Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric, Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Temperature dependence of diamond growth by a hot-filament method in a low temperature range

A. Yamaguchi, M. Ihara, and H. Komiyama

Department of Chemical Engineering, Faculty of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan

Temperature dependence of the growth rate and morphology of diamond grown using a hot filament-assisted chemical vapor deposition (HFCVD) method was experimentally determined. Emphasis was placed on the low substrate temperature ranging from 210 to 700 °C. The growth rate was determined from the particle sizes for at least two different deposition times as measured by scanning electron microscopy. The activation energy for the growth of diamond was as small as a few kilocalories per mole. The morphology of the diamond particles depended strongly on the substrate temperature. At 210 °C, most of the particles were octahedron faceted with only a {111} surface. With increasing temperature, cubo-octahedron faceted with both {100} and {111} surfaces appeared.

1. INTRODUCTION

Seemingly inconsistent experimental results have been reported on growth rates of diamonds grown using various CVD methods [1-6]. We reported that diamonds grow on a substrate even at as low a temperature as 135 °C [7]. Temperature dependence of the growth rate of diamond were studied by a number of researchers, resulting in the activation energy which has not been established. Activation energy of diamonds grown using CVD methods ranges from 10 to 25 kcal/mol in the substrate temperature range above 600 °C [1-6]. If the nominal activation energy of 15 kcal/mol is valid where the value is taken from previous studies, then diamond growth at low temperatures should be extremely slow. For example, the growth rate at 135 °C is five orders of magnitude lower than that at 700 °C. Because the nominal growth rate at 700 °C is 1 μm/h [3], diamonds could not actually grow at 135 °C. Because research on the hot filament-assisted chemical vapor deposition (HFCVD) method at low substrate temperatures is scarce, this present study was undertaken to determine the growth rate of diamonds deposited using a HFCVD method for a wide temperature range.

2. EXPERIMENTAL

Diamond particles were deposited on a substrate using the HFCVD method. Essential parts of the experimental apparatus as well as the deposition process itself were similar to those described elsewhere [7]. The substrate used here was a 8-mm × 8-mm × 0.5-mm silicon wafer that had been polished by diamond paste. Its temperature was able to be controlled between 210 °C and 700 °C using an electric heater and a stream of cooling water, and was measured with a thermocouple inserted into a hole in the substrate holder. The difference in temperature between the measured point and the substrate surface was no greater than 10 °C [7]. A tantalum filament was placed 4 mm above the substrate, and using a dual-band pyrometer, its temperature was measured to be 2700 ± 20 °C. The feed gas was methane (0.5%) diluted by hydrogen, and the gas flow rate was 300 sccm. The total pressure of the gas was 50 Torr.

3. RESULTS

Scanning electron micrographs of the diamond particles deposited for different times were taken, which showed clearly the existence of an incubation period. The growth rate was determined from the plot of the average particle size versus the deposition time at each substrate temperature.

Figure 1 shows an Arrhenius plot of the temperature dependence of the growth rate for substrate temperatures ranging from 210 to 700 °C. The apparent activation energy was as small as 1~5 kcal/mol, which was much smaller than that reported for high temperatures above 600 °C [1-6]. Also seen in the figure is that the apparent activation energy shows a tendency to decrease slightly with decreasing substrate temperature. Similar behavior was reported by Snail *et al.* [7] for substrate temperatures of 444~1200 °C. Those results along with ours suggest that diamond growth is not a process that can be characterized by a single rate-controlling step.

Figure 2 shows the scanning electron micrographs of diamond particles synthesized on substrates that were at 250 °C or 700 °C. In the case of 250 °C, diamond particles were octahedron-faceted with only a {111} surface. In the case of 700 °C, diamond particles were cubo-octahedron -faceted with both {100} and {111} surfaces. Temperature-dependent crystallography was studied previously by Spitsyn *et al.* [8]. We observed that as the substrate temperature decreased from 900 °C to 800 °C

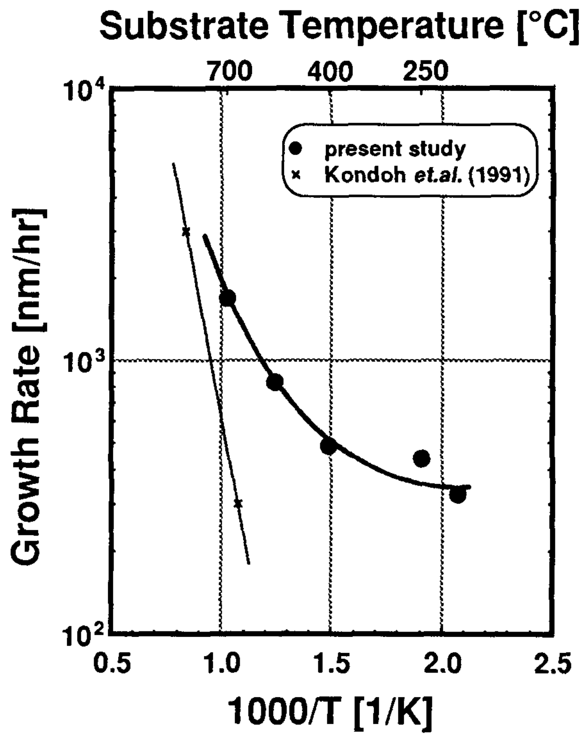
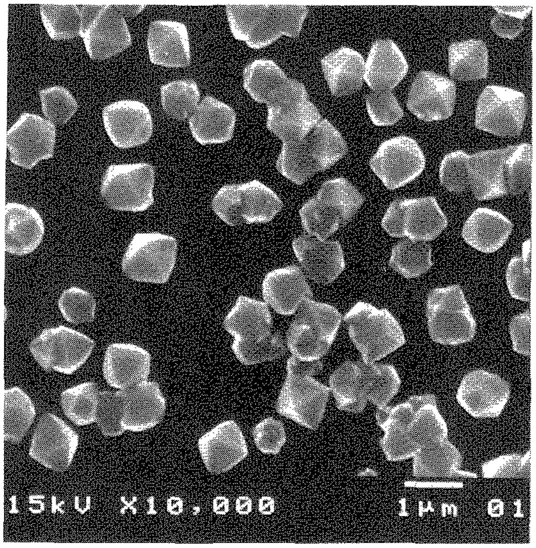
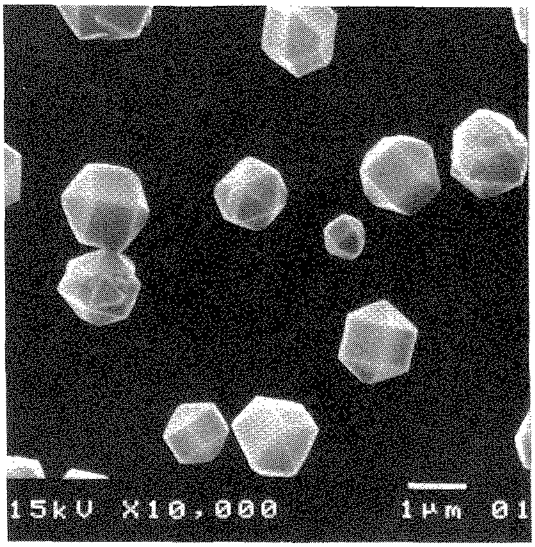


FIG. 1. Temperature dependence of diamond growth rate at substrate temperatures of 210~700 °C (solid circles). The marks of x are the data from Ref. 3.



(a)



(b)

FIG. 2. Scanning electron micrographs of diamond particles synthesized at a low and high substrate temperature, (a) 250 °C, deposition time of 120 minutes, (b) 700 °C, deposition time of 52 minutes, respectively.

or lower, the ratio of the growth rate in the {100} and {111} directions (i.e., $v(100)/v(111)$) increased; consequently, the appearance of the {100} surface gradually decreased. This tendency was more evident at the lower temperatures.

4. DISCUSSION

The mechanism responsible for the weak and non-Arrhenius type of dependency of the growth rate on temperature at low substrate temperatures may be interpreted two ways. One possibility is that the chemical composition adjacent to the substrate surface depends on the substrate temperature. The sticking probability of a chemical species is usually a function of temperature [9-11], which thus makes the surface concentration dependent on temperature. If the concentrations of the gaseous components, for example H, C_2H_2, and CH_3 [12,13], are temperature dependent, then the Arrhenius relationship doesn't hold. Another possibility is the existence of multiple mechanisms of crystal growth characterized by different activation energies. Changes observed experimentally in the crystallography support this possibility. On the other hand, process-dependent temperature dependencies support the former possibility. Further study is now under way to clarify the mechanism involved.

5. CONCLUSIONS

In conclusion, the growth rate for diamonds grown using a HFCVD method was less dependent on the substrate temperature for temperatures ranging from 210 °C to 700 °C. The apparent activation energy, determined from an Arrhenius plot of the substrate temperature versus diamond growth rate, decreased from 5 to 1 kcal/mol with decreasing temperature.

REFERENCES

(1) B. V. Spitsyn, J. Cryst. Growth 99, 1162 (1990).
(2) D. W. Kweon, J. Y. Lee, and D. Kim, J. Appl. Phys. 69, 8329 (1991).
(3) E. Kondoh, T. Ohta, T. Mitomo, and K. Ohtsuka, Appl. Phys. Lett. 59, 488 (1991).
(4) C. J. Chu, R. H. Hauge, J. L. Margrave, and M. P. D'Evelyn, Appl. Phys. Lett. 61, 1393 (1992).
(5) K. A. Snail and C. M. Marks, Appl. Phys. Lett. 60, 3135 (1992).
(6) M. Kamo, T. Ando, Y. Sato, K. Bando, and J. Ishikawa, Diamond and Related Materials 1, 104 (1992).
(7) M. Ihara, H. Maeno, K. Miyamoto, and H. Komiyama, Appl. Phys. Lett. 59, 1473 (1991).
(8) B. V. Spitsyn, L. C. Bouilov, and B. V. Derjuguin, J. Cryst. Growth 52, 219 (1981).
(9) B. J. Wood and H. Wise, J. Phys. Chem. 66, 1049 (1962).
(10) H. J. Kim, Y. Egashira, and H. Komiyama, Appl. Phys. Lett. 59, 2521 (1991).
(11) Y. Shimogaki et al., Extended Abstracts Vol. 93-1, spring meeting, Honolulu, Hawaii, May 16-21, p. 1753 (The Electrochemical Society, Inc., NJ, Pennington, 1993).
(12) F. G. Celli, P. E. Pehrsson, H. T. Wang, and J. E. Butler, Appl.Phys. Lett. 52, 2043 (1988).
(13) S. J. Harris, A. M. Weiner, and T. A. Perry, Appl. Phys. Lett. 53, 1605 (1988).