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# Characterization of crystalline quality of diamond films by Raman spectroscopy

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We have measured Raman spectra of diamond films prepared by a hot-filament method and found that diamond layers on Si substrates are under compressive strain. The degree of the strain is found to increase with increasing nondiamond component in the diamond films. It is shown that Raman spectroscopy is a powerful method to estimate the crystalline quality, especially the strain in the diamond films.

Diamond films have been prepared by several methods such as the glow discharge, plasma chemical vapor deposition, and hot-filament methods.<sup>1-6</sup> Diamond films have a number of excellent properties, viz., hardness, chemical inertness, optical transparency, and thermal conductivity. They are expected to have applications as heat sink of electronic devices, protective films, and transistors operating at high temperature. However, the diamond films grow epitaxially only on diamond substrates and not on other kinds of substrates for a variety of reasons such as strain in the films and formation of  $sp^2$  carbons, etc.

Raman spectroscopy is a powerful tool in characterizing carbon materials. For example, a single peak is observed at  $1333\text{ cm}^{-1}$  (Refs. 5 and 7) for diamond and at  $1581\text{ cm}^{-1}$  for graphite.<sup>8</sup> In glassy carbon and pyrolytic graphite which consist of amorphous  $sp^2$  structures, two broadbands are observed at 1360 and  $1590\text{ cm}^{-1}$ .<sup>9</sup> An asymmetric broadband is observed at around  $1530\text{ cm}^{-1}$  in diamond-like amorphous carbon (*a-C*) films.<sup>10-12</sup> Raman spectra of diamond films have been measured by a few authors.<sup>4-6</sup> So far, Raman spectroscopy has been used to confirm the existence of diamond structure in the films but has not been used to estimate the crystalline quality of diamond in the films. In this letter we focus on crystalline quality, especially stress estimations in the diamond films using Raman spectroscopy.

The diamond films were prepared by a hot-filament method,<sup>6</sup> depositing carbon on a silicon substrate from a mixture of ethanol and  $\text{H}_2$ . A tungsten filament was placed  $\sim 10\text{ mm}$  above the substrate and electrically heated to  $\sim 2300^\circ\text{C}$ . The quartz tube reaction chamber was placed in an electric furnace and heated to  $800^\circ\text{C}$ . The total pressure was kept at  $\sim 80\text{ Torr}$ . Four kinds of samples were prepared by changing the ethanol concentration from 0.1 to 0.5%. A scanning electron microscopy (SEM) image of the surface of sample A is shown in Fig. 1.

Raman spectra were measured at room temperature with 4579 and 5145 Å lines of an argon ion laser and a 6471 Å line of a krypton ion laser. The Raman spectra were recorded with a Jobin-Yvon-Ramanor U-1000 double monochromator equipped with a photomultiplier and photon-counting electronics. Raman spectra were measured in a  $90^\circ$  scattering geometry and recorded at relatively low power  $\sim 50\text{ mW}$  on the samples. The spectral slit width is  $\sim 8\text{ cm}^{-1}$

and  $3\text{ cm}^{-1}$  for low- and high-resolution measurements, respectively.

Figure 2 shows Raman spectra of the diamond film deposited on a silicon substrate excited at various wavelengths. A sharp line of diamond at  $\sim 1333\text{ cm}^{-1}$  and an asymmetric broadband centered at  $\sim 1530\text{ cm}^{-1}$  are observed in the spectra excited by the 5145 Å line. The spectral profile of the diamond film coincides well with that of *a-C* films except for the sharp line of diamond.<sup>10-12</sup> The position of the sharp line of diamond does not depend on the excitation wavelength, whereas that of the asymmetric broadband shifts to the lower frequency side with an increase of the excitation wavelength. The spectral variation of the diamond film with the excitation wavelength agrees well with that of *a-C* films. In a previous paper,<sup>10-12</sup> we suggested that the Raman spectral

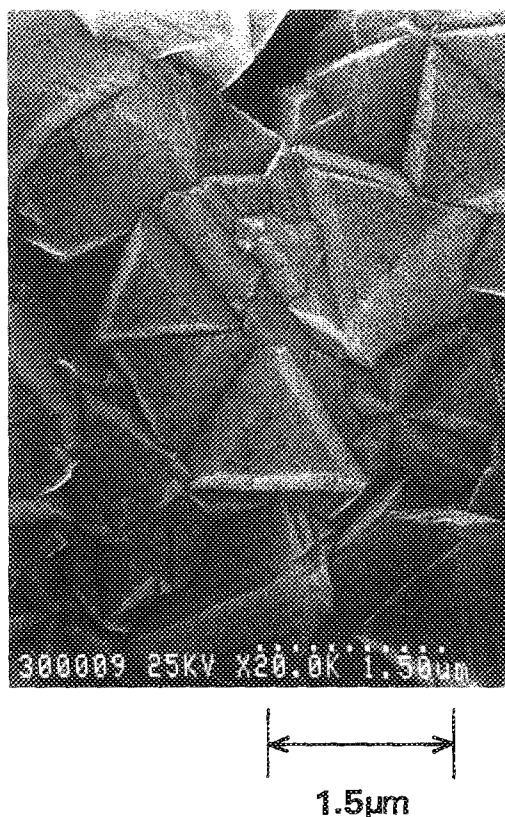


FIG. 1. SEM photograph of sample A (the ethanol concentration 0.1%).

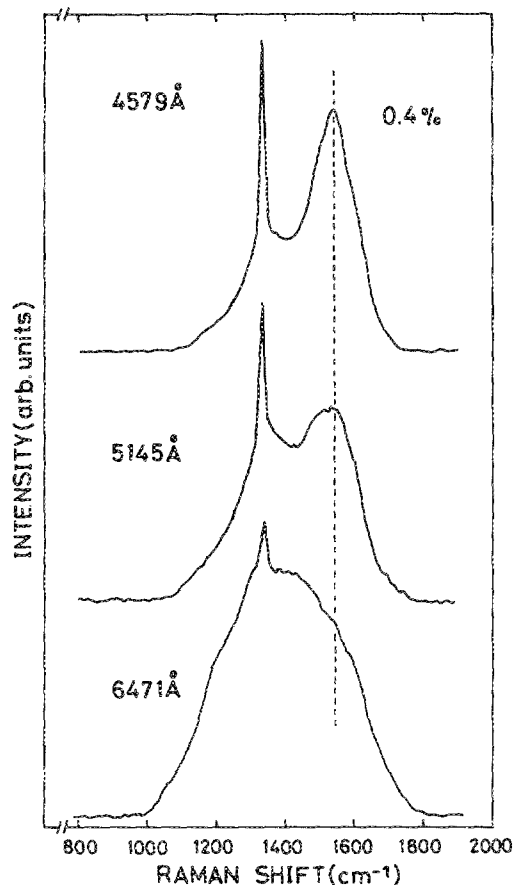


FIG. 2. Raman spectra of the diamond film obtained by various excitation wavelengths. The Raman spectra of sample *D* (the ethanol concentration 0.4%) were corrected by subtracting the background due to the luminescence.

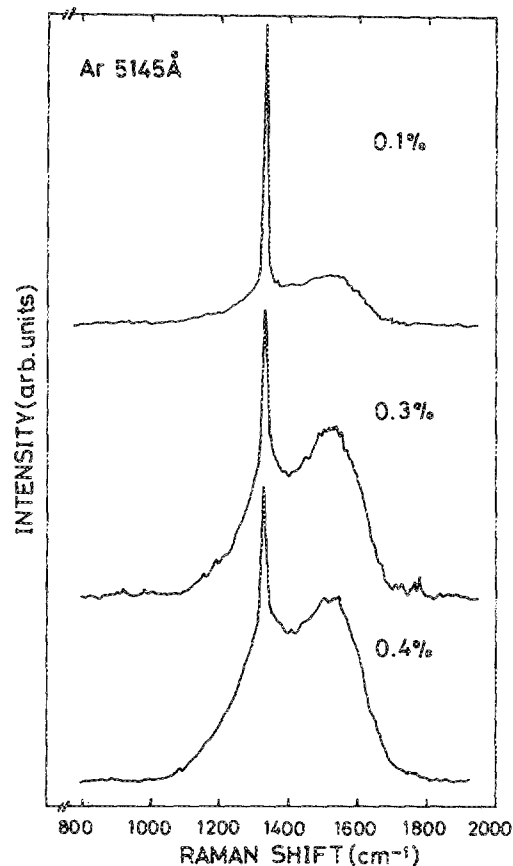


FIG. 3. Raman spectra of samples *A* (the ethanol concentration 0.1%), *C* (0.3%), and *D* (0.4%) excited at 5145 Å line. The Raman spectra were corrected by subtracting the background due to the luminescence.

variation of *a*-C films was interpreted in terms of the  $\pi$ - $\pi^*$  resonant Raman scattering from  $\pi$ -bonded ( $sp^2$ ) carbon clusters with various sizes. The comparison of the Raman spectra of the diamond film with *a*-C films confirms that the asymmetric broadband at  $\sim 1530 \text{ cm}^{-1}$  in the diamond film originates from  $sp^2$  carbon clusters with various sizes. Raman spectra of the diamond films prepared by changing the ethanol concentration are shown in Fig. 3. As seen in Fig. 3, the intensity of the asymmetric broadband assigned to  $sp^2$  carbon clusters relative to that of the sharp line of diamond tends to increase with the increase of the ethanol concentration.

Figure 4 shows high-resolution Raman spectra of diamond in the diamond films. A Raman line of natural diamond is given in Fig. 4 for comparison. The Raman spectra were fitted with a Lorentzian line shape. The peak frequencies and linewidths obtained by the Lorentzian fit to the data and the peak frequency shifts were listed in Table I. The relative intensity, that is, the integrated intensity of the sharp line of diamond normalized by that of  $1530 \text{ cm}^{-1}$  band, is also shown in Table I. The measurements were repeated twice for each sample and the average values are summarized in Table I. As seen in Fig. 4 and Table I, the Raman line of diamond in the diamond films shifts to a higher frequency by  $1\text{--}3 \text{ cm}^{-1}$  compared to that of natural diamond. Furthermore, the linewidth of the Raman line is significantly larger

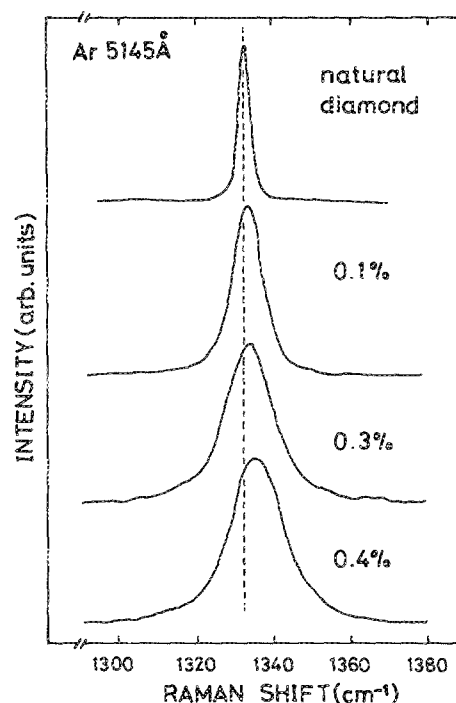


FIG. 4. Raman spectra of diamond for samples *A*, *C*, *D* and the natural diamond excited at the 5145 Å line. The Raman spectra were measured with high resolution and corrected by subtracting the background due to the luminescence.

TABLE I. Peak frequencies, linewidths, and the peak frequency shifts of the Raman lines of diamond, and the relative intensities for various samples. The peak frequency shift indicates the changes in frequency from that of the natural diamond. The linewidth designates the full width at half maximum of the spectrum. The relative intensity reveals the integrated intensity of the Raman line of diamond against that of the asymmetric broadband.

Sample	Ethanol (%)	Peak frequency (cm <sup>-1</sup> )	Peak Linewidth (cm <sup>-1</sup> )	Peak frequency shift (cm <sup>-1</sup> )	Relative intensity
A	0.1	1333.5	8.5	+0.8	0.39
B	0.5	1333.9	13.0	+1.2	0.01
C	0.3	1334.2	13.5	+1.5	0.06
D	0.4	1335.4	14.9	+2.7	0.03
Natural diamond	...	1332.7	3.3	+0	...

than that for natural diamond. It indicates that the crystal-line quality of the diamond films is not as good as that of the natural diamond.

A Raman line of silicon shifts to higher and lower frequency under compressive and tensile stresses, respectively, in silicon films.<sup>13</sup> The degree of stress is estimated by measuring the peak frequency shift. It has also been reported that Raman lines of diamond shift to higher frequency with the increase of a compressive stress.<sup>14</sup> Referring to the above results, the peak frequency shift of the Raman line of diamond here indicates the presence of compressive stress. The lattice constant is 3.567 Å in diamond and 5.430 Å in silicon. If a diamond film is deposited on the silicon substrate, it is expected that the lattice constant expands in the diamond layers and contracts in the silicon layers because of the lattice mismatch. Consequently, the diamond film on the silicon substrates should be under a tensile stress. Hence, the compressive stress in our diamond films cannot be explained by the mismatch of the lattice constants.

In Table I the relative intensity, which designates the ratio of the content of diamond against that of nondiamond, tends to decrease with an increase in the degree of stress. This tendency suggests that the formation of nondiamond is closely related to the strain of the diamond structures. A formation of *sp*<sup>2</sup> carbon clusters might cause the strain of diamond structures and vice versa.

For uniaxial stress parallel to either the <100> or <111> directions the *k* ≠ 0 triply degenerate optical phonon in diamond-type materials is split into a doublet and a singlet.<sup>13,14</sup> From the selection rule, only the singlet can be observed in backscattering geometry. The frequency of the singlet is given by

$$\nu_s = \nu_0 + 2\nu_H - (2/3)\nu_U, \quad (1)$$

where

$$\begin{aligned} \nu_H &= (p + 2q)(s_{11} + 2s_{12})X/6\nu_0, \\ \nu_U &= (p - q)(s_{11} - s_{12})X/2\nu_0 \quad \text{for } \langle 100 \rangle \\ &= rs_{44}X/8\nu_0 \quad \text{for } \langle 111 \rangle; \end{aligned} \quad (2)$$

*s*<sub>11</sub>, *s*<sub>12</sub>, and *s*<sub>44</sub> are the elastic compliance constants, *X* is the strength of the stress, and *p*, *q*, and *r* are the changes in the

spring constant due to the strain. The peak frequency shift  $\Delta\nu_s = \nu_s - \nu_0$  is linear to the stress *X*. Using the values of *s*<sub>11</sub>, *s*<sub>12</sub>, *s*<sub>44</sub> and *p*, *q*, *r* taken from Refs. 15 and 16, that is,

$$\begin{aligned} s_{11} &= 9.524 \times 10^{-14} \text{ cm}^2/\text{dyn} \quad p = -1.071 \times 10^{28} \text{ s}^{-2}, \\ s_{12} &= -0.9913 \times 10^{-14} \text{ cm}^2/\text{dyn} \quad q = -5.260 \times 10^{28} \text{ s}^{-2}, \\ s_{44} &= 1.736 \times 10^{-13} \text{ cm}^2/\text{dyn} \quad r = -7.707 \times 10^{28} \text{ s}^{-2}. \end{aligned}$$

The following equation is obtained:

$$\begin{aligned} X(\text{dyn/cm}^2) &= -1.08 \times 10^{10} \Delta\nu_s (\text{cm}^{-1}) \quad \text{for } \langle 100 \rangle \\ &\quad -2.63 \times 10^{10} \Delta\nu_s (\text{cm}^{-1}) \quad \text{for } \langle 111 \rangle. \quad (3) \end{aligned}$$

We measured the Raman line of diamond in a 90° scattering geometry because of the weak intensity of the Raman line and surface roughness of the films. Although the singlet and doublet are generally observed in this geometry, the coefficient for the doublet is not appreciably different from that for the singlet in Eq. (3). In addition, our films are polycrystalline and Eq. (3) cannot be directly applied. However, we can roughly estimate that the value of compressive stress for our samples is the order of 10<sup>10</sup> dyn/cm<sup>2</sup> and that the corresponding strain is *e* = 0.1–0.2% using the relation *e* = (*s*<sub>11</sub> + *s*<sub>12</sub>)*X*.

The lattice constants of the films were determined by the x-ray diffraction method. The values obtained range from 3.562 to 3.566 Å. Although the recognized difference among the lattice constants of the films could not be found, the peak frequency of the Raman line of diamond varies remarkably with the samples. This indicates that Raman scattering is a sensitive technique for the study of crystalline quality, especially strain fields of the diamond films.

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