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LASER-INDUCED FLUORESCENCE AND TIME-RESOLVED EMISSION SPECTROSCOPY OF LASER ABLATION PLASMA

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Abstract. Based on the results of quantitative spectroscopic diagnostics the character of relaxation of parameters (n_e, T_e, n_a) of recombining laser produced plasma and processes (recombination, chemical reactions, cluster formation) which determine the plasma composition evolution were analyzed and the correlation of these processes with initial conditions of plasma creation were established.

Pulsed laser ablation plasmas produced by high power laser radiation near a solid target have numerous applications. These include deposition of thin layers, vaporization of sample material for spectrochemical analysis, formation of atomic, molecular and cluster beams. In the recombination phase such plasmas are attractive for generation of laser oscillations and as X-ray and vacuum ultraviolet sources. (Schriever *et al,* 1998, Ohyanagi *et al,* 1996). For optimization of these applications and refined management of ablation plume characteristics it is of great importance the understanding the basic physical and chemical processes governing the plasma composition at the various stages of its evolution.

The distinctive feature of pulsed laser ablation plasma is a complex spatio-temporal structure and a wide range of varying of plasma parameters during the plasma existence time. The plasma parameters are heavily dependent on irradiation conditions such as incident laser fluence, irradiation spot dimension, environment atmosphere composition and pressure. In a study of such plasmas one has to cope with a combination of short time scales (ns), small spatial dimensions (mm) and consequently strong plasma density gradients and the low density of the active species. In order to obtain the quantitative information on plasma parameters, like electron temperature, electron density, spatial and temporal evolution of transient species the currently available techniques should be adopted and laser aided diagnostics must be developed, which combine high sensitivity with a good spatial and temporal resolution.

In the present paper the laser-induced fluorescence method (LIF) combined with the time resolved emission spectroscopy was adopted to measure the spatial and temporal distributions of ions, atoms, and molecules, electron temperature and density in the laser ablation plasma. Based on the obtained results of diagnostics of plasma composition and its spatial-temporal changes at different irradiation conditions relaxation aspects of laser-produced plasma dynamics have been analyzed.

Details of the experimental apparatus employed in studies of laser-produced plasma composition have been described elsewhere (Burakov *et al,* 1997). Briefly, plasma was produced by focusing of a Nd:YAG (1064nm, 10ns, 10^8-10^{10} W/cm^2) or XeCl (308nm,10ns,10^8-10^9 W/cm^2) laser radiation on the surface of the metallic (Al, Ti) and graphite samples in the helium (air) atmosphere at pressures of 10^{-3}-500 Torr. The densities, temperatures, time-space distributions of various ablated species (Al, Al^+, Ti, Ti^+, AlO, TiO, C_2) were obtained.

Optical observation of the plasma emission was performed by imaging the section of the plasma plume onto the entrance slit of monochromator equipped by the fast photomultiplier. The emission spectra of plasma were recorded in the UV and visible region (spectral resolution of $\Delta\lambda \geq 3 \bullet 10^{-2}$nm) at different distances from the target surface. The detection of the photomultiplier signals was accomplished by a transient digitizer, connected to a personal computer for data processing, storage and analysis.

For LIF measurements a tunable dye laser radiation at the fundamental wavelength (560 - 630 nm) or its second harmonic was used to probe the ground state atoms and ions with the different delays after ablating laser pulse. The quantitative interpretation of LIF measurements was performed by using the three-level atomic and four-level molecular approximations, the measured collisional quenching rates of the excited states as well as taking into account the temporal shape of the excitation laser pulse and the temporal variation of the absorption linewidth. The fluorescence signals were calibrated against the fluorescence of dye solutions with known quantum yield (Burakov *et al,* 1989, Burakov *et al,* 1992). The final expression for the LIF measurements of absolute concentrations of atoms, (molecules) could be written as:

$$N = \alpha S_f / S_k, \quad (1)$$

where $\alpha = f(B_{ij}u, A_{ji}, Q_{ji})$, A_{ji} is the Einstein coefficient for spontaneous emission, $B_{ij}u$, $B_{ji}u$ are the coefficients for laser stimulated processes, Q_{ji} is

the collisional quenching rate; u is the laser spectral intensity, and S_j, S_k are the LIF and calibration signals, respectively.

The electron density (n_e) was determined from the emission linewidth measurements according to the Stark broadening theory. The shapes of some selected lines were analyzed at different delay times (with respect to the leading edge of the laser pulse) in order to obtain the temporal evolution of n_e. The choice of the emission lines for the n_e measurements was made according to the following rules: (i) the emission linewidth had to be sensitive enough to the Stark effect to ensure that this was the main broadening process under typical experimental conditions; (ii) the emission had to remain strong even at large distances from the target in order to permit time and space resolved measurements; (iii) self-absorption of the emission line had to be negligible.

The full width at half maximum intensity (FWHM) of the Stark broadened line ($\Delta\lambda$) and its Stark shift ($\delta\lambda$) are related to the electron density n_e by the expressions (Griem H.R.,1974):

$$\Delta\lambda(\text{Å}) = 2[1+1.75\bullet10^{-4}n_e^{1/4}\gamma(1-0.068n_e^{1/6}T_e^{-1/2})]\bullet10^{-16}wn_e, \qquad (2)$$

$$\delta\lambda(\text{Å}) = [d/w+2\bullet10^{-4}n_e^{1/4}\gamma(1-0.068n_e^{1/6}T_e^{-1/2})]\bullet10^{-16}wn_e, \qquad (3)$$

where w is the electron impact width parameter and γ is the ion-broadening parameter; both weak functions of temperature.

The electron temperature (T_e) was deduced by the relative intensities of lines from a given state of ionization. This is a standard approximation for the determination of T_e needed in the Stark broadening measurements. The validity of this approximation was confirmed by results of T_e determination from relative populations of three levels n_i, n_j, n_k using method developed by (Biberman L.M.and Vorob'ev V.S., 1982) for nonequilibrium recombining plasmas.

$$\frac{n_j}{g_j}\exp\left[-(I_{pj}-E_j)/T_e\right]\{X_j(y)-X_k(y)\} = \frac{n_i A_{in}}{g_i}\exp\left[-(I_{pj}-E_i)/T_e\right]\{X_j(y)-X_k(y)\} + \frac{n_k A_{kl}}{g_k}\exp\left[-(I_{pj}-E_k)/T_e\right]\{X_i(y)-X_j(y)\} \qquad (4)$$

where $X_m(y) = 4/\sqrt[3]{\pi}\int_0^y z^{3/2}\exp(-z)dz$, $y = (I_{pi}-E_m)/T_e$;

I_{pi} is the ionization potential, E_i ,and g_i are the energy and degeneracy of the state i, respectively.

The emission spectra, electron temperature and density are found to be influenced by the irradiation conditions and ambient atmosphere.

For example, the temporal evolution of electron density deduced from Stark broadening of the AlI 396.15nm line in the aluminum/air plasma and time dependence of electron temperature are shown in the Fig.1.

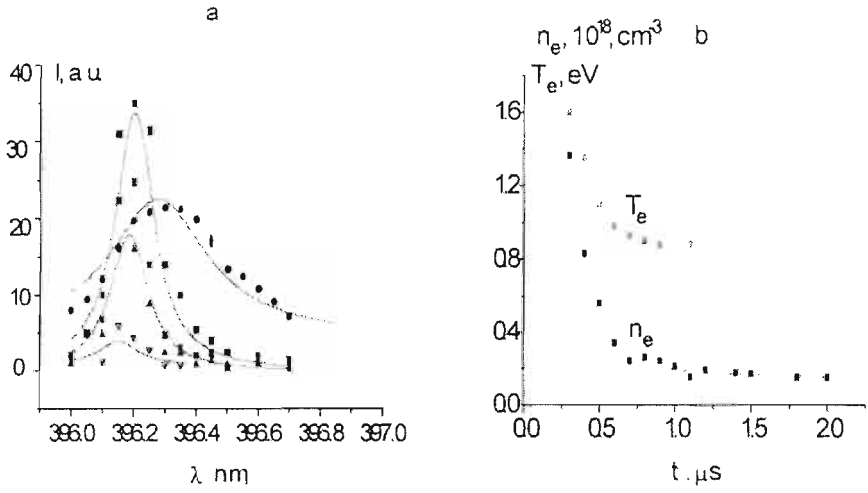

Fig.1. (a) AlI 396.15nm line Stark profiles at delays 0,4(•), 0,7(¦), 1,0(Δ), and 2 μs (∇) after the ablating laser pulse and (b) time evolution of electron density (n_e) and temperature (T_e) in aluminum/air plasma at distance of 0.5mm from the target and laser irradiance of 500 MW/cm^2. The dotted lines in Fig.1. (a) represent the Lorentzian fits.

The measured values of n_e are in the range of $1.4 \bullet 10^{18}$ -$3.5 \bullet 10^{17}$ cm^{-3} in the time interval of 0.3 - 0.6μs after the laser pulse, while the electron temperature drops from 1.6 eV to 1 eV. The electron temperature rapidly decreases in the time interval where maximal line emission is observed. After this time T_e begins to decrease more slowly, showing that there is a quasistationary equilibrium between the rates of cooling of electrons and their recombination heating. The temporal evolution of n_e for each distance can be characterized by an approximately biexponential decrease. The initial more fast decay rate can be attributed to the propagation of the recombining plasma, while the slow decay is preferably due to the recombination

processes. The temporal evolution of densities of electrons and excited atoms was explained in terms of three-body electron-ion recombination, ionization and gasdynamical expansion (Burakov *et al,* 1997).

The similar behavior of recombination dynamics has been observed in recombining titanium/air laser produced plasma. Fig.2,3 presents typical temporal history of species-resolved structure of this plasma illustrating the major periods where spectra of various species are usually observed. Temporal behavior of TiI 461,7 nm line emission indicates the rapid decay of its intensity during several microseconds, but the excited Ti-atoms are available to tens of microseconds. In this time interval the maximum of the ground-state Ti-atoms and electronically excited TiO molecules were observed.

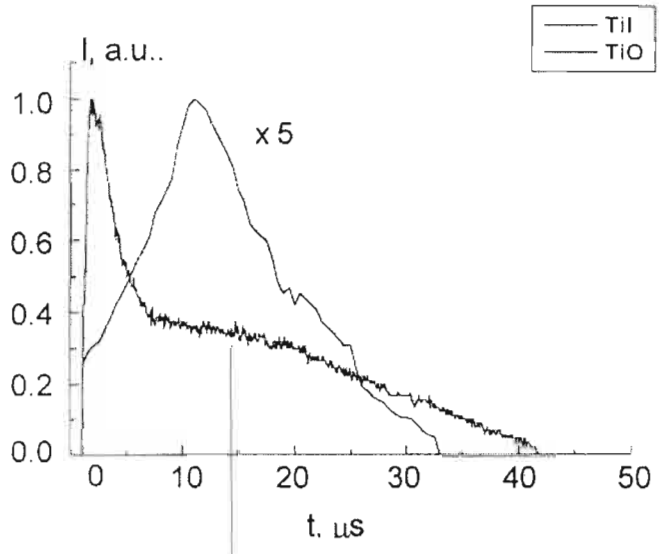

Fig.2. Temporal evolution of emission intensities of the TiI 461.7 nm line and TiO molecules at 560,2 nm, (0-0)-band of β-system at the distance of 1 mm from the target and laser irradiance of $1 \bullet 10^{10}$ W/cm^2.

The absolute measurements of concentrations of atoms, ions and molecules in laser ablation plasmas were performed by the LIF method. The temporal profiles of atoms and ions in the plume have the form of curves (Fig.3) with maxima whose value and position are dependent on the conditions of focusing of radiation onto the target. In the vicinity of the target surface the maximal density of ground-state atoms is reached at 15 μs,

ions - at 10 μs after starting of laser action. The observed temporal profiles are formed predominantly by recombination processes and cannot be explained by only the time-of-flight characteristics of the plasma. The range of the concentrations of Ti atoms of $2 \bullet 10^{13}$-$1.1 \bullet 10^{15}$ cm^{-3} and ions of $2.5 \bullet 10^{12}$-$4.5 \bullet 10^{13}$ cm^{-3} was recorded in the titanium/air plasma. TiO molecules were detected at the stages of plasma expansion and afterglow in the time interval of 5-60 μs after ablation laser pulse and up to 3 mm from the target surface (Fig.3). With the plasma evolution the density decreases up to 1 10^{13} cm^{-3} (60 μs) as well as with increasing of a distance from a target. Noteworthy, the strong dependence of species densities on the laser beam size was observed.

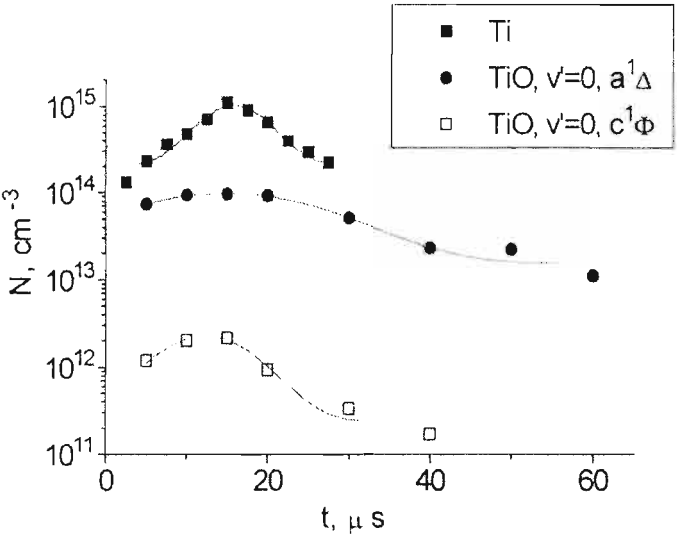

Fig.3. Concentrations of the ground state Ti atoms and TiO molecules in states $a^1\Delta$, $v'=0$ (•) and $c^1\Phi$, $v''=0$ (□) in the titanium/air plasma as a function of the delay from the ablation laser pulse at the distance of 1 mm from the target and laser irradiance of $1 \bullet 10^{10}$ W/cm^2.

Dynamics of recombination indicated a slow recombination of ions with electrons in the late stage of plasma decay. The characteristic recombination time essentially exceeded the gasdynamical expansion one. So, plasma has had time to fly apart without a complete recombination. It was supported by the temporal dependence of relative concentrations of ions

and atoms as determined by fluorescence measurements. Such situation in recombination dynamics called "frozen" ionization is caused by decreasing of electron density and delivering the kinetic energy to them in the recombination process and as result there exist a tendency to maintain the plasma temperature. The conservation of charged particles in the late stages may be favourable to the intensification of clustering process because the ions become the centres of condensation.

So, the investigations showed, that it possible to distinguish two main stages in the time and space evolution of laser-induced plasma in gas environment. The first stage is associated with an plasma expansion. Plasma evolution in this stage is ruled mainly by processes with charged species (ionization by electron impact, and three-body electron-ion recombination). At the end of this stage plasma involving electrons and multicharged ions is turned to plasma consisting of atoms (molecules) and one-charged ions (predominantly in ground states). The processes that govern the ablation plume-gas dynamics in this stage are chemical kinetics of the ablated species with background gas, for example oxidation reactions during laser ablation in the oxidant atmosphere (air), material or thermal diffusion in background gas, and cluster/particulate formation (condensation) as plasma cools (Burakov V.S., et al., 1995).

The formation of molecular carbon during laser ablation of graphite target in helium atmosphere was investigated by LIF monitoring of the time-space distributions of the C_2 and C_3 molecules in the ablated plasma. The presence of C_2 and C_3 molecules in plasma was considered to be as a first step in the formation of carbon clusters. The emission spectrum was dominated by the C_2 Swan bands ($d^3\Pi_g$ - $a^3\Pi_u$) in the Δv = -2; -1; 0; +1; +2 sequences. The emission spectra in the wavelength range 390 - 410 nm can be identified as the C_3 bands. The C_2 high pressure bands in the spectra were recorded including the (6 - 7) band at 543.4 nm and (6 - 8) band at 589.9 nm. These bands were thought to be either thermally excited or formed from atomic carbon recombination. The high vibrational temperatures of C_2 species (17800-12200K) estimated under various helium pressure support that, the recombination of free carbon atoms is the most likely mechanism for the production of C_2 molecules.

The experiments performed demonstrate the great diagnostic capabilities of the LIF combined with the time resolved emission spectroscopy for the analysis of plasma dynamics during the laser induced ablation of solid samples. Based on the quantitative data provided by LIF measurements the details about the densities, temperatures and kinetic

energies of various ablated species were obtained. The experimental results show a rather complex evolution of plume particles. In the initial stage of plasma decay the gasdynamical expansion and recombination processes play a major role in plasma evolution. The results permitted to elucidate the effects of oxidation kinetics and dimer (cluster) formations on the relative concentrations in ablation plasmas at the late stages. The role of excited and metastable reagents in oxidation kinetics has also been established (Burakov V.S., et al.,1999).

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