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Spectroscopic Characterization of Indium-Tin Laser Ablated Plasma

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***Abstract*—**In the present research work we present the optical emission studies of the Indium (In) – Tin (Sn) plasma produced by the first (1064 nm) harmonic of an Nd: YAG nanosecond pulsed laser. The experimentally observed line profiles of neutral Indium (In I) and Tin (SnI) are used to extract the electron temperature (T_e) using the Boltzmann plot method. Whereas, the electron number density (N_e) has been determined from the Stark broadening line profile method. The T_e is calculated by varying the distance from the target surface along the line of propagation of plasma plume and also by varying the laser irradiance. Beside we have studied the variation of N_e as a function of laser irradiance as well as its variation with distance from the target surface.

***Keywords*—**Indium – Tin plasma, laser ablation, optical emission spectroscopy, electron temperature, and electron number density.

I. Introduction

Laser Induced Breakdown Spectroscopy (LIBS), is a very simple and straightforward promising analytical technique being used for all types of matter. It is based on optical detection of certain atomic and molecular species by monitoring their emission signals from the laser induced plasma either in vacuum or open air at atmospheric pressure [1]. In the present study we have employed LIBS technique for the optical emission studies of In – Sn plasma produced by the fundamental (1064 nm) harmonic of a Q-switched Nd: YAG laser. We present the spatial evolution of the In-Sn plasma in which, experimentally observed line profiles of neutral Indium and tin have been used for the determination of Te using the Boltzmann plot method, whereas, the determination of Ne has been made from the Stark broadening line profile method. Apart from that, we have studied the variation of electron temperature (Te) and electron number density (Ne) as a function of laser irradiance.

II. The Sample

The sample under this study is Indium -Tin. A small piece (15 mm diameter and 3 mm thickness) was used as target material. The mass % of the Indium and Tin in the sample was 77.08 and 22.92 respectively as shown in Fig. 1. The Scanning Electron Microscope (SEM) photograph of the In-Sn is shown in Fig. 2.

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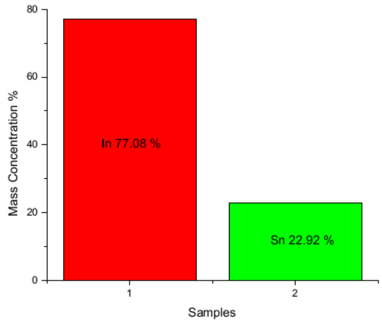

Fig. 1 Mass % of the sample components

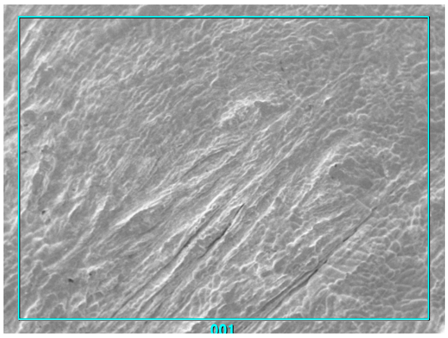

Fig. 2 SEM photograph of In-Sn sample showing its morphology

III. The Experimental Setup

The experimental setup is shown in Fig. 3, and is same as that described in our previous work [2]-[5]. Briefly we used a Q-switched Nd: YAG (Quantel Brilliant) pulsed laser having pulse duration of 5 ns and 10 Hz repetition rate which is capable of delivering 400 mJ at 1064 nm, and 200 mJ at 532 nm. The laser pulse energy was varied by the flash lamp Q-switch delay through the laser controller, and the pulse energy was measured by a Joule meter (Nova-Quantel 01507). The laser beam was focused through a 20 cm focal length quartz lens. The sample was mounted on a three dimensional sample stage, which was rotated to avoid the non-uniform pitting of the target. The distance between the focusing lens and the sample was kept less than the focal length of the lens to prevent any breakdown of the ambient air in front of the target. The spectra were obtained by averaging 10 data of single shot under identical experimental conditions. The radiation emitted by the plasma were collected by a fiber optics (high-OH, core diameter: 600 µm) having a collimating lens (0-45o field of view) placed at right angle to the direction of the laser beam. The optical fiber was connected with the LIBS-2000 detection system (Ocean Optics Inc.), to measure the plasma emission. The emission signal was corrected by subtracting the dark signal of the detector through the LIBS software. The LIBS-2000 detection system is equipped with five spectrometers each having slit width of 5 µm, covering the range between 220 to 720 nm. The uncertainty in the measurements is ≈ 0.02 nm. All the five spectrometers installed in the LIBS2000 are manufactured calibrated in efficiency using the DH-2000-CAL standard light source. The data acquired simultaneously by all the five spectrometers were stored on a PC through the OOILIBS software for subsequent analysis. In the experiments, the time delay between the laser pulses and the start of the data acquisition is about 3.5 µs, whereas the system integration time is 2.1 ms. In order to record the emission spectrum, the LIBS-2000 detection system was synchronized with the Q-switch of the Nd: YAG laser. The flash lamp out of the Nd: YAG laser triggered detection system through a four-channel digital delay/Pulse generator (SRS DG 535).The LIBS-2000 detection system triggered the Q-switch of the Nd: YAG laser.

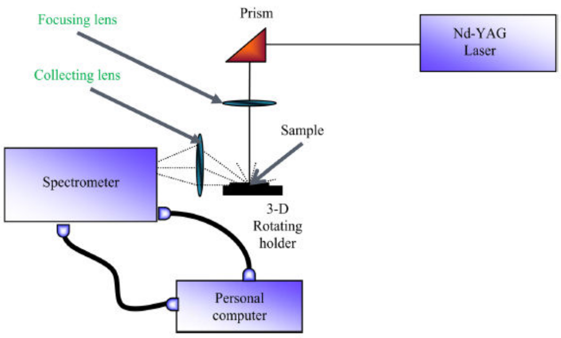

Fig. 3 Block diagram of the experimental setup

IV. Results and Discussions

A. Emission studies

In the first set of experiments, we have recorded the In-Sn plasma produced by the fundamental (1064 nm) harmonics of the Nd: YAG laser. The laser beam was focused on the target surface by a quartz lens with a focal length of 20 cm. The plasma was recorded at different positions along the direction of propagation of the plasma plume. Fig. 4 shows the window of emission spectrum covering the spectral region from 250 to 340 nm. In this spectral region, neutral (In I) as well as singly ionized (In II) lines of indium and few neutral lines of tin (Sn I) are present. The assignment of these spectral lines are well known and are shown in Tables I & II based on NBS (NIST) database [6] and using [7].

TABLE I
Spectroscopic Parameters of the Observed Neutral Indium Lines

Wavelength λ (nm)	Statistical weight gk	Transition probability A (s-1)	Excitation energy E (cm -1)
260.17	3	1.14×107	40363.98
271.02	6	3.14×107	39098.38
275.38	3	1.46×107	36301.86
325.85	4	3.76×107	32892.23

TABLE II
Spectroscopic Parameters of Observed Neutral Tin Lines

Wavelength λ (nm)	Statistical weight gk	Transition probability A (s-1)	Excitation energy E (cm -1)
231.72	7	2.217 ×108	51754.9
248.34	5	2.264 ×107	43682.7
257.15	7	4.768 ×107	47487.7
266.12	3	1.609 ×107	39257.1
286.33	3	5.40 ×107	34 914.2

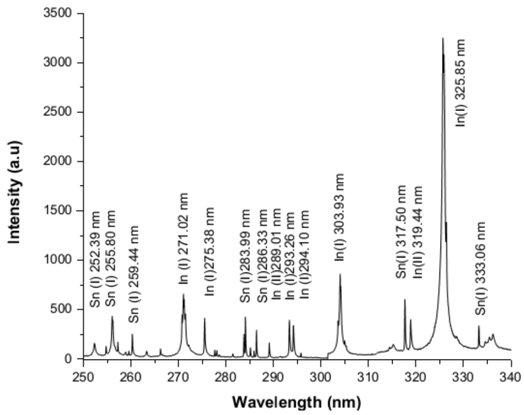

Fig. 4 The emission spectrum of Indium-Tin plasma produced by fundamental harmonic of the laser

B. Determination of Electron Temperature (Te)

The electron temperature (Te) is determined using the Boltzmann plot method from the relative intensities of the observed lines. The relative intensities are normally proportional to the population of the pertinent upper levels. The following relation has been used to extract the electron temperature [1]:

$$\ln\left(\frac{I_{ki}\,\lambda_{ki}}{A_{ki}g_k}\right)=\ln\left(\frac{N(T)}{U(T)}\right)-\frac{E_k}{kT} \qquad (1)$$

where, Iki is the integrated line intensity of the transition involving an upper level (k) and a lower level (i), λki is the transition wavelength, Aki is the transition probability, gk is the statistical weight of level (k), N(t) is the total number density, U(T) is the partition function, Ek is the energy of the upper level, K is the Boltzmann constant and T is the excitation temperature. A plot of ln (λI/gA) versus the term energy EK gives a straight line with a slope equal to (-1/ KT). Thus the Te can be determined without the knowledge of the total number density or the partition function. The line identifications and different spectroscopic parameters such as wavelength (λki), statistical weight (gk), transition probability (Aki) and term energy (Ek) are listed in Table I. For the determination of Te we have used four neutral indium lines at 260.17, 271.02, 275.38 and 325.85 nm respectively as shown in Fig. 5. Similarly, for tin, we have used four neutral tin (Sn I) lines at 231.72, 248.34, 257.15 and 266.12 nm as shown in Fig. 6. Errors are bound to be present in the determination of the electron temperature by this method therefore; the temperature is determined 5040 and 5100 K for In and Sn respectively with ± 200 K uncertainty, which is coming mainly from the transition probabilities and the measurement of the integrated intensities of the spectral lines. We have also studied the spatial behaviour by moving detector from the target material along the line of propagation of plasma plume. The electron temperature of the plasma close to the target surface (0.05 mm) is estimated as 6470 and 6360 K that varies to 4990 5190 K at a distance of 2 mm from the target surface for In and Sn respectively as shown in Fig. 7.

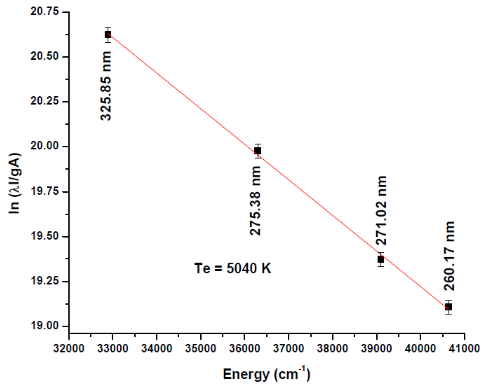

Fig. 5 Boltzmann plot based on four neutral indium spectral lines

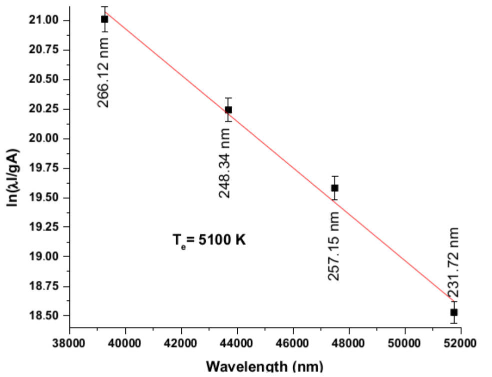

Fig. 6 Boltzmann plot based on four neutral tin (Sn I) spectral lines

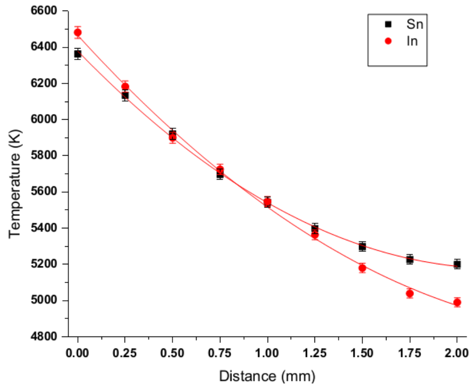

Fig. 7 Variation of the electron temperature along the direction of propagation of the plasma plume

C. Determination of Electron Number Density (N_e)

For the determination of electron number density (Ne), we have employed one of the most reliable techniques by using the measured Stark broadened line profile of an isolated line of either neutral atom or single charge ion. The full-width at half maximum (FWHM) of the Stark broadening profile is related with the number density through the following relation [1], [8]:

$$\Delta\lambda_{1/2} = 2\omega\left(\frac{N_e}{10^{16}}\right) + 3.5A\left(\frac{N_e}{10^{16}}\right)^{1/4}\left[1-\frac{3}{4}N_D^{-1/3}\right]\omega\left(\frac{N_e}{10^{16}}\right) \quad (2)$$

where, ω is the electron impact width parameter, A is the ion broadening parameter, Ne is the electron number density and ND is the number of particles in the Debye sphere. The first term in (2) refers to the broadening due to the electron contribution, whereas, the second term is attributed to the ion broadening. Since the contribution of the ionic broadening is normally very small, therefore, it can be neglected. Therefore, (2) reduces to:

$$\Delta\lambda_{1/2} = 2\omega\left(\frac{N_e}{10^{16}}\right) \quad (3)$$

Here Δλ1/2 is the width of the spectral line, ω is the electron impact broadening parameter and Ne is the electron number density. The observed line shape was corrected by subtracting the instrumental width from the observed width

$$\Delta\lambda_{\text{true}} = \Delta\lambda_{\text{observed}} - \Delta\lambda_{\text{instrument}} \quad (4)$$

The instrumental width of the LIBS 2000 spectrometer system is extracted as 0.05 (2) nm using a narrow line-width dye laser. The Stark broadening parameter is relatively independent of the temperature. The Ne was determined from the line profiles of the isolated neutral tin (Sn I) line at 286.33 nm using (3) for which the value of ω was adopted from reference data [9]. Fig. 8 (a) shows the spectral lines recorded from the plasma generated by the first harmonic of the laser. The laser energy was varied from 115 to 125 mJ for the various corresponding values of Q switch delay. The widths of the line profile increases as the laser energy is increased and its value is maximum at 25µs delay. Fig. 8 (b) shows the Stark broadened profile of neutral tin (Sn I) line at 286.33 nm recorded from the plasma along with the least squares fit of a Lorentizion line shape which yields the widthΔλ1/2of this line. The variations of Ne with respect to distance for In and Sn is shown in Fig. 9.

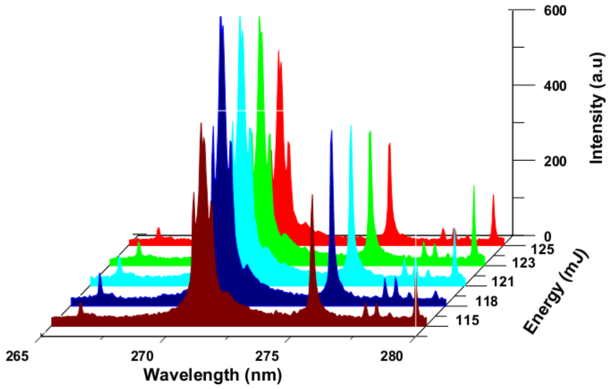

Fig. 8 (a) Variation in the signal intensity and width of the neutral tin line at 286.33 nm corresponds to several Q-Switch delays using first (1064 nm) harmonic of the laser

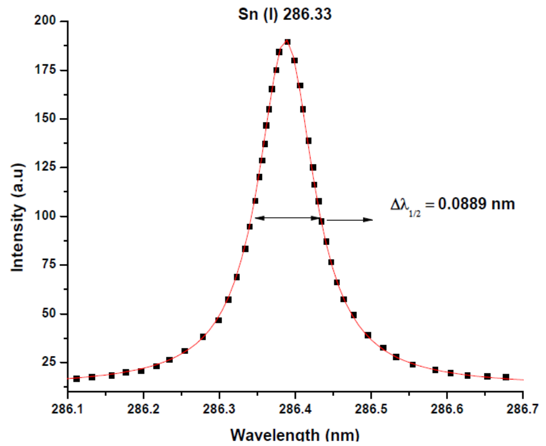

Fig. 8 (b) Stark broadening profile of the neutral tin line at 286.33 nm. The dots represent the experimental profile and the solid line is Lorentzian fit

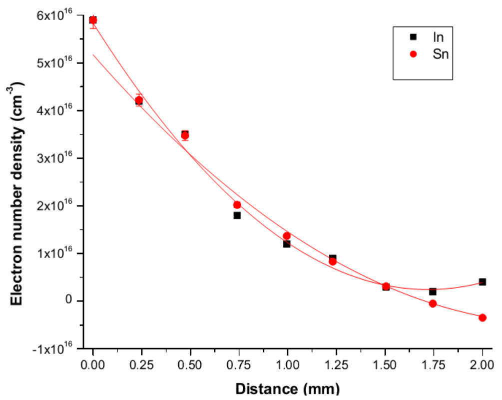

Fig. 9 Variation of the electron number density along the direction of propagation of the plasma plume

D. Effects of Laser Irradiance on Plasma Parameters

In the second set of experiments, we have determined the electron temperature and electron number density for different values of the laser irradiance using Nd: YAG laser at its fundamental (1064) harmonics. We have observed that the intensities and widths of the spectral lines increase with the increase in the laser irradiance. The electron temperature has also been determined by varying the laser irradiance from 2 x 1010 to 6.5 x 1010 W cm-2. The variation of Te with laser irradiances for In and Sn is shown in Fig. 10. Similarly, variation of Ne with laser irradiances is shown in Fig. 11. The decrease in the number density at large distance is mainly due to the recombination of electrons and ions.

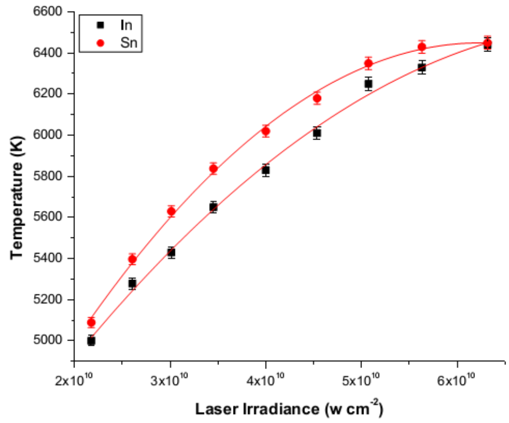

Fig. 10 Variation of the electron temperature with the laser irradiance

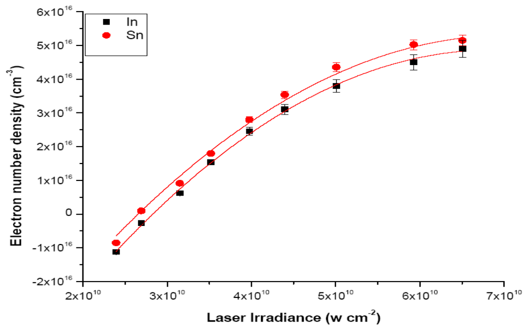

Fig. 11 Variation of the electron number density with the laser irradiance

E. Validity of Local Thermodynamic Equilibrium (LTE) Condition

The condition that the atomic states should be populated and depopulated predominantly by electron collisions, rather than by radiation, requires an electron density which is sufficient to ensure the high collision rate. The corresponding lower limit of the electron density is given by the McWhirter criterion to check the condition for the validity of the local thermodynamic equilibrium (LTE) [10]:

$$N_e \geq 1.6\times10^{12}\, \mathrm{T}^{1/2}(\Delta E)^3 \qquad (5)$$

where T (K) is the plasma temperature and ΔE (eV) is the energy difference between the states, which are expected to be in LTE. At ~ 6470 K temperature, (5) yields Ne ≈ 1016 cm-3. The electron number densities determined in our experiments are higher than this required number density to satisfy the LTE conditions. When the laser beam is focused on the target, the ablation of target takes place and due to the density gradient, the plasma rapidly expands.

V. Conclusion

We have used a Q-switched Nd: YAG laser at its fundamental (1064 nm) harmonic to study the indium – tin plasma produced at atmospheric pressure. The optical emission spectrum of the plasma reveals transitions of neutral and singly ionized indium and tin respectively. The electron temperature and the electron number density have been determined along the axial positions of the plasma plume. It is observed that the spatial behaviour of the electron temperature and electron density close to the target (0.05 nm) is maximum and decreases along the distance from the target. Variations of the electron temperature and the electron number density with the laser energy show that these both parameters increase with the increase in the laser energy. The observed increase in these plasma parameters with the increase of the laser irradiance is due to the absorption and/or reflection of the laser photon by the plasma, which depends upon the plasma frequency. In our experiment, frequency for fundamental (1064) harmonics of the Nd: YAG laser is 2.8 x 1014 Hz, whereas the plasma frequency is νp = 8.9 x103 √Ne. The electron number density is Ne ≈ x 1016 cm-3, therefore, νp ≈ x 1012 Hz which is less then the laser frequency, and shows that, the energy loss due to the reflection of the Nd: YAG laser from the plasma is insignificant.

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