Femtosecond laser-induced ablation of graphite

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Abstract: The dynamics of fs-laser ablation of graphite has been investigated experimentally and theoretically. Molecular dynamics caculations, incorporating changes of the interatomic potentials due to electronic excitation, support the experimental observation of two different ablation mechanisms.

OCIS Codes: 320.0320 Ultrafast optics, 320.7130 Ultrafast processes in condensed matter, including semiconductors, 350.0350 Other areas of optics, 350.3390 Laser materials processing.

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Femtosecond laser ablation of solid materials has attracted increasing interest in the past few years, both from a fundamental physics point of view, and with respect to technical applications of ultrashort laser pulses for material processing. With such short pulses transient extreme states of matter can be reached, opening unique paths for structural modifications and material removal. Recently we have shown [1] that near-threshold ablation of absorbing solids with femto- and picosecond pulses exhibits a material-independent behavior, which is characterized by a distinct transient interference phenomenon in the nanosecond time range. In this work we present a combined experimental and theoretical study of ultrashort laser pulse ablation of graphite, emphasizing how the specific, but still not well characterized features of the carbon phase diagram modify the observed *universal* ablation behavior.

Highly oriented pyrolytic graphite (HOPG) and quasi-crystalline graphite were excited with single 100fs laser pulses. Using time resolved microscopy [2], the reflectivity of the irradiated surface was monitored with 100fs temporal and micrometer spatial resolution. Fig. 1 shows a sequence of micrographs covering a time span from a few picoseconds after excitation up to the appearance of the final modifications of the surface.

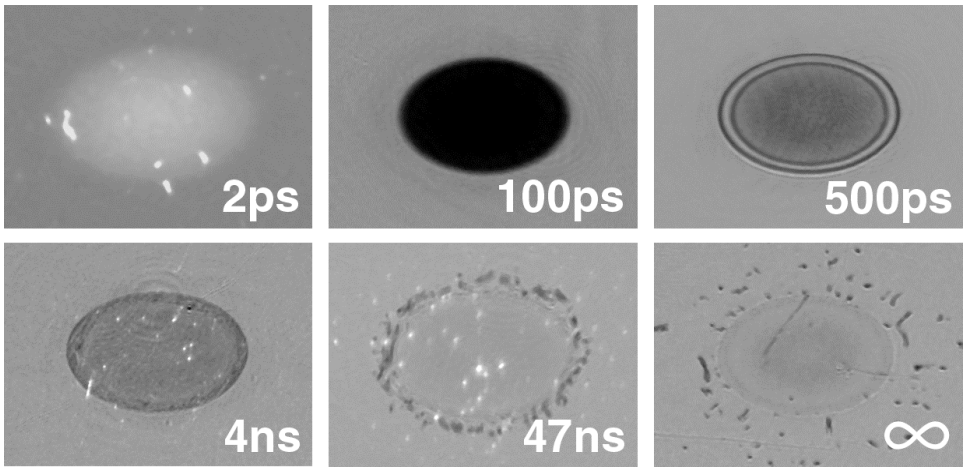

Fig. 1: Sequence of micrographs of a graphite surface excited with a 100fs, 500mJ/cm^2 laser pulse for different delay times between pump and probe pulse.

For early times the surface exhibits an increase in reflectivity (Δt=2ps) which has been also observed previously [3] and interpreted as ultrafast melting of the material. Compared to other group IV and III-V semiconductors [4,5] the reflectivity increase upon melting is less pronounced and *not* fluence-independent. As already pointed out in [3] and supported by recent theoretical calculations [6] this can be explained by a metallic liquid state with less than four electrons per atom, which is resistively saturated (plasma-frequency - relaxation time product $\omega_P\tau \approx 1$). The initial state of high reflectivity, indicative of the high-density molten phase of carbon, *survives* only for a few picoseconds. For fluences below the ablation threshold (F_{ab1} = 185mJ/cm^2) a reflectivity value between the level of the initial liquid and that of solid HOPG is reached within 10-20ps. It must be noted that in graphite the melting threshold F_m = 165mJ/cm^2, as determined from a *post-mortem* analysis of the final surface modifications, is very close to the ablation threshold.

As can be seen in the viewgraph for Δt=100ps, the onset of ablation is marked by a drastic decrease of reflectivity to values well below the level of the solid. At the periphery of the excited area (low fluences) this zone of decreased reflectivity subsequently transforms into the interference pattern typical for the near-threshold ablation of absorbing solids [1] (Δt=500ps). The interference indicates the existence of an optically steep ablation front towards vacuum. Its formation can be explained by a *thermal* ablation model, which describes material removal as hydrodynamic expansion of the laser-generated, highly pressurized fluid layer through the liquid-gas coexistence regime of the phase-diagram [1,7]. In contrast to all the other materials investigated so far, the interference observed on graphite does not just vanish due to the progressive transformation of expanded liquid material to the gas phase. Instead, the area covered by interference fringes appears to be the source of µm-sized fragments which are ejected at later times (Δt=47ns) and finally deposited in solid form in and around the ablation crater (Δt=∞). We relate this behavior to the peculiar and still not well understood properties of the liquid state of carbon. The high temperatures and pressures required to observe l-C and the possibility of a liquid-liquid phase transition [8-10] will surely influence the ablation dynamics. Therefore, the formation and the ejection of the fragments may indicate solidification of the liquid component of the ablation plume before a complete transformation into the gas-phase can occur.

Above a threshold fluence of $F_{ab2} \approx$ 250mJ/cm^2 we neither observe the interference phenomenon, nor the formation of fragments. This is quite obvious from the viewgraphs in Fig. 1, where for Δt=500ps the interference is confined to a narrow region at the periphery of the spot. From the very same region formation of the fragments occurs at later times (Δt=4ns). This observation is confirmed by Fig. 2, which shows transient images of the irradiated surface for a delay time of 1.5ns (left) and micrographs of the final surface morphology (right) for fluences below (top row) and above (bottom row) the second threshold.

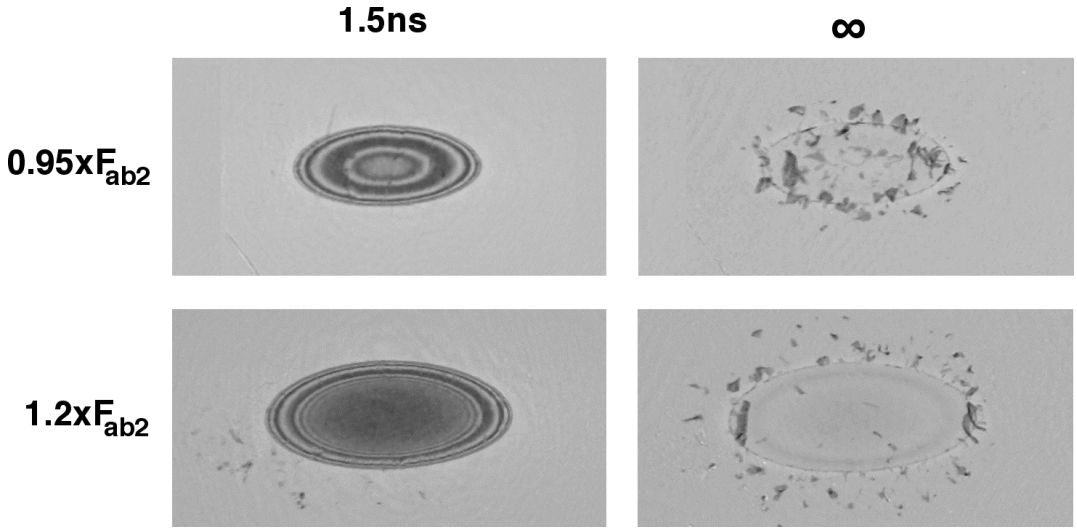

Fig. 2: Micrographs of a laser-irradiated graphite surface for two fluences below (top row) and above (bottom row) the second ablation threshold. On the left side transient images, taken at a pump-probe delay of 1.5ns, are shown. The right side displays the final appearance of the surface.

Below F_{ab2} the whole spot exhibits transient interference and is finally covered with sheet-like fragments. Above F_{ab2} no interference is visible in the central part of the spot. Moreover, this region is free of fragments. According to our understanding of femtosecond ablation [1], the absence of interference implies that hydrodynamic expansion of the laser-generated fluid does *not* include the passage through the liquid-gas co-existence regime of the phase diagram, but proceeds most likely *above* the critical point. In this frame of interpretation the ablating material can be completely transformed into a volatile phase (atomic gas, clusters) and will be permanently removed form the surface, explaining the absence of fragments in this case.

The ablation process has been also theoretically studied using molecular dynamics simulations. These calculations allow a separate treatment of the electronic and ionic degrees of freedom and are therefore able to model the interaction of ultrashort laser pulses with solids [11]. Although a direct comparison of simulation and experiment is difficult due to the fact that the 100ps- to ns-time-scale is not accessible for these calculations, the numerical results show also two distinct ablation thresholds corresponding to different microscopic processes. For lower intensities material removal is due to the ejection of complete graphite layers. In this process the excitation leads to a disruption of the bonds between the layers. At higher intensities a second threshold indicates the onset of bond breaking within an individual graphite layer. As a consequence of this process single atoms and small cluster are emitted.

In conclusion, we have studied the dynamics of melting and ablation of graphite after femtosecond laser-excitation, using time- and space-resolved measurements of the optical reflectivity. Compared to other covalently bonded materials, the experimental data on graphite reveal significant differences, which might be related to the unique features of the carbon phase diagram. Supported by theoretical simulations, two different pathways of ablation are identified leading to different final states of the removed material.

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