Model of the competitive growth of amorphous carbon and diamond films

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Recent experiments by D. S. Olson, M. A. Kelly, S. Kapoor, and S. B. Hagstrom [J. Appl. Phys. **74**, 5167 (1993)] have demonstrated that depending on the ratio of the fluxes of carbon and atomic hydrogen onto a substrate in a chemical vapor deposition reactor, either an amorphous carbon deposit, or a crystalline diamond film, may be produced. A simple interpretation of these findings is proposed, based on a set of phenomenological rate equations for various growth and etching processes. The model is simple enough to admit analytical solutions in certain circumstances, which may provide insights into the optimisation of carbon film deposition methods. © *1995 American Institute of Physics.*

I. INTRODUCTION

Diamond and diamond-like carbon films have remarkable properties, with great potential for useful applications (for reviews see Refs. 1–3). A tremendous amount of research has been directed in recent years towards understanding the methods by which they are produced, which are mostly chemical vapour deposition (CVD) techniques. The ultimate aim of this effort is to improve the properties of the coatings, for example the adhesive strength, homogeneity, or hardness; or the economics of production, which would include the rate of growth of the films, and the nature of the precursors.

Modelling studies which interpret experimental data can help to clarify the underlying growth mechanisms. Much attention has been devoted to identifying sequences of attachment of various reactive species to a growing film.[4–9] This has been coupled to models of the chemical dissociation of the gaseous precursors in various types of CVD reactor, and the transport of the products to the surface.[10–13] In a more phenomenological approach, rate equations for growth have been developed, based on an assumed molecular attachment mechanism but calibrated using experimental data.[14,15]

Film deposition experiments of a particularly simple nature were recently carried out by Olson et al.[16,17] It was demonstrated that films could be deposited on a silicon wafer mounted on a rotating platform, which was exposed sequentially to fluxes of sputtered carbon, and hot filament-generated atomic hydrogen, respectively. The rates of incidence of each species during each exposure period could be controlled separately, and the cycle time could also be varied. The character of the deposit was investigated for a range of exposures of the substrate to the carbon and hydrogen sources.

Most interestingly, for particular relative fluxes of the two species, no film could be grown. If the ratio of fluxes was shifted away from this condition, then either amorphous carbon films could be deposited (for an increase in the carbon flux) or diamond films were produced (by increasing the flux of hydrogen). The rate of growth of each type of film

increased as the flux ratio moved away from the no-growth situation, and in the case of a diamond product, the quality of the film (measured by its Raman spectrum) also improved.

These observations were taken by Olson et al.[18] to suggest that the etching of carbon by hydrogen is an important ingredient in the overall film growth mechanism. The differential etch rates of sp^2 and sp^3 bonded carbon has often been thought to be important as a means of stabilising the diamond structure.[19] In this paper, a simple set of rate equations is developed to express the same ideas mathematically. This is presented in the next section. Some solutions to the equations in the amorphous and crystalline growth regimes are then given in Sec. III, and their properties are discussed and compared with the experimental observations. A summary and some conclusions are given in Sec. IV.

II. MODEL DEVELOPMENT

The recent demonstration by Olson et al.[16,17] that a diamond film could be grown using pure hydrogen and carbon fluxes implies that surface interactions control the deposition, and that the simplest ingredients, namely H and C atoms, are all that are required for diamond synthesis to occur. It was suggested[18] that three processes take place: the addition of disordered carbon to the surface, the etching of this material from the surface by atomic hydrogen, and the conversion of disordered carbon into diamond, mediated by hydrogen. The latter represents the bonding of the adsorbed carbon into the correct lattice position, and is assumed to occur only where the diamond is coated with a monolayer of disordered carbon, so that the atom is free to reorient, and also so that hydrogen may assist the process. The conversion process might simply be the formation of a second bond between an adsorbed carbon and the substrate. Atomic hydrogen would assist this by removing any hydrogen bonded in positions which might prevent this taking place. Even then, conversion may occur only at a suitable site for crystal growth, such as a ledge.

This set of processes can be modelled using rate equations. 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

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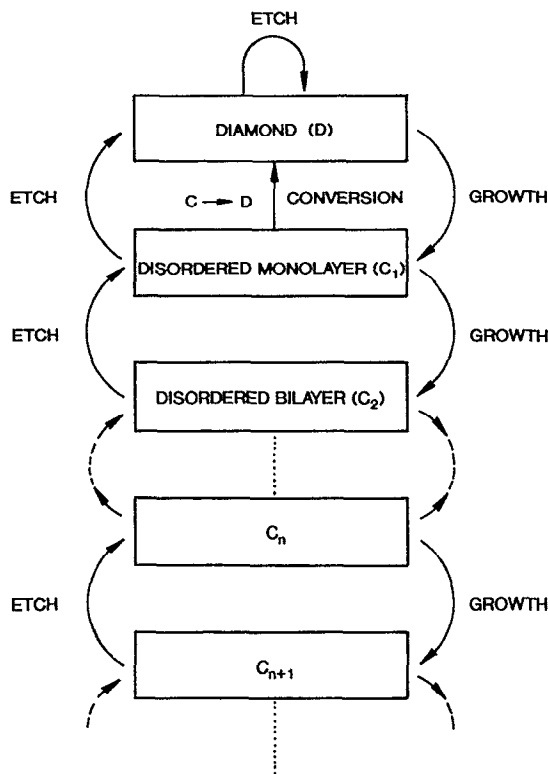
FIG. 1. Processes involved in the film deposition scheme.

exposed be D, and the corresponding fractions where n layers of disordered carbon have deposited be C_n. Then the evolution equations for these populations are

$$\frac{dD}{dt} = \phi_H K C_1 - \phi_C A D + \phi_H E_C C_1 \qquad (1)$$

$$\frac{dC_1}{dt} = - \phi_H K C_1 + \phi_C A D - \phi_H E_C C_1 - \phi_C A C_1 + \phi_H E_C C_2 \qquad (2)$$

$$\frac{dC_n}{dt} = \phi_C A C_{n-1} - \phi_H E_C C_n - \phi_C A C_n + \phi_H E_C C_{n+1}, \quad n > 1 \qquad (3)$$

where ϕ_C and ϕ_H are the fluxes of atomic carbon and hydrogen at the surface, A is the carbon sticking probability; E_C is the carbon etching probability and K the disordered carbon to diamond ($C \rightarrow D$) conversion probability, both processes driven by hydrogen. For example, the fraction of diamond surface sites can change, according to Eq. (1), either by $C \rightarrow D$ conversion, attachment of carbon from the gas phase to form a disordered carbon monolayer site, or the etching of a disordered carbon monolayer site, respectively. The deposition of material to form the diamond lattice directly is assumed to be very unlikely, or impossible. The rates of hydrogen-induced $C \rightarrow D$ conversion and carbon etching are assumed to be proportional to the hydrogen flux. The equations are examples of the *birth and death* equations often used in the study of nucleation processes. A box-model illustration of the various processes possible is given in Figure 1.

$C \rightarrow D$ conversion can occur only where a ledge in the underlying diamond crystal is covered by a carbon monolayer, so the conversion probability K represents the product of the conversion probability for such a site multiplied by the fraction of all sites which are potential growth sites.

III. SOLUTIONS TO RATE EQUATIONS

A. Diamond film growth

The equations must be solved subject to a normalization condition:

$$D + \sum_{n=1}^{\infty} C_n = 1, \qquad (4)$$

and it can be shown that time-independent solutions are possible only if

$$x = \frac{\phi_C A}{\phi_H E_C} < 1, \qquad (5)$$

in which case

$$D = \frac{(1 + K/E_C)(1 - x)}{(1 + K/E_C)(1 - x) + x} \qquad (6)$$

$$C_1 = \frac{xD}{(1 + K/E_C)} \qquad (7)$$

$$C_n = x C_{n-1}, \quad n > 1. \qquad (8)$$

The populations of adsorbed carbon columns overlying the perfect diamond lattice decrease with increasing thickness, so that there is always an appreciable density of the disordered carbon monolayer to be converted to diamond by the incident hydrogen flux. The rate of growth of diamond is

$$R_d = \phi_H K C_1 - \phi_H E_D D, \qquad (9)$$

in atoms per unit area per second. The second term represents the process of diamond etching with probability E_D per site per incident H atom. Neglecting this process, which is slow, R_d can be written
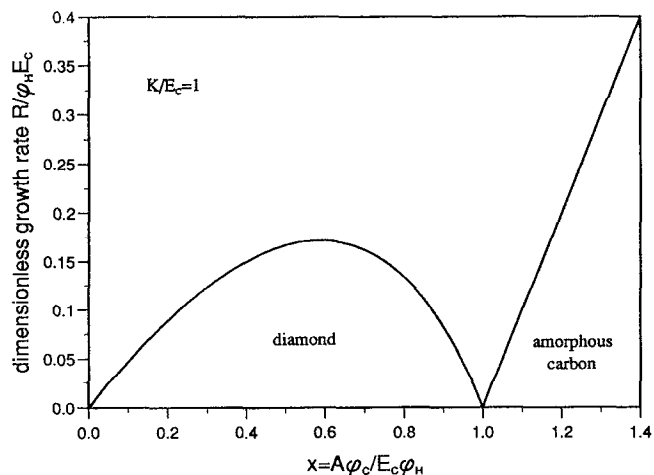

FIG. 2. Film growth rate against ratio of rate coefficients x. For $x < 1$ the material deposited is diamond, while for $x > 1$ it is amorphous carbon.

$$R_d = \frac{\phi_C A(1-x)K/E_C}{1+(1-x)K/E_C} = \frac{\phi_H K x(1-x)}{1+(1-x)K/E_C}. \qquad (10)$$

If $K \gg E_C$, then $R = \phi_C A$, which is the maximum possible rate of growth, and $D \approx 1$ so that the surface is then virtually entirely ordered in the diamond lattice arrangement. In the opposite extreme, $K \ll E_C$, the growth rate becomes very small, as is to be expected if $C \rightarrow D$ conversion is unlikely. Another feature of Eq. (10) is that there exists an optimum flux ratio of C to H atoms for maximum growth: too little C (small x) and no monolayer is deposited; too much C (large x) and the potential diamond growth sites are smothered by unproductive disordered carbon multilayers, and an amorphous carbon film is then deposited. The dependence of R_d on x (for $x < 1$) is illustrated in Figure 2. The deposition of amorphous carbon when $x > 1$ is discussed in the next section.

If the C to H flux ratio can be related to the proportions of hydrocarbons and hydrogen in the reactor gas mixture, then an optimum gas mixture for growth is implied, which is indeed found in practice. The maximum rate of diamond film growth, for a constant hydrogen flux, occurs at

$$x = \frac{E_C}{K}\left[1 + \frac{K}{E_C} - \left(1 + \frac{K}{E_C}\right)^{1/2} \right], \qquad (11)$$

or $x \approx 1/2 + K/(8E_C)$ for small K/E_C.

Two problems prevent the direct use of Eq. (10) in real cases: the relationship between the atomic fluxes and the gas mixture proportions is not known, as are the values of the sticking, etching and conversion probabilities. In order to overcome the first difficulty, it is necessary to model the gas reactions in the reactor, in particular the dissociation of the hydrogen and hydrocarbon precursors, and the transport processes towards the substrate.[10] As for the unknown coefficients, one can either fit them to diamond growth rate data, or use separate effect data such as graphite etch rates in a hydrogen plasma.[20]

B. Amorphous carbon film growth

For $x > 1$ no steady state solutions to the rate equations exist. The new situation represents runaway disordered carbon deposition with complete smothering of the active diamond growth sites. A snapshot of the developing populations is shown in Figure 3 for particular choices of the rate coefficients such that $x = 4/3$. The peak moves towards the right as time progresses, and the width of the distribution depends on the choice of rate coefficients. In this case, the surface is particularly rough: the width of profile is of the same order of magnitude as the mean film thickness. The velocity of the C_n profile towards larger values of n increases as the carbon flux increases. In fact the deposition rate of amorphous carbon, in conditions when $D \ll 1$, is given by

$$R_a = (\phi_C A - \phi_H E_C)\Sigma C_n = \phi_H E_C(x-1), \qquad (12)$$

which is indicated in Figure 2. At $x = 1$, there is an exact balance between the deposition and etching of carbon, and no films are grown.
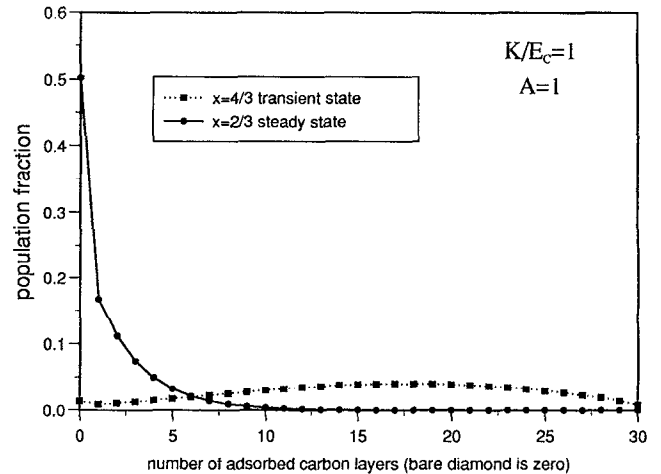

FIG. 3. Surface fractions of adsorbed carbon layers for a case of steady state diamond growth, and a case of time-dependent amorphous carbon deposition.

In the case where a flux of hydrogen is absent, the equations can be solved analytically for large enough times. The populations are then given by:

$$C_n = \frac{(\phi_C A t)^n}{n!}\exp(-\phi_C A t), \qquad (13)$$

and the mean value of n is equal to $\phi_C A t$. The rate of growth of amorphous material increases linearly with carbon flux [which is the correct limit of Eq. (12)], and so does the roughness of the deposit.

In contrast, the steady state distribution for $x = 2/3$ [given by Eqs. (6)–(8)] is also shown in Figure 3. The diamond growth rate is proportional to the C_1 population, which is large and time-independent for $x = 2/3$, and small and decreasing with time for $x = 4/3$.

Olson et al.[17] observed that diamond could be grown only for a ratio of H to C fluxes greater than about 3000–5000. The growth rate of diamond increased as the flux ratio
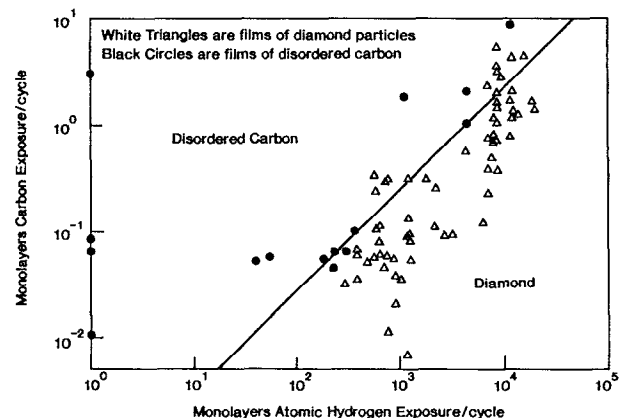

FIG. 4. Growth regimes for carbon films: dependence on exposure to sputtered carbon and atomic hydrogen. The solid line is a fit of the zero-deposition line in the model to the boundary between the two regimes.

was increased above this threshold, and similarly, the growth rate of a disordered carbon film increased as the ratio was reduced below this value. The model is consistent with this behavior if $A/E_C \approx 4000$. Sticking probabilities are commonly taken to be unity and so $A = 1$. The observed growth rate of the diamond film fixes the remaining parameter K and the model is then complete. A comparison with Olson et al.'s growth regime observations[17] is given in Figure 4. The axes give the exposure of the substrate to each species during each cycle of the processing procedure and the solid line represents $x = 1$, the zero-deposition rate condition.

Data was gathered only for a particular substrate temperature, and etch rates are in principle temperature dependent, so additional parametrisation would be necessary for a more generally applicable model. Furthermore, instead of being constants, the attachment and etch rates might depend on the local environment at a site, particularly the presence of adsorbed species on adjacent sites. Such a development would be reminiscent of some features of the KPZ continuum growth model.[21] The effect would be to reduce the roughness in the films since exposed atoms would be more likely to be removed, and troughs would be filled in. This would also result if surface transport were allowed. The model would therefore require some development before being generally predictive.

IV. CONCLUSIONS

Rate equation descriptions of diamond growth have been suggested previously,[14,15] but have been somewhat limited in the range of processes which are considered, in particular, etching has not been described explicitly. The present model describes carbon deposition in two competing modes: as an ordered diamond lattice, and as a disordered amorphous carbon layer. Material deposited by both modes can be etched away by atomic hydrogen, but the diamond structure resists this more strongly. Furthermore, atomic hydrogen is assumed to induce the conversion to diamond of an adsorbed monolayer of disordered carbon. This conversion may be pictured as the formation of additional bonds, of the correct orientation, between an adsorbed carbonaceous group and the diamond substrate. These ideas have been suggested by Olson et al.,[18] and are represented here using simple rate equations for the surface fractions of various populations. The processes are illustrated in Figure 1.

It has been shown that two distinct growth regimes are described by the equations. For a low ratio of carbon flux to atomic hydrogen flux, diamond is deposited in a steady state process. The equations can be solved analytically and predict an initially increasing growth rate as the carbon flux increases. This behavior eventually reverses, and there exists an optimum C:H flux ratio for which the growth rate is at a maximum. In the model, diamond deposition relies on a balance between the deposition of carbon, and its subsequent modification by atomic hydrogen, and the maximum rate of diamond deposition occurs when the balance is just right.

The rate of diamond deposition falls to zero as the ratio of C to H fluxes increases above the optimum value. The critical ratio for zero deposition corresponds to complete etching of all carbon deposited. For ratios greater than the critical value, amorphous carbon films are deposited. The process is not a steady state, since even for a constant growth rate, the roughness of the surface always increases. The rate of growth is proportional to the carbon flux.

The model is very simple, and not yet calibrated for general conditions of substrate temperature, but the framework developed might easily be extended to allow this, if data were available for the evaluation of various rate coefficients. More importantly, the model can account for several observed phenomena, and if the interpretation is correct, then this might help to identify the carbon film growth mechanism.

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