NUCLEATION PROCESS OF DIAMOND BY PLASMA CVD

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The pre-treatment of substrate surfaces is known to exert a significant influence on the growth of diamond by plasma CVD. The ultrasonic treatment method newly proposed by our group proved to increase the density of nucleation more than 10 times over that of the conventional finger polishing method and to grow diamond particles with uniform sizes below 0.5 μm. This method also made it possible to carry out a quantitative study of the nucleation mechanisms. It turned out that size defects about several tens to hundred angstroms act as very effective nucleation sites. The size of the critical diamond nucleus was estimated to be about 30 Å. It was also found that erosion of substrate surfaces by hydrogen plasma was so great as to hinder the nucleation. This erosion effect should also be taken into consideration in the study of diamond growth.

1. Introduction

Diamond has been attracting great interest in various fields due to its excellent physical, mechanical and electrical properties. In the growth of diamond by chemical vapor deposition (CVD), the inclusion of amorphous carbon had been the greatest problem, until Spitsyn et al.\(^1\) succeeded in selectively etching amorphous carbon during the growth by introducing atomic hydrogen. This idea has since been utilized to develop a variety of improved CVD methods for diamond growth\(^2-5\).

At present, however, there still remain many unsolved problems in the growth mechanisms, among which the nucleation of diamond at the initial growth stage is very important. Its study will give us much useful information about the possibility of growing single crystalline diamond films.

The growth of diamond requires a high degree of carbon supersaturation, which, however, enhances the growth of amorphous carbon. Introduction of a large amount of hydrogen gas suppresses not only the growth of amorphous carbon but also the nucleation of diamond, as well as causing erosion of the substrate surface by radical atomic hydrogen generated in the plasma.

Recently, we have demonstrated that the surface morphology of substrates greatly affected the nucleation of diamond\(^5\). In this paper, we propose a new surface treatment method, “ultrasonic treatment.” This method can introduce very tiny defects in the surface adequate for the nucleation of diamond, and at the same time control the nucleation density quantitatively by the treatment time. Nucleation mechanisms will also be discussed in relation to the defect size and density.

2. Experimental

Figure 1 shows a schematic diagram of the plasma CVD apparatus used for the growth of diamond films. The center part of a reactive quartz tube 3 cm in diameter was placed in a hole made through a microwave guide operated at 2.45 GHz. The substrate was set in the center of the plasma. The substrate temperature was controlled by an auxiliary infrared light via a quartz rod. Methane diluted with hydrogen at carbon concentrations of 0.3–3% was flown at pressures of 400–4000 Pa. The input power of the microwave was 300 W.

The diamond growth was carried out on Si(111) surfaces. Substrate surfaces were damaged by our newly developed ultrasonic treatment method; the substrates were immersed in alcohol containing diamond powder and were subjected to ultrasonic vibration. This method was able to introduce very tiny defects in the substrate surface with controlled densities and sizes.

The powder diameters used in the experiment were 0–1, 5–10, 20–40 and 40–60 μm. Diamond growth was carried out on these damaged substrate surfaces with powder diameter, powder density and treatment time as parameters. For comparison, growth was also carried out on substrate surfaces scratched by the conventional finger polishing method.

3. Results and discussion

According to observations by electron microscopy, the size of defects caused in the substrate surface by finger polishing with diamond paste extended up to several micrometers, whereas those caused by ultrasonic treatment were distributed only below several hundred angstroms. Figure 2 compares scanning electron microscopy (SEM) micrographs of diamond particles grown on these treated substrates. In both cases, the surface treat-

Fig. 2. SEM micrographs of grown diamond particles. Upper: on a finger-polished substrate. Lower: on a substrate subjected to ultrasonic treatment.

ment was carried out with diamond powder with grain sizes of 0–1 μm for 30 minutes. It is found that the ultrasonic treatment shows a decided superiority over finger polishing in terms of nucleation density.

The size of defects, which was dependent on the grain size of diamond powder, proved to affect the density of nucleation. Figure 3 shows the relation between the density of nucleation and the treatment time for various grain sizes of diamond powder (0–1, 5–10, 20–40 and 40–60 μm). In this experiment, 1 gram of diamond powder was dispersed in 20 ml of ethanol and subjected to ultrasonic vibration for 10, 100, or 1000 sec. The

Fig. 3. A relation between the density of nucleation and the ultrasonic treatment time for various grain sizes of diamond powder.
growth was carried out in methane plasma for 10 minutes.

The nucleation density increased slowly with increasing treatment time for the grain sizes of 0–1 and 5–10 μm, whereas it increased more rapidly for 20–40 μm. In contrast, it tended to decrease with treatment time for the grain sizes of 40–60 μm. Figure 4 shows the distribution profiles of the size of the diamond particles grown versus the growth time on substrate surfaces treated with diamond powder with supposedly optimum grain sizes of 20–40 μm. The profile is nearly Gaussian, ranging below 0.5 μm with small deviations. The mean particle size is plotted against the growth time in Fig. 5; it increased with the growth time with a saturation at about 0.3 μm. At the saturation, the nucleation density was about 10 μm⁻³. These results imply that the nucleation occurred first for a short time on the defect sites, and that each nuclei grew uniformly with time until the lateral growth was limited by the neighbouring diamond particles. Because of the small particle sizes and their narrow distribution profiles, the films looked very smooth to the naked eye and exhibited interference colors.

As is seen from the above results, ultrasonic treatment increased the nucleation density more than ten times and yielded increased uniformity in the size of diamond particles compared with the conventional finger polishing method. This result suggests that diamond nucleation is greatly related to the size and the density of defects, and that the optimization of the shape and size of defects is essential to the growth of high-quality diamond films by plasma CVD.

Next, the growth products at the initial growth stages were observed by transmission electron microscopy (TEM). Replicas of the substrate surfaces were prepared after growth times of 30 sec and 120 sec on Si substrate surfaces subjected to 1000 sec ultrasonic treatment. Fig. 6(a) is a TEM micrograph of a replica after 30 sec of growth and (b) after 120 sec of growth. Figure 6(a) shows diamond particles with a density more than 10¹⁰/cm² as well as a number of remaining tiny
is the number of atoms in the nucleus of radius \( r \), \( v \) is the volume per one atom, \( \sigma_f \) is the free surface energy of the diamond, \( \sigma_A \) is the surface energy of the diamond at the contact with the substrate, \( \gamma \) is the contact energy between diamond and substrate, and \( C_f \) and \( C_{AB} \) are the geometrical factors. \( \Delta \mu \) is the change in the chemical potential for the transformation from gas to solid phase and is given by

\[
\Delta \mu = kT \log \left( \frac{p}{p_a} \right),
\]

where \( k \) is the Boltzmann constant, \( T \) is the temperature of the atmosphere, and \( p \) and \( p_a \) are the carbon vapor pressures of the surroundings and at equilibrium, respectively. The radius of the critical nucleus (the critical radius) for the growth of the crystal is obtained from the extreme value of Eq. (1) and is given by the following equation:

\[
r^* = \frac{2\sigma_f}{\Delta \mu}.
\]

According to Spitsyn et al.\(^1\), carbon partial pressure of \( 10^{-6} \) Torr is necessary to grow diamond films at a growth rate of 1 \( \mu \)m/hr, and this corresponds to a supersaturation of \( 10^7 \) for the equilibrium carbon pressure of diamond of \( 10^{-13} \) Torr at 1300°C. Using the (111) surface energy of diamond (3700 erg/cm\(^2\)) and neglecting the contact energy, we obtain a critical radius of about several Å in this case. As the critical radius is a slow function of supersaturation, the above estimation may also approximately hold for our growth conditions. The discrepancy between the above estimation and our experimental results may be ascribed to plasma etching of growing diamond nuclei by atomic hydrogen, as shown in Figs. 6(a) and (b).

Defects artificially introduced in the substrate surface are considered to have the following effects. The surface energy of (111) silicon is 1240 erg/cm\(^2\), which is much smaller than that of diamond. Therefore, diamond tends to grow on silicon as particles after the Volmer-Weber type growth mechanism, as the contact angle is large and the contact area is small. At the same time, these defects may increase the contact energy between the diamond nuclei and substrate surface.

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Fig. 6. TEM micrographs of the replicas of substrate surfaces after growth for (a) 30 sec and (b) 120 sec.

Defects introduced by the ultrasonic treatment. Even diamond particles smaller than 100 Å in size are well-faceted. Note that diamond particles smaller than about 30 Å are not found. For 120 sec growth, the substrate surface became smoother and the diamond particles grew to sizes mostly larger than 100 Å. The density of diamond particles was about \( 10^9 \)/cm\(^2\), one order smaller than for the 30 sec growth time. This reduction may be caused mainly by the strip-off of diamond nuclei generated at an early growth stage by atomic hydrogen radicals, as well as by the extinction of nucleation centers due to erosion of the substrate surface. This result implies that erosion by atomic hydrogen is very detrimental to diamond nucleation. From the observed minimum size of the diamond particles in Fig. 6(a), the critical nucleus for the onset of nucleation is estimated to be about 30 Å in diameter.

The size of the critical nucleus is related to the supersaturation of the carbon gas pressure, the surface energies of diamond and substrate material, and the contact energy. The increment of the free energy due to the formation of a nucleus is given by

\[
\Delta G(r) = -n\Delta \mu + n^{2/3} \left\{ \sum \sigma_f C_f + (\sigma_A - \gamma)C_{AB} \right\},
\]

(1)

Here,

\[
n = \frac{4\pi r^3}{3v}
\]

(2)
lowering the contact angle and then the critical radius. The experimental value of about 15 Å for the critical radius may be determined by the balance between plasma etching and the above defect effects.

For defects to effectively act as nucleation sites, their size and shape should be optimum such that the contact area between diamond nuclei and defects is large. TEM observation of the silicon surface subjected to ultrasonic vibration with diamond powder showed defects about 100 Å or smaller in size. This means that the defect size comparable to the critical radius is optimum for nucleation.

4. Conclusion

In the growth of diamond by plasma CVD, high substrate temperatures and the high surface energy of diamond, as well as the erosive effect of hydrogen radicals make diamond nucleation difficult. A conventional method to enhance the nucleation is to introduce scratches artificially in the surface by finger polishing with diamond paste. However, very few studies have been carried out on the role of these defects and their optimum shape and size. This paper performed SEM and TEM analysis of diamond grown on surfaces treated with our newly proposed ultrasonic method, and gave information on the size of the critical nucleus and the shape and size of defects optimum for nucleation. With this method, a nucleation density more than 10 times that for the conventional polishing method was obtained. Resultant films, composed of very uniform, fine diamond particles with their sizes below 0.5 μm, had very smooth surfaces. The critical nucleus was estimated to be about 30 Å in diameter in this experiment. It was also found that the re-evaporation of many nuclei occurred during the initial stage of nucleation due to erosion by hydrogen radicals. In conclusion, defects which are comparable in shape and size to critical nuclei and can withstand erosion act as very effective nucleation sites, and our ultrasonic treatment method can introduce such defects at high densities, resulting in a high density of diamond nucleation.

REFERENCES