

Diamond growth with CF₄ addition in hot-filament chemical vapour deposition

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Tetrafluoromethane (CF₄) was added to standard CH₄/H₂ mixtures for diamond growth in hot-filament-assisted chemical vapour deposition. CF₄ concentrations in the range of 0.3%–3% were studied. Mass spectrometry of the exhaust gas showed that only a small fraction (<15%) of CF₄ was thermally dissociated for filament temperatures over 1800 °C. The observed stable products of its dissociation were mainly C₂H₂, CH₄ and HF. This CF₄ addition considerably enhanced the nucleation and growth characteristics on silicon and molybdenum. Diamond growth was observed with substrate temperature as low as 390 °C. A comparative study for the growth dependence on substrate temperature with and without CF₄ addition in the gas mixture is presented. The growth rate was measured by post-growth weighing with a micro balance. An activation energy of 11 kcal mol⁻¹ for growth with CF₄ addition was obtained. Raman spectra and atomic force microscopy were used to characterize the diamond films.

1. Introduction

The growth of polycrystalline diamond films by chemical vapour deposition (CVD) has been considerably developed in the last few years. Since the discovery that diamond could be grown on substrates other than diamond at growth rates over 1 μm h⁻¹ [1], many laboratories have worked to improve this technology. Typically, mixtures of diluted hydrocarbons in hydrogen, and various techniques for activation of the gas phase, ranging from hot filaments to plasma arc jets, have been used. Growth rates between 1 μm h⁻¹ to almost 1 mm h⁻¹ have been reported. Relatively low growth temperatures have been reported, but the best growths occur between 700 and 900 °C. The addition of small amounts of oxygen in the gas mixture helps to improve the film quality and extend the growth to lower temperatures. These and many other features of this development are the subject of some good reviews that show its importance from the scientific and technological viewpoint [2–6].

Another branch of diamond CVD that has been introduced is the halogen-based system. Halogen-hydrocarbon or halocarbon-hydrogen mixtures are used instead of the conventional mixture of hydrocarbons with hydrogen. Some experiments have shown that the presence of halogens promotes the formation of solid carbons, including diamond [7]. The preferential etching of the graphitic phase by halogens has also been experimentally shown [8].

The growth of diamond with the halogen-based system has been shown to be very encouraging. After the original work of Patterson *et al.* [9–11] many authors [12–18] have been able to enhance diamond growth by the use of halogenated gas mixtures. Bai *et al.* [19] have reported evidence of preferential growth from methyl chloride when isotope-labelled methyl chloride and methane are both introduced into a hot-filament reactor. Pan *et al.* [20] have reported a fully chlorine-activated reactor, in which they measured lower activation energy for diamond growth.

Thermochemistry studies [21] have shown that, in the absence of hydrogen, halogenated surfaces are stable enough to avoid the diamond growth, but if hydrogen or hydrocarbons are added the growth is quite favourable. It has also been depicted that typical gas-phase reactions of hydrocarbons and fluorine have higher rate coefficients with much lower activation energy than their counterparts with hydrogen [22]. This is very likely to happen also for surface reactions. The abstraction of hydrogen atoms from the diamond surface, considered a limiting step for diamond growth at low temperatures, is expected to be enhanced by fluorine reactions with a much smaller dependence on temperature.

In this work we studied the CF₄ addition to regular CH₄/H₂ gas mixture, in a hot-filament reactor. Our main interest was in low temperature growth. We observed that, with CF₄ addition, diamond grows at

lower temperatures at reasonable rates. The growth rates for $\text{CF}_4/\text{CH}_4/\text{H}_2$, CH_4/H_2 and CF_4/H_2 mixtures were compared, and the growth rate by post-growth weighing was measured with a micro balance. Atomic force microscopy (AFM) and Raman spectroscopy were used to characterize the films grown with and without the presence of CF_4 . The stable species in the exhaust gas were also studied by mass spectrometry.

2. Experimental procedure

The experimental apparatus is shown in Fig. 1. The hot-filament reactor was constructed inside a 60 mm o.d. Pyrex tube. The filament was 2.5 cm long, made of 150 μm tungsten wire. The substrates were small pieces of around 15 mm^2 centred on the substrate holder made of a 125 μm thick molybdenum sheet fastened to water-cooled copper posts. The distance between the filament and the substrate was maintained at 3 mm for all experiments. The filament temperature was measured by an uncorrected disappearing filament pyrometer. The voltage and current on the filament were also monitored to observe variations in filament power consumption. There was good control over substrate temperature. The lowest substrate temperature was controlled by varying the length of the molybdenum foil of the substrate holder. A power supply provided current, up to 50 A, to heat the substrate holder over this lowest temperature. The substrate was attached to the substrate holder with a thin layer of high-temperature molybdenum grease to guarantee a good thermal contact. With this apparatus it was possible to control the substrate temperature between 250 and 1000 $^\circ\text{C}$.

Either silicon, molybdenum or diamond substrates were used for these experiments. Silicon and molybdenum were used to characterize the nucleation and long-term growth. These substrates were scratched with 1 μm diamond paste and rinsed with acetone before growth. The diamond substrates were used for growth-rate measurements. The diamond substrates were previously grown over molybdenum in a similar reactor, with a gas mixture of 0.4% CF_4 , 2% CH_4 balanced with hydrogen. Freestanding films of around 100 μm were grown during 24 h, for a filament temperature of 2200 $^\circ\text{C}$, a substrate temperature of 800 $^\circ\text{C}$,

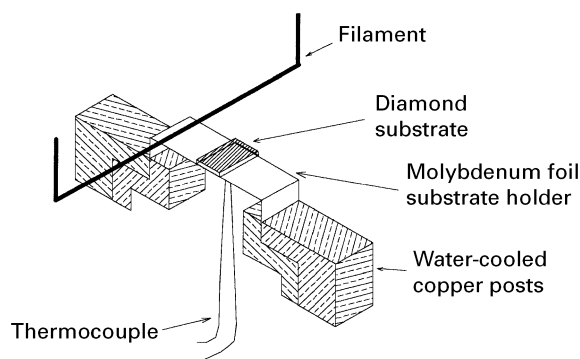


Figure 1 Experimental apparatus. Detail of the filament and substrate geometry, showing the molybdenum foil substrate holder.

a flow rate of 100 standard $\text{cm}^3 \text{min}^{-1}$ and a gas pressure of 50 torr (1 torr = 133.322 Pa). After growth, the molybdenum substrate was dissolved and the 200 mm^2 diamond wafer was laser cut to give the small 15 mm^2 diamond substrates [23].

The diamond substrates were submitted to acid cleaning, before and after growth, to remove metal residues. The use of diamond substrates reduced the error in growth-rate measurement because there was no mass loss during growth or cleaning procedures and, also, the growth-induction time was considerably reduced.

In the present experiments, growth occurred over the back surface of these diamond substrates. The very small grain size in this surface allows a better observation of the newly grown diamond. Scanning electron microscopy (SEM), AFM images and Raman spectroscopy were performed after growth on this surface [24].

For some experiments a mass spectrometer was used (Balzers QMG 421-C) to analyse the stable species in the exhaust gas. The mass spectrometer was also used to verify the calibration of the mixtures, within an error of 5%. For the growth experiments, variable amounts of CH_4 and CF_4 were added to hydrogen. The mass spectrometry was focused on the H_2 (2 u), CH_4 (15 or 16 u), HF (20 u), C_2H_2 (26 u), C_2H_4 (28 u) and CF_4 (69 u). The mass spectrometer was calibrated for the measurements of CH_4 , C_2H_2 and CF_4 diluted in hydrogen. The HF and C_2H_4 measurements were only relative. The observation of mass 69 and mass 51 together show that the mass 69 was only due to CF_4 , without the influence of CHF_3 or other compounds that may be fragmented to CF_3 in the mass spectrometer.

3. Results and discussion

3.1. Filament activity and growth characteristics

The filament activity in a hot-filament reactor has been shown to be influenced by the feed-gas mixture. This influence is explained by the poisoning of the filament surface by a carbon layer deposit. As Sommer and Smith [25, 26] have shown, this carbon deposit is in equilibrium with the carbon content in the gas phase, at the filament temperature. They have shown this dependence for different carbon contents and also for the oxygen addition in the mixture.

The measurement of the filament emissivity is the main indication of the change in the filament activity. An abrupt decrease of filament emissivity was correlated with an overall increase on chemical activity in the reactor. The filament temperature measured with the one-colour pyrometer was used only as a reference because the correction for the variation of the filament emissivity was not precisely known. In particular, the substrate temperature was very dependent on the filament activity. The substrate temperature dependence on filament temperature for gas mixtures without CF_4 and with CF_4 is shown in Fig. 2. Over some filament temperature the filament activity increased, as is shown by the change in the trend of the solid line. The

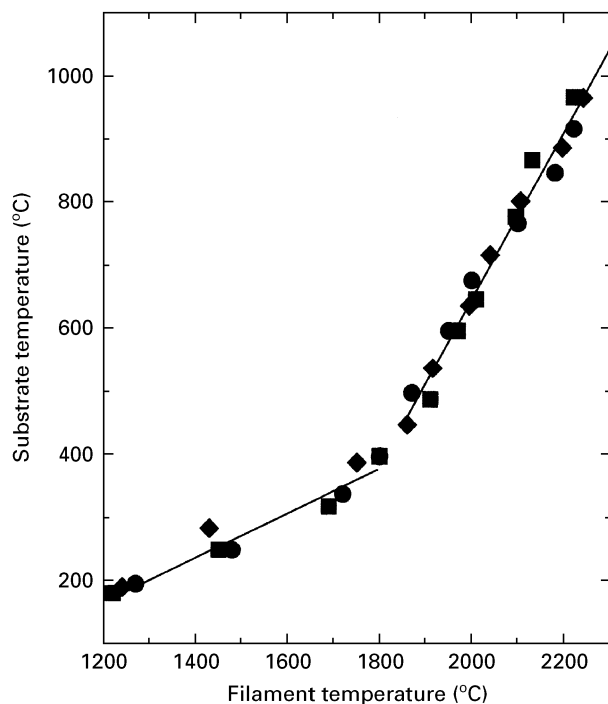


Figure 2 Dependence of substrate temperature on filament temperature for various gas mixtures: (●) 0.5% CH₄, (■) 0.5% CH₄+0.5% CF₄, (◆) 0.5% CH₄+2% CF₄.

temperature at which this happens should depend on the carbon content in the gas phase. Despite the high variation of carbon content with the CF₄ addition, variation of this temperature was only observed when methane content was varied. This observation indicates that the carbon added with the CF₄ had a small influence on the carbon chemistry over the filament surface. This result is consistent with a small dissociation of the CF₄, as confirmed by the mass spectrometry of the exhaust gas.

The filament temperature for the growth experiments was 2200 °C, a region of high filament activity for all gas mixtures tested. The growth characteristics at a substrate temperature of 800 °C, on silicon and molybdenum substrates were very different in this system. Silicon substrates were etched during the growth process. For CF₄ concentrations higher than 1%, the surface damage and the nucleation density were considerably reduced. A nucleation enhancement was clearly observed for CF₄ concentrations lower than 0.7%. Molybdenum substrates were not etched in the reactor and an enhancement of the nucleation process was observed for all the CF₄ concentrations tested, up to 2%. We observed a faster nucleation and a faster lateral growth of isolated particles [27]. Also, the CF₄ addition made possible the growth of good quality film with higher methane concentration in the feed gas. Fig. 3 shows the Raman spectrum of a 250 μm thick film grown with a mixture of 4% CH₄ and 0.5% CF₄ balanced with hydrogen.

The filament did not carbonize at any filament temperature, and no diamond growth was observed for experiments with mixtures of only CF₄ in hydrogen.

Only molybdenum substrates were used to test growth at lower temperatures. We were able to ob-

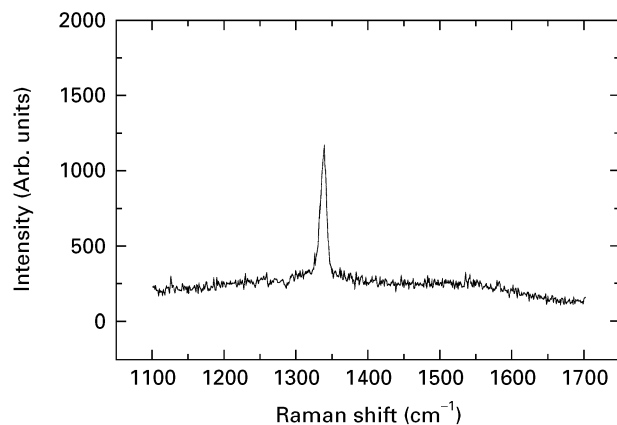


Figure 3 Raman spectrum of a diamond sample grown on molybdenum during 36 h with a mixture of 4% CH₄+0.5% CF₄ in H₂.

serve well-faceted diamond for temperatures as low as 390 °C. An excessive induction time, of more than 10 h was necessary for temperatures lower than 350 °C, and the films showed only ball-like particles.

3.2. Growth on diamond substrates and growth-rate measurements

Each diamond substrate was weighed in a microbalance before and after growth to obtain the mass variation, Δm . Each substrate area, A , was also measured. Considering that the diamond substrate is small enough to have a uniform deposit over its area, the growth rate was calculated, $G = \Delta m/At$, where t is the deposition time. The growth rate, G , is given in units of $\mu\text{g cm}^{-2} \text{h}^{-1}$. The specific mass of the deposit was not evaluated to measure the linear growth rate.

Fig. 4 shows the dependence of diamond growth rate with substrate temperature, for growth with three different gas mixtures. The data are shown as an Arrhenius plot. From this plot we obtained an activation energy of around 11 kcal mol⁻¹ for diamond growth with CF₄ addition. This is about half the activation energy measured for growth with CH₄/H₂ mixture, in the range between 560 and 800 °C. Other authors [28–30] have also reported activation energies in the order of 22 kcal mol⁻¹ for growth with CH₄/H₂ mixtures. Some difficulty has been reported in growing diamond at low temperatures [31, 32]. Ihara *et al.* [33] reported diamond growth even at 135 °C with CH₄/H₂ mixtures, but growth-rate data given in their paper show a much smaller activation energy. Hong *et al.* [14] have reported a growth rate of 0.05 μm h⁻¹ at 380 °C with a CCl₄ mixture. The minimum growth rate we observed, considering a film density of 3.52 g cm⁻³, was 0.13 μm h⁻¹ at 390 °C with the 1.5% CH₄+1.5% CF₄ mixture.

With CF₄ addition, growth was observed at temperatures as low as 250 °C. For these low temperatures most of the growth was of spherical particles indicating a low-quality diamond. Raman spectroscopy can clearly show the decrease in diamond quality for substrate temperatures under 390 °C, as shown in Fig. 5. The same conditions (filament temperature, gas pressure and flow rate) were used for all experiments, with

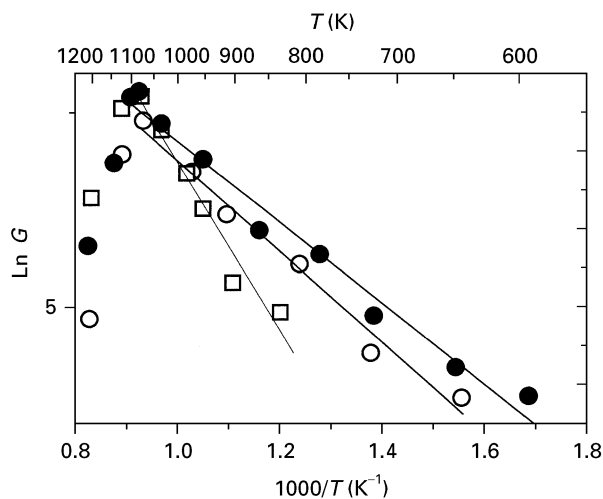


Figure 4 Dependence of diamond growth rate on substrate temperature for different gas mixtures: (□) 1.5% CH₄, (○) 1% CH₄+0.5% CF₄, (●) 1.5% CH₄+1.5% CF₄.

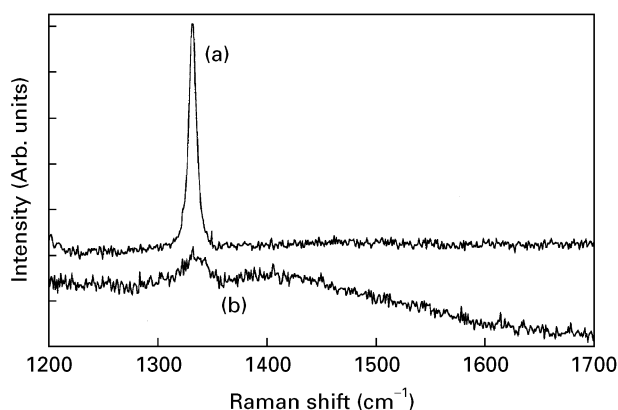


Figure 5 Raman spectra for samples grown on a diamond substrate with a gas mixture of 1% CH₄+0.5% CF₄ for two different substrate temperatures: (a) 450 °C and (b) 330 °C.

and without CF₄ addition. The lower activation energy observed may indicate that the presence of fluorine chemistry in the gas phase was responsible for a growth enhancement at lower temperatures.

The morphology of these films was also investigated by AFM and SEM. The direct observation of the AFM and SEM images shows that the grain size increases with the increase of substrate temperature. Fig. 6 shows the roughness histogram obtained from AFM images for some of the samples grown at different temperatures. The vertical roughness decreases with temperature increase, and saturates at the higher temperature limit. Also the grain coalescence is better at higher temperatures, as observed by the bearing area analysis shown in Fig. 7. The figure was made possible by combining the excellent vertical and lateral resolution of the AFM images to calculate the area covered by the films at different depths, called the bearing area.

3.3. Mass spectrometry

A complete mass spectrum of the exhaust gas in the reactor, with a filament temperature of 2200 °C, and

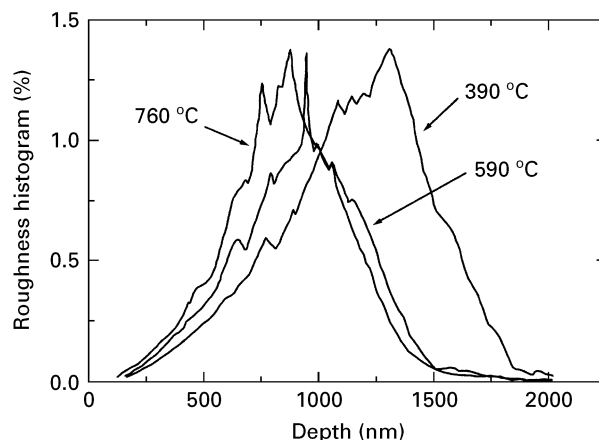


Figure 6 Roughness histogram obtained from AFM images for samples grown on diamond substrates with a gas mixture of 1% CH₄+0.5% CF₄, for the substrate temperatures indicated.

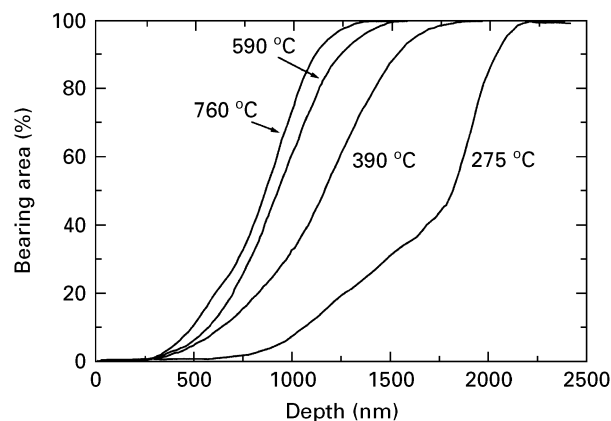


Figure 7 Bearing ratio curve for films grown on diamond substrates with a gas mixture of 1% CH₄+0.5% CF₄, for the substrate temperatures indicated.

the gas mixture with the addition of 2% CF₄, shows that the main stable species in the reactor are H₂, CH₄, C₂H₂, CF₄, C₂H₄ and HF, with only lesser amounts of C₂H₆. No fluorinated hydrocarbons are observed, indicating that CF₄ and HF are the only fluorinated stable species present in the conditions of a hot-filament reactor. This is very similar to a result presented in a previous paper [27], despite the much higher resolution of the present mass spectrometer. With this observation, the mass spectrometry studies were concentrated only on these stable species.

We observed that the CH₄ and the C₂H₂ mole fractions increase with increasing CF₄ concentration. An analysis of the carbon balance indicates that most of the carbon from CF₄ dissociation is incorporated on CH₄ and C₂H₂.

The observation of CF₄ dependence on the substrate temperature, measured at the substrate surface by the collection of gas through a quartz microprobe, only shows an increase of CF₄ mol fraction at lower temperatures that is consistent with thermal diffusion.

Equilibrium calculations show that CF₄ should be completely dissociated in the pressure and temperature conditions of this experiment. The relative

stability of CF_4 to thermal dissociation indicates that CF_4 dissociation is limited kinetically. The beginning of CF_4 dissociation coincides with the overall increase of filament activity. This suggests that with a filament clean of a carbon layer the probability of CF_4 dissociation increases. The CF_4 dissociation may occur by direct thermal dissociation or by atomic hydrogen attack. It may also dissociate catalytically on the clean filament surface. The increase in the filament activity is accompanied by an increase in the atomic hydrogen production that is known to be responsible for the increased conversion of methane into acetylene. The overall coincidence of the increase in the chemical activity may suggest that the same agent, the atomic hydrogen, is also responsible for the CF_4 dissociation. The fact that only CF_4 and HF were detected, indicates other fluorinated species are not stable in the hot-filament conditions. This observation also indicates that fluorinated radicals have a very short life time. A long lived radical could react at colder regions of the reactor to produce other stable species.

The increase in acetylene mole fraction was very pronounced. For a fixed filament temperature, the $[\text{C}_2\text{H}_2]/[\text{CH}_4]$ ratio increased approximately linearly with CF_4 in the reactor, as shown in Fig. 8. In a regular hot-filament system with a CH_4/H_2 mixture, the increase of the carbon content by the increase of CH_4 concentration in the feed gas tends to decrease the $[\text{C}_2\text{H}_2]/[\text{CH}_4]$ ratio, because of the reduction in the atomic hydrogen content. This means that the addition of carbon to the hot-filament system through the addition of CF_4 is not equivalent to the addition of CH_4 , despite the fact that both convert mainly to CH_4 and C_2H_2 in the reactor.

It is expected that the partitioning of carbon between CH_4 and C_2H_2 is controlled by the establishment of a steady state in the regular hot-filament reactor. There is evidence of a rapid equilibration. Gas kinetic modelling of these systems gives a simplified picture of the gas-phase chemistry: the methane/acetylene inter-conversion is controlled by the hydrogen atom production; once H and $[\text{C}_2\text{H}_2]/[\text{CH}_4]$ are set, the concentration of all radical species follows from partial equilibrium of hydrogen-abstraction reactions [34].

It is very likely that such a steady state between CH_4 and C_2H_2 concentrations is also reached in the present case, independently of the mechanism that produces the hydrocarbons from the dissociation of CF_4 . However, the observation of Fig. 8 indicates that there is no net consumption of atomic hydrogen due to the addition of CF_4 to the gas mixture.

The observation of C_2H_4 concentration shows a linear dependence on the fraction of CF_4 dissociated. Because C_2H_4 is an intermediate product in the formation of C_2H_2 from hydrocarbons, it may indicate that acetylene is directly formed from the CF_4 dissociation mechanism.

Once the CF_4 is dissociated by the reaction

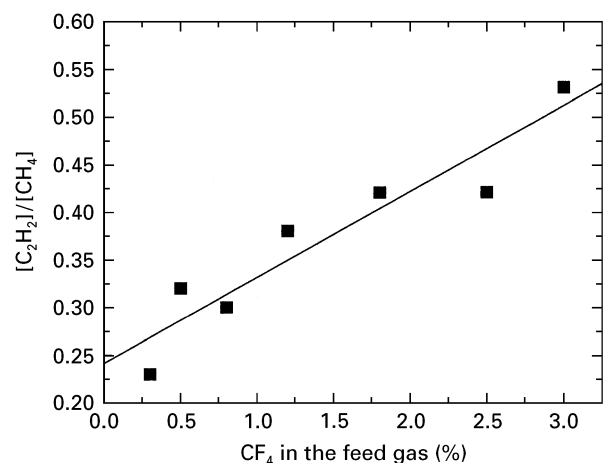
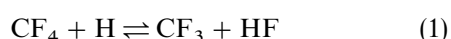
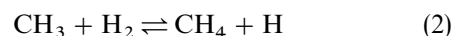


Figure 8 $[\text{C}_2\text{H}_2]/[\text{CH}_4]$ ratio dependence on CF_4 added to a mixture of 0.5% CH_4 in the feed gas, for a filament temperature of 2200°C .

the CF_3 radical may dissociate or attack H_2 with the production of excess hydrogen atoms and HF . The observation of no halogenated hydrocarbons, together with the observation of the behaviour of C_2H_4 , indicates that Reaction 1 proceeds rapidly through the change of fluorine by hydrogen in reactions with H_2 , up to the production of intermediate radicals in the formation of C_2H_4 , including methyl radical. Fox *et al.* [35] observed the increase of methyl radical mole fraction with the increase of CF_4 concentration in the feed gas, with their molecular beam mass spectrometer. Methane is probably produced through the equilibrium of the reaction



This reasoning indicates a possible mechanism for the formation of acetylene and methane from the dissociation of CF_4 , without a net consumption of atomic hydrogen. A complete understanding of such a mechanism depends on an accurate modelling of the gas-phase chemistry. This modelling is difficult due to the lack of important kinetic data.

The high stability of HF indicates that probably there are no free fluorine atoms in the hot-filament reactor. On the other hand, the erosion of the silicon substrate, the diamond films free of amorphous carbon even for high CH_4 content in the feed gas, and also the lower activation energy observed, are evidence of a gas phase very reactive with the substrate surface.

Independently of the probable benefit of the fluorine presence over the surface chemistry, in the hydrogen abstraction to create growth sites or in the stabilization of the diamond phase, the benefits of CF_4 addition over the gas-phase chemistry are very clear. Its high thermal stability prevents its carbons from poisoning the filament. No loss of filament activity was observed. The CF_4 is dissociated only after the filament is already free of a poisoning carbon layer. After CF_4 dissociates, the overall chemistry adds its carbons to the growth species, probably without a net consumption of atomic hydrogen. This may lead to a favourable environment for diamond growth.

4. Conclusion

The effect of CF₄ addition in the regular CH₄-H₂ mixture for diamond growth in a hot-filament reactor, was studied. The effect of CF₄ addition on the filament activity was observed. Growth experiments were performed to study the effects of CF₄ addition in nucleation, growth morphology, film quality and growth rates. Growth was found to be possible at low temperatures and an activation energy of 11 kcal mol⁻¹ for growth with CF₄ addition, was measured. Mass spectrometry was also used to analyse the stable species in the reactor.

The mass spectrometry shows that only a small fraction (<15%) of CF₄ is thermally dissociated in the reactor. This dissociation starts only after the observed increase in filament activity. The CF₄ dissociation scales with the CF₄ concentration in the feed gas. This suggests that the CF₄ dissociation occurs either catalytically on the filament surface or by hydrogen attack. We also observed that CF₄ dissociation is considerably enhanced by applying a forward bias voltage between the substrate and the filament [27]. The only stable species observed that contain fluorine are CF₄ and HF. The CF₄ dissociation produces mainly CH₄, C₂H₂ and HF. Acetylene is the main hydrocarbon product from CF₄ dissociation and probably there is no net consumption of atomic hydrogen in this process.

Growth experiments show that the CF₄ addition increases considerably the nucleation density, reducing the induction period for diamond growth on such foreign substrates as silicon and molybdenum. Most of the enhancement is already observed only with small amounts of CF₄ dissociated. The increase in the amount of CF₄ dissociated has a smaller effect on growth characteristics. For larger amounts of CF₄ dissociated, the Raman spectrum starts to show a broad peak around 1500 cm⁻¹ due to graphitic inclusion, probably as a result of the excess acetylene in the gas phase.

The most impressive difference obtained with CF₄ addition is the smaller activation energy. This result may imply a different growth mechanism. For growth only from hydrocarbon-hydrogen mixtures, the growth models preview three hydrogen abstraction reactions, that are considered responsible for most of the observed activation energy. The smaller activation energy observed may suggest that the hydrogen abstraction reactions may have a smaller activation energy in this system, probably because fluorine participates in them.

Bai *et al.* [19] have shown some evidence that a new growth species, probably the CH₂Cl, is more effective than CH₃ in systems containing methyl chloride. It is not evident from our experiments if a fluorinated hydrocarbon radical may or may not be a more effective growth species in this system. The fact that stable fluorinated hydrocarbons were not observed by mass spectrometry indicates that fluorinated hydrocarbon radicals have a very short life time in this system. The *in situ* detection of these radicals by Fox *et al.* [35], showed a result similar to ours.

From these arguments, we conclude that fluorine atoms and fluorinated hydrocarbon radicals have a very short life time and, if they contribute to enhance the growth characteristics in this system, they must be produced very close to the substrate surface. This may be possible if CF₄ is dissociated by atomic hydrogen attack just on the surface. The silicon substrate etching and the diamond films free of a graphitic phase, even for high methane concentrations in the feed gas, are evidence of a system very reactive with the substrate surface.

From a practical viewpoint, the addition of a small amount of CF₄ to the regular CH₄-H₂ mixture considerably enhances the diamond nucleation, grows good-quality diamond even at high hydrocarbon content in the feed gas, and promotes the growth at lower temperatures.

Acknowledgements

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