

# Boundaries of the diamond domain in the C–H–O diagram of carbon film deposition

I J Ford†

Department of Materials, University of Oxford, Parks Road, Oxford, Oxfordshire OX1 3PH, UK

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**Abstract.** Chemical vapour deposition experiments using gas mixtures of hydrocarbons with carbon dioxide can produce films of either diamond or a graphitic, amorphous form of carbon. The boundaries of the diamond growth domain in the triangular C–H–O gas composition diagram appear to be straight lines. It is shown that this is consistent with a simple model of the competition between the deposition of diamond and amorphous carbon phases. Gas phase carbonaceous fragments can attach to the surface of a growing film. Hydrogen in the gas phase etches poorly bound carbonaceous material from the surface, and also assists the incorporation of carbon into the diamond lattice. Oxygen in the gas phase forms carbon monoxide, and oxygen-bearing species also etch carbonaceous material. With these simple ingredients a rate equation approach is developed which also predicts the rate of diamond growth within the diamond domain, and indicates that oxygen can improve the efficiency of the process.

## 1. Introduction

Diamond films are grown in chemical vapour deposition (CVD) reactors by breaking carbonaceous gas phase molecules into reactive fragments using an energy supply (for example a hot filament or an electromagnetically driven plasma) and allowing the fragments to condense onto the surface to be coated. In many cases, the reactor gas mixture contains hydrocarbons such as methane or ethyne, together with hydrogen, carbon dioxide or carbon monoxide. The process has received a great deal of attention because diamond films are thought to be ideal for many possible applications, ranging from protective coatings to electronic devices [1].

The low-pressure deposition conditions in CVD reactors are well outside the high-pressure/high-temperature region of the carbon phase diagram where diamond is the stable allotrope. The formation of diamond is believed to be favoured, however, by the presence of highly reactive hydrogen atoms in the activated gas mixture. It is thought that the lifetime of any non-diamond carbon deposited on the surface is limited due to etching by hydrogen atoms. For hydrogen-rich mixtures, therefore, diamond deposition will occur.

However, for carbon-rich gas mixtures, the disordered, graphitic phase is favoured. As the carbon fraction in the gas mixture increases, the steady state surface composition

during growth changes, with non-diamond material being deposited in between the growing diamond crystallites. Similarly, the bulk quality of the diamond, measured in terms of its non-diamond content, changes. Eventually, for a sufficiently carbon-rich mixture, only the non-diamond phase is present on the surface and in the film. There is therefore a (somewhat blurred) boundary in the triangular C–H–O gas composition diagram introduced by Bachmann *et al* [2] between the diamond and graphitic deposition domains. On the other hand, if the oxygen fraction in the gas mixture is progressively increased, a point is reached where no carbon deposits are produced. This defines the other boundary of the diamond domain in the Bachmann diagram, adjacent to the no-growth regime [2].

The competition between the growth modes has been described recently using a set of rate equations [3]. According to the model, which was developed for C–H gas mixtures in response to a series of experiments conducted by Olson *et al* [4], the transition to the graphitic domain occurs at a critical ratio of the surface fluxes of reactive carbon species and hydrogen atoms, denoted  $\phi_C$  and  $\phi_H$  respectively, i.e.

$$\frac{\phi_C}{\phi_H} = \beta \quad (1)$$

with  $\beta$  a parameter which may be temperature dependent. If it is assumed that  $\phi_C$  and  $\phi_H$  are related to the carbon and hydrogen elemental fractions in the gas mixture, then this can be translated into a critical elemental mixture corresponding to the boundary between diamond and

† Now at: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.

graphitic deposition. Within the graphitic and diamond domains, relative deposition rates are predicted [3].

The situation is made more complicated if oxygen is added to the gas mixture, for example in the form of O<sub>2</sub>, CO or CO<sub>2</sub>. Although too much oxygen cuts off all growth, adding some oxygen can increase the growth rate of diamond compared to a C–H mixture. This has been demonstrated very clearly in recent CVD experiments using a sequential reactor [5]. In this paper, the simple phenomenological model described earlier [3] is extended to allow for the presence of oxygen in the gas mixture. Using the simplest assumptions, it is shown that the geometry of the diamond domain in the C–H–O phase diagram can be understood, and that an oxygen-induced enhancement in the diamond growth rate can also be obtained. These themes are developed in the following three sections. Conclusions are then drawn in section 5.

## 2. Extended model for C–H–O mixtures

The deposition process will be described in the same way as previously [3]. Rather than investigate the attachment and removal of groups in microscopic detail, a coarse scale approach is used, concentrating on the deposition of layers of material of various character. Three key surface processes are considered. Firstly, the attachment of reactive carbonaceous groups, such as methyl radicals, from the gas phase. Secondly, the removal of such groups driven by etchant species, principally hydrogen atoms, but also any radicals deriving from oxygen in the gas mixture. The third step is the conversion of an attached, randomly oriented and therefore non-diamond carbonaceous group into a correctly bonded diamond structural unit. This step is considered to be driven by hydrogen atoms, since unwanted hydrogens generally need to be removed from the attached group. These three steps are given more substance in the Harris mechanism of diamond growth [6]. The conversion, or cementation, step corresponds to the bonding of an attached methyl group at a step on the (hydrogen terminated) diamond surface by the elimination of two hydrogens. Rather than specify a particular mechanism, however, the present model is developed in a more general manner in order to encompass a wider range of microscopic models which fit into the basic three-process pattern.

It is implicit that carbonaceous material can attach to a group which has not yet been cemented into place as diamond. In this way, one can consider carbonaceous bilayers, trilayers, etc. This is a slightly inappropriate nomenclature, since the layering of a disordered material is imprecise, but the approximate terminology is useful. Multilayer carbonaceous group deposition would lead to a film which would almost certainly contain hydrogen, and which would be amorphous in structure. The key to diamond growth is to maintain a rate of diamond cementation without the surface being smothered with amorphous material to deeper and deeper thicknesses.

In order to model these processes, we construct, as before [3], rate equations describing the evolution of the fractional area of the surface covered by amorphous carbonaceous layers with various thicknesses. The area

fraction occupied by exposed diamond is  $D$ , and the corresponding fractions where  $n$  disordered layers of carbonaceous material have deposited are denoted  $C_n$ . Then the evolution equations for these populations are

$$\frac{dD}{dt} = \phi_H K C_1 - \phi_C A D + (\phi_H E_H + \phi_O E_O) C_1 \quad (2)$$

$$\frac{dC_1}{dt} = -\phi_H K C_1 + \phi_C A (D - C_1) - (\phi_O E_O + \phi_H E_H) (C_1 - C_2) \quad (3)$$

$$\frac{dC_n}{dt} = \phi_C A (C_{n-1} - C_n) - (\phi_O E_O + \phi_H E_H) (C_n - C_{n+1}) \quad (4)$$

for  $n > 1$

where  $\phi_H$ ,  $\phi_C$  and  $\phi_O$  are the surface fluxes of hydrogen atoms, carbonaceous fragments, and oxygen-containing etchant species respectively.  $A$  is the carbonaceous fragment sticking probability;  $E_{H,O}$  are the fragment etching probabilities due to hydrogen and oxygen species respectively; and  $K$  the disordered carbonaceous monolayer to diamond conversion, or cementation, probability. In principle, the attachment and removal coefficients should depend on  $n$ , i.e. the depth of the disordered layer, but for simplicity  $n$ -independent values are used.

The various terms describe the dynamics of the surface populations of different layer thicknesses. For example, the addition of a carbonaceous group transfers population from an  $n$ -layer to an  $(n + 1)$ -layer. Etching performs the reverse. Cementation is the unique process in the scheme which converts carbonaceous monolayers ( $C_1$ ) into diamond ( $D$ ). A box model of the population dynamics is shown in figure 1.

The terms in the rate equations which differ with respect to the earlier scheme [3] involve the oxygen species flux  $\phi_O$ . They are introduced to represent two empirical facts: that oxygen can etch a carbon film, but does not seem to drive diamond growth [5]. It is in this second role that oxygen species differ from hydrogen atoms. The simplest way in which this key difference can be modelled is to add an oxygen flux term to the etch rates in the equations, but to use hydrogen alone as the driver of diamond cementation.

The rate equations can be solved in the steady state, making use of the normalization condition  $D + \sum_{i=1}^{\infty} C_i = 1$ . The results are

$$D = \frac{(1 + y + K/E_H)(1 + y - x)}{(1 + y + K/E_H)(1 + y - x) + x(1 + y)} \quad (5)$$

$$C_1 = \frac{x(1 + y - x)}{(1 + y + K/E_H)(1 + y - x) + x(1 + y)} \quad (6)$$

$$C_n = \frac{x}{1 + y} C_{n-1} \quad n > 1 \quad (7)$$

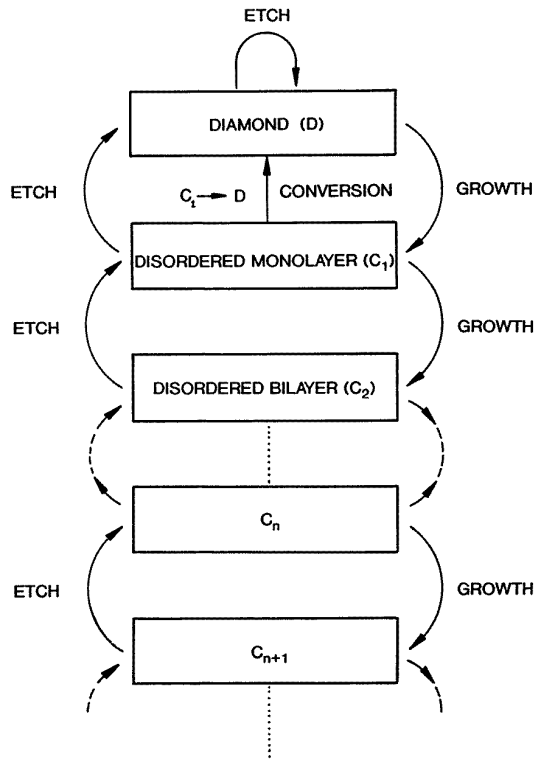
where

$$x = \frac{\phi_C A}{\phi_H E_H} \quad (8)$$

and

$$y = \frac{\phi_O E_O}{\phi_H E_H} \quad (9)$$

The rate of diamond growth, in atoms per unit area per second, is then given by  $R_d = \phi_H K C_1$  if the etching of



**Figure 1.** Box model of the population dynamics of diamond/amorphous carbon deposition. Each arrow corresponds to a term in the appropriate rate equation.

diamond itself by hydrogen or oxygen (represented by the self-terminating loop on the  $D$  box in figure 1) is neglected.

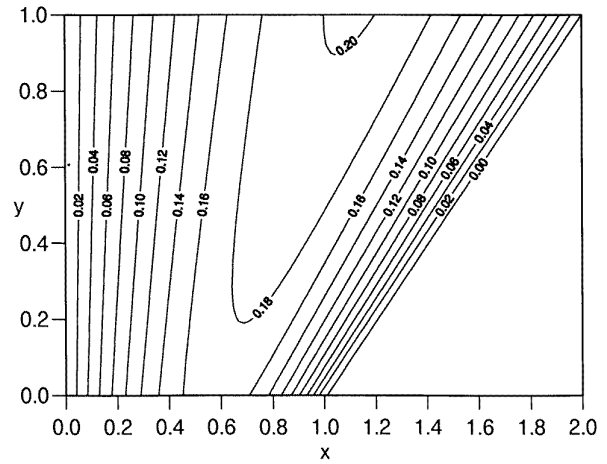
The condition for deposition of diamond rather than amorphous carbon is

$$x \leq 1 + y \quad (10)$$

which generalizes the result  $x \leq 1$  obtained in [3], which is equivalent to equation (1) with  $\beta = E_H/A$ . The diamond domain in the  $x - y$  plane is shown in figure 2, plotted using an assumed value of  $K/E_H$  of unity. It lies between  $x = 0$  and  $x = (1 + y)$ . For  $x > (1 + y)$  the surface becomes covered with thicker and thicker graphitic layers. Contours of  $C_1$ , which is also the dimensionless growth rate  $R_d/K\phi_H$ , are shown for a value of  $K/E_H = 1$ . The dimensionless growth rate along the  $x$ -axis was given in [3]. We therefore see that a flux of a reactive oxygenated species (a non-zero value of  $y$ ) allows diamond deposition to occur at higher carbon/hydrogen ratios than would be permitted in its absence. For a given value of  $x$  it can be shown that the maximum in  $C_1$  occurs on the line  $x = (1 + y)/2$  and is given by

$$C_1^{max}(x) = \frac{x}{4x + K/E_H} \quad (11)$$

which is apparent in the shape of the contours. Clearly, the addition of oxygen makes possible, within the model, a higher rate of diamond growth (per incident hydrogen atom), as long as the carbon flux is adjusted to satisfy the above condition. In simple terms the oxygen performs the etching task leaving more hydrogen available to carry out



**Figure 2.** Monolayer surface fraction  $C_1$  against carbon and oxygen flux parameters  $x$  and  $y$ , for  $K/E_H = 1$ .

the diamond cementation. The highest surface fraction of diamond for a given  $x$  is given by

$$D^{max}(x) = \frac{2x + K/E_H}{4x + K/E_H} \quad (12)$$

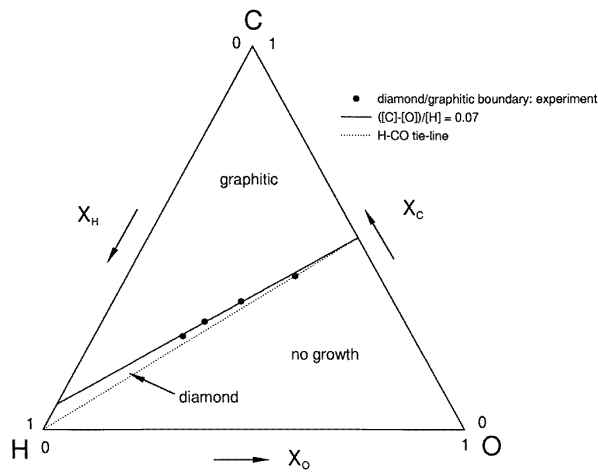
which falls with increasing  $x$ . On the other hand, the growth rate rises and then falls with  $x$ , at a fixed  $y$ . In the model, therefore, the fastest growing films do not necessarily have the largest surface area fraction of exposed diamond during deposition.

The contours of  $C_1$  in the  $x - y$  plane correspond to those of the diamond growth rate per hydrogen atom. The growth rate per incident carbonaceous group is given by  $R_d/(A\phi_C) = (K/E_H)C_1/x$  and a similar plot to figure 2 could be constructed, with the diamond domain lying between the same boundaries, but with a different set of contours.

The diamond domain in the  $x - y$  plane must now be translated into conditions in the C–H–O gas composition diagram. This means we need to relate the fluxes of active species to the elemental concentrations in the gas mixture. A simple treatment of this problem is suggested in the next section.

### 3. Mapping into the Bachmann diagram

The connection between gas phase composition and the concentrations of reactive species is provided by studying the chemical thermodynamics of C–H–O mixtures [7, 8]. Instead of applying the full thermodynamic treatment, however, a simpler approach will be used here. Studies have strongly suggested that the most stable oxygenated gas phase species is carbon monoxide. The carbon tied up in this species will not take any part in the growth dynamics. Making the approximation that the bulk of the oxygen is present in the form of CO, the flux of carbonaceous fragments onto the surface should therefore be a function of the difference between the carbon and oxygen elemental concentrations in the mixture:  $\phi_C \propto \mathcal{F}([C] - [O])$ , where the square brackets denote elemental



**Figure 3.** Phase diagram for carbon film deposition, showing experimental points on the diamond/graphite domain boundary [9], and a straight line fit corresponding to  $([C]-[H])/[O] = 0.07$ .

concentrations. This immediately yields the diamond/no-growth boundary condition  $[C] = [O]$  corresponding to  $x = 0$ : this origin of the diamond/no-growth boundary has been suggested before [9]. As for the etching species, the simplest approach possible is to make  $\phi_H$  and  $\phi_O$  functions of the elemental concentrations  $[H]$  and  $[O]$  respectively. While the representation of  $\phi_H$  in this way is probably reasonable,  $\phi_O$  should perhaps be more complicated, in view of the formation of the CO species. However, we shall pursue the simplest approach, and not only use these representations, but also assume that each relationship is linear. Then  $x = (1 + y)$  is equivalent to

$$[C] - [O] = \mathcal{A}[H] + \mathcal{B}[O] \quad (13)$$

introducing temperature-dependent coefficients  $\mathcal{A}$  and  $\mathcal{B}$ . This condition describes a straight line on the triangular C–H–O gas composition diagram introduced by Bachmann *et al* [2] shown in figure 3. Each vertex represents a pure element, and all possible C–H–O mixtures are contained within the triangle. The coordinates along the sides are

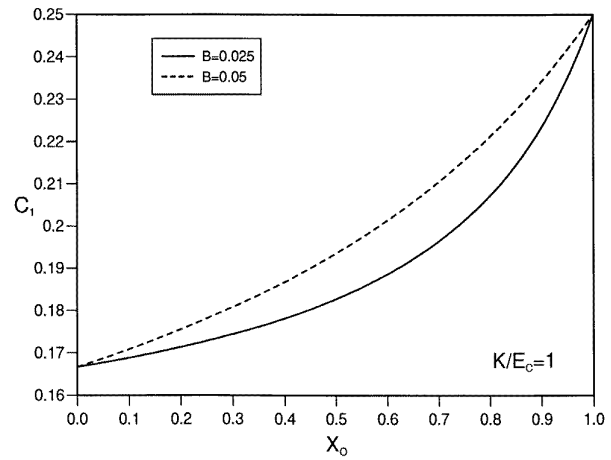
$$X_C = [C]/([C] + [O]) \quad X_O = [O]/([O] + [H])$$

$$X_H = [H]/([H] + [C]).$$

The straight line described by equation (13) joins the points at  $\{X_C = (1+\mathcal{B})/(2+\mathcal{B}); X_H = 0\}$  and  $\{X_H = 1/(1+\mathcal{A}); X_O = 0\}$ . We now compare this expectation with results from some experiments.

#### 4. Discussion

The nature of the deposited phase for a range of compositions of the gas phase has been studied recently by Marinelli *et al* [9, 10]. Chemical vapour deposition experiments were conducted using mixtures of hydrocarbons and carbon dioxide in the gas phase. As the proportion of hydrocarbon was increased, the process



**Figure 4.** Variation in monolayer surface fraction  $C_1$ , and specific growth rate of diamond, along the centre line of the diamond domain.

moved from the no-growth regime into the diamond domain and finally the graphitic domain.

Points representing the transition from diamond to graphitic deposition for experiments using  $\text{CO}_2$  with  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  are shown, from left to right, as full circles in figure 3 [9]. It is apparent that a straight line corresponding to the condition  $([C]-[O])/[H] = 0.07$  can account for the tendency of the diamond domain to broaden as the mixture moves towards the H vertex. This experimental boundary fits the expected condition given in equation (13) with  $\mathcal{B} \ll 1$ , and with  $\mathcal{A} = 0.07$ . Unfortunately, it is difficult to obtain a more precise fit to the parameter  $\mathcal{B}$  since data are lacking in the region close to the pure CO composition. An estimated upper limit for  $\mathcal{B}$  is 0.05.

It was pointed out in [9] that the observed diamond growth domain in the hydrocarbon/ $\text{CO}_2$  experiments had a different shape to that proposed originally by Bachmann *et al* [2]. In the original conception, the domain widened towards the upper right, with upper and lower boundaries approximately given by straight lines joining points  $\text{CO}_{0.75}$  and  $\text{CO}_{1.2}$  respectively to the H vertex. The diamond/graphite boundary would in this case be consistent with equation (13) with  $\mathcal{B} = 1/3$ . The simple linear mapping of the diamond domain from the  $x - y$  plane into the C–H–O diagram would therefore seem to be able to account for either this diamond domain, or the data produced by Marinelli *et al* [9]. The common feature of the two representations of (different) experimental data is the straight line boundaries, which is a natural prediction from the present model.

Although the straight line boundary seems consistent with the experiments of Marinelli *et al* in the centre of the C–H–O diagram, its extrapolation onto the C–H axis reduces to  $[C]/[H] = 0.07$ , representing, for example, a mixture of approximately 14% by volume of methane in hydrogen. This is perhaps three times too much methane than found experimentally at the diamond/graphite boundary, which suggests that the simplified mapping from the  $x - y$  plane to the Bachmann diagram used above is

inadequate close to the H vertex. This suggests that a better representation of the gas phase chemistry ought to be attempted in this region.

We now consider the variation in the specific diamond growth rate within the diamond domain. A surface plot of  $C_1$  (which is proportional to the diamond growth rate) within this region is difficult to display, due to the narrow geometry of the domain. It would correspond to a distorted version of figure 2: lines of constant  $x$  correspond to straight lines on the C–H–O diagram emanating from the centre of the C–O side, and lines of constant  $y$  correspond to lines parallel to the C–H side of the triangle.  $C_1$  rises from zero at each boundary of the diamond domain and peaks along a ridge line corresponding to the condition

$$2([C] - [O]) = A[H] + B[O] \quad (14)$$

which approximately bisects the angle between the no-growth and diamond/graphite boundaries of the diamond domain, and which is equivalent to the line  $x = (1 + y)/2$ . The maximum in  $C_1$  for a given value of  $x$  along this line was given by equation (11). Converting this to elemental concentrations, we write

$$C_1^{ridge} = \frac{A[H] + B[O]}{(4 + K/E_H)A[H] + 4B[O]} \quad (15)$$

Note that values of  $C_1$  along the ridge line denote maxima with respect to a change in oxygen fraction at a given value of  $([C] - [O])$ . Maxima with respect to oxygen change for a mixture with a fixed  $[C]/[H]$  ratio will be slightly different.

The variation in specific growth rate (equation (15)) along the ridge line (equation (14)) is shown in figure 4 for  $K/E_H = 1$ ,  $A = 0.07$  and for two values of  $B$ . The maximum value of  $C_1$  forecast in equation (11) is only realized when quite close to the ‘CO’ limit. Nevertheless, there is a steady increase in diamond growth rate per incident hydrogen atom as the oxygen content of the mixture is increased.

Since we are restricted to considering only the relative abundances of C, H and O in the mixtures, we can only predict relative and not absolute growth rates. The rate of diamond growth is proportional to  $\phi_H$ , and so the deposition rate will depend not only on the hydrogen fraction, but also on the gas partial pressures. The simple model described here would suggest that diamond growth could be enhanced simply by increasing these pressures, and the high growth rates found using gas torch deposition equipment at atmospheric pressure may be a reflection of this. However, the microwave and hot-filament driven CVD reactors work best at low pressure, and so the situation is not so straightforward. The fluxes of active fragments do not seem simply to increase as the partial pressures of feed gases increase.

## 5. Conclusions

A simple model of the competition between the growth of diamond and amorphous, graphitic carbon has been extended to include oxygen within the mixture of gases used in a chemical vapour deposition (CVD) process.

The model is based on rate equations which describe the addition and removal of layers of carbonaceous material on the surface of a substrate placed within the CVD reactor. Gas phase carbonaceous species provide reactive fragments which attach to the surface. Gas phase hydrogen selectively removes poorly bonded carbonaceous material, and also strips off unwanted structures which prevent attached groups bonding as the diamond phase. Gas phase oxygen can also etch carbonaceous material and, in addition, tie up a proportion of the available gas phase carbon in the form of CO, which reduces the flux of reactive carbonaceous groups to the surface. Starting with these simple assumptions, and also making some simple representations of the surface fluxes of various species in terms of the elemental composition of the gas phase, it is possible to account for the shape of the diamond growth domain within the C–H–O gas composition diagram. In addition, the variation in the rate of growth of diamond per incident hydrogen atom can be predicted for mixtures within the diamond domain. This specific growth rate peaks along a line running (to a good approximation) down the centre of the domain, and increases somewhat with oxygen content.

In contrast to models where many possible surface and gas phase reactions are considered, the present model makes the simplest possible assumptions about the key processes, and is then able to account for various tendencies seen in experimental data. Whether the model can be made predictive, rather than a tool for interpretation, is another matter. This would depend on amassing sufficient data to fix the four unknown rate coefficients in the model.

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