HFCVD OF DIAMOND AT LOW SUBSTRATE AND LOW FILAMENT TEMPERATURES

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ABSTRACT

It has been discovered that the addition of a small amount of oxygen to the CH₄ and H₂ feed gas permits HFCVD of diamond at significantly lower filament and substrate temperatures. The effective O/C ratio here is much lower than that used in most studies of the oxygen effect. Careful control of the O/C and C/H ratios were found to be crucial to success. The effects of substrate and filament temperatures on growth rate and film quality were studied. Optimum conditions were found that gave reasonable growth rates (~0.5 μm/h) with high film quality at filament temperatures below 1750 °C and substrate temperatures below 600 °C. As a result, low temperature deposition has been realized. Power consumption can be reduced 50%, and the filament lifetime is extended indefinitely.

INTRODUCTION

It has been commonly accepted that diamond deposition in a hot filament assisted chemical vapor deposition (HFCVD) reactor requires a filament temperature higher than 1900 °C to activate the gas. Production of atomic hydrogen, along with activated growth species, is considered vital to this technology. [1, 2] The combined effects of high temperature and carburization of the filament results in frequent breaking and severe distortion of the tungsten filaments. Diamond growth rates reach a maximum at a substrate temperature around 950 °C. 700 °C is considered to be a lower limit for the substrate temperature, below which significant amounts of non-diamond carbon are co-deposited on the substrate.

Addition of oxygen has been found to increase the growth rate, reduce non-diamond carbon content in the film, and allow deposition at lower substrate temperatures. [3, 4, 5] Most of the studies of the oxygen effect have been conducted in microwave systems. Only a few of the studies were in HFCVD systems. [6, 7] Low substrate temperature growth has been attempted by using a high filament temperature (2300 °C). [8] Application of higher concentrations of hydrocarbon is often associated with oxygen addition. An O/C ratio between 50% to 200% is most commonly used.

In this investigation, it has been discovered that addition of a small amount of oxygen (~10³ ppm) to the CH₄ and H₂ mixture can allow diamond deposition in a
HFCVD reactor at significantly lower filament and substrate temperatures. Diamond has been observed to grow at filament temperatures as low as 1400 °C or at substrate temperatures as low as 450 °C without significant co-deposition of non-diamond carbon. High quality films have been grown with reasonable growth rates by careful control of feed gas composition and substrate and filament temperatures.

EXPERIMENTAL

Most of the experiments were conducted in a conventional quartz tube HFCVD reactor with independent control of substrate and filament temperature. The filament was a 7-loop, 4 mm diameter coil made from 0.5 mm diameter, 50 mm long tungsten wire, typically held 6 to 7 mm above the substrate. The filament brightness temperature was measured using a single-color disappearing-filament pyrometer. No corrections were applied. The substrate temperatures reported here were measured using an S-type thermocouple buried in the substrate holder. Comparing the thermocouple reading at higher temperatures with that from a pyrometer looking directly at the back of the Si substrate, it is found that the temperature indicated using the thermocouple is no more than 50 °C lower than the actual temperature when the filament is below 1750 °C. Computer control guaranteed that both the filament and the substrate temperature remained constant during deposition. The results shown in Fig. 1 were obtained in a reactor without independent substrate heating. For this data, the actual substrate temperature is unknown. However, since only a single filament temperature (1500 °C) was used and the same filament lasted throughout the series of measurements, the substrate temperature is assumed to have been constant. An unknown but constant substrate temperature should not alter the conclusions drawn from this series of measurements in which the effect of gas composition was the focus.

Si(100) was used as the substrate. Each substrate was scratched over one-half of its surface using diamond paste before deposition so that both the film and individual particles could be examined. The growth rates referred to in this paper were average rates measured from isolated particles. Raman spectra of the films were recorded using a Dilor XY spectrometer with a confocal microscope and CCD detector. All spectra were recorded at 514.5 nm excitation with the confocal aperture adjusted to yield ~ 8 μm lateral and vertical sampling. The spectrometer was configured in a double-subtractive mode of operation which yielded a FWHM of 3.7 cm⁻¹ on the 1332 cm⁻¹ line for a natural diamond sample. The film quality is represented here by the intensity ratio of the Raman line near 1332 cm⁻¹ to the maximum in the 1500 ~ 1600 cm⁻¹ region characteristic of sp² carbon (I(dia)/I(gra)). All the depositions lasted 16 hrs, were at 40 torr chamber pressure, and at a total gas flow rate of 50 sccm.

RESULTS AND DISCUSSION

Effects of O/C and C/H Ratios

The choice of an optimum oxygen to carbon atomic ratio O/C was found to be crucial for the success of low temperature deposition. This ratio is significantly smaller than what is commonly used, and the acceptable range is much narrower. Fig. 1 shows
the effect of the O/C ratio on the growth rate and film quality for different CH₄ percentages in the feed gas at a 1500 °C filament temperature (Tf). A minimum O/C ratio was observed, below which mostly non-diamond carbon was deposited. A slight increase from the minimum O/C ratio resulted in a dramatic improvement in both growth rate and film quality. Soon afterwards, a maximum growth rate was reached. Films with the highest quality always appeared with O/C ratio above that for the maximum growth rate. A further increase in O/C resulted in rapid deterioration of both the growth rate and film quality. The optimum O/C ratio shifted to higher values with increases in the C/H ratio. Typically, for a 0.5% CH₄ feed gas, the O/C ratio had to be higher than 8%. The growth rate reached a maximum at 13% O/C ratio, and 15% O/C ratio yielded the highest film quality. An O/C ratio between these two later values is considered to be the optimum O/C ratio. In this case, the width of the range is only 2%. Although this width will expand with increases in filament or substrate temperature, it is limited to a much narrower range compared to conventional depositions. Thus, precise control of O/C ratio to the optimum value is important. In microwave systems, there have been reports that growth rates maximize at an O/C ratio less than 50%. However, since the growth rate remains high and film quality improves with higher O/C ratios, a much higher O/C ratio and, at the same time, higher C/H ratio are commonly used.

As is shown in Fig. 1, the C/H ratio affects the optimum O/C ratio. An interesting question is: whether or not it is possible to use higher C/H ratios and always find a corresponding optimum O/C ratio so that higher growth rates can be achieved, as in conventional depositions? However, we found that with higher CH₄ concentrations, and higher O/C ratios, the non-diamond carbon content in the film increases substantially and the growth rate decreases. This behavior can already be seen in Fig. 1, in the 1% CH₄ growth, where graphitic carbon increases in the films throughout the O/C ratio range tested. The growth rate of this low quality film was no higher than those grown with lower CH₄ percentage. Experiments at different conditions showed that the optimum C/H ratio is closely related to filament temperature. The lower the filament temperature, the lower the C/H ratio that can be tolerated (and vice versa).

Effects of Substrate Temperature

Fig. 2 shows the effect of substrate temperature on growth rate and film quality at 1600 °C filament temperature, 1% CH₄ and 19% O/C feed gas composition. The growth rate reaches a maximum as the substrate temperature is increased. The highest growth rate occurred at about 750 °C instead of 950 °C, as in conventional depositions. The most striking feature of these results is that the best film was achieved at the lowest substrate temperature. Non-diamond carbon content was dramatically reduced as the substrate temperature decreased. These results have been observed repeatedly regardless of changes in other conditions.

Effects of Filament Temperature

The relationship between filament temperature and growth rate also changes with oxygen addition. As shown in Fig. 3, an increase in filament temperature does not always mean an increase in growth rate. The growth rate at 1700 °C and at 2000 °C are comparable, whereas the film quality improves significantly at 2000 °C. However, there
was not enough gain in either growth rate or film quality to justify the filament at 2000 °C instead of 1800 °C. The substrate temperature was 780 °C, and 0.5% CH4 and 13% O/C ratio were used. The specific temperature at which growth rate decreases with filament temperature (1700 °C in this case) changes when the feed gas composition or the substrate temperature are changed. There can also be more than one local maximum growth rate. The span over which the growth rate recovers (from 1700 °C to 2000 °C in this case) varies. Another interesting phenomenon is that the graphitic carbon component in the film will eventually decrease as the filament temperature becomes very low. This phenomenon was also observed in experiments at different conditions.

Combining all the information, it is possible to select optimum conditions to deposit high quality films at a moderate growth rate using significantly lower filament and substrate temperatures. Fig. 4 shows diamonds grown under the conditions: T_f=1700 °C, T_s=580°C, 0.5% CH4 and 13% O/C ratio, and the corresponding Raman spectrum. The crystal surfaces are smooth, twinning is low, and almost no graphitic carbon is detected by Raman spectroscopy. (I(dia)/I(gra) is greater than 250.) The FWHM of the diamond first order Raman line is 6.2 cm⁻¹. This spectrum indicates a better quality film than most of those grown under conventional conditions. Note that the feed gas used here is the same as that used in Fig. 3. Compared to the data at T_f=1700 °C in Fig. 3, one can see that a 200 °C decrease in substrate temperature greatly improved the film quality. The growth rate of this sample was about 0.2 μm/h. Higher growth rates can be achieved by adjusting operating parameters.

Power Consumption and Filament Durability

Fig. 5 shows the strong relationship between power consumption and filament temperature. At 1700 °C, the filament requires only 50% of the power needed at 2000 °C. Since higher filament temperature does not always benefit the growth rate, or film quality, operating the filament at a lower temperature can save a significant amount of energy.

Another benefit of operating the filament at lower temperatures is that its distortion is substantially eliminated and the lifetime is extended indefinitely. This durability of the filament not only saves the time and labor involved in frequently changing the filament, but also makes the duplication and control of deposition conditions much easier.

CONCLUSIONS

By careful control of the feed gas composition of C, H, and O, high quality diamond can be deposited at significantly lower filament and substrate temperatures than those normally used while retaining growth rates comparable to those of conventional HFCVD. As a result, power consumption can be reduced by 50% and the filament lifetime extended indefinitely.

Deposition of diamond at these low filament and substrate temperatures, and the unique behavior of growth rate and quality change with these temperatures are not consistent with the present understanding of the HFCVD diamond growth mechanism. Exploration of mechanisms that can explain these phenomena should be at least as
important as the results. Some work has been done in this respect and will be presented elsewhere [9].

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Fig. 1. a) Growth rate vs O/C ratio for different CH$_4$ percentages in the feed gas. 

b) Corresponding intensity ratio of Raman lines near 1332 cm$^{-1}$ and 1500 to 1600 cm$^{-1}$ vs O/C ratio. Deposition conditions: T$_f$=1500°C, T$_s$ < 700 °C and unknown.
Fig. 2. Effect of substrate temperature on growth rate and film quality. Deposition conditions: $T_f = 1600 \, ^\circ\text{C}$, 1\% CH$_4$, O/C=19\%.

Fig. 3. Effect of filament temperature on growth rate and film quality. Deposition conditions: $T_s = 780 \, ^\circ\text{C}$, 0.5\% CH$_4$, O/C=13\%.
Fig. 4 a) Scanning electron microscopy image of diamonds and corresponding Raman spectrum. Growth conditions: $T_f=1700$ °C, $T_s=580$°C, 0.5% CH$_4$, 13% O/C.