

## Raman scattering from ion-implanted graphite

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Ion-implanted graphite is studied by Raman scattering. Highly oriented pyrolytic graphite is implanted with  ${}^7\text{Li}$ ,  ${}^9\text{Be}$ ,  ${}^{11}\text{B}$ ,  ${}^{12}\text{C}$ ,  ${}^{31}\text{P}$ , and  ${}^{75}\text{As}$  ions at 100 keV normally incident upon the  $c$  face. Ion fluences in the range  $1 \times 10^{14}$  to  $2.5 \times 10^{16}$  ions/cm $^2$  are used. The lattice damage upon implantation is monitored by observation of the disorder-induced Raman line at  $\sim 1355$  cm $^{-1}$  in the first-order spectra and at  $\sim 2970$  cm $^{-1}$  in the second-order spectra. The Raman results indicate that an abrupt transformation to an amorphous surface layer occurs at a critical fluence which varies with the mass of the implanted ion. Results for first- and second-order Raman spectra are also presented for the same ion-implanted samples upon isochronal vacuum annealing at various annealing temperatures, showing a partial restoration of the graphite ordering. The second-order Raman spectra are even more sensitive than the first-order spectra to the creation of lattice damage by ion implantation and to the subsequent partial restoration of lattice order by annealing.

### INTRODUCTION

Intercalation has been widely used as a mechanism for chemical introduction of foreign species into layered host materials such as graphite. Graphite intercalation compounds are interesting because of the large varieties of behavior that can be produced by intercalation, such as the occurrence of superconductivity in  $\text{C}_8\text{K}$ , where neither C nor K are superconducting, the increases by nearly two orders of magnitude in the in-plane conductivity  $\sigma_a$  and the increase by more than two orders of magnitude in

the electrical anisotropy ratio  $\sigma_a/\sigma_c$  where  $\sigma_c$  is the  $c$ -axis conductivity.

Ion implantation provides a physical mechanism for the introduction of foreign species into these host materials, making possible the introduction of species that do not intercalate by chemical means. Because of the high kinetic energy of insertion, it may be possible to create more stable materials with lower affinities for desorption of the guest species. This kinetic energy, however, introduces lattice disorder which affects various physical properties of these materials. Therefore the lattice damage must

be monitored.

As an implanted ion (typically of  $\sim 100$  keV energy) slows down and comes to rest, it makes many violent collisions with lattice atoms, displacing them from their lattice sites. Some of these displaced atoms have enough kinetic energy to displace others, giving rise to a cascade process. The net result is the production of a highly disordered region around the path of the ion with the dominant disorder occurring near the end of the ion trajectory, as shown schematically in Fig. 1(a). At sufficiently high dosage, these individual disordered regions begin to overlap [Fig. 1(b)] until finally a noncrystalline or amorphous layer is formed [Fig. 1(c)]. Such a mechanism for the introduction of disorder is well known from studies of Si and Ge.<sup>1</sup>

The method of ion implantation in fact provides a technique for artificially producing disordered regions of varying sizes [Fig. 1(b)] by appropriate selection of the dose of implanted ions. Ion implantation allows study of the evolution of the microscopic structural properties of a very important sequence of regimes: crystalline-microcrystalline-amorphous.

This paper focuses on the use of Raman scattering as a tool to monitor the ion-implantation process in graphite. Since ion implantation takes place within an optical skin depth, Raman scattering which probes the sample within an optical skin depth provides a sensitive tool for monitoring the implantation process. Raman scattering has in fact been widely exploited to characterize ion-implanted silicon<sup>2-4</sup> and to some extent also graphite.<sup>2,5-7</sup> Since graphite is a crystalline material, the profile and range of the ion-induced disorder is sensitive to the angle of ion incidence to the layer planes, so that control of the disorder generation is more difficult than for amorphous or glassy substrates. The first- and second-order Raman spectra reported here for boron-implanted graphite provide evidence for the three regimes of behavior delineated above.

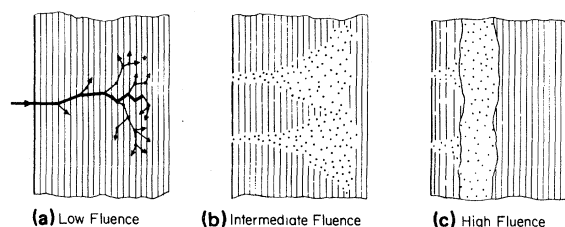


FIG. 1. Schematic view of the disordered region in graphite caused by implantation at (a) low, (b) intermediate, and (c) high fluence.

The Raman spectra of several forms of graphite have been reported by Tuinstra and Koenig.<sup>8</sup> It has been noted that while single-crystal graphite and highly oriented pyrolytic graphite (HOPG) exhibit a sharp Raman line [Fig. 2(a)] at  $\sim 1580$   $\text{cm}^{-1}$ , more poorly ordered graphite materials, such as activated charcoal<sup>8</sup> or glassy carbon,<sup>5</sup> exhibit two Raman lines [Fig. 2(b)], one near  $\sim 1580$   $\text{cm}^{-1}$  and an additional line near  $\sim 1355$   $\text{cm}^{-1}$  where the phonon density of states has a strong maximum. Tuinstra and Koenig<sup>8</sup> have shown that the relative intensity of the disorder-induced  $1355\text{-cm}^{-1}$  line relative to the Raman-active  $1580\text{-cm}^{-1}$  line,  $I(1355)/I(1580)$ , varies inversely with the crystallite size  $L_a$  of the graphite sample. For thin ( $\ll 2500$  Å) amorphous carbon films deposited on glass substrates,<sup>9</sup> the two lines are no longer resolved and a very broad asymmetric Raman line is observed [see Fig. 2(c)]. However, thick carbon films ( $\geq 2500$  Å) deposited on glass exhibit a two-peak Raman spectrum.

Previous studies on ion-implanted graphite<sup>2,6</sup> have yielded the broad line characteristic of the amorphous regime [see Fig. 2(c)]. The first measurements by Crowder *et al.*<sup>2</sup> were made on graphite implanted with  $^{40}\text{Ar}$  ions at a fluence of  $1 \times 10^{16}$  ions/ $\text{cm}^2$ , and the overall study was directed toward an elucidation of the effect of ion implantation on the tetrahedral bonding arrangement in common semiconductors. Crowder *et al.*<sup>2</sup> showed that a similar broad asymmetric Raman line, characteristic of the amorphous regime, was obtained upon ion

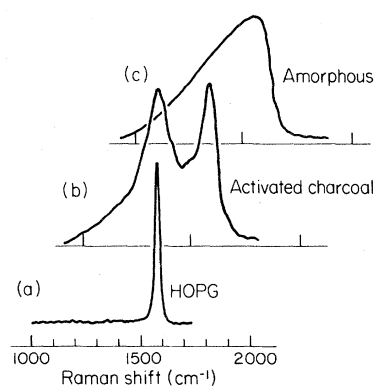


FIG. 2. Experimental Raman spectra from various kinds of graphite. (a) Single-crystal graphite and HOPG with a single line near  $1580$   $\text{cm}^{-1}$ . (b) Activated charcoal showing the Raman-active  $E_{2g_2}$  line near  $1580$   $\text{cm}^{-1}$  and a disorder-induced line near  $1355$   $\text{cm}^{-1}$ . (c) A broad asymmetric line from an amorphous film peaked near  $1500$   $\text{cm}^{-1}$  (from Ref. 9).

implantation of either graphite or diamond, showing that ion implantation destroyed the local tetrahedral bonding arrangement of diamond. Later work by Wright *et al.*<sup>6</sup> was carried out on ultra superior purity graphite (USP) samples, showing Raman spectra similar to Fig. 2(b) prior to implantation with 10–15 keV <sup>1</sup>H, <sup>2</sup>D, and <sup>4</sup>He ions and fluences up to  $4 \times 10^{19}$  ions/cm<sup>2</sup>. Their first-order Raman spectra also exhibited the broad asymmetric line after implantation [see Fig. 2(c)]. Annealing at 1040 °C for 3 h restored the double-peaked spectra [see Fig. 2(b)] for USP samples that had been implanted with <sup>2</sup>D ions at 15 keV to a fluence of  $2.7 \times 10^{19}$  ions/cm<sup>2</sup>. A broadening effect of ion implantation on the second-order spectra was also reported by Wright *et al.*<sup>6</sup> Raman spectroscopy has also been used to monitor the effect of fast neutron irradiation at low temperature (5 K) followed by room-temperature annealing,<sup>7</sup> in which the focus was on monitoring the radiation damage of reactor materials.

In the present study, attention is focused on implanted ions with masses comparable to that for the graphite host. A relatively low fluence ( $10^{14} \lesssim \phi \lesssim 10^{16}$  ions/cm<sup>2</sup>) has been used, which permits us to investigate for the first time the disorder produced by ion implantation prior to the formation of the amorphous layer (see Fig. 1). Results for the effect of annealing on the implanted samples are reported for the range of fluences near the threshold for formation of the amorphous layer. Our measurements of the second-order Raman scattering show the second-order spectra to be even more sensitive than the first-order spectra to monitoring the threshold for formation of the amorphous layer.

### EXPERIMENTAL

Samples of highly oriented pyrolytic graphite (HOPG) have been implanted with carbon ions and ions of atomic mass less (<sup>6</sup>Li, <sup>9</sup>Be, <sup>11</sup>B) and greater (<sup>31</sup>P, <sup>75</sup>As) than that of carbon. Carbon ions are of special interest because only carbon impurities are introduced during the implantation process, thereby making it possible to distinguish the effects caused by the ion implantation itself from the effects caused by the implantation of ions differing from the host material. An Accelerators Inc. 300R ion implanter was used for the implantation and the ion beam was directed normal to the graphite *c* face. The samples were implanted at ambient temperatures, with fluences in the range  $1 \times 10^{14}$  ions/cm<sup>2</sup> to  $2.5 \times 10^{16}$  ions/cm<sup>2</sup>, and at an accelerating voltage of 100 keV.

The Raman scattering experiments were per-

formed at room temperature using a Brewster angle backscattering geometry. Incident radiation of 4880 Å and ~200 mW was provided by a cw argon-ion laser. The scattered radiation was collected 90° to the sample surface, analyzed by a double-grating monochromator and detected by a cooled photomultiplier tube.

Repeated Raman spectra showed the ion-implanted samples to be stable with respect to time and ambient laboratory atmosphere. At the low laser powers used in the Raman scattering measurements, no laser annealing effect was expected or observed. The ion-implanted samples were isochronally vacuum annealed in quartz tubes in the temperature range  $700 < T < 1000$  °C.

### RESULTS AND DISCUSSION

Raman spectra of HOPG implanted with <sup>9</sup>Be, <sup>11</sup>B, <sup>12</sup>C, and <sup>31</sup>P at a fixed fluence of  $1 \times 10^{14}$  ions/cm<sup>2</sup> are presented in Fig. 3. These spectra are from unannealed samples and for the case of the <sup>9</sup>Be, <sup>11</sup>B, and <sup>12</sup>C ions correspond to the low-fluence regime (as discussed below). All spectra show the appearance of Raman intensity in the

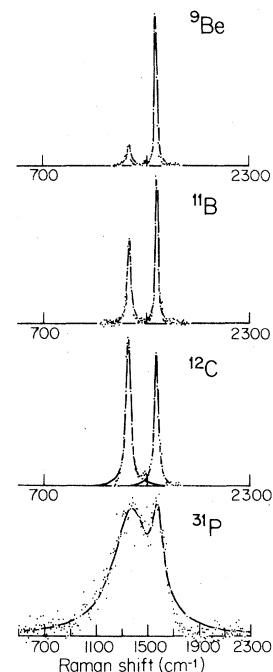


FIG. 3. Room-temperature Raman spectra showing lines at 1355 and 1580 cm<sup>-1</sup> for unannealed HOPG samples ion implanted with <sup>9</sup>Be, <sup>11</sup>B, <sup>12</sup>C, and <sup>31</sup>P at the same fluence,  $1 \times 10^{14}$  ions/cm<sup>2</sup> at 100 keV. The abscissa is linear in wave number and the points are experimental.

vicinity of  $\sim 1355 \text{ cm}^{-1}$ , indicative of disorder-induced scattering.<sup>8,9</sup>

As seen from Fig. 3, the intensity of the  $1355\text{-cm}^{-1}$  line relative to that at  $1580 \text{ cm}^{-1}$  and denoted by  $I(1355)/I(1580)$ , depends on the atomic mass of the implanted species, the heavier implanted ions giving larger magnitudes for  $I(1355)/I(1580)$ . The results for atomic masses less than or equal to carbon show well-resolved peaks, in contrast to the behavior for the phosphorus ions ( $M = 31$ ) where the Raman spectrum appears to be qualitatively similar to that for amorphous carbon [Fig. 2(c)]. Expect for the barely resolved doublet structure, the spectrum for the  $^{31}\text{P}$  implanted sample at a fluence of  $1 \times 10^{14} \text{ ions/cm}^2$  (Fig. 3) is qualitatively similar to that reported by Wright *et al.*<sup>6</sup> for an  $^{40}\text{Ar}$  implanted sample at a fluence of  $1 \times 10^{16} \text{ ions/cm}^2$ . Our results for the Raman spectra of  $^{75}\text{As}$ -implanted graphite are qualitatively similar to those for P, indicating a saturation as a function of ion mass and fluence of the intensity ratio  $I(1355)/I(1580)$  once the Raman line shape characteristic of amorphous carbon is obtained. For equal incident kinetic energy, the heavier ions are slowed down over a shorter penetration depth, thereby giving rise to a greater density of collision events and a larger cross-sectional damage area per ion. Thus it is reasonable that the transition from the disordered regime [Fig. 1(a)] to the amorphous regime [Fig. 1(c)] occurs at a lower implantation dose as  $M$  increases.

As can be seen from Fig. 3, the linewidth of both the  $1355\text{-cm}^{-1}$  and  $1580\text{-cm}^{-1}$  lines increases with increasing atomic mass  $M$  of the ions. The increase in linewidth is gradual as  $M$  is increased from 9 in Be to 12 in C, in contrast to the dramatic increase in linewidth for the case of phosphorus where  $M = 31$ .

Insight into the linewidth behavior shown in Fig. 3 is also provided by study of the dependence of the Raman spectra on ion fluence for a single ion species, as shown in Fig. 4(a) for boron  $^{11}\text{B}$  ions. This figure shows a gradual increase in relative intensity  $I(1355)/I(1580)$  and linewidth of both lines as the fluence is increased from  $1 \times 10^{14} \text{ ions/cm}^2$  to  $5 \times 10^{14} \text{ ions/cm}^2$  to  $1 \times 10^{15} \text{ ions/cm}^2$ . As the fluence of boron is further increased to  $5 \times 10^{15} \text{ ions/cm}^2$ , a dramatic change in linewidth and intensity occurs and above that fluence the results at  $1 \times 10^{16}$  and  $2.5 \times 10^{16} \text{ ions/cm}^2$  show little further change. Results at  $1 \times 10^{14} \text{ ions/cm}^2$  and 100 keV for phosphorus (Fig. 3) and arsenic (not shown) appear to be in the same regime of behavior as that which is observed with boron for fluences of  $5 \times 10^{15} \text{ ions/cm}^2$  and above. The spectra for sam-

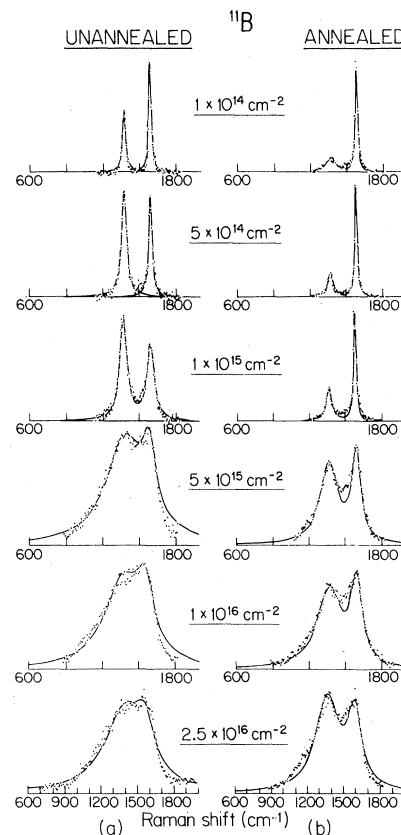


FIG. 4. Raman spectra for various fluences ( $1 \times 10^{14}$  to  $2.5 \times 10^{16} \text{ ions/cm}^2$ ) of  $^{11}\text{B}$  ions implanted into six HOPG samples. The spectra on the left (a) are for the unannealed samples, and on the right (b) are for the same samples annealed at  $950^\circ\text{C}$  for 0.5 h. The abscissa is linear in wave number and the points are experimental.

ples with high ion concentrations are asymmetric, though two broad lines can be resolved by deconvolution, fitting each component to a Lorentzian line shape. The deconvolution procedure for high ion concentrations, however, results in considerable error in the determination of peak frequencies and linewidths.

Raman spectra are shown in Fig. 4(b) for the same samples that are shown in Fig. 4(a), but after annealing at  $950^\circ\text{C}$  for 0.5 hours. We find that annealing at a temperature as low as  $700^\circ\text{C}$  is sufficient to yield two clearly resolved Raman peaks from samples which have been implanted with  $^{11}\text{B}$  ions to fluences in the range  $5 \times 10^{15} \leq \phi \leq 2.5 \times 10^{16} \text{ ions/cm}^2$ , and had exhibited the broad asymmetric line shape characteristic of the amorphous layer [see Fig. 4(a)]. Thus annealing provides a partial restoration of the structural order of the pristine graphite, consistent with the annealing results obtained by others.<sup>6,9</sup> From studies on Si

and Ge it has been shown that the effect of annealing is more sensitive to the annealing temperature than to the time of annealing, provided that the time is sufficient for the samples to reach thermal equilibrium. Annealing studies of graphite implanted with high fluences of the light ions  $^1\text{H}$ ,  $^2\text{D}$ , and  $^4\text{He}$ , however, showed a weak dependence on the annealing time.<sup>6</sup> It is clear from Fig. 4 that for all ion concentrations shown, annealing at  $950^\circ\text{C}$  causes a partial restoration of crystalline order. With regard to the disorder-induced  $1355\text{-cm}^{-1}$  line, annealing causes both the intensity and linewidth to decrease. For the Raman-active  $1580\text{-cm}^{-1}$  line, annealing causes an increase in intensity and a decrease in linewidth. For both unannealed and annealed samples the line shapes for fluences  $\phi \geq 5 \times 10^{15}$  ions/cm<sup>2</sup> are qualitatively different from the behavior below this fluence. In these spectra no evidence for carbide formation in terms of carbide-specific Raman lines was found for our experimental conditions. The absence of such lines may be due to the low annealing temperatures or the relatively low implanted-ion concentrations used in these experiments.

A summary of results for the first-order Raman spectra is given in Figs. 5 and 6, where the linewidths (FWHM) of the  $1355\text{-cm}^{-1}$  and  $1580\text{-cm}^{-1}$  lines are, respectively, plotted as a function of  $\log_{10}\phi$ , where  $\phi$  is the boron fluence. Also plotted on this figure are the results obtained after annealing at two different temperatures. The linewidths are determined by fitting the experimental data to a Lorentzian line shape. Figure 5 dramatically shows

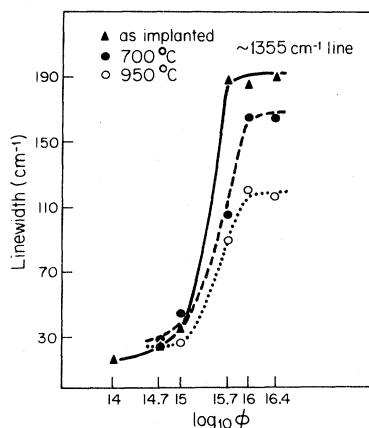


FIG. 5. Graph of the  $1355\text{-cm}^{-1}$  linewidth (FWHM) versus  $\log_{10}\phi$  for  $^{11}\text{B}$  ion implanted HOPG, where  $\phi$  is the boron fluence. Results are presented for unannealed samples and for the same samples annealed at  $700^\circ\text{C}$  and  $950^\circ\text{C}$ .

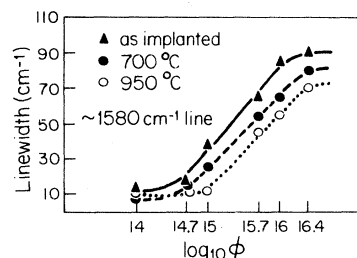


FIG. 6. Graph of the  $1580\text{-cm}^{-1}$  linewidth (FWHM) versus  $\log_{10}\phi$  for  $^{11}\text{B}$  ion implanted HOPG where  $\phi$  is the boron fluence. Results are presented for unannealed samples and for the same samples annealed at  $700^\circ\text{C}$  and  $950^\circ\text{C}$ .

the rapid change in linewidth of the  $1355\text{-cm}^{-1}$  line in the vicinity of a fluence of  $\phi \geq 1 \times 10^{15}$  ions/cm<sup>2</sup>. The linewidth changes with annealing are very small for  $\phi \leq 1 \times 10^{15}$  boron ions/cm<sup>2</sup> and are very significant above this fluence, though the fluence range over which the change in linewidth in Fig. 5 occurs is not sensitive to annealing for annealing temperatures  $\leq 950^\circ\text{C}$ . Noting that the Raman-active  $1580\text{-cm}^{-1}$  line is much narrower than the disorder-induced  $1355\text{-cm}^{-1}$  line at low fluences, the order-of-magnitude increase in linewidth from low to high boron-ion fluence is of comparable size for both the  $1355\text{-cm}^{-1}$  and  $1580\text{-cm}^{-1}$  lines. However, the fluence range over which this increase in linewidth occurs is larger for the  $1580\text{-cm}^{-1}$  line than for the  $1355$  line. The percent reduction in linewidth due to annealing is larger for the  $1355\text{-cm}^{-1}$  line than for the  $1580\text{-cm}^{-1}$  line.

In connection with the linewidths of the first-order spectra, it is of interest to note that the introduction of guest species by chemical intercalation does not significantly increase the linewidths of the first-order Raman spectra,<sup>10</sup> even for the lowest-stage compounds (i.e., highest intercalate concentration), indicating that intercalation does not radically reduce the in-plane graphite crystallite size. The anomalous broadening of the first-order Raman spectra for the stage 1 alkali metal compounds is attributed to a strong coupling between the discrete  $E_{2g_2}$  mode and a continuum of phonon states, and not to a reduction in the in-plane graphite crystallite size.<sup>11</sup> On the other hand, the  $E_{2g_2}$  mode frequency is known to vary with intercalation, being upshifted linearly as a function of reciprocal stage ( $1/n$ ) for acceptor intercalants and downshifted for donor intercalants.<sup>12</sup> It is also well known<sup>13</sup> that the disordering of the graphite lattice upshifts the first-order Raman  $E_{2g_2}$  mode frequency, with a sensitivity to crystallite size that depends on the ra-

quency (up to  $12\text{ cm}^{-1}$ ) with decreasing crystallite size is suggested to be a consequence of both a breakdown in the wave-vector selection rule and a phonon dispersion branch that rises away from the zone center, thereby admixing phonons with both larger wave vectors and higher frequencies.

These considerations inspired investigation of the behavior of the frequency shift of the  $1580\text{-cm}^{-1}$  line relative to that for HOPG and the results are shown in Fig. 7 for samples implanted with boron. A dramatic change in the mode frequency shift ( $\nu - \nu^{\text{HOPG}}$ ) is found for fluences  $\phi$  in the range where the linewidth changes rapidly. This behavior suggests that at low fluence there is an upshift of the  $E_{2g_2}$  mode, consistent with the increasing disorder [Fig. 1(a)] and formation of microcrystallites [Fig. 1(b)]. At high fluence, where the structure becomes amorphous, the downshift of the  $E_{2g_2}$  mode might be associated with an expansion of the C—C in-plane distance, similar to the effect observed in donor graphite intercalation compounds.<sup>12,14,15</sup> The behavior of the annealing data in Fig. 7 is particularly interesting and may upon detailed examination yield information on activation energies for the transition of an ion from an interstitial to a substitutional site.

Second-order (two phonon) Raman spectra have been reported for various types of graphite samples, exhibiting a variety of crystallite sizes.<sup>13</sup> The dominant feature in the second-order spectrum is an intense line at  $2735\text{ cm}^{-1}$ . A very sharp but weak

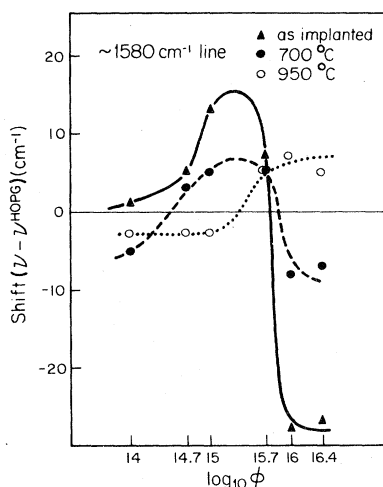


FIG. 7. Graph of the frequency shift of the  $1580\text{-cm}^{-1}$  line with respect to that of unimplanted HOPG versus  $\log_{10}$  of the boron fluence  $\phi$ . Results are given for both the unannealed samples and for the same samples annealed at  $700$  and  $950^\circ\text{C}$ .

feature at  $3248\text{ cm}^{-1}$  and a feature at  $2970\text{ cm}^{-1}$  which is caused by lattice disorder, have also been reported.<sup>13</sup> Nemanich *et al.* show that the feature at  $\sim 2735\text{ cm}^{-1}$  becomes broader, the one at  $\sim 2970\text{ cm}^{-1}$  becomes more intense, and the one at  $3248\text{ cm}^{-1}$  is suppressed with decreasing crystallite size.<sup>13</sup> In contrast, the second-order Raman spectra for single-crystal graphite and HOPG show no structure at  $2970\text{ cm}^{-1}$  and a partially-resolved doublet structure at  $2735\text{ cm}^{-1}$ .<sup>13,16,17</sup> Our measurements on HOPG show additional sharp features in the second-order spectra at  $2327\text{ cm}^{-1}$ ,  $2435\text{ cm}^{-1}$ , and a broader feature at  $2468\text{ cm}^{-1}$  (see Fig. 8). Wright *et al.*<sup>6</sup> have also reported a broad feature at  $2445\text{ cm}^{-1}$  in USP graphite, corresponding to the doublet structure in Fig. 8 at  $2435\text{ cm}^{-1}$  and  $2468\text{ cm}^{-1}$ . This feature is also evident in the second-order spectra for HOPG shown in Ref. 17. The sharp feature at  $2327\text{ cm}^{-1}$ , reported here for the first time, was observed using laser excitation wavelengths of  $4880$  and  $5145\text{ \AA}$ .

Previous workers have identified the  $2970\text{-cm}^{-1}$  feature in the second-order spectra with disorder-induced scattering, analogous to the  $1355\text{-cm}^{-1}$  line in the first-order Raman spectra.<sup>6,13,16,17</sup> The identification of this feature in the second-order spectra can be made using the density of phonon states<sup>18</sup> calculated on the basis of the graphite phonon dispersion relations of Maeda *et al.*<sup>19</sup> The main peaks in the phonon density of states occur at  $1620$ ,  $1360$ ,  $850$ ,  $830$ , and  $570\text{ cm}^{-1}$ . Thus  $2(1620)\text{ cm}^{-1} = 3240\text{ cm}^{-1}$  and  $2(1360)\text{ cm}^{-1} = 2720\text{ cm}^{-1}$  correspond, respectively, to the peaks at  $3248$  and  $2730\text{ cm}^{-1}$  in the second-order Raman spectra. The disorder-induced peak at  $2970\text{ cm}^{-1}$  corresponds to  $(1620 + 1360)\text{ cm}^{-1} = 2980\text{ cm}^{-1}$  and therefore involves two phonons at somewhat different points in the Brillouin zone, consistent with a disorder-induced mechanism. We also note that the doublet structure in the density of states at  $830$  and  $850\text{ cm}^{-1}$  combines with the  $1620\text{-cm}^{-1}$  peak to

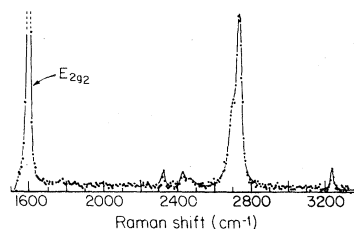


FIG. 8. Second-order Raman spectra of HOPG. An intense line occurs at  $2735\text{ cm}^{-1}$  and a very sharp feature at  $3248\text{ cm}^{-1}$ .

yield 2450 and 2470  $\text{cm}^{-1}$ , which are close to the observed peaks in the second-order Raman spectra at 2435 and 2468  $\text{cm}^{-1}$ . No identification has been made of the sharp feature in the second-order spectrum at 2327  $\text{cm}^{-1}$ .

Results for the second-order Raman spectra from HOPG samples implanted with various fluences of 100-keV boron ions are given in Fig. 9(a). These spectra also show a strong dependence on boron fluence, with results analogous to the first-order spectra for the ion-implanted samples. However, in the case of the second-order spectra, additional interesting phenomena are observed with increasing concentration of implanted ions. As boron ions are introduced, a feature at 2970  $\text{cm}^{-1}$  appears, and its intensity is increased with increasing boron-ion dosage up through a fluence of  $5 \times 10^{14}$  ions/ $\text{cm}^2$ . For a fluence of  $1 \times 10^{15}$  ions/ $\text{cm}^2$ , the 2970- $\text{cm}^{-1}$  feature becomes broadened and shows a decrease in peak intensity. At fluences of  $5 \times 10^{15}$  ions/ $\text{cm}^2$  and above, the feature at 2970  $\text{cm}^{-1}$  cannot be resolved from the broad background. In comparison to second-order spectra previously reported for

samples with various crystallite sizes,<sup>13</sup> the results in Fig. 9(a) indicates that the effect of implantation of 100-keV boron ions is the introduction of disorder and reduction of the ordered crystallite size. We may identify the onset of amorphous behavior with the disappearance of the second-order spectral features. Second-order Raman spectra have previously been reported by Wright *et al.* for  $4.1 \times 10^{19}$   $^1\text{H}$  ions/ $\text{cm}^2$  at 15 keV showing a very broad band, peaking at 2890  $\text{cm}^{-1}$ , and a weaker broad feature at 2150  $\text{cm}^{-1}$ , not found in graphite and identified with the occurrence of conjugated acetylenic bonds.<sup>6</sup> We note that a combination of two peaks in the phonon density of states ( $1620 + 570$ )  $\text{cm}^{-1} = 2190 \text{ cm}^{-1}$ , which suggests a disorder-induced second-order feature analogous to the feature at 2970  $\text{cm}^{-1}$ .

As shown in Fig. 9(b) the effect of annealing in this case is even more dramatic than for the first-order spectra. For fluences of  $5 \times 10^{14}$  ions/ $\text{cm}^2$  and below, annealing at a temperature as low as 700  $^{\circ}\text{C}$  sharpens the 2730  $\text{cm}^{-1}$  line and reduces the intensity of the 2970  $\text{cm}^{-1}$  feature, indicating some restoration of order by the annealing process. For the sample that had been implanted at  $10^{15}$  ions/ $\text{cm}^2$ , this low-temperature (700  $^{\circ}\text{C}$ ) anneal restored the second-order Raman spectra to an extent corresponding approximately to that for the  $5 \times 10^{14}$  ions/ $\text{cm}^2$  unannealed sample. However, for fluences of  $5 \times 10^{15}$  ions/ $\text{cm}^2$  and above, annealing at 700  $^{\circ}\text{C}$  (or at temperatures up to 1000  $^{\circ}\text{C}$ ) did not restore any of the features in the second-order spectra. From comparison of Figs. 4 and 9 we suggest that the second-order lines are much more sensitive to the restoration of order by annealing than the first-order lines.

Results for the first- and second-order Raman spectra for graphite implanted with boron ions indicate three regimes of behavior. At low fluence ( $\phi \leq 5 \times 10^{14}$  ions/ $\text{cm}^2$ ), the first- and second-order Raman spectra show relatively sharp features which we identify with an ordered sample containing pockets of disorder caused by ion implantation. At a fluence of  $\sim 1 \times 10^{15}$  ions/ $\text{cm}^2$ , the first-order spectrum starts to broaden while the second-order spectrum becomes greatly attenuated, although it is partly restored by annealing. We suggest that at a fluence of  $1 \times 10^{15}$  ions/ $\text{cm}^2$ , the regions of disorder (see Fig. 1) begin to coalesce (percolate), forming islands of ordered regions surrounded by disorder. This may be called the microcrystalline regime. At this fluence level, annealing has the most significant effect on the first- and second-order spectra, consistent with the restoration of sufficient order

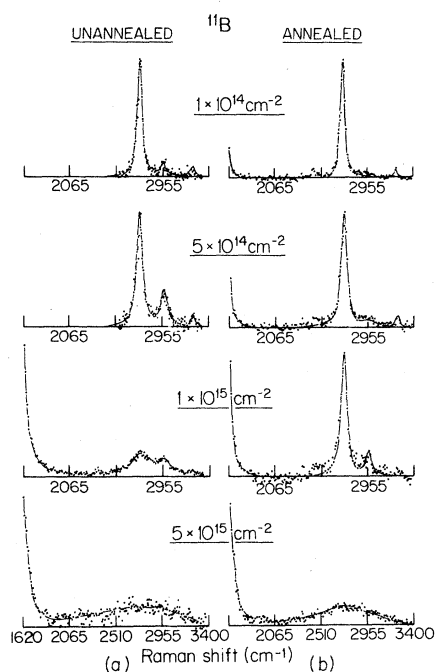


FIG. 9. Room-temperature second-order Raman spectra for various fluences ( $1 \times 10^{14}$  to  $5 \times 10^{15}$  ions/ $\text{cm}^2$ ) of  $^{11}\text{B}$  ions implanted into four HOPG samples. Results are given for the unannealed samples (a) and for the same samples annealed at 700  $^{\circ}\text{C}$  for 0.5 h (b).

to inhibit the coalescence of the disordered regions. At higher fluences where the coalescence of the disordered regions is well established, the microcrystalline regions shrink in size, and annealing is ineffective in inhibiting the coalescence of the disordered regions. This may be called the amorphous regime.

Work is in progress to explore the behavior of the electrical conductivity in these three regimes of ion fluence and to correlate the behavior of the electrical conductivity with the Raman spectra reported here.

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- <sup>1</sup>J. W. Mayer, L. Eriksson, and J.A. Davis, *Ion Implantation in Semiconductors* (Academic, New York, 1970).
- <sup>2</sup>B. L. Crowder, J. E. Smith, Jr., M. H. Brodsky, and M. I. Nathan, *Proceedings of the Second International Conference on Ion Implantation in Semiconductors* (Garmisch-Partenkirchen, Federal Republic of Germany, 1970), p.255; J. E. Smith, Jr., M. H. Brodsky, B. L. Crowder and M. I. Nathan, *J. Non-Cryst. Solids* **8-10**, 179 (1972).
- <sup>3</sup>R. Beserman and T. Bernstein, *J. Appl. Phys.* **48**, 1548 (1977).
- <sup>4</sup>Herbert Engstrom and J. B. Bates, *J. Appl. Phys.* **50**, 2921 (1979).
- <sup>5</sup>M. I. Nathan, J. E. Smith, Jr., and K. N. Tu, *J. Appl. Phys.* **45**, 2370 (1974).
- <sup>6</sup>R. B. Wright, R. Varma, and D. M. Gruen, *J. Nucl. Mater.* **63**, 415 (1976).
- <sup>7</sup>H. Maeta and Y. Sato, *Solid State Commun.* **23**, 23 (1977).
- <sup>8</sup>F. Tuinstra and J. L. Koenig, *J. Chem. Phys.* **53**, 1126 (1970).
- <sup>9</sup>S. A. Solin and R. J. Kobliska, *Proceeding of the 5th International Conference on Amorphous and Liquid Semiconductors* (Taylor and Francis, London, 1974), p. 1251; N. Wada, P. J. Gaczi, and S. A. Solin, *J. Non-Cryst. Solids* **35** and **36**, 543 (1980).
- <sup>10</sup>M. S. Dresselhaus and G. Dresselhaus, in *Physics and Chemistry of Materials with Layered Structures*, edited by F. Lévy (Reidel, Dordrecht, Holland, 1979), Vol. 6, p. 423; M. S. Dresselhaus and G. Dresselhaus in *Light Scattering in Solids*, edited by L. Cardona and G. Güntherodt (Springer, Berlin, 1981) (in press).
- <sup>11</sup>P. C. Eklund, G. Dresselhaus, M. S. Dresselhaus, and J. E. Fischer, *Phys. Rev. B* **16**, 3330 (1977); P. C. Eklund and K. R. Subbaswamy, *ibid.* **20**, 5157 (1979).
- <sup>12</sup>S. Y. Leung, G. Dresselhaus, and M. S. Dresselhaus, *Synth. Met.* **2**, 89 (1980).
- <sup>13</sup>R. J. Nemanich, G. Lucovsky, and S. A. Solin, *Mater. Sci. Eng.* **31**, 157 (1977).
- <sup>14</sup>D. E. Nixon and G. S. Parry, *J. Phys. C* **2**, 1732 (1969).
- <sup>15</sup>S. A. Solin, *Mater. Sci. Eng.* **31**, 153 (1977).
- <sup>16</sup>R. J. Nemanich and S. A. Solin, *Phys. Rev. B* **20**, 392 (1979).
- <sup>17</sup>P. C. Eklund, D. S. Smith, V. R. K. Murthy, and S. Y. Leung, *Synth. Met.* **2**, 99 (1980).
- <sup>18</sup>S. Y. Leung, M. S. Dresselhaus, and G. Dresselhaus, *Physica* (in press).
- <sup>19</sup>M. Maeda, Y. Kuramoto, and C. Horie, *J. Phys. Soc. Jpn.* **47**, 337 (1979).