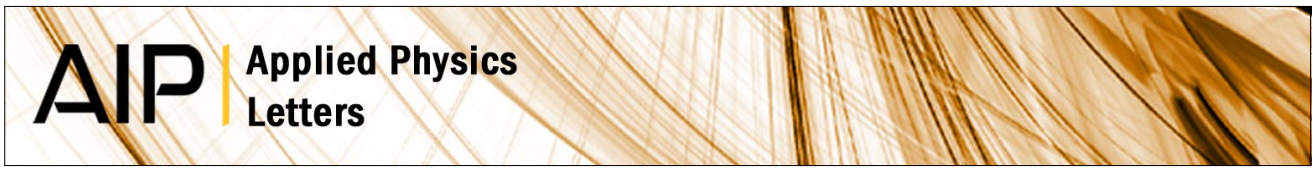

Electronic temperature and density of the plasma produced by nanosecond ultraviolet laser ablation of LiF

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Electronic temperature and density of the plasma produced by nanosecond ultraviolet laser ablation of LiF

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Optical emission spectroscopy is used to investigate the spatial evolution of the electron temperature (T_e) and electron density (N_e) in the plasma generated by laser ablation in a vacuum of a wide-band-gap material, such as LiF, with a pulsed 193 nm excimer laser operating at a fluence of 1.5 J cm^{-2} close to the threshold. It is found that, whereas N_e (in the range of 10^{16} cm^{-3}) decreases by a factor of 2 as the distance to the target increases, T_e exhibits a sharp decrease (from 1.85 eV to 0.66 eV) between 1 and 2 mm from the target and it remains practically constant for longer distances from the target. These results provide direct measurements of the electron temperature and density during nanosecond laser ablation of LiF. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1922574]

Laser ablation has become a very promising tool for both advanced micromachining and thin film deposition.[1] In most of the cases, a plasma formed by neutral and ionized species is produced whose dynamics has been widely studied in order to understand the physical mechanisms controlling the thin film deposition process and properties.[2,3]

Lithium fluoride (LiF) is a wide- (~13.5 eV) band-gap material with interesting applications in integrated optics.[4] However, the synthesis of LiF thin films has scarcely been reported in literature. LiF films have mostly been grown by thermal evaporation leading to low-quality films.[5–7] In addition, there has only been one successful trial[8] to grow good-quality LiF thin films by pulsed laser deposition (PLD) out of different experiments resulting in rough films.[9,10] The main difficulties found when synthesizing LiF films by PLD have been related to the ultraviolet (UV)-induced defect formation and to the ejection[9] of particles of sizes of up of 2 μm at high laser fluences.[8]

A limited number of works have been focused to the study of the fundamental plasma parameters in PLD, such as the electron temperature and/or the electron density, that can be of interest for the study of the plasma reactivity, the energy transport into the plasma, the role played by plasma ions (whose concentration equal that of the electrons) and the plasma formation process when irradiating wide-band-gap materials with pulsed UV radiation from excimer lasers.[11–15] A recent work[16] reports interesting results on the comparison between nanosecond (ns) and femtosecond (fs) PLD of LiF at relatively high laser fluences (12.5 J/cm^2) including extensive optical emission spectroscopy (OES) studies, although no measurements of N_e and T_e were provided. In this regard, measurements of N_e and T_e in the near-surface region of the luminous plume formed by laser ablation of wide-band-gap materials have only been indirectly or partially reported.[11–14] Therefore, the aim of the present work is to determine the spatial evolution of N_e and T_e in the plasma produced by pulsed UV laser ablation of LiF crystals.

The plasma was generated by ablating a LiF crystal with 193 nm (6.4 eV photons) laser pulses from an ArF excimer laser having a full width at half maximum (FWHM) pulse duration ≅20 ns and a repetition rate of 10 Hz. The target was mounted in a rotating holder and placed in a vacuum chamber evacuated to a residual pressure of 1.0×10^{-6} mbar. The angle of incidence of the laser beam was 45°, and the laser energy density at the target surface was 1.5 J cm^{-2} (irradiance ~0.075 GW cm^{-2}) which is slightly above the threshold for seeing a visible plasma. The plasma was ×2 imaged onto the 20 μm entrance slit of a 0.75 m monochromator with a spectral resolution of 0.045 nm. This image was scanned along the normal to the target with a spatial resolution of 0.18 mm. The light was finally collected by a photomultiplier (15 ns rise time) connected to a boxcar averager/gated integrator with a gate wide enough to catch the main part of the transient, which means about 700 ns. The results presented here start at a distance of 1 mm from the target to be sure that the contribution from the continuum can be neglected. The collected intensities are corrected by normalized factors considering the spectral response of the photomultiplier and the grating of the spectrometer.

The estimation of N_e has been carried out by measuring the Stark broadening of the spectral profiles of an isolated line of Li I. The latter is a well-established and reliable technique for measuring electron densities in medium to high-density plasmas.[17] Stark broadening of well-isolated lines from neutral atoms is predominantly caused by electron-atom collisions, the FWHM of the Stark-broadened lines, d, being related to N_e (in cm^{-3}) by:[17]

$$d = 2W\frac{N_e}{10^{16}}\text{Å}, \tag{1}$$

where W is an electron impact parameter which, for the chosen Li I line [$\lambda_0 = 610.3$ nm from the triplet ($3d^2D_{3/2,5/2} \rightarrow 2p^2P_{1/2,3/2}$)], is a weak function of the temperature and only changes by a factor less than 1.07 over the temperature range of 2500 K–20 000 K.[18] We have used $W = 0.216$ Å to determine N_e.[18]

In order to extract the Stark broadening from the total experimentally measured line broadening, we have to previously deconvolute the different effects that contribute to the

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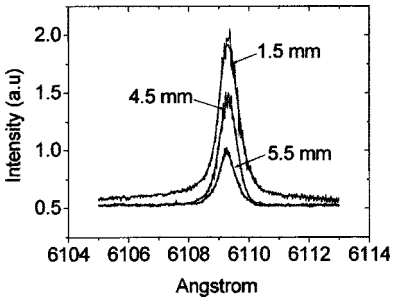

FIG. 1. Representative wavelength resolved OES spectra of the 610 nm Li line at three distances from the LiF target. The raw experimental line and the smoothed line are shown together at each distance.

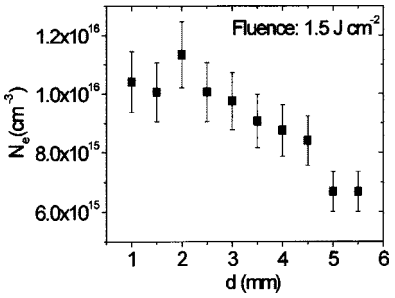

FIG. 2. N_e as a function of the distance to the target surface using the time-integrated configuration.

broadening of the spectral line: The instrumental broadening (linked to the spectral resolution of the monochromator) and Doppler and Stark broadenings. The contribution from Doppler broadening ($\sim$0.1 Å at FWHM) can be neglected when compared to the Stark broadening resulting from collisions of neutral atoms with charged particles that dominate for plasma densities above 10^{14} cm^{-3}.[17] Thus, the total FWHM, b, can reasonably be approximated by the expression:[19,20]

$$b \cong \left(\frac{d^2}{4} + g_{\mathrm{Ins}}^2\right)^{1/2} + \frac{d}{2}, \tag{2}$$

which has an accuracy of 1%,[19] and where d is the FWHM due to Stark broadening, and $g_{\mathrm{Ins}}=0.45$ Å is the measured contribution of the instrumental function (considered Gaussian). In order to determine g_{Ins}, a lithium hollow cathode lamp was used. Since b and g_{Ins} are known, the Stark broadening d can be derived from Eq. (2) and related to N_e through expression (1). Assuming that the error in measuring the instrumental FWHM is $\pm$5%, the use of expression (2) would produce an error in the Stark width and in the derived N_e that is less than $\pm$10%. Therefore, we think that the procedure followed is robust enough to allow the derivation of reliable values for N_e.

The experimental recorded emission spectrum only exhibited a few lines of the easily excitable Li I. Neither the (very difficult to excite) Li II lines nor the F I lines (visible F I emission lines require excitation of energy levels above 12 eV)[21] appear in the spectrum. F I emission lines have been recently observed by other authors[16] in PLD of LiF but only using fs laser pulses and much higher laser fluences than the ones used in the present work.

Figure 1 shows representative wavelength resolved OES spectra of the 610 nm Li line at three distances (1.5 mm, 4.5 mm, and 5.5 mm) from the LiF target. The raw experimental lines are shown together with the corresponding smoothed lines. It can be seen from this figure that there is no self-absorption. Consequently, we can use this optically thin line to extract the Stark width from its FWHM.

Figure 2 shows the time-integrated N_e calculated from expression (1) and (2) as a function of the distance to the LiF surface. The N_e values show a variation of less than a factor of 2 within the 5 mm length region analyzed. It is interesting to note that the present experimental N_e data cannot be fitted to the $1/d$ law predicted for a free expansion (from a point source into a large volume) which has been usually reported in plasmas produced by laser ablation of metals,[22] graphite,[23] and $YBa_2Cu_3O_7$,[24] but not of wide-band-gap materials.

The determination of T_e is done using the well-known Boltzmann plot technique and assuming local thermodynamic equilibrium (LTE).[20,25,26] Therefore, we have considered three spectral emission lines from Li I (610.3 nm, 460.2 nm, 413.2 nm) corresponding to the transitions with the greatest difference between their corresponding upper energy levels so as to make the method selected for measuring T_e more accurate.[25] In addition, these three Li I emission lines were selected in such a way that none of them end in the ground energy level of Li I so as to minimize their self-absorption by the plasma.

Figure 3 shows a Boltzmann plot at a distance of 3 mm from the target where the straight line is given by equation:[20,26]

$$\ln\left(\frac{I_i \lambda_i}{g_i A_i}\right) = -\frac{1.44}{T_e} E_i + C, \tag{3}$$

where C is a constant and I_i is the relative intensity of the emission line of wavelength λ_i (nm), g_i is the statistical weight of the upper excited level with energy E_i(cm^{-1}), and A_i(s^{-1}) is the transition probability for spontaneous radiative emission taken from the Kurucz atomic line database maintained by the Harvard–Smithsonian Centre for Astrophysics.[27]

In general, the closer the experimental points to the straight line fit, the better accuracy is achieved in obtaining T_e.[20,25] Thus, the good linear fitting to the experimental data of the three-point Boltzmann plot presented in Fig. 3 indicates that LTE really holds in our plasma as expected from the relatively high values of the measured electron density. Moreover, a necessary (though not sufficient) condition for having LTE is that $N_e(\mathrm{cm}^{-3}) \geqslant 1.4\times10^{14}\times T_e^{1/2}\times(\Delta E)^3$.[17] If we apply this rule to the less favorable case of our set of measurements, that is, the transition associated with the wavelength 413.2 nm of Li I with $\Delta E \cong 3.00$ eV and T_e

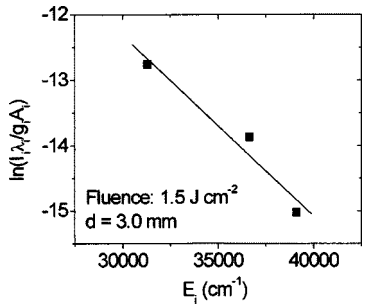

FIG. 3. Boltzmann plot performed at 3 mm away from the LiF target surface. The solid line shows a linear fit of the experimental data from whose slope the electron temperature is obtained.

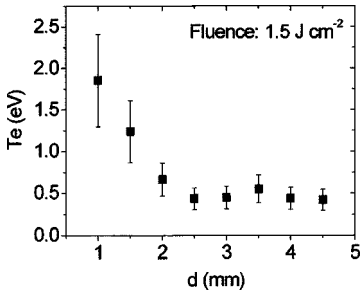

FIG. 4. Time-integrated T_e from the LiF plasma as a function of the distance to the LiF surface.

$=1.85$ eV, we have that LTE might start to hold for $N_e \geqslant 5.1\times10^{15}$ cm^{-3}. The latter value is lower than the ones we have determined here for N_e as seen in Fig. 2.

Figure 4 shows the dependence of the time-integrated T_e as a function of distance to the target. It is seen that T_e decreases sharply (from 1.85 eV to 0.66 eV) along the first millimeter and then T_e reaches an almost constant value around 0.45 eV. The latter behavior is in agreement to what has been reported for plasmas produced by laser ablation of metals,[22] graphite,[23] and $YBa_2Cu_3O_7$.[24]

In conclusion, we have performed direct measurements of the spatial evolution of T_e and N_e in the plasma produced by the ablation of a LiF crystal by 193 nm laser pulses at a fluence close to the ablation threshold (1.5 J cm^{-2}). We found that T_e exhibits a sharp decrease in agreement with previous studies of plasmas produced from the laser ablation of other materials. However, N_e shows a dependence on the distance d that does not follow the usual $1/d$ law observed in the plasmas formed after nanosecond laser ablation of several other materials other than wide-band-gap ones.

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