Raman Studies of Graphitic Carbons Modified by High Power Laser Irradiation

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Abstract. Conventional Raman and Raman Microprobe spectroscopy are used to determine the structural changes which occur in graphite after being irradiated with a high power Ruby laser. The Raman spectra for graphite suggest that the microstructure of the laser irradiated region of the sample consists of randomly oriented crystallites of about 100Å size. The microprobe analysis revealed a highly disordered boundary zone betwen the irradiated spot and the surrounding unirradiated region.

The properties of carbon close to its melting point remain largely unexplored because of the experimental difficulties imposed by the high melting temperatures. It has recently been demonstrated[1] that the near surface region of graphite can be brought to the high temperature regime, and even melted, by high power pulsed laser irradiation thus providing a convenient way to investigate the physical properties of carbon in the temperature region close to the solid-liquid phase transition. We have used Raman spectroscopy to study the changes in the crystalline structure associated with the melting and resolidification process since these changes provide important information about the evolution of the near surface region during the heating and cooling processes.

Thin ~0.5cm^2 sections of highly oriented pyrolytic graphite (HOPG) were irradiated with pulses of a Ruby laser ($\lambda \approx 6910$Å) of ~30 nsec FWHM duration and energy densities in the range 0.1 to 5.0 J/cm^2. Raman spectra were taken using the ~4880Å line of a cw argon-ion laser in two different systems: a conventional set-up in the backscattering configuration and a Raman microprobe which could be focused down to a spot of ~4μm^2 to study the spatial variations of the crystallinity.

The main features of the Raman spectrum of HOPG consist of a first-order zone center mode at ~1580cm^{-1} and a second-order overtone at ~2720cm^{-1} (See Fig. 1a). Upon irradiation with laser energy densities of about 1J/cm^2 a disordered region is seen to form as evidenced by the growth and line broadening of the disorder-induced ~1360cm^{-1} line in the first-order Raman spectrum and the formation of a broad band in the second-order spectrum. As the pulse energy density is increased between 1J/cm^2 and 3J/cm^2 the line at ~1360cm^{-1} grows at the expense of the ~1560cm^{-1} line while the two

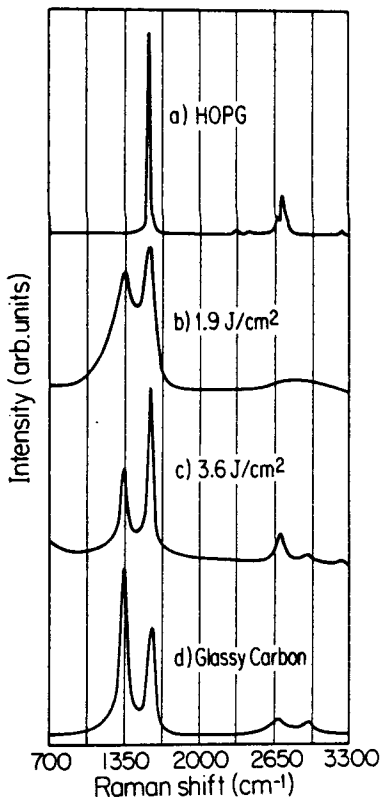

Figure 1. First and second order Raman spectra for pristine HOPG (a), laser irradiated HOPG (b) and (c) and glassy carbon (d). Pulse energy densities for the laser irradiated samples are indicated.

lines further broaden and coalesce. This behavior is represented by Fig. 1b. A useful estimate of the degree of crystallinity of the lattice is provided by the relative intensity of the disorder induced ~1360cm^{-1} line relative to the Raman-allowed ~1580cm^{-1} line = I_{1360}/I_{1580} which was shown to vary inversely with the crystallite size L_a of the graphite structure. In addition, the linewidths (FWHM) of the ~1360cm^{-1} and 1580cm^{-1} lines, reflect the degree of disorder induced in the lattice.[2] A summary of the results for the first-order Raman spectra of the pulsed-laser irradiated HOPG is given in Figs. 2a and 2b where the intensity ratio I_{1360}/I_{1580} as well as the linewidths of the two lines are, respectively, plotted as a function of the energy density of the laser pulse. Figures 2a and 2b show that irradiation with pulse energy densities between 0.6J/cm^2 and 3J/cm^2 produce a highly disordered region with very small crystallite sizes. However, as the laser pulse energy density is further increased above 3J/cm^2 the behavior changes significantly: in the first-order spectrum the two lines at ~1360cm^{-1} and ~1560cm^{-1} narrow and become well defined, and in the second-order spectrum, instead of the broad band, two peaks at 2720cm^{-1} and 2945cm^{-1} become clearly defined. Figs. 1c and 1d and Figs. 2a and 2b show that after irradiation with pulse energy densities of about ~4J/cm^2 the Raman spectrum of the irradiated HOPG shows a strong resemblance to the Raman spectrum of glassy carbon, suggesting

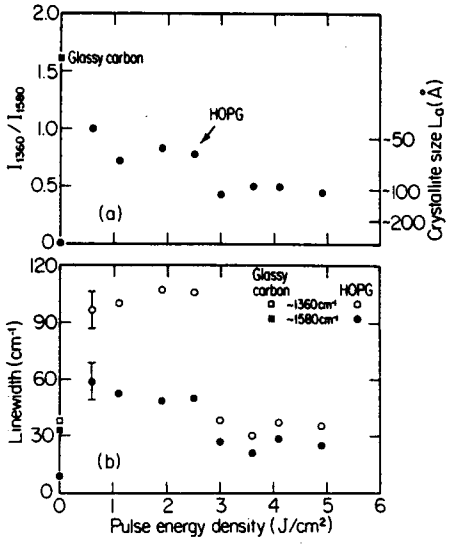

Figure 2. a) Relative intensity of the disorder induced ~1360cm^{-1} line to the Raman allowed ~1580cm^{-1} line as a function of laser pulse energy density.
b) Linewidths (FWHM) of the disorder induced ~1360cm^{-1} line and Raman allowed ~1580cm^{-1} line as a function of laser pulse energy densities. Note the change in behavior for pulse energy densities larger than 3J/cm^2.

that at this high energy density the microstructure of the disordered region consists of randomly oriented crystallites of about 100Å size. TEM studies support this observation.[1]

Analysis with the Raman microprobe system permitted identification of three regions on the samples surfaces with quite different characteristics. In the region well beyond the irradiated spot, the characteristic spectra of pristine HOPG were observed. Within the irradiated zone the spectra were similar to those obtained with the conventional Raman system. The interesting feature revealed by the microprobe analysis was the large amount of disorder in the boundary region between the outer region and the irradiated zone. This behavior was explained [3] in terms of the thermo-mechanical stresses induced in the graphite structure because of the large temperature changes during the irradiation.

The changes in the structure of HOPG induced by the high energy laser pulses can be explained in terms of the previously proposed melting model[1] by comparing with the extensively studied behavior of silicon under pulsed laser irradiation.[4] The crystalline structure of silicon after laser irradiation depends strongly on the velocity of the solid-liquid interface during the solidification of the molten layer. For pulses with relatively low energy density, the heating and cooling processes are very fast and the crystalline structure is left in the amorphous phase. This behavior would correspond to pulse energy densities smaller than 3J/cm^2 in the case of graphite. For pulses with larger energy densities ($\gtrsim$ 3J/cm^2 in the case of graphite), the cooling rate is slower so that the substrate remains at high temperatures for longer time, thus allowing for the nucleation and growth of crystallites; the resulting state is therefore polycrystalline. In the case of silicon, a third type of behavior is observed at even larger pulse energy densities, where the regrowth velocity is slow enough to allow epitaxial regrowth. This behavior has not been observed in our pulsed laser irradiation studies of graphite.

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