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Abstract. A model is developed which describes the growth of graphitic and amorphous carbon, and diamond. The results of detailed calculation illustrate that diamond and amorphous carbon grow simultaneously in the process of diamond chemical vapour deposition, and that their growth rates depend strongly on the substrate temperature and the flux ratio of hydrogen- and carbon-containing species. In addition, it was found that there are critical values for the substrate temperature and the flux ratio of hydrogen- and carbon-containing species below which only graphitic carbon film can grow.

1. Introduction

Research on the growth of crystalline diamond films by the chemical vapour deposition (CVD) method has been intensified in recent years. Diamond can be grown from a gas mixture of a carbon compound and hydrogen under conditions for which diamond is thermodynamically metastable. During deposition, molecules which contain carbon and hydrogen are excited. Some excited carbon species condense on the substrate surface and combine to form sp^2 and sp^3 carbon hybridization states [1–3], i.e., to form thermodynamically stable graphitic and amorphous carbon, and metastable diamond structures [4].

Modelling the CVD diamond process which interprets experimental results can help to clarify the underlying growth mechanisms. A number of theoretical models have been proposed to describe the surface processes occurring during diamond CVD [5–7]. Recently, we proposed a theoretical model on the basis of Ford's model [8] to describe the dependence of the diamond growth rate on the substrate temperature [9], which gives some explanation of the experiment results. However, the theory only treats the growth of diamond. In most experimental cases there is not only diamond growth but also to a certain extent there is amorphous carbon or graphite growth. Therefore in an extended theory the growth of diamond and the growth of amorphous carbon or graphite should be treated simultaneously. In this paper, we modify the previous model presented in [9], and give an extended theory for the growth of graphitic and amorphous carbon, and diamond film.

2. Model development

In this model, we introduce the concept of 'germs', as intermediate species in the formation of diamond, which is taken from Avrami's work where the kinetic equation for the phase

change is described [10].

We assume that the diamond can only be transformed from germs and not from disordered carbon directly. Then, the diamond growth mechanism is described as follows: (1) the adsorption of carbon-containing species onto the surface; (2) the formation of germs from the disordered carbon; and (3) the diamond growth when the germs incorporate into the diamond lattice. Meanwhile disordered carbon may also be deposited on the surface or may be etched away by H atoms, and the process of the conversion of carbon-containing species into disordered carbon is neglected. We further assume that the germs grow by the conversion of disordered carbon, and this process can occur only where diamond or germs are coated with a monolayer of disordered carbon.

As for the previous model [8, 9], the processes of film growth can be modelled using rate equations. Let the fraction of the surface sites at which diamond and germs are exposed be D and G, and the corresponding fractions where n layers of disordered carbon have been deposited be C_n. Then the evolution equations for these populations are

$$dD/dt = n_h K_1 G_1 - n_c SD + n_h E p C_1 \tag{1}$$

$$dG/dt = -n_h K_1 G + n_h K_2 C_1 - n_c SG + n_h E q C_1 \tag{2}$$

$$dC_1/dt = -n_h K_2 C_1 + n_c S(D + G) - n_h E C_1 - n_c SC_1 + n_h E C_2 \tag{3}$$

$$dC_n/dt = n_c SC_{n-1} - n_h E C_n - n_c SC_n + n_n E C_{n+1} \qquad (n > 1) \tag{4}$$

where K_1 and K_2 are the probabilities of conversion of the germs to diamond and of the disordered carbon to germs per second, and E is the carbon etching probability per second; all of the three processes are driven by hydrogen. Also S is the carbon sticking probability per second. The relation between K_2, E and S is

$$K_2 + E + S = 1. \tag{5}$$

p and q are the probabilities of diamond and germs above which only one layer of disordered carbon has been deposited. Their relation is

$$p + q = 1. \tag{6}$$

This equation means that there is either diamond or germs under a single layer of disordered carbon on the surface. And

$$p = \frac{D}{D + G} \tag{7}$$

$$q = \frac{G}{D + G}. \tag{8}$$

n_h and n_c are the fractions occupied per site by hydrogen and carbon atoms:

$$n_h = N_h/\Sigma \tag{9}$$

$$n_c = N_c/\Sigma \tag{10}$$

where N_h and N_c are the surface hydrogen and carbon atom concentrations, and Σ is the number of surface sites per unit area.

The rate equation of the surface hydrogen concentration can be written as

$$dN_h/dt = J_h - J_{h0}\sigma N_h - N_h/\tau \tag{11}$$

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 (11) 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

$$\tau^{-1} = \tau_0^{-1} \exp(-q_1/RT) \tag{12}$$

where R is the universal gas constant, T is the substrate temperature, and q_1 is a constant to be determined.

The parameters K_1, K_2 and E are functions of the surface temperature, and are often written as

$$E = A \exp(-q_2/RT) \tag{13}$$
$$K_1 = B \exp(-q_3/RT) \tag{14}$$
$$K_2 = C \exp(-q_4/RT) \tag{15}$$

where A, B, C, q_2, q_3 and q_4 are constants to be determined.

In the above processes, it is proposed that the growth of disordered carbon forms graphitic carbon whose Raman shift is at 1580 cm^{-1}, and the growth of the germs forms amorphous carbon whose Raman shift is centred at about 1550 cm^{-1}.

3. Solutions

Under steady-state conditions, we have

$$dD/dt = 0 \tag{16}$$
$$dG/dt = 0 \tag{17}$$
$$dN_h/dt = 0. \tag{18}$$

The fractions $D, G, C_1, \ldots, C_n$ satisfy a normalization condition:

$$D + G + \sum_{n=1}^{\infty} C_n = 1. \tag{19}$$

From equations (1)–(4), (16), (17) and (19), we obtain

$$C_1 = \frac{p(1-p)}{1 + (1-p)K_2/E} \tag{20}$$

$$G = \frac{n_h K_2(1 + K_2/E)}{(n_h K_1 + n_c S)(1 + K_2/E) - n_h E} C_1 \tag{21}$$

$$C_n = pC_{n-1} \qquad (n > 1) \tag{22}$$

$$p = n_c S/n_h E. \tag{23}$$

Here p is the ratio of the carbon sticking rate to the etching rate. Neglecting surface reflection, i.e., for $J_h = J_{h0}$, N_h can be derived from equation (11) and equation (18):

$$N_h = \frac{J_h}{J_h \sigma + 1/\tau}. \tag{24}$$

When p is less than 1, diamond and amorphous carbon can grow. In this case the rate equations have steady-state solutions. The rates of the diamond and the amorphous carbon growth are defined as

$$R_d = n_h K_1 G \tag{25}$$
$$R_g = n_h K_2 C_1 - R_d \tag{26}$$

in atoms per site per second, and the growth rate of the whole film is

$$R = R_d + R_g = n_h K_2 C_1. \tag{27}$$

When p is larger than 1, graphitic carbon film will grow; the deposition rate is given by

$$R_c = (n_c S - n_h E) \sum_{n=1}^{\infty} C_n = n_h E(p - 1). \tag{28}$$

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 cm^{-2} s^{-1}, $\sigma = 10^{-16}$ cm^2, $\tau_0 = 10^{-13}$ s and $\Sigma = 10^{13}$ cm^{-2}). We take $q_1 = 54.61$ kcal mol^{-1}, $q_2 = 38.0$ kcal mol^{-1}, $q_3 = 63.5$ kcal mol^{-1}, $q_4 = 46.0$ kcal mol^{-1}, $A = 10^6, B = 10^{10}$ and $C = 10^7$. The values of $J_h, \sigma, \tau_0, A, B, q_1$ and q_2 were taken according to experimental results and the theoretical work of Erents *et al* [11]. The value of Σ was taken as the maximum value of the diamond nucleation density, and the values of C, q_3 and q_4 were taken according to the fit of the calculation results to the experimental observations.
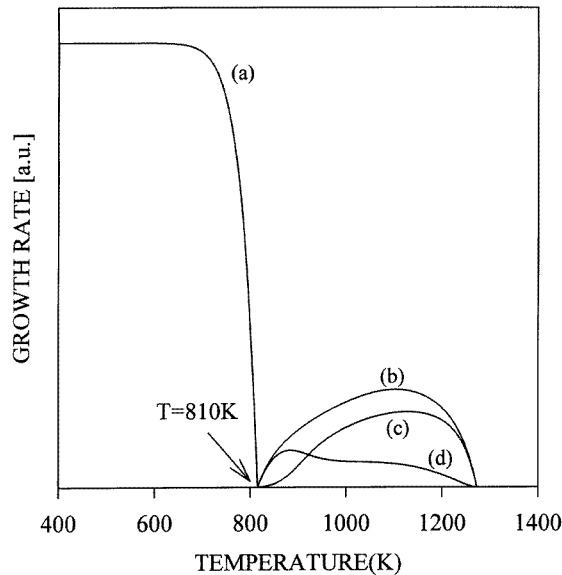

Figure 1. The growth rates of: (a) graphitic carbon film; (b) the diamond–amorphous carbon film; (c) diamond; (d) amorphous carbon, against the substrate temperature, with $J_h/J_c = 12\,000$.

4. Calculations and discussions

In figure 1, the calculated growth rates of diamond, amorphous carbon, the film made up of diamond and amorphous carbon combined ($p < 1$), and the graphitic carbon film ($p > 1$) are shown as functions of the substrate temperature (T) with J_h/J_c fixed. We can find from the figure the following features.

(1) When T is less than a critical value (810 K), graphitic carbon film will grow. Its growth rate drops sharply until zero is reached, when T is close to the critical value. This is because the rate of etching of carbon by hydrogen becomes more important than the deposition rate as T gets nearer to the critical value.

(2) There is a range of substrate temperature for which diamond and amorphous carbon can grow simultaneously as shown in figures 1 as curves (c) and (d). The two forms have
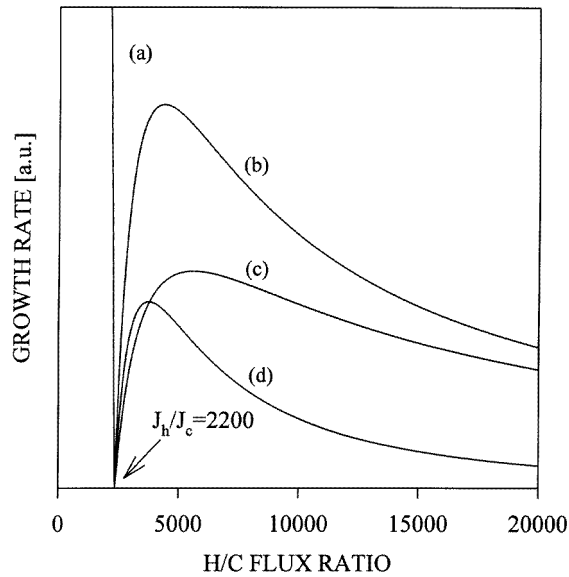
Figure 2. The growth rates of: (a) graphitic carbon film; (b) the diamond–amorphous carbon film; (c) diamond; (d) amorphous carbon, against the H/C flux ratio J_h/J_c, with the substrate temperature fixed ($T = 1100$ K).

their highest growth rates at about 1160 K and 870 K, while the film growth rate takes its highest value at about 1130 K.

(3) It can also be noted that when T is less than 930 K, the film contains more amorphous carbon than diamond. However, the diamond constituent becomes dominant in the film with the increase of the substrate temperature. This trend is consistent with the experiment results [12] where the ratio of the diamond and amorphous carbon in the film is determined by the heights of their Raman peaks centred at 1333 cm^{-1} and 1550 cm^{-1}.

Figure 2 shows our calculation results on the dependence of the growth rates on J_h/J_c when T is fixed at 1110 K. There also exists a critical value of J_h/J_c ($J_h/J_c = 2200$) below which the graphitic carbon film grows quickly and linearly with the decrease of J_h/J_c. When J_h/J_c is larger than the critical value, the deposition of the film containing both diamond and amorphous carbon commences and the growth rate goes through a maximum at about $J_h/J_c = 4000$. In addition, it can be noted that when J_h/J_c is larger, the growth rate of diamond decreases more slowly than that of amorphous carbon. So the film possesses more diamond as J_h/J_c increases. The calculation results agree with the experimental results [12, 13] if we assume that J_h/J_c is related to the ratio of H$_2$/CH$_4$ directly.

In conclusion, an extended model has been developed which treats the growth of graphitic and amorphous carbon, and diamond. Their growth rates were calculated as functions of the substrate temperature and the flux ratio of hydrogen- and carbon-containing species, respectively. The results are consistent with those of experiment: that diamond and amorphous carbon grow simultaneously in the process of diamond CVD, and that both of their growth rates are greatly influenced by the substrate temperature and the flux ratio of the hydrogen- and carbon-containing species. We also find that there are critical values for the two factors below which only graphitic carbon film can grow.

References

[1] Tsai H C and Bogy D B 1987 *J. Vac. Sci. Technol.* A **5** 3287
[2] Sharma S C, Green M, Hyer R C, Dark C A and Black T D 1990 *J. Mater. Res.* **5** 2424
[3] Beeman D, Silverman J, Lynds R and Anderson M R 1984 *Phys. Rev.* B **30** 870
[4] Kobashi K, Nishimura K, Kawate Y and Horiuchi T 1988 *Phys. Rev.* B **38** 4067
[5] Frenklach M 1992 *J. Chem. Phys.* **97** 5794
[6] Harris S J 1992 *J. Chem. Phys.* **96** 2371
[7] Butler J E and Woodin R L 1993 *Phil. Trans. R. Soc.* A **342** 209
[8] Ford I J 1995 *J. Appl. Phys.* **78** 7573
[9] Shen M-R, Wang H, Ning Z-Y, Ye C and Ren Z-X 1996 *J. Phys.: Condens. Matter* **8** 8953
[10] Avrami M 1939 *J. Chem. Phys.* **7** 1103
[11] Erents S K, Braganza C M and McCracken G M 1976 *J. Nucl. Mater.* **63** 399
[12] Kondoh E, Ohta T, Mitomo T and Ohtsuka K 1993 *J. Appl. Phys.* **73** 3041
[13] Olson D S, Kelly M A, Kapoor S and Hagstrom S B 1993 *J. Appl. Phys.* **74** 5176