LOW TEMPERATURE DIAMOND GROWTH WITH CF_4 ADDITION IN A HOT FILAMENT REACTOR

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ABSTRACT

In this work we show that the addition of a small amount of CF_4 to a regular CH_4-H_2 gas mixture allows diamond growth at lower temperatures with reasonable growth rates. We used a hot filament assisted reactor and observed diamond growth with a substrate temperature as low as 390 °C. We present a comparative study for the growth dependence on substrate temperature with and without CF_4 addition in the gas mixture. The growth rate is measured by post growth weighting with a micro balance. Raman spectroscopy, SEM and AFM images show the good quality of the films grown at low temperatures when CF_4 is added to the feeding gas.

I -- INTRODUCTION

The growth of diamond with the halogen-based system has been shown to be very promising. Patterson et al. [1] reported deposition of diamond films at substrate temperatures as low as 250 °C and with relatively small gas activation in a simple flow tube reaction chamber, heated only up to 950 °C. Rudder et al. [2] reported direct deposition of diamond films on silicon, with dense nucleation, without any surface pre-treatment, in a rf-plasma reactor. Hong et al. [3, 4] have obtained enhanced growth in a hot filament reactor by the use of halogenated methane in the gas mixture. Baranauskas et al. [5] have shown atomic resolution AFM images obtained from films grown in a hot filament reactor when CF_4 was added to the gas mixture. Kadono et al. [6] reported the diamond growth from CF_4-H_2 mixtures in a microwave plasma system. Corat et al. [7] have reported a mass-spectrometric study of CF_4 addition in hot-filament chemical vapor deposition (HFCVD). Trava-Airoldi et al. [8] have reported better diamond adherence on carbides with low temperature growth when CF_4 is added in HFCVD.

Further theoretical and modeling studies on the halogen influence on diamond growth are still due, probably by the lack of sufficient kinetic data on reactions for halocarbon and halogens with hydrocarbons and hydrogen. Thermochemistry studies [9] 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 favorable. It has been also depicted that typical gas phase reactions of hydrocarbons and fluorine have higher rate coefficients which have much lower activation energy than their counterparts with hydrogen [10]. This is very likely to happen also for surface reactions. The abstraction of H 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.

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In this paper we study the CF_4 addition to a regular CH_4/H_2 gas mixture, in a hot filament reactor. Our main interest is on low temperature growth. We observed that with CF_4 addition diamond grows at lower temperatures at reasonable rates. In this work we made a comprehensive study of low temperature growth with CF_4 addition. We compare the growth rates for $CF_4/CH_4/H_2$, CH_4/H_2 and CF_4/H_2 mixtures. We measured the growth rate with a micro balance for post growth weighting. SEM, AFM and Raman spectroscopy are used to characterize the films grown with and without the presence of CF_4.

II -- EXPERIMENTAL

The experimental apparatus is shown in Fig. 1. The hot filament reactor is constructed inside a 60 mm OD Pyrex tube. The filament is 2.5 cm long, made of 150 μm tungsten wire. The substrates are small free standing diamond pieces of around 15 mm^2. The substrate holder is made of a 125 μm thick molybdenum sheet fastened to water cooled copper posts. The distance between the filament and the substrate is maintained at 3 mm for all experiments. The filament temperature is measured by an uncorrected disappearing filament pyrometer. The voltage and current on the filament are also monitored to observe variations in filament power consumption. The substrate temperature is measured by a chromel-alumel thermocouple spot welded to the center of the substrate holder back surface. This allows reliable temperature measurements to be made. We have a good control over substrate temperature. We control the lowest substrate temperature through the length of the molybdenum foil of the substrate holder. A power supply provides current, up to 50 A, to heat the substrate holder over this lowest temperature. The diamond substrate is attached to the substrate holder with a thin layer of high temperature grease to guarantee a good thermal contact. With this setup we have been able to control the substrate temperature between 250 and 1000 °C.

The diamond substrates were previously grown over molybdenum in a similar reactor. We used a gas mixture of 0.4% CF_4, 2% CH_4 and hydrogen balance. We grew a 100 μm free standing film during 24 hours, for a filament temperature of 2200 °C, a substrate temperature of 800 °C, a flow rate of 100 sccm and a gas pressure of 50 Torr. After growth the molybdenum substrate was dissolved. The 200 mm^2 diamond wafer was laser cut to give the small 15 mm^2 diamond substrates [11].

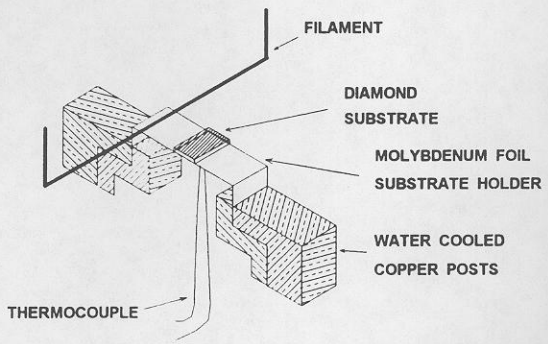

Figure 1: Experimental setup showing the filament substrate geometry in detail.

The diamond substrates were submitted to acid cleaning before and after growth to remove metallic residues. The use of diamond substrates reduces the error in growth rate measurement because the growth induction time is considerably reduced.

The growth rate (G), given in units of $\mu g/(cm^2.h)$, is obtained by weighting the mass of each substrate before and after growth. Each substrate area is also measured. We consider that the diamond substrate is small enough to have a uniform deposit over its area.

In the present experiments we have grown over the back surface of these diamond substrates. The very small grain size in this surface allows a better observance of the new grown diamond. SEM and AFM images and the Raman spectra are obtained after growth on this surface.

III -- RESULTS AND DISCUSSION

Fig. 2 shows the dependence of diamond growth rate with substrate temperature, for growth with three different gas mixtures. The data is shown as an Arrhenius plot. From this plot we obtained an activation energy of around 11 kcal/mole for diamond growth with CF_4 addition. This is about half the activation energy we measured for growth with a CH_4/H_2 mixture, in the range between 560 and 800 °C. Other authors [12, 13, 14, 15] have also reported activation energies on the order of 22 kcal/mol for growth with CH_4/H_2 mixtures. Some difficulty in growing diamond at low temperatures has been reported [16, 17]. Ihara et al. [18] reported diamond growth even at 135 °C with CH_4/H_2 mixtures, but growth rate data given in their paper show a much smaller activation energy. Hong et al. have reported a growth rate of 0.05 µm/h at 380 °C with a CCl_4 mixture. Considering a film density of 3.52 g/cm^3, we observed growth rates from 0.13 µm/h at 300 °C to 7 µm/h at 800 °C, with the

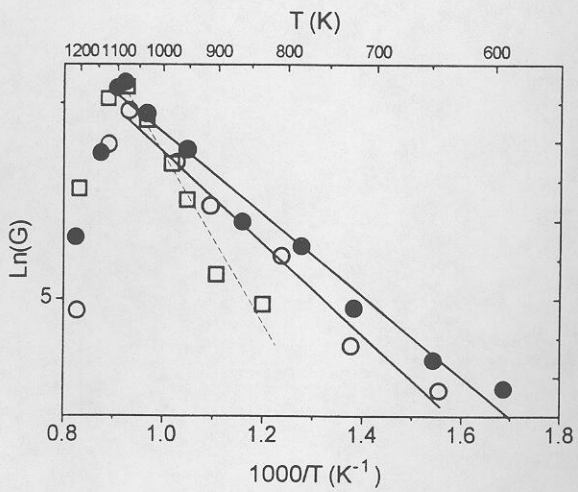

Figure 2: Arrhenius plot for three gas mixtures: ○ 1% CH_4 + 0.5% CF_4; ● 1.5% CH_4 + 1.5% CF_4; □ 1.5% CH_4. The lines are linear regression fits for the corresponding data.

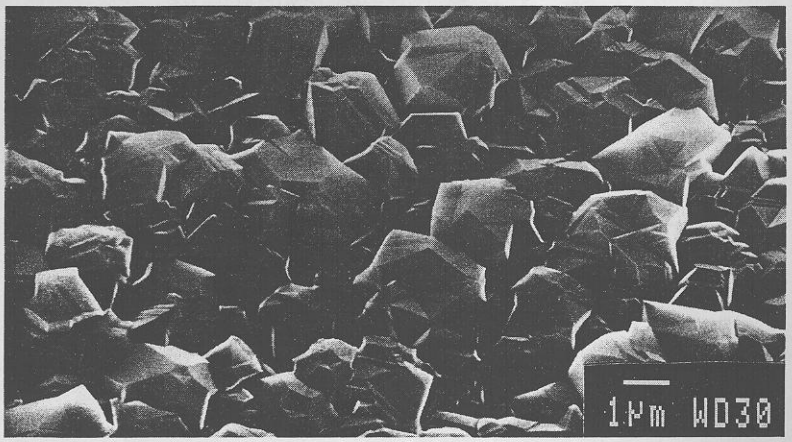

Figure 3: SEM picture of a small region of a sample grown at 300 °C.

1.5% CH_4 + 1.5% CF_4 mixture.

We did not observe any growth for our experiments with CF_4/H_2 mixtures. We used 0.5% and 2% CF_4 concentrations and the same growth conditions described. This confirms our previous observation that the amount of CF_4 dissociated is very small in a hot filament reactor [7].

With CF_4 addition we have been able to grow diamond at temperatures as low as 250 °C. For these low temperatures most of the growth is of spherical particles, but at some small regions we can observe very well faceted particles, as shown by SEM in Fig. 3. The same

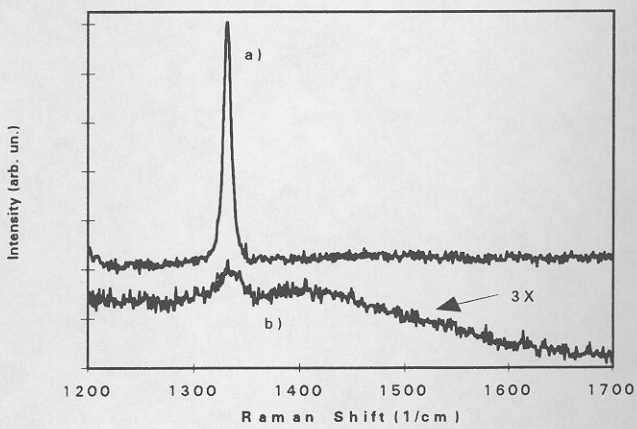

Figure 4: Raman spectra for samples grown with 1.0% CH_4 + 0.5% CF_4: a) 450 °C, b) 330 °C with the scale multiplied by a factor of 3.

conditions (filament temperature, gas pressure and flow rate) are used for all experiments. These experiments show that the presence of fluorine chemistry in the gas phase probably is responsible for an enhancement compared to growth with regular CH_4/H_2 mixtures.

Raman spectroscopy is not able to discriminate adequately between the diamond substrate and the new deposit, but it can clearly show the decrease in quality under 375 °C, as shown in Fig. 4. Separate growths on molybdenum substrates actually show that the diamond Raman signature at 1332 cm^{-1} appears only for substrate temperatures higher than 390 °C.

The morphologies of these films were also investigated by AFM. The direct observation of the AFM image shows that the grain size increases with substrate temperature increase. Fig. 5 shows the roughness histogram 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 bearing area analysis [8].

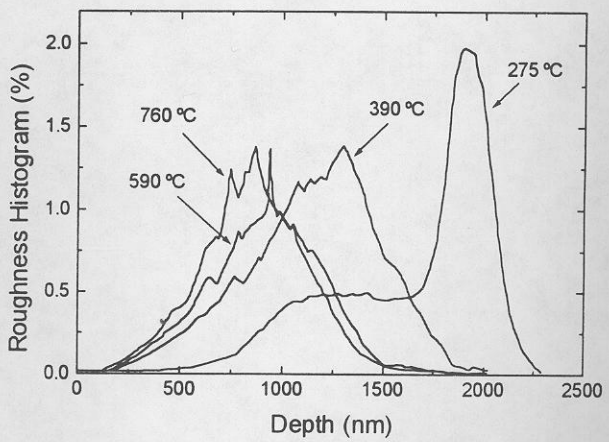

Figure 5: Roughness histogram obtained from AFM image, for samples grown with the mixture of 1.5% CH_4 + 1.5% CF_4, at the indicated temperatures.

In summary we have grown diamond at temperatures as low as 390 °C with CF_4 addition in the regular CH_4/H_2 mixture in a hot filament reactor. We measured an activation energy of 11 kcal/mole that is much lower than the activation energy for diamond growth from CH_4/H_2 mixtures. Raman spectroscopy shows good quality diamond for most of these experiments. SEM and AFM images show characteristic diamond faces. Bearing area and roughness measurements from the AFM images show smooth and dense diamond grown at temperatures higher than 390 °C.

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REFERENCES

1. D.E. Patterson, B.J. Bai, C.J. Chu, R.H. Hauge and J.L. Margrave, in Proc. of the 2nd Intern. Conf. on the New Diamond Science and Technology, edited by R. Messier, J.T. Glass, J.E. Butler and R. Roy (Materials Research Society, Pittsburgh,PA,1991), p. 433
2. R.A. Rudder, G.C. Hudson, J.B. Posthill, R.E. Thomas and R.J. Markunas, Appl. Phys. Lett., **59**, 791 (1991)
3. F.C.-N. Hong, G.T. Liang, D. Chang and S.C. Yu, in Applications of Diamond Films and Related Materials, edited by Y. Tzeng, M. Yoshikawa, M. Murakawa and A. Feldman (Elsevier Science Publishers B.V., 1991), p. 577
4. F.C.-N. Hong, J.-C. Hsieh, J.-J. Wu, G.-T. Liag and J.H. Hwang, Diamond and Related Materials, **2**, 365 (1993)
5. V. Baranauskas, M. Fukui, C.R. Rodrigues, N. Parizotto and V.J. Trava-Airoldi, Appl. Phys. Lett., **60**, 1567 (1992)
6. M. Kadono, T. Inoue, A. Miyanaga and S. Yamazaki, Appl. Phys. Lett., **61**, 772 (1992)
7. E.J. Corat, D.G. Goodwin and V.J. Trava-Airoldi, in Proc. of the 2nd Intern. Conf. on the Applications of Diamond Films and Related Materials, edited by M. Yoshikawa, M. Murakawa, Y. Tzeng and W.A. Yarbrough (MYU, Tokio,1993), p. 697
8. V.J. Trava Airoldi, B.N. Nobrega, E.J. Corat, E. Del Bosco, N.F. Leite and V. Baranauskas, to be published in Vacuum.
9. S.J. Harris and D.N. Belton, Appl. Phys. Lett., **59**, 1949 (1991)
10. M. Frenklach, in Proc. of the 2nd Intern. Symposium on Diamond Materials, edited by A.J. Purdes, B.M. Meyerson, J.C. Angus, K.E. Spear, R.F. Davis and M. Yoder (The Electrochemical Society, Inc., Washington, DC,1991), p. 142
11. V. Baranauskas, A. Peled, V.J. Trava-Airoldi, C.A.S. Lima, I. Doi and E.J. Corat, to be published in Applied Surface Science **79-80**, (1994)
12. E. Kondoh, T. Ohta, T. Mitomo and K. Ohtsuka, Appl. Phys. Lett., **59**, 488 (1991)
13. B.V. Spitsyn, L.L. Bouilov and B.V. Deryagin, J. Cryst. Growth, **52**, 219 (1981)
14. W. Zhu, R. Messier and A.R. Badzian, in 1st Intern. Symposium on Diamond and Diamond-Like Films (The Electrochemical Society, 1989), p. 61
15. Y.Mitsuda, T. Yoshida and K. Akashi, Rev. Sci. Instrum., **60**, 249 (1989)
16. W.A.Yarbrough, A.R. Badzian, D. Pickrell, Y. Liou and A. Inspektor, J. Cryst. Growth, **99**, 1177 (1990)
17. Y. Liou, A. Inspektor, R. Weimer and R. Messier, Appl. Phys. Lett., **55**, 631 (1989)
18. M. Ihara, H. Maeno, K. Miyamoto and H. Komiyama, Appl. Phys. Lett., **59**, 1473 (1991)