Optical emission spectra of ZnMnO plasma produced by a pulsed laser

J Uzuriaga, J C Chamorro, R A Marín and H Riascos
Grupo Plasma, Láser y Aplicaciones, Universidad Tecnológica de Pereira A.A. 097, Pereira, Colombia.
E-mail: hriascos@utp.edu.co

Abstract. Optical emission lines from the plasma generated by a laser ablation process have been investigated to gather information on the nature of the chemical species present. In particular, the experiments were carried out during the laser ablation of a ZnMnO target, in presence of a controlled oxygen atmosphere. The resolved emission spectra are dominated by the atomic neutral or singly ionized emission lines from Zn species, while the Mn I line was detected in emission spectrum at 40 mTorr only. The background continuum, intensities and widths of all observed lines increased with increasing gas pressure. The electron density and electron temperature were calculated for various gas pressures. The electron density was found to increase with the increment of the argon gas pressure, whereas electron temperature decreased. The electron temperature and density are found to be similar to those obtained in the well-known pulsed laser deposition (PLD) process.

1. Introduction
Pulsed Laser Deposition (PLD) of material processing is a technique which has given good results for various applications of thin films of wide range materials [1–6]. In PLD, a pulsed laser is focused onto a target of the material to be deposited. For sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material creating a plasma plume. The ablated material is ejected from the target in a highly forward-directed plume. In PLD, the properties of the film growth are mostly affected by laser-ablation plasma; the composition of the plume is nearly identical to that of the target although there could be some mismatch due to incongruent melting of the target and/or intentional supply of atoms from the ambient gas. When the deposition is performed in a reactive ambient, in addition, the chemical reactions of the ablated species with the species in the reactive ambient play a crucial role in film deposition. Hence, the characteristics of the plume produced by pulsed laser ablation and the understanding of the processes involved in film deposition are of great interest. In this respect, it would be important to elucidate the correlation between plasma parameters and deposited film properties [7], one of the ultimate goals of the research on PLD mechanisms. The characterization of laser-ablation plasmas through the determination of their main parameters, as electron temperature and number densities of the different species present in the plasma, has gained high interest in recent years, allowing to improve the process control and providing better understanding of these complex and versatile spectroscopic sources. The most widely used method to determine the temperature of laser-ablation plasmas has been the Boltzmann plot method, which provides the excitation temperature from the measurement of line emissions
from a single species. In its simplest form, only two emission lines, which differ on their upper level energies, are necessary to obtain the excitation temperature [9]. In some works, Boltzmann plots have been obtained from a higher number of emission lines [8–11]; in this case, a good correlation of the experimental data to a linear fitting indicates the validity of the Boltzmann equation. In some cases, the measured line intensities corresponded to the emission from the whole plasma [12–14], so the Boltzmann plot method provided a single value of the excitation temperature of the plasma. Also, time resolution is used in light detection, as the plasma temperature is known to experience a rapid decrease due to the plasma expansion. In other cases, the emission from the plasma is spatially resolved in order to obtain the temperature at a given distance from the sample [9]. In this work, we present experimental results on the laser ablation of a ZnMnO target in Oxygen atmosphere, calculating the temperature and density of plume by using the optical emission spectroscopy method. Optical emissions from the excited molecules, as well as atomic species—both ionic and neutral—were observed as a function of the gas pressure and temperature of vacuum chamber.

2. Experiment

The oxygen gas was introduced at the vacuum chamber to obtain a pressure of several mTorr. The chamber was first pumped at a pressure of 10^{−6} Torr with a turbo- molecular pump.

An Nd:YAG pulsed laser operating at 1064 nm and a pulse width of 9 ns was used as a power source for ablation of ZnMnO target. The power of the laser pulse was about 1.2 W and the elliptical spot was below 0.05 cm². The plasma plume was created by illuminating the focused laser pulse onto the target at an angle of 45°C with respect to the normal direction of the target by a plane-convex lens of a 22 cm focal length. The target had a set rotating speed of 2.4 rpm to avoid the non-uniform pitting of the target and the target-to-substrate distance was 60 mm. The light emitted by the plume was measured along the direction perpendicular to the ejection through a spectrometer (Jobin Yvon Triax550) with a spectral resolution of 2 nm. The spectrometer was equipped with a 1200 lines per mm diffraction grating. The Optical Emission Spectroscopy (OES) measurements were carried out at the different temperature and oxygen pressures.

3. Plume characteristics

Figures 1 and 2 show optical emission spectra of the plume recorded at various pressures of oxygen gas and at different chamber temperature. The optical emission spectra of plasma plume were recorded in the wavelength range from 400 to 800 nm at various gas pressures and chamber temperature. The optical spectroscopy showed that the plasma emission is mainly due to atomic and singly ionized Zn for both gas pressures and chamber temperature variation. The observed line intensities are higher in ambient gas as compared to temperature. Since the plasma expands in ambient gas highly energetic particles produced in the early stage of plasma undergo collisions with the ambient atmosphere resulting in enhanced cooling. The strongest emissions were observed around 481.05 nm and 636.23 nm from the neutral Zn atoms (Zn I) and 773.25 nm from the singly ionized Zn atoms (ZnII) in the all gas pressure, others neutral spectral lines such as 468.01 nm, 472.1 nm, and the ionic line 492.4 nm appear in all pressures except at 13 mTorr. Practically at 13 mTorr there are a few presences of Zn emission lines.

We detected also following many weaker lines: three belonging to Mn I at 602.23 nm, 754.15 nm, and 768.02 nm, and of O I 610.62 nm. It is interesting to note that for the spectra at room temperature and 13 mTorr and at 300°C and 46 mTorr appear 481.05 nm, 636.23 nm and 773.25 nm lines only.

Significant variations in the intensities of emission lines of various atomic and ionic species of the plasma were observed with changes ambient gas pressures, it is observed that both electronically excited Zn atoms and the singly ionized Zn atoms peaks increase linearly with
The strongest observed emission lines of the plume are listed in table 1 with corresponding spectroscopic data [15].

| Wavelength | Transitions    | $g_k$ | $g_i$ | $A$ (s$^{-1}$) | $E_k$ (eV) |
|------------|----------------|-------|-------|----------------|------------|
| 468.01     | $4s5s^3S_1 \rightarrow 4s4p^3P_0$ | 3     | 1     | $1.55 \times 10^7$ | 6.654      |
| 472.21     | $4s5s^3S_1 \rightarrow 4s4p^3P_1$ | 3     | 3     | $4.58 \times 10^7$ | 6.654      |
| 481.05     | $4s5s^3S_1 \rightarrow 4s4p^3P_2$ | 3     | 5     | $7.00 \times 10^7$ | 6.654      |
| 636.23     | $4s4d^1D_2 \rightarrow 4s4p^3P_1$ | 5     | 3     | $4.65 \times 10^7$ | 7.744      |

Gas pressure as shown in figure 2. The strongest observed emission lines are listed in table 1 with corresponding spectroscopic data [15].

**Figure 1.** Spectra at various pressures.

**Figure 2.** Spectra at different chamber temperature.

### 4. Electron temperature

The characterization of the laser-induced plasma through the determination of their main parameters, i.e., electron temperature ($T_e$) and electron number density ($N_e$), is important to understand the dynamics of the process. Assuming plasma in local thermodynamic equilibrium (LTE), the electron temperature can be estimated using ratio of intensity of transitions belonging to the same atomic species and same ionization state for the optically thin plasma given by

$$\frac{I_1}{I_2} = \frac{A_1 g_1 \lambda_2}{A_2 g_2 \lambda} \exp \left( -\frac{E_1 - E_2}{k_B T_e} \right)$$

where $I$, $\lambda$, and $E$ are the intensity, wavelength (nm), and excitation energy of upper state (eV) of the corresponding OES peaks; $g$ and $A$ are the statistical weight of upper state and Einstein transition probability (s$^{-1}$); $k$ is the Boltzmann constant; and $T$ is the excitation temperature of the species under investigation. Subscripts 1 and 2 refer to the transition from respective states. The slope of the plot of

$$\ln \frac{I_{1mn} \lambda_{mn}}{g_m} A_{mn}$$

against $E_m$ gives the electron temperature (eV).
To calculate the electron temperature of the plasma, we have used four (Zn I) lines at 468.01, 472.25, 481.05 and 636.3 nm using the Boltzmann plot method and is shown in figures 3 and 4. Errors are bound to be present in the determination of the plasma temperature by this method; therefore the temperature is determined with approximately 15% uncertainty, mainly coming from the transition probabilities and the measurement of the integrated intensities of the spectral lines.

The electron temperature was calculated as a function of the gas pressure as well as the chamber temperature. In the former, the temperature varies from 11500 K to 38500 K, presenting the maximum electron temperature at 46 mTorr, whereas, in the latter it varies from 18200 K to 39300 K as gas pressure varied from 13 to 95 mTorr and the chamber temperature varied from room temperature to 400 °C respectively as shown figures 3 and 4. The electron temperature increases up to 46 mTorr and for higher pressures decreases. As shown on figure 4, in contrast with the case chamber temperature, the electron temperature behave very different, there were no a clear trend of increasing electron temperature with increasing chamber temperature.

![Figure 3. Electron temperatures as a function of gas pressure.](image1)

![Figure 4. Electron temperatures as a function of chamber temperature and constant gas pressure.](image2)

5. Electron number density
Spectral width of lines is composed of three contributions, namely, Doppler broadening, resonance pressure broadening and Stark broadening. It is assumed that the Stark contribution largely dominates the broadening of spectral lines in LTE.

The broadening of well-isolated lines from non-hydrogen neutral atoms and singly ionized ions is predominantly caused by electron impact. Since the perturbations caused by ions is negligible compared to electrons, the ion correction factor can safely be neglected. In this work, the ZnMnO plasma was assumed to be optically thin. With these simplifications the full width at half-maximum (FWHM) of the Zn line is related to plasma density (Ne) by the relationship [16,17].

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

(3)

where \( W \) is electron impact parameter [18]. From the above equation, it is clear that the electron density \( N_e \) is proportional to \( \Delta \lambda_{1/2} \). Strong Zn II spectral lines were also observed in the case of ablation in oxygen, which confirms that the zinc plasma is actually formed. The zinc plasma
formed above the target surface may absorb part of the laser energy and decrease the efficiency of the laser energy available for ablation of the target material.

Figure 5 shows the electron number density determined using Stark broadening of isolated lines of Zn at different gas pressures. At the pressure of 46 mTorr a maximum density was observed equal to $1.4 \times 10^{16}$ cm$^{-3}$, for higher pressures the density decreases. Figure 6 shows that the electron density values are not much affected by the presence of the temperature chamber, the electron density seems to be constant and equal to $1.44 \times 10^{16}$ cm$^{-3}$ at 46 mTorr.

![Figure 5. Plasma density determined by Stark broadening for different gas pressure.](image1)

![Figure 6. Plasma density determined by Stark broadening for different chamber temperature.](image2)

6. Conclusions
The electron temperature was calculated as a function of gas pressure as well as chamber temperature, ratio of intensity of transitions belonging to the same atomic species and same ionization state for the optically thin plasma, Its value as function of gas pressure and temperature chamber varied slightly. The electron density seems to be constant and equal to $1.44 \times 10^{16}$ cm$^{-3}$ at 46 mTorr for temperature chamber and gas pressure.

References
[1] Harilal S 2007 J. Appl. Phys. 102 1
[2] Geohegan D et al 2006 Photon-based Nanoscience and Nanobiotechnology (Springer)
[3] Wang X et al 2002 Chem. Phys. Lett 353.
[4] Ferrando V et al 2003 Supercond. Sci. Technol. 16 241
[5] Dauscher A, Thomy A and Scherrer H 1996 Thin Solid Films 280 61-66
[6] Miller J and Richard P 1998 Laser Ablation and Desorption (UK: Academic Press)
[7] Saji J, Joshy N and Jayaraj M 2006 J. Appl. Phys. 104 053307
[8] Aragón C and Aguilera J A 2008 Spectrochim. Acta Part B 63 893-916
[9] Shukla G and Khare A 2009 Appl. Surf. Sci. 255 8730-8737
[10] Shaikh N M, Hafeez S, Baig M 2007 Spectrochim. Acta Part B 62 1311-1320
[11] Griem H R 1964 Plasma Spectroscopy (McGraw-Hill Book Company).
[12] Harilal S 2001 Appl. Surf. Sci. 172 103
[13] Voevodin A, Jones J and Zubinski J 2000 J. Appl. Phys. 88 1088
[14] Amoruso S, Bruzzese R, Spinelli N and Velotta R 1999 J. Phys. B 32 R131
[15] NIST Atomic Spectra Database, http://physics.nist.gov, Kurucz output Atomic Spectral Line database
[16] I. Gornushkin B, King L A, Smith B W, Omenetto N and Winefordner J D 1999 Spectrochim. Acta Part B 54 1207
[17] Marr G V 1969 Plasma Spectroscopy (Elsevier Publishing Company)
[18] Dimitrijević M S and Sahal-Bréchot S 1999 Serb. Astron. J. 160 21-33