

RAMAN SPECTRA OF DIAMONDLIKE AMORPHOUS CARBON FILMS

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Raman spectra of diamondlike amorphous carbon (a-C) films prepared by the plasma CVD method have been measured. From a comparison between Raman and infrared absorption spectra, the relative intensity of Raman bands is found to decrease with an increase of sp^3 content in a-C films. It is confirmed that the relative intensity can be used as a parameter for sp^3 content. It is suggested that a-C films prepared by the plasma CVD method contain more polyene structures than those prepared by the sputtering method.

1. Introduction

Diamondlike amorphous carbon (a-C) films show a number of interesting properties such as great hardness, electrical insulation, chemical inertness and infrared transparency. A number of analytical techniques have been employed to characterize the microstructure of a-C films including Raman spectroscopy¹⁾⁻³⁾, infrared spectroscopy (IR)⁴⁾, electron energy loss spectroscopy (EELS)⁵⁾ and other optical measurements^{6),7)}, and a-C films are confirmed to consist of a mixture of tetrahedral (sp^3) and trigonal (sp^2) bonding structures.

We have measured Raman spectra of a-C films prepared by plasma CVD and sputtering methods. A relatively sharper Raman band at around 1530 cm^{-1} and a broad shoulder band at around 1400 cm^{-1} were observed in the spectra of a-C films. In a previous paper^{1),2)}, we demonstrated that the spectra of a-C films could be well resolved to two bands with Gaussian line shapes, and proposed that these bands originated from carbon clusters with an sp^2 configuration from a comparison between the spectra of sp^3 - and sp^2 -bonded materials. Furthermore, it was found that the Raman spectral profiles varied in excitation wavelength depending on the electronic absorption spectra associated with π - π^* electronic transitions. The spectral variation was interpreted in terms of π - π^* resonant Raman scattering from aromatic rings of various sizes^{1),2)}.

It is reported that hydrogenation introduces

many sp^3 sites into a-C films and that the sp^3/sp^2 bonding ratio varies with the hydrogen content in a-C films. In a previous paper³⁾, we have measured the Raman spectra of several samples prepared by changing the hydrogen gas content in the sputtering atmosphere. The relative intensity of Raman bands was found to decrease with increases of the optical gap and decreases of the refractive index. It was suggested that the relative intensity could be used as a parameter for sp^3 content in a-C films³⁾.

In this work, we will measure the infrared absorption spectra from which the sp^3/sp^2 bonding ratio of a-C films is estimated and try to elucidate the relation between the sp^3 content of a-C films and Raman spectral profiles.

2. Experimental

a-C films were deposited on silicon substrates held at 120°C . Mixtures of C_2H_4 and H_2 were used. Two types of samples were obtained by changing the gas ratio (A: $\text{C}_2\text{H}_4/\text{H}_2=1/0$, B: $\text{C}_2\text{H}_4/\text{H}_2=1/50$). The total pressure was kept at about 1 Torr.

The Raman spectra were measured at room temperature with the 5145 \AA line of an argon ion laser. The Raman spectra were recorded by a Jobin Yvon Ramanor U-1000 double monochromator equipped with a photomultiplier and photon-counting electronics. The Raman spectra were measured in a backscattering geometry and recorded with a laser power of 40–60 mW.

The absorption spectra were measured from a-C films deposited on glass substrates. The optical gap was estimated as 1.0 eV. The refractive index and thickness of a-C films were determined by ellipsometry. The refractive index of samples A and B was about 2.1–2.3 at 6328 Å. The thickness of samples was about 1000–2000 Å.

3. Results and discussion

Figures 1(a) and (b) show the Raman spectra of a-C films prepared by the plasma CVD method. A relatively sharper Raman band at around 1530 cm^{-1} and a broad shoulder band at around 1400 cm^{-1} are observed in the spectra of a-C films prepared by the sputtering method. In a previous paper^{2),3)}, we have suggested that the Raman bands at around 1400 and 1530 cm^{-1} originate mainly from aromatic rings of large and small sizes, respectively. In addition, a weak shoulder band was observed at about 1200 cm^{-1} in the spectra of a-C films prepared by the plasma CVD method. Raman spectra of a-C films can be decomposed into two bands with Gaussian line shapes; a typical result of the

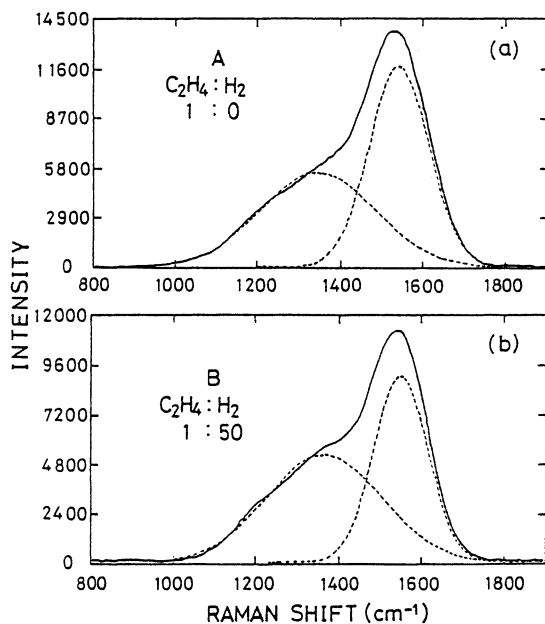


Fig. 1. Raman spectra of a-C films. Figures 1(a) and (b) show the Raman spectra of sample A ($\text{C}_2\text{H}_4/\text{H}_2=1/0$) and sample B ($\text{C}_2\text{H}_4/\text{H}_2=1/50$), respectively. The decomposed bands are also shown in Figs. 1(a) and (b) as broken lines.

lineshape analysis for samples A and B is also shown in Fig. 1. The relative intensity of the 1400 cm^{-1} band against the 1530 cm^{-1} one for samples A and B is 0.9 and 1.2, respectively.

Figure 2 shows the absorption spectra of a-C films for samples A and B. The C-H stretching absorption bands due to hydrogens bonded to sp^2 and sp^3 carbons ($\text{C}_{\text{sp}^2}\text{-H}$ and $\text{C}_{\text{sp}^3}\text{-H}$ bands) are observed at around 3000 and 2900 cm^{-1} , respectively. Absorption spectra are resolved to six bands with Gaussian line shapes. From the relative intensity between the $\text{C}_{\text{sp}^3}\text{-H}$ and $\text{C}_{\text{sp}^2}\text{-H}$ bands, we estimate that 72% and 69% of the carbon atoms are sp^3 bonded for samples A and B, respectively.

Combining the results of the Raman and IR measurements, the decrease of the relative intensity of Raman bands is considered to be caused by the increase of sp^3 content in a-C films. The relative intensity of the 1400 cm^{-1} band against 1530 cm^{-1} one can be used as a parameter for sp^3

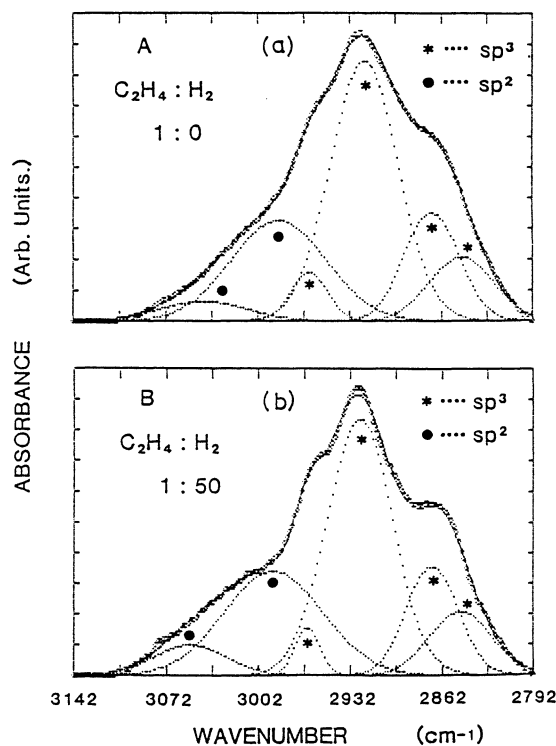


Fig. 2. Absorption spectra of a-C films. Figures 2(a) and (b) show the absorption spectra of samples A and B, respectively. The open circles are experimental data points. The decomposed bands are shown in Figs. 2(a) and (b) as broken lines.

content. The decrease of the intensity of the 1400 cm^{-1} band may suggest that the sp^2 carbon clusters with large sizes are converted into sp^3 structures.

The agreement between the observed Raman spectra and calculated lines for a-C films prepared by the plasma CVD method is not better than that for ones prepared by the sputtering method, because an additional shoulder band is observed at about 1200 cm^{-1} in the former films. The intensity of the additional shoulder band for sample B is stronger than that for sample A. The ν_3 mode for transpolyacetylene is observed at about 1170 cm^{-1} in the spectra excited by the 5145 \AA line⁸⁾, whereas a broad Raman band for amorphous diamond is expected to be observed at around 1200 cm^{-1} from the calculation of the density of states¹⁾. Referring to the results that the sp^2/sp^3 bonding ratio for sample B is larger than that for sample A and that the Raman scattering cross-section of diamond is much lower than that of sp^2 bonded materials⁹⁾, the shoulder band at about 1170 cm^{-1} is considered to originate from polyene structures such as poly-

acetylene rather than amorphous diamond. Based on this assignment, we conclude that a-C films prepared by the plasma CVD method contain more polyene structures than those prepared by the sputtering method.

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