

The Optical Properties of Graphite Under Intense Picosecond Laser Illumination¹

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Picosecond laser ellipsometry has been used in the visible to estimate for the first time the index of refraction of highly oriented pyrolytic graphite samples at high temperatures. While recent experiments seem to indicate that molten graphite behaves in many respects as a metal, investigation of optical properties with picosecond laser pulses consistently shows a reduced reflectivity value as soon as the threshold value of laser fluence for surface melting is exceeded. This occurrence may be interpreted as a reduced conductivity of the liquid phase. The experimental conditions are discussed, and in particular, the possible occurrence of optically thick layers of matter in front of the hot surface during the measurements is evaluated.

KEY WORDS: ellipsometry; graphite; high temperatures; laser pulse; index of refraction; melting; reflectivity.

1. INTRODUCTION

Investigations on the high-temperature phases of graphite have been published since the beginning of this century [1], nevertheless, several aspects still remain to be clarified. In particular, a consensus on the electronic properties of the liquid phase of graphite has not been reached. It was a well-established experimental fact that graphite sample would sublime when heated at atmospheric pressure. However, by providing the energy for melting in sufficiently short periods of time, it is conceivable to be able to melt the surface of a sample before substantial evaporation occurs. Along this line of reasoning, pulse laser heating techniques applied to this

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problem have provided substantial evidence of transient melting at atmospheric pressure of thin layers of graphite. An added advantage of this techniques is that, if heating occurs in a sufficiently short time, evaporation from the surface can be avoided altogether for short periods of time after melting. So the optical properties of liquid layers of graphite may be studied directly by time-resolved optical probing of the surface.

Laser investigations in the nanosecond regime [2], although achieving surface melting of graphite samples, as evicted from postmortem analysis, could not [3] follow the evolution of the optical properties of the hot graphite surface due to sublimation of the material. With picosecond laser excitation [4], instead, heating of the surface is accomplished before substantial evaporation takes place and therefore direct observation of optical properties such as reflectivity and/or transmission becomes possible under suitable temporal resolution. In particular, a substantial decrease in the reflectivity upon melting has been observed in the visible, infrared, and ultraviolet.

Recently, femtosecond excitation and melting of graphite and diamond have been achieved [5] following other femtosecond excitation studies [6] on the solid phase of graphite which revealed an extremely rich evolution of the optical response in this time domain. The results showed a distinct new high reflectivity phase, lasting less than 5 ps, characteristic of the molten phase. On a longer time scale, the data showed a reduction in reflectivity, in agreement with earlier picosecond observations. Finally, pulsed electrical heating experiments on carbon whiskers [7] resulted in a liquid phase for graphite consistent with a metallic behavior. All these data were corroborated by recent molecular dynamical calculations [8] which evaluated a metallic high-temperature steady-state behavior of graphite at low pressures.

In line with systematic investigations of the optical properties of graphite at high temperatures, we present here the results of picosecond ellipsometry performed on graphite samples excited above melting temperature by picosecond laser pulses. This technique has been used in order to evaluate on a transient basis the complex index of refraction of solid surfaces. The data refer to visible radiation ($\lambda = 0.53 \mu\text{m}$) and extend similar measurements in the near-infrared performed earlier [9]. The results consistently show a reduction of both real and imaginary parts of the index of refraction, in agreement with previous picosecond measurements. The implications of these results in the light of contrasting data mentioned are briefly discussed.

2. LASER HEATING AND DIAGNOSTIC TECHNIQUES

The kinetics of laser interaction with strongly absorbing solids has been discussed in detail by many authors, in different temporal regimes [10]. When efficient heating is the main concern, as in the present situation, picosecond laser pulses have distinctive advantages over other excitations in different temporal domains. Basically, heating for shorter times does not produce more rapid heating since electron-phonon interactions occur on this time scale. Conversely, heating for longer times delivers more energy to the sample, which may result in sublimation of the surface and heating of thicker layers of material. The main points on picosecond laser interaction of relevance in the present topic may be summarized as follows.

Within times of the order of the laser pulse duration heat is deposited into a layer of thickness $d_{\text{abs}} = 1/\alpha$, α being the absorption coefficient of the radiation, thermal diffusion not playing any role. Also, evaporation may be negligible on this scale since there is little time for the atoms at the surface to move considerably and generate an optically thick layer of matter [10]. Finally, ionization of the material at the surface and production of plasma may occur at high laser intensities, however, the threshold for this effect to occur is decreasing with pulse duration. Picosecond laser plasma effects are thus likely to occur only at fluences many times above the melting threshold. It should be noted that shorter laser pulses need more intensity ($\text{W} \cdot \text{cm}^{-2}$) in order to reach the same temperature, since to do so they need to provide the same energy to the target. Therefore, it may be possible that the threshold fluence for plasma formation with femtosecond pulses is considerably lower than with picosecond laser pulses.

The picosecond domain of interaction, therefore, seems most suited for efficiently heating the matter at high temperature.

Observations of the phase transition of the surface of the sample is most readily accomplished by monitoring the evolution of the reflectivity. By using a weak laser pulse slightly delayed with respect to the heating pulse and focused in the center of the exposed area, one can measure the reflectivity with a temporal resolution given by the duration of the probing pulse itself. This method, known as optical pump and probe, provides excellent results in a temporal region inaccessible by electronic detectors.

In the present measurements, both the real part and the imaginary part of the index of refraction of liquid graphite are evaluated. Clearly, a single reflectivity measurement does not provide sufficient information. Two independent measurements are required. This may be obtained by using ellipsometry, that is, by measuring the reflectivity in two mutual perpendicular polarization directions. By doing so, inversion of the Fresnel formulas provides the required values of n and k . This derivation is based

on the assumption of a sharp interface and of a bulk material, i.e., a uniform surface layer thicker than the penetration depth of the probing radiation.

3. EXPERIMENTAL RESULTS

In the present experiment, samples of highly oriented pyrolytic graphite (HOPG) are used, with the *c*-axis perpendicular to the surface of the sample. The initial, room temperature reflectivity and therefore the index of refraction of this sample have been measured to correspond to the values quoted in the literature within the experimental errors.

The laser source used in the present experiment is an actively passive mode-locked Nd:YAG laser delivering a few millijoules of laser energy at $1.06\ \mu\text{m}$ in 30-ps pulses. A second harmonic generator provides frequency-doubled radiation in the visible ($0.53\ \mu\text{m}$, 20 ps). The infrared laser pulses are used to heat the material, while green light pulses monitor the instantaneous reflectivity of the sample. All beam transverse profiles are gaussian in shape. The temporal evolution of the pulse has been checked via standard autocorrelation techniques. A long-focal length ($\approx 1\text{-m}$) lens provides an excitation spot $\approx 0.2\ \text{mm}$ in diameter. At its center, the green probe spot $\approx 30\ \mu\text{m}$ in diameter probes a uniformly heated portion of the sample. The geometry of the apparatus can be described as one-dimensional across the depth of the sample.

Three silicon detectors, equipped with suitable diffusers and interference and neutral density filters have been used throughout the experiment. Their linearity has been carefully checked against a pyroelectric energy meter in the appropriate range of laser excitations. The output of the detectors is proportional to the laser fluences of the pump beam at the target, to the reflected and incident fluences of the probing beam. The ratio of the two latter channels is proportional to the instantaneous reflectivity of the sample through calibration constants which are determined by using samples of known reflectivity. The output from the detectors is then fed to a data acquisition system that shapes the analog data in a form directly compatible with a standard analog-to-digital converter card of a personal computer, where data are analyzed and stored. For each laser pulse, the surface of the sample is moved into the focal plane of the lenses so as to expose each time a fresh portion of the sample. Visual inspection of the irradiated area is performed via an on-line microscope.

Figures 1 and 2 illustrate a set of the data obtained. Plots of the reflectivity of HOPG samples versus pump laser fluence are presented for two mutually perpendicular polarizations of the probing beam and different delays of the probe with respect to the pump pulses. The angle of incidence

is 70° . In this set of experiments excitation is provided by infrared laser pulses, in contrast with previous measurements [4] in which green pulses have been used for heating the HOPG sample surface. Due to the increased absorption coefficient α , the heated layer is reduced as well as the threshold pump fluence at which melting first occurs. While the linearity of our fluence scales in Figs. 1 and 2 has been carefully checked, it has not been possible to achieve a correspondingly good absolute calibration. The scales shown are therefore merely indicative of the range of pump fluence covered

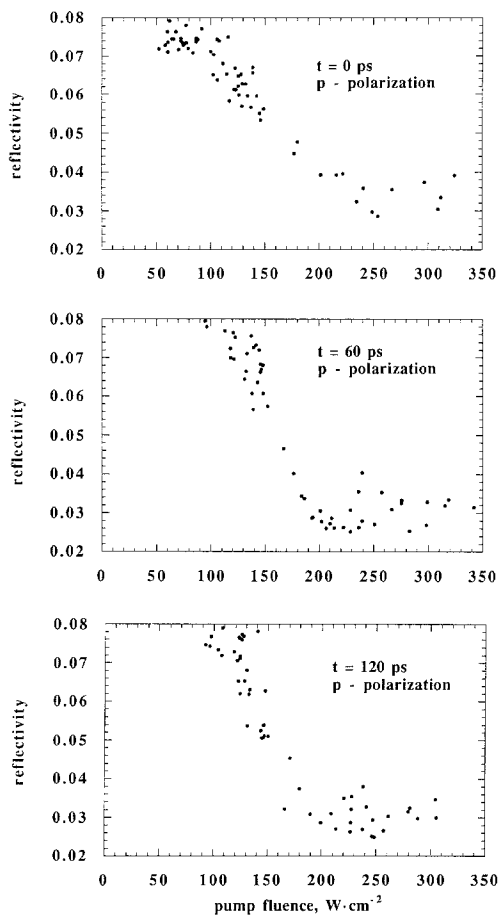


Fig. 1. Reflectivity of highly oriented pyrolytic graphite at $0.53 \mu\text{m}$ for an angle of incidence of 70° versus pump laser fluence ($\text{W}\cdot\text{cm}^{-2}$) for the delays t shown from the peak of the excitation pulse. The reflectivities refer to p-polarization of the probe beam.

by the measurements. On the other hand, the reflectivity scales shown turn out to be strongly different for the two polarizations at this angle of incidence, as expected for reflections close to the pseudo-Brewster angle in directions parallel (p) and perpendicular (s) to the plane of incidence of the probing beam.

All the data in the figures show a sharp decrease in the reflectivity of the sample as soon as a critical fluence value for the pump beam has been exceeded. This critical value is coincident with the appearance of damage on the surface of the sample. Melting of the surface has therefore occurred. The amount of decrease in the reflectivity is extremely large. Both reflectivities drop by a factor ≈ 3 , well within the laser pulse duration. This is

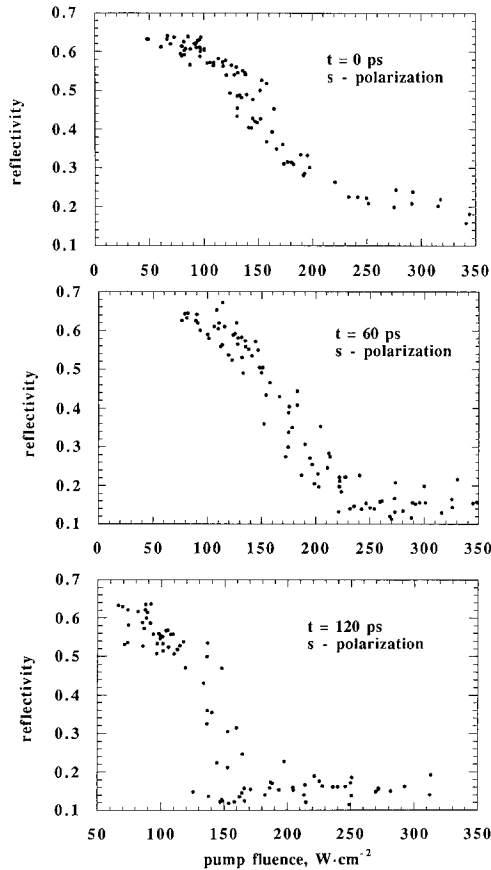


Fig. 2. Same as Fig. 1 but with s-polarization of the probe beam.

indicative of the amount of disruption caused by the interaction. Despite the scattering of the experimental data, due to both sample irregularities and noise in the detector system, increasingly steep negative slopes are observed at longer delay times. Two different mechanisms may contribute to this behavior. First, the finite duration of the pump and the probe pulses implies that the observed reflectivity values are in fact convoluted values with a characteristic duration of the order of $\tau_{\text{eff}} \approx [\tau_{\text{pump}}^2 + \tau_{\text{probe}}^2]^{1/2}$, where $\tau_{\text{pump}} = 20$ ps and $\tau_{\text{probe}} = 30$ ps are the durations of the two laser pulses. Therefore, a smoothing of the reflectivity values is expected when temporal overlap of the two laser pulses occurs. Second, when the pump fluence is close to the threshold value, very thin layers of material are molten and some contribution to the reflectivity from the solid bulk material is expected. At higher laser fluences this effect disappears, as Figs. 1 and 2 show.

Similar sets of data have been taken for different values of the angle of reflection. The behavior of the reflectivity plateau observed after melting does not change for delay times longer than 120 ps. A slow recovery of the reflectivity is observed at delay times above 0.5 ns, as already reported. The constant values of the reflectivity at 120 ps have thus been taken as representative of the reflectivity of the molten phase of graphite.

Upon inversion of the Fresnel formulas the resulting values for the complex index of refraction at $0.53 \mu\text{m}$ have been evaluated and are illustrated in Fig. 3, together with corresponding solid-state values. Also, previous measurements in the infrared are illustrated. The error bars refer to measurements in a single angle of incidence and are well representative of the uncertainties involved in such measurements. The errors in the real

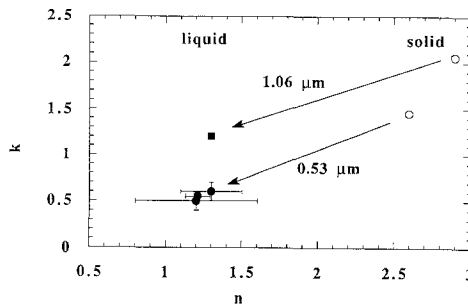


Fig. 3. Values of the complex index of refraction of HOPG graphite in the solid phase at room temperature (open circles) and in the liquid phase (filled circles and squares) for 0.53- and 1.06- μm radiation.

part of the index of refraction are larger when deduced from smaller angles of incidence, where the inversion procedure is less accurate. In all cases a reduction of both the real and the imaginary part of the index is observed.

4. DISCUSSION AND CONCLUSIONS

The data obtained in the present experiment all point to a strong reduction of the index of refraction of graphite upon melting and are consistent with the observations previously performed in the infrared [9]. This variation of the index of refraction corresponds therefore to a decrease in the dielectric function also in the visible. Both the real and the imaginary parts of ϵ are decreasing at the phase transition. This might suggest that less metallic conditions exist in the liquid phase as compared to the solid phase of graphite, unless a compensation between the Drude term and the bound electron contribution in the dielectric constant occurs at high temperatures. However, the considerable decrease in the imaginary part of the index of refraction, k , should be stressed. Under the assumptions used here this means that visible radiation can penetrate a factor ≈ 2 deeper into molten graphite than in the solid. Also, if this process is iterated, the more the radiation penetrates into the liquid, the deeper the molten layer becomes and considerable thicknesses may be formed by this mechanism. Therefore, from postmortem examination of the sample, misleading conclusions may have been drawn by attributing the thickness of the molten layers to metallic thermal diffusivity instead.

The question whether the observations are referring to the hot surface of the sample rather than to an optically thick layer is now addressed. As already mentioned in other publications [10, 11], it is unlikely that at the fluence levels near threshold for melting an optically thick vapor cloud

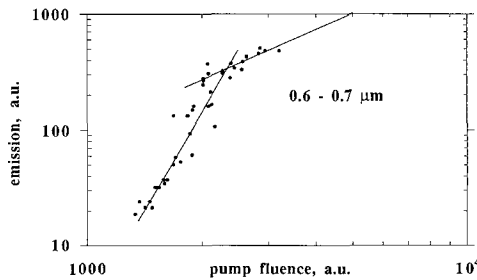


Fig. 4. Time-integrated radiation emitted in the range 0.6–0.7 μm by graphite samples interacting with 30-ps, 1.06- μm laser pulses as a function of the pump laser fluence. The arrow indicates the onset of surface melting, deduced by the appearance of surface damage.

might be formed in tens of picoseconds. Besides these semiquantitative arguments, experimental evidence [9] has been given that reflectivity increases have been observed in these experiments for very high angles of incidence and p-polarization, indicating that consistent surface conditions were observed rather than optically thick media.

Figure 4 provides a plot of the integrated radiation emitted by the sample in the spectral region 600–700 nm as a function of the infrared pump fluence. These measurements were simply performed by collecting the radiation emitted from the hot surface with a bundle of optical fibers connected through suitable color filters with a photomultiplier. The data were corrected for the spectral sensitivity of the photocathode and the overall transmission of the filters. The emission of radiation from the hot solid has a very steep behavior that in the logarithmic representation might well be interpolated with a power law. However, as soon as the critical value for surface melting is reached, a sudden change of the slope of the curve is observed, indicative of changed emission conditions upon melting. This behavior is once more consistent with emission from a hot surface that melts and further supports the notion of an unobscured hot surface being probed by optical means.

In summary, the observed optical properties of liquid graphite in the picosecond excitation regime are consistent with those observed with femtosecond laser pulses. The short-lived high reflectivity phase of molten graphite observed in the latter experiments has been interpreted as a metallic-behavior liquid carbon [5]. The same conclusions have been drawn from the nanosecond electrical heating experiments [7]. Clearly, no relation exists between the two sets of experiments and the difference in temporal regime does not convey mutual support to the conclusions. On the contrary, the reflectivity drop observed on the picosecond time scale with femtosecond excitation is in contrast with the pulsed electrical experiments. Indeed, other electrical heating experiments have shown a different behavior of graphite at high temperatures [12]. In other words, experimental consistency exists between laser heating experiments, although the interpretation of the results is still subject of speculation. Added support to these experimental observations from theoretical models is so far still elusive due to the equilibrium assumptions implied in their development. Further systematic experiments are therefore needed to prove the validity of the assumptions used in the interpretation of the data.

Finally, it is to be noted that the suggested existence of two different phases of liquid carbon [13] has led to a plausible unified picture consistent with all the experimental findings [14]. Moreover, paths in the carbon phase diagram [15] have been discussed which could explain the kinetics of the phase transition under different regimes.

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