

Atomic scale KMC simulation of {100} oriented CVD diamond film growth under low substrate temperature

—Part II Simulation of CVD diamond film growth in C-H system and in Cl-containing systems

Xizhong An¹⁾, Yu Zhang²⁾, Guoquan Liu¹⁾, Xiangge Qin¹⁾, Fuzhong Wang¹⁾, and Shengxin Liu¹⁾

1) Materials Science and Engineering School, University of Science & Technology Beijing, Beijing 100083, China

2) Applied Science School, University of Science & Technology Beijing, Beijing 100083, China

(Received 2002-01-28)

Abstract: The growth of {100}-oriented CVD diamond film under two modifications of J-B-H model at low substrate temperatures was simulated by using a revised KMC method at atomic scale. The results were compared both in Cl-containing systems and in C-H system as follows: (1) Substrate temperature can produce an important effect both on film deposition rate and on surface roughness; (2) Atomic Cl takes an active role for the growth of diamond film at low temperatures; (3) {100}-oriented diamond film cannot deposit under single carbon insertion mechanism, which disagrees with the predictions before; (4) The explanation of the exact role of atomic Cl is not provided in the simulation results.

Key words: CVD diamond film; atomic Cl; revised KMC (Kinetic Monte Carlo) method; atomic scale simulation

[This project was supported by National Natural Science Foundation of China (No.59872003).]

1 Introduction

Synthesis of diamond films by chemical vapor deposition (CVD) from a precursor gas mixture containing a small amount of hydrocarbon (usually methane, acetylene, *etc.*) and hydrogen as the carrier gas at sub-atmospheric pressures has become commercially viable over the last decades [1-5]. And there are several CVD methods through which diamond films can grow in high rate and high quality. One significant drawback to most of the current growth processes, however, is that they are carried out at high substrate temperatures (above 1000 K). Substrates that melt or undergo problematic phase changes at these temperatures cannot therefore be employed. It is excited that low temperature (below 1000 K) growth of diamond is one of the most important aims of CVD diamond synthesis, which requires diamond film deposition in C-H-Cl system or in C-H-O system. A decrease of the substrate temperature T_s would allow many new CVD diamond film applications [6, 7].

Several growth models of CVD diamond film in C-H system at high temperature have been the subjects of extensive investigation, both experimentally and

theoretically [8-14]. However, fewer researchers have gone in for the mechanism study of CVD diamond film growth under low temperature in Cl containing system. Recently, Joe, *et al.* reported a new model through which diamond film can grow by insertions of single carbon species at C-H bond under low substrate temperature in C-H-Cl system, and they finished the numerical simulation of diamond film formation by this mechanism [14]. The growth of diamond film under low substrate temperature is completely ascribed to the insertions of single carbon species in Joe-Badgwell-Hauge (J-B-H) model. In Part I of this two-part paper [15], The growth of {100}-oriented CVD diamond film under J-B-H model was simulated from atomic scale by using a revised Kinetic Monte Carlo (KMC) method [16]. However, through simulation we cannot make sure whether the insertions of single carbon species or atom Cl dominate the whole deposition process. To ascertain this phenomena, we revised J-B-H model and simulated the film growth under these modified models.

2 Method

Diamond is usually deposited at sub-atmospheric

pressure (about 2660 Pa in this paper). The typical deposition conditions are as follows. A feed gas of H_2 containing a small fraction of some hydrocarbon precursor (often 1% CH_4 by volume) and in some cases Cl_2 is supplied to the growth reactor and activated by exposure to a heat source (a hot filament in this paper). The growth substrate is in contact with this activated gas and diamond deposition that occurs mainly by the reaction of the substrate with H, C, CH, CH_2 and Cl *etc.* according to a set of chemical reactions listed in **tables 1 and 2**, respectively. The model in table 1 (cited as "modification 1 (mod.1)" hereafter) shows the diamond film growth by insertions of single carbon species in C-H system, where all the chemical reactions and the kinetic data are both from reference [14]. This mechanism can demonstrate the key role of single-carbon insertions during {100}-oriented CVD diamond film growth, *i.e.* whether there are open sites on the growth surface or not, there will be possible to deposit diamond on diamond substrate. In table 1, C_d is the diamond atom on the growth surface, and D is the diamond atom formed after the insertion reaction

occurs. The model in table 2 (as "modification 2 (mod.2)") indicates the growth of diamond film in C-H-Cl system. This model is helpful to examine the critical role of atom Cl during {100}-oriented CVD diamond film growth under low temperature, *i.e.* the substrate surface must be activated either by hydrogen abstraction or disadsorption to create open sites at first; then the growth species in precursor near the substrate will interact with the activated sites to finish the chemical adsorption of hydrocarbon, which will lead to the growth of diamond film. The atom Cl does not involve in the incorporation to diamond film lattice, but it can react with those species adsorbed on the surface to accelerate the process of reactions. Part of the reactions and kinetic data in table 2 are from references [11, 12, 14]. C_d represents the diamond atom on the surface, species separated by a bullet (\bullet) are dimer bonded, and an asterisk (*) represents a surface biradical. CVD diamond film can grow on {100}-oriented substrate by homoepitaxy. The growth conditions and size are all the same as in Part I [15].

Table 1 Surface-phase reactions in modification 1 of J-B-H model

No.	Surface-phase reaction	$A / (\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1})$	n	$E / (\text{J}\cdot\text{mol}^{-1})$
1	$C_dH + H \Rightarrow C_d + H_2$	7.30×10^{13}	0.0	35700.0
2	$C_d + H \Rightarrow C_dH$	1.70×10^{13}	0.0	0.0
3	$C_d + CH_3 \Rightarrow C_dCH_3$	5.00×10^{12}	0.0	0.0
4	$C_dCH_3 + H \Rightarrow C_dCH_2 + H_2$	1.00×10^{14}	0.0	43680.0
5	$C_dCH_2 + H \Rightarrow C_dCH_3$	1.70×10^{13}	0.0	0.0
6	$C_dCH_2 + H \Rightarrow C_d + CH_3$	3.00×10^{13}	0.0	0.0
7	$C_dH + CH_2 \Rightarrow C_dCH_3$	5.00×10^{13}	0.0	21000.0
8	$C_d + CH_2 \Rightarrow C_dCH_2$	5.00×10^{12}	0.0	0.0
9	$C_dH + CH \Rightarrow C_dCH_2$	5.00×10^{13}	0.0	21000.0
10	$C_d + CH \Rightarrow C_dCH$	5.00×10^{12}	0.0	0.0
11	$C_dCH + H \Rightarrow C_dCH_2$	1.70×10^{13}	0.0	0.0
12	$C_dH + C \Rightarrow C_dCH$	5.00×10^{13}	0.0	21000.0
13	$C_d + C \Rightarrow C_dC$	1.00×10^{13}	0.0	0.0
14	$C_dC + H \Rightarrow C_dCH$	1.70×10^{13}	0.0	0.0
15	$C_dC + H_2 \Rightarrow C_dCH_2$	1.70×10^{13}	0.0	0.0
16	$C_d + C_dCH_2 \Rightarrow D + C_dH_2 + D$	3.00×10^{13}	0.0	0.0
17	$C_dCH + C_dH \Rightarrow D + C_dH + D$	3.00×10^{13}	0.0	0.0
18	$C_dC + C_dH \Rightarrow D + C_d + D$	3.00×10^{13}	0.0	0.0

The diamond film growth simulations start on an H-passivated diamond substrate. All lattice sites are fixed at their diamond cubic positions. The temporal evolution of the diamond surface is simulated by means of a modified Kinetic Monte Carlo (KMC) method [16]. As the surface evolves according to this KMC method, it will be covered by various combina-

tions of radical sites, H atoms, Cl atoms and hydrocarbons chemisorbates, all of which will evolve according to the site-by-site reaction either in table 1 or in table 2. The program is written in Visual C language and run in a Pentium III 800 personal computer. The memory is 256 M and the running time is about 1 to 4 s.

Table 2 Surface-phase reactions in modification 2 of J-B-H model

No.	Surface-phase reaction	$A / (\text{mol}\cdot\text{cm}^{-1}\cdot\text{s}^{-1})$	n	$E / (\text{J}\cdot\text{mol}^{-1})$	$\Delta H / (\text{J}\cdot\text{mol}^{-1})$	$\Delta S / (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$
1	$\text{C}_d\text{H} + \text{H} \rightleftharpoons \text{C}_d + \text{H}_2$	1.30×10^{14}	0	30660.0	-41580.0	22.26
2	$\text{C}_d + \text{H} \rightleftharpoons \text{C}_d\text{H}$	1.00×10^{13}	0	0.0	-406980.0	-137.76
3	$\text{C}_d\text{CH}_2 + \text{H} \rightleftharpoons \text{C}_d + \text{CH}_3$	3.00×10^{13}	0	0.0	-103320.0	33.18
4	$\text{C}_d + \text{CH}_3 \rightleftharpoons \text{C}_d\text{CH}_3$	5.00×10^{12}	0	0.0	-297780.0	-176.40
5	$\text{C}_d\text{CH}_y + \text{H} \rightleftharpoons \text{C}_d\text{CH}_{y-1} + \text{H}_2$	2.80×10^7	2	31340.0	-47460.0	27.72
6	$\text{C}_d\text{CH}_y + \text{H} \rightleftharpoons \text{C}_d\text{CH}_{y+1}$	1.00×10^{13}	0	0.0	-348600.0	-143.22
7	$\text{C}_d \cdot \text{C}_d \rightleftharpoons \text{C}_d + \cdot + \text{C}_d$	1.00×10^{13}	0	0.0	20580.0	1.68
8	$\text{C}_d\text{H} + \text{Cl} \rightarrow \text{C}_d + \text{HCl}$	1.70×10^{13}	0	84.0	—	—
9	$\text{C}_d\text{CH}_3 + \text{Cl} \rightarrow \text{C}_d\text{CH}_2 + \text{HCl}$	1.62×10^{13}	0	3024.0	—	—
10	$\text{C}_d + \text{Cl} \rightarrow \text{C}_d\text{Cl}$	2.40×10^{13}	0	0.0	—	—
11	$\text{C}_d\text{Cl} + \text{H} \rightarrow \text{C}_d + \text{HCl}$	1.10×10^{13}	0	19320.0	—	—
12	$\text{C}_d + \cdot + \text{C}_d\text{C}_x\text{H}_y \rightarrow \text{C}_d + \text{C}_d\text{C}_{x-1}\text{H}_y + \text{C}_d$	2.00×10^{13}	0	36960.0	—	—

Note: “•”—dimer bonded; *—surface biradical.

3 Results and discussion

In the process of diamond film growth, substrate temperatures play an important role. Their effects on deposition rate, surface roughness (R_q) and height of the film can be characterized. Definitions of deposition rate and surface roughness are the same as that in reference [12]. Conditions of CVD diamond film are as following: $T_s = 900$ K, $w_{\text{Cl}} = 0.023\%$, $w_{\text{CH}_3} = 0.023\%$, $w_{\text{H}_2} = 90\%$ (w , mass fraction) and $P = 2.66$ kPa. We call this the standard case for comparison. Keeping other process parameters in standard case constant, we simulated {100}-oriented CVD diamond film growth under two modified models when the substrate temperatures are 1000, 900 and 800 K, respectively.

3.1 Simulation of CVD diamond film growth under different models at 1000 K

The evolution of diamond film deposition rate with simulation time at 1000 K is shown in **figure 1**. This plot indicates that the shape of each curve is in accordance with that in Part I of this two-part paper [15], which are all due to the morphology of the substrate surface. The diamond film deposited in Cl containing system (such as in J-B-H model [14] or in modification 2) has higher growth rate than that deposited under single carbon species insertions in C-H system. This phenomenon indicates that atom Cl is very effective in low temperature growth of diamond film, which is in well agreement with the conclusions drawn by several researchers [17-21]. And this made us doubt the role of the single carbon insertions on C-H bond in diamond film CVD process at low substrate temperatures.

Even though the growth rate in Cl containing system is higher than that in C-H system at low tempera-

tures (see **figure 1**), it also has higher surface roughness which can produce significant effects on film quality (as shown in **figure 2**). Therefore, the substrate temperature of 1000 K is not suitable for the growth of diamond film of good quality. In order to acquire the desired diamond film, suitable substrate temperature should be carefully chosen.

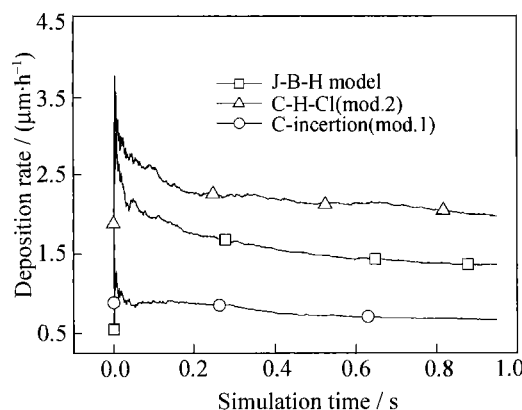


Figure 1 Evolution of diamond film deposition rate with simulation time at 1000 K.

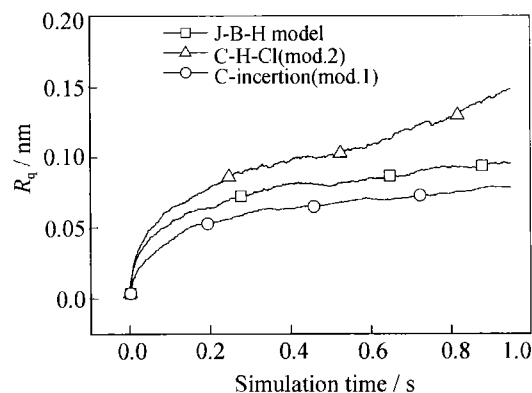


Figure 2 The evolution of diamond film surface roughness with simulation time at 1000 K.

The slope of the film height curve shown in **figure 3** represents the growth rate of diamond film in quan-

tative, *i.e.* a steep curve corresponds to a high deposition rate (see both figure 1 and figure 3).

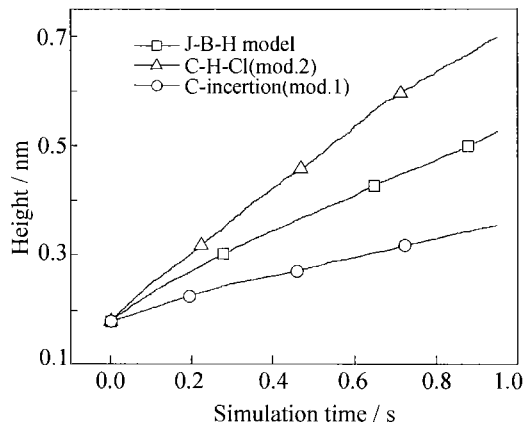


Figure 3 The evolution of diamond film height with simulation time at 1000 K.

3.2 Simulation of CVD diamond film growth under different models at 900 K

When T_s is 900 K, the difference of diamond film deposition rate between Cl containing system and single carbon insertion system becomes very evident (as shown in figure 4), and the latter made the growth rate of diamond film drop rapidly. Such low rate will have no sense for actual production of diamond film. From figure 4, it is also found that there is still disparity of growth rate in two Cl containing systems, which means the single carbon insertion cannot accelerate the film deposition.

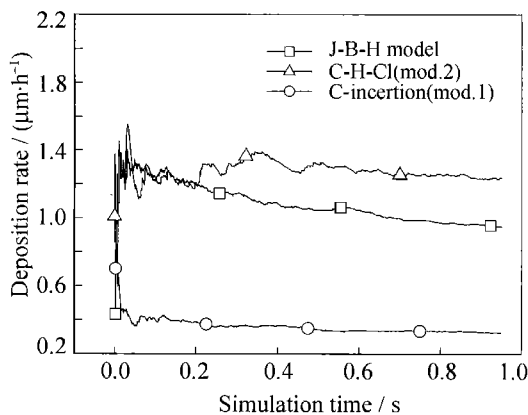


Figure 4 The evolution of diamond film deposition rate with simulation time at 900 K.

From the surface roughness curve in figure 5, it is found that smoother diamond films can be produced both in Cl containing system and in C-H system at low temperatures, compared with those created at somewhat higher temperatures (see figure 2).

3.2 Simulation of CVD diamond film growth under different models at 800 K

When the substrate temperature drops to about 800

K, it is found that in single carbon insertion system the diamond film can hardly grow. In Cl containing systems, however, the deposit rate of diamond film is relatively high (as shown in figure 6). This once again proves the important role of atomic Cl in the process of diamond chemical vapor deposition. Figure 7 is the evolution of diamond film surface roughness with simulation time. Undoubtedly, such smooth diamond film should be due to the key role of atomic Cl, not of single carbon insertion.

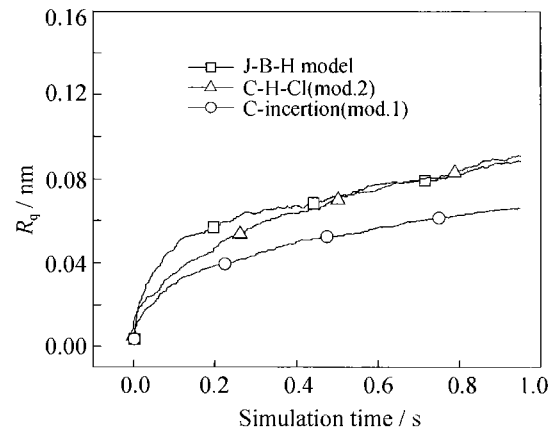


Figure 5 The evolution of diamond film surface roughness with simulation time at 900 K.

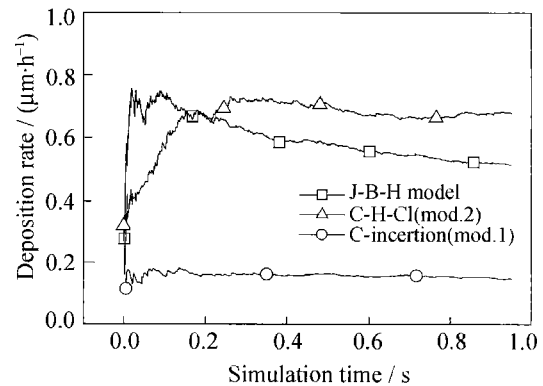


Figure 6 The evolution of diamond film deposition rate with simulation time at 800 K.

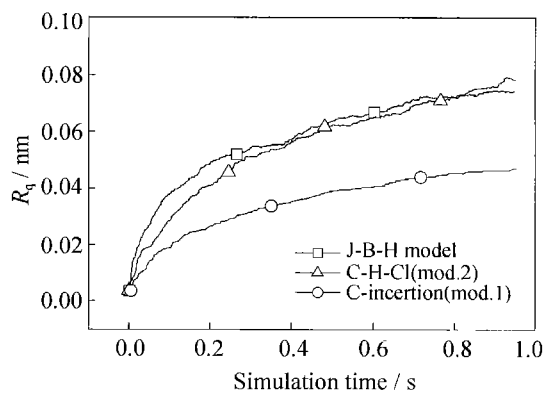


Figure 7 The evolution of diamond film surface roughness with simulation time at 800 K.

4 Conclusions

(1) Two modifications of J-B-H model have been accomplished in order to ascertain the role of atomic Cl and single carbon species insertion in CVD diamond process.

(2) The simulation results indicate that the substrate temperature (T_s) plays an important role in diamond film growth process. As the elevation of T_s , the diamond film showed a high growth rate and meanwhile a coarse surface. Therefore, considering the relationship between the deposition rate and the surface roughness, a moderate T_s should be chosen.

(3) Atomic Cl can increase the growth rate of diamond film and create smooth film in relative low T_s , but it should be constrained to a suitable concentration.

(4) Through our simulation, no predominance of single carbon species insertion has been found. On the contrary, {100}-oriented diamond film cannot deposit at a high enough rate on such mechanism as single carbon insertion at low substrate temperature. This result is in disagreement with the report before.

(5) Even though atomic Cl can produce positive effects on diamond film growth and realizes diamond film deposition at low substrate temperatures, however, what is the exact reason for atomic Cl in the process of diamond film growth still needs further study.

References

- [1] K.E. Spear, Diamond-ceramic coating of the future [J], *J. Amer. Ceram. Soc.*, 72(1989), p.171.
- [2] H. Schiomi, K. Tanabe, Y. Nishibayashi, and N. Fujimori, Epitaxial growth of high quality diamond film by the microwave plasma-assisted chemical-vapor-deposition method [J], *Jpn. J. Appl. Phys.*, 29(1990), p.34.
- [3] L.F. Suteu, C.J. Chu, M.S. Thomposon, R.H. Hauge, J.L. Margrave, and M.P. D'Evelyn, Atomic force microscopy of (100), (110), and (111) homoepitaxial diamond films [J], *J. Appl. Phys.*, 71(1992), p.5930.
- [4] F.C. Hong, G. Liang, J. Wu, D. Chang, and H. Hsieh, Diamond deposition from halogenated methane reactants in a hot-filament chemical vapor deposition reactor [J], *Appl. Phys. Lett.*, 63(1993), No.23, p.3149.
- [5] M. Okkerse, M.H.J.M. De Croon, C.R. Kleijn, G.B. Marin, and M. Okkerse, A surface and a gas-phase mechanism for the description of growth on the diamond (100) surface in an oxy-acetylene torch reactor [J], *J. Appl. Phys.*, 84(1998), No.11, p.6387.
- [6] I. Schmidt and C. Benndorf, Using fluorine and chlorine in the diamond CVD process [J], *Diamond and Related Materials*, 8(1999), p.231.
- [7] S. Proffitt, C.H.B. Thompson, A. Gutierrez-Sosa, N. Paris, N.K. Singh, R.B. Jackman, and J.S. Foord, Understanding the chemistry of low temperature diamond growth: an investigation into the interaction of chlorine and atomic hydrogen at CVD diamond surfaces [J], *Diamond and Related Materials*, 9(2000), p.246.
- [8] S.J. Harris, Mechanism for diamond growth from methyl radicals [J], *Appl. Phys. Lett.*, 56(1990), No.23, p.2298.
- [9] S. Skokov, B. Weiner, and M. Frenklach, Elementary reaction mechanism of diamond growth from acetylene [J], *J. Phys. Chem.*, 98(1994), p.8.
- [10] M. Frenklach, Monte Carlo simulation of diamond growth by methyl and acetylene reactions [J], *J. Chem. Phys.*, 97(1992), No.8, p.5794.
- [11] C.C. Battaile, D.J. Srolovitz, J.E. Butler, A kinetic Monte Carlo method for the atomic-scale simulation of chemical vapor deposition: Application to diamond [J], *J. Appl. Phys.*, 82(1997), No.12, p.6293.
- [12] M. Grujcic, S.G. Lai, Atomistic simulation of chemical vapor deposition of (111)-oriented diamond film using a kinetic Monte Carlo method [J], *Journal of Materials Science*, 34 (1999), p.7.
- [13] D. Takeuchi, S. Yamanaka, H. Watanabe, S. Sawada, H. Ichinose, H. Okushi, and K. Kajimura, High quality homoepitaxial diamond thin film synthesis with high growth rate by a two-step growth method [J], *Diamond and Related Materials*, 8(1999), p.1046.
- [14] R. Joe, T. A. Badgwell, and R. H. Hauge, Atomic carbon insertion as a low-substrate-temperature growth mechanism in diamond CVD [J], *Diamond and Related Materials*, 7(1998), p.1364.
- [15] X.Z. An, Y. Zhang, G.Q. Liu, X.G. Qin, F.Z. Wang, S.X. Liu, and J.Y. Li, Simulation of CVD diamond film growth under Joe-Badgwell-Hauge model [J], *J. Univ. Sci. Technol. Beijing*, 9(2002), No.5, p.367.
- [16] Y. Zhang, *Computer Simulation and Visualization of Growth Processes of Chemical Vapor Deposition Diamond Film* (in Chinese) [D], University of Science & Technology Beijing, Beijing, 2001.
- [17] J.-J. Wu and F.C.-N. Hong, Diamond growth by injecting thermally decomposed chlorine atoms into methane / hydrogen mixture [J], *J. Appl. Phys.*, 81(1997), p.3652.
- [18] J.-J. Wu and F.C.-N. Hong, Effect of chlorine addition on diamond growth using methane/hydrogen reactions [J], *J. Appl. Phys.*, 81(1997), p.3647.
- [19] I. Schmidt, F. Hentschel, and C. Benndorf, Low temperature diamond growth using halogenated hydrocarbons [J], *Solid State Ionics*, 101/102(1997), p.97.
- [20] I. Schmidt and C. Benndorf, Mechanisms of low temperature growth of diamond using halogenated precursor-gases [J], *Diamond and Related Materials*, 7(1998), p.266.
- [21] M. Asmann, J. Heberlein, and E. Pfender, A review of diamond CVD utilizing halogenated precursors [J], *Diamond and Related Materials*, 8(1999), p.1.