PHYSICAL REVIEW B VOLUME 59, NUMBER 21 1 JUNE 1999-I

Laser-irradiation-induced structural changes on graphite

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(Received 2 October 1998)

Pyrolytic graphite has been irradiated with high-energy density laser pulses (248 nm wavelength, 20 ns duration, and up to 250 J/cm^2 energy density). Craters with depth up to 5 μm have been obtained by irradiating with a single pulse and the bottom of the craters has been analyzed with many techniques to investigate the possible morphological and structural modifications induced in the irradiated material where temperature and pressure fields, appropriate to the graphite-diamond phase transition, may be achieved. Melting of the surface layers of the irradiated graphite was realized, as established with scanning electron microscopy, while the estimated and measured pressure attained a maximum value on the order of 2.5 GPa. The temperature profile depends on the depth below the irradiated surface and the observed structural modifications are associated with different depths. Just below an ordered sp^2 hybridized nanocrystalline graphite surface layer, a disordered graphitic layer was formed, within which diamond particles with spheroidal geometry are embedded. [S0163-1829(99)12921-7]

Laser irradiation may induce structural changes in irradiated targets, in connection to the temperature and pressure fields experienced by the irradiated materials. The pulsed laser ablation (PLA) process is widely utilized for thin-film deposition: basically, this requires that the plume, expanding out of the irradiated surface, impinges onto a substrate.[1]

Carbon films deposited by this technique, under appropriate irradiation conditions, appear interesting because of their diamondlike properties.[1] However, much less attention has focused on the changes induced by the laser irradiation of graphite targets, with laser parameters appropriate to generate strong ablation. In this case the target may experience pressures in the GPa range and temperatures of several thousands degrees K, which may provide suitable conditions to induce significant structural modifications in the irradiated material.

In this work we report on the structural and morphological modifications of pyrolytic graphite samples (purity 99%, density 1700 kg/m^3, average crystallite size 7 nm) subjected to PLA both in air and in vacuum. We used a Lambda Physik LPX220i KrF excimer laser (wavelength 248 nm, pulse duration 20 ns) by which fluences up to 250 J/cm^2 and power densities up to 12.5 GW/cm^2 may be deposited on a surface area of $0.3\times 0.9\,\mathrm{mm}^2$.

By irradiating the graphite target with a single laser pulse, visible craters, irregular in shape, with a depth up to about 5 μm have been obtained. By a DEKTAK profilometer, lateral dimensions and depth of craters were evaluated as a function of the pulse energy (in the range from 50 to 250 J/cm^2), and pulses number (between 1 and 1000). As a rule, the first pulse ablates much more material than all the subsequent ones, suggesting that it induces structural and optical changes in graphite at the crater bottom;[2] at a fluence of 250 J/cm^2, the average depth of the crater produced by the first pulse is 5 μm and the mass of the ablated material is 2 μg. Scanning electron microscope (SEM) pictures clearly show that the crater bottom (Fig. 1) is always covered by a layer, a few tens of nm thick, with regular and rounded contours, which suggests the occurrence of a melting and resolidification process. Indeed, the surface tension in liquid carbon is

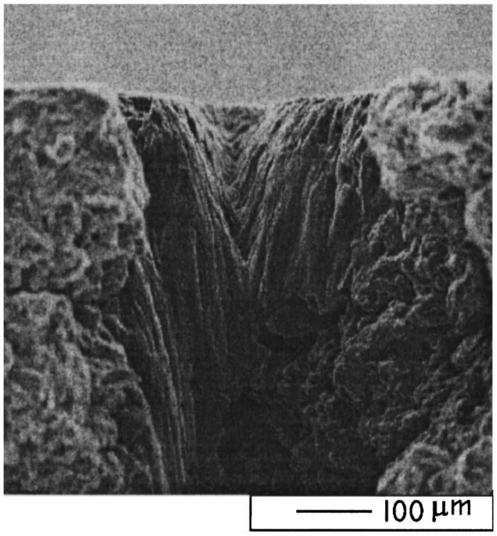

FIG. 1. SEM picture showing that the crater bottom is covered by a layer, a few tens of nm thick, with regular and rounded contours suggesting the occurrence of a melting and resolidification process.

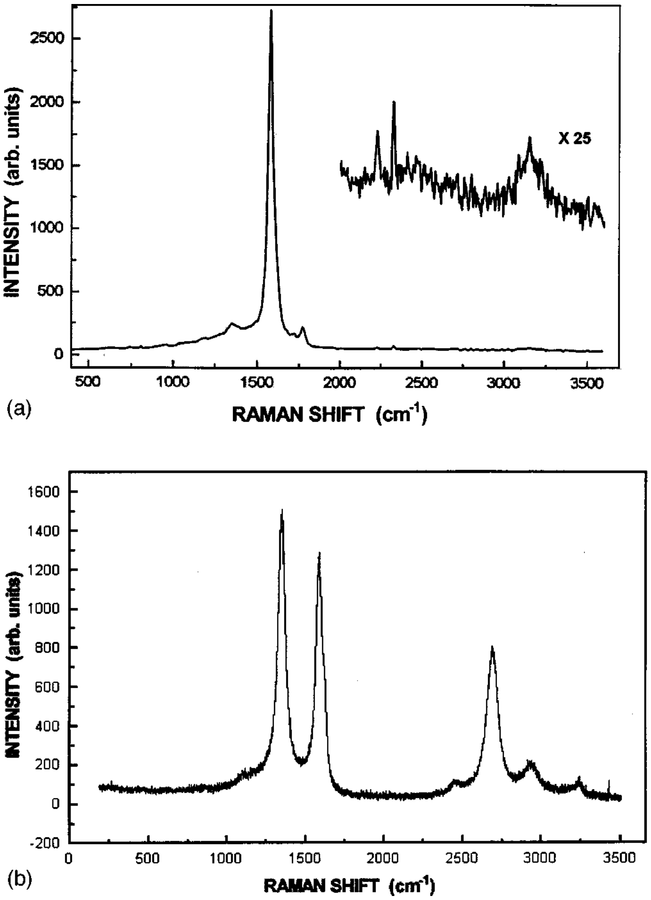

FIG. 2. (a) UV μ-Raman spectra (wavelength 244 nm, 1 μm spot diameter, and probe penetration depth comparable to that sampled by XRD) of the crater bottom on a laser-ablated region, showing that the material appears as an ordered graphite. (b) μ-Raman spectra taken in the visible region (wavelength 514.5 nm, probe penetration depth of about 100 nm) from the same region as (a) showing a considerable degree of structural disorder, with average crystallite size of 1.5 nm.

very high while the wettability of the basal plane of pyrolytic graphite is quite poor.

X-ray-diffraction (XRD) spectra of crater bottoms (not reported here) were recorded in the Seeman-Bohlin configuration, at an incidence angle of 1°, thus providing structural information from a depth of about 30 nm; no significant changes were observed with respect to the structure of the virgin samples.

From the same crater bottoms, UV μ-Raman spectra (wavelength 244 nm, spot diameter 1 μm, probe penetration depth comparable to that sampled by XRD) were taken. Again, the material appears to be ordered graphite, as shown in Fig. 2(a). Conversely, μ-Raman spectra taken in the visible region (wavelength 514.5 nm, probe penetration depth of about 100 nm) from the same regions of the target [Fig. 2(b)] show a considerable degree of structural disorder, with an average crystallite size of 1.5 nm, as estimated from the ratio ID/IG between the intensities of the D and G peaks, centered at about 1355 and 1580 cm^{-1}, respectively.[3] The evolution of the peaks in Raman spectra in the visible region as a function of pulse number, between 1 and 1000, as well as of fluence, in the range 50–250 $\mathrm{J/cm}^2$, do not show evident trends: no substantial differences are observed with respect to the features of the spectrum reported in Fig. 2(b).

Energy-dispersive spectroscopy of the virgin graphite (not reported) shows some oxygen contamination, presumably trapped in the pores; after irradiation, the relative oxygen content at crater bottoms is lowered, thus indicating a transition to a more compact, less porous material, down to a depth of about 1 μm.

The results of the above analyses are likely to indicate that the structure of the laser-irradiated graphite undergoes different changes at different depths. Such a modification can be interpreted, starting from literature estimates of the achieved temperature[4,5] and pressure values under irradiation.[6,7] To describe the thermodynamic conditions experienced by the irradiated target, it is necessary to infer about the space and time evolution of both pressure and temperature. Temperature evolution as a function of time and depth in the target has been calculated:[4] in the surface layer, which directly absorbs radiation, temperature rises up to values close to the thermodynamic critical value (6800 K in graphite); the superheated material most probably undergoes thermodynamic phase explosion[8] and is ejected out of the target surface. At depths below the absorbing surface layer, the temperature increases through the heat diffusion mechanism: in the layers where the temperature overcomes the melting point (4800 K in graphite), the material undergoes a solid-liquid transition. Moving more in depth, there are regions where temperatures do not exceed the melting point. The appropriate depths that are interesting in each of the above temperature regimes (thermodynamic critical temperature, melting temperature, and temperature below the melting point) depend on the deposited energy density and on the position with respect to the center of the laser spot on the target. The lifetime of the transient temperature fields depends on depth and on the presence of the liquid phase as well: as an order of magnitude, such a lifetime is about ten times the pulse duration in the region where the material remains solid and it lasts about 50 times the pulse duration in the liquified region.[6,8] The pressure trend depends on the plume evolution; indeed, the generated plume has an internal pressure, besides exerting a pressure (momentum conservation) on the surface from which it departs. The transferred momentum was calculated and measured;[7,9] we estimated it from the oscillations of a pendulum stricken by a single laser pulse (energy = 450 mJ and energy fluence $=215\,\mathrm{J/cm}^2$) and it resulted in about 3.5×10^{-5} Ns, corresponding to an average pressure of 0.8 GPa. The intensity of such a pressure pulse decreases on moving towards the periphery of the area irradiated by the laser and is proportional to the flux of the ejected particles. The maximum pressure, as evaluated from the Gaussian spatial profile of the ejected particles, is 2.5 GPa. The duration of the pressure impulse depends on plume evolution: we estimate that 200 ns after the laser shot, most of the generated plume is far from target surface, which therefore experiences no additional mechanical load. By considering together the time evolution of both pressure and temperature and including it into the C-phase diagram, we obtain some hints on the pressure-temperature path followed by the laser-irradiated target region and consequently on the structural changes it undergoes. The liquified material solidifies in the thermodynamic stability region of graphite: such a

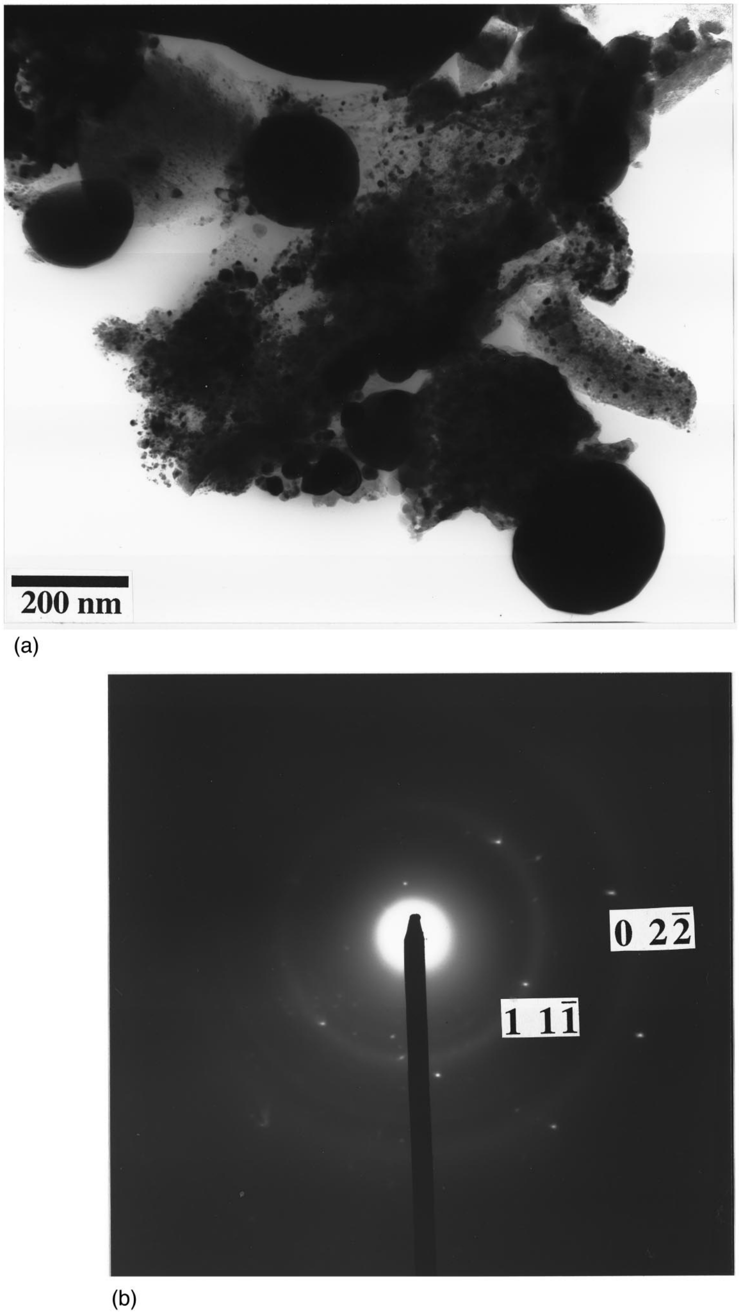

FIG. 3. Bright-field image (a) and corresponding to a selected area diffraction pattern (b) of the laser-ablated sample. Spherical crystallites are visible. The diffraction pattern exhibits diffuse halos, typical of an amorphous structure, and crystalline spots. A set of spots shows a near [011] orientation of the diamond cubic phase, according to which it has been indexed.

transition lasts for a time (50 times the pulse duration, see above) sufficient to nucleate and grow graphite crystals with nanometric size. On the contrary, the graphite below the liquified layer undergoes a solid-state phase transition because of the high temperature it experiences while it is brought to a pressure near that required by the pressure-temperature phase diagram to attain the diamond structure. The above considerations on the pressure-temperature profiles induced in the laser-irradiated graphite may explain the ubiquitous presence of a structurally ordered thin surface layer, covering a thicker layer of disordered material, which undergoes conditions similar to those induced in shock compression experiments. Therefore, it is likely that locally, pressure-temperature values are attained appropriate to graphite-diamond solid-state transition with formation of diamond crystallites. These were not revealed by Raman spectroscopy in the visible range, due to the low (1/60) cross section for anelastic light scattering of sp^3 hybridized atoms with respect to sp^2 ones.[10] We analyzed by transmission electron microscopy (TEM) several areas at the crater bottom of targets irradiated with 1000 pulses at 200 J/cm^2. Besides polycrystalline graphite regions, with an average crystallite size of 5–50 nm, we observed spheroidally shaped, isolated crystallites, with typical diameter ranging from 20 to 150 nm, having cubic structure [Fig. 3(a)]. The diffraction pattern of the selected area [Fig. 3(b)] displays both the halos due to a carbon amorphous structure, and a set of spots. Such a reflection can be indexed according to the diamond phase as shown in Fig. 3(b). The possibility that such a pattern is due to impurities is ruled out by the low impurity concentration of the virgin samples as compared to the spheroidal particle size.

Before concluding, some words should be said about the time scale (≈ 200 ns) involved in the suggested graphite-diamond solid-state transition. An inspection of the literature, concerning radiation-induced structural changes in solids, seems to indicate that under appropriate conditions (high temperature and high pressure) phase transition may occur in a ns regime without involving a liquid phase.[11] However, work is in progress to further clarify this point by also considering the possibility that partially molten layers may be involved in the observed phase transition.

In conclusion, structural modifications of graphite targets irradiated with high fluence laser pulses have been obtained. The depth dependence of such modifications is explained on the basis of the C-phase diagram and on the time evolution of temperature and pressure fields associated with the laser irradiation process. Just below an ordered sp^2 hybridized nanocrystalline graphite layer, a disordered graphitic layer is formed, within which diamond particles with spheroidal geometry are embedded.

We thank Dr. R. Tagliapietra (Renishaw S.p.A.) for UV Raman spectroscopy measurements and Dr. R. Kelly and Professor C.E. Bottani and Professor G. Caglioti for useful discussions.

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