Effect of residual stress on the Raman-spectrum analysis of tetrahedral amorphous carbon films

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Tetrahedral amorphous carbon (ta-C) films deposited by the filtered vacuum arc process have large compressive residual growth stresses that depend on the atomic-bond structure. We observed that the G peak of the Raman spectrum shifts to higher frequency by $4.1\pm0.5\,\mathrm{cm}^{-1}$/GPa due to the residual compressive stress. This value agrees well with the calculated Raman-peak shift of the graphite plane due to applied stress. By considering the effect of residual stress on the G-peak position, we also observe a similar dependence between the G-peak position and the atomic-bond structure in both ta-C and hydrogenated amorphous carbon (a-C:H) films; namely, that a higher sp^2 bond content shifts the G-peak position to higher frequency. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1343840]

Raman spectroscopy is a relatively simple and nondestructive analysis tool to characterize the structural change of carbon materials. It has therefore been widely used to analyze the structural variation in amorphous carbon materials such as hydrogenated amorphous carbon (a-C:H), or tetrahedral amorphous carbon (ta-C) films, as well as diamond or graphite.[1–3] The Raman-spectrum analysis of amorphous carbon films includes deconvolution of the spectrum with two Gaussian peaks: the G and D peaks. It is well known that the G peak originates from E_{2g} phonons among the zone center modes of graphite sheet.[4] On the other hand, the D-peak intensity is closely related to the sp^2 cluster size, although there is still some controversy regarding the exact origin of the D peak.[5]

The atomic-bond structure of the carbon film can be deduced from the intensity ratio, the full width at half maximum (FWHM) values, or the position of each peak. In a-C:H films, for example, it has been shown empirically that the G-peak position shifts to a higher wave number as the graphitic component in the film increases.[6] However, in ta-C films, a consistent relationship between the G-peak position and the atomic-bond structure has not been observed. For example, Tamor and Vassell reported that the G-peak position of ta-C film shifted to a lower wave number as the graphitic component increased.[7] Assuming that the origin of the G peak is the same in both ta-C and a-C:H films, this inverse behavior is hard to understand. It was argued that the reason for this difference in behavior is that the Raman peak for ta-C film is much lower in intensity and more symmetric than that of a-C:H films due to a higher sp^3 hybridization fraction. Thus, the deconvolution can induce a larger error for ta-C films. Other methods were therefore suggested to determine the atomic-bond structure of ta-C films.[2,8,9] However, the inconsistency in the change in the G-peak position still remains to be resolved.

In the present work, we investigate the residual stress effect on the G-peak position. As reported for diamond and graphite,[10,11] residual stress in the carbon materials changes the lattice spring constants, which can in turn change the Raman-peak position. The residual stress for ta-C films is at least three times larger than that of a-C:H films. Hence, residual stress can significantly influence the Raman spectrum of ta-C films. Ager *et al.* showed that the residual compressive stress of ta-C film shifted the Raman peak in carbon to a higher wave number by 1.9 cm^{-1}/GPa.[12] However, the result was not sufficiently quantitative to clarify the inconsistency in the change in the G-peak position for ta-C and a-C:H films. Furthermore, their result was obtained from a carbon Raman peak that had not been deconvoluted. Hence, the result cannot be simply related to the G-peak position, so it is not easy to compare the stress-induced peak shift with theoretical predictions for the graphite plane.[12] In the present work, we show that the inconsistency comes from the high residual compressive stress of ta-C films, by comparing the G-peak position between stressed and stress-relieved ta-C films.

Using energetic condensation of carbon ions from a filtered vacuum arc plasma, 100-nm-thick ta-C films were deposited on 510-μm-thick Si(100) wafers. Details of the deposition equipment have been described elsewhere.[13] During the deposition, a dc bias voltage ranging from 0 to -500 V was applied to obtain films with various atomic-bond structures. In order to measure the residual stress of the film, a 100 ± 5-μm-thick Si(100) wafer was also used as the substrate. The residual stress of the film was obtained from the curvature of film/substrate composite using the Stoney equation.[14] Nanoindentation, low energy EELS, and RBS were employed to characterize the mechanical properties and atomic-bond structures of the films. Raman spectra of stressed film were obtained from a-C film adhered to a Si wafer. A Jobin Yvon T64000 triple-Raman spectroscope was used to collect the Raman spectra. The spatial resolution was

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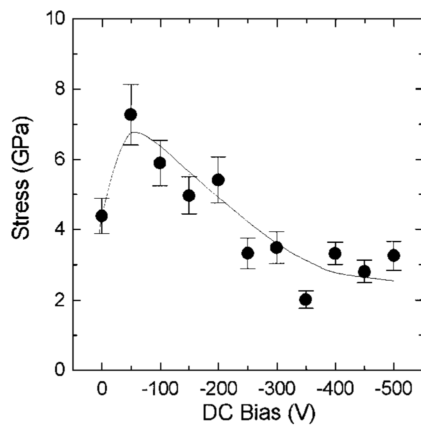

FIG. 1. Residual stress of ta-C film as a function of applied negative bias voltage during film deposition. The line in the figure is not a fitted curve, but is included only to guide the eye.

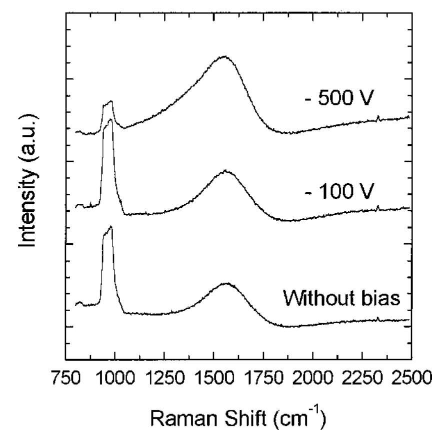

FIG. 2. Raman spectra of ta-C films for various negative bias voltages. The spectra were normalized to the film thickness and shifted upward for ease of comparison.

1 μm and the spectral resolution 1 cm^{-1}. The spectra were obtained in the range of 450–2000 cm^{-1}. An Ar ion laser of 514.5 nm wavelength was used to induce the Raman spectrum.

The Raman spectrum of the stress-relieved ta-C film was obtained from a ''freehang'' ta-C sample prepared by a Si etching technique using HF and HNO_3 solutions.[15] This etching process relieves the residual stress of the film by removing the mechanical constraint of the Si substrate. By using this etching technique, the edge of the sample was restored to its unstressed length, which had a periodic sinusoidal shape.[15] The etching depth was greater than 30 μm, which would adequately relieve the residual stress of the film. The Raman spectrum was obtained at distances larger than 30 μm from the etch front of the Si substrate. In order to avoid thermal degradation of the film, the laser power on the surface and the collection time were limited to 2 mW and 4 min, respectively. After each measurement, the ta-C film was examined under an optical microscope, and then another Raman spectrum was observed at the same site, to check for thermal degradation. Degradation was not observed in the present experimental conditions.

Figure 1 shows the dependence of the residual stress of the film on the applied negative bias voltage. The residual compressive stress increased from 4 to 7 GPa as the negative bias voltage was increased from 0 to 100 V. However, the residual stress decreased when the negative bias voltage was higher than 100 V. At a negative bias voltage of 500 V, the residual stress had decreased to about 3 GPa. Hardness, measured by nanoindentation, and mass density obtained from the RBS spectrum showed the same dependence on the negative bias voltage. Values of maximum hardness of 65 ± 5 GPa and density of 3.5 ± 0.4 g/cm^3 were observed when the negative bias voltage was about 100 V.

Figure 2 shows the Raman spectra of the stressed ta-C films. Because of the higher sp^3 content in ta-C films, the Raman peak for carbon in ta-C films is generally much smaller than that from a-C:H films. Furthermore, the D-peak shoulder is much weaker in ta-C films, resulting in a more symmetric carbon Raman peak. The peak at 960 cm^{-1} is the second-order peak of the Si substrate. Hence, the intensity of the Si peak is a measure of the optical transparency of the film. Figure 2 shows that the film deposited at 500 V has a smaller Si secondary peak and a higher carbon peak than for film deposited at 100 V. This result shows that the higher negative bias voltage (>100 V) increased the content of sp^2 bonds. Hence, the decrease in residual stress, hardness, and density for negative bias voltages higher than 100 V (Fig. 1) is mainly due to an increase in the sp^2 content. This relationship could also be confirmed by low-energy EELS spectra, where the intensity of the π-plasmon loss peak at about 7 eV increased with increasing negative bias voltage for bias voltages greater than 100 V. This behavior as a function of negative bias voltage agrees well with previous reports.[16,17]

The results of Figs. 1 and 2 show that the residual compressive stress is proportional to the content of sp^3 bonds in the film. Therefore, the Raman-spectrum analysis result will be presented in terms of the residual stress of the film. Figure 3 shows typical results of Raman spectra from stressed and unstressed films deposited at a negative bias voltage of 50 V. In the Raman spectrum of stressed film, the Si secondary peak between 900 and 1050 cm^{-1} was excluded from the fitting process. As can be seen from the symmetric shape of the carbon Raman peak, the spectrum was deconvoluted into a broad D peak and a sharp G peak. The broad D peak seems to represent a higher degree of disorder in sp^2 domain boundaries. Consequently, there were relatively large errors in determining the ratio I_D/I_G, the D-peak position, and the full width at half maximum (FWHM) of each peak. However, the error in the G-peak position is sufficiently small to allow the structural change of ta-C films to be reflected. The error in the G-peak position, estimated to be ± 1.5 cm^{-1}, is mainly due to uncertainty in the baseline correction. Figure 4 shows the change in the G-peak position as a function of residual compressive stress of the film. In spite of the scatter in the data, the result shows that the G-peak position of stressed ta-C film (adherent to the Si wafer) is shifted to higher wave numbers with increasing residual compressive stress. This behavior agrees with the previous result reported by Tamor and Vassell.[7] However, the G-peak position of the ta-C freehang sample shows the opposite behavior; the G peak is shifted to lower wave numbers with increasing residual stress of the deposited film. This result definitely shows that the discrepancy in the movement of the G-peak position for ta-C and a-C:H is due to the high residual compressive stress of ta-C films.

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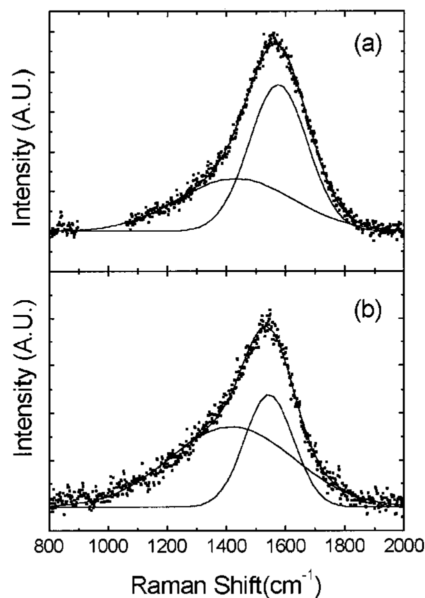

FIG. 3. Typical fitting result of the Raman spectra of (a) stressed, and (b) stress-relieved ta-C film, deposited at a negative bias voltage of 50 V.

By comparing the difference in G-peak position for stressed film and freehang samples with the residual stress relieved by the etching technique, we can quantitatively estimate the stress-induced G-peak shift. The result is summarized in Fig. 5. The difference in G-peak position is linearly proportional to the residual stress of the film. From the slope of the data, the stress-induced G-peak shift was obtained as $4.1 \pm 0.5\,\mathrm{cm}^{-1}$/GPa. It should be noted that this value agrees well with the calculated Raman-peak shift (4.9 cm^{-1}/GPa) with applied biaxial stress, as obtained by averaging over orientation in randomly oriented graphite planes.[12] This agreement is not surprising if one considers that the origin of the G peak is the E_{2g} phonon mode of the graphite plane, and the orientation of the sp^2 domains should be random in an amorphous carbon film. Therefore, in order to obtain information specific to the atomic-bond structure from the Raman-spectrum analysis, this value should be considered in determining the G-peak position.

In summary, it was observed that the G peak of Raman spectra shifted to higher wave numbers as a result of residual compressive growth stress. By comparing the G-peak position between stressed and stress-relieved ta-C films, the stress-induced G-peak shift was estimated to be $4.1 \pm 0.5\,\mathrm{cm}^{-1}$/GPa. The present work also shows that the inconsistency in the G-peak position change between ta-C and a-C:H is caused by the high level of residual compressive stress in ta-C films. After considering the residual stress effect on the G-peak position, the dependence of the G-peak position on the atomic bond structure exhibited the same behavior for both ta-C and a-C:H films: that is, a higher content of sp^2 bonds resulted in a shift of the G peak to higher wave numbers.

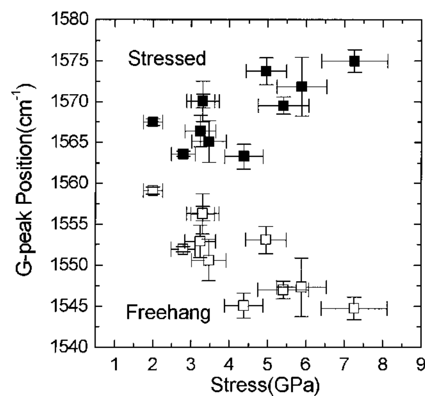

FIG. 4. G-peak position of stressed (solid squares) and a stress-relieved free hang (open squares), as a function of the residual compressive stress.

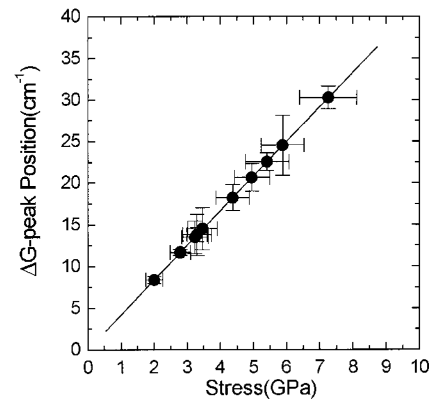

FIG. 5. G-peak position shift due to residual compressive stress as a function of the relieved residual stress.

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