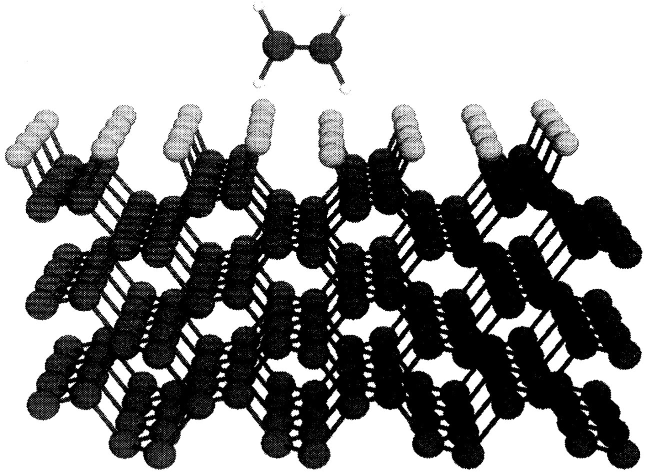

FIG. 1. Side view of the fluorinated diamond (110) surface. The atom diameters are 50% of their covalent radii. An ethylene molecule is also shown. Note that this geometry is favorable for ethylene addition parallel to the surface.

confirm the self-limiting aspect of the reactions. We thus examined the energetics of adding more than one layer during an exposure to a single reactant. Assume that the fluorinated surface, obtained as the result of reaction (3), continues to be exposed to C_2F_4. For continued growth on this surface one would need to desorb two F_2 molecules per each C_2F_4 adsorbed. However, we compute a substantial energetic loss for this reaction:

$$\mathrm{C(110):F} + \mathrm{C_2F_4} \longrightarrow \mathrm{C(110):F} + 1\ \mathrm{C\ layer} + 2\mathrm{F_2} - 2.65\ \mathrm{eV/(surface\ C)}, \qquad (5)$$

where the energy of the reaction was obtained in the limit of adding one full layer. The reaction (3) is thus clearly self-limiting, in the sense that a continued growth using C_2F_4 is energetically very unfavorable.

The self-limiting character of the second reaction was examined in a similar way. Continued growth of the completely hydrogenated surface using C_2H_4 would require the desorption of two H_2 molecules per each adsorbed C_2H_4. This reaction can be expressed as

$$\mathrm{C(110):H} + \mathrm{C_2H_4} \longrightarrow \mathrm{C(110):H} + 1\ \mathrm{C\ layer} + 2\mathrm{H_2} + 0.53\ \mathrm{eV/(surface\ C)}. \qquad (6)$$

From reaction (6) it would appear that reaction (4) is not self-limiting, since there is an energy gain of 0.53 eV. However, in order to realize this gain, a two-center reaction must take place, so that the C═C bond breaks simultaneously with the formation of two H_2 molecules. This is a very unlikely process. [In the reactions with the fluorinated surface, Eq. (4), the high binding energy of HF provides the driving force for ethylene addition *without* the simultaneous breakage of the C═C bond.] The lack of reactivity of ethylene towards the diamond surface is also clear from experimental data, since growth of diamond from hydrocarbons requires either a plasma discharge or filament-induced decomposition of the feed gas. Therefore, both growth reactions are most likely self-limiting with a single bilayer forming in each cycle. When used in an alternating fashion, ALE growth should result.

It is also possible to use alternative monolayer ALE cycles based on the main growth reactions (3) and (4). The reactions described below alternate between using one of the growth reactions together with a "switching" reaction that changes the termination of the surface. The first possibility is the reaction of F_2 with a uniformly hydrogenated (110) surface:

$$\mathrm{C(110):H} + \mathrm{F_2} \longrightarrow \mathrm{C(110):F} + \mathrm{HF} + 4.35\ \mathrm{eV/(surface\ C)}. \qquad (7)$$

This reaction has a large energy gain, primarily due to the exchange of the weak F_2 bond for the strong HF bond. The remaining fluorine atom replaces the hydrogen adatom as the terminating adatom.

One could also use a flux of atomic F to abstract H from the surface, which would be followed by fluorine adsorption at the surface. For the (110) surface this gives

$$\mathrm{C(110):H} + 2\mathrm{F} \longrightarrow \mathrm{C(110):F} + \mathrm{HF} + 7.48\ \mathrm{eV/(surface\ C)}. \qquad (8)$$

The difference between the energies of reactions (7) and (8) is due to the binding energy of F_2, which is well known to be overestimated by the local density theory [18]. Nevertheless, it is obvious that the use of atomic F would increase the energy gain, and likely also reduce the initial energy barriers.

The equivalent reactions of diatomic and atomic hydrogen with fluorinated surfaces have also been studied. We obtain

$$\mathrm{C(110):F} + \mathrm{H_2} \longrightarrow \mathrm{C(110):H} + \mathrm{HF} + 1.33\ \mathrm{eV/(surface\ C)} \qquad (9)$$

and

$$\mathrm{C(110):F} + 2\mathrm{H} \longrightarrow \mathrm{C(110):H} + \mathrm{HF} + 6.17\ \mathrm{eV/(surface\ C)}. \qquad (10)$$

These reactions thus also exhibit large energy gains.

Any of the reactions (7)–(10) can be combined with the appropriate growth reaction (3) or (4) to obtain a monolayer per cycle ALE growth mechanism. Furthermore, the reactions (7)–(10) are obviously self-limiting. However, there exists a possibility of etching, in particular for the atomic species. Since atomic H is generated in large concentrations during plasma-assisted chemical-vapor-deposition growth of diamond, it is unlikely to etch diamond at a high enough rate to inhibit growth. In fact, it has been speculated that atomic H may be beneficial for the formation of diamond by preferentially etching graphitic precursors. Atomic F, although well known to etch Si, does not etch diamond to a significant extent [17]. It has been suggested that this is due to the large radius of the F atom, which prevents its diffusion into subsurface layers. Such in-diffusion is necessary for etching silicon.

The most promising monolayer ALE mechanism would consist of reaction (3) together with either (9) or (10) to alternate the surface adatoms. This mechanism would be self-limiting, and it exhibits substantial energy gains at each step of the cycle. In addition, it avoids the usage of the highly reactive atomic and diatomic fluorine.

In summary, we have identified several highly favorable reactions that have the potential of achieving a controlled layer-by-layer growth of diamond. All of the reactions should be self-limiting and can be appropriately combined into atomic layer epitaxy cycles with either monolayer or bilayer growth per cycle. Specifically, the reactions involve the exposure of gaseous hydrospecies and fluorospecies to a hydrogenated or fluorinated diamond (110) surface. C_2H_4 and C_2F_4 are used as growth precursors when exposed to an oppositely terminated surface. Atomic and diatomic hydrogen and fluorine react with the oppositely terminated surface and lead to switching of the surface-terminating adatoms. This can be used to achieve monolayer growth per cycle. All of the reactions are very favorable energetically. This is mainly due to the formation of strongly bonded HF molecules during each of the reactions.

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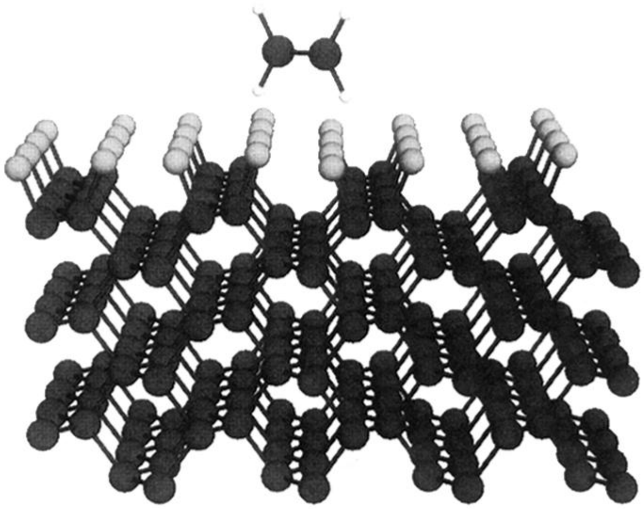

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