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Investigation of Dependency of Laser Irradiance on Plasma Parameters for Silica by Using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract

The influence of changing laser irradiances on the plasma parameters, i.e. the electron temperature (Te) and electron number density (Ne), have been investigated by using Laser Induced Breakdown Spectroscopy (LIBS). This work aims to determine electron temperature and electron number density by analyzing the radiation emitting from the fused silica. For this purpose, evacuate the chamber to a base pressure of 10-6 Torr with the help of a turbo molecular pump. For the enhancement of emission intensity, the argon gas was filled at 20 Torr. The irradiance varies from 7.3 TW/cm2 to 10.7 TW/cm2. The calculated electron temperature from the Boltzmann plot method varies from 4950 K to 4975 K. Results showed the increasing trends of electron temperature with an increase in laser irradiances. Electron number density was calculated from the Stark-Broadened line profile, and it varies from 4.2 × 1017 cm-3 to 9.9 × 1017 cm-3. This study revealed that at low laser irradiance, the electron number density decreases, whereas at higher laser irradiance, the electron number density increases.

Keywords: System Laser, Electron, Temperature, Irradiance, Quartz, LIBS.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is an easy, useful, and non-destructive technique that uses high energetic pulses for the excitation of samples [1]. It leads the optical access to the sample for the detection of impurities or trace elements in solids, liquids, gases, and biological samples [2]. CF-LIBS method is used for the elemental analysis of the materials. Quantitative and qualitative analysis of materials can also be carried out by this method. High-energy pulses focused on the surface of the sample with the help of a suitable focusing lens. The focusing high-energy pulses ablate, evaporate, ionize, and form high-pressure plasma on the surface of the sample. The plasma plume formed has an extremely high temperature of a few thousand Kelvin and consists of positive ions and high-speed electrons. The plasma cools down by a process called plasma expansion. Radiation emitted from the sample is carried out to the spectrometer through optical fibers [3].

When the laser falls on the quartz sample, partial energy is transmitted (depending on the transmittance) and absorbed by the sample. As a result of the de-excitation process, samples re-emit radiation. [4]. Within a short time, LIBS detects simultaneously the neutral and ionized species by the spectral lines coming out from the sample [5]. The plasma formed due to the high-pulsed laser is transient in nature and depends upon the irradiance conditions, mainly the laser fluence, intensity, wavelength, ambient pressure, and pulse duration [6]. The thermodynamics parameters of plasma i.e. the electron temperature (Te) and the electron number density (Ne) depend on the laser irradiance [7]. In Laser- Induced Breakdown Spectroscopy (LIBS), the atoms are excited to higher energy states and eventually de-excited to their ground state, during which high energetic radiation is emitted [8]. These radiations are used for the measurements of the plasma parameters of the sample [3, 9].

The present work aims to determine the plasma parameters, i.e. electron temperature and the electron number density by analyzing the radiation emitting from the fused silica. The Nd: YAG laser having a wavelength of 1064 nm, pulsed duration of 10 ns, with its maximum energy of 105mJ has been used. Argon (Ar) gas is filled in the vacuum chamber at 20 Torr for the enhancement of emission intensity. The Boltzmann plot method has been used for the evaluation of electron temperature. The electron number density is calculated from the Stark-broadening line profile.

2. Experimental Setup

The schematic diagram of the experimental setup is shown in Figure 1. The laser beam generated from the Q-switched Nd: YAG laser (CFR 200 Big Sky laser Technologies Quantel France), operating at a wavelength of 1064 nm with an energy of 75 – 105mJ, pulse duration of 10 ns, a repetition rate of 10 Hz, and with laser irradiance varying from 7.3 TWcm-2 to 10.7 TWcm-2 was used for the plasma formation on the surface of Silica. A focus lens with a focal length of 20 cm is used to focus the laser on the fused silica sample. The sample was highly polished and cleaned with acetone before the experiment started.

A sample holder is used to slowly rotate with the help of a stepping motor to avoid the drilling of the sample. The sample was held perpendicular to the incident beam of the laser so that maximum laser energy fell on the sample. The plasma emission is viewed with the help of a quartz window at a right angle to the plasma generated from the material. The air present in the chamber gets ionized due to the high-energy laser that is why the chamber evacuated to a pressure of 10 – 6 Torr with the help of a vacuum pump.

An argon gas was filled into the chamber at a pressure of 20 Torr. Emissions from the fused silica are carried out by a bundle of optical fibers having CCD (charge-coupled devices) detectors for a broad band of 200 - 980 nm. The optical fibers carried the radiations to the LIBS 2500 - 7 spectrometer system (Ocean Optics lnc, USA). The Laser-Induced Breakdown Spectroscopy (LIBS) system has an optical resolution of 0.1 nm.

All the measurements have been performed with a time window of the order of 2.1ms. The time length between the laser strikes on the sample surface and the beginning of the measurements (called the delay time) was 2.15 µs. This delay is the time that the material gets ablated and vaporized, so the spectrometer begins to collect the signals.

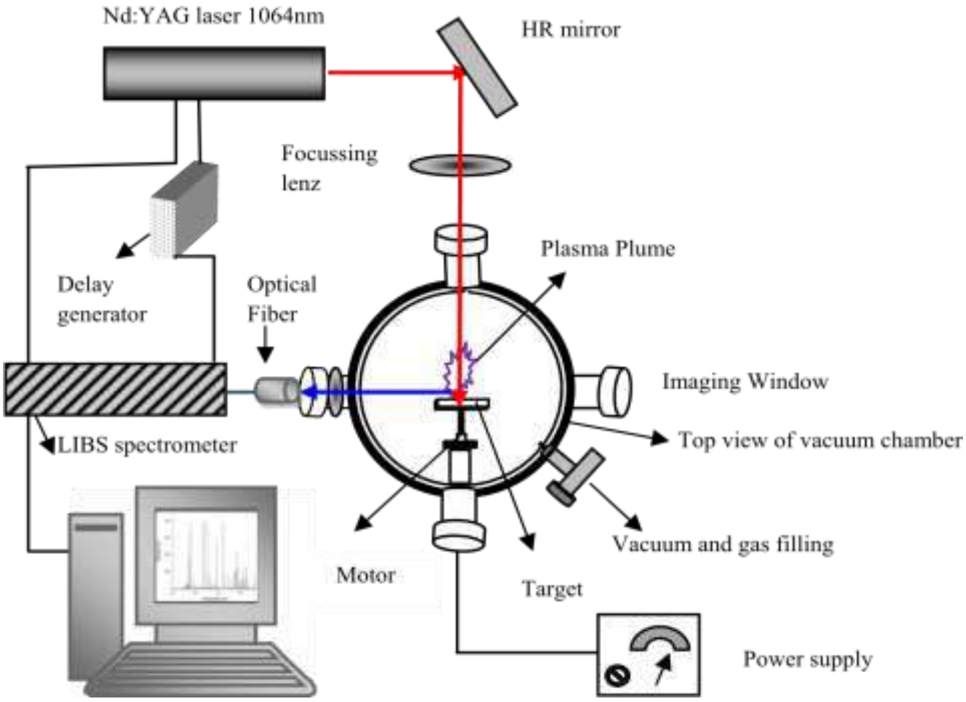

Fig. 1. The schematic diagram of LIBS set-up.

1.1 Measurement of parameters

The parameters measured by LIBS are electron temperature, calculation of width parameters, calculation of fluences, calculation of irradiance and the electron number density. The electron temperature and the electron number density are two important parameters of plasma. The plasma formed on the surface of the quartz consists of neutral as well as ionized species. The incident laser interacts with the plume in a complex manner, further exciting and ionizing ablated material in the plume. The de-excitation of the exited species in the plume results in the emission of radiation. After expanding to distances of a few mm plasma plumes are usually optically thin and exhibit many atomic neutral and ionic lines. The emission of spectra from the plume is used to calculate the electron temperature of the plasma plume. The irradiance of the plasma is calculated from the fluence, fluence is the energy per unit area. A specific line of wavelength 251.94nm is used for the Stark broadening by using which we have calculated the electron number density.

3. Results and Discussions

3.1 LIBS Analysis for Determination of the Plasma Parameters

3.1.1 Electron Temperature (Te)

Electron temperature (Te) and electron number density (Ne) are two important plasma parameters. The plasma formed on the surface of the fused silica consists of neutral as well as singly and doubly ionized species. The temperature and the density of plasma are remarkably high. A laser beam incident on the sample absorbs and excites the atoms of the sample. Electrons jumped to higher energy levels within a short interval of time, come back to their ground states and emit high energetic radiation. After expanding to a distance of a few mm plasma plumes usually exhibit many atomic neutral and ionic lines [10].

The electron temperature is important to understand the ionization, dissociations of atoms, and excitation process taking place in the plasma. The plasma is in the state of Local Thermal Equilibrium (LTE), and the temperature of the plasma depends on the energy of the incident laser. The emissions from the sample are used to calculate the electron temperature of the fused silica. Atoms and ions of plasma follow the Boltzmann distribution, and the electron temperature is calculated by the Boltzmann plot method, using eqn. 01 [11].

$$ln\,(\lambda_{mn}\mathrm{I}_{mn}/g_m A_{mn}) = -E_m/kT_e + ln(N(T)/\,U(T) \quad (1)$$

Where λ_{mn} and I_{mn} are the wavelengths and the intensity, respectively. And gm, A_{mn}, & E_m are the statistical weight, transition probability, and the energy of the upper state, respectively. K, Te, N(T), and U(T) denote Boltzmann constant, electron temperature, total number density, and partition function, respectively. Boltzmann plot between ln ($\lambda_{mn}I_{mn}$/gm A_{mn}) and the E_m for a specific spectrum gives a straight line as shown in Figure 2. The slope of the Boltzmann plot is equal to -1/kT_e and by using this slope electron temperature can be calculated, without knowing the values of N(T) and U(T). Spectroscopic parameters for silicon needed in calculations are obtained from the NIST database and are listed in Table 1. Figure 3 shows that the electron temperature is directly proportional to laser irradiances. The irradiance of the plasma is calculated from the fluence, while irradiance is the energy per unit area per unit time. As the irradiance of the laser increased the electron temperature increased as well. The electron temperature varied from 4950 K to 4975 K as the variation in irradiance changed from 7.3 KW/cm^2 to 10.7 TW/cm^2.

Table 1. Spectroscopic parameters for silicon obtained from the NIST database.

Wavelength(nm)	Intensity (I_{mn})	Statistical weight(gm)	Transition Probability108 (Amn)	Ek(J)
578.1987	151	3	2.97E+05	56578.26
579.9467	151	7	2.53E+05	57198.03
220.867	150	3	2.62E+07	45276.19
221.736	153	7	4.54E+07	45321.85
221.243	150	3	1.81E+07	45293.63
243.589	149	5	4.43E+07	47351.55
250.766	152	5	5.47E+07	39955.05
251.508	151	3	7.39E+07	39760.29
251.687	149	5	1.68E+08	39955.05

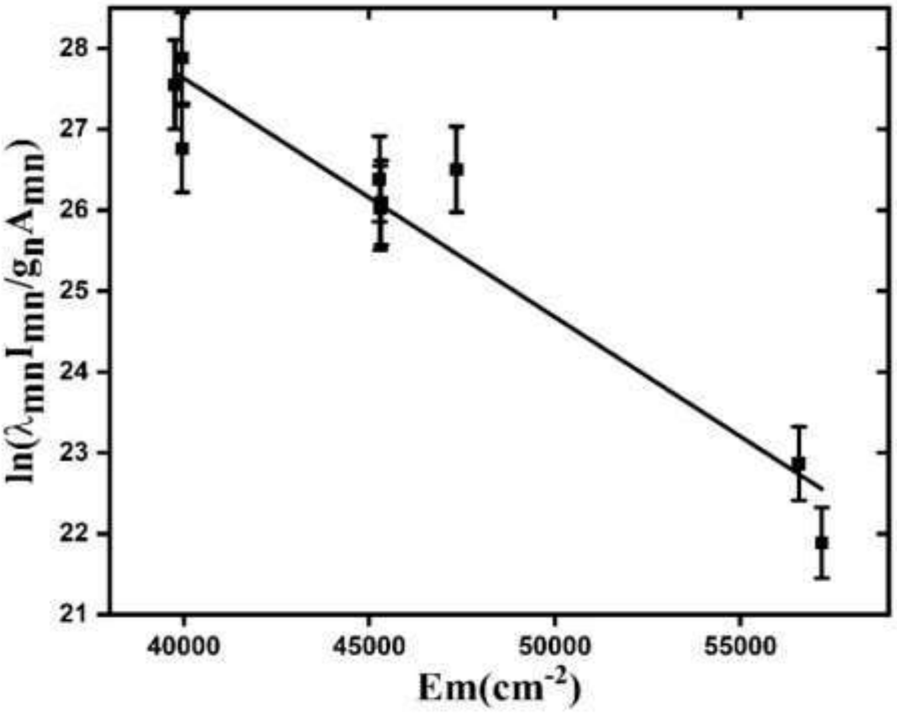

Fig. 2. The slope of Boltzmann plot obtained by using LIBS data for fused silica.

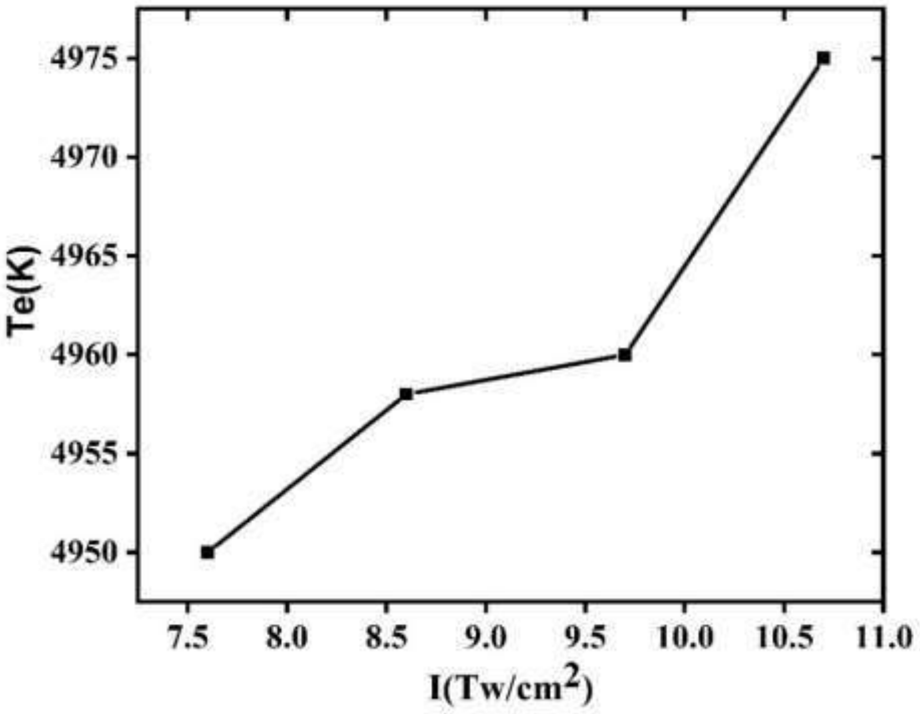

Fig. 3. The variation of irradiance of laser and electron temperature.

3.1.2 Electron Number Density

Electron number density is an important parameter of plasma, which shows the number of electrons when plasma forms on the surface of the sample. The electron numbers depend on the incident laser irradiance. There will be more ablation, and ionization of the material if the energy of the laser is high. The density of the plasma may be so high that the incident laser may not reach the sample, which is known as opaque plasma. At these conditions, plasma absorbs or reflects the incident laser. The plasma will expand within a few microseconds, so its temperature drops down, this process is known as plasma expansion. The electron number density can be calculated by the Saha-Boltzmann equation [12].

The electron number density can be calculated by various methods, such as Doppler broadening and Stark broadening. Among these methods, the electron density can measure with reasonable accuracy by Stark broadened line profile of an isolated atom. The plasma formed on the surface of the sample is in Local thermodynamics equilibrium (LTE), but this method can be used even if the plasma is not in LTE. The plasma number density determination using the stark broadening method is in the range of 1014 cm^{-3} to 1018 cm^{-3} [13]. The collisions between the charged species result in a broadening of lines and a shift in the peak wavelength.

The full-width half maximum (FWHM) of the Stark broadened lines $\lambda_{1/2}$ is related to the electron number density by the expression [14, 15].

$$\lambda_{1/2} = 2\omega(Ne/1016) + 3.5A(Ne/1016)1/4\,[1 - 1.2N_D - 1/3\,] \times \omega(Ne/1016) \tag{2}$$

Where ω is the electron impact width parameter, Ne is the electron number density (cm−3), and A is the ion broadening parameter. ND is the number of particles in the Debye Sphere. The electron impact parameter width (ω) can be calculated from the formula.

$$\omega = 4.8767 \times 10 - 4 + 1.6385 \times 10 - 8 \times T_e - 1.8473 \times T_e \times 10 - 13 \times T_{2e} \tag{3}$$

The first term in equation (2) refers to the electron broadening and the second term contributes to the ion broadening, and in our case, it is very minimal, so we neglected this factor, and Eqn. 2 reduced as.

$$\Delta\lambda_{1/2} = 2\omega\,(Ne/1016) \tag{4}$$

The Si I at a wavelength of 251.94 nm was selected for the determination of the electron number density, its shape is well-fitted by a Lorentzian function. A Lorentzian fit of 251.94 nm line used for the evaluation of electron number density is shown in Figure. 4. Electron temperature and electron density normally increase as the irradiance of the laser increases.

The calculated range of electron density is 4.25 ×1017 cm^{-3} to 9.98 × 1017 cm^{-3}, with the variation of laser irradiance from 7.3 TWcm^{-2} to 10.7 TWcm^{-2}. At lower irradiance of laser, the electron number density is low, but as the irradiance increased its value also increased to a maximum value. Calculated values of the electron number densities are given in Table 2.

A necessary criterion for the local thermodynamics' equilibrium condition imposes is given in Eqn. 5 [13].

$$Ne \geq 1.4 \times 1014\,Te\,\Delta E_3 \tag{5}$$

Where, Ne is the electron number density (cm^{-3}), and ΔE is the maximum energy difference between the states expected to be in LTE condition. In this work the electron density is between 4.25×1017 cm-3 to 9.98 × 1017 cm^{-3}.

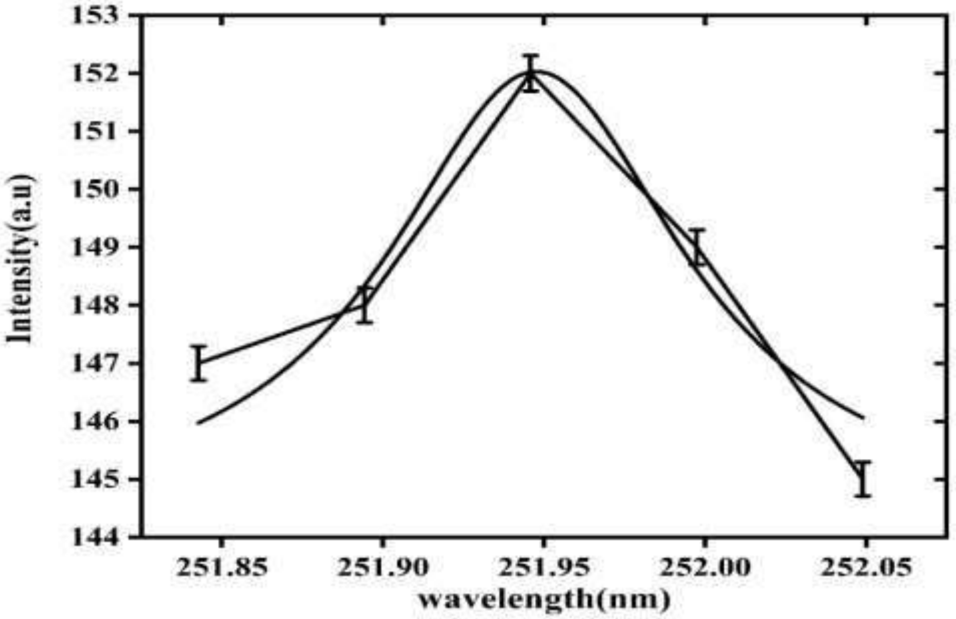

Fig. 4. A Lorentzian fit of 251.94 nm line used for the evaluation of electron number density of Si.

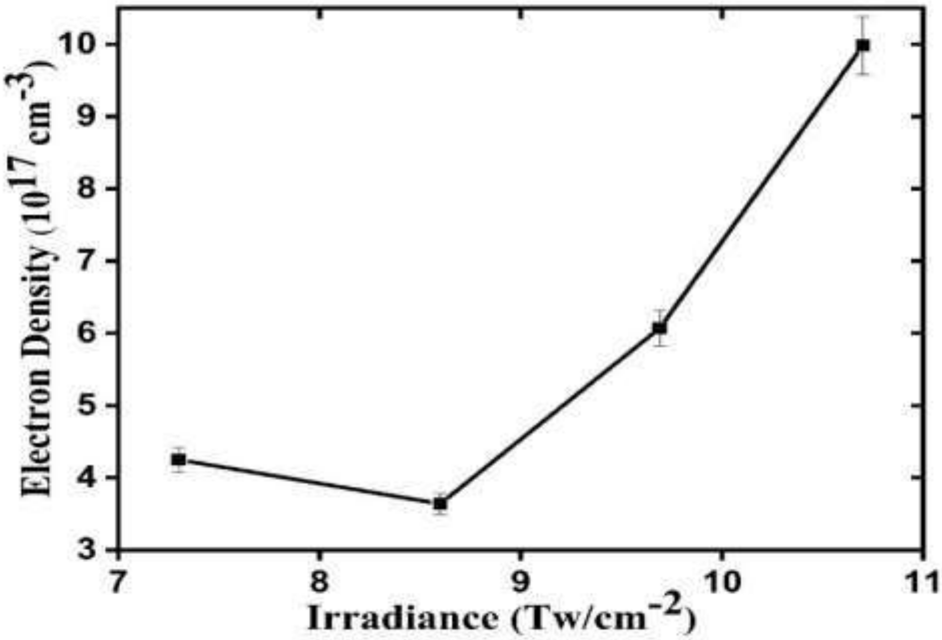

Fig. 5. The variation in electron number density of fused silica at various irradiances under Ar environment at a 20 Torr pressure.

Table 2. The calculated values of electron number densities at different temperatures vary from 4.25×1017 to 9.9×1017 cm-3.

Temperature T(K)	**T^2**	**ω(T) nm**	**FWHM Δλ (nm)**	**Ne=Δλ×10^16/2w (cm^{-3})**
4950	24502500	0.000564249	0.048	4.25 × 10^17
4958	24581764	0.000564366	0.04114	3.64 × 10^17
4960	24601600	0.000564386	0.06857	6.07 × 10^17
4975	24750625	0.0005646	0.11275	9.9 × 10^17

4. Conclusion

This study investigated the effect of laser irradiance on the plasma parameters of fused silica. LIBS analysis showed that the electron temperature and the electron number density are strongly dependent on the laser irradiance. They increase by increasing irradiance and attaining a maximum value at the maximum irradiance of 10.7 TWcm-2. All measurements are performed in the presence of Ar gas under a pressure of 20 Torr. The enhancement of the plasma parameters is due to more collisions, excitations, and de-excitation of the atoms. The maximum electron temperature calculated is 4975 K and the maximum electron number density is 9.9 x 10^{16} cm-3.

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