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The mechanical properties of polycrystalline diamond films

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The mechanical properties of polycrystalline diamond films grown by a filament-assisted chemical vapor deposition, with and without dc bias applied between filaments and a substrate, were investigated. The bias application influenced the morphology and the crystallinity of the film. The internal stress turned from a relatively large compressive stress to a tensile one with increasing bias current. The maximum fracture strength measured in a bulge test was 3150MPa. It was revealed that the mechanical properties for the diamond film were strongly affected by the amount of nondiamond carbon component and grain size of the film.

1. INTRODUCTION

With the advent of chemical vapor deposition (CVD) techniques for synthesis of polycrystalline diamond film, there is increasing interest in a variety of applications. For optical applications, the prominent optical transmissive property, not only from ultraviolet to far infrared [1] but also X-ray wavelength region, is applicable to high efficiency optical windows and X-ray lithography masks.[2,3] These applications require a membrane form (a free-standing film partly supported by a substrate) a few microns thick, and the mechanical strength of the membrane is very important. In addition, adequate tensile stress (~10MPa) is necessary in the film to allow fabricating a taut membrane. Although the mechanical properties are assumed to be very sensitive to the microstructure, impurities and defects, few studies have been reported up to now. In this study, polycrystalline diamond films were prepared using a filament-assisted CVD under various experimental conditions. The internal stress, Young's modulus and burst pressure for the diamond films were measured. The relationship between these mechanical properties and the film structures is discussed, especially the grain size and nondiamond carbon content in the films.

2. EXPERIMENTAL

2.1. Diamond growth and characterization

Polycrystalline diamond films were deposited onto 2-inch (100) oriented silicon wafers by the hot filament CVD method. The detailed setup for the apparatus is described in ref.4. The source gas was a mixture of methane and hydrogen. The filament and substrate temperatures were fixed at 2100°C and 850°C, respectively. The morphology and crystallinity were controlled by changing the following parameters: 1) pretreatment diamond powder size; fine (0-1μm), medium (8-16μm) and rough (40-60μm); 2) oxygen addition to the source gas; 0.1%; 3) total gas pressure; 20 or 150 Torr; 4) dc bias application between filaments and a substrate (the substrate was positively biased); 2-25mA/cm^2.

The deposited film quality were

Table 1 CVD diamond film growth conditions

Series	Powder size	CH4[vol%]	Pressure[Torr]	Bias[mA/cm²]	Grain size[μm]
A	fine,medium,rough	1	20	none	1.2—2.5
B	fine	1	150	0-25	0.3—0.6
C	fine	1+O_2 0.1%	20	0-25	0.2—0.8

evaluated by Raman scattering spectroscopy. The integrated Raman spectra intensity ratio diamond at 1332cm^{-1} to amorphous and/or graphitic carbon around 1500cm^{-1} ($I_{dia}/I_{a\text{-}C}$) is assumed to be the index which represents the crystallinity. The surface morphology and average grain size of the diamond film were examined with a scanning electron microscopy (SEM) and an atomic force microscopy (AFM).

2.2. Mechanical properties measurement

The internal stress for a thin film can be calculated from the distortion of a substrate, using the following equation for a circular substrate:[5]

$$\sigma=\frac{Eb^2}{6(1-\nu)Rt} \qquad (1)$$

where E/(1-ν) is biaxial modulus for the substrate, R is the change in radius curvature for the substrate, and b and t are the substrate and film thickness. R was determined by laser reflection technique, calculating the optical interference fringes. According to compressive or tensile stress in the film, a negative and a positive sign are assigned, respectively. The value of Young's modulus for the diamond films was measured with a specially developed apparatus designed for thin films.[6] The values of Poisson's ratio for the diamond films were assumed to be equal to that for single crystal diamond (0.29).[7] A circular-aperture (ϕ15mm) diamond membrane was prepared by partially etching away the silicon substrate using hydrofluoric and nitric 1:1 acid mixture for the bulge test. The setup for the bulge test was as follows. A membrane was rigidly settled on a small chamber and pressure was gradually increased on the sample by input gas (N_2), using a needle valve on the diamond growth surface. Pressure was applied to the membrane until it bursts. The bursting pressure was monitored by a diaphragm pressure gauge. The fracture strength for the membrane was calculated by employing the following equation:[8]

$$M=0.374[E/(1-\nu)]^{1/3}(P_b r/t)^{2/3} \qquad (2)$$

where M is the fracture strength, P_b is the burst pressure, r is the aperture radius (ϕ15mm) and t is the film thickness (1μm).

3. RESULTS AND DISCUSSION

3.3 Structural changes in diamond

Three series, twelve samples were prepared for characterization. They are listed in Table 1. Figure 1 shows a plot of the crystallinity ($I_{dia}/I_{a\text{-}C}$) as a function of grain size. As the pretreatment powder size becomes larger, the grain size increases from 1.2μm to 2.5μm. In this series, every sample is well faceted. The bias current application also influence the grain size and the crystallinity. In series B, the grain size decreases monotonically from 0.6μm to 0.3μm as the bias current

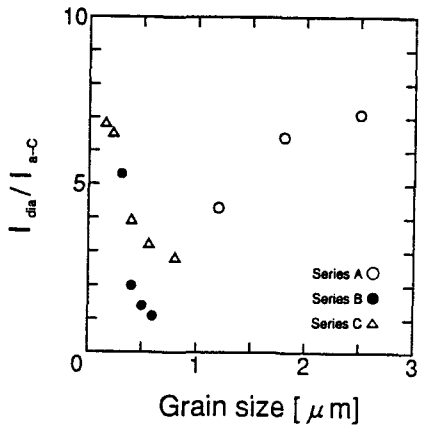

Figure 1. Crystallinity dependence on grain size, as determined from Raman spectra.

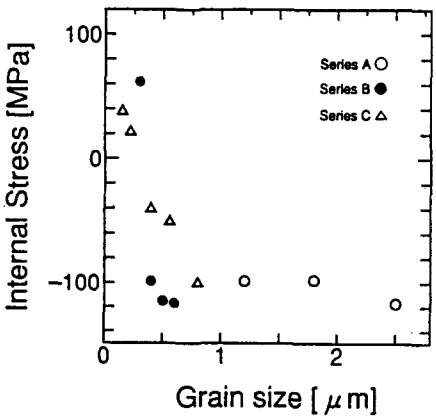

Figure 2. Internal stress variation with grain size.

increases. The nondiamond carbon content gradually decreases with the increase in bias current. Oxygen addition to the source gas is also effective to decrease the nondiamond carbon component. In Fig.1, the crystallinity for series A has a positive relation to the grain size. This phenomenon suggests that the non diamond carbon component, namely, amorphous and/or graphitic carbon, is mainly present in the grain boundaries. However, in the bias application series, B and C, the crystallinity decreases with increasing grain size. Under the biased conditions, the surface of the substrate is exposed to the bombardment electrons and ionic species during diamond film growth. Zhu et al. reported that graphitic carbon can be etched selectively by hydrogen plasma.[9] The variation of B and C can be explained by this hydrogen plasma effect at higher bias voltage.[10]

The internal stress of the diamond film is shown in Fig.2 as a function of grain size. Relatively large compressive stress is observed in most samples. In contrast, the internal stress turned to a tensile stress for the film which has small grain size and relatively high crystallinity. Total internal stress in a thin film is expressed as a sum of thermal stress and intrinsic stress. Thermal stress is caused by the difference in the thermal expansion coefficient between the film and the substrate. The thermal stress for diamond on silicon was estimated as a compressive stress with several hundred MPa in the present deposition conditions. Therefore, a tensile stress observed in the film comes from a large intrinsic tensile stress, surpassing the thermal compressive stress. This can be explained qualitatively by the grain boundaries relaxation model.[11] This model requires a constrained relaxation in a grain boundary during film growth to produce stress. Applying this model to our diamond films, the estimated grain size necessary to compensate for the thermal stress is about 0.2μm. It corresponds roughly to that for the film exhibits tensile character. However, there are the films that show compressive character, though the constrained relaxation effect also be expected with submicron grain sizes. The authors assumed that relatively large content of nondiamond carbon within the films produced compression. Thus, the combined effect of its small grain size and low nondiamond carbon content give tensile stress in a polycrystalline diamond film.

Figure 3 shows the fracture strength calculated using eq.(1) from the experimental data for Young's modulus and the burst

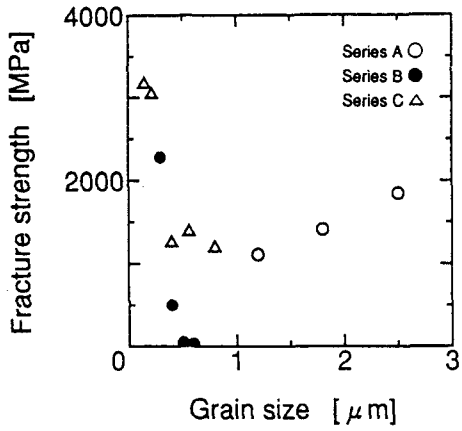

Figure 3. Diamond membrane fracture strength as a function of grain size.

pressure. In series A, the fracture strength increases with increasing the grain size. The one reason for this is that the film consisting of smaller grain size has higher nondiamond carbon content. It is noticeable that the films which exhibit over 2000MPa strength have a tensile character. They have relatively high quality and small grain size at the same time.

Membrane burst is due to the occurrence and propagation of cracks. In the polycrystalline diamond, microscopic cracks would be generated at the grain boundaries, where the nondiamond carbon is localized. From the cross-sectional SEM observation, the film grown without bias application reveals a typical columnar growth structure. On the other hand, the film grown with the biased condition has a microcrystalline structure showing fine agglomerated grains. Assuming that the propagation of cracks occurs mostly along the grain boundaries, the columnar growth structure is considered to be more brittle than the microcrystalline structure, since the microcrystalline structure has a longer crack length before it bursts. At the same time, the content of nondiamond carbon is the fairly important factor in improving the fracture strength of the diamond.

4. CONCLUSION

The mechanical properties of polycrystalline diamond film were investigated as a function of grain size. The maximum fracture strength of 3150MPa was obtained when 25mA/cm^2 bias was applied and oxygen was added to the source gas at the same time. The sample has expected to have potential applicability as a membrane because of its tensile character and sufficiently high mechanical strength for practical use, as demonstrated by the present study. The authors found that smaller grain size and less impurities are necessary in order to achieve a membrane with higher fracture strength. Bias application in the hot-filament CVD method is one effective method of achieving high mechanical strength.

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