Microbalance measurements of diamond growth rates

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In-situ measurements of growth rates during hot-filament assisted chemical vapor deposition of diamond were made using a microbalance. The source gases were CH_4, C_2H_2, C_2H_4 and C_2H_6. Hydrogen flow rate was kept constant at 200 sccm. Total pressure was fixed at 10 or 20 Torr and the input concentration of hydrocarbon was varied by controlling the hydrocarbon flow rate. We find that for source gas concentrations from 0.3% to 1% the deposition is first-order for methane and approximately half-order for the two-carbon source gases. Below 0.3%, the reaction shifts from half-order to first-order for two-carbon source gases. These results indicate that the two-carbon source gases decompose to one-carbon species and provide further support for CH_3 as the dominant growth species in hot-filament assisted diamond deposition. At methane concentrations above 1% the reaction order approaches zero. This behavior suggests that surface adsorption processes, not contemplated in current proposed mechanisms for attachment kinetics, may play a role in diamond growth. The observed diamond growth rates can be rationalized with a Langmuir-Hinshelwood type mechanism in which some surface sites are blocked by non-diamond carbon.

1. BACKGROUND

The mechanism for the nucleation and growth of diamond is of great interest. Recent reviews have been given by Celii and Butler [1], Angus et al. [2] and Butler [3]. Because of the high substrate temperatures, typically around 800°C, few in-situ measurements of growth kinetics have been reported. In-situ microbalance measurements, however, provide a means for monitoring the average growth rate during deposition. There have been some earlier microbalance studies [4, 5, 6, 7], but the method has not been widely used.

Microbalances can be employed during hot-filament deposition despite the extremely large temperature gradients near the substrate, typically on the order of 2000°C/cm. Because of the low density of the reaction gas, in our case primarily H_2 at 10 - 20 Torr, convective effects are minimized. The estimated value of the Grashof number at these conditions is approximately 0.5. (The Grashof number is a measure of the relative magnitude of buoyancy forces to viscous forces.) Three-dimensional computer modeling of the deposition chamber confirms a slow, approximately 0.10 m/sec, convection velocity rising in the center of the reaction zone defined by the filaments. The rising gas in the center region of the reactor gives rise to a large steady state convective cell that fills the entire reactor. See Figures 1 and 2. The convective gas motion in the cell is steady and does not perturb the measurements. If the filament temperature is increased, the increased drag force from the increased vertical convective flow gives rise to a step decrease in the apparent measured mass.

In this paper, we describe measurements of reaction order and the effect of oxygen additions and cyclic deposition conditions. The measured reaction orders will be used to discuss proposed reaction mechanisms.

2. EXPERIMENTAL

The deposition chamber is shown in Figure 1. It is an 80 liter stainless steel bell jar. The reaction zone is defined by two vertical filaments, 3 cm long. Filaments of W, Ta and
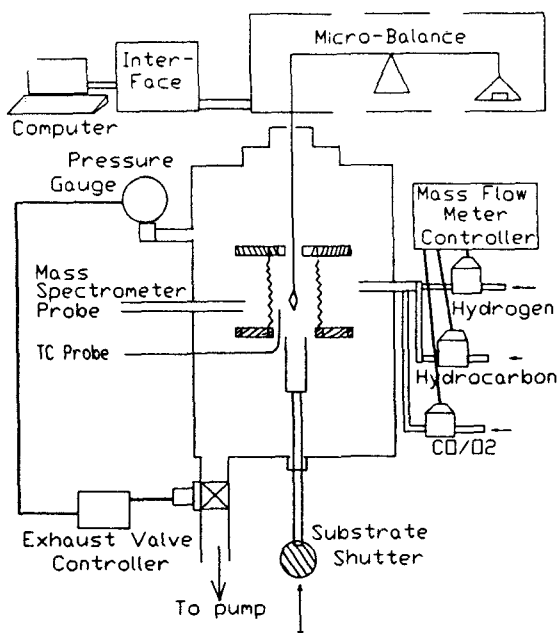
Figure 1.   Schematic drawing of hot-filament microbalance reactor.

Figure 2.   Computed convective flow velocity vectors for H_2 at 20 Torr. Reactor diameter is 34 cm and height is 54 cm.

Re were used Platinum foil substrates were suspended by a thin nichrome or platinum wire from a Cahn, model D-200, microbalance. The ultimate sensitivity of the microbalance was 0.1 µg; at reaction conditions sensitivities from 0.20 µg to 0.5 µg were obtained. A mass change of 0.2 µg corresponds to a thickness of diamond of 60 Å on our substrates that have a total area of approximately 10 mm^2.

Measurements of mass were made as a function of time. All of the reaction order data were taken on substrates that were fully covered with a well faceted diamond film. The hydrogen flow rate was fixed at 200 sccm and the flow rate of hydrocarbon was varied to get the desired concentration. The reported data points are average rates of mass change, in mg/hour, observed after steady state growth was achieved. A new data point was taken by changing the flow rate of hydrocarbon and waiting until a new steady state was achieved. In most runs the concentration of methane was ramped up and then down, to insure there were no hysteresis effects. The estimated average residence time in the reactor is 8 min. and time to reach a new
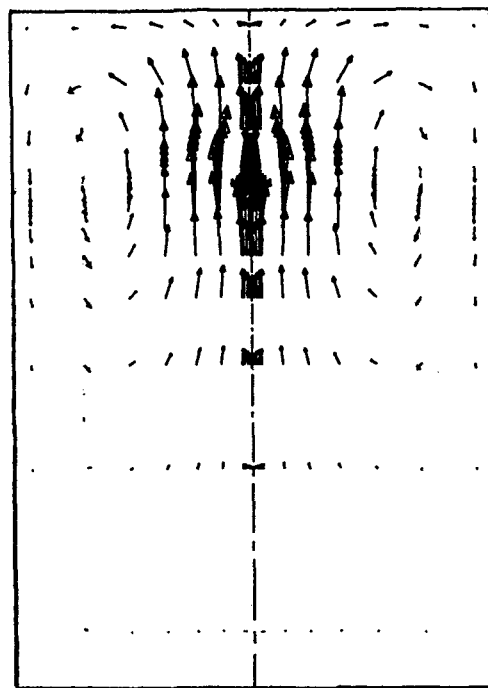
steady state growth rate was approximately 60 min. The filament and substrate temperatures were kept constant at 2300°C and 800°C respectively. Pressures were 10 and 20 Torr.

There was a significant induction period when a bare platinum substrate was subjected to the diamond growing environment. It has previously been reported by us that during this period graphite appears on the substrate [2, 7]. After several hours, the graphite disappears and only diamond is present on the substrate. After steady state diamond growth is achieved, the substrate is covered with a well faceted diamond film with a Raman peak at 1332 cm^{-1} with a FWHM of 5 cm^{-1} [2, 7].

3. RESULTS

The growth rate data were correlated initially using a simple power law expression.

$$\frac{dM}{dt} = k\left[C_xH_y\right]^m \qquad (1)$$

where m is the reaction order and $[C_xH_y]$ is the concentration of the hydrocarbon in the source

gas.

Two series of data taken using methane and acetylene source gases are shown in Figures 3 and 4. Several features of the data are immediately apparent. First, the methane source gas shows first order kinetics at concentrations below approximately 1%. At concentrations greater than 1% CH_4, the rate approaches approximately zero order.

For acetylene, the rate is approximately half order in acetylene concentration above 0.3%. At concentration less than 0.3% C_2H_2, the reaction becomes first order. Possible reasons for the observed reaction order behavior will be given in the discussion section.

The observed reaction rates with C_2H_4 and C_2H_6 were close to that observed with C_2H_2 [7]. Also, both C_2H_4 and C_2H_6 gave approximately half-order rate expressions. This behavior may be explained by the rapid conversion of C_2H_6 and C_2H_4 to C_2H_2. Preliminary modeling of the gas phase reactions supports this view.

Addition of O_2 to the source gases led to a decrease in the growth rate. See Figure 5. On the other hand, addition of CO to the source gases gave no change in growth rate (Figure 6). These results indicate that CO is sufficiently stable that it is not decomposed efficiently in the present hot-filament reactor. At higher filament temperatures or in plasma reactors CO may decompose.

A set of experiments was performed in which steady state growth was achieved with a gas mixture of 1.5% CH_4 and 0.5% O_2 in hydrogen. After steady state growth was achieved, the CH_4 flow was abruptly shut off. After approximately 30 minutes the growth rate dropped to zero and the CH_4 flow was restarted. This process was repeated cyclically. The growth rate after the first CH_4 shut off was approximately 25% greater than the steady state growth rate before the CH_4 flow was shut off. The enhanced growth rate was recovered each time during repeated cycling.

4. DISCUSSION

We use very simplified reaction sets to rationalize the observed reaction orders. These mechanisms are clearly over-simplified. They can, however, give insight into the major processes taking place.

For example, half-order behavior typically occurs when a bi-atomic species is converted into a monatomic species.

$$X_2 \underset{\leftarrow}{\overset{\rightarrow}{}} 2X \qquad (2)$$

followed by subsequent reactions of the monatomic species. In the present case, X_2 is acetylene, C_2H_2, and X is a single carbon atom species, CH_n. It should be noted that in this case reaction (2) does not refer to a single elementary reaction. Rather, it refers to a set of elementary reactions, whose net result is the interconversion of acetylene into one or more single carbon species, CH_n. The conversion of C_2H_2 to CH_n species through action of the hot filament is complex and not known with certainty. However, once formed, the CH_n species have several reaction pathways. First, they can diffuse out of the reaction zone, where they are irreversibly lost, for example to wall reactions.

$$CH_n \rightarrow W \qquad (3)$$

Alternatively, they can diffuse to the region immediately adjacent to the substrate surface.

$$CH_n \rightarrow (CH_n)_s \qquad (4)$$

The CH_n species adjacent to the surface can attach to the surface forming diamond

$$(CH_n)_s + S \rightarrow D \qquad (5)$$

where S indicates a free surface site and D is diamond.

Steady state analysis of this reaction system shows half-order kinetics when $k_2 k_{-2}[C_2H_2] > k_3^2$ and first order kinetics when $k_2 k_{-2}[C_2H_2] < k_3^2$. This is in qualitative agreement with the observed behavior, i.e., half order kinetics at high $[C_2H_2]$ and first order at low $[C_2H_2]$. In the above discussion k_i is the rate constant for the ith reaction; a negative value of i signifies the reverse reaction. It should again be emphasized that in the above mechanism, reaction (2) refers to a set of reactions; it is not an elementary reaction.

Half order behavior is also observed with C_2H_4 and C_2H_6 [2, 7]. Though not conclusive, these results give additional support to the view
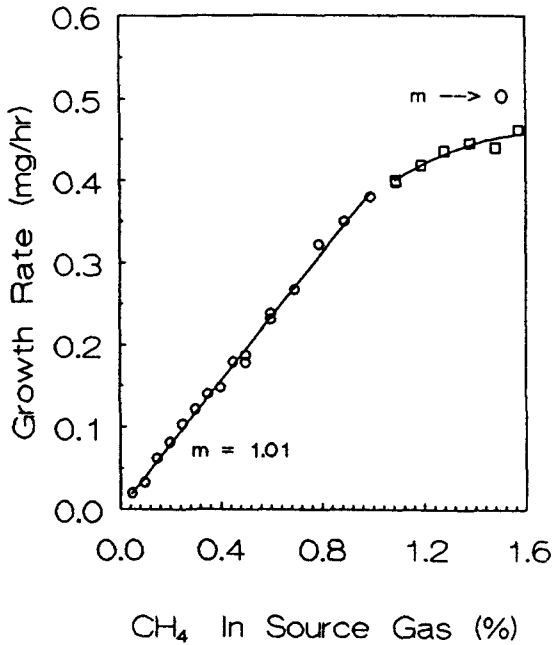
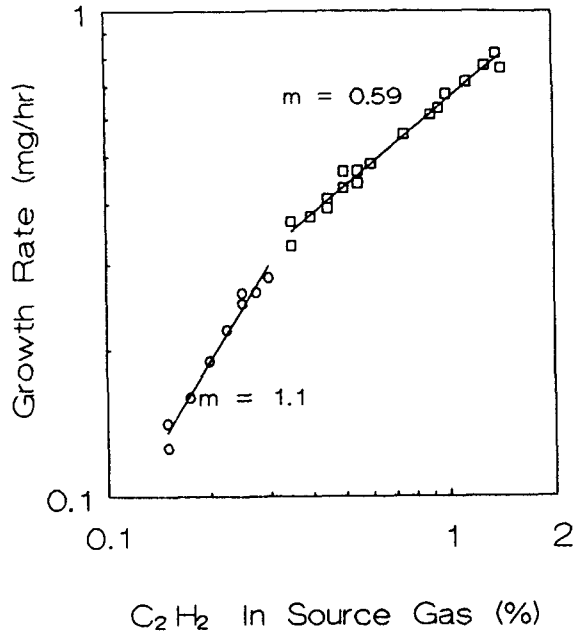Figure 3. Growth rate, mg/hour, versus methane concentration in source gas. Pressure was 20 Torr.

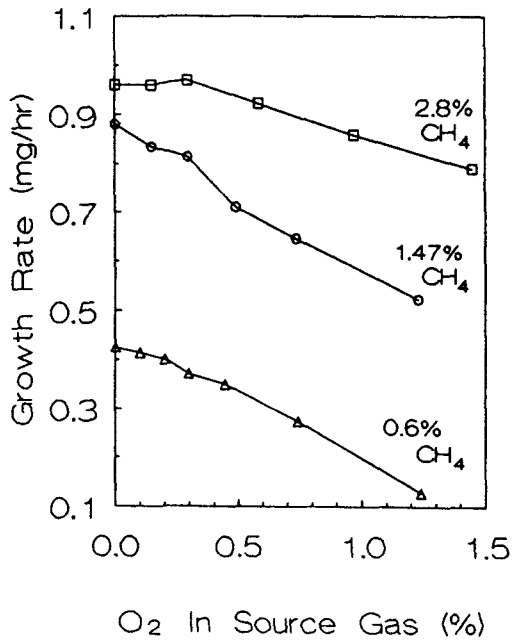Figure 4. Growth rate, mg/hour, versus acetylene concentration in source gas. Pressure was 20 Torr.

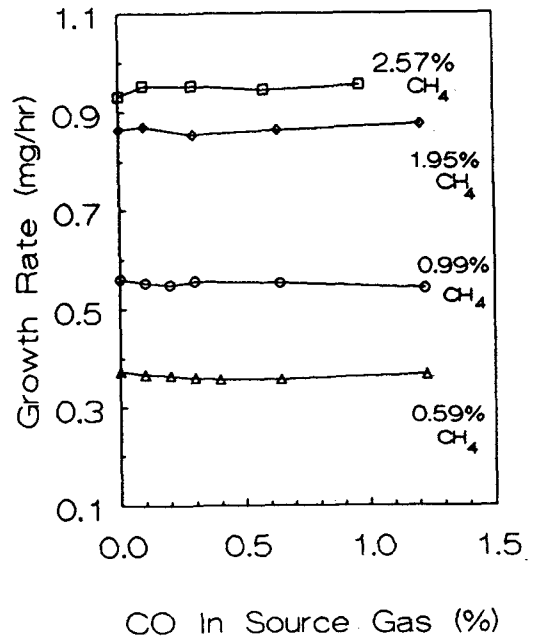Figure 5. Effect of O_2 on growth rate. Pressure was 20 Torr.

Figure 6. Effect of CO on growth rate. Pressure was 20 Torr.

that C_1H_n species are primarily responsible for diamond growth.

The first order behavior observed for CH_4 can be rationalized by a number of possible mechanisms. A simple reaction scheme giving first order behavior in both CH_4 and H was given earlier [7]. Methyl radicals are formed by reaction with atomic hydrogen.

$$CH_4 + H \rightarrow CH_3 + H_2 \qquad (6)$$
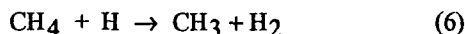
The methyl radicals can diffuse out of the reaction zone

$$CH_3 \rightarrow W \qquad (7)$$

or to the vicinity of the substrate surface

$$CH_3 \rightarrow (CH_3)_s \qquad (8)$$

where they can react with a free radical surface site, S, to form diamond, D.

$$(CH_3)_s + S \rightarrow D \qquad (9)$$

Steady state analysis of this reaction set shows first order behavior in both H and CH_4 [7]. The first order dependence on CH_4 is in agreement with the present data.

The gradual change to zero order kinetics at high CH_4 concentrations is most easily explained by a competition for available surface sites. One mechanism that leads to this behavior is obtained by replacing reaction (9) with

$$(CH_3)_s + S \underset{\leftarrow}{\overset{\rightarrow}{}} X \qquad (10)$$

$$X \rightarrow D \qquad (11)$$
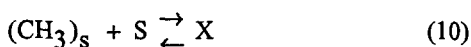
where X is a surface adsorbed intermediate and

$$[X] + [S] = 1 \qquad (12)$$

Steady state analysis of reactions (6), (7), (8), (10), (11) and (12) gives a kinetic expression of the form.

$$\frac{dM}{dt} = \frac{K_a\,CH_4]}{1 + K_b\,[CH_4]} \qquad (13)$$

Equation (13) is of the classic Langmuir -

Hinshelwood type. It gives first order kinetics when $K_b\,[CH_4] \ll 1$ and zero order when $K_b CH_4] \gg 1$. This is in agreement with the observed reaction orders. Langmuir - Hinshelwood kinetics are often seen in gas/solid reaction systems where there is a competition for surface sites.

The details of the reaction mechanism are certainly more complex than that described by reactions (6) - (12). Nevertheless, the change from first to zero order kinetics is suggestive that surface adsorbed intermediates may play a role in diamond growth kinetics.

An enhancement of growth rates by cycling during combustion synthesis of diamond has been previously reported by Mucha et al. [8] and Ravi et al. [9] and a theoretical anlaysis presented by Frenklach and Wang [10]. The reason for this phenomenon is not understood. It may be caused by the removal of non-diamond forms of carbon on the surface that block the active growth sites. Alternatively, it could change the surface reconstruction.

More detailed in-situ molecular level probes of the diamond surface during reaction will be required to establish detailed molecular mechanisms with certainty. Nevertheless, the microbalance studies provide data that proposed kinetic models must explain.

5. ACKNOWLEDGMENTS

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