

SOME THERMODYNAMIC ASPECTS OF CVD FILAMENT PROCESS FOR DIAMOND GROWTH

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INTRODUCTION

Low pressure synthesis of diamonds from hydrocarbons has seen an enormous resurgence in the last decade. After the pioneering work by Eversole in 1958 and decades of patient - but often non-reproducible - work by Deryagin and co-workers, the recent work in Japan by Matsumoto and co-workers has led to the universal acceptance of the viability of low pressure, metastable growth of crystalline diamond (ref. 1). As a result of recent work, not only has the chemical vapor decomposition (CVD) of diamonds by a simple thermal decomposition process been confirmed, but a plethora of low pressure processes have been developed - among them, plasma assisted CVD (RF, microwave, and DC), electron beam and laser assisted CVD, and deposition from ion beams, to name a few.

Despite the wide diversity of processes and operating conditions there are a few observations that have gained a near universal acceptance:

1. An abundant supply of atomic hydrogen is required at the growing diamond surface.
2. The exact chemical nature of the starting carbon source is not crucial. Almost any form of carbon source has been found satisfactory for growing diamonds. Alkanes, alkenes, alkynes, aldehydes, alcohols, and ketones have been used successfully to date.
3. Carbon concentration in the gas phase should be very low. An excessive amount leads to graphitic deposits.
4. For the thermal, filament process carbide-forming refractory metal filaments are successful in growing diamonds; carbon filaments apparently do not work. Other filaments such as platinum also do not work.

Finally, while it is generally believed that the reaction is kinetically limited, the exact rate limiting step and the growth mechanism are still topics of controversy. There have been many proposals as to which carbon specie is critical for the diamond growth with the list being made up of free radicals like $\text{CH}_3\cdot$ and $\text{C}_2\text{H}\cdot$, gaseous carbon atoms and clusters, molecules like CH_4 or C_2H_2 , and ionic species e.g., CH_3^+ .

The objective of this paper is to apply thermodynamic analyses to the diamond CVD process, on the one hand to give insights as to what some of the "universal" observations tell us about the process, and on the other to provide a framework for evaluating alternate hypotheses for growth mechanisms. Following a long-standing tradition at GE, our group is involved in research on a wide variety of processes for diamond synthesis, including those mentioned above. However, for the purpose of this paper, we have selected only one process - the hot filament, thermal process - primarily because it is the simplest CVD process and likely to be more amenable to thermodynamic analyses than others. In the following sections we will present results of thermodynamic equilibrium calculations aimed specifically at answering such questions as why carbon filaments do not work, or which carbon species are unlikely to be critical in diamond growth.

Thermodynamic Calculations

Thermodynamics of thermal decomposition of hydrocarbons has long been a topic of interest in the context of deposition of coke or pyrolytic carbon (ref. 2). However, most of this work has dealt with atmospheric and higher pressures, and is of little direct use to the diamond CVD process. More recently, there have been a few studies aimed especially at diamond CVD (e.g., ref. 3); we hope that this paper will serve to augment such studies and provide a slightly different perspective.

Equilibrium calculations presented here were carried out using the JANAF database, with 14 gaseous species containing C and H, and one condensed specie - graphite. Diamond phase was not included since the free energy difference between graphite and diamond is quite small compared to that between gaseous species and graphite; in our opinion, the resultant simplification well justifies incurring relatively minor errors in carbon activities and gas phase specie concentrations.

Why do carbon filaments not work?

A logical place to begin an investigation of why carbon filaments apparently do not work is to examine the condensed phase activity using conditions typical of filament growth. We have selected a feed composition of 1.5 mole% methane in hydrogen at a pressure of 0.01 atmosphere (7.6 torr or 10.13 mbar) with substrate temperatures from 700C to 1100C and filament temperatures from 2000C to 2600C. Figure 1 shows the carbon activity as a function of temperature. Over the entire range of filament temperatures the condensed phase activity is below unity, thereby indicating that the gas phase is below saturation with respect to solid carbon. Conversely, substrate temperature range shows carbon activity to be significantly greater than unity, reaching a peak supersaturation of 100 in the vicinity of 1000C. This strongly suggests that it is necessary for the filament to operate with a carbon activity in the range of 0.25 to 0.9; carbide forming refractory metals meet this criterion, but carbon filaments require that the gas phase be saturated with respect to carbon.

Another way to illustrate the same point is to calculate the carbon atom fraction in the gas phase in equilibrium with solid carbon at filament temperatures. This is shown in Figure 2. In order to be in equilibrium with a carbon filament, the reactor feed needs to be as high as 28% methane at the upper end of the range, decreasing to just below 2% at a filament temperature of 2000C which may be too low to produce an adequate amount of atomic hydrogen. This would explain why the use of a carbon filament produces graphitic deposits, similar to those obtained with an excessive amount of carbon in the feed. Lower melting filaments, such as platinum, are also unsuccessful because they are unable to generate an adequate supply of atomic hydrogen.

Equilibrium distribution of hydrocarbon species

Next, let us examine the equilibrium distribution of hydrocarbon species as a function of temperature. Figure 3 is a plot of the partial pressure (in atmospheres on a logarithmic scale) over the entire temperature range for the selected case of 1.5% methane in hydrogen as a feed. Several features can be noted from the figure.

Filament region:

1. Atomic hydrogen concentration increases rapidly from less than 10% at 2000C to over 50% at 2600C.

2. Almost all of the carbon is present as either C_2H_2 or C_2H , with all the other minor species accounting for roughly 0.5% of the total carbon. Only when the temperature exceeds 2500C do the species C and C_3 account for more than 1% of the carbon. The concentration of methyl radical is well below 0.1% over the entire temperature range.

Substrate region:

1. The predominant species are molecular hydrogen and methane.
2. At temperatures above 900C acetylene concentration increases gradually, overtaking methane between 1000C & 1100C - reportedly the preferred range for growing good diamond crystals. Ethylene is a distant third accounting for at best 1% of the carbon at its peak.

From these observations one is led to conclude that the role of the filament is to convert molecular hydrogen to atomic hydrogen, and to convert methane - or, for that matter, any other hydrocarbon source - to primarily acetylene and C_2H . The insensitivity of the process to the exact source of hydrocarbon suggests that this rearrangement proceeds fairly rapidly producing an equilibrium distribution of species, thereby obliterating any history of the feed composition. At the substrate, reverse reactions producing molecular hydrogen and methane take place, in addition, of course, to a rather slow carbon deposition reaction to form diamonds. In view of the extremely low mass transfer Peclet number in a typical filament reactor, which makes it behave more like a continuous stirred-tank reactor (CSTR), the steady-state concentrations of hydrocarbon species is determined by a balance between the source and sink rates at the filament and the substrate.

Calculated impingement rates of the various carbonaceous species using equilibrium concentrations at the filament, which provide an absolute upper bound for all species except methane and ethylene, can be compared with the observed growth rates of diamond films to obtain an estimate of the incorporation ratio (fraction of collisions resulting in film growth) required for a specific specie to be the critical one for diamond growth. Based on typical growth rates of 1 to 10 microns/hour, an average incorporation rate is approximately 4×10^{-8} g-atoms/cm²/sec. At this growth rate, the required incorporation ratio for acetylene and C_2H is roughly 1 in 1000, while that for C & C_3 is roughly 1 in 10. Since these ratios have been calculated assuming the maximum possible concentrations (equilibrium at the filament and no re-combinations thereafter), and since the substrate surface is supposedly almost totally covered with hydrogen, acetylene and C_2H appear to be the most likely candidates for the critical species, with C_3 and C being less likely (but possible) ones, particularly at high filament temperatures. Other free radicals such as CH , CH_2 , and particularly CH_3 are at too low a concentration to account for the growth rates. Methane is always a possible candidate since it can be abundant near the substrate, and ethylene can not be ruled out if one assumes complete equilibrium at the substrate. A substantial back-conversion of acetylene to methane has been experimentally observed by us based on reactor gas sample analyses, confirming the importance of the back-conversion reaction.

Simultaneous deposition of diamond and etching of graphite

It is often mentioned that one of the key elements of low pressure growth of diamonds is the ability of atomic hydrogen to etch away any graphite that may get deposited leaving behind only the diamond phase. In a process that operates in a cyclic manner (whether in time or space) there would be no inconsistencies in alternating between graphite deposition and etching conditions. In a steady-state process, however, to

maintain that bulk graphite can be deposited and then etched away would constitute a serious thermodynamic violation, since it would imply a carbon activity that was simultaneously greater than unity for deposition and less than unity for etching. If one were to invoke non-uniform temperatures on the substrate, as seen from Figure 1 parts of the substrate would have to be above 2000C for the activity to drop below unity. Experimentally, we have observed many instances where graphite is nucleated on a growing diamond film and then grows alongside the diamonds for the remainder of the experiment. This proves that once graphite is deposited during the course of diamond growth, it is there to stay unless the reactor conditions are altered.

A more difficult question to address is what happens when one uses a graphite substrate in a filament reactor: During the early stage of diamond nucleation is the graphite substrate etched? In the absence of the filament (e.g., in a furnace at 1000C) the answer would, of course, be no. Even with the filament, if the homogeneous phase were in local thermodynamic equilibrium there could be no etching. However, in the close proximity of the filament the presence of non-equilibrium concentration of atomic hydrogen makes thermodynamic arguments inapplicable. An experimental resolution of this question, while beyond the scope of this paper, is also made difficult by the fact that in the early stage of the experiment the filament is gradually coming to equilibrium with the gas by incorporating carbon, thereby significantly affecting the gas phase composition. Only a series of careful experiments can hope to resolve this very interesting question.

CONCLUSIONS

Thermodynamic equilibrium calculations were carried out for the hot filament CVD process for diamond deposition under typical conditions. It was shown that the carbon activity is considerably below unity at the filament and very high at the substrate. The failure of carbon filaments to grow diamonds was shown to be due to the gas phase in equilibrium with the filament to be excessively rich in carbon, thereby exceeding the supersaturation limits for diamond growth. Details of the gas phase concentrations were used to evaluate the likelihood of the various gas species to be critical for diamond growth.

ACKNOWLEDGEMENTS

The author would like to thank the management of GE Research and Development and GE Superabrazives for their permission to publish this paper. The author would also like to thank Dr. Steve Spacil for his valuable assistance on the program for thermodynamic calculations, Mr. R.J. Kehl for his help with the experiments, and Drs. Tom Anthony and Bill Banholzer for many valuable discussions.

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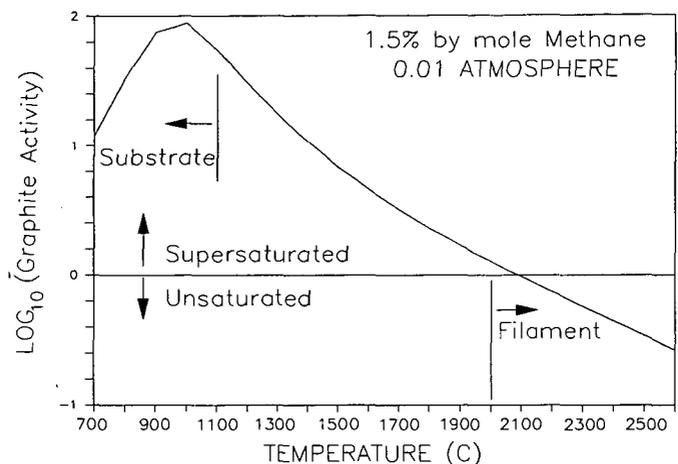


Figure 1: Graphite Activity as a function

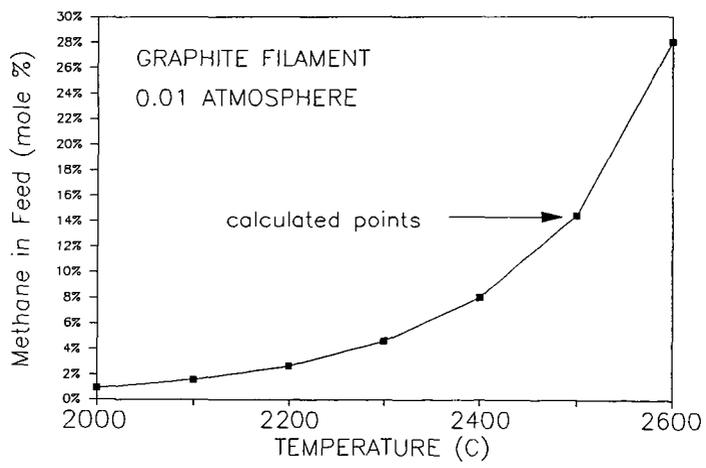


Figure 2: Feed Methane Concentration in Equilibrium with Carbon Filament

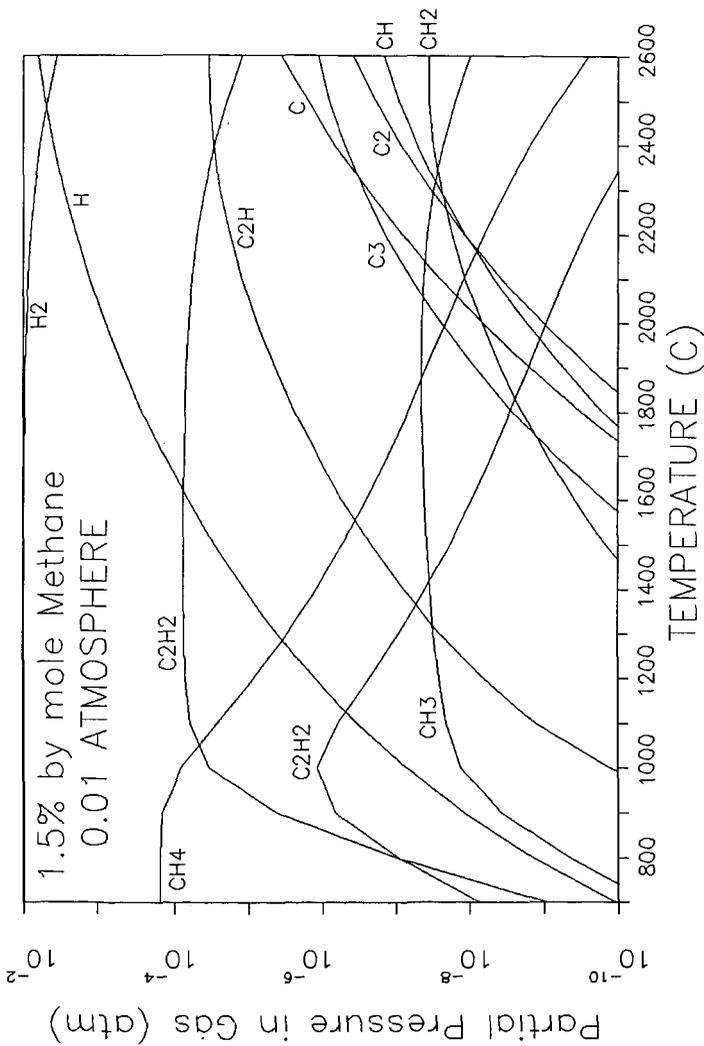


Figure 3: Equilibrium Partial Pressures in Gas