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Spectroscopic Studies of Tin Plasma Using Laser Induced Breakdown Spectroscopy

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Abstract. Laser-induced Sn plasma generated at different laser intensities has been characterized using visible emission spectroscopy. A CO_2 laser pulse 85 ns in duration is used to generate plasma from a planar Sn sample in a vacuum of 10^{-5} torr. The plasma electron temperature is inferred by the Boltzmann plot method from singly ionized Sn emission lines, and plasma electron density is inferred using Stark broadened profiles. Electron temperature is measured in the range of (0.53 - 1.28) eV, and electron density is measured in the range of (9.19×10^{15} - 7.45×10^{16}) cm^{-3}, as the laser intensity is varied from (1×10^{10} to 2.5×10^{10}) W/cm^2. The plasma shielding effect has been observed within the laser intensities of (2×10^{10} – 2.5×10^{10}) W/cm^2.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a powerful and flexible tool for qualitative and quantitative elemental studies in a wide class of applications from material science to medicine. The ablation process using long pulse duration lasers (> 1 ns) is divided into three stages. In the first stage, the laser light interacts with the solid resulting in rapid ionization of the target surface into plasma on a time scale short compared with the pulse duration. In the second stage, the laser light is efficiently absorbed by the plasma which expands isothermally. In the third stage, after the end of the laser pulse, the resultant plasma plume expands quasi-adiabatically in a medium, which can include vacuum or a background gas, with or without applied fields [1,2].

Laser produced Sn plasma is the most promising candidate for the next generation extreme ultraviolet (EUV) light source used in the semiconductor lithography industry to produce microchips with feature size of 32 nm or smaller. It is considered as a potential EUV source due to its high conversion efficiency from laser to EUV light, and also due to the ability to control the ionic plasma debris [3,4]. Here we use the LIBS technique to study laser produced Sn plasma.

Most of the previous studies [5-7] using visible emission spectroscopy of laser-produced Sn plasma have used 1064 nm Nd:YAG laser radiation, and there have been minimal efforts to study the visible emissions from Sn plasma produced by a CO_2 laser with 10.6 µm wavelength. Here we measure the visible spectrum radiated by laser-produced Sn plasma using a CO_2 laser at intensities from 1×10^{10} to 2.5×10^{10} W/cm^2. The spectral line intensities allow the deduction of electron temperature and electron density in space and time and thus give information regarding the fundamental plasma physics involved.

2. Experimental setup

The experimental setup shown in figure 1 is one variation of the LIBS technique in practice. The laser used in the experiments consists of a master oscillator and power amplifier. The gas mixture ratio of the oscillator is (CO_2:N_2: He = 20:4:76 %), optimized to remove the long μs tail and enahnce the peak power of the oscillator to 1 MW. The pulse duration of the laser from the oscillator is shortened by an air-breakdown plasma shutter. The plasma shutter is triggered by free electrons from an air-breakdown plasma induced by a Q-switched Nd:YAG laser and pumped by the oscillator itself.

A 2 mm thick 98.4% pure Sn sample was mounted in the vacuum chamber on a 3-dimensional motorized stage which was translated in the focal plane before each shot to provide a fresh surface. The vacuum was maintained below 10^{-5} torr throughout the experiments. The CO_2 laser with pulse duration of 84 ns was focused on the target surface at normal incidence by an F/10 meniscus lens. The optical emission from the plasma plume was collected normal to the target surface with a 1:1 imaging system. The optical system consisted of a collimating and focusing lens used to image the visible plasma radiation to the entrance slit of a 0.5m Czerny–Turner spectrograph (Acton Pro, Spectra-Pro 500i). The spectrograph was equipped with three gratings: 150, 600 and 2400 grooves/mm. The output of the spectrograph was coupled to an intensified charge-coupled device (PI MAX, Model 512 RB) camera that was operated with vertical binning of the 512 × 512 pixel array to provide spectral intensity versus wavelength. A programmable timing generator enables the acquisition of time resolved plasma spectra by controlling the delay between the laser pulse arrival and the detector system, as well as the intensification (exposure) time. The highest resolution grating (2400 groove/mm) was used for better resolution when measuring the Stark broadened transition lines; these lines being used to estimate the electron number density. For the measurement of the excitation temperature, the 600 groove/mm grating was used.

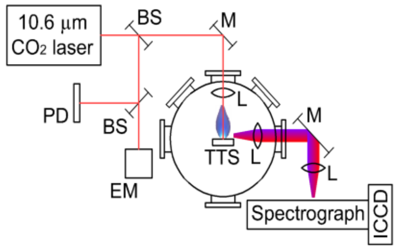

Figure 1. Experimental arrangement – BS-beam sampler, M-mirror, PD-photodiode, EM-laser energy monitor, TTS-target translation stage, L-lens, ICCD – intensified charge-coupled device camera, Spectrograph – Acton 500i SpectraPro.

3. Result and discussion

A sample of the emission spectrum covering the spectral region from 554 – 581 nm belonging to neutral (Sn I) and singly ionized (Sn II) is reproduced in Figure 2. In order to study the effects of the laser intensity on the emission characteristics of the laser produced Sn plasma in detail, the intensities of the Sn (II) lines at 556.19 nm (6d $^2D_{5/2} \rightarrow$ 6p $^2P_{3/2}$), 558.89 nm (4f $^2F_{5/2} \rightarrow$ 5d $^2D_{3/2}$), and 579.92 nm (4f $^2F_{7/2} \rightarrow$ 5d $^2D5_{3/2}$) were measured at various laser intensities. Figure 3 shows the dependence of the normalized intensities on the laser intensity. It is found that emission intensity of the Sn (II) transition lines at 556.19 nm, 558.89 nm and 579.92 nm increases by a factor of 13.0, 9.0, and 7.7 times with the increases of laser intensities from 1×10^{10} W/cm^2 to 2.5×10^{10} W/cm^2, whereas at the higher values of laser intensity from 2×10^{10} W/cm^2 to 2.5×10^{10} W/cm^2 a negligible variation is observed. As the emission intensity is associated with the density and temperature of the ablated material, so at the higher CO_2 laser intensity, which produces the dense plasma generated by the leading edge of the laser pulse, prevents light from reaching the surface. Therefore, most of the energy in the remaining part of the laser pulse will be absorbed by material in front of the surface prevent the tailing part of the laser pulse. Thus the laser energy delivered at high intensity is less effective in causing vaporization than the energy delivered at lower intensity.

In addition, we have recorded the spatial variation of the three transition lines from the Sn plasma along the normal to the target surface. In this experiment, the plasma is generated at a constant laser intensity of 1.5×10^{10} W/cm^2. Figure 4 shows the variation of the optical emission of Sn ions at different positions along the normal axis. It is found that emission intensity of the Sn (II) transition lines are all weaker close the surface up to a distance of 2 mm where a peak is reached, and then decay

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from 2 mm to the limit of our experimentation (5 mm). Up to 2 mm from the target surface, the intensities of the ionic lines are increasing because the collision process is dominant in this region which re-excites such ionic levels. Past 2 mm, the electron- ion recombination is fast as to result in a decrease of the emission intensities.

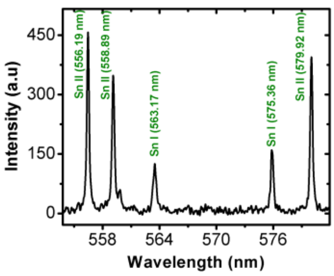

Figure 2. Emission Spectrum of the Sn plasma.

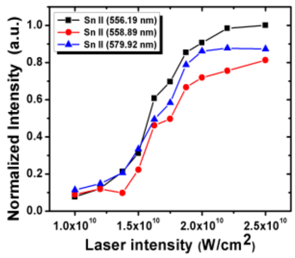

Figure 3. Variation in the integrated intensity of the Sn II transitions with laser intensity.

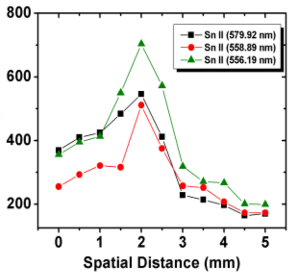

Figure 4. Spatial variation in the integrated intensity of the Sn II transitions.

3.1. Temperature and Electron Number Density

The key parameters of laser ablated plume are electron density and electron temperature. These parameters have been estimated under the assumption of local thermodynamic equilibrium as discussed in our previous work [8]. Five Sn II lines at 533.23 nm (6d $^2D_{3/2}\rightarrow$ 6p $^2P_{1/2}$), 556.19 nm (6d $^2D_{5/2}\rightarrow$ 6p $^2P_{3/2}$), 558.89 nm (4f $^2F_{5/2}\rightarrow$ 5d $^2D_{3/2}$), 645.35 nm (6p $^2P_{3/2}\rightarrow$ 6s $^2S_{1/2}$) and 684.4 nm (6p $^2P_{1/2}\rightarrow$ 6s $^2S_{1/2}$) have been employed in the Boltzmann plot method under the assumption of local thermodynamic equilibrium (LTE).

The shape and width of the spectral lines emitted by the plasma are governed by the collisional processes perturbing the emitting atoms and ions. Hence, the plasma density can be inferred from the profile of line spectra. The FWHM of the Stark broadened profile of Sn (II) lines at 556.19 nm has been used to estimate the electron number density [5,8]. The FWHM of the 556.19 nm is obtained by fitting the lorentizan profile shown in figure 5. The Stark broadening parameter ω was taken from Ref. [7]. Spectroscopic constants of Sn (II) lines used for the estimation of temperature have been taken from the NIST database [9]. The minimum criteria for LTE proposed by McWhirter [10] have also been verified and found to be the minimum electron number density $N_e \geq 2.2\times10^{15}$ cm^{-3} to justify the LTE assumption.

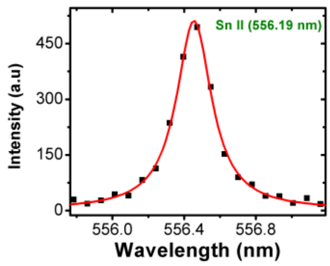

Figure 5. Lorentian fit on the Sn II transition line at 556.19 nm

Figure 6 shows the estimated values of the plasma temperature and number density of the Sn plasma dependence on the laser intensity. It is found that the T_e in the range of (0.53 - 1.28) eV, increases by the factor of 2.4 and the N_e is in the range of (9.19×10^{15} - 7.45×10^{16}) cm^{-3}, increases by the factor of 8 with the increase in the laser intensity from 1×10^{10} to 2.5×10^{10} W/cm^2. With increase in laser irradiance, the temperature and number density are found to increase up to the 2×10^{10} W/cm^2 laser irradiance and then to saturate. The saturation in temperature and number density above the 2×10^{10} W/cm^2 laser irradiance level is presumably due to plasma shielding, i.e., absorption and/or reflection of the laser photons by the plasma plume.

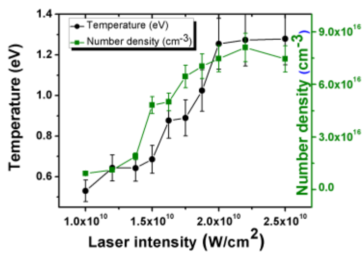

Figure 6. Dependence of T_e and N_e of the Sn plasma with laser intensity.

In the Previous reported work of O'Shay *et. al*.[6] measured higher temperatures and electron densities of Sn plasma generated by a 1.064 µm Nd:YAG laser than the work presented here. The laser parameters such as wavelength, spot size, pulse lengths and laser intensity used in Ref. 6 are 1.064 µm, 58 µm, 10 ns and 3.8 $\times 10^{11}$ W/cm^2 respectively, whereas in the present work we used as 10.6 µm, 200 µm, 84 ns, (1 - 2.5) $\times 10^{10}$ W/cm^2 respectively. The analytical properties of the laser ablated plasma are highly influenced by these parameters. Besides the longer pulse duration, higher spot size and lower intensity in the present work, the most important factor that influence the lower values of the temperature and number density is the laser wavelength, which directly affects the critical electron density (N_{cr}). The critical electron density at which the plasma becomes opaque to laser radiation is inversely proportional to the square of the incident laser wavelength. Thus critical electron density for 1.064 µm, Nd: YAG laser is two orders of magnitude greater than the CO_2 laser, whereas the optical depth of the 10.6 µm CO_2 laser in the target surface is less than the 1.064 µm Nd:YAG laser. This difference in laser absorption density explains the lower measured electron density in CO_2 laser-produce plasma plumes.

4. Summary

The effects of the CO_2 laser intensity on the emission, T_e and N_e of the Sn plasma have been studied. The variation in T_e and N_e with the laser irradiance shows that both the parameters increase with the increase in the laser intensity. It is found that emission intensity of the Sn (II) transition lines at 556.19 nm, 558.89 nm and 579.92 nm increases by the factor of 13.0, 9.0 and 7.7 and the T_e and N_e increases by the factor of 2.4 and 8 with the increases of laser intensities from 1×10^{10} W/cm^2 to 2.5×10^{10} W/cm^2, whereas at the higher values of laser intensity from 2×10^{10} W/cm^2 to 2.5×10^{10} W/cm^2 a negligible variation is observed. Plasma shielding effect has been observer within the laser intensity of (2×10^{10} – 2.5×10^{10}) W/cm^2.

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