STRUCTURAL FEATURES OF DIAMOND GROWN AT LOWER TEMPERATURES

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INTRODUCTION

Although diamond can be synthesized at a temperature lower than 500℃ in CVD processes, a substrate is generally maintained at a temperature between 800 and 1100℃ for the growth of high quality diamond with practical growth rates. The growth rate at the lower temperature is not necessarily high due to suppression of the decomposition of the starting carbon compounds. However, since reaction rate of graphitic carbon with gaseous atomic hydrogen goes through a maximum at about 500℃[1], it is possible to produce better quality diamond free from carbon impurities at temperatures lower than 800℃.

The growth rate has been stimulated using oxygen containing compounds as a starting gas, or by activation methods such as heating a filament in a suitable gaseous mixture in a hot filament method. In a microwave plasma method, several methods could be considered as acceleration methods of the growth rate. For example, the application of higher microwave power, the addition of oxygen containing compounds, and irradiation by light are applicable.

In this paper, growth features of diamond at a temperature lower than 700℃ have been reported, including the effects of UV light irradiation, water as an additive and microwave power. The efforts were focused on increasing of the growth rate and improving the quality of diamond.

EXPERIMENTAL

Diamond was deposited by a microwave plasma-assisted CVD system which is essentially the same as that reported previously[2]. Though the substrate temperature was usually controlled by adjustment of microwave power, a substrate holder cooled by flowing water was also used for experiments supplying higher microwave power. The temperature was measured by radiation pyrometers equipped with silicon and germanium detectors.

As a UV light source, a super high-pressure mercury lamp was used. The light emission was in the range of 230-580nm. The stronger lines in the UV region are at 366, 405 and 436nm. The lamp was usually run at a fixed power of 500W. The UV light was fed to the chamber through a silica glass window after being reflected by a mirror, and was focused to a 50mm diameter. The beam was vertically incident on the substrate surface.

A copper sample holder cooled by water was used for growth of diamond at higher microwave power. A substrate temperature was controlled by adjustment of the flow rate of water. Individual cubo-octahedral crystals of about 2-5μm produced at substrate temperatures higher than 800℃ were employed as seeds and were subjected to the growth. Grown samples have been studied using scanning electron microscopy and Raman spectroscopy.

RESULTS AND DISCUSSION

Typical examples of an early growth stage at 500 ℃ and 0.3% methane showed that pyramids were formed on all (100) faces of the seed crystal. And it was shown that the lateral growth which fills in the lower-level face proceeds simultaneously with the vertical growth and the crystal finally becomes an octahedron.

The peak position and line width($2.7cm^{-1}$) expressed as full width at half maximum (FWHM) in the Raman spectrum of the crystal grown on the seed at 500℃ and 0.3% methane concentration indicated that the crystal was of reasonably high quality. The growth at 400℃ and 0.3% showed a similar morphological change to that observed at 500℃. At 300℃, a granular form was found on the (100) faces, differing from the crystals grown at higher temperatures. The growth rates at 500, 400 and 300℃ were estimated to be about 150 Å /h, 60

Å /h and 10 Å /h, respectively.

No distinction in morphology was observed between diamond particles obtained at 500℃, both with and without UV irradiation. In the Raman spectra of the particles, no appreciable difference in FWHM, and in luminescence background was found.

Though diamond grown with irradiation at 500 ℃ exhibited an octahedral morphology a with smooth (111) surface, UV irradiation at 400℃ made a morphological change, and the surface was heavily devastated. The steps on the (111) face seemed to have triangular forms aligned along the same direction. The size of particles grown under UV irradiation is larger than that obtained with no irradiation. UV light appears to be effective in enhancing the growth rate. The effect of UV irradiation on the Raman spectra of the particles grown at 400℃ was appreciable. The intensity of the broad Raman line around 1400cm^{-1} is stronger in diamond grown under UV irradiation than in that grown without UV light. Additionally, the FWHM is larger in the irradiated sample than in the unirradiated one. The results indicate that diamond grown with UV light exhibits higher carbon impurities and lower quality compared with diamond obtained without UV light.

UV irradiation on the growth at 300℃ resulted in ball-like deposits of diameters below 0.2μm on the (100) faces. Such deposits were rarely observed on the other surfaces. It is inferred from the surface morphology and shape that the growth layer may be polycrystalline, and that the quality is highly deteriorated. The tendency is similar to the result obtained from the layer grown at 400℃.

The use of UV light is effective in enhancing the growth at temperatures lower than 500℃. It should be noted that no appreciable effect on the growth rate and morphology has been observed at temperatures higher than 600℃.

The surface of the crystals grown at 500℃ at 380W and 500W seemed to show slightly more disorder on the (111) surface compared with that of crystals grown at 280W. The increase in growth rates of crystals with an increase of microwave power was observed. The results indicate that higher microwave power is effective for increasing the growth rate. Broad Raman lines at around 1500cm^{-1} due to double-bonded carbon are found in the spectra of the samples grown at 380 and 500W, though they have a different relative intensity. The double-bonded carbon is hardly detectable in the crystal obtained at 280W. Moreover, an increase in luminescence background throughout the higher wave number region was observed in all spectra. The higher the microwave power which was supplied, the larger the 1332cm^{-1} line width became. The results indicate that the higher power induce some structural disorder and/or defects in the growth layer, and does not always result in better quality diamond.

SUMMARY

Growth of diamond from gaseous mixtures of methane and hydrogen by means of microwave plasma assisted chemical vapor deposition have been studied at substrate temperatures lower than 700℃. The effects of UV light and microwave power were also studied. The growth rate of (100) face was found to be greater than that of (111) face in the early growth stage. The uses of UV light and higher microwave power during diamond growth in microwave plasma CVD have proved to be effective in enhancing the growth at temperatures lower than 500℃.

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