SPECTROSCOPIC STUDY OF $(TiO_2)_{1-x}(CuO)_x$ PLASMA GENERATED BY Nd:YAG LASER

Sabah N. Mazhir
Department of Physics, College of Science for Women, University of Baghdad, Iraq
E-Mail: drsabah6688@gmail.com

ABSTRACT

Laser-induced $(TiO_2)_{1-x}(CuO)_x$ plasma, which is produced by laser. A pulse of Nd:YAG laser is supplied for duration 10 ns produce plasma from a planar $(TiO_2)_{1-x}(CuO)_x$ sample placed in a vacuum having a pressure of 10^{-3}mbar. The temperature of the plasma electrons is calculate by the Boltzmann plot methodology from of Ti and Cu emission lines of singly ionized, and the density of the plasma electron is calculated with the use of Stark broadened profiles. As well as the electron temprature is calculated within the values of (0.699 - 0.781) eV, and the density of electron is measured in the values of $(34.7\times10^{18} – 50.5\times10^{18})$ cm^{-3}.

Keywords: boltzmann plot, plasma diagnostic, optical emission spectroscopy.

1. INTRODUCTION

The knowledge about free electron number densities, Ion, atom and their temperatures is very essential to describe the laser-induced plasma (LIP) which is crucial for modeling and analytical objectives. The above parameters are usually determined indirectly through the assistance of optical emission measurements, under the hypotheses is that plasma in local thermodynamic equilibrium (LTE) [1, 2, 3, 4].

Laser-induced plasma can constitute from the interaction of high-power Nd:YAG laser with solid medium. The produced laser can be utilized in many fields for instance, the elemental analysis that is depend on plasma emission. This process is called “laser-induced breakdown spectroscopy (LIBS)” [5, 6].

In comparison to other numerous diagnostic techniques that recognizes other transient processes/ occurrences, the optical emission spectroscopy (OES) has many advantages, such as obtaining information of the constituted elements, in addition of studying plasma expansion dynamics [7]. Normally, LIBS has the capacity to be utilized for the purpose of chemically describing the majority of the samples, which can include of metals, rocks, glasses, etc. The applications of LIBS “under gaseous condition” have shown considerable developed in the field of scientific research [8]. Showing a great capacity for development as a tool for space exploration, it is also considered as an accepted form of analysis in challenging applications[9]. In the case of high-speed practices, flow control process of laser-based has numerous merits with regards flow control applications [10]. In LIBS measurement, there are two main factors to explain laser-induced plasma: plasma temperature, as well as electron density. In terms of diagnostic techniques, temperature plasma can be clarified by integrated line intensities ratio, line intensity ratio to accompanying continuum, and the continuum spectrum shape [11,12].

2. ELECTRON TEMPERATURE CALCULATION

All types of internal energy (vibrational, rotational and electronic) represent a single temperature in LTE plasmas, the temperatures of Boltzmann and LET depend on atomic lines intensities. [13].

In this work, the method of Boltzmann plot is utilized in order to calculate the electron’s temperature T_e which is taken from the gradient of this method. By the same token, the peaks of this approach are very essential to calculate Te. These peaks can be obtained by the identical stage of ionization and the identical atomic species. However, a the latter method is superior to the ratio method because the lines having greater optical thickness can be readily localized amongst the large deviation of the data points.

The line intensity of spectral is calculated by [14]:

$$Iij = \frac{hc\ Ag\ n}{\lambda ij\ U(T)} e^{\frac{Ej}{KT}} \tag{1}$$

where I_{ij} and λ_{ij} denote the intensity and wavelength that match the transition from i to j respectively, h is the Planck’s constant, c is the light of speed, n is the number density of emitting species, $U\ (T)$ refers to partition function, Aij means the transition probability between level i and j, Boltzmann’s constant k, excitation temperature T, gj stands for the statistical weight of upper energy level and Ej means upper energy level [14].

From equation (1), minor rearrangement yields:

$$\frac{\lambda ji\ Iji}{hc\ Aji\ gi} = \frac{n}{U(T)} e^{\frac{-Ej}{KT}} \tag{2}$$

From the above equation, getting the natural logarithm on both sides, the result will be:

$$ln\left(\frac{\lambda ji\ Iji}{hc\ Aji\ gi}\right) = -\frac{1}{KT}(Ej) + \ln\left(\frac{N}{U(T)}\right) \tag{3}$$

Equation (3) gives linear relationship when $ln\left(\frac{\lambda ji\ Iji}{hc\ Aji\ gi}\right)$ is plotted viruses E_j [14].

3. ELECTRON DENSITY CALCULATION

The spectral line width and its final shape are influenced by numerous mechanisms such as of broadening types (natural, Doppler, Stark and instrumental). However, the Stark broadening which is related to the local electric fields developed by the adjacent particles which are charged, specially the electrons which are found in the vicinity of the emitting atoms, as a function of their density and energy is important and hence allows a more convenient manner to assess the density of the density of the electrons and the field strength. Hence, in plasma spectroscopy field, Stark broadening regarded as the single most important aspects of spectral line broadening which supplies the electron density with the known electron temperature of the plasma [15].

The density of the electron can be outlined by the equation:

$$\ln ne = 1.2\ln(\Delta\lambda\, {}^{1}/_{2}) + 44.2476 - 0.60\ln(Te) \qquad (4)$$

T_e refers to the electron temperature in K
ne refers to the electron number density in cm^{-3} [16].

$$\Delta\lambda\, {}^{1}/_{2} = 2[1 + 1.75\alpha(1 - 0.75r)]\omega \qquad (5)$$

Where ω is the electron impact half widths in nm, α is the ion broadening parameter in nm, r is the mean distance between ions divided by the Debye length [15].

4. DEBYE LENGTH MEASUREMENTS

Debye length is the measure of the penetration depth of the external electrostatic fields, i.e. of the thickness of the boundary sheath over which charge neutrality may not be maintained [17].

The Debye length λ_D can be calculated by the applied electrical potential and as shown in the following equation [16]:

$$\lambda_D = \left(\frac{\varepsilon_o k_B T_e}{n_e e^2}\right)^{1/2} \qquad (6)$$

where n_e is the density of the electrons (m^{-3}) , ε_O is permittivity of free space.

The foremost condition for the existence of plasma is the Debye length, which should be minute when compared to the system dimension (L) i.e.λ_D<<< L[18].

5. DEBYE NUMBER N_D MEASUREMENT

An additional plasma parameter which has an association with the Debye length is the particles number (N_D) in a Debye sphere has a radius equal to λ_D. When the Debye sphere includes many electrons, the effect shielding can form.

Depending on Debye sphere and number of electrons, it is easy to calculated Debye number as given in the following equation [19]:

$$N_D = \frac{4}{3}\pi n_e \lambda_D^3 \qquad (7)$$

6. EXPERIMENTAL DETAILS

The pellets $(TiO_2)_{1-x}(CuO)_x$ has been prepared from Nano shell Company with a purity 99.99% and Copper oxide with purity 99.99% were mixed at different concentrations Copper oxide of (x= 0.0, 0.05, 0.1, 0.15, 0.2) Wt. %. Optical emission spectroscopy measurements are performed to obtain the electron temperature and electron number density of Plasma Generated by Laser-the pellets $(TiO_2)_{1-x}(CuO)_x$ interaction under the vacuum of (10^{-3}mbar), by PLD technique, Nd:YAG laser was utilized to deposited thin films from TiO_2:CuO. The characteristic feachers of Nd:YAG laser were (λ= 1064 nm) SHG Q-switching laser beam at 800 mJ, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it as shown in Figure-1. Emission spectrum ranging from (100-1100 nm) is recorded in axial and radial directions by using ocean spectrometer (S3000-UV-NIR). The electron temperature is determined from the slope of Boltzmann's plot that uses the intensity of several spectral lines versus their corresponding excitation energies.

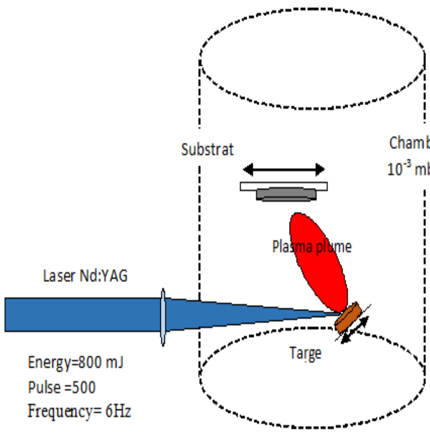

Figure-1. PLD set up using Nd:YAG with λ= (1064 nm) under the vacuum of (10^{-3}mbar).

7. RESULTS AND DISCUSSIONS

Plasma composition can be detected by OES by the careful monitoring of electronically the stimulated species and their intensities in the discharges produced by Ar plasma torch. Within the range (200 -1100) nm and utilizing a spectrometer (S2000), the spectra were detected. The S2000 is of great sensitivity, receives light energy emitted via optical fiber and spreads it through a fixed grating across the detector. The emission spectrum that covering the region of spectral (200 – 1000) nm that belongs to neutral (Ti I), (Cu I), (OI) and singly ionized (Ti II), (Cu II), (O 5II) as a function wavelength were reproduced in Figure-2.

ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

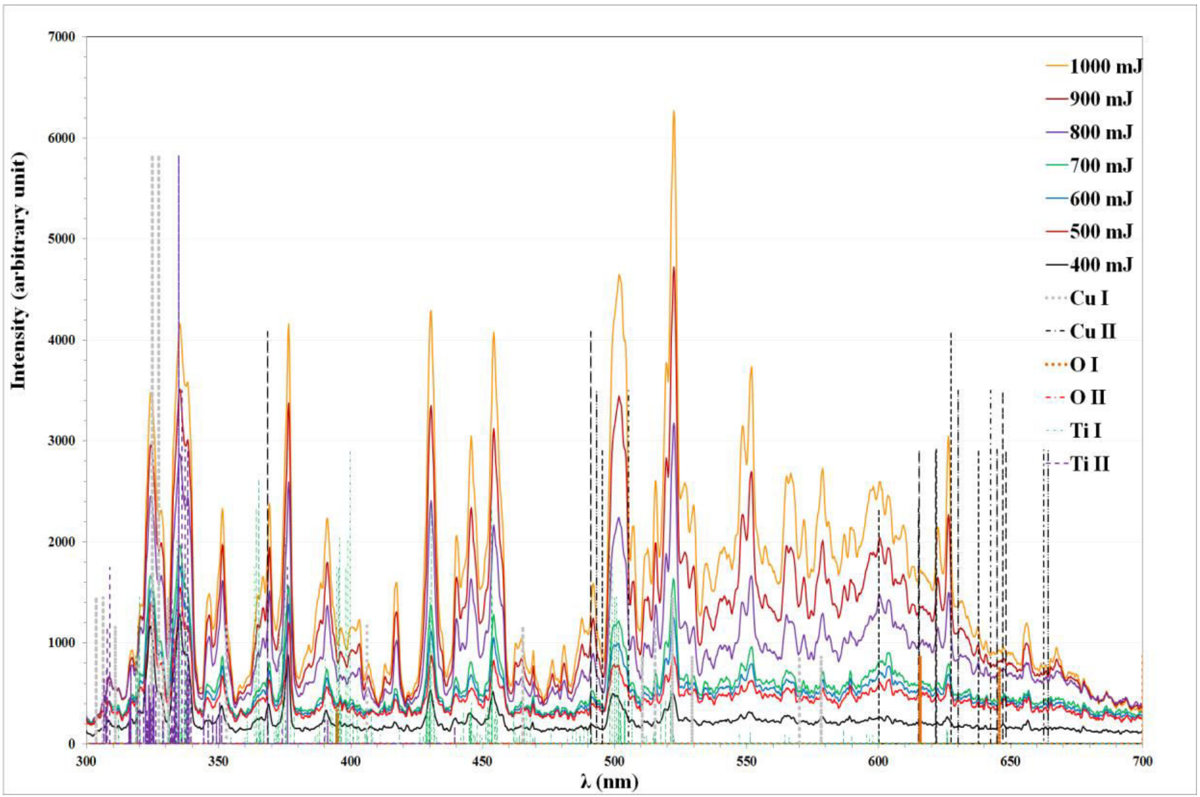

Figure-2. Illustrates the intensity of spectral line in $(TiO_2)_{1-x}(CuO)_x$ plasma as a function of wavelength.

Figure-3 Shows samples of the method of Boltzmann plots, which are calculated various plasma energy levels, starting from 400 mj - 1000mj. According to the linear nature shown by the Boltzmann plots, it is concluded that an equilibrium state was made between neutral species and the electrons. The high energy states of nonstationary conditions clarified the discrepancies with ion species LTE. This result was backed up by the ionization energy that resulted to be higher than the characteristic energy of plasma expansion.

ARPN Journal of Engineering and Applied Sciences

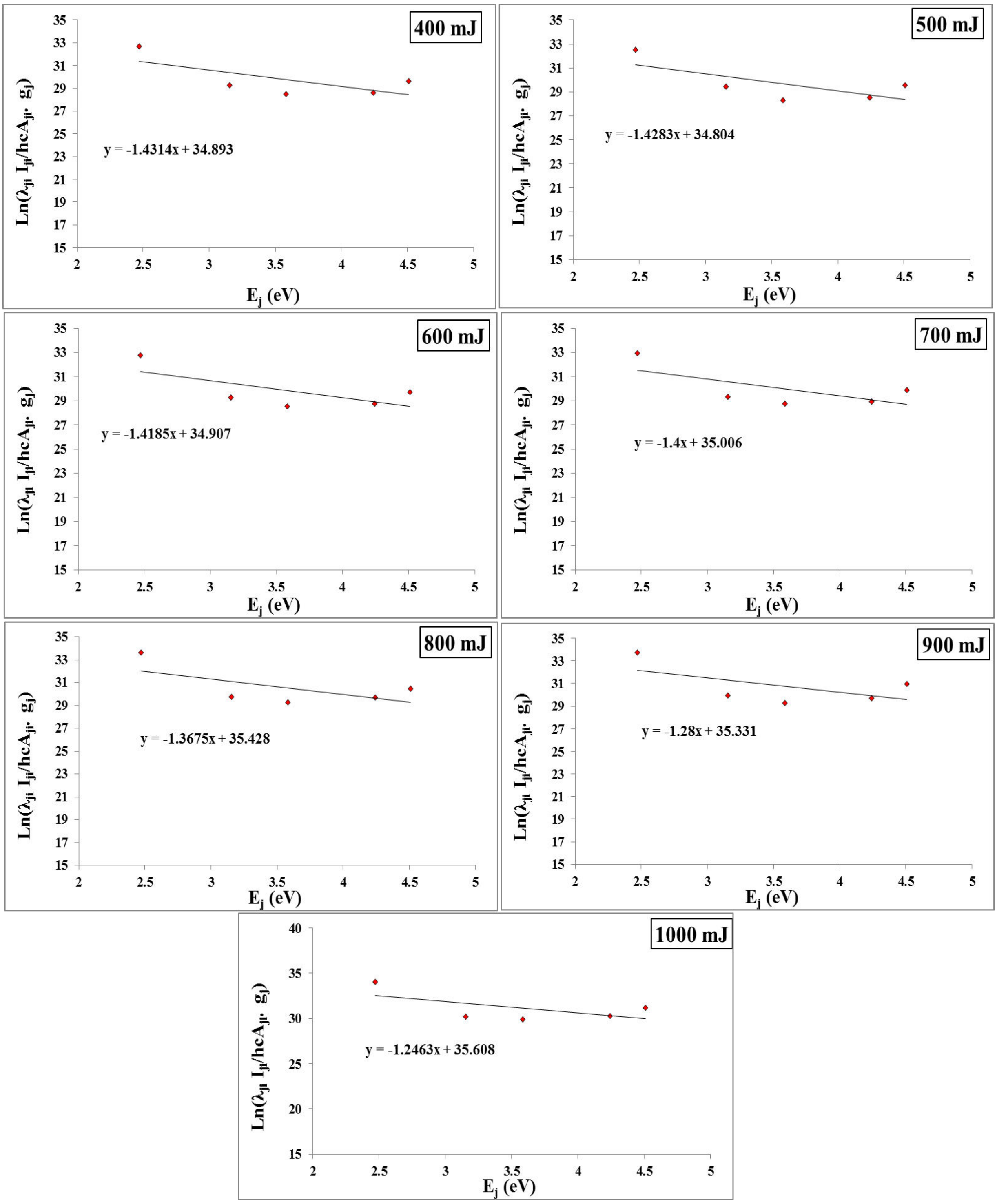

Figure-3. Clarify plots of Saha Boltzmann depicting the LIP produced by a Nd:YAG laser from an Titanium Oxide and copper Oxide target at different energies: (a) 400 mj, (b) 500 mj, (c) 600 mj, (d) 700 mj,(e) 800 mj,(f) 900 mj, and (g)1000mj

Figure-4. Illustrates the predicted values of the Lorention fit on the Cu I,Ti I and Ti II transition lines as a function wavelength at different laser energies. Under the hypothesis of local thermodynamic equilibrium (LTE), the parameters such as electron number density and plasma temperature have been calculated by utilizing Boltzmann plot method. The plasma-emitted spectral line's shape and width are determined via the perturbing collision processes of the emitted atoms and ions. Therefore, the density of the plasma can be determined from the profile of the line spectra. The FWHM of the Stark broadened profile of Cu I,Ti I and Ti II lines have been utilized to estimate the density of electron number [7, 10]. The parameter of Stark broadening was obtained from past studies and papers [9].

ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

Depending on the NIST database, spectroscopic constants of Cu I,Ti I and Ti II lines have been utilized to estimate the temperature [11].

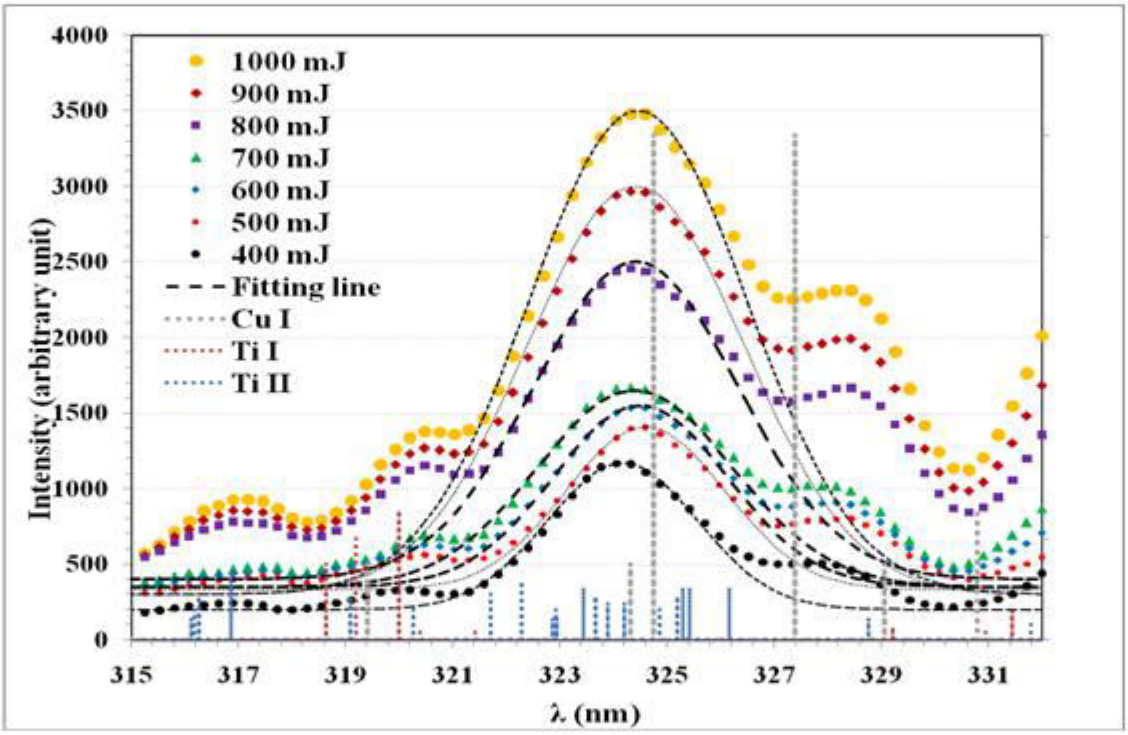

Figure-4. Shows the estimated values of the Lorentian fit on the Cu I,Ti I lines.

Figure-5 depicts the predicted values of the plasma temperature and number density of the Ti plasma that depend on the intensity of laser. It is noticed that the T_e which was between the range of (0.699 – 0.781) eV, showed an increase by the factor of 1.11 and the Ne fell which was in the range of $(34.7\times10^{18} – 50.5\times10^{18})$ cm^{-3}, rose by the factor of 1.45 along with the rise in the laser energy from 400 to 1000 mj. Along with the rise in laser irradiance, the temperature as well as the number density were found to rise to a level of 1000mj irradiance of laser and to saturate later on. The temperature's saturation along with the number density which was over the 1000mj radiance level is thought to occur due to the effect of shielding of plasma, In other word, it means absorption and/or reflection laser photons mode by the plume of plasma.

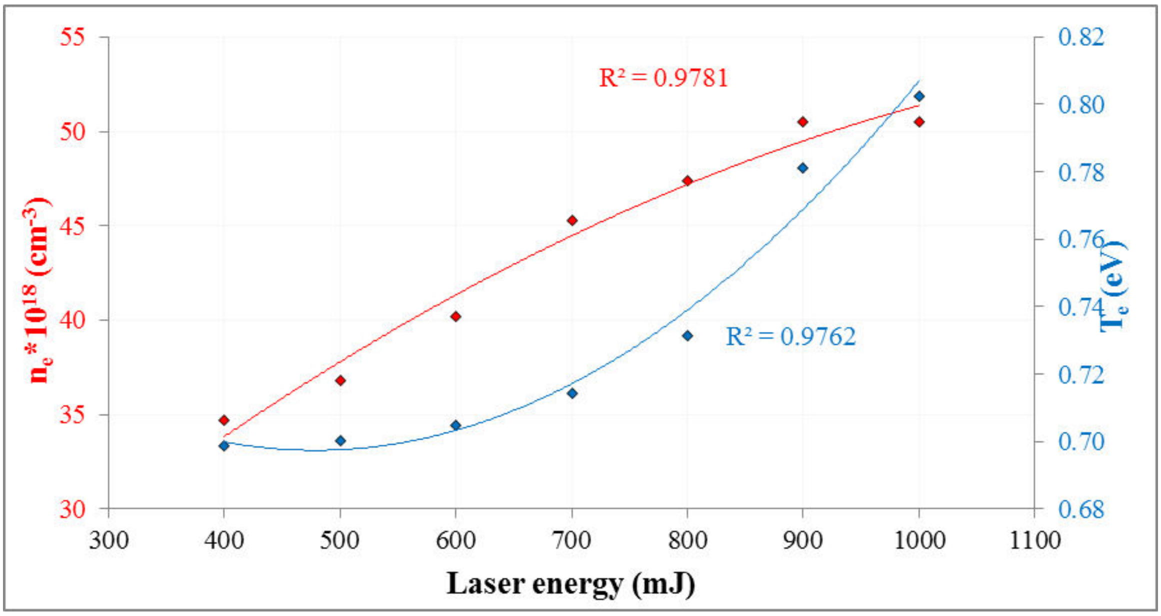

Figure-5. Shows the dependence of Te and Ne of the Ti and Cu plasma with laser energies.

8. CONCLUSIONS

This paper has critically evaluated the development which has been made experimentally on properties of laser-induced plasmas. This was achieved by utilizing OES to determine plasma physical parameters. In addition, this paper studied the Nd:YAG laser intensity effects T_e and N_e of the Ti and Cu plasma. The changes in the aforementioned parameters with irradiance of laser indicated that T_e and N_e increase with the increase in intensity of laser. It is also noticed that the Te, which was between the range of (0.699 - 0.781) eV, showed an increase by the factor of 1.11 and the Ne fell, which was in the range of $(34.7\times10^{18}$ - $50.5\times10^{18})$ cm^{-3}, rose by the factor of 1.45 along with the rise in the laser energy from 400 to 1000 mj. Along with the rise in laser irradiance, the temperature as well as the number density were found to rise to a level of 1000mj.

REFERENCES

[1] M. Cvejić, K. Dzierżęga and T. Pięta. 2015. Investigation of thermodynamic equilibrium in laser-induced aluminum plasma using the H α line profiles and Thomson scattering spectra, Applied Physics Letters. 107: 024102.

[2] S. N. Mazhir, N.H. Harb. 2015. Influence of concentration on the structural, optical and electrical properties of TiO_2: CuO thin film Fabricate by PLD, IOSR Journal of Applied Physics (IOSR-JAP). Volume 7, Issue 6 Ver. II (Nov. - Dec. 2015), pp. 14-21.

[3] S. N. Mazhir, G. H. Mohamed, A. A. Abdullah, M. D. Radhi. 2015. UV Photovoltaic detector based on Bi doped TiO_2 Fabricated by Pulse Laser Deposition. International Journal of Advanced Research. 3(5): 1060-1070.

[4] A. M. van der Mullen. 1990. On the atomic state distribution function in inductively coupled plasmas-II. The stage of local thermal equilibrium and its validity region. Spectrochim. Acta Part B 45, 1-13.

[5] B. G. Morgan. 1975. Laser-induced breakdown of gases, Rep. Prog. Phys. 38(5): 621.

[6] Bekefi G. 1976. Principles of Laser Plasma (New York: Wiley-Interscience).

[7] J. Camcho, L. Diaz, M. Santos. 2010. Time-resolved optical emission spectroscopy of laser-produced air plasma, J. Appl. Phys. 107: 083306.

[8] A. J. Effenberger and Scott J R. 2010. Effect of Atmospheric Conditions on LIBS Spectra, Sensors. 10: 4907-4925.

[9] A.K. Knight, N.L. Scherbarth, D.A. Cremers, M.J. Ferris. 2000. Characterization of breakdown spectroscopy (LIBS) for application to space exploration. ppl. Spectrosc. 54: 331-340.

[10] N. Glumac, G. Elliott. 2007. The Effect of Ambient Pressure on Laser-Induced Plasmas in Air”. Opt. Lasers Eng. 45(1): 27-35.

[11] Griem H. R. 2005. Principles of Plasma Spectroscopy (Cambridge: Cambridge University Press).

[12] K. A Yahya, S. N Mazher, Z. A. Hafidh. 2007. Study of Density Distribution in Entrained Plasma, Um-Salama Science Journal,2007; 4(2): 305-309.

[13] C.O. Laux, T.G. Spence, C.H. Kruger and R.N. Zare. 2003. Optical diagnostics of atmospheric pressure plasmas. Plasma source sci. Technol.12: 125-138.

[14] H.H. Ley, A. Yahya, R.K. Raja Ibrahim. Analytical methods in plasma Diagnostic by optical emission spectroscopy: A tutorial Review.

[15] F. Deeba, A. Qayyum, N. Mahmood. 2014. Optical emission spectroscopy of 2.45GHz microwave induced plasma, Academic editor: Yong- Cheol Hong 12 June.

[16] D. O' Connell, L.J. Cox, W.B. Hyland, S.J. McMahon, S. Rreuter, W.G. Graham, T. Gans, and F.J. Currell. 2011. Cold atmospheric pressure plasma jet interactions with plasmid DNA. Applied Physics letters98, 043701;doi:10.10631/1.3521502.

[17] T. J. M. Boyd and J.J. Sanderson. 2003. The physics of plasmas. Cambridge University Press, UK.

[18] P.M. Bellan, 2004. Fundamentals of plasma physics. Academic press, New York, USA.

[19] R. O. Dendy. 1990. Plasma Dynamics. Clarendon Press, Oxford. p. 161.