Laser induced aluminium plasma analysis by optical emission spectroscopy in a nitrogen background gas

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Abstract. We studied an Al plasma generated by a Nd:YAG laser with a laser fluence of 4 J/cm², a wavelength of 1064 nm, energy pulse of 500 mJ and 10 Hz repetition rate. We studied their spectral characteristics at various ambient nitrogen pressures by optical emission spectroscopy (OES). The N₂ gas pressure was varied from 20 mTorr to 150 mTorr. In Al plume, both atomic and ionic spectra were observed. The electron temperature and electron number density of the plume as a function of the ambient gas pressure were determined. The electron temperature was calculated by using the Boltzmann-plot method and the number density was calculated considering the stark effect as dominating on the emission lines.

1. Introduction
Pulsed laser deposition (PLD) has emerged as a potential technique for the fabrication of thin films and nanostructures of various materials because of the ability to control the size and shape of nanodeposits by varying the laser parameters, the gas atmosphere, target-substrate distance and substrate temperature [1-5]. This technique is highly suitable for depositing thin films at a relative high deposition rate and low cost. However, the interaction of laser light with the solid targets is a complicated process and is not yet completely understood. It consists of different stages: the laser ablation of the target; plasma generation; laser interaction with the plasma; plasma expansion and collision with a substrate. Laser-produced plasma is transient in nature with characteristic parameters that evolve quickly and are highly dependent on irradiation conditions such as incident laser intensity and pulse duration, laser wavelength, irradiation spot size, ambient gas composition, and ambient pressure. The stages of the plasma generation, laser interaction with plasma and plasma expansion play a very important role in the thin film growth process. In fact, during temporal evolution of the laser induced plasma (LIP), excitation and ionization of the evaporated material occurs, therefore, it is important to define its thermodynamic parameters, such as electron number density $N_e$ and temperatures of electrons $T_e$. In order to optimize and control the thin film growth process it is necessary to study the dependence of these parameters of the LIP on the deposition conditions and to develop suitable diagnostics. For measuring and controlling the parameters of the LIP the method of OES is used extensively [6]. It is based on the study of the spectral distribution of line intensity and broadening in emission spectra. In this paper we report on optical emission spectroscopic studies of AlN plasma plume accompanying pulsed laser ablation.

Atomic species are identified through the characteristic emissions in recorded spectra. The electron temperature $T_e$ and number density $N_e$ are determined from relative atomic and ionic line intensity...
measurements using the Boltzmann plot method. The properties of the created plume were investigated by acquiring spectra at different ambient pressures.

2. Experimental setup

The plasma was produced by ablating a Al target in a N$_2$ background gas. We used a short-pulse, Q-switched Nd:YAG laser which provided 7 ns, 500 mJ laser pulses at a wavelength of 1064 nm with a 10 Hz repetition rate. The experiment took place in a stainless steel vacuum chamber configured as a six-way cross of 10 cm inner diameter tubes forming a central 10 cm diameter target chamber evacuated to 10$^{-5}$ mTorr, and flushed with pure nitrogen (99.99%) at different flow rates during experiments. The laser beam was focused with a 20 cm focal length lens on an Al target (99.99%) with a 45° angle of incidence, giving an energy density of approximately 4 J/cm$^2$. Nitrogen gas (99.99%) was injected to the chamber as a reactive gas, and the flow of such was accurately controlled by a needle valve. During laser ablation, nitrogen pressure was varied from 20 to 150 mTorr as measured by a vacuum gauge. The substrate was placed at a distance of 60 mm from the target. The films were deposited on silicon substrates that had previously been ultrasonically cleaned in acetone. Emission spectra were collected, imaged onto spectrograph TRIAX 550™ with 1200 grooves/mm grating and a resolution of 0.025 nm using two 10 and 13 cm focal length lenses positioned outside the reactor. For time-integrated spectra measurements, the spectrograph was equipped with a CCD linear sensor (1024 × 256). Most of the spectra were collected with integration times of 0.5 s.

![Figure 1. Optical emission spectra of laser induced aluminum plasma at different nitrogen pressures.](image)

3. Results and discussion

3.1. Analysis of plasma

Figure 1 shows optical emission spectra of the plume, recorded at various pressures of nitrogen gas. The optical emission spectra of plasma plume were recorded in the wavelength range from 200 to 800
nm at different pressures; the general structure does not vary much with the N\textsubscript{2} pressure. In the spectra shown in figure 1, the most intense lines are related to the emission from the aluminum species. Apparently, the main emitting species in the laser-produced plasma are excited single (Al II) and double ionized (Al III) ones. The lines with the highest intensity in the plasma spectrum are Al III at 563.15 nm and Al II at 273.4 nm, 302.66 nm, 376.25 nm, 452.64 nm, 616.15 nm and 695.02 nm. In addition, the most intense lines of nitrogen gas observed are neutral and multiple-ionized atoms of nitrogen; the lines are at 376.260 nm (N\textsc{iii}), 282.364 nm (N\textsc{ii}) and 496.398 nm (N\textsc{i}).

### 3.2. Determination of electron temperature

Determination of electron temperature was made assuming LTE resulting from collisions in the plasma, so that the populations of the bound states follow the Boltzmann distribution. The relative line intensities from a particular state can then be used to calculate the electron temperature of the plasma [7-8].

\[
\ln\left(\frac{I_{mn}\lambda_{mn}}{A_{mn}g_{mn}}\right) = \ln\left(\frac{N}{Z}\right) - \frac{E_m}{kT_e}
\]

where \(\lambda_{mn}\) is the transition wavelength, \(I_{mn}\) the intensity of the observed transition line, \(A_{mn}\) the transition probability, \(g_{mn}\) the degeneracy of the upper level, \(E_{mn}\) the energy of the upper level, \(k\) the Boltzmann constant, \(N\) the total number of states, \(Z\) the partition function, and \(T_e\) the electron temperature. For the transition, the upper state is labeled as \(m\) and the lower state by \(n\). The slope \((-1/kT_e\)) of the plot of \(\ln(I_{mn}\lambda_{mn}/A_{mn}g_{mn})\) versus \(E_m\) yields the temperature.

![Figure 2](image2.png) **Figure 2.** Calculation of electron temperature using the Boltzmann-plot method at different pressures.

![Figure 3](image3.png) **Figure 3.** Variation of plasma electron density at different nitrogen pressures, calculated from Stark broadening.
3.3. Estimation of electron density

There are three possible broadening mechanisms that can occur in the laser-ablated plume. The Doppler broadening, resulting from motion of the atoms, the Stark-broadening from collisions with charged species, and the resonance broadening arising from collisions between the neutral species exciting strong resonance lines [7]. Estimation of electron density depends principally upon the measurement of the Stark and Doppler broadening of some optical lines [8]. Doppler broadening is estimated by using the formula \( \Delta \lambda_{1/2} = 7.16 \times 10^{-7} (T_e/M)^{1/2} \), where \( T_e \) is the electron temperature in Kelvin and \( M \) the atomic mass [9]. In our case, Doppler broadening can be ignored. Stark broadening of an isolated line in the plasma was, thus, used to estimate electron density in the plasma. The \( S^3_{d1}D^{-} - S^{16}_{f1}F \) transition of atomic Aluminum (Al II) at 617.2949 nm was used for electron density measurements. The Stark-broadened profiles were recorded at various pressures and fitted to the Lorentzian profile. FWHM \( (\Delta \lambda)_{1/2} \) of the Stark broadened of a line is related to the electron density through the expression [7, 9].

\[
\Delta \lambda_{1/2} = 2W \left( \frac{n_e}{10^{16}} \right) + 3.5 A \left( \frac{n_e}{10^{16}} \right)^{1/4} \left( 1 - \frac{3}{4} N^{-1/3} \right) W \left( \frac{n_e}{10^{16}} \right)
\]  

(2)

this is the sum of two (electron impact and ion-impact) terms. \( A \) is the ion broadening parameter and \( W \) is the electron impact-width parameter. Both \( W \) and \( A \) are nearly temperature independent [8]. \( N_D \) is the number of particles in a Debye sphere is given by

\[
N_D = \frac{1.72 \times 10^9 [T_e (eV)]^{3/2}}{[n_e (cm^{-3})]^{1/2}}
\]  

(3)

the contribution is almost entirely due to electron impact, and the half-width of the Stark broadened transition can be estimated by the first term in equation (2) to a good approximation [10]. Expression (2) reduces to:

\[
\Delta \lambda_{1/2} = 2W \left( \frac{n_e}{10^{16}} \right)
\]  

(4)

where \( n_e \) is the electron density in \( cm^{-3} \); the \( W \) and \( A \) parameters can be found in [7, 11].

| \( \lambda \) (nm) | \( A_k (s^{-1}) \) | \( E_i (eV) \) | \( E_k (eV) \) | Configuration | \( J_i - J_k \) | \( g_i - g_k \) |
|-----------------|-----------------|-----------------|-----------------|--------------|-----------------|-----------------|
| Al II 270.6435  | 3.326e+06       | 13.071346       | 17.651076       | 3s4p - 3s7d  | 0 - 1           | 1 - 3           |
| Al II 373.4715  | 2.954e+06       | 15.062085       | 18.383310       | 3s4d - 3s11f | 2 - 3           | 5 - 7           |
| Al II 617.2949  | 5.103e+06       | 16.604633       | 18.612722       | \( S^3_{d1}D^{-} - S^{16}_{f1}F \) | 2 - 3           | 5 - 7           |
| Al II 697.3449  | 7.445e+05       | 16.604633       | 18.382210       | \( S^3_{d1}D^{-} - S^{16}_{f1}F \) | 2 - 3           | 5 - 7           |

4. Conclusions

We used the optical emission spectroscopy method to analyze the spectra plasma generated by Nd:YAG pulsed-laser of nanosecond pulsed inciding on Al target in a nitrogen atmosphere. Emission
spectra were mainly due at single ionized and double ionized Al species, also we observed neutral and single ionized Nitrogen species. The electron temperature $T_e$ has been determinated from the Boltzmann plot method and electron number density $N_e$ is estimated from the stark broadened profile of the spectra lines. The electron density found to be decrease with increase in Nitrogen pressure; besides, it is observed that the electron temperature achieves a maximum value at 67 mTorr of Nitrogen gas pressure.

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