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Modelling the substrate-temperature-dependence of diamond film growth

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Abstract. A model has been developed which describes the process of substrate-temperature-dependent diamond film growth. Detailed calculations were performed for the dependence of the diamond growth rate on the substrate temperature and the flux ration of hydrogen- and carbon-containing species above the surface. The theoretical results were fitted well with the experimental observation and data for diamond deposition by the hot-filament CVD method, illustrating that the model gives a satisfactory description of the diamond formation process.

1. Introduction

Since Eversole [1] first patented his technique for diamond growth by the pyrolysis of hydrocarbon gases, it has been recognized and further established that atomic hydrogen is the species responsible for the etching of graphite during the diamond growth process [2]. However, because of the extensive use of hydrogen and hydrocarbon gas mixtures for diamond synthesis, understanding the fundamental processes of nucleation and growth in their entirety has been impeded by the complexity of the gas-phase chemistry [3,4].

In order to understand the diamond deposition process, Olson *et al* [5] constructed a novel sequential reactor which has four isolated gas environments. High-quality diamond film was obtained in this reactor by alternately exposing a substrate to a source of sputtered carbon atoms from a graphite target in a helium DC glow discharge and to one emitting atomic hydrogen generated by a hot tungsten filament. On the basis of their work, it was proposed that the growth of diamond films was governed by surface reaction and the necessity of gas-phase precursors could be precluded. They further suggested [6] that three processes might occur during diamond growth: (i) the addition of disordered carbon to the surface; (ii) the etching of this material from the surface by atomic hydrogen; and (iii) the conversion of disordered carbon into diamond mediated by atomic hydrogen. The three processes of diamond growth were then modelled by Ford [7] in terms of a set of rate equations. However, the model is very simple, especially in that it is independent of substrate temperature and insufficient to explain the experimental phenomena. If the processes of diamond growth described above were correct for general hot-filament CVD, the processes would in principle be strongly temperature-dependent, so it is necessary to develop a generally applicable model.

In this paper, we propose a model for substrate-temperature-dependent diamond film growth on the basis of Ford's model. Detailed calculation was performed and the results were compared with the experimental observations.

2. The development of the model

In a general hot-filament CVD system, we describe the diamond growth mechanism as follows: the adsorption of carbon-containing species onto the surface and finally the incorporation of the carbon atoms into the diamond lattice mediated by hydrogen atoms. Meanwhile disordered carbon may also be deposited on the surface or etched away by H atoms. Here we neglect the process of the conversion of carbon-containing species into disordered carbon on the surface and assume that the diamond grows by the conversion of disordered carbon and that this process can occur only where diamond has been coated with a monolayer of disordered carbon, so that the atom is free to re-orientate.

We focus our attention to the substrate surface where the diamond film growth occurs at a suitable site for crystal growth. Assume that the surface of the film consists of sites where carbon has bonded correctly to form a diamond lattice and sites where disordered carbon has deposited to various thicknesses. Let the fraction of the surface sites where diamond is exposed be D and the corresponding fraction where n layers of disordered carbon have been deposited be C_n . Then, in the framework of Ford, the evolution equations for the populations can be expressed as

$$dD/dt + n_h K C_1 - n_c S D + n_h E C_1 \quad (1)$$

$$dC_1/dt = -n_h K C_1 + n_c S D - n_h E C_1 - n_c S C_1 + n_h E C_2 \quad (2)$$

$$dC_n/dt = n_c S C_{n-1} - n_h E C_n - n_c S C_n + n_h E C_{n+1} \quad (n > 1) \quad (3)$$

where K is the conversion probability of the disordered carbon to diamond per second and E is the carbon etching probability per second, both processes being driven by hydrogen. S is the carbon sticking probability per second. The relation among them is

$$K + E + S = 1. \quad (4)$$

Let N_h and N_c be the surface hydrogen and carbon atom concentrations and Σ the quantity of the surface sites per unit area. n_h and n_c are defined as

$$n_h = N_h/\Sigma \quad (5)$$

$$n_c = N_c/\Sigma. \quad (6)$$

These two parameters denote the fractions that hydrogen and carbon atoms occupy per site.

The surface hydrogen concentration is determined by the balance of its adsorption and desorption. Here, we consider the ion-induced desorption and thermal desorption. The rate equation of the surface hydrogen concentration can be written as

$$dN_h/dt = J_h - J_{h0}\sigma N_h - N_h/\tau \quad (7)$$

where J_h is the flux of H from the bulk to the surface and J_{h0} is the actual bombarding flux. The second term on the right-hand side of equation (7) accounts for the de-trapping of near-surface hydrogen by ion-induced desorption, which is described by the cross section σ . The third term accounts for hydrogen loss by thermal desorption at a rate given by

$$\tau^{-1} = \tau_0^{-1} \exp[-q_1/(RT)] \quad (8)$$

where R is the universal gas constant, T is the substrate temperature and q_1 is a constant to be determined. A similar expression was used by Erents *et al* [8] to explain the strong temperature-dependence of the chemical erosion yield of graphite by hydrogen impact.

Because of the low concentration of carbon in diamond deposition, we assume that N_c is independent of T and equal to the flux of carbon-containing species from the bulk (J_c) in unit time.

The parameters K and E can be regarded as the rate of reaction of surface H atoms with reactive carbon. They are functions of surface temperature and often written as

$$E = A \exp[-q_2/(RT)] \quad (9)$$

$$K = B \exp[-q_3/(RT)] \quad (10)$$

where A , B , q_2 and q_3 are constants to be determined.

We note that the rate equations (1)–(3) are similar to those in Ford's model. However, the parameters in the equations have been re-defined with consideration of the substrate temperature. So the whole process in the model is substrate-temperature-dependent.

3. Solutions for diamond film growth

Under steady-state conditions, we have

$$dD/dt = 0 \quad (11)$$

$$dN_h/dt = 0. \quad (12)$$

The fractions D , C_1, \dots, C_n satisfy a normalization condition:

$$D + \sum_{n=1}^{\infty} C_n = 1. \quad (13)$$

From equations (1)–(3), (11) and (13), it can be obtained that

$$C_l = \frac{p(1-p)}{1+(1-p)K/E} \quad (14)$$

$$C_n = pC_{n-1} \quad (n > 1) \quad (15)$$

$$p = n_c S / (n_h E) \quad (16)$$

where p is the carbon sticking-to-etching-rate ratio. Neglecting surface reflection, namely $J_h + J_{h0}$, N_h can be derived from equations (7) and (12) to be

$$N_h = \frac{J_h}{J_h \sigma + 1/\tau}. \quad (17)$$

The diamond film growth can occur only when p is less than 1 and only in this case do the rate equations have steady-state solutions. The rate of the diamond growth is defined as

$$G = n_h K C_1 \quad (18)$$

in atoms per site per second.

In the following section, we perform detailed calculations using reasonable values for J_h , σ , τ_0 and Σ ($J_h = 1.6 \times 10^{16}$ atoms $\text{cm}^{-2} \text{s}^{-1}$, $\sigma = 10^{-16}$ cm^2 , $\tau_0 = 10^{-13}$ s and $\Sigma = 10^{13}$ cm^{-2}). We take q_1 , q_2 and A according to [8]: $q_1 = 54.61$ kcal mol^{-1} , $q_2 = 38.0$ kcal mol^{-1} and $A = 10^6$. The values of q_3 and B are taken as $q_3 = 54.0$ kcal mol^{-1} and $B = 10^9$.

4. Calculations and conclusions

The diamond growth rate was calculated as a function of the substrate temperature when J_h/J_c is fixed (shown in figure 1). It can be seen from figure 1 that the growth rate has its highest value at about 1150 K and that it increases almost linearly with substrate temperature in the lower temperature region and decreases quickly in the higher region. This qualitative behaviour of the calculated growth rate agrees well with the experiment

result (see [9]). That is, a relatively sharp maximum in the growth rate is observed. Within the model a simple explanation can be given as follows. At low temperature, the hydrogen desorption from the surface is small; the rate of diamond growth is determined mainly by the reactions between hydrogen and carbon atoms. With increasing deposition temperatures, the reactions become faster, resulting in a higher growth rate. Above a certain temperature, the desorption of the hydrogen atoms becomes more important than the reactions and the growth rate decreases sharply. We can further obtain from figure 1 that the growth rates can be expressed approximately by the Arrhenius equation [10] in the lower temperature region. Then an effective activation energy for diamond growth of about 16 kcal mol^{-1} can be obtained, which is close to the experimental value of about 22 kcal mol^{-1} [10].

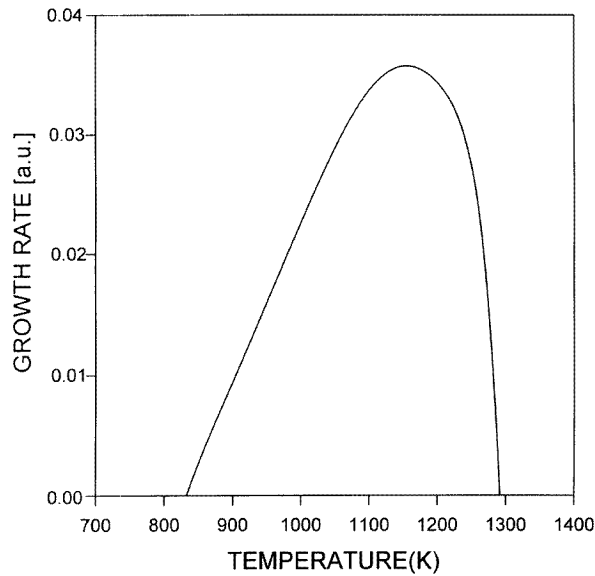


Figure 1. A plot of the diamond growth rate against the substrate temperature with $J_h/J_c = 12000$.

From figure 1, it can also be noted that there is a range of the substrate temperature within which diamond growth can occur. The low and high critical values of the temperature are determined by $p = 1$ and $p = 0$ respectively. From equations (16) and (17), it is not difficult to find that, when T is fixed, p is normal to J_c/J_h . So, for a certain T , J_h/J_c must be larger than a critical value, ensuring the condition of diamond growth ($p < 1$). The critical value of $(J_h/J_c)_{cri}$ at a certain value of T can be obtained when $p = 1$. Figure 2 shows the relation between $(J_h/J_c)_{cri}$ and the substrate temperature T . We note that, when $T < 1200 \text{ K}$, $(J_h/J_c)_{cri}$ increases linearly with T , which illustrates that a higher substrate temperature needs a higher $(J_h/J_c)_{cri}$ above which diamond can grow. However when $T > 1200 \text{ K}$, $(J_h/J_c)_{cri}$ decreases with T . In the experiment of Olson *et al* [5], it was reported that diamond could be grown only for a ratio of H to C fluxes greater than about 4000 at a substrate temperature of $1070 \pm 50 \text{ K}$. Our theoretical result is consistent with this point.

Another observation in their experiment is that the diamond growth rate increased greatly as the flux ratio increased above this threshold. Figure 3 shows our calculation result of the dependence of the growth rate on J_h/J_c when T is fixed at 1100 K . From figure 3

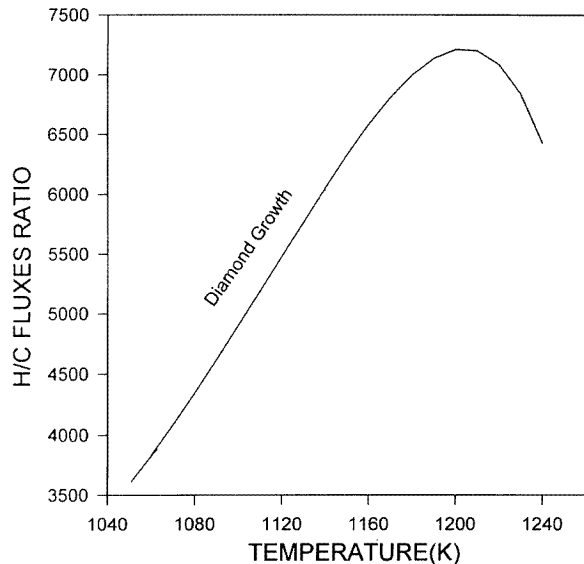


Figure 2. The critical values of the H/C fluxes ratio $(J_h/J_c)_{cri}$ as a function of the substrate temperature.

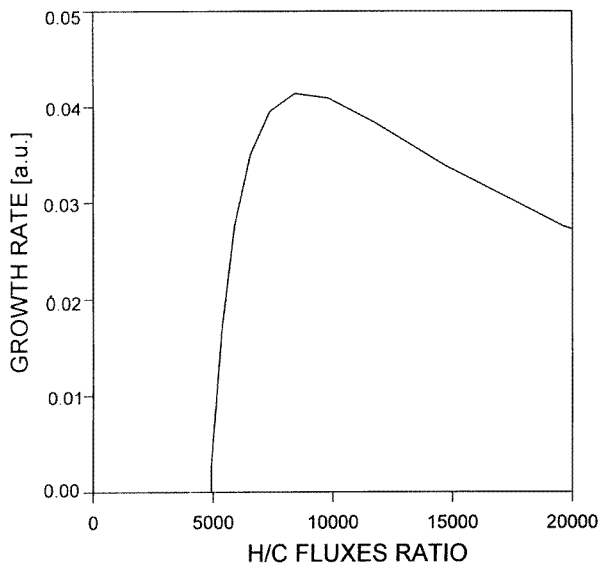


Figure 3. A plot of the diamond growth rate against the H/C fluxes ratio J_h/J_c with the substrate temperature fixed ($T = 1100$ K).

it can be found that the calculation result conforms to the experimental observation when J_h/J_c is less than a value of about 9000. When J_h/J_c is larger than this value, the growth rate decreases with increasing J_h/J_c . This is reasonable because the carbon source will not be abundant enough to supply the diamond growth if J_h/J_c is too large. Furthermore, in

a general hot-filament CVD system, it is reported that there is an initial rise in diamond growth rate for increasing methane fractions and that a very sharp drop occurs at a certain methane content [11]. The calculation result agrees with this experimental result if we assume that J_h/J_c is related directly to the H_2/CH_4 ratio.

In conclusion, a model was developed for substrate-temperature-dependent diamond growth by a general hot-filament CVD method. Through the detailed calculation, we obtain that: (i) the diamond growth rate depends strongly on the substrate temperature and there exists a maximum growth rate at an appropriate substrate temperature; (ii) the diamond growth rate is also influenced greatly by the flux ratio of hydrogen- and carbon-containing species to the surface; (iii) it must be larger than a critical value above which diamond growth can occur; and (iv) we predict an effective activation energy for diamond growth of about 16 kcal mol^{-1} in the lower temperature region, close to the observed one. These results agree well with the experimental results, which proves that our model gives a sufficiently good description of the diamond formation process with different substrate temperatures.

Here, we only consider the case of diamond film growth ($p < 1$). When $p > 1$, which is the case for graphite growth, the solutions of the rate equations become unsteady. So a different method of treatment of the rate equations should be involved. In addition, in most experimental cases, there is not only diamond growth but also a certain amount of graphite. Thus, for a more general theory, the growth of diamond and graphite should be treated simultaneously. This will be our further work.

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