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Laser Nanoablation of Graphite in Argon Atmosphere

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Abstract—The results of comparative studies of laser ablation of highly oriented pyrolytic graphite in air and in an inert medium upon exposure to nanosecond pulsed laser irradiation with an energy density in the range $E = 0.4 - 3$ J/cm^2 are presented. It is found that the nanoablation mode is established below the evaporative ablation threshold ($E < E_a \approx 1$ J/cm^2) in both cases (the average ablation rate is lower than 10^{-3} nm/pulse); in this case, the nanoablation rate in argon is lower than in air by a factor to 6. The experimental data count in favor of the oxidation mechanism of graphite nanoablation.

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Laser nanoablation, i.e., removal of individual material clusters and even atoms upon exposure to low-intensity light flux, is of undoubted fundamental interest; as a practical matter, it has a high potential for ultraprecision materials processing, including etching of single atomic layers. The nanoablation effect first detected in diamond and diamond-like films [1, 2] was explained by graphitization of their surface followed by oxidation. Atmospheric oxygen plays here a crucial role, and the oxidation reaction is directly associated with material removal.

Recently, we have experimentally found that the nanoablation mode is also implemented in highly oriented pyrolytic graphite (HOPG) during target irradiation in air with a laser beam of UV and visible regions with an energy density in a pulse above $E_0 \sim 0.4$ J/cm^2 [3]. As the laser energy density E exceeds the threshold $E_a \sim 1$ J/cm^2, the evaporative mode of laser ablation is initiated [3, 4].

Presumably, the graphite nanoablation mechanism is similar to that in diamond, i.e., the nanoablation mechanism is based on oxidation of the irradiated sample surface. To test this hypothesis, in this work, we comparatively studied the process of laser-induced graphite removal in air and in Ar inert gas atmosphere.

Experiments were performed using an Ntegra Spectra M scanning probe microscope (SPM) at room temperature. Samples were placed into a working chamber filled with air or argon at normal atmospheric pressure; to increase the pumping efficiency, the argon feeding nozzle was brought to the objective focusing laser radiation (to a distance of ~1 cm). Gas inflow was controlled by a humidity sensor. As the chamber was filled with argon, the relative humidity RH decreased and became close to $RH = 0\%$. After 10-min storage under these conditions, experiments on ablation began. Accordingly, when filling the chamber with air, the establishment of equilibrium humidity (~35–40%) in the sample region was waited. A solid-state Nd:YAG laser with wavelength $\lambda = 532$ nm and pulse duration $\tau = 7$ ns was used. The laser pulse repetition rate was $f = 1$ kHz, the graphite sample exposure time was 60 s (the number of laser pulses was $N = 6 \cdot 10^4$). The laser beam was focused into a spot ~0.5 μm in diameter on the sample surface. The morphology of nanometer-depth craters was analyzed by scanning the area exposed to the SPM probe in the tapping mode before and immediately after laser irradiation.

At the beginning of the study, the minimum energy density in a pulse at which changes in the material surface relief in the laser irradiation region are reliably detected was determined (the detectability of such measurements is mostly controlled by the initial sample surface roughness). This value was in the range

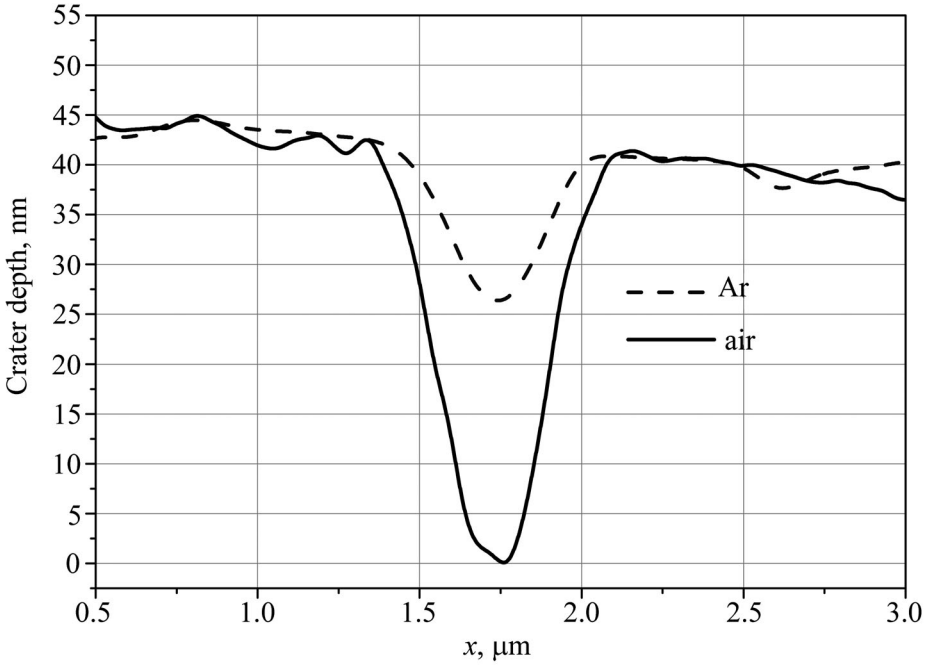

Fig. 1. Crater profiles at $E \sim 0.5$ J/cm^2 in air and in Ar atmosphere.

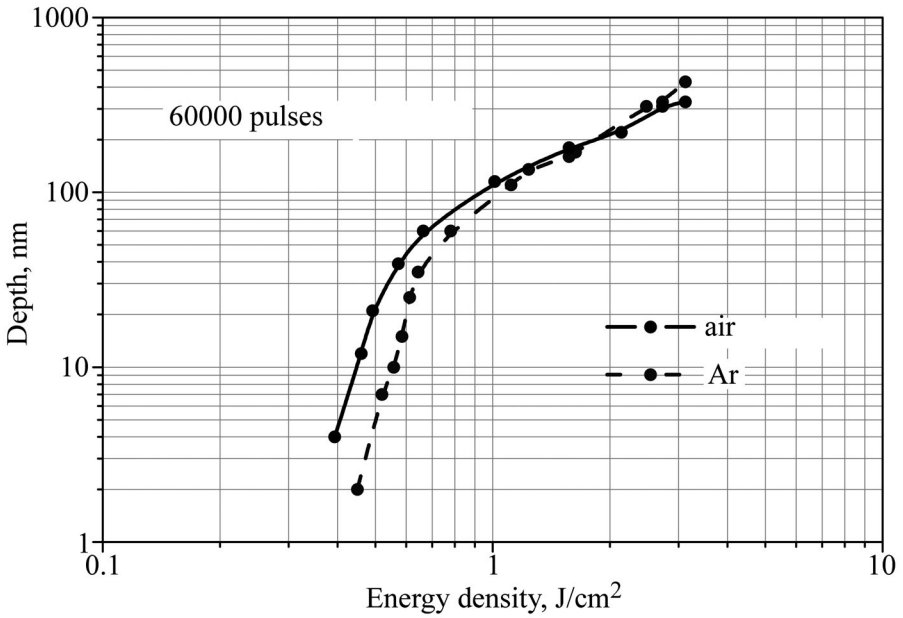

Fig. 2. Dependence of the crater depth in graphite on the laser pulse energy density in air and in Ar atmosphere.

of $\sim$0.4–0.5 J/cm^2; in this case, craters $\sim$1 nm deep and $\sim$0.5 μm in diameter appeared on the surface. The ablation rate averaged over a large number of pulses was $\sim 7 \cdot 10^{-5} - 3 \cdot 10^{-4}$ nm/pulse in air and $\sim 3 \cdot 10^{-5} - 10^{-4}$ nm/pulse in Ar, which suggests that the term "nanoablation" is applicable in the case at hand.

Figure 1 shows the crater profiles at the laser radiation energy density in a pulse $E \sim 0.6$ J/cm^2. We can see that the craters obtained in an argon atmosphere are smaller (by a factor of $\sim$2.5), and the region of the laser radiation impact on the sample surface is narrower than in the case of air medium.

A series of exposures at various laser radiation energies made it possible to determine the dependence

of the depth D of obtained craters on the energy density E per pulse up to $E = 3$ J/cm^2. This dependence $D(E)$ constructed for clarity in the log–log plot is shown in Fig. 2. It should be noted that the evaporative ablation threshold determined by the dependence $D(E)$ inflection and direct observations of the plasma plume in the laser irradiation region is $E_a = 0.7 - 0.8$ J/cm^2 which is in good agreement with the evaporative ablation threshold ($E_a \sim 1$ J/cm^2) determined in previous studies [3, 4].

The behavior of the $D(E)$ curves in Fig. 2 clearly shows that the ablation rate significantly decreases (by a factor to 6) in the nanoablation mode ($E < E_a$) in argon in comparison with that in air.

Thus, the data obtained evidently count in favor of the reactive mechanism of laser nanoablation of graphite in air. In this case, the nanoablation rate is probably controlled, as in diamond, by low-temperature oxidation on the graphite surface of both initial (before laser irradiation) and laser-induced defects.

As E_a is exceeded, the dependences $D(E)$ almost merge, which indicates the transition to the evaporative mechanism of material removal in both cases. Noteworthy is the trend toward a more rapid increase in the ablation rate in argon than in air, observed in the range $E = 2 - 3$ J/cm^2 (see the corresponding curves in Fig. 2). It is possible that this effect is caused by more efficient ionization of air than argon (nitrogen, oxygen, and argon ionization potentials are 14.5, 12.1, and 15.7 eV, respectively [5]). At the levels $E \sim 2 - 3$ J/cm^2, the emission intensity becomes close to the threshold one I_B for optical breakdown in gas, which is $\sim 10^8 - 10^9$ W/cm^2 when plasma is initiated near the evaporating target with the result that incident laser radiation is in part screened [6]. In argon, the plasma density is lower, and larger laser pulse fraction reaches the graphite surface, being not scattered or absorbed, thus providing higher ablation rate.

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