Measurement of Thermodynamic Parameters of Graphite by Pulsed-Laser Melting and Ion Channeling

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The effect of 30-ns, 6943-Å, high-power laser irradiation on the surface of pristine and ion-implanted graphite has been studied by Rutherford-backscattering channeling spectrometry (RBS). The experimental results are explained by a model in which at a threshold energy density of 0.6 J/cm^2 the graphite surface melts, and the melt-depth measurements provide a simple estimate of the melting temperature (~ 4300 K) and the latent heat of fusion of graphite ($\sim 16 \pm 5$ kcal/mol).

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In the last few years laser annealing of isotropic solids has been extensively[1,2] studied and calculations and experiments with nanosecond pulses support the idea that at sufficiently high laser energy densities the surface of a semiconductor can be melted. Laser melting of amorphous and crystalline silicon layers has led to the measurement of important thermodynamic parameters of silicon and a better understanding of the amorphous/crystalline[3] phase. Rutherford-backscattering channeling spectrometry[4] (RBS) is ideally suited for these experiments, enabling measurement of composition, crystallinity, and stoichimetry of solid surfaces with adequate depth resolution (a few 100 Å).

Recently, it has been shown[5,6] that highly oriented pyrolytic graphite (HOPG), despite its polycrystallinity (grain sizes of approximately a few micrometers), channels high-energy ions since the mosaic spread of the c axis of the individual crystallites is comparable to the channeling critical angle. Thus the RBS and channeling technique provides a sensitive probe for the modification of the crystallinity of the near-surface layers of these samples.[7] The pulsed-laser heating of graphite is particularly intriguing because of the high basal-plane thermal conductivity and the poor conductivity of the material along the c axis. As a result, the surface of the material can be heated to very high temperatures; thereby melting could occur. The experiment takes on added significance because the measured phase diagrams of carbon are not complete and particularly at atmospheric pressures there are no reliable data on the phase diagram close to the accepted melting point of carbon. The measurements of Bundy[8] by flash heating at static pressures seem consistent with earlier published results[9] and their pressure dependence of the melting temperature of graphite is given by $T_m = -0.1163P^2 + 15.66P + 4000$, with T_m in kelvins and P in kilobars. Muncke,[10] using a model for the difference in chemical potential between liquid carbon and graphite and accepting Bundy's value for the heat of fusion of graphite, estimated the value for the heat of fusion of graphite at 0 kbar to be $H(0) = 23.8$ kcal mol^{-1}. This value is much higher than the heat of fusion predicted by Pitzer and Clementi.[11] In the present work we report measured values of these parameters obtained by laser melting of the surface of graphite using short, high-energy pulses and we obtained the value 16 ± 5 kcal mol^{-1}.

The HOPG samples were obtained from Union Carbide and the typical c-axis mosaic spread of the crystallites (average grain size, ~ 1 μm) was $\sim 0.4° \pm 0.1°$ as measured by the x-ray diffraction technique. Channeling was observed in these crystals with use of 2-MeV He^+ ions and the measured half-angle of 0.3° and minimum yield of 32% are consistent with the expected mosaicity of the crystallites.[6] Some of the HOPG samples were implanted with 1×10^{15} to 5×10^{15} As$^+$/cm^2 at 230 keV to produce a disordered near-surface region to study the laser irradiation effects. Fast impurity diffusion effects were studied in connection with the surface melting phenomena discussed below. The ruby laser pulses were generated in an oscillator (JK Lasers) and further amplified before entering a tapered quartz homogenizer. The sample when placed in proximity to the homogenizer received uniform irradiation over a diameter of 6 mm. The laser energy monitor was calibrated with use of the reproducible, threshold energy density required to melt the surface of an amorphous layer of silicon on a single-crystal substrate.[12] Typical laser pulses were Gaussian in time with a full width at half max-

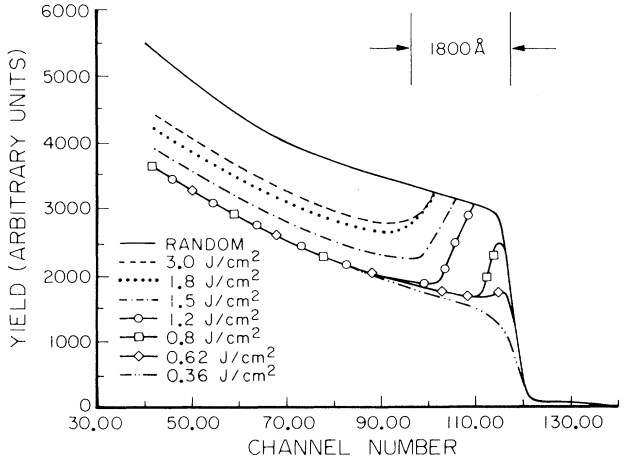

FIG. 1. The 2-MeV–He^+-ion channeling spectra of HOPG irradiated at various energy densities of 6943-Å ruby laser pulses. The spectrum at 0.36 J/cm^2 coincides with the spectrum from a pristine sample.

imum of 30 nsec.

In Fig. 1 is shown the channeling spectra of unimplanted HOPG for various laser energy densities incident on the sample. For laser energy densities of 0.62 J/cm^2 and above, a disordered region is seen to form. This region grows linearly in depth with increasing laser energy density (as shown in Fig. 2) and eventually saturates at an energy density of 1.8 J/cm^2. The extrapolation of the linear region to zero depth defines the threshold laser energy density of ~ 0.6 J/cm^2. The microstructure of these disordered layers was examined with transmission electron microscopy (TEM) and Raman spectroscopy. Selected-area TEM diffraction patterns in Fig. 3 demonstrate that above but near threshold this layer is amorphous [Fig. 3(a)] but at energy densities exceeding 2 J/cm^2 randomly oriented graphite crystals are seen [Fig. 3(b)].

The above data can be explained by surface melting. Using the values of specific heat[11] measured between $300 < T < 4000$ K and a penetration depth for 6943-Å laser light of ~ 700 Å, one estimates a melting temperature of ≈ 4300 K, identifying the threshold energy laser density of 0.6 J/cm^2 (Fig. 2) with melting of the near-surface region. The heat lost by thermal conduction is relatively insignificant during the first 30 nsec of the heating process. At energy densities greater than the melt threshold, the thickness of the disordered region increases linearly with laser energy density, suggesting that the energy coupled in by the laser goes mainly into melting the surface region, with insignificant heat losses due to conduction and radiation.[13] However, the molten layer will eventually cool by a conduction mechanism, though more slowly than an isotropic solid like silicon (i.e., ≤ 1 m/s), because of the highly anisotropic nature of the thermal conductivity of graphite, with poor thermal conduction along the c axis. At higher energy densities (> 2 J/cm^2), the regrowth velocity is expected to be slower, which may explain the appearance of graphite carbon under these conditions. This is analogous to the amorphization of Si with very

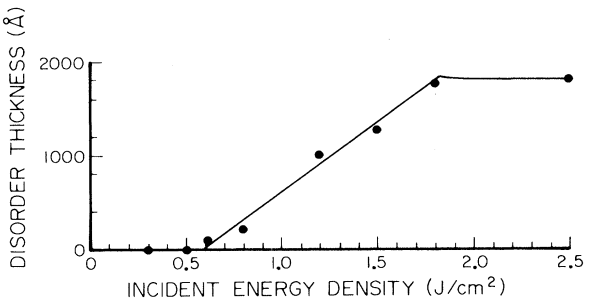

FIG. 2. The disorder layer thickness vs laser energy density. The threshold energy density of 0.6 J/cm^2 is indicated.

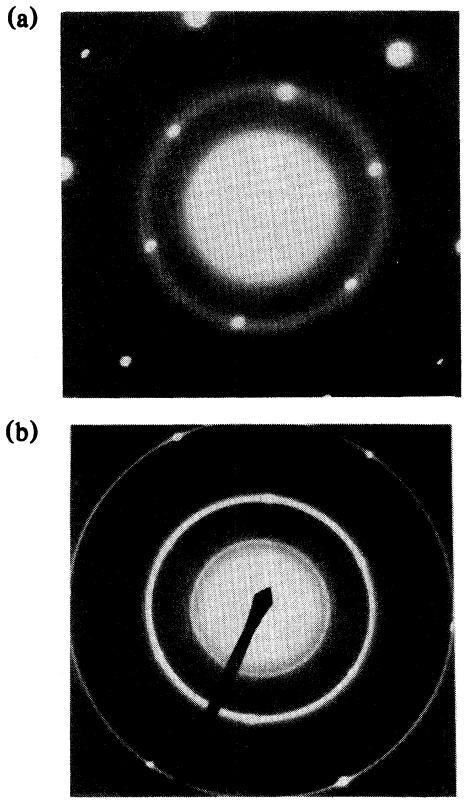

FIG. 3. Selected-area TEM diffraction patterns of HOPG surface layers irradiated with laser energy density of (a) 1.2 J/cm^2 and (b) 3.5 J/cm^2.

short pulses.[14] One important aspect of Fig. 3(b) is the appearance of the (001) spacing (the smallest-radius diffraction ring) which indicates the formation of crystallites with some having their c axis orthogonal to the original c axis of the substrate. It is difficult to explain this polycrystalline formation by a solid-phase process. This observation provides strong evidence for a melting transition having occurred. But as the deeper molten layers are produced, the surface temperature gets higher and remains molten longer, resulting in mass loss by evaporation. This evaporation causes an attenuation of the incident laser pulse and results in a saturation of the thickness of the disordered layer. The formation of an absorptive gaseous layer was directly confirmed by a cw probe laser beam[15] at 6328 Å, which was attenuated when the initial part of the high-energy pulse had been coupled into the surface of the solid. From the slope of the curve Fig. 2, we estimate a heat of fusion for graphite of 16 ± 5 kcal mol^{-1}.

The pulsed-laser modification of ion-implanted layers offers further evidence for melting, through observation of a reproducible laser energy threshold and the production of sharp order-disorder interfaces. Figures 4(a) and 4(b) show the depth profiles of the implanted As at various laser energy densities. At energy density of 0.8 J/cm^2 some of the surface damage is annealed out with some epitaxial regrowth and the As peak is split into two parts: one, weak and at the surface and the other close to the as-implanted position (1080 Å). It has been shown[7] that in graphite the implanted As does not diffuse along the c axis for isochronal anneals of 20 min at temperature as high as 2300 °C. Lateral diffusion is found to dominate. Hence the observed profiles of the As and the increased segregation of the impurity to the surface can only be explained by the formation of a molten layer which sweeps the As in the melt to the surface where most of the As vaporizes. Otherwise, to explain the motion of As to the surface would require a diffusivity of 10^{-4} cm^2 s^{-1}, too large for any solid-state diffusion process. This idea is supported further by the increasing arsenic segregation to the surface with increasing melt depth.

We therefore conclude that the effect of high-energy laser pulses leads to melting of the surface of graphite. The evidence for melting is as follows: (1) The existence of a sharp order-disorder boundary. (2) The segregation of impurities to the surface. The propagation of such impurities by a diffusion mechanism would require $D \sim 10^{-4}$ cm^2 s^{-1}, which is much too large for a solid-state diffusion process. (3) The existence of a sharp threshold in laser energy density in producing a disordered layer at the surface. (4) The linear increase in the width of the disordered layer with the laser energy density. (5) The formation of crystallites with c axes orthogonal to the original c axis of the substrate after high-dose irradiation.

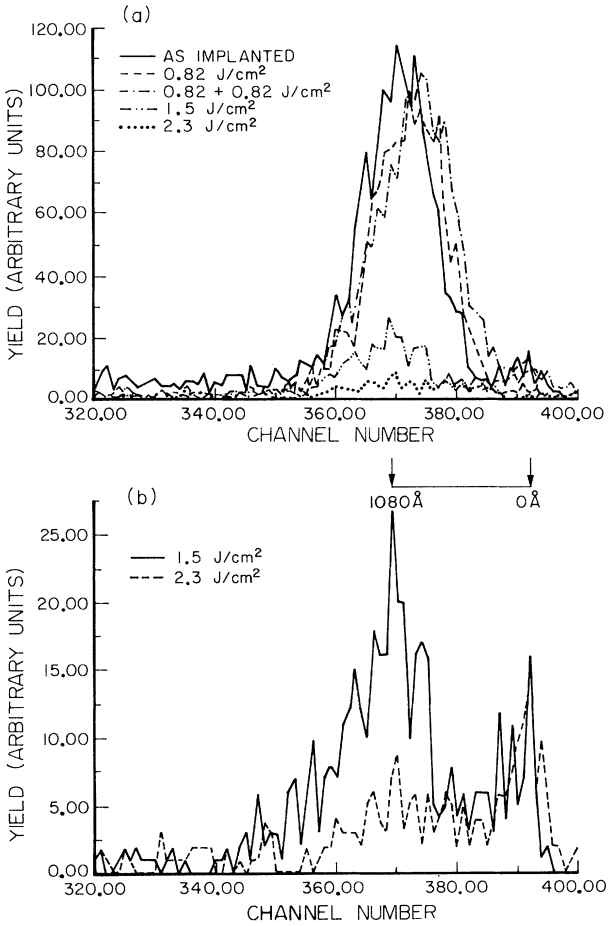

FIG. 4. Rutherford-backscattering spectra of As depth profile in HOPG implanted with 5×10^{15} As$^+$/cm^{-2} at 230 keV. (a) At various laser energy densities; in the case of $0.82+0.82$ J/cm^2, two 0.82-J/cm^2 pulses were used. (b) With the vertical scale magnified.

On the basis of the melting model we can extract a melting temperature of 4300 K and a heat of fusion of 16 ± 5 kcal mol^{-1}. Thus, pulsed laser irradiation and channeling provides a convenient way to study the thermodynamic properties of highly crystalline, refractory material systems close to the solid-liquid phase transition. Such studies would be otherwise difficult because of the high temperatures involved.

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[12]The ruby-laser energy density threshold required to melt ion-implanted silicon (As, $5\times10^{15}/\text{cm}^2$ at 150 keV) is 140 mJ/cm^2 as determined independently at Bell, Malvern, and Sandia Laboratories.

[13]Similar results have been observed in the case of laser melting of Si and Ge as well. The thermodynamic parameters calculated directly from the data with neglect of heat diffusion lead to answers which are $\sim 50\%$ different from those from a detailed calculation including thermal diffusion. Our simple calculation is justified in the case of graphite since (a) the thermodynamic parameters are not known as accurately and (b) the thermal conductivity of graphite along the c axis is very small.

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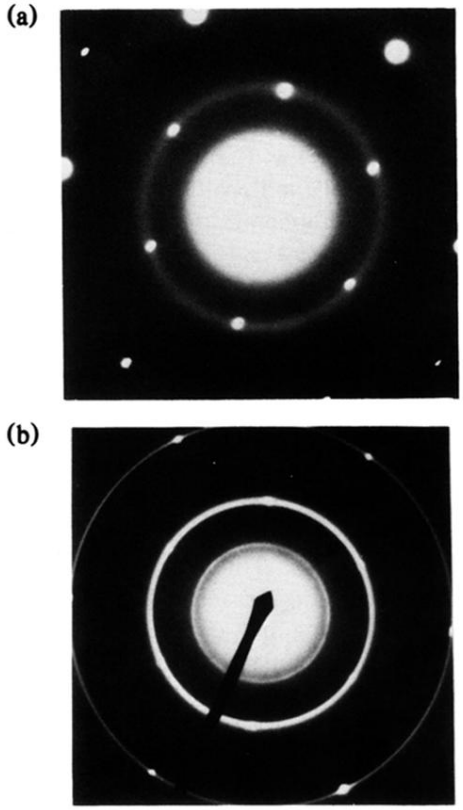
[15]Even at low energy density the As peak moves towards the surface (Fig. 4) supporting our idea of the loss of carbon by sublimation. However, this will not explain the segragation of As to the surface.



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