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High efficiency deposition of diamond film by hot filament chemical vapor deposition

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A new designed reaction chamber with new relative distribution of filament and substrates has been adopted in order to increase the deposition area of diamond films and thus increase the deposition efficiency in conventional hot filament chemical vapor deposition (HFCVD) systems. The relatively small reaction chamber was cuboid shaped ($50 \times 25 \times 25$ mm^3) and composed of molybdenum wafers. It was established in the vacuum chamber. A tungsten filament was hung up vertically in the center of the small chamber and parallel to the gas flow path. At the four inner sides of the reaction chamber, four Si(100) substrates ($30 \times 10 \times 0.5$ mm^3) were installed to grow diamond films. The deposition results indicate that uniform diamond films can be obtained on the four substrates, and the film growth rate is the same at both ends of the substrates. The diamond film growth rate was about 1–2 μm/h, which is similar to those of the conventional HFCVD method. Thus, the deposition area and efficiency can be increased four times in the case without the filament number, gas flow rate, and power consumption.

Since Spitsyn's *et al.* report[1] in 1981, many chemical vapor deposition methods have been developed for diamond growth, such as hot filament CVD (HFCVD),[2] microwave plasma (MPCVD),[3] RF-,[4] plasma jet,[5] and O_2–C_2H_2 flame,[6] etc. Because of its high potential application in wear resistance, optical, heat sink, and semiconducting devices, many researchers have been trying to industrialize it. Large area deposition of diamond film has been studied intensively,[7] especially by HFCVD, MPCVD, and plasma jet. However, some problems are still unsolved. HFCVD is an attractive candidate among various methods though there exist some disadvantages such as its low growth rate, impurities, etc. In most cases, the substrate size or deposition area is approximately equal to the filament distribution area or even smaller. When the deposition area increases further, some technical problems become prominent. For example, it is a little difficult to keep the filaments straight and stable; meanwhile, the deposition efficiency was not increased and seems quite low too, and the growth rate reaches hardly more than 10 μm/h because of its relatively low filament temperature compared to that of plasma jet and O_2–C_2H_2 flame.[8]

In this paper, we report a new designed reaction chamber in which we have changed the setup of the filament and the substrates to increase the growth area and thus increase the deposition efficiency while the filament number, gas flowrate, and power consumption are kept the same as those in conventional HFCVD. The deposition area can be increased by at least two times in our experiments.

Our experiments were performed in a conventional HFCVD apparatus. A quartz tube with diameter of 120 mm and length of 500 mm was used as the vacuum chamber. In its center, a much smaller cuboid-shaped reaction chamber made of Mo wafers was installed. At the bottom of each Mo wafer, it was folded at a width of 5 mm toward the inner side, and thus the substrate can be gripped vertically. The chamber size was $50 \times 25 \times 25$ mm^3. A 40 mm long tungsten filament (ϕ0.3 mm) coiled into 20 turns of ϕ4 mm was vertically installed in the center of the chamber (Fig. 1) and parallel to the gas flow direction. The substrates were put on the four inner sides of the small chamber. A mixture of high purity hydrogen (99.999%) and methane were inlet into the small chamber through a ϕ10 mm stainless steel tube. The single crystalline Si(100) wafers with each size of $30 \times 10 \times 0.5$ mm^3 were used as the substrates. They were polished by 0.5 μm diamond paste to increase diamond nucleation density. The CH_4 concentration was 0.2–3.0 vol% mixed with hydrogen in a total flow rate of 100 sccm. The filament temperature was 2100 °C during deposition, as measured by an optical pyrometer. The substrate temperature was 800–900 °C, measured by a W–25% Re thermocouple

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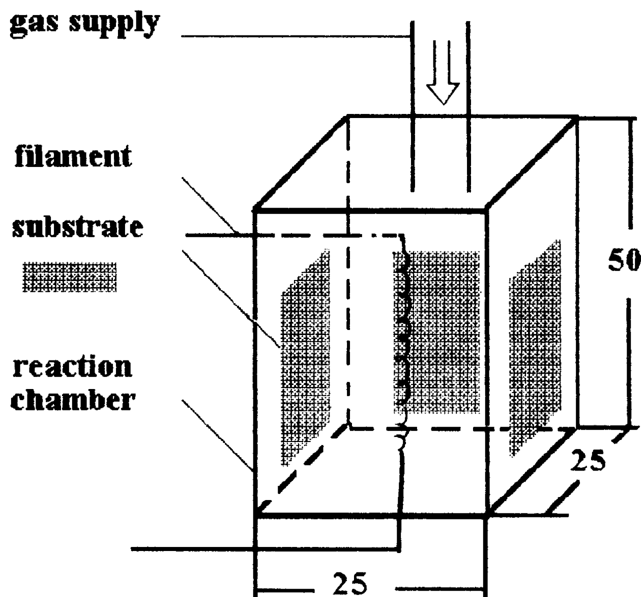

FIG. 1. Schematic drawing of the small reaction chamber.

which was fixed in contact with the back of the substrate. The pressure during deposition was 30 Torr, as measured by a barometer. The films obtained were analyzed by x-ray diffraction (XRD), Raman spectroscopy (Raman), and scanning electron microscopy (SEM). Cross sections of the films were observed by SEM to calculate the growth rate of the as-grown films.

Figure 2 gives the Raman spectra of one of the four grown films deposited at the concentration of $CH_4 = 1.5$ vol% on both ends. Sharp diamond peaks appeared at 1333 cm^{-1}. The Raman peak of graphite at 1580 cm^{-1} is not prominent. From this result we see that high quality diamond films have been obtained. Figure 3 is the XRD pattern of the obtained films of Fig. 2(a). The intensity of the (220) peak is stronger than those of (111) and (400), and is different from the powder pattern result

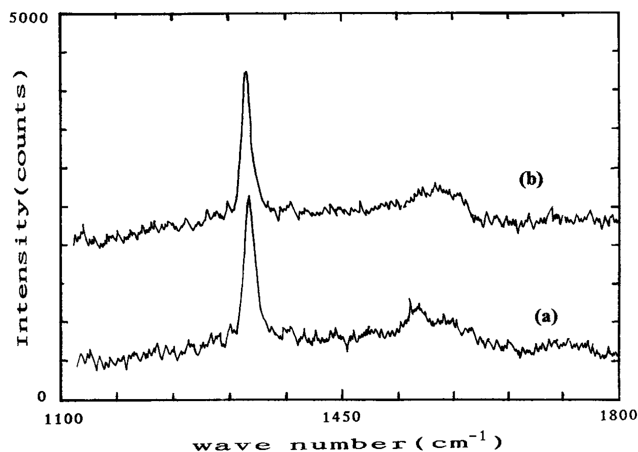

FIG. 2. Raman spectra on both ends of the substrates after being deposited at $CH_4 = 1.5$ vol%: (a) top end, and (b) lower end.

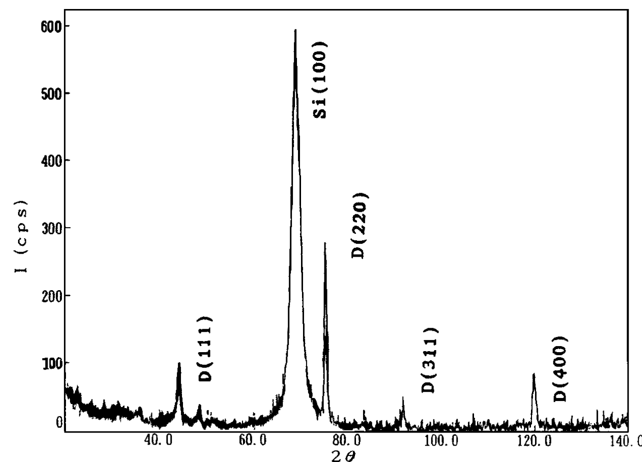

FIG. 3. XRD pattern of the same sample as that of Fig. 2(a).

(ASTM-628). The result indicates a (110) preferred growth. Figure 4 show the SEM photomicrographs of the film surface at the two ends grown at a concentration of 1.5%. As the polycrystalline surface morphology observed, most of the crystal grains are not the square (100) facet or triangular (111) facet. The growth rate is calculated to be 1.5 μm/h from the SEM cross-section measurement. The growth rates of the films on the two ends of the substrate are equal. The same results are obtained by analyzing the other three samples shown.

When we changed the methane concentration from 0.2 vol% to 3 vol%, the crystal morphology experienced a change from (111), (100), to polycrystalline successively. The range is 0.2–0.5 vol% for (111) predominate, and 0.5–1.3 vol% for (100). Large methane concentration is favorable to polycrystalline facet. This is similar to other reports,[9] while the methane concentration in our experiment can be a little larger.

Debroy *et al.*[10] have discussed the two main transport mechanisms of the active species (CH_3, C_2H_2), i.e., the convection and diffusive mass transports in HFCVD system. Their calculation and experiments indicate that the diffusive mass transport caused by temperature and concentration gradient is the dominant mechanism of diamond growth (30 Torr), and the convection, both of free and forced, is unimportant in determining the quality and growth rate of the films. In our experiments, the filament was hung up vertically, and the temperature field was perpendicular to it. It is this gradient field that determines the transport of the active species to the substrate surface. The gas flow direction has no great influence on the diamond growth. Symmetry of the gradient field around the filament enabled the diamond films deposited on the four inner sides of the Mo holder. The four-sided substrate holder is only one design among various arrangements. Other cases can be chosen if necessary, such as the two-sided or three-sided

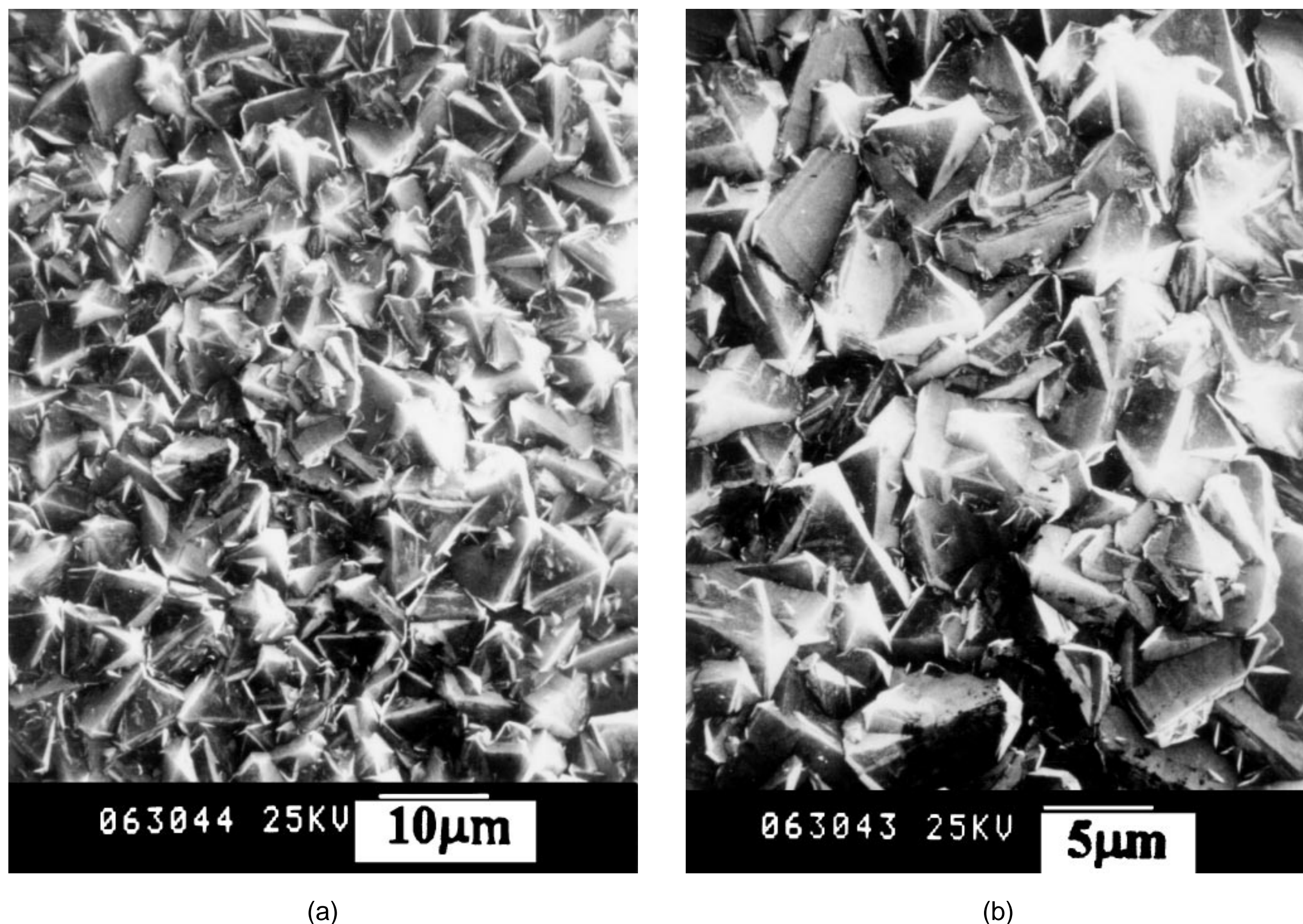

FIG. 4. SEM photomicrographs of both ends of the obtained films grown at $CH_4 = 1.5\%$: (a) top end, and (b) lower end.

pattern, etc. Since the filament is kept straight during the diamond growth, there are no intense temperature and concentration gradients existing in the vertical direction. The transport of the active species from the filament to the substrates is uniform, so it is not surprising that the diamond film growth rate is the same on both ends of the substrate.

In our experiments, a large methane concentration can be used to deposit high quality diamond films. The reason seems to be that the produced atomic hydrogen by hot filament was confined in the small space of the reaction chamber and promoted etching of the graphite formed during the diamond deposition. In most of the HFCVD results, the methane concentration of more than 2 vol % is not suitable for high quality diamond film growth.[2,8]

The increasing of the deposition area, while the gas flow rate and the filament power consumption remain the same as that in conventional HFCVD, means the increase of the growth efficiency. In HFCVD method, when acetone or other organic compound is applied to replace the methane[11] or when the electron assistance[12] is added, the growth rate can reach 5–10 μm/h. Since the deposition efficiency can be increased three or four times, our method has opened the door for industrial application.

In conventional HFCVD, the filaments are horizontally installed over the substrates,[2] or hung up vertically with the parallel substrates, where the gases flow directly across filaments to the substrates with a high speed to improve the uniformity of the film.[7] Our designed reaction chamber has changed the filament and substrate distributions. When more filaments are adopted to deposit large area diamond films, some other kind of filaments and substrate distributions can be constructed to increase the deposition efficiency according to our idea, while the gas flow direction need not be considered. The pattern which shows that the substrates can be installed surrounding the filaments may eliminate the former limitation that the deposition area must be smaller than the filament's distribution area in multifilament cases. Thus we can deposit a large area of diamond film in a relatively small vacuum chamber. According to this, we can construct more types of filaments and substrate distributions to increase the diamond deposition efficiency.

In conclusion, a new type of filament-to-substrate distribution has been employed to increase the dia-

mond film growth efficiency. This method is suitable for depositing high quality diamond films. The growth regularity of diamond film in this case is similar to that in the conventional HFCVD.

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