TEXTURE OF VAPOR DEPOSITED DIAMOND FILMS AS REVEALED BY PLASMA-ETCHING

Chiemi HATA\(^1\), Mutsukazu KAMO\(^2\), and Yoichiro SATO\(^2\)

\(^1\)Hoya Corporation, 3-3-1 Musashino, Akishima, Tokyo 196, Japan
\(^2\)National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

Polycrystalline films were grown on silicon substrates by microwave plasma-assisted vapor deposition from a gaseous mixture of methane and hydrogen for methane concentrations ranging from 0.3% to 5.0%. The films were then subjected to reactive etching in air-plasma under reduced pressure. A variety of etching patterns was observed on the surfaces and cross-sections of the films: films obtained at lower methane concentrations of 0.3% to 0.5%, where well-defined (111) and (100) faces appear, became porous by etching, with pores located mainly at grain boundaries. Films obtained at 3.0% to 4.0%, whose surfaces consisted predominantly of square (100) faces, were found to have typical columnar structures. The intergrain regions of these films were etched away rapidly by the etching and thin rods or needles of single crystalline diamond remained. Films obtained at 5%, in which the crystalline morphology disappears, became highly porous by etching, looking like a spider's web.

1. Introduction

One of the characteristic features of “diamond” grown by chemical vapor deposition is that the structure, texture and morphology of the deposits depend on growth conditions, e.g., carbon content in the gas phase or substrate temperature. The change should be closely related to the growth mechanism in which the relative rate of formation of single and double bonds, as well as the relative growth rates of specific crystalline surfaces, e.g., (111) and (100) depend strongly on gas composition and substrate temperature.\(^{1-4}\)

Detailed characterization of the deposits grown under different conditions is therefore very important in understanding the growth mechanism as well as the properties of the diamond films obtained by chemical vapor deposition. As an effort in this direction, oxidative plasma etching has been employed in this study: vapor deposited diamond films were subjected to reactive etching in air-plasma under reduced pressure. Comparisons of morphology and Raman spectra of etched films with those of as-grown films have been found to be highly informative as to growth and structural features.

2. Experimental

Deposition of diamond was carried out using a gaseous mixture of methane and hydrogen by the microwave plasma-assisted chemical vapor deposition method. The apparatus is shown schematically in Fig. 1. It consists of a silica tube reaction chamber equipped with a sample holder, microwave generator, waveguide, gas feeding system and an evacuation pump.

![Fig. 1. Schematic drawing of the microwave plasma-assisted chemical vapor deposition system.](image-url)
Diamond films were grown on surface-treated silicon wafers under the following conditions:
Gas source: gaseous mixture of CH\textsubscript{4} and H\textsubscript{2}
Methane concentration (CH\textsubscript{4}/CH\textsubscript{4}+H\textsubscript{2}): 0.3–5.0 vol\%
Flow rate: 100 ml/min (STP)
Total gas pressure: 40 Torr
Microwave power: 400 W
Temperature of substrate (measured by an optical pyrometer): 850°C
Duration of deposition: 30–300 Hrs

Reactive etching experiments on the films were done using the same apparatus as that used for deposition under the following conditions:
Etching gas: air or pure oxygen
Flow rate: 100–300 ml/min
Gas pressure: 10–40 Torr
Microwave power: 100–300 W
Duration of etching: 10 min–1 Hr

Both as-grown films and etched films were characterised by scanning electron microscopy (SEM), Raman spectroscopy and density measurement.

A number of natural diamonds of Type Ia and Type IIa as well as synthetic diamond made under high pressure and high temperature using nickel as catalyst have been used as a standard for Raman spectroscopy. The peak position of the Raman line of diamond observed at room temperature with each of these single crystals agreed within ±0.1 cm\textsuperscript{-1}, and was postulated to be at 1332.5 cm\textsuperscript{-1}.\textsuperscript{5)} The peak positions of the vapor deposited samples have been determined in reference to this value.

3. Results and discussions

Characteristic changes in texture and surface morphology were observed with the diamond films obtained at different methane concentrations ranging from 0.3% to 5%. They are divided into four groups in terms of their methane concentrations as follows; A) 0.3–0.5%, B) 1.0–2.5%, C) 3.0–4.0% and D) 5%.

The SEM photographs in Fig. 2 compare the surface morphology of as-grown films obtained under different methane concentrations (CH\textsubscript{4}/CH\textsubscript{4}+H\textsubscript{2}; 0.5, 2.0, 4.0, 5.0 vol%) with those of etched films. Figure 3 shows the cross-sectional views of the same samples as those in Fig. 2.

The film obtained at the lower methane concentration of 0.5% shows surface morphology which is characterized by well-defined crystal habits and frequent appearance of twinning. The grain boundaries are apparent from the morphology observed by SEM. In contrast, its cross-section shows a complicated fracture pattern as shown in Fig. 3, in which grain boundaries are not so apparent as at the surface. The film obtained at 2.0% methane shows that its surface consists of smooth (100) faces and rough (111) faces. Its cross-sectional view is also complicated. The surfaces of the films obtained at higher methane concentrations of 3 to 4% consist predominantly of square or rectangular (100) faces which lie nearly parallel to the substrate surface. Their cross-sections show a typical columnar structure. The film obtained at 5% has an appearance quite different from other films in that both the surface and cross section are smooth, almost entirely lacking in crystalline morphology.

Raman spectra of these films are shown in Fig. 4. It is noted that the Raman bands due to non-diamond structures increase in relative intensity with increasing methane concentration; the broad band around 1500 cm\textsuperscript{-1}, which may be assigned to some disordered structures including double bonds, increases in intensity at higher concentration. In addition, the bands due to highly disordered graphite which appear simultaneously at about 1600 cm\textsuperscript{-1} and 1360 cm\textsuperscript{-1} are predominant at 5%, as shown in Fig. 4. The Raman lines of diamond of as-grown and etched films observed by Raman microprobe are shown in Fig. 5, in which the line width and position are of interest.

The density measured by the sink-float method is shown in Fig. 6. The values of the films prepared at methane concentrations of 0.3% and 0.5% agree with the value of 3.515 g/cm\textsuperscript{3} reported for natural diamond within the experimental scatters, which are shown by the error bars. Density decreases gradually with methane concentration to 4% and then drops sharply to about 3.30 g/cm\textsuperscript{3} (ca. 94% of
the density of natural diamond) at 5%.

It was found that a film obtained at lower methane concentrations is more resistant to oxidative plasma etching than the one obtained at higher concentrations. The etching proved to be particularly useful in revealing the details of texture in cross-section, which is important in understanding how a film grows.

On the surface of the film prepared at a methane concentration of 0.5%, etch pits are found to be concentrated mainly at grain boundaries, penetrating along the boundaries. Smaller etch pits are
found at twin boundaries and also on crystalline faces. In the cross sections, dendritic grains outlined by etch pits are clearly observed. Dendrites are thinner at the substrate side and some of them grow thicker as they go away from the substrate, while others disappear. These etch patterns suggest that grain boundaries are in fact most defective. They also indicate that there are defects in the twin boundaries and that the crystal grain itself is not free from defects.

The Raman line of the film is much broader than that of standard single crystal diamond. The
line width measured as full width at half maximum (FWHM) is 7–8 cm$^{-1}$ for the film while FWHM for the standard is about 2 cm$^{-1}$. The peak position is found to be located at a higher Raman shift by about 1 cm$^{-1}$. After etching, the position goes close to the standard position, while the line width remains much the same.

Similar etch patterns have been observed with the sample prepared at 2%. At the surface, large etch pits are found on (100) faces. The Raman line is broad and slightly shifted. The etching seems to have an unappreciable effect on the Raman line.

Films obtained at methane concentrations of 3 to 4% show (100) preferred orientation and their cross sections show a typical columnar structure. The Raman line of diamond is located at a higher wavenumber than the high pressure synthetic diamond used as standard, with its FWHM of 3 to 4 cm$^{-1}$. After etching, it is found that the intergrain regions were etched away rapidly and thin rods or needles remained. The Raman line of the needles is

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**Fig. 4.** Raman spectra of diamond films deposited under different methane concentrations.

**Fig. 5.** Microprobe Raman spectra of diamond films: As-grown (solid line) and etched (dotted line).

**Fig. 6.** Density of diamond film vs. methane concentration.
the same in peak position and FWHM as that of standard diamond.

Film obtained at 5% has an appearance quite different from other films in that both surface and cross section are smooth, almost entirely lacking in crystalline morphology. The Raman line of diamond is extremely weak and broad band at 1450 to 1550 cm⁻¹ due to disordered structures involving double bonds which became stronger. The etched film appears highly porous, looking like a spider's web.

4. Conclusion

It has been shown that the reactive plasma etching is useful in revealing the details of the texture of vapor-deposited diamond films and in understanding where the defects and graphitic components are, as well as how the films grow.

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REFERENCES