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Surface morphology of polycrystalline diamond films etched by Ar^+ beam bombardment

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Polycrystalline diamond films etched by Ar^+ beam bombardment were investigated by scanning electron microscopy and Raman spectroscopy. In an ion sputtering apparatus, an etching rate of 14 $\mu m\ C^{-1}$ was obtained when 10 kV-accelerated Ar^+ ions penetrated with an angle of 15–30° from the normal. A number of cavities were created on the surface treated at low incidence angle. In contrast, micro-prominence was seen under the condition of high incidence angle. The degree of surface roughness on etched films was also changed with the incidence angle of the beam. A relatively smooth surface appeared after the treatment with an incidence angle of $\geqslant 15°$. Raman spectroscopy revealed that the physical etching of diamond is effective in obtaining high quality surface of polycrystalline diamond films.

1. Introduction

In order to realize successful applications of synthetic diamond in micro-electronics and optics, there has been increasing interest in the chemical and/or physical etching of diamond. Among early works using single crystal diamond as a target, several ion etching techniques have been successfully employed to prove that the etching rate of diamond depends on the bombardment conditions. For argon ion beams, Whetten *et al.* [1] reported that an increase in the sputter yield of (1 0 0) single crystal diamond was observed as the angle of incidence was varied from the normal, with a maximum occurring at approximately 60°. This result shows good agreement with the calculated result using the formula proposed by Witcomb [2] who described the energy dependence of the maxima of the sputter yield curves. In addition, they indicated that sputter due to Ar^+ bombardment yield was reduced by more than a factor of 2 along the [1 1 0] channelling direction. In the case of polycrystalline diamond films, since the facets of each crystallite on the film surface are randomly oriented, the etching characteristics may differ from those of single crystal diamond. One of our aims is to describe the change in the surface roughness and the etching rate of the etched polycrystalline diamond films as a function of the angle of Ar^+ incidence.

Several results of reactive ion etching describe oxygen as having an important role in the etching process [3–6]. The etching proceeds through graphitization by ion bombardment, followed by oxidation of the graphitic material [7]. Since the etching rate of non-diamond carbon is faster than that of diamond using the reaction gases involving oxygen [8], a relatively high etching rate is given for diamond. In contrast, Ar^+ bombardment can selectively etch out mechanically weak materials such as graphitic carbon. For instance, Kamata *et al.* [9] suggested that the etching rate of sp^2 bonded graphitic carbon is higher than that of sp^3 structure in the chemical vapour deposition process enhanced by electron cyclotron resonance plasma with CH_4–H_2–Ar gas system. We provided an oxygen free Ar^+ beam to estimate the preferential etching for graphitic materials in the films. In this communication, Raman spectra obtained from the etched and non-etched regions are demonstrated to discuss the effect of Ar^+ bombardment on the etching for non-diamond carbon.

2. Experimental Procedure

Polycrystalline diamond films were synthesized by a combustion flame technique with a gas mixture of C_2H_2 and O_2. The flow rates of O_2 (quoted minimum purity of 99.5%) and C_2H_2 (quoted minimum purity of 98%) were kept constant at 36.5 and 37.2 $mL\ s^{-1}$, respectively. The substrate temperature was measured by an optical pyrometer without any correction for emissivity. Using the flow rate of the cooling water, the temperature of the water cooled stage for the substrate was varied between 1140 and 1500 K. The diamond films deposited on Si single crystal wafer had an average crystal size of 5 μm and the film thickness of 10–20 μm as the result of 0.5–1.5 h deposition. The height change on the film surface reached was 15 μm maximum. Ar^+ ion beam was irradiated on the diamond surface in an ion sputtering apparatus under a total gas pressure of 1×10^{-3} Pa. The distance

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between the ion source and diamond was 280 mm. Using an ion lens, the spot size of the ion beam was varied on the film surface. The incidence angle of the beam was varied from 0–75° from the normal. The surface morphology of the diamond before and after etching was observed by a scanning electron microscope (SEM). SEM was also used to estimate the etching rate through cross-sectional observation for the film. Raman spectroscopy was conducted to determine the quality of the diamond films.

3. Results and discussion

Prior to the etching experiment, the etching rate was defined as

$$S_E = (d_1 - d_2)/q, \qquad (1)$$

where d_1 and d_2 are thickness of the diamond film before and after Ar^+ bombardment at the centre of the irradiated region, and q is the charge of argon ions which bombard the surface of the sample. In the range between 0–10 kV in accelerated voltage, there is a threshold voltage to determine whether the diamond film is etched or not. Under the conditions of the accelerated voltage beyond 6 kV, the etching rate of 10–13 $\mu m\, C^{-1}$, showing slight dependency on the accelerated voltage, was obtained. By varying the lens voltage for a given beam focus and angle of ion incidence, the sputtering area on the diamond film was changed. A minimum area of $3 \times 3\ mm^2$ was obtained at an incidence angle of 0° from the normal with good focus. With an incidence angle of 45°, the ion beam was defocused on the surface. Therefore, etching area was enlarged to approximately $4 \times 6\ mm^2$. This monotonously increases with the incidence angle of the beam. However, the etching rate has no relation with area of the irradiated surface on the film. The dependence of the etching rate of the diamond film on the incidence angle is shown in Fig. 1. At the incidence angles of 15° and 30°, the etching rate reached 14 $\mu m\, C^{-1}$, corresponding to 16 $\mu m\, h^{-1}$.

After the irradiation of 0.1 C- Ar^+ beam at an incidence angle of 0°, the surface of the polycrystalline film received light etching. The crystal edges became gradually blunted. A number of cavities having 2–3 μm in diameter were created on the facets of the diamond. It seems that the etching of diamond proceeds with growth of these cavities on the facets. As indicated in Fig. 2, surface morphology of diamond films irradiated with a charge of 0.5 C were remarkably changed with the Ar^+ incidence angle. On the surface with an incidence angle of 0°, Fig. 2a, there were many cavities having approximately 5 μm in diameter. Degree of surface roughness was essentially unchanged before and after the etching procedure. By increasing the angle, the diameter of the cavities was enlarged and film surface became smooth. The samples as shown in Fig. 2b and c were etched with a relatively high etching rate of 14 $\mu m\, C^{-1}$. Under the conditions of high incidence angle, as shown in Fig. 2d–f, micro-prominence is uniformly distributed over the whole surface irradiated by Ar^+ beam. The direction of beam incidence

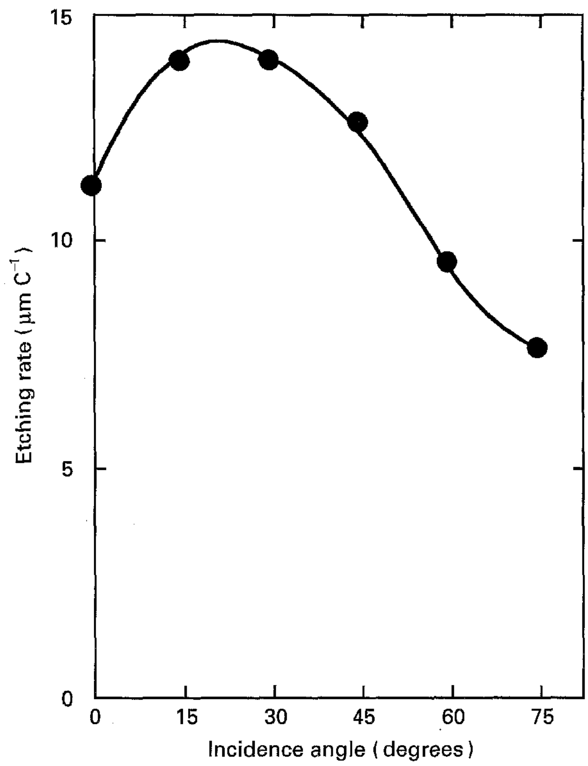

Figure 1 Etching rate of diamond films by Ar^+ bombardment with an accelerated voltage of 10 kV.

corresponds to that of the arrow as indicated in the pictures. The degree of surface roughness is also small on these samples.

In the 1980s, various studies confirmed that the transition from sp^2 hybridized carbon to sp^3-bonded diamond-like carbon occurs when the carbon films are subjected during their growth to bombardment by accelerated ions [10, 11]. Furthermore, Kamata *et al.* [9] suggested that the etching rate of sp^2 hybridized amorphous carbon is higher than that of sp^3 structure in chemical vapour deposition process enhanced by electron cyclotron resonance plasma with CH_4–H_2–Ar gas system. In this system, Ar^+ generated in the plasma strongly attacks the substrate. These reports lead us to the speculation that the Ar^+ bombardment possesses structural selectivity. This introduces preferential etching for graphitic non-diamond materials. As indicated in Fig. 3a, polycrystalline diamond films obtained by the combustion flame method indicated a peak of F_{2g} Raman active mode of typical diamond at 1332 cm^{-1} and a broad peak at $\sim$ 1400 cm^{-1} on the Raman spectrum. The latter one is attributable to the Raman active vibrational mode of sp^2 hybridized, non-crystalline carbon. With the irradiation of 0.5 C- Ar^+ beam, the broad peak became small and shifted toward a high wave number as shown in Fig. 3b. At this condition, diamond film was sputtered 6 μm in depth. This result strongly suggests that the physical etching of diamond is effective to obtain high quality surface polycrystalline diamond films.

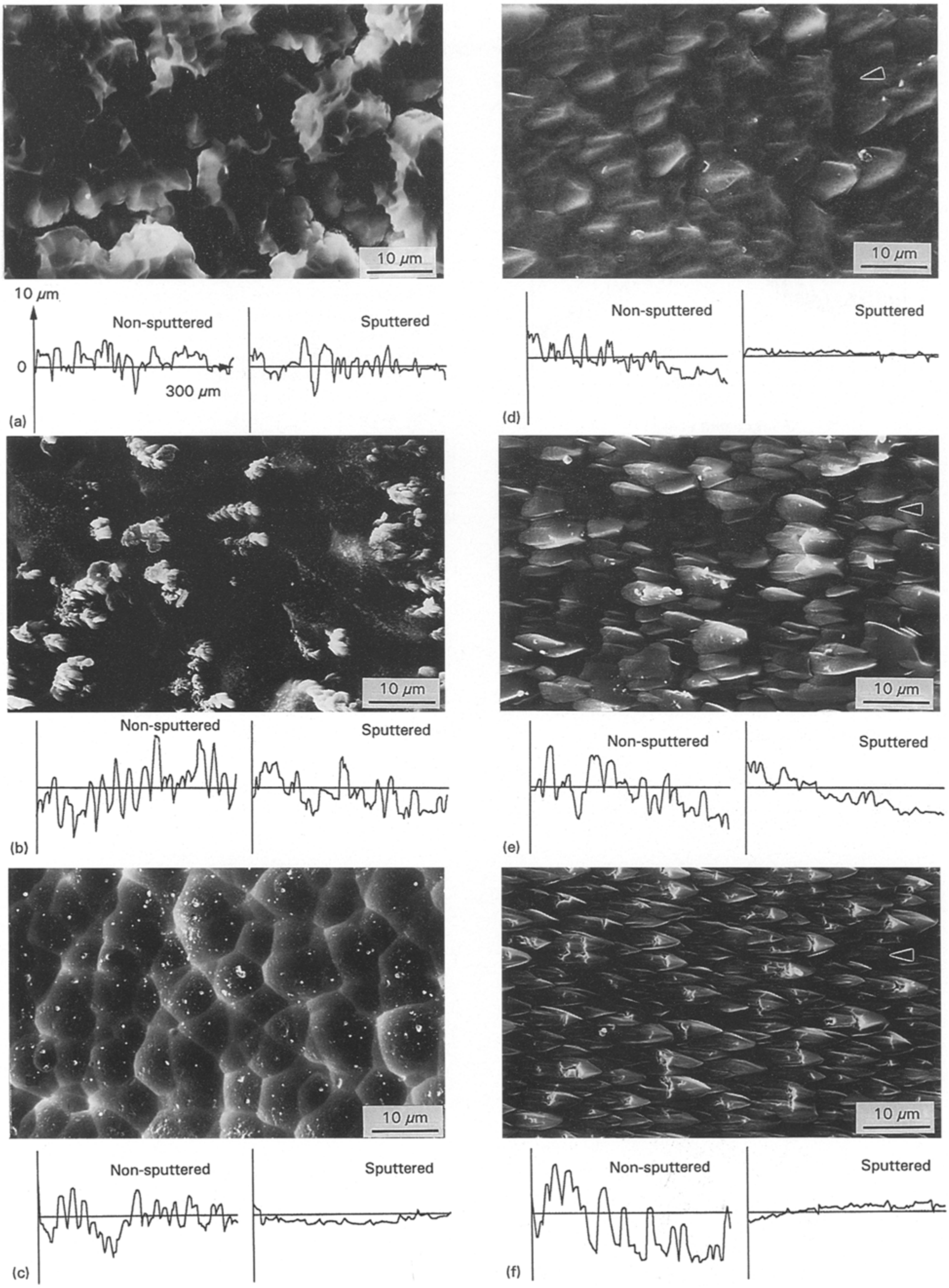

Figure 2 SEM micrographs and one-dimensional surface profile of the diamond films. These were taken as a function of incidence angle from (a) 0° to (f) 75° in 15° steps.

4. Conclusions

Polycrystalline diamond films were physically etched by Ar^+ beam to obtain a smooth surface. The etching rate of the polycrystalline diamond films changes with the incidence angle of Ar^+ beam. The degree of the surface roughness became small with the creation of cavities having approximately 10 μm diameter at an angle of 30°. In addition, the Raman

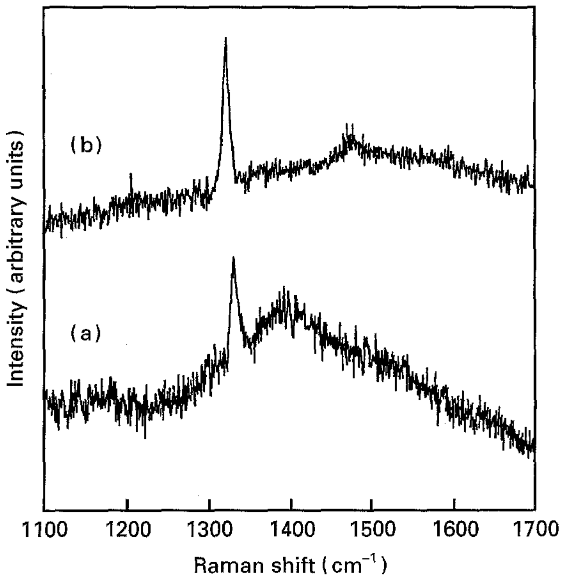

Figure 3 Raman spectra of the diamond film; (a) as-grown and (b) etched.

spectrum suggested that non-diamond carbon on the film surface is preferentially etched by ion bombardment.

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