Brief Reports

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Disorder-induced line broadening in first-order Raman scattering from graphite

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First-order Raman scattering from graphite irradiated by an electron beam has been studied by using the laser microprobe technique. An approximately linear relation is exhibited between the linewidth of the E_{2g} mode and the reciprocal of the crystallite size. The observed linewidths are larger than those calculated by using the known dispersion curve and the wave-vector uncertainty.

I. INTRODUCTION

The Raman scattering of graphites is sensitive to the structural disorder of those surfaces.[1-7] The first-order Raman spectrum of crystallite graphite shows a strong band, which has been assigned to the in-plane E_{2g} zone-center mode, at around 1580 cm^{-1} (G). In microcrystallite graphite and disordered carbon, additional bands appear at around 1360 cm^{-1}(D) and 1620 cm^{-1}(D'). The additional features have been assigned to arise from non-zero-center phonons and to be related to peaks in the density of states.[2,3] The intensity ratio (R) of the D band to the G band has been reported to be inversely proportional to the microcrystallite planar size (L_a).[1,6]

In addition to the appearance of new bands, a finite crystallite size can also induce broadening in the G band line.[3,5] However, quantitative studies on the dependence of the linewidth on crystallite size have not been well established because of the limitation of range on crystallite size in graphites.

In the present work we have studied the first-order Raman spectrum from isotropic graphite irradiated with an electron beam to elucidate the relation between linewidth and microcrystallite size. This is because a wide variety of crystallite sizes can be obtained in the same sample by electron beam irradiation.[8,9] The disorder introduced by ion implantation has also been studied by Raman spectroscopy.[10,11] In addition we discussed the broadening from a wave-vector uncertainty by using the known dispersion curve.

II. EXPERIMENT

Microlaser Raman spectroscopy was performed for isotropic graphite irradiated with the high-current-density electron beam. The isotropic polycrystal graphite ($T-6P$) was obtained from the Ibiden Co. The high-current-density electron beam was formed from a hollow-cathode-type ion gun with Ar gas, and focused to the surface of the sample mounted on a water-cooled copper sample holder. Details of the experimental procedure for the electron beam irradiation were described in a previous paper.[8]

Raman spectra were measured with an NR-1100 spectrometer (Japan Spectroscopic Company Ltd.) in the range of 1200 to 1700 cm^{-1}. The 488.0-nm line of an Ar-ion laser with 400-mW power was introduced with an objective lens (×50). The illuminated area was as small as 2μm in a diameter. The scattered light was collected in the backscattering configuration and analyzed with a double-grating monochromator. Peak positions and integral intensities of Raman bands were determined by computer simulation, in which the numerical deconvolution method was used by assuming a Lorentzian line shape for all Raman bands.

III. RESULTS

Figure 1(a) shows the Raman spectrum of the graphite before the electron beam irradiation. The observed spectrum consists of three peaks at 1358, 1576, and 1615 cm^{-1}. These three lines are attributed to the D, G, and D' bands, respectively. The microcrystallite size L_a was estimated to be 80 Å from the integral intensity ratio (R) of the D band to the G band by using the method of Tuinstra and Koenig.[1] After the electron beam irradiation, the intensities of three bands were varied at various positions on the sample. Figures 1(b) and 1(c) show a typical example of Raman spectra for the irradiation center and the edge of the sample, respectively. The L_a estimated from the integral intensity ratio was varied from the irradiation center to the sample edge. Detailed descriptions on the position dependence of L_a were given in a previous paper.[9]

Figure 2 shows the relation on the integral intensity between the D' and D bands on the basis of that of the G band. The intensity of the D' band increases linearly with the increase of that of the D band. From the slope of this curve, an estimate of the intensity ratio of the D'

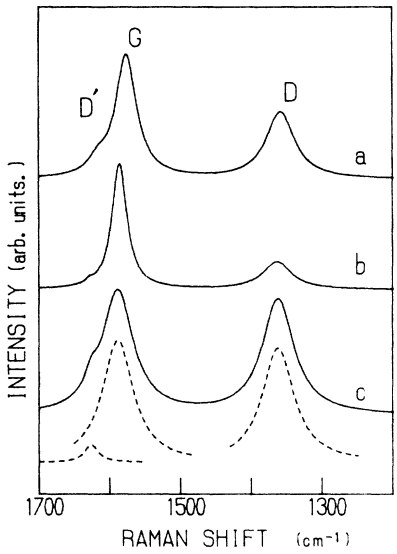

FIG. 1. Raman spectra of the graphite irradiated with electron beam. (a) Obtained before irradiation: (b) obtained from the center of the irradiated part after irradiation ($E=40$ eV and $\phi\sim 9\times 10^{20}$ electrons/ cm^2); and (c) obtained from outside the irradiated part ($E=40$ eV and $\phi\lesssim 10^{19}$ electrons/cm^2). The dashed line indicates a typical example of numerical deconvolution.

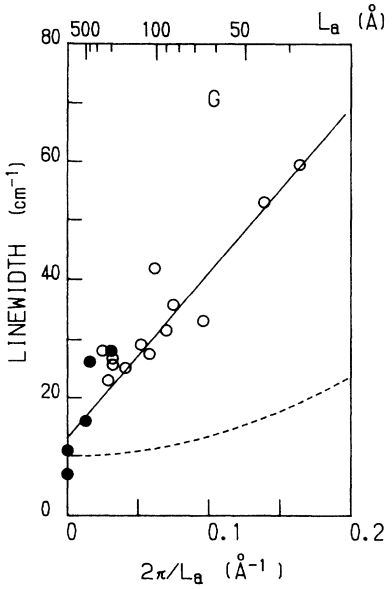

FIG. 3. Dependence of the linewidth of the G band on microcrystallite size L_a. (○) indicates the present data and (●) indicates the data taken from Refs. 4, 5, 12, and 13. The solid line indicates the least-squares fit, and the dashed line indicates the values obtained by the calculations from the dispersion curves.

band to the D band is about 0.15.

Figure 3 shows the linewidth (half-width at half-maximum intensity) of the G band versus $2\pi/L_a$, where $2\pi/L_a$ is the wave-vector uncertainty determined by the uncertainty principle. Open and solid circles indicate the

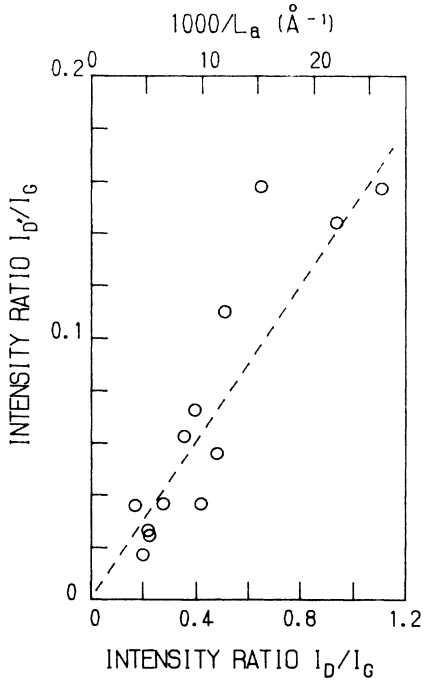

FIG. 2. The relative intensity of the D' band to the G band vs that of the D band to the G band. The dashed line indicates the least-squares fit.

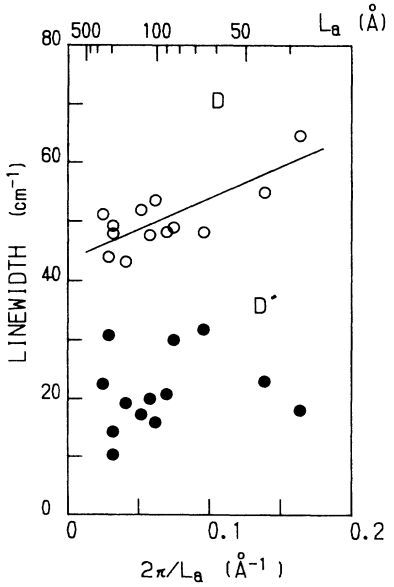

FIG. 4. Dependence of the linewidths of the D and D' bands on microcrystallite size L_a. (○) indicates the D band, and (●) indicates the D' band. The solid line indicates the least-squares fit for the D bands.

data obtained by the present work and those taken from the literature,[4,5,12,13] respectively. The linewidth increases almost linearly with the decrease of L_a. A similar relation holds for the D band (Fig. 4).

IV. DISCUSSION

Figure 3 clearly shows that the linewidth of the G band is closely related to the crystalline size L_a (planar domain size): the linewidths increase with decreasing L_a. We attempted to calculate the linewidth of the G band from a wave-vector (q-vector) uncertainty by using the known dispersion curve, since the G band has been attributed to the in-plane E_{2g} zone center mode.

Finite crystalline size produces an uncertainty in the wave vector[3,14] ($\Delta q = 2\pi/L_a$). This wave-vector uncertainty can be converted into an uncertainty in frequency ω by using the phonon dispersion relation. The phonon dispersion relation for graphite has been calculated by a number of workers with force-constant models to fit the experimental neutron data.[5] We assumed the dispersion curve for the E_{2g} mode to be parabolic[15] near $q=0$ ($\Delta\omega = Cq^2$). The coefficient C was determined to be 340 cm^{-1} $\mathrm{\AA}^2$ in order to fit the dispersion curve calculated by Maeda, Kuramoto, and Horie[16] below $k = 0.3\mathrm{\AA}^{-1}$. Using these relations, the linewidth due to the phonon dispersion can be calculated. Then we calculated the linewidth of the G band as the sum of the intrinsic width of the zero-center phonon and the additional width due to the wave-vector uncertainty, where the intrinsic width was estimated to be 10 cm^{-1} from the spectrum of the highly oriented pyrolytic graphite (HOPG).[5] The calculated linewidth, which is shown in Fig. 3 by the dashed line, qualitatively explains the line broadening with decreasing L_a, but does not fit experimental data. A similar relation between the linewidth of the E_{2g} mode peak and $1/L_a$ has been observed for boron nitride microcrystals by Nemanich, Solin, and Martin.[17] Crystalline boron nitride also has D_{6h}^4 space-group symmetry. They suggested that the vibrational excitation lifetime is influenced by surface and boundary scattering and the linewidth is dependent upon the surface-to-volume ratio, which can be expressed with L_a.

Another candidate for the origin of the additional line broadening is the stress produced by the temperature gradient, since in the present experiment the central part of the surface irradiated with the electron beam is strongly heated up.[9] However, Wada has studied the G band of the Raman spectrum as a function of hydrostatic pressure and has reported no apparent change in its shape under pressure.[18] The effect of the stress for the line broadening may therefore be small, but a distribution of C—C bond distances caused by the electron beam irradiation could be one of the candidates for the line broadening.

An approximately linear relation holds between intensities of D and D' bands and both intensities relate to L_a (shown in Fig. 2). Both disorder-induced features (D and D' bands) have been attributed by Lespade, Al-Jishi, and Dresselhaus[2] to arise from non-zero center phonons and relate to peaks in the vibrational density of states. In contrast, Nakamizo and Tamai[19] have observed the D' band in surface oxidized graphite, and they suggested that the D' band arises from a CO stretching mode or a hexagonal ring stretching mode in small crystallites with surfaces covered with CO complexes. The present results (shown in Fig. 4) show that the relation between the linewidth of the D band and L_a is similar to that in the G band, but an apparent relation between the linewidth and L_a is not observed in the D' band. The relation between $I_{D'}/I_G$ and I_D/I_G suggests that the intensity of the D' peak is dependent upon the crystallite size (L_a), which is related to the surface-to-volume ratio. If the D' peak arises from nonzero phonons in a similar manner to the D peak, the linewidth of the D' peak should depend on L_a. On the other hand, if the D' peak arises from the vibration of species attached to the surface of microcrystals such as C-O, the linewidth of the D' peak may be independent on L_a. We therefore propose that the disorder-induced D' band does not arise from the normal lattice vibration of graphite.

V. CONCLUSION

An approximately linear relation holds between the linewidth of the E_{2g} mode and the reciprocal of the crystallite size. The observed linewidths are larger than those calculated by using the known dispersion curve. The relation between linewidth and crystallite size is similar in G and D bands, but no apparent relation can be seen in D' band.

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