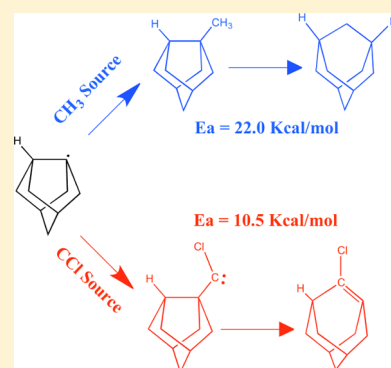


# CCl Radicals As a Carbon Source for Diamond Thin Film Deposition

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**ABSTRACT:** We use first-principles quantum mechanical calculations to study diamond thin film growth on the (100) surface using CCl radicals as the carbon source. Our results show that CCl inserts into the surface dimer C–C bonds with a barrier of 10.5 kcal/mol, roughly half of the energy required for traditional CH<sub>2</sub> insertion (22.0 kcal/mol). In addition to this, CCl has improved surface mobility (~30.0 kcal/mol barrier, versus 35 kcal/mol for CH<sub>2</sub>, along the C–C dimer chain direction), and hydrogen abstraction from the surface is also favored via atomic Cl in the vapor phase. These results explain the lower substrate temperatures achieved in crystal diamond growth from the use of chlorinated sources in CVD processes, as opposed to the more traditional CH<sub>4</sub>/H<sub>2</sub> derived species. Our results also suggest that further reductions in substrate temperatures are possible from using CCl as the only carbon source.



**SECTION:** Kinetics and Dynamics

Synthesis and deposition of diamond and amorphous diamond-like (DLC) thin films at low temperatures and pressures has attracted a great deal of interest due to the unique optical, mechanical, and thermal properties of diamond.<sup>1</sup> Various techniques have been used to this end, including chemical vapor deposition (CVD), radio frequency (RF) and direct current (DC) plasma deposition, laser plasma sources, mass-separated ion beam deposition, and sputtering.<sup>2–7</sup> Traditionally, CVD of thin diamond has used CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> or H<sub>2</sub> gas precursors, requiring high temperatures (1000–1200 K) for the substrate. This has severely limited the choice of substrates that can be used.

A significant amount of effort has been invested toward understanding the traditional CVD process. This effort has focused on mechanics of insertion and migration of CH<sub>2</sub> groups on the different crystallographic surfaces of diamond, using quantum mechanical (QM) and hybrid quantum mechanics/molecular mechanics (QM/MM) cluster methods.<sup>8–11</sup>

Experiments using CH<sub>4–n</sub>Cl<sub>n</sub> ( $n = 1–4$ ) precursors in H<sub>2</sub> and CH<sub>4</sub>/Cl<sub>2</sub>/H<sub>2</sub> mixtures as the source gas for diamond growth have shown that chlorine atoms play an important role in the creation of active surface growth sites.<sup>12,13</sup> Kotaki and Amada<sup>14</sup> reported that CCl radicals from a plasma jet containing CCl<sub>4</sub> contribute to deposit diamond, while Asmann et al.<sup>15</sup> demonstrated that the use of chlorine precursors such as Cl<sub>2</sub>, CCl<sub>4</sub>, and CHCl<sub>3</sub> reduce the CVD temperature requirements for diamond, from 800–1000 to ~400 °C. Ab initio calculations on the chemisorption of fluorine, chlorine, hydrogen fluoride, and hydrogen chloride on diamond (100) surfaces have been reported;<sup>16</sup> yet, the exact mechanisms for understanding how halogenated species affect the surface growth chemistry of diamond as a function of substrate temperature have yet to be elucidated.

In this Letter, we use QM-based density functional theory (DFT) and periodic slab models to examine the diamond thin film growth mechanisms when using CCl radicals as the carbon source, in contrast to CH<sub>2</sub>, and explain why it enables lower substrate deposition temperatures. The (100) diamond surface was chosen considering its cubic morphology and because CVD samples exhibit low defect densities and a low indexed surface. We find that the CCl radical has a low barrier for insertion into the C–C dimer on a (100) 2 × 1 bulk reconstructed surface and a relatively high surface mobility when compared to CH species. Previous experimental studies show that halogenated hydrogen–carbon CVD enhances low-temperature growth of diamond and improves its nucleation density and crystal quality when compared to the more conventional nonhalogenated counterpart.<sup>12,15</sup>

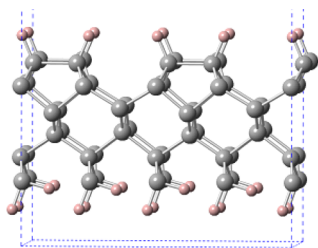
DFT calculations with periodic boundary conditions were performed using the Perdew–Burke–Ernzerhof (PBE) functional,<sup>17</sup> as implemented in the Quantum Espresso code.<sup>18</sup> We used the Vanderbilt ultrasoft pseudopotentials (USPPs) with a plane wave basis set and a cutoff energy of 30 Ry for wave functions and 240 Ry for charge density. The Brillouin zone was sampled with 1 × 2 × 1 Monkhorst–Pack  $k$ -point grid. A 10 Å vacuum between adjacent slabs was used to prevent the interaction between neighboring replicas along the  $z$  direction. Transition states were determined by using the “climbing-images” nudged elastic band (CI-NEB) method.<sup>19</sup>

A six-layered 4 × 2 reconstructed diamond slab (100) surface was used, with a one hydrogen per carbon passivation layer on one side and two hydrogens per fixed carbon on the other to maintain sp<sup>3</sup> hybridization (Figure 1). The dehydrogenation

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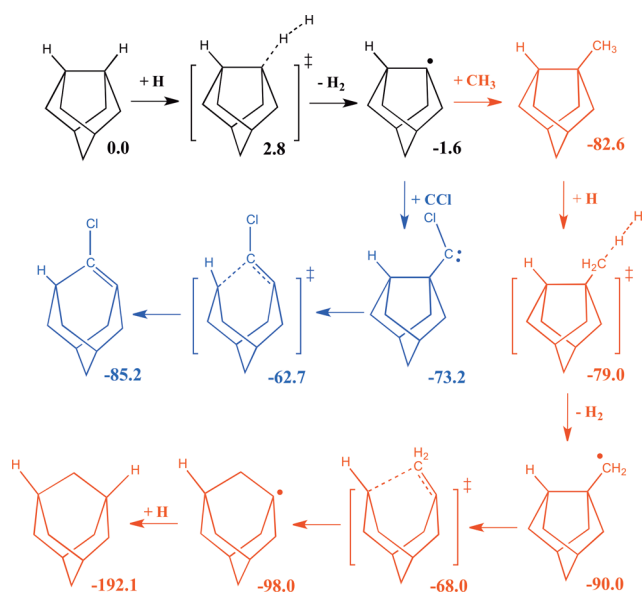
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**Figure 1.** Atomistic model used to simulate the diamond (100)  $2 \times 1$  bulk reconstructed surface. The carbon atoms in the bottom layer are fixed at their bulk positions, while others are unconstrained (carbon and hydrogen are represented by gray and pink balls, respectively).

energies of the diamond (100) surfaces using five-, six-, seven-, eight-, and nine-layer models were calculated to determine the minimum cell size under fully periodic boundary conditions. The corresponding reaction energies are 53.0, 50.5, 50.5, 50.5, and 50.6 kcal/mol for five-, six-, seven-, eight-, and nine-layer models, respectively, suggesting that the six-layer model represents the best compromise between size and accuracy. To confirm surface size independence for the reaction energies of  $H_2$  abstraction from the dimer, three different surface sizes were tested, namely,  $4 \times 2$ ,  $6 \times 2$ , and  $4 \times 4$ . All three surface models have similar energies, 82.7, 82.3, and 82.8 kcal/mol, respectively; hence, for computational efficiency reasons, we chose the  $4 \times 2$  model.

The most important step in diamond growth on the reconstructed (100) surface is the carbon incorporation onto the surface, either by insertion into a reconstructed dimer bond through the ring-opening/closing mechanism or via the trough bridging mechanism.<sup>10,20–22</sup> Figure 2 shows the classical ring-opening/closing reaction pathway of C addition to a (100) reconstructed surface using a  $CH_3$  radical adsorbant. The first step in the growth sequence is the  $CH_3$  chemisorption onto a radical vacancy site, typically created by the abstraction of a passivating H from the surface dimer by means of an atomic H in the chemical vapor phase. The abstraction process is



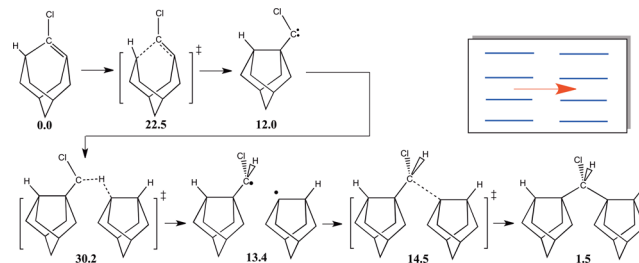
**Figure 2.** Traditional ring-opening/closing reaction pathway using  $CH_3$  (red) and  $CCl$  (blue) as precursors. The energies for intermediate states are given in blue numbers and kcal/mol units.

thermodynamically favorable and has a low reaction barrier of 2.8 kcal/mol (consistent with prior results, which obtained  $\sim 6.3$  kcal/mol),<sup>9</sup> while the  $CH_3$  chemisorption is energetically downhill. For growth to proceed, a H abstraction from this pendant  $CH_3$  needs to occur. This will form a  $CH_2$  radical that initiates the five-membered ring opening and six-membered ring formation (closing). The selective abstraction of H from the  $CH_3$  is 3.6 kcal/mol (consistent with an existing report,  $\sim 7.1$  kcal/mol).<sup>9</sup> The  $CH_2$  radical is then incorporated into the diamond dimer, via C–C bond scission of the surface dimer chain and subsequent formation of a bridge between the dimer carbons. This ring-opening/closing reaction barrier is 22.0 kcal/mol (again, consistent with prior reports, 20 kcal/mol).<sup>9</sup>

We did not observe the open ring intermediate, although such an intermediate is found to be a local minimum in the previous computational study.<sup>9</sup> Our results are consistent with a more recent study using high-level ab initio calculations that also confirm that such an intermediate is unstable.<sup>23</sup>

A key requirement for growth using  $CH_3$  radicals (e.g.,  $CH_4/H_2$  precursors) as growth species is the selective abstraction of H to form  $CH_2$ . This step conventionally involves reactions between atomic H, from the vapor phase, and the specific surface sites (depicted by the black circle in Figure 2). Instead, by using  $CCl$  radicals as the growth species, we avoid the need for a selective H abstraction step, and the reaction barrier for the ring-opening/closing decreases from 22.0 to 10.5 kcal/mol. The reaction pathway using  $CCl$  radical is also shown in Figure 2. This is clear evidence that the CVD process using  $CCl$  radicals as the growth species may proceed at lower temperatures, in comparison to the conventional nonhalogenated precursors.

Phenomenological analysis of experimental results and theoretical studies often suggests the importance of C species surface migration in the diamond growth progress.<sup>22,24–29</sup> Two primary migration mechanisms occur, migration along the dimer chain (trough) and that along the dimer row.<sup>11,26</sup> Here, we report on these migration mechanisms for  $CCl$  radicals. Figure 3 shows the corresponding migration reaction

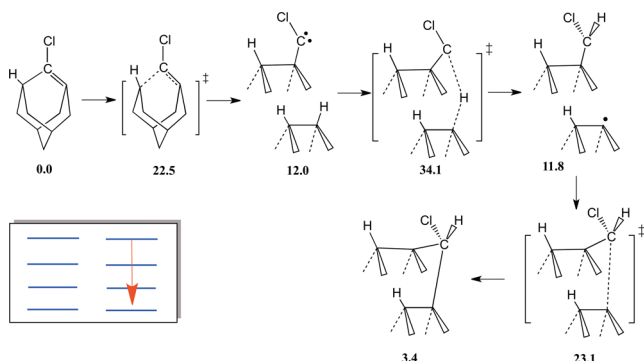


**Figure 3.**  $CCl$  migration barriers across the trough.

mechanism across the trough. The first step corresponds to the ring opening, which has a reaction barrier of 22.5 kcal/mol. The  $CCl$  radical then reacts with the adjacent surface H to form a reaction site on the neighboring C. A  $CClH$  bridging ring structure forms between the two dimers along the chain direction. The highest reaction barrier for the  $CCl$  radical to move along the dimer chain direction is 30.2 kcal/mol, which is again lower than the corresponding  $CH_2$  migration barrier of  $\sim 35$  kcal/mol (from previous calculations).<sup>9,11</sup> This migration direction is therefore within the temperature reach of traditional CVD processes, and we estimate that it could proceed below 200 °C. However, the key point here is that this

particular CCl radical migration does not require selective H abstraction from the surface in order to proceed.

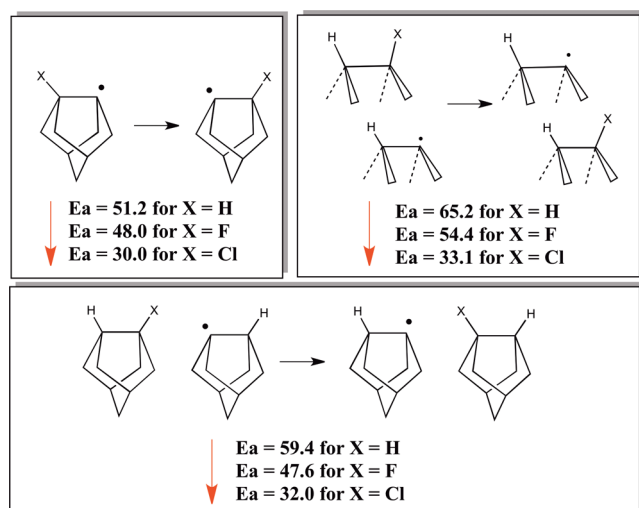
Figure 4 shows the migration reaction mechanism along the dimer row direction using a CCl radical as the growth species.



**Figure 4.** CCl migration barriers along the dimer row.

As in the dimer chain direction, it also forms a CClH bridging ring structure between two surface dimer units in a row. The overall energy barrier for a CCl radical to move along this direction is 34.1 kcal/mol. In contrast, the overall reaction barrier using  $\text{CH}_2$  growth is 26.6 kcal/mol (based on published results).<sup>9</sup> This means migration across the trough direction is favored over that in the dimer row direction when using CCl radicals as growth species.

The surface migration of H also plays an important role in the traditional CVD process.<sup>24</sup> Therefore, we expect that the migration of halogens is also important for diamond growth in halogenated carbon–hydrogen CVD processes. Consequently, we examined the surface migration barrier of Cl, H, and F. The reaction mechanisms and the corresponding energies are shown in Figure 5. The overall reaction barrier for Cl migration along



**Figure 5.** The surface migration of the Cl atom compared with H and F.

the dimer chain direction is 30.0 kcal/mol, which is much lower than that for the other species, that is, 51.2 kcal/mol for F and 48.0 kcal/mol for H. When migration occurs along the dimer row direction, the reaction barrier for Cl is 33.1 kcal/mol, which is again much lower than that for F (65.2 kcal/mol) and H (54.4 kcal/mol). From this result, we conclude that the

migration of Cl on the diamond (100) surface is relatively facile and thermodynamically favored for low-temperature CVD deposition.

Finally, to test the chemical and thermal stability of the strained CCl-inserted surface, we carried out ab initio molecular dynamics (AIMD) NVT (constant volume and temperature, with a Nosé–Hoover thermostat) ensemble simulations on a fully periodic system of 65 atoms (49 C, 15 H, and 1 Cl) in an orthogonal box ( $5.04 \times 10.09 \times 19.81 \text{ \AA}$ ) at 400 K. These calculations use the Vienna ab initio simulation package (VASP),<sup>30–32</sup> with the PBE approximation for exchange and correlation and a plane wave cutoff set to 400 eV. A Verlet algorithm with a time step of 1 fs was used to integrate the equations of motion during a 4 ps equilibrated dynamic trajectory. The surface structure remains stable during the 4 ps, suggesting that selective Cl cleavage would complete the diamond growth cycle.

To summarize, we have examined the mechanisms of carbon insertion into a reconstructed C–C dimer bond using CCl radicals and their dominant migration mechanisms (along the dimer chain and along the dimer row). In contrast with the nonhalogenated  $\text{CH}_2$  radicals, we find that surface CCl pendants have a lower insertion barrier into the diamond surface C–C dimer, as well as enhanced surface mobility. Most importantly, CCl radicals do not require the selective abstraction of H species for six-membered ring formation (a critical step for diamond growth). Cl atoms also have higher mobility on the diamond surface when compared to H. We contend that these factors are the primary reason for the experimentally observed decrease in substrate temperatures found for chlorinated CVD processes in diamond growth, in addition to the high surface radical vacancy concentration attainable from H abstraction by gaseous atomic Cl. Furthermore, the  $\beta$ -scission reaction when the carbon in the CCl group forms a double bond that leads to the dimer bond breaking is the key step for adsorbate incorporation into the diamond lattice (similar to the  $\text{CH}_2$  case). In contrast to the  $\text{CH}_2$  case, the Cl pendant avoids the formation of sp and sp<sup>2</sup> carbon sites on the surface and may be selectively cleaved.

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### Notes

The authors declare no competing financial interest.

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