

## Study the Copper Plasma Generated Laser-Induced Breakdown Spectroscopy

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**Abstract:** In the present work, the optical emission spectra of Copper (Cu) plasma have been recorded and analyzed using the Laser Induced Breakdown Spectroscopy technique (LIBS). The emission line intensities and plasma parameters were investigated as a function of laser energy. The electron number density ( $n_e$ ) and electron Temperature ( $T_e$ ) were determined using the Boltzmann plot method and McWhirter criterion. Measured values of  $n_e$  and  $T_e$  are in the range of 9323 K-11871 K and ( $n_e$ ) is  $2.3 \times 10^{16}$ - $2.6 \times 10^{16} \text{ cm}^{-3}$  at the fundamental wavelength (1064 nm).

**Key words:** LIBS, copper plasma, plasma parameter, electron density number, determined, fundamental

### INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is a technique which was first reported in early 1960s and then reviewed by several researchers (Harilal *et al.*, 2005). This sensitive technique is based on an optical detection for certain atomic and molecular species by monitoring their emission signals from the laser induced plasma. It provides a useful tool to determine the chemical and physical properties of a wide range of materials including metals, liquids, aerosols, plastics, minerals and biological tissues, etc. (Harilal *et al.*, 2005; Pleslic and Andreic, 2005). It is a simple technique as compared with many other types of elemental analysis because of its straight forward experimental set-up. In this technique a pulsed laser is required to generate micro-plasma on the target surface (Tao *et al.*, 2007). Elemental analysis is accomplished by study the emission from plasma plume. The characteristics of laser induced plasma depend upon several parameters characterizing the features of the target, properties of the ambient medium, laser wavelength and pulse duration etc. (O'Shay *et al.*, 2007). The first direct spectral analysis made by LIBS can be attributed to Rung *et al.* (Abdellatif *et al.*, 2010; Mayo *et al.*, 2008). Copper is the most widely used metal for various applications of plasmonic materials due to its high electrical conductivity and optical properties. Gaudiuso *et al.* (2010) the objective of the present work was to characterize the laser induced copper plasma in term of spectral line intensities and plasma parameter ( $n_e$  and  $T_e$ ) under different laser power energy using LIBS technique.

### MATERIALS AND METHODS

**Experimental work:** The experimental setup that used in this study consist from: Q-switched Nd:YAG (Quantel brilliant) laser operating at 1064 nm (6 ns pulse duration



Fig. 1: Copper target

and 10 Hz repetition rate) was used as an ablation source with maximum pulse reach to 850 mJ per pulse. The laser pulse energy was varied by the flash lamp Q-switch delay through the laser controller and measured by an energy meter (Nova-Quantel P/niz01507). Optical system consist of: convex lens of 10 cm focal length, reflected mirrors made from brass with diameter about 50 mm and thickness about 5 mm. The emission spectra were obtained by recorded the emission with high intensity of shot under identical experimental conditions. The radiation emitted by the plasma were collected by an optical fiber model ocean optic (high-OH, core diameter: 600  $\mu\text{m}$ ) having a collimating lens (0-450 field of view) placed at right angle to the direction of the laser beam. This optical fiber was connected with the HR 4000 spectrometer (Ocean optics Inc.). The HR 4000 spectrometer consist of 14 grating available with entrance slit 5, 10, 25, 100 or 200 mm, covering the spectrum range from 200-1100 nm with optical resolution of 0.03 nm (FWHM), integration time 3.8 msec-10 sec. The sample was mounted on a three-dimensional sample stage from ocean optics which was rotated to avoid the non-uniform pitting of the target. The copper target was 3.0 mm diameter and 0.3 cm thickness as show in Fig. 1.

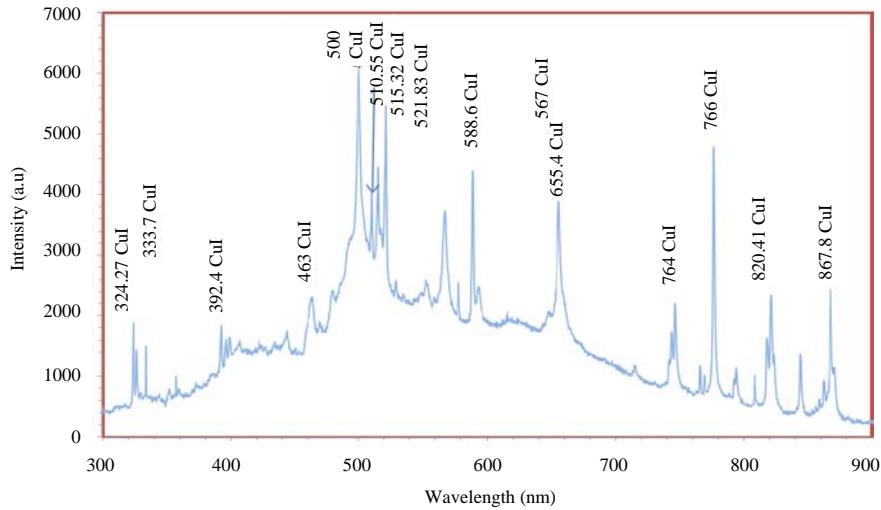


Fig. 2: Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5 mm, 81.5 mJ laser energy covering the region 300-900 nm spectral window

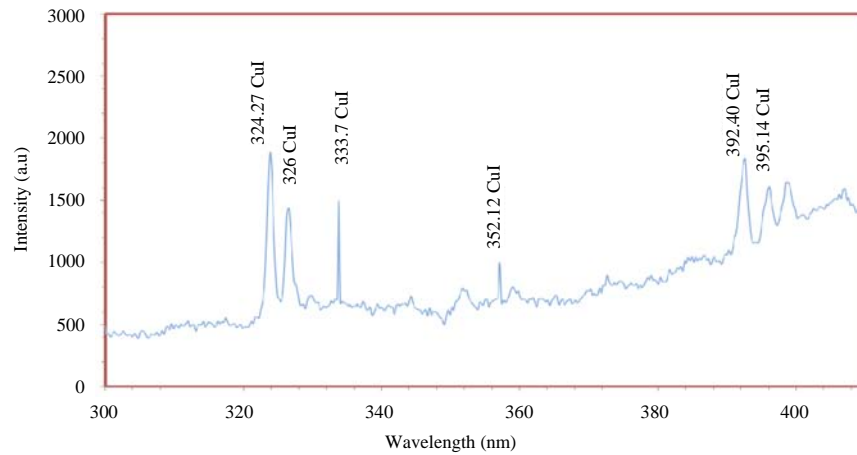


Fig. 3: Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5 mm, 81.5 mJ laser energy covering the region 300-400 nm spectral window

**RESULTS AND DISCUSSION**

**The optical emission spectra of copper plasma:** In the present research, copper plasma is generated using Nd:YAG laser at the first harmonic generated with 6 ns pulse duration 10 Hz repetition rate. The plasma emission was recorded as a definition of laser intensity to the surface of Cu target. Figure 2 shows the emission spectrum of copper plasma generated by laser energy at 81.2 mJ. Emission that recorded was covering the spectral region from 300-900 nm.

In Fig. 3 and 4 it is seen emission spectrum of copper plasma related to these spectrum region between 300-400 nm. Most of the lines in this region belong to emission of neutral copper. The lines at 324.75 and

333.78 nm are the strongest that are identified as  $3d^4P^{12}P_{3/2}$  to  $4S^{12}S_{1/2}$  and  $3d4P1^2P_{1/2}$  to  $4S^1S_{1/2}$  and  $3d4S4P4F_{7/2}$  to  $4S^{22}D_{5/2}$  transitions, respectively.

In Fig. 4 show the emission spectrum in the region between 400-550 nm. The dominating lines belong to emission of neutral copper besides a couple of lines attached to singly ionized copper the strongest lines of Cu I identified as  $4d^4d^2D_{5/2}$  to  $4P^2P_{3/2}$  at line 521.83 nm. The singly ionized line at 467.76 and 515.32 nm are identified as  $3d 4s 5s_2 D_{5/2}$  to  $4P^4F_{5/2}$  and  $3d 4d^2D_{5/2}$  to  $4P^2P_{1/2}$ , respectively. It is noticed that the lines of neutral copper are strong and sharp whereas that of singly ionized copper broad. The Cu II line at lower wavelength belongs to the  $4P^2 P_{3/2}$  to  $3d 4S^2 2 D_{5/2}$  transition.

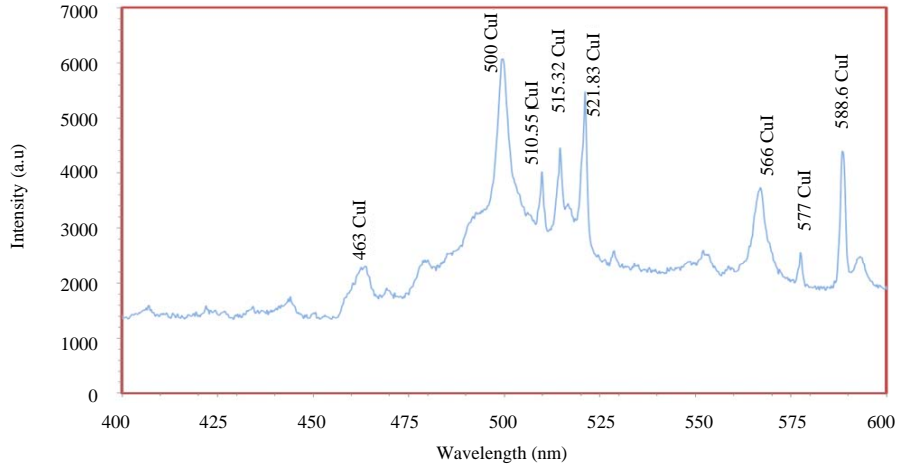


Fig. 4: Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5 mm, 81.5 mJ laser energy covering the region 400-600 nm spectral window

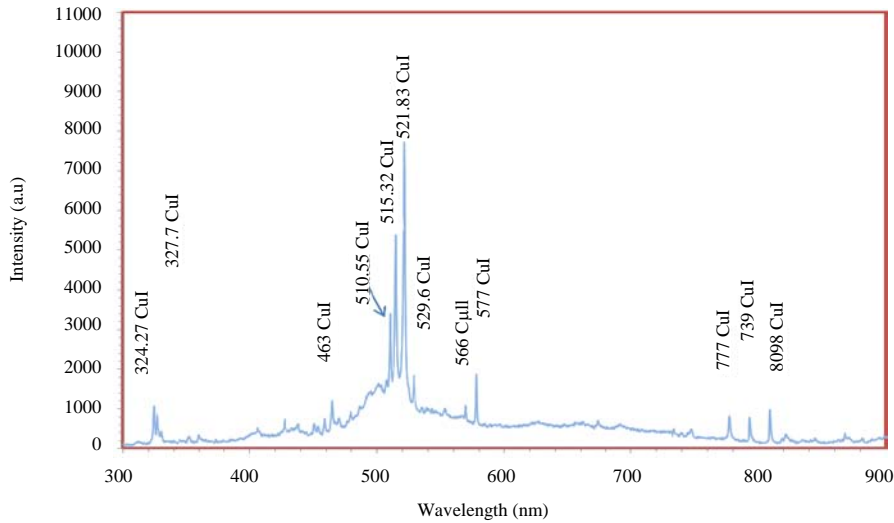


Fig. 5: Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5 mm, 134.5 mJ laser energy covering the region 300-900 nm spectral window

When the laser energy increased the spectral lines intensities and widths increase with the increasing laser energy. As shows in the Fig. 5 and 6 the emission of copper plasma at 1064 nm laser wavelength and 134.5 mJ laser energy. The emission spectrum of copper plasma using nanosecond laser is shown as in the Fig. 6. The intensity of CuI lines are more pronounced at transitions  $[4p^2P-4d^2D]$ , i.e., 515.324,  $[4p^2P-4d^2D]$  i.e., 521.820 and  $[4s^2D-4p^2P]$  i.e., 510.554 nm while Cu II lines such as  $[4p^1F-6d^3D]$  i.e., 324.7 nm and  $[5p^3P-5d^3D]$ , i.e., 577.721 nm have relatively low intensity. No Cu III lines were detected in these regions.

**The plasma temperature:** In the present research, the plasma temperature of the laser induced-copper plasma

has been determined using the Boltzmann plot method for which the plasma assumed to fulfill the LTE condition must be optically thin and the number densities in the excited states follow the Boltzmann distribution. Under these conditions, the electron temperature has been estimated using silver lines of the same ionization stage as give in Eq. 1:

$$\ln \frac{I_{ki} \lambda_{ki}}{A_{ki} g_k} = \ln \frac{N(T)}{U(T)} - \frac{E_k}{KT} \quad (1)$$

Where:

$I_{ki}$  : The integrated line Intensity of the transition involving upper level (k) and a lower level (I)

$\lambda_{ki}$  : The transition wavelength

- $A_{ki}$  : The transition probability
- $g_k$  : The statistical weight of level (k)
- $N(T)$ : The partition function
- $E_k$  : The energy of upper level
- (K) : The Boltzmann constant
- (T) : The exaction Temperature

Plot between  $\ln(I\lambda/gA)$  and upper level Energy ( $E_k$ ). The slope of this plot is equal to  $(-1/kT)$ . From this slope, plasma Temperature (T) can easily be estimated without knowing the partition function. The line identifications and different spectroscopy parameter such as wavelength ( $\lambda$ ), ( $g$ ) statistical weight, ( $A$ ) transition probability and term E Energy (Miziolek *et al.*, 2006) are listed in Table 1. Taking from NIST database (NIST). Five lines used to determine the plasma temperature by using Boltzmann plot method the copper lines is (510, 515, 521, 342 and 578 nm). The electron temperature behavior was studied as a laser energy function of the plasma generated by 1064 nm wavelength of laser irradiance. The electron temperature at 81.5 mJ to be 9323 K until reach to 11871 K at 221 mJ with increase the laser energy the electron temperature increase it is noted that the electron temperature increases with the energy which is surely due to higher energy transfer at this energy level. The region near the surface of the target material constantly absorbs radiation during the exposure time of laser pulse, responsible for enables the electron to

gain temperature and so on (Noll, 2012). The higher value of the temperature near the surface is due to the absorption of laser radiation by inverse bremsstrahlung absorption process and decrease in the temperature is due to the fact that the thermal energy is converted rapidly into kinetic energy (Cremers and Radziemski, 2006). The kinetic energy is used to attain maximum expansion velocities and is responsible for decreasing plasma temperature way form the target surface during expansion. Ying *et al.* also reported similar results for ArF excimer laser irradiance (Unnikrishnan *et al.*, 2010) Fig. 7 and 8 shows the Boltzmann plot that used to determine the electron temperature.

**The electron density number:** Electron density is given by McWhirter equation which is the condition for reached to smallest ND to ensure the warrant of the LTE (Singh and Thakur, 2007):

$$N_e \geq 1.6 \cdot 10^{12} T^{1/2} (\Delta E)^3$$

When  $t(k)$  as plum temperature and  $\Delta E$  (EV) it energy different between levels must been with local thermodynamic equilibrium. In our experiment the electron number density range satisfy the local thermodynamic equilibrium. When the laser focused on the target the ablated Cu surface take a placed with according to the density gradient plasma fasting expansion (Hanif *et al.*, 2012). Also the electron number density was calculated for different energy laser. It was observed increasing in electron temperatures and end with increasing the  $E_i$  it is came from absorption, reflection of laser photon by plum. With increase the exaction flounce, more species, ion and electron are generated the laser pulsed interacts with species. Resulting in further heat and

Table 1: Spectroscopy parameter of the singly/second ionized and Cu line data take from reference (NIST)

Transitions	$E_i$ (eV)	$A_{ji}$ ( $s^{-1}$ )	$g_i$	$\lambda$ (nm)	Atom/ion
$4S^2^2D4P^2P$	3.820	$2.0 \cdot 10^6$	4	510.55	CuI
$4P^2P4d^2D$	6.191	$6.6 \cdot 10^7$	4	515.32	CuI
$4P^2P4d^2D$	6.192	$7.5 \cdot 10^7$	6	521.82	CuI
$4S^2^2D4P^2P$	3.760	$1.65 \cdot 10^6$	4	578.21	CuI
$3d4p^2p_{3/2}$	33.780	$1.37 \cdot 10^8$	4	324.31	CuI

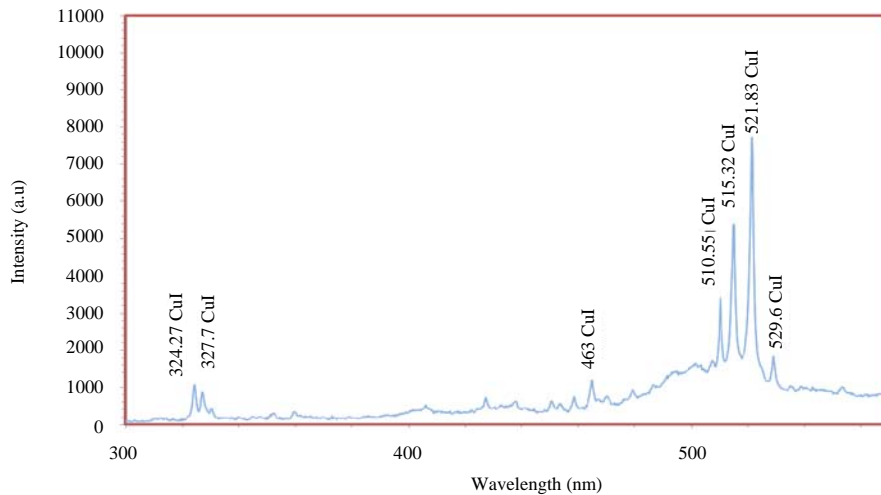


Fig. 6: Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5 mm, 134.5 mJ laser energy covering the region 300-600 nm spectral window

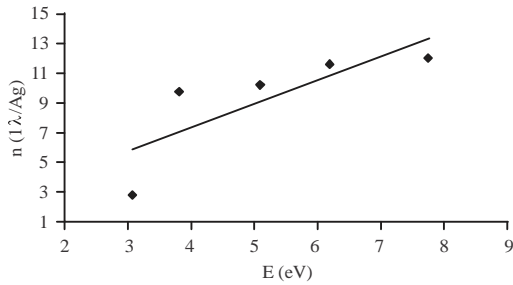


Fig. 7: Boltzmann plot for 5 neutral spectral line in 81.5 mJ by using 1064 nm for Nd:YAG laser

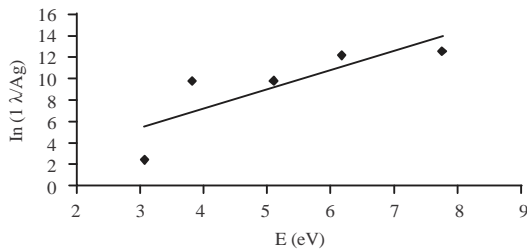


Fig. 8: Boltzmann plot for 5 neutral spectral line in 134.5 mJ by using 1064 nm for Nd:YAG laser

ionization and respectively, increasing consumption of incoming laser pulsed (Hanif *et al.*, 2011; Griem, 1974).

### CONCLUSION

We have used Q-switched Nd:YAG laser at fundamental 1064 nm to study the laser produce copper plasma. The emission spectrum of the plasma reveals transitions of natural and singly ionizes copper. The electron temperature and the electron density number have been determine along the axial positions of the plasma plum. It is observed that the plasma parameter will increase with increase the laser energy from 81.5-134.5 mJ. For the electron temperature in 81.5 mJ to be 9323 K and for 134.5 mJ to be 9500 K and the electron density number was  $2.3 \times 10^{16}$  and  $2.6 \times 10^{16} \text{ cm}^{-3}$ .

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