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Gated ICCD Photography of the KrF-Laser Ablation of Graphite into Background Gases

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Gated ICCD Photography of the KrF-Laser Ablation of Graphite into Background Gases

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The dynamics of the KrF-laser ablation ($\Phi = 20 \text{ J cm}^{-2}$) of graphite into 300 Torr of He, Ne, Ar, and Xe has been studied by fast imaging of the visible plasma emission using a gated intensified CCD array (ICCD) camera system. In each case, the soot which was redeposited on the graphite rod following ablation was highly fullerene deficient compared to the material collected on a sample disk 1.5 cm from the rod, as determined by laser desorption Fourier Transform Mass Spectrometry (FTMS).

The ICCD photographic investigations of the plasma plume propagation in the different gases reveal three common phases to the expansions: (1) forward motion, deceleration and stopping of the leading edge of the plume, (2) an apparent reflected shock within the plume which propagates backward and partially reflects from the rod surface, leaving "redeposited" material, (3) a secondary forward propagation and coalescence of the material reflected from the rod surface, resulting in continued expansion and dissipation of the plasma and the appearance of glowing ultrafine particles. Detailed sequencing of the plasma expansion into argon is presented here which shows at least two sets of reflected shocks. The possible explanation of the observed difference in fullerene content is discussed on the basis of different plasma phases resulting in soot deposition on the rod and disk.

1. INTRODUCTION

The interaction of a laser-generated ablation plume with a background gas^{1,2} is of current interest for several materials-fabrication applications. During pulsed laser deposition (PLD) of thin films by laser ablation, for example, an ambient background gas (pressures usually $\leq 300 \text{ mTorr}$) is often employed. This gas slows and scatters the plume atoms, reducing their maximum kinetic energies from hundreds of eV to less than 0.1 eV within a few centimeters. During this process, the slower atoms in the plume coalesce with the faster atoms in the plume which have undergone collisions, resulting in the subsequent propagation of a contact or "shock" front, as revealed by fast photography with a gated intensified CCD array camera system (ICCD).²

At higher gas pressures laser ablation can be utilized to produce novel clusters, such as fullerenes and doped fullerenes by the ablation of graphite into inert gases.³⁻⁸ The dynamics of fullerene assembly in the ablation plume are unclear, however production of fullerenes seems clearly related to the pressure and temperature within the confined plasma bubble. At the 300 Torr pressure used in this study, several effects suspected to occur in PLD plumes become observable by ICCD imaging, including the redeposition of material on the target surface, reflected shocks within the plume, and details of the plume coalescence into a stable shock front.

In addition to the detection of the extremely bright plasma plume, gated ICCD photography is also capable of detecting blackbody emission in the photon-counting regime from slow-moving hot particulates ejected from the target under PLD conditions.⁹ At high pressures, blackbody emission is also emitted from clusters formed by ablation of graphite into rare gases.¹⁰ In this study, ICCD photography is used to view the expansion and thermalization of the laser-generated graphite plume into background gases from the extremely bright hot plasma stage into the photon counting regime of blackbody emission from hot clusters.

2. EXPERIMENTAL

Imaging and soot deposition experiments were made in a stainless steel chamber which was pumped out to 10^{-6} Torr and filled with 300 Torr of buffer gas. A 1/4"-diameter graphite rod target was rotated by a motorized feedthrough. Laser ablation was performed by a focused KrF-laser beam ($\lambda = 248 \text{ nm}$, 46-ns FWHM, $1 \times 1 \text{ mm}^2$ area, energy density = 20 J/cm^2) incident at 30° to the normal of the flat rod end. The rod was viewed side-on as shown in Figs. 1 and 2.

The experimental apparatus for gated ICCD photography has been previously described.² A lens-coupled, gated-intensified, CCD-array camera (Princeton Instruments ICCD-576G/RB with

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Figure 1: Gated ICCD photographs of the visible plume following KrF-laser ablation (20 J cm^{-2} , 46ns FWHM pulse) of graphite into 300 Torr helium, neon, argon and xenon after a time delay of 1 microsecond following arrival of the arrival of the laser pulse.

105 mm Nikkor-UV lens) was responsive over a 200–820 nm wavelength range and gateable with "shutter speeds" $\geq 5 \text{ ns}$. Each image represents a different laser shot.

For the soot deposition experiments, a 16.5 mm -stainless steel sample disk for FTMS was located in front of the laser plume at 15.4 mm from the rod surface. The repetition rate of the pulsed laser was 5 Hz and irradiation time for all four buffer gases used was 30 minutes. The analysis of the soot deposited on the sample disks and on the sides of the graphite targets were performed with an Extrel FTMS-2000 Fourier Transform Mass Spectrometer equipped with a Quanta Ray DCR-11 Nd:YAG pulsed laser. The details of this analysis have been described previously.⁸ Both positive and negative ions were examined.

3. RESULTS AND DISCUSSION

Side-on images of the visible emission from the graphite ablation plasmas in 300 Torr of helium, neon, argon and xenon are shown in Figure 1 at a time delay of 1 microsecond following laser irradiation. At this time delay, each plume has undergone viscous slowing to nearly stop expansion in the forward direction and each displays a different mixture of hydrodynamic development. For example, the backward-moving component of the argon plume is in the process of reflecting from the rod surface while this component of the xenon plume has not yet progressed as far. This hydrodynamic behavior was extremely reproducible from shot to shot, to time delays out to at least 100 μs .

Figure 2 shows a series of images which detail the graphite plume expansion into 300 Torr argon.

The gate widths of the camera remained at 5 ns for $\Delta t \leq 10 \mu\text{s}$, 20 ns for $4 \mu\text{s} < \Delta t \leq 100 \mu\text{s}$, and 5 μs for $\Delta t = 500 \mu\text{s}$. The exposures (f-stops) and microchannel plate gain were varied to compensate for a decrease in brightness over an estimated 10 orders of magnitude, however, and the peak intensity was normalized for display in Fig. 2.

Within 300 ns, the plume is slowed dramatically and a backward-propagating front is noted at $\Delta t = 400 \text{ ns}$. This appears to be material reflected from the front contact surface of the plume. This is more easily recognized in Fig. 3, where the corresponding images from Fig. 2 have been presented such that the digitized intensity is plotted along the vertical axis. At 600 ns this reflected component appears to reach the rod surface and from $800 \text{ ns} < \Delta t \leq 1 \mu\text{s}$, a reflection from the rod face occurs. The portion of backward-propagating plume which extends around the side of the rod face results in plasma emission "behind" the rod surface in the images from $1 \mu\text{s} \leq \Delta t \leq 30 \mu\text{s}$, and in a band of "redeposited" soot on the side of the rod as shown in the inset of Fig. 2.

Another reflection from the front contact surface appears to occur circa 3 μs , resulting in another set of interfering traveling waves within the plume and a complex interference pattern from $5 \mu\text{s} \leq \Delta t \leq 10 \mu\text{s}$.

The final expansion stage is presented in Fig. 4 for the $10 \mu\text{s} \leq \Delta t \leq 100 \mu\text{s}$ images in which a stable forward-propagating front of material slowly emerges to generally maintain its shape to very long times. The plasma emission diminishes to yield the glow from hot microparticulates which are separated spatially from the rod surface region, as indicated in the 500 μs image of Fig. 2.

Figure 5 plots the position-time behavior of the leading edge of the argon plume in the first microsecond showing fits to the data of both drag

Figure 2: Gated ICCD photographs of the visible plume following KrF-laser ablation (20 J cm^{-2} , 46ns FWHM pulse) of graphite into 300 Torr Argon at the indicated time delays following laser arrival. Exposures were varied and normalized (see text). The side-on view of the graphite rod, scale, and band of redeposited soot is shown in the inset (the rod surface in the 20–100 μs images is offset by 1.5 scale-mm further left). Several reflected shocks are evident. The first begins $\sim 300 \text{ ns}$, resulting in backward-moving material leading to redeposition of soot on the rod sides, and another reflected shock from the rod surface ($\sim 1 \mu\text{s}$). This process is repeated, the plume expanding in stages, until glowing microparticulates are observed away from the target at very long times (see 500 μs image).

Figure 3: Selected data from Figure 2 tracing the evolution of the plasma plume from KrF-laser irradiated graphite into 300 Torr Argon. In this 3D representation, the intensity of the light in Fig. 2 is plotted along the vertical axis. Following rapid expansion in the first 300 ns, a reflected shock propagates back and collides with the surface of the rod from 400 ns to 1 μ s. Plasma emission wrapping around the side of the rod causes the apparent emission "behind" the rod surface. The reflection of material from the rod surface influences a secondary forward expansion.

Table 1

Drag and shock wave propagation model fit parameters for the first microsecond of graphite plume expansion

Model		units	Helium	Neon	Argon	Xenon
Drag	x_f	mm	4.1	2.7	2.0	1.5
	β^{-1}	μ s	0.25	0.20	0.19	0.23
Shock wave	a	mm	4.4	3.1	2.5	1.9
	α		0.49	0.43	0.39	0.42

($x = x_f [1 - \exp(-\beta t)]$) and shock ($x = at^\alpha$) propagation models.^{2,11} Results of fits to the He, Ne, Ar, and Xe data are given in Table 1.⁸

From Fig. 1 and the drag model fits of Table 1, the plume range x_f decreases with increasing mass of the background gas. From Fig. 5 and the values of β^{-1} in Table 1, the velocity of the leading edge of the plume drops to 10% of its initial velocity within ~500 ns for all the gases studied. The drag model incorrectly predicts stoppage of the plume while the shock model overestimates the expansion at later times (for a single spherical expansion front $x \sim t^{0.4}$). Both models neglect the effects of reflected shocks within the plume.

The amount of brown-colored soot deposited 1.5 cm away from the rod onto a sample disk was the largest for He and smallest for Xe. FTMS spectra of this soot showed pronounced C₆₀, C₇₀ as well as other fullerene peaks for all the gases used. Quantitative comparison of the absolute amount of the C₆₀, C₇₀ shows that He and Xe give the highest yield of fullerene compared to Ne and Ar. Another interesting feature of these mass spectra is the shift of the fullerene distribution to the higher masses for Xe compared to He.⁸ In addition, large amounts of black-colored soot were redeposited onto the side surface of the graphite target rod. As shown in Fig. 2, the soot produced a cylindrical black band a few millimeters in width starting from the front edge

Figure 4: Selected data from Figure 2 tracing the final expansion stage of the plasma plume from KrF-laser irradiated graphite into 300 Torr Argon (the intensity of the light in Figure 2 is plotted here along the vertical axis).

Figure 5: Plume position (leading edge) versus time for 20 J/cm² KrF-laser ablation of graphite into 300 Torr of Argon as measured from sets of ICCD photographs. Fits to the *drag model* (solid line) and the *shock wave propagation model* (dashed line) are given for the 0–1.0 μs phase of the expansion.

Figure 6: Scanning electron microscope photograph of the redeposited soot on the graphite rod surface following 20 J/cm² KrF-laser ablation of graphite into 300 Torr Argon. The full width of the photograph represents 3.7 μm.

of the graphite rod. The largest bands were formed for Xe and Ar and much less redeposited material was found for He and Ne. Only trace amounts of C_{60} were found in the redeposited soot when He and Ne were used as buffer gases. Notably, C_{60} was not found in the redeposited material for Ar and Xe. In addition, there are no higher-mass fullerenes (up to $m/z = 2000$) in the spectra.

Figure 6 shows a Scanning Electron Microscopy (SEM) image of the soot deposited back onto the rod following 9000 laser shots in 300 Torr argon. SEM images of all of the targets showed a broad distribution of particle sizes ranging from 10 nm to 1 μm (where the larger particles, upon closer examination, are comprised of coalesced smaller particles).

4. CONCLUSIONS

The ICCD photographic investigations of the plasma plume propagation in the different gases reveal three common phases to the expansions: (1) forward motion, deceleration and near-stopping of the leading edge of the plume, (2) an apparent reflected shock within the plume which propagates backward and partially reflects from the rod surface, leaving "redeposited" material, (3) a secondary forward propagation and coalescence of the material reflected from the rod surface, resulting in continued expansion and dissipation of the plasma and the appearance of glowing ultrafine particles. Detailed sequencing of the plasma expansion into argon presented here shows at least two sets of reflected shocks. In this case, phases (2) and (3) above are repeated at least once.

The laser beam creates a plasma with a front-edge propagation velocity about 1.4×10^6 cm/s ($v_0 = \beta x_f$ from Table 1). This is at least one order of magnitude higher than the sound velocity in the surrounding buffer gas. This plasma contact front locally compresses the surrounding buffer gas until the pressure inside the plasma bubble reaches that of the locally compressed buffer gas. During this process, a reflected shock is generated within the plasma bubble which moves in the opposite direction until it reaches the rod surface. This shock wave travels within the plume material, collides and reflects from the rod, and propagates with lower velocity into the buffer gas.

The KrF-laser ablation of graphite rod in 300 Torr of He, Ne, Ar, and Xe produces two different kinds of soot. The soot deposited on the side surface of the graphite rod was fullerene deficient for all buffer gases used. The ablated material collected on

the sample disk contains fullerenes whose mass distribution depends on the buffer gas used. The difference in fullerene content between the material deposited on the rod and on the sample disk may be rationalized if one takes into account that disk soot deposition occurs after 500–1000 μs (the third phase) when the ablated material has cooled and mixed well with the buffer gas.

The soot deposited on the rod consists of ultrafine particles which either condensed from atomic vapor during the redeposition process or evaporated from the rod. The backward plasma results in the deposition of this material on the rod surface. A fraction of the backward-moving material reflects from the rod surface and travels with the long-lived plasma, anneals, and gives rise to fullerene growth. These growing clusters finally deposit on the sample disk. The observation of hot ultrafine particles in the buffer gas well after the plasma has decayed raises questions as to its importance in fullerene growth and annealing.

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