Isotope Enrichment in Laser-Ablation Plumes and Commensurately Deposited Thin Films

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A highly efficient isotope enrichment process is observed directly in laser-ablation plumes generated from ultrafast laser pulses focused on a solid surface. Data are presented for boron nitride and gallium nitride targets using laser pulses of 150–200 fs at 780 nm wavelength. Isotope ratios for B and Ga are observed in a time-of-flight spherical-sector electrostatic analyzer. Enrichment factors of 2 or more above natural abundance are observed for the ratios of B^{10}/B^{11} as well as for Ga^{69}/Ga^{71}. These same plumes are used to deposit isotopically enriched films of boron nitride on silicon.

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We have discovered an unusually efficient isotope enrichment process occurring in plasma plumes generated by laser ablation from solid surfaces [1]. These results have been obtained for two different elements, boron (B) and gallium (Ga), as observed directly in the ablation plumes from BN and GaN, using a sector-field electrostatic analyzer. The phenomena are also observed in thin films of BN deposited from the laser-ablation plume. The experimental setup consists of conventional laser-ablation geometry with the laser beam focused by a lens through a vacuum window and incident on the target at a 45° angle. The ablation plume expands normal to the target surface, with no external fields. Films are deposited by introducing a silicon substrate at approximately 7 cm from the ablation target. Ion spectra are obtained by removing the silicon substrate and allowing the plume to traverse a 1.1-m distance into a differentially pumped vacuum chamber containing the spherical-sector electrostatic analyzer with microchannel plates (MCPs). There are two 4-mm apertures defining the entrance to the analyzer chamber and the analyzer itself has a 2-mm acceptance aperture. The base pressure of the ablation chamber is 5×10^{-9} Torr and is backfilled with N_2 gas for experiments on plume background-gas interactions. Ablation is initiated by 150–200 femtosecond pulses from a Ti:sapphire chirped-pulse amplified laser operating at 780 nm with S polarization and a 10 Hz repetition rate. Typical laser intensities on target are 10^{13} to 10^{15} W/cm^2. Experiments have been done on boron ablated from a boron nitride target and on gallium ablated from a gallium nitride target.

Figure 1 shows a typical example for an ion time-of-flight spectrum observed during the ablation of a boron nitride target using 200 fs pulses with a fluence of 50 J/cm^2 providing an intensity of 2.5×10^{14} W/cm^2. The spectrum shown is obtained in the direction normal to the target surface on the center of the plume and is the accumulated average over multiple laser pulses. This averaging smoothes out shot-to-shot fluctuations. The various peaks are identified in the figure, where charge states +1 through +5 are present for the two isotopes of boron and charge states +1 to +4 for nitrogen. It is immediately obvious, for the conditions associated with the figure, that the relative heights of the boron isotopes for charge states +3 and +4 are much greater than the 1 to 4 ratio expected from the natural abundance of B^{10} (19.78%) and B^{11} (80.22%). The spectrum in Fig. 1 is obtained for a specific voltage setting on the analyzer sector plates and corresponds to an energy-to-charge ratio (E/q) of 1 keV. By stepping the voltage settings across an appropriate range on the sector plates, one can sweep out a full energy distribution for each of the charge states present in the ablation plume. For the experiment, the detector is scanned in voltage, by a computer-controlled step and acquire process, resulting in relatively rapid accumulation of the charge-state-separated energy distributions. Such distributions, corrected for MCP detector efficiency (as a function of ion energy), are seen in Figs. 2(a) and 2(b). Figure 2(a) shows the results as observed in vacuum, where, as previously observed, the higher charge-state distributions are systematically centered at higher energies [2]. It is determined, as seen in Table I, that the total B^{10}

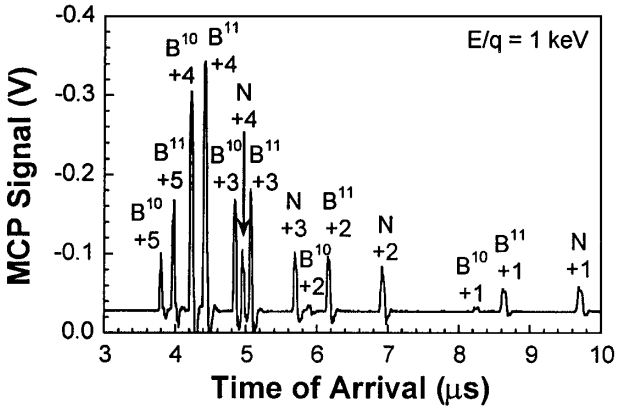

FIG. 1. Ion time-of-flight spectrum for ablation of the BN target with $E/q = 1$ keV. The laser intensity on target is 2.5×10^{14} W/cm^2 using 200 fs pulses.

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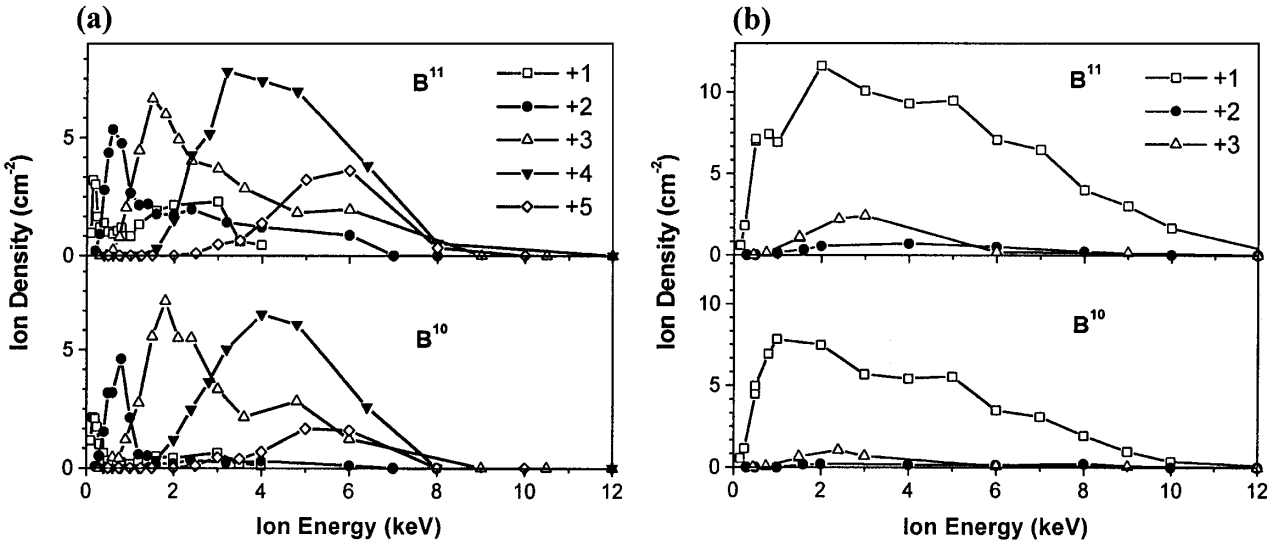

FIG. 2. Ion energy spectra of B^{11} and B^{10} for BN ablation plumes in (a) vacuum, and (b) 0.8 mTorr N_2. The laser intensity on target is 2.5×10^{14} W/cm^2 using 200 fs pulses.

yield is substantially above the 20% level that would be expected from natural abundance considerations. By introducing a background gas of 0.8 mTorr N_2 into the ablation chamber, one would expect the higher charge states to be reduced through charge-exchange collisions with the gas. The consequences of these collisions can be seen in Fig. 2(b), where the same experiment as in Fig. 2(a) was run except for the inclusion of the background N_2 gas in the ablation chamber. It is clear that the total ion signal in Fig. 2(b), as now defined primarily by charge state +1 (into which the higher charge states collapsed), contains a significantly larger proportion of B^{10} than would occur from the 20% natural abundance levels. From Table I, the ratio of the total amounts of B^{10} to B^{11} in the plume for Figs. 2(a) and 2(b) is 0.66 and 0.55, respectively. This is to be compared to 0.25 as obtained from the natural abundance ratio.

Similar experiments have been done for Ga^{69} (60.4%) and Ga^{71} (39.6%). Trends in the energy distributions for gallium were similar to that for boron. Significant enrichment of the lighter Ga^{69} component of the spectrum was observed. In Fig. 3(a) is shown the ratio of B^{10}/B^{11} obtained from Fig. 2(b) as a function of ion energy for charge state +1 as observed through the N_2 background gas. In Fig. 3(b) is presented a similar analysis as obtained for Ga^{69}/Ga^{71} taken from gallium nitride ablation that is obtained in a similar fashion as that for boron. The laser pulses used for the GaN case were 150 fs with a fluence of 3.3 J/cm^2 yielding an intensity of 2.2×10^{13} W/cm^2. Also shown in the figures, as dashed horizontal lines, are the natural abundance ratios that would normally be expected for both elements. It is observed in Fig. 3 that, for charge state +1, which is the predominant ion species under background-gas conditions, the ratio of the lighter to heavier isotope is significantly larger than that expected from natural abundance considerations. Average values for boron are observed to be 0.62 compared to a natural abundance ratio of 0.25 and for gallium, 2.8 compared to 1.5.

TABLE I. Total ion counts (integrated over ion energy), separated by isotope and charge state from Fig. 2. Laser-ablation plumes are from 200 fs, 50 J/cm^2 laser pulses in vacuum, and in 0.8 mTorr N_2 backfill.

Charge state	Vacuum B^{10}	Vacuum B^{11}	Vacuum Ratio	N_2 Backfill B^{10}	N_2 Backfill B^{11}	N_2 Backfill Ratio
+1	1.77	6.06	0.29	42.19	72.44	0.58
+2	3.65	10.48	0.35	1.34	3.70	0.36
+3	19.03	20.09	0.95	2.94	7.90	0.37
+4	22.68	30.96	0.73			
+5	5.04	10.92	0.46			
Total	52.17	78.50	0.66	46.47	84.04	0.55

Since our detector is observing these ionic yields in a narrow cone angle normal to the ablation target surface, one would expect that the very center of a film area, deposited by this method, should also show a similar enrichment of the lighter isotopes. This follows since these ablation plumes, in vacuum, are highly ionic, as observed by the sector analyzer. In order to investigate this, films of BN_x (where $x < 1$) were grown, in vacuum, by intercepting the ablation plumes associated with these highly enriched isotopic plasmas. The boron isotope ratios in the films were then analyzed for commensurate enrichment effects.

Figure 4 shows the results of analyzing the B^{10}/B^{11} ratios in one of these films using 2.5 MeV He^+ Rutherford backscattering spectrometry (RBS). A 3-mm beam spot was positioned at successively larger radii away from the central portion of the film which had intercepted the

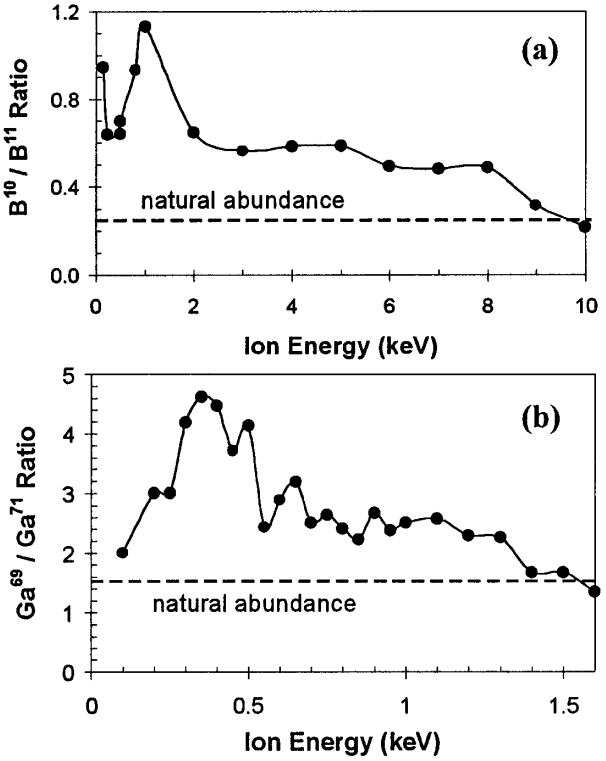

FIG. 3. Lighter isotope enhancement in laser-ablation plumes for (a) B^{+1} with 200 fs, 50 J/cm^2, 2.5×10^{14} W/cm^2 laser pulses, and (b) Ga^{+1} with 150 fs, 3.3 J/cm^2, 2.2×10^{13} W/cm^2 laser pulses, both in 0.8 mTorr N_2 backfill. (Note different energy ranges of B and Ga ions.)

central zone of the plume. The highest isotopic ratios are seen to occur near the portion of the film that is commensurate with the central portion of the plume (spot 1). The B^{10}/B^{11} ratio at this point is 0.45. The ratio gradually decreases away from the central portion. At the edge of the wafer, one inch from the center, the ratio has decreased to a value close to that expected for natural abundance. Several such films have been analyzed resulting in similar trends as that observed in Fig. 4. A distinct absence of oxygen and carbon impurities in the films (and therefore the plume) was also confirmed by these RBS measurements.

Table I shows the integrated areas under each of the charge-state curves presented in Fig. 2(a). The ratios of these areas are also presented which provides a measure of the total isotope enrichment associated with each charge state of boron. An interesting pattern is seen in the case of vacuum ablation where charge state +3 has the largest (nearly 1:1) ratio of the light to heavy isotope. This is followed by charge state +4 which has the next most highly enriched condition. It is also observed that the highest total yield of ions is for the +4 charge state.

The enrichment effects observed in this work most probably involve the interaction of charged ion species in the laser plasma with intense magnetic fields formed by the laser just ahead of the plume expansion process. It is very unlikely that the observed effects are associated with isotope production through laser-induced nuclear reaction processes. The laser intensities used in this work (10^{13}–10^{15} W/cm^2) are much too low for such events to occur. Intensities 4 to 5 orders of magnitude greater would be necessary for photoinduced (n, γ) reactions to occur via optically energized electrons [3].

It is known that both toroidal and axial magnetic fields are generated within laser-induced plasmas and that these fields, near the surface of the ablation target, are on the order of 0.6 MG for laser intensities around 10^{15} W/cm^2 [4,5]. The time development of the toroidal field precedes that of the axial field and in so doing provides a transradial impulse to the ion velocities. The presence of an axial field provides the conditions for a plasma centrifuge mechanism to operate in producing the isotope separation we observe. The intensity of both fields decreases

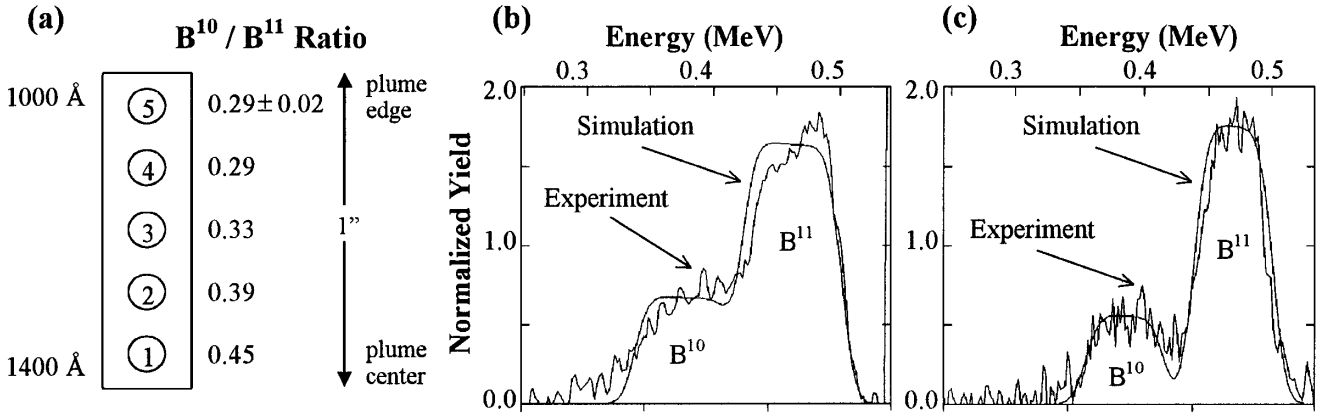

FIG. 4. Rutherford backscattering of 2.5 MeV He^+ from the BN thin film showing the isotope enhancement of B^{10} over B^{11}. (a) Thickness and B^{10}/B^{11} ratio variation across the sample. (b) RBS measurement and RUMP simulation (Rutherford Materials Program; see Ref. [10]) at spot 1. (c) RBS measurement and RUMP simulation [10] at spot 5.

monotonically away from the surface of the ablating target. Published data [6] demonstrate that an inverse power law decrease in the axial field occurs over distances of about 150 μm from the ablation surface. By extrapolating an initial 0.5 MG field to large distances, one can estimate the axial field strength along the path toward a deposition substrate on which the isotopically enriched films are grown. Using a -0.33 power law dependence for the axial field strength as a function of distance [6] for a laser intensity of 2×10^{14} W/cm^2, we obtain a spatially averaged field strength of 44 kG across the 7 cm distance from our ablation target to the deposition substrate. Since the axial field is claimed to be produced by a dynamo action within the plasma itself [5], one might expect that the field is retained within the plasma plume as it moves toward the deposition site. This would provide the necessary geometry for a plasma centrifugelike condition to be established. Physical instruments, based on such a principle, are well established as devices for plasma isotope enrichment [7]. Such a process provides a mechanism by which enrichment of the light isotope would occur on the zero radial spot of the plume, similar to what we observed.

The basic plasma centrifuge equation, as given by Krishnan *et al.* [8], yields a separated enrichment ratio in terms of the radial distance from the center of an axial magnetic field: $R(r)/R_0 = \exp(\Delta m \omega^2 r^2/2kT)$, where $R(r)$ is the ratio of the heavier to lighter ion species at radius r normalized to the ratio on axis, R_0. The enrichment depends on the isotope mass difference Δm, the angular plasma rotation rate ω, Boltzmann's constant k, and the plasma temperature T. Based on the data shown in Fig. 4, for a factor of 2 enrichment and a radial separation of enriched isotopes of 2.5 cm, we arrive at a rotation rate of 3.3×10^5 rad/sec. The value of the equilibrium plasma temperature is taken as 0.5 eV and is based on typical electron temperatures we measured for similar pulses in titanium using optical emission line ratios from spectroscopic emission data. Comparing our results with the operating parameters of conventional plasma centrifuges [7] allows for an estimate of the magnetic fields involved in our experiments. Using this approach, our minimum plasma rotation rate corresponds to a uniform axial magnetic field distributed over the space between the ablation target and film substrate of 4 kG. As stated above, the extrapolated spatially averaged field across this region is 44 kG. Thus, the predicted average axial field is more than sufficient to cause the isotope separation observed in our experiments. With these estimates, a plasma centrifuge mechanism is a reasonable explanation of the results presented here.

These results suggest an interesting method for measuring internal magnetic fields of laser-ablation plasmas. This is a uniquely valuable scientific result superimposed on the more practical matter of using the technique as a simple and direct means to obtain isotopically enriched materials. It is probable that other fundamental information about laser plasmas could also be derived from such observations. Information about ion and electron densities, temperatures, collision rates, and electromagnetic fields could be probed in this way. Moreover, from a practical standpoint, the direct deposition of engineered isotopically enriched thin films is a clear application area [9].

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