Low-frequency feature in the first-order Raman spectrum of amorphous carbon

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In the first-order Raman spectrum of amorphous carbon (*a*-C) there is a low-frequency feature in the 200–900-cm^{-1} region. This feature is characteristic of the highly disordered amorphous-carbon materials. We note that the intensity of this feature is very sensitive to the thermal history of samples, thus suggesting that it is an important measure of the degree of disorder of the *a*-C materials. We also discuss the relationship between this feature and the phonon density of states of graphite.

There is considerable interest in understanding the mechanisms for structural changes in carbon networks. Raman spectroscopy has proven to be a useful tool in the study of bonding of nonmetals. Many studies have been conducted on the Raman spectrum of carbon including amorphous carbon.[1–6] We note that there is a saddle-shaped, low-frequency (200–900 cm^{-1}) feature in the spectra of sputtered *a*-C film samples. This feature may be related to the feature of the phonon density of states of graphite. We have studied this feature recently and find that it is a sensitive probe of changes in short-range order in *a*-C materials.

The most distinct characteristic of the first-order *a*-C Raman spectrum is an asymmetric feature in the 1000–1800-cm^{-1} region with the summit at about 1550 cm^{-1}. This feature has been frequently used in the discussion of the structure of amorphous-carbon materials.[1–3] In addition to this feature which is the strongest one, for certain kinds of *a*-C materials-such as the carbon thin film made by sputtering-there is also a saddle-shaped, less-intense, low-frequency (200–900 cm^{-1}) feature in the first-order Raman spectrum. In the early studies of *a*-C Raman spectra this low-frequency feature was noted.[7–9] But recent reports on Raman study of carbon thin film, almost without exception, have ignored the spectral range where the low-frequency feature is found.[1,2] This is unfortunate since the region of 1000 to 1800 cm^{-1} usually chosen for analysis is complicated by the presence of Raman scattered light from both fully amorphous carbon and from partially ordered regions that are more graphitic. On the other hand, the low-frequency feature can be seen to occur in a region devoid of features observed in graphitized samples opening the potential for their use as measures of ordering occurring in *a*-C.

The carbon films used in the study are about 400 nm thick and are deposited on Si wafers by dc-magnetron sputtering. Some samples were annealed at different temperatures in a vacuum chamber with Ar gas flow. The 488-nm Ar^{+} laser line was used to excite the Raman scattering. The laser beam was incident on the sample with an angle about 70° to the normal of the sample and the light power at the surface of the sample was about 70 mW. The scattered light was collected in the direction of the normal of the sample. The Raman spectra were obtained by a SPEX 1877 Triplemate, and a photomultiplier (EMI 7981B) was used as the photon detector. The whole Raman system was calibrated by using a tungsten-halogen lamp (Optronic Laboratories Standards).

Figure 1 shows the Raman spectra of as-deposited and annealed carbon films at three stages of annealing. From the spectrum of the as-deposited sample it can be seen that the intensities of the maxima of the low-frequency feature, one at about 400 cm^{-1} and another around 800 cm^{-1}, are only about one-fourth as intense as that of the peak at about 1550 cm^{-1}, but are stronger in intensity

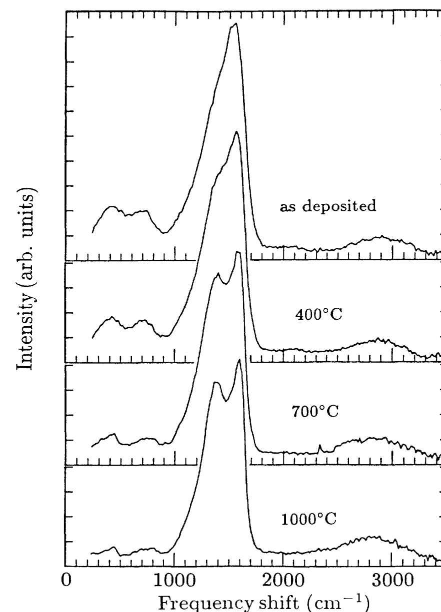

FIG. 1. Raman spectra of as-deposited and annealed *a*-C samples. *a*-C samples are made by dc-magnetron sputtering. The annealing is done in a vacuum chamber with argon gas flowing.

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than the second-order Raman feature around 2900 cm^{-1}. Limited by the rejection of Rayleigh scattering of the spectrometer, the spectra lower than 250 cm^{-1} could not be recorded.

Some trends can be clearly seen in the spectra of samples annealed at progressively higher temperatures. First, the entire low-frequency feature becomes less pronounced and the two maxima shift toward higher frequency. In spite of this decrease the feature and the two maxima are, however, still visible even for the sample annealed at 1000° C. Second, the shoulder at about 1360 cm^{-1} gradually grows higher and becomes distinct from the strongest peak at about 1580 cm^{-1} and, lastly, is resolved as a separated peak. In addition, the 1580-cm^{-1} peak itself seems to shift to higher frequency. Third, the maximum intensity of the feature in the 1000–1800-cm^{-1} region does not change substantially as the annealing temperature increases. Changes in the second-order spectrum are not noted.

Thermally induced changes in the strong feature are well known although the question of interpreting the changes is very much alive. Rouzaud, Oberlin, and Benz-Bassez[10] studied the graphitization process of evaporated carbon films by a variety of techniques including Raman spectroscopy. They heated their samples under an inert gas flow from 25 to 2700° C and obtained polycrystalline graphite as the product of the highest temperatures. They observed the narrowing of the first-order Raman features and the increasing of the relative intensity of the peak at about 1360 cm^{-1} early in the graphitization process. Our study shows that, for sputtered carbon film, another important characteristic of this period is the reduction in intensity of the low-frequency feature in the 200–900-cm^{-1} region. In fact, the relative decrease in its intensity is more pronounced, and should be easier to quantify, than the changes in the main peak.

It is generally believed that the *a*-C Raman spectrum is related to the phonon density of states (PDOS) of graphite.[8–11] The theoretical calculation given by Shuker and Gamon[12] indicates that the measured Raman spectrum of an amorphous solid is composed of the Bose-Einstein factor, the $1/\omega$ harmonic-oscillator factor, the transition probabilities, and the vibrational density of states. Only changes in the density of states can produce peaks in the spectra since all other factors vary relatively slowly. A decade ago Wada, Gaczi, and Solin[9] found that the reduced Raman spectrum of the *a*-C film compares well with the Gaussian-broadened one-phonon density of states of graphite.

In general, one way to verify the assumption that a broad spectrum is the broadened version of a core spectrum is to convolute the core spectrum with a known or assumed spread function and compare the result with the broad spectrum. Wada, Gaczi, and Solin took this approach. Another way is to eliminate or reduce the effect of the spread function from the broad spectrum (i.e., deconvolution) and to compare the result with the core spectrum. We think this way has more advantages since it may allow a comparison of two spectra with narrower features. Based on the same assumption that the spread function has a Gaussian function form, we have deconvoluted the Raman spectra of *a*-C films.[13]

Figure 2 shows the deconvolution result for an as-deposited *a*-C film and the PDOS of graphite for comparison. The open circles in Fig 2(a) are the experimental Raman data and the lower solid curve is the result of deconvoluting the data. To check the deconvolution method we reverse the process by convoluting the lower solid curve with the same spread function used in the deconvolution and compare the result with the experimental data. The convolution result is indicated by the upper solid curve in Fig. 2(a) which coincides almost exactly with the original data. The deconvolution of the spectrum of as-deposited *a*-C film yields peaks at about 410, 760, 1310, 1410, and 1600 cm^{-1}, respectively. In this frequency region the high density peaks in the phonon density of states of graphite calculated by Niclow, Wakabayashi, and Smith[14] are at about 468, 773, 1335, 1425, and 1610 cm^{-1}, respectively [see Fig. 2(b)]. The peak position agreement between the deconvoluted spectrum and PDOS of graphite is fairly good, except in the 400–500-cm^{-1} region.

Assuming that the 410- and 760-cm^{-1} peaks in the deconvoluted spectrum of *a*-C are related to the 468- and 773-cm^{-1} peaks in the PDOS of graphite, respectively, and using data given by Nemanich and Solin[15] and fol-

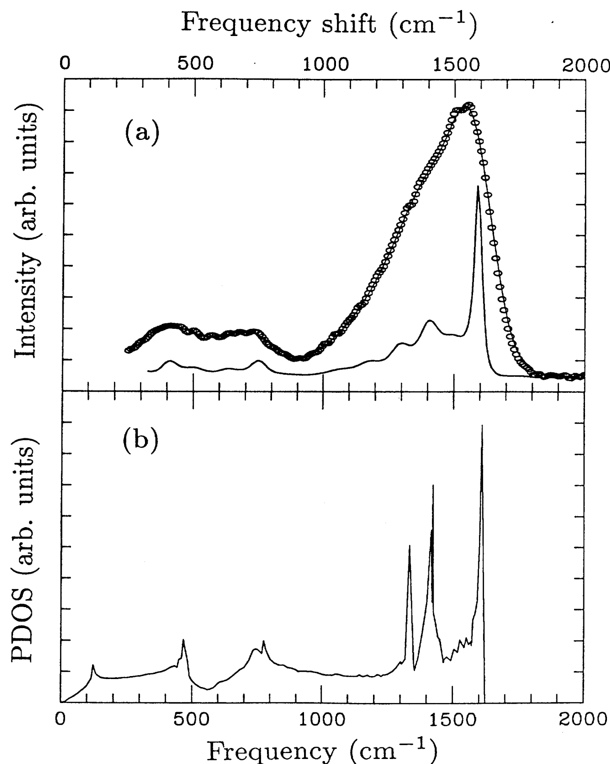

FIG. 2. (a) Circles are measured *a*-C Raman data. The lower solid curve is the deconvolution result of the measured data. The upper solid curve is obtained by convoluting the lower curve with the same spread function used in the deconvolution. (b) Phonon density of states of graphite calculated by Niclow, Wakabayashi, and Smith (Ref. 14).

lowing their discussion, the 760-cm^{-1} peak is from both the M-point zone boundary phonon mode with "out-of-plane" displacement and the M-point mode with "in-plane" displacement, whereas the 410-cm^{-1} peak is solely from the M-point mode with "out-of-plane" displacement.

There is only one sharp peak at 1580 cm^{-1} in the Raman spectrum of single crystal graphite which is the result of the selection rules related to the symmetry of the crystal structure. The appearance of all other peaks and features in the Raman spectra of different kinds of carbon materials is caused by the relaxation of the selection rules due to the disorder in the structure of the materials.[4] The intensity and the width of those disorder-related features depend on the degree of disorder in the samples. For example, all amorphous-carbon samples show the presence of such a 1350-cm^{-1} feature. It occurs as a distinct peak in annealed samples, which show some ordering, or as a shoulder in as-deposited materials, which are more disordered. The low-frequency feature is observed in all our sputtered a-C samples and the as-deposited sample shows the most pronounced low-frequency feature. It is reasonable to believe that this low-frequency feature is also disorder induced.

Whether the sputtered a-C films are uniquely disordered remains to be seen. Since most previous investigations were not made with an eye toward observing and quantifying the low-frequency feature, it is not possible to ascertain whether materials prepared in other ways are less or as disordered, with respect to the low-frequency feature, as sputtered a-C material. It should be noted that in any future discussions of the relative disorder in a-C materials, the low-frequency feature should take an important role since it is more easily quantified.

It is worth reflecting on other important aspects of the Raman spectroscopy in the study of amorphous materials. The benefit is twofold. First, a Raman spectrum can be used to monitor the process of phase change. It is possible to tell what happens in each step by observing the changes of Raman intensities for different modes. Some interesting studies have already been done in this area. Second, using the deconvolution method, the Raman spectrum of amorphous materials may be used to obtain the phonon density of states of corresponding crystalline materials. This is possible because most phonon modes are Raman active for highly disordered amorphous materials. One of the advantages of this method is the wide energy span of the Raman spectrum which enables the study of the whole phonon energy range.

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