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Nanomaterial and Laser Induced – Breakdown Spectroscopy (LIBS)

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Abstract

In the present work, the optical emission spectra of Nano- 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 (ne) and electron temperature (Te) were determined using the Boltzmann plot method and McWhirter criterion.

Keywords: Nano- Copper (Cu)plasma, spectroscopy technique (LIBS), laser energy.

Introduction

Laser induced breakdown spectroscopy (LIBS) is a technique, which was first reported in early 1960s and then reviewed by several researchers. 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 [1-3]. It is a simple technique as compared with many other types of elemental analysis because of its straightforward experimental set-up. In this technique a pulsed laser is required to generate micro-plasma on the target surface. 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. The first direct spectral analysis made by LIBS can be attributed to RUNG et al [4-5]. In 1980s, this technique was increasingly applied as an analytical tool in research [6].Copper is the most widely used metal for various applications of plasmonic materials due to its high electrical conductivity and optical properties.[7,8] The emission characteristics and plasma parameters of Copper are of great importance not only in the laboratory plasma diagnostics but also for a number of technological applications, such as for nano-particles, cluster production, contacts of low-voltage switching devices, and as metal films.[9–10] Shuaibov etal.[11] investigated the time-averaged spectra (200–600 nm) of Ag produced by the 1064 nm laser irradiation in vacuum (3–5 torr) at a distances of (1-7mm) from the target surface. Chuchmann and Shuaibov[12] reported the temporal dependence of the populations of excited atomic states of silver and copper at the (1-7mm) distance from the target surface. Roberts et al.[13] reported the femtosecond laser (130 fs) ablation of silver foil using the single and double pulse configurations. Rashid et al.[14] reported the comparative study on the effect of the inter-pulse delay and the ratio of the laser pulse energies on the silver emission line intensities, enhancement for collinear and orthogonal pre-ablation dual pulse configurations using the (1064nm) and (532 nm) of Nd:YAG laser. The objective of the present work was to characterize the laser induced Nano-Copper plasma in term of spectral line intensities and plasma parameter (n_e and T_e) under different laser power energy using LIBS technique.

Experimental work

A: Synthesis of Nanomaterial (Cu Nanoparticles)

- The formation of copper nanoparticles was complete with utilized of ancestor copper nitrate Cu $(NO_3)_2$ and sodium hydroxide the copper nitrate was weighing at room temperature with (3.0gm) with (5 ml) from NaOH solution dissolved in deionized water 100 ml.
- NaOH solution was slowly dropped under constant stirring until homogenous blue solutions appear maxising was on the magnetic stirrer for 30min at 250°C upon cooling temperature.
- Later it was diluted by adding 5ml from triethylamine (TEA) as catalyst for Solvthermal process. The obtained solution was washed several times by using DI water in centrifuged to ensure that no any impurities in the solution.
- The result solution used as thin film on glass surface. The processing to clean the glass surface was first cleaned by a commercial detergent, then in ethanol for half an hour in ultrasonic cleaner. Finally, the glass surface was rinsed with DI and dry in figurative.
- The liquid mixture was obtained was espionage on the glass surface in air under 125°C until it dried later the thin film annealed at 250°C for 30 min in the air.

B: The LIBS system

The schematic diagram of the experimental setup used for the investigation of Copper plasma is shown in Fig. 1.

- Q-switched Nd:YAG (Quantel Brilliant) laser operating at 1064 nm (6 ns pulse duration 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 (50mm) 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 µm) 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 200µm , covering the spectrum range from 200-1100nm with optical resolution of 0.03 nm(FWHM), integration time 3.8ms-10sec.

- 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 Nano-Copper target was 3.0mm diameter and 0.3cm thickness

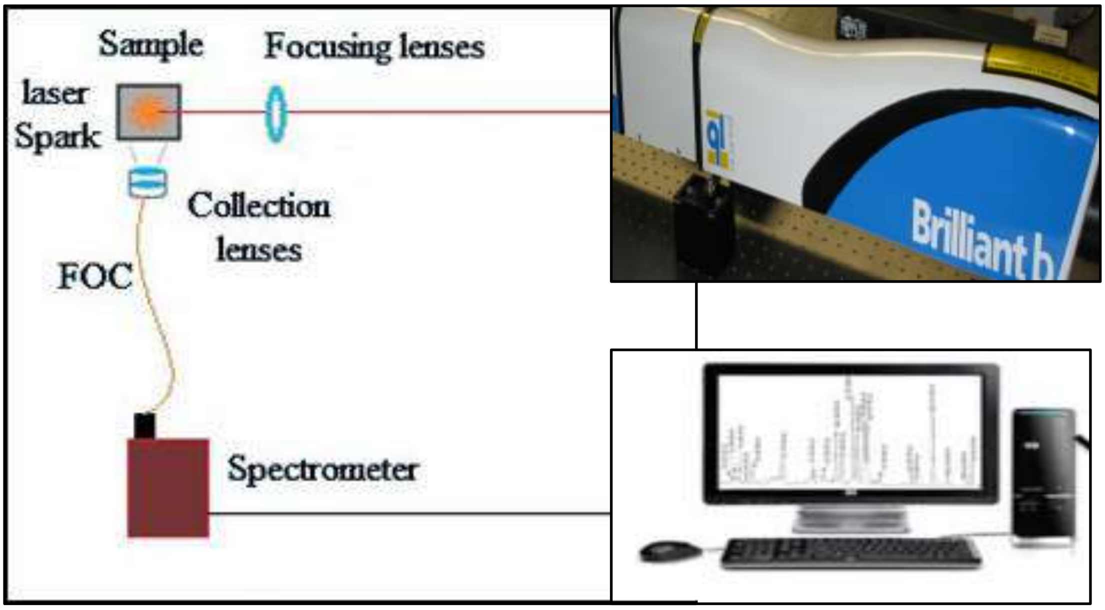

Fig 1: laser induced breakdown spectroscopy diagram of test

Result and discussion

Structural properties

X-ray Diffraction Result

Through studying the X-ray diffraction spectrum one can understand the crystalline growth nature of Nano- Cu prepared by Solvthermal method on glass surface at annealing temperature 300°C became crystalline as prepared Cu NPs is explained in Figure 2. Which show a single-phase with a monoclinic structure. Lattice parameters are a = 4.84 Å, b = 3.47 Å, c = 5.33 Å. The intensity and peak positions are in good concordance with the presented values (JCPDS file No. 05-661). Corresponding to plane (002) and (111) ,(222) ,(113) in consecutively as show in Figure 3.

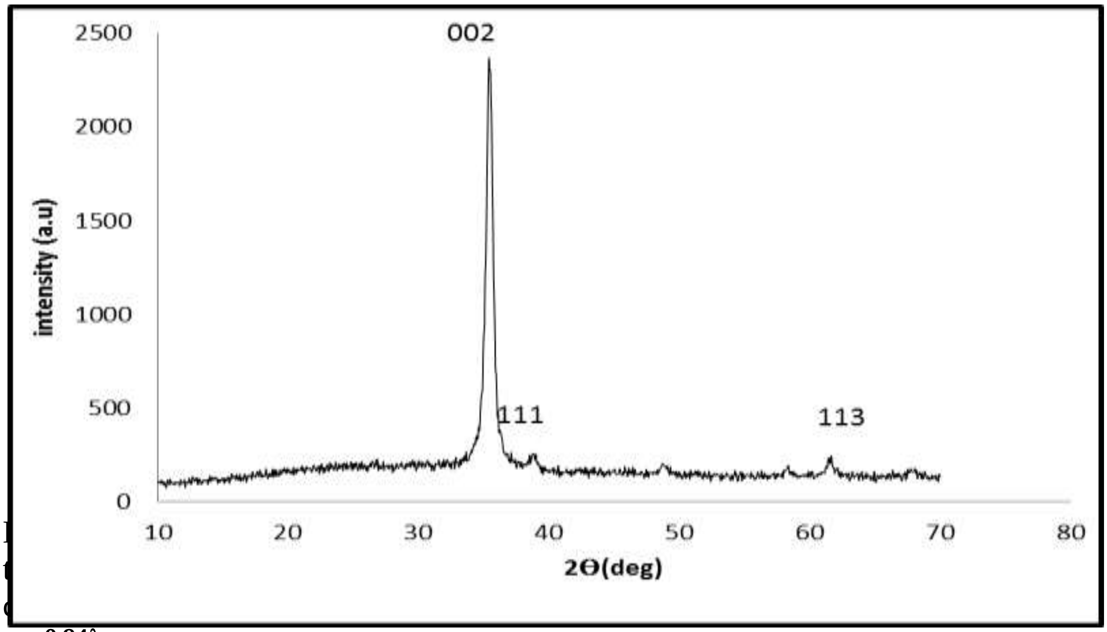

Figure 2: the XRD of Cu Nanoparticles

where

λ : is the x-ray wavelength (A°)

$\Delta_2\theta$: FWHM (radian)

θ: Bragg diffraction angle of the XRD peak (degree)

Scanning Electron Microscopes (SEM)

To be acquainted the overall structure of growth sample of Cu NPs. Scanning electron microscopic was utilized and result display in the Figures with the Cu *NPs* was synthesized by the Solvthermal method, which include chemical reaction with watery solutions of $Cu(NO_3)_2$ as nitrate .5 H_2O 0.1M and NaOH 0.9M solution whose pH value was 13 at room temperature. As can you see from the low – magnification image show as deposited Cu having several aggregated molecular nanostructure. When the nanoparticles was check at magnifying. The acquire samples was in round shape tiny nanoparticles with rang 16-45 nm

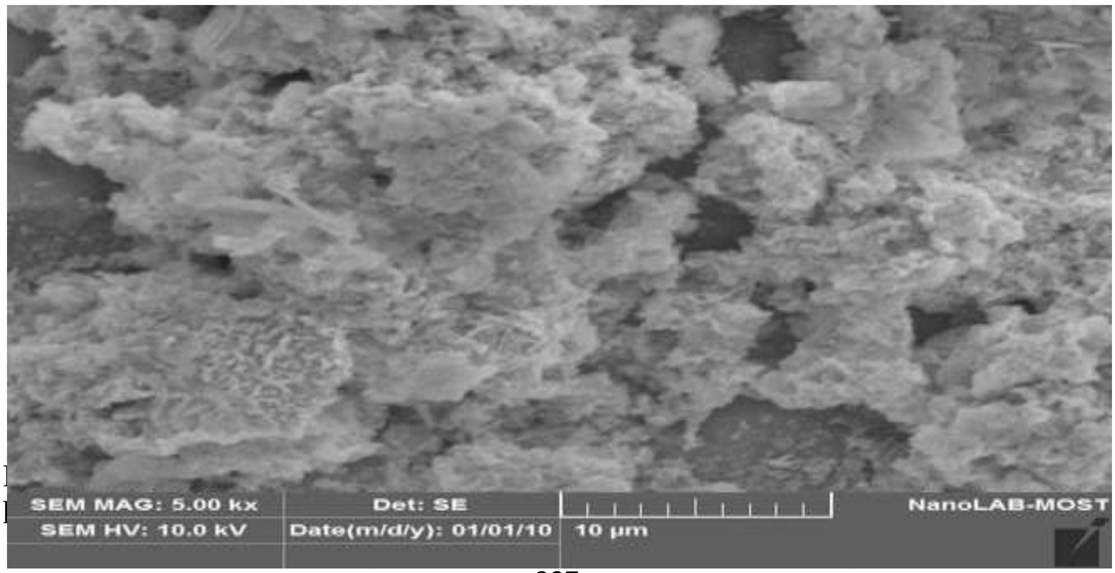

Figure 3:SEM image of the Cu Nanoparticles

work Cu (NO_3) .5H_2O was used to prepare spherical shaped Nano Cu at mild reaction temperature. The same morphology was obtained when using Cu $(NO_3)_2$. 3H_2O . And the surface exhibited smooth particles with a homogenous surface morphology, with a wide size distribution of particles size of aggregated particles.

Atomic Force Microscopic (AFM)

The grain size (grain diameter) and average roughness and root mean square roughness (RMS) of Cu Nanoparticles are measured by using AFM as shown in Figure 4. The AFM images of the Cu Nanoparticles There are many Nano- structure on the surface homogeneously in the film so the particle keep size as deposited on the surface on substrate.

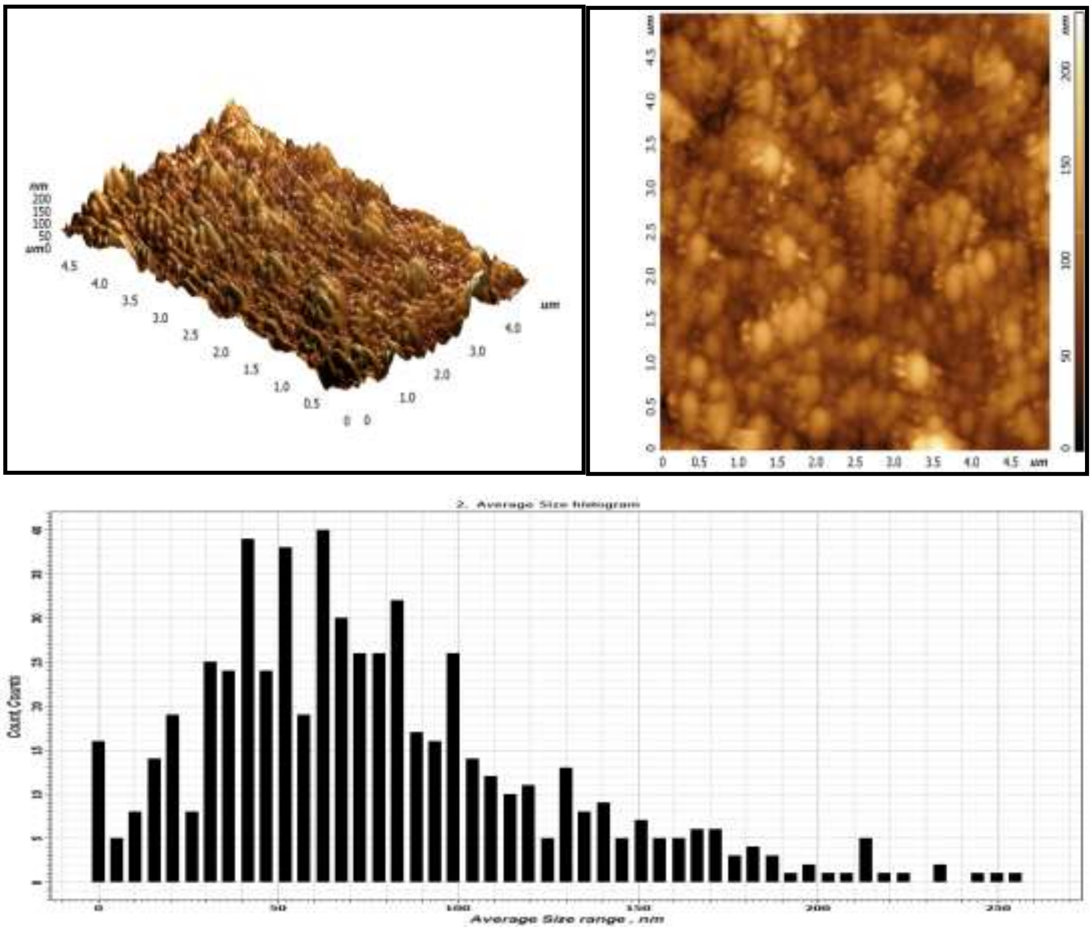

Figure 4:AFM for Cu Nanoparticles

Result of Emission Spectrum

The laser - induce plasma process can be classified into three regimes: evaporation of the target material, interaction of the evaporated cloud with incident laser beam resulting in cloud heating and plasma formation, and expansion and rapid cooling of the plasma .Observations were made of the plasma created by the interaction of the laser beam with the target in a direction perpendicular to that of the laser beam. Plasma produced by a high intensity laser pulse expands normal to the target surface due to shock waves [3] In the present work, produced Nano- copper plasma with different laser energy at (20-30 mj) by Q- Switched Nd:YAG laser at (1064) nm wavelength, 6ns pulse duration , 10Hz repeation rate was generated .the laser was focused on the target surface i.e. perpendicular to the target surface , whereas , the plum emission was register as a function of the laser energy . Figure (5) shows the emission spectrum of Nano- copper plasma generated by laser energy at 20 mj. Emission that recorded was covering the spectral region from (300 to 900) nm.

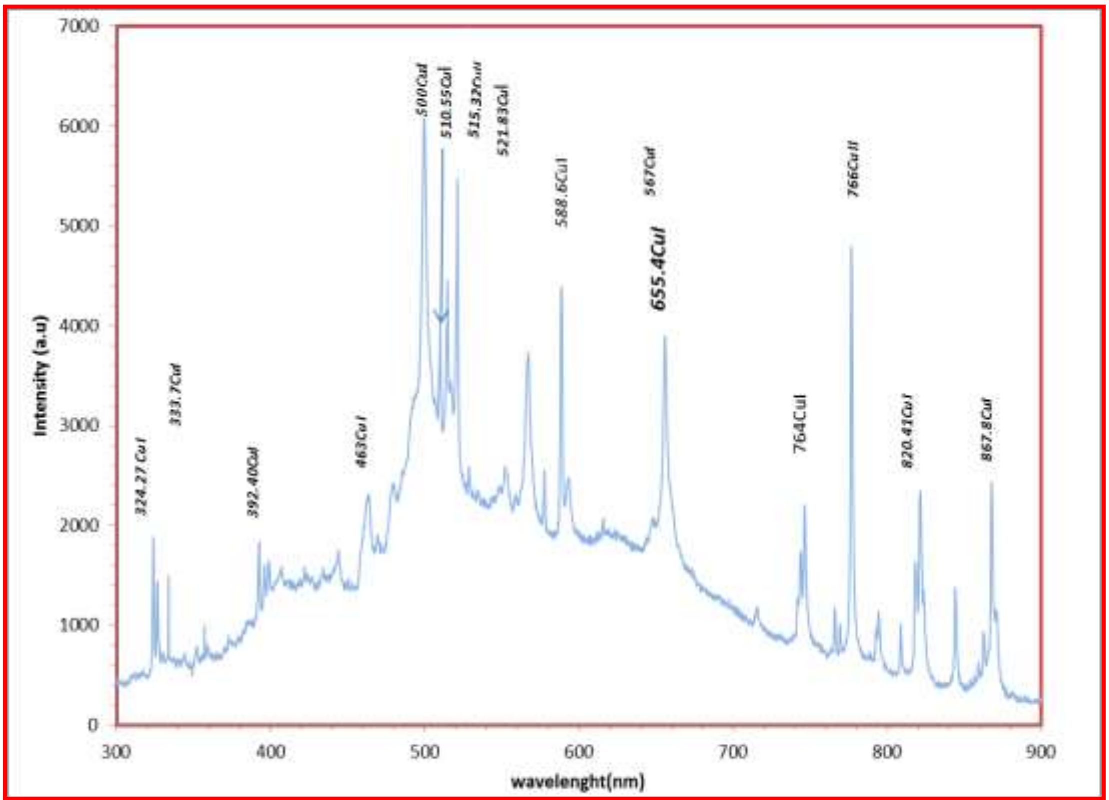

Fig (5): Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5mm,20 mj laser energy covering the region 300-900 nm spectral window.

In the Figure (6 and 7) it is seen emission spectrum of copper plasma related to these spectrum region between (300 to 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 $3d^4P^1\ ^2P_{3/2}$ to $4S^1\ ^2S_{1/2}$ and 3d4P1 $^2P_{1/2}$ to $4S^1S_{1/2}$ and $3d4S4P4F_{7/2}$ to $4S^2\ ^2D_{5/2}$. Transitions, respectively.

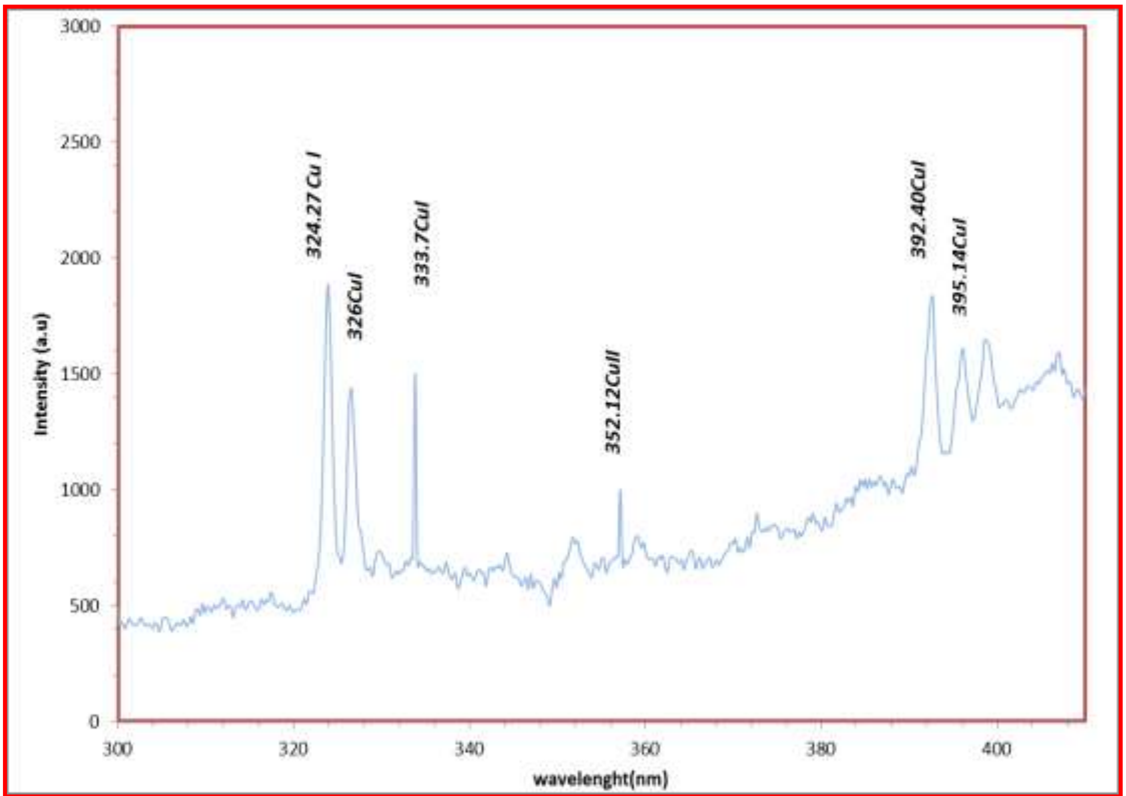

Fig (6): Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5mm,20 mj laser energy covering the region 300-400 nm spectral window.

In Figure (6) show the emission spectrum in the region between (400 to 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 $^2D_{5/2}$ 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 $4P^2P_{3/2}$ *to* $3d4S^2\ ^2D_{5/2}$ transition.

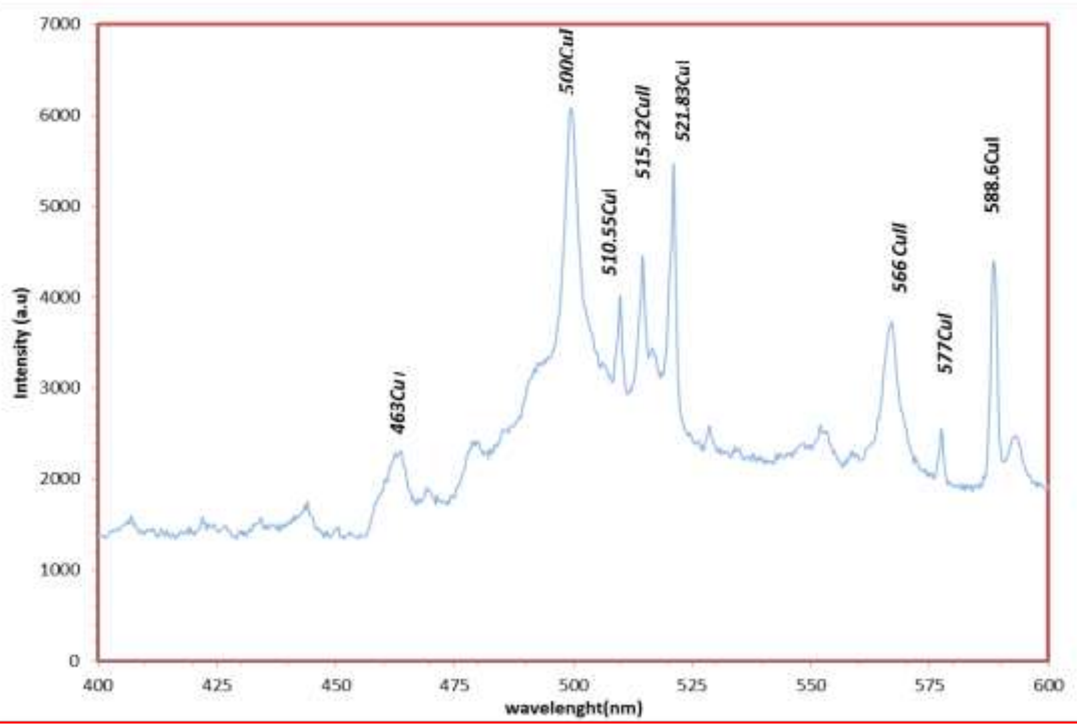

Fig (6): Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5mm,20 mj laser energy covering the region 400-600 nm spectral window.

When the laser energy increased the spectral lines intensities and widths increase with the increasing laser energy. The emission of copper plasma at 1064 nm laser wavelength , and 30 mj laser energy. The emission spectrum of copper plasma using nanosecond laser is shown as in the figure (7). The intensity of Cu I lines are more pronounced at transitions [4p ^{2}P-4d^{2}D] i.e. 515.324, [4p ^{2}P-4d ^{2}D] i.e. 521.820 and [4s^2 ^{2}D-4p ^{2}P] i.e. 510.554nm while Cu II lines such as [4p ^{1}F-6d ^{3}D] i.e.324.7nm and [5p ^{3}P-5d ^{3}D] i.e. 577.721 nm have relatively low intensity. No Cu III lines were detected in these regions.

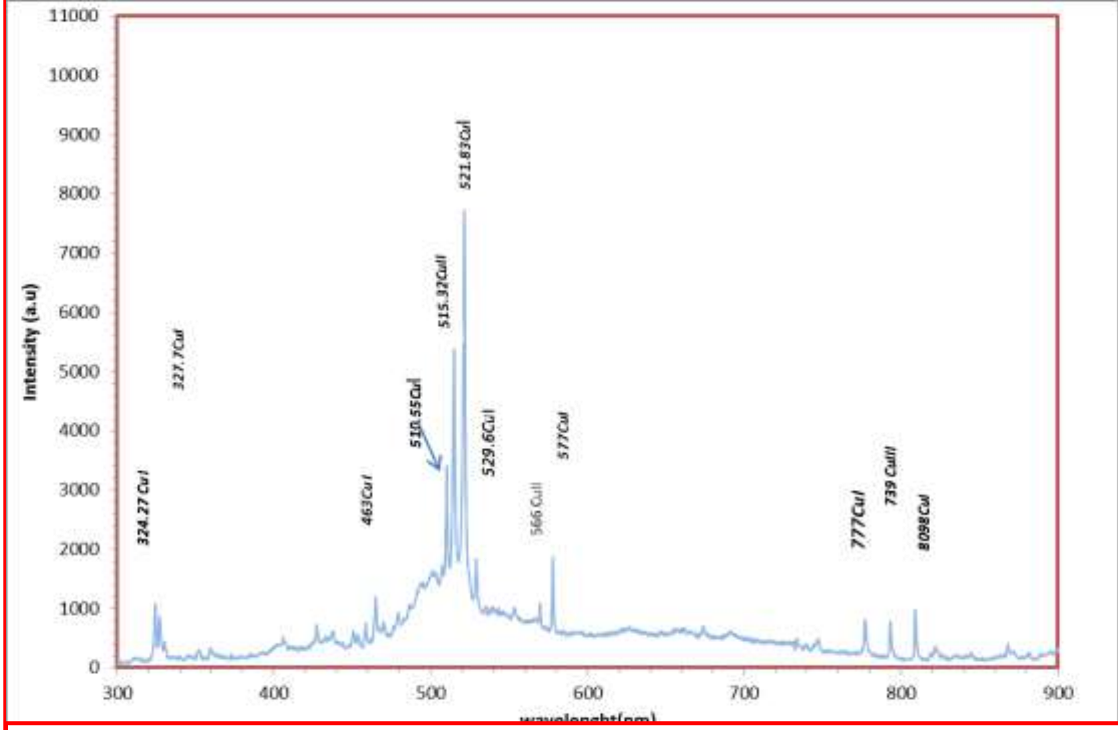

Fig (7): Emission spectrum of neutral and ionized copper plasma generated by the 1064 nm laser at distance 5mm,30 mj laser energy covering the region 300-900 nm spectral window.

A typical spectrum is characterized by atomic, ionic emission lines and by continuum emission. At the beginning, after the plasma formation, the light emission is dominated by the continuum emission, which is caused by recombination radiation (free-bound) and bremsstrahlung emission (free-free)[15] . As time passes, the continuum emissions decrease dramatically, and ionic and atomic emissions begin to increase.

Effect of exaction source

The nature and characteristics of LIBS was depending on the laser energy The size, temperature and hence the extent of ionization is very much dependent on the laser pulse energy. This laser pulse energy is the source of energy for evaporation, atomization and ionization of the target.

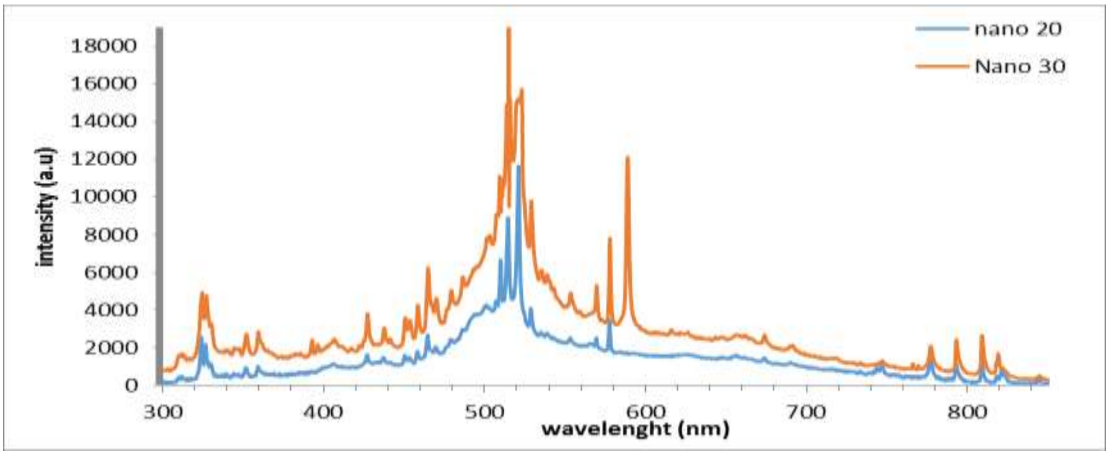

Figure 8:Spectrum of Cu NPs of the area (300-900nm) generated by 1064nmlaser at 20, 30 mj laser energy

Determination of electron temperature and number density of plasma

The plasma temperature was determine by using Boltzmann plot method from relatives intensity of observed lines; the relatives intensity normally proportional to the population of the pertinent upper levels[16,17]. The following relation has been used to extract the plasma temperature [13]:

$$\ln\frac{I_{ki}\,\lambda_{ki}}{A_{ki}\,g_{k}} = \ln\frac{N(T)}{U(T)} - \frac{E_{k}}{KT} \quad \ldots\ldots\ldots\ldots\ldots 1$$

Where I_{ki} is the integrated line intensity of the transition involving upper level (k) and a lower level (i), λ_{ki} is the transition wavelength, A_{ki} is the transition probability,g_k the statistical weight of level (k) ,N(T) is the partition function, E_k is the energy of upper level , (K) is the Boltzmann constant and (T) the exaction temperature .Plot between Ln (I λ /g A) 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 (λ), (g) statistical weight, (A) transition probability and term E energy [18,19], are listed in Table (1). Taking from NIST database [20].The atomic lines of Cu element are used to determine the electron temperature are selected as

- They must be reasonable, rare to prevent the interference with other line.
- They must be non-resonant lines with lower level more with the ground state specials' with elevated compositions of the lines interest to prevent maximum emission intensity according to self-absorption of the plasma spectrum .

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 and as shows in figure (9-10) behavior was studied as a laser energy function of the plasma generated by 1064 nm wavelength of laser irradiance at 20mj, The electron temperature increased between 6564 to 10698 k also the electron number density was calculated for different energy laser. As show in result note that END varying between 9.36×10^{16} to $1.19\times10^{17}cm^{-3}$. 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 [21]. 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[[17,14].

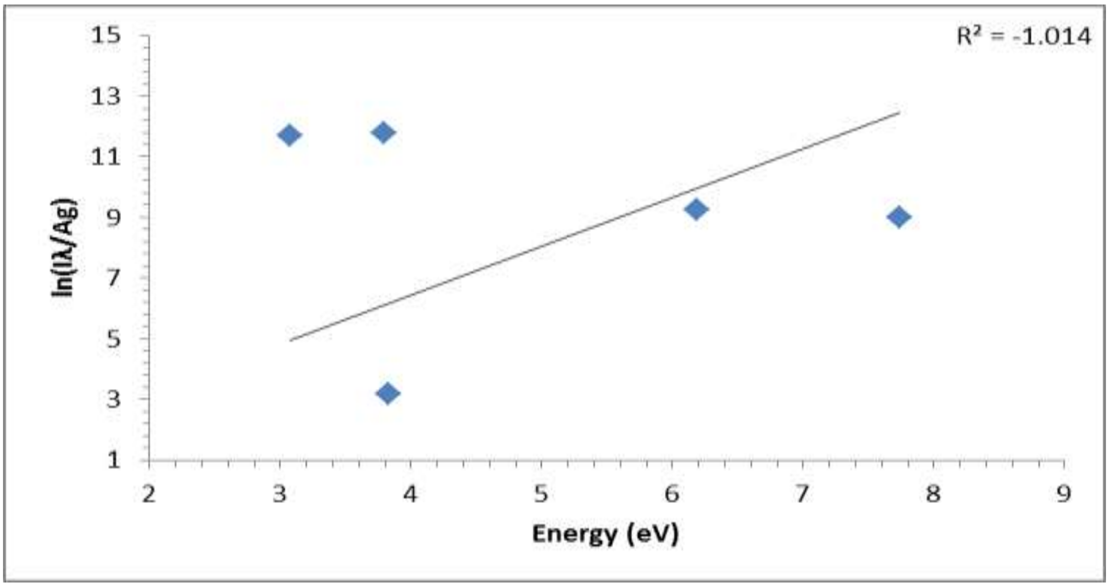

Figure 9: Boltzmann plot for 5 neutral spectral line in 20mj by using 1064nm for Nd:YAG laser

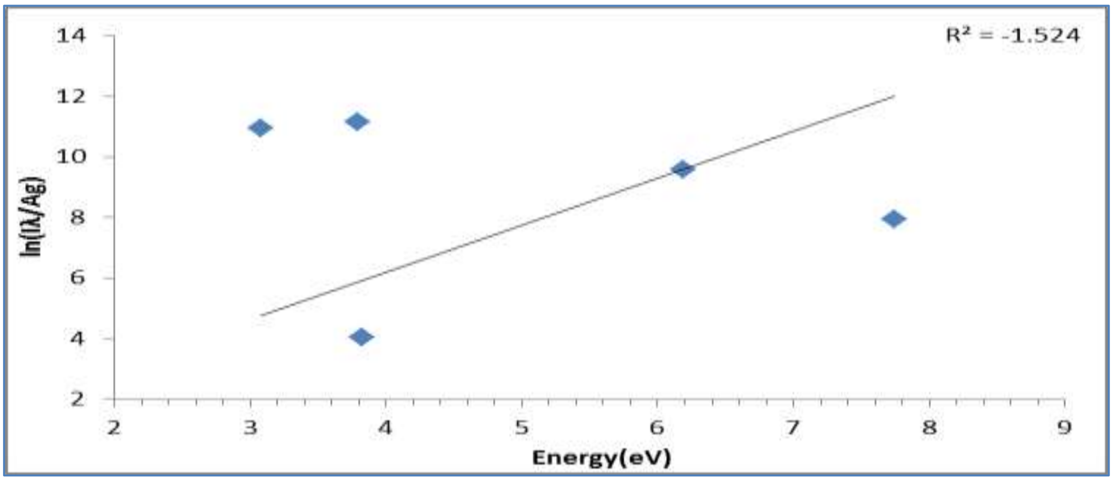

Figure 10: Boltzmann plot for 5 neutral spectral line in 30mj by using 1064nm for Nd:YAG laser

Table (1): Spectroscopy parameter of the singly / second ionized and Cu line data take from reference [30].

Atom/ ion	λ(nm)	g_j	Aji($^{s-1}$)	Ej (ev)	Transition
Cu I	510.55	4	$2.0*10^6$	3.82	$4S^2\ ^2D4P^2P$
Cu I	515.32	4	$6.6*10^7$	6.191	$4P^2P4d^2D$
Cu I	521.82	6	$7.5*10^7$	6.192	$4P^2P4d^2D$
CuI	578.21	4	$1.65*10^6$	3.76	$4S^22D4P^2P$
Cu1	324.31	4	$1.37*10^8$	33.78	$3d4p^2p_{3/2}$

Where E_k=Upper level energy, A = Transition probability

Conclusion

Nd:$y_3Al_5O_{15}$ laser in the 1064nm wavelength to diagnosis the copper plasma. ET and END was measured on the axis direction of plum. It observed was noted that the plasma temperature and END increased with increasing laser temperature.

Conflict of Interests.
There are non-conflicts of interest .

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الخلاصة

في العمل الحالي، تم تسجيل وتحليل أطياف الانبعاث البصري لبلازما النانو والنحاس (Cu) باستخدام تقنية التحليل الطيفي الناجم عن الليزر (LIBS). تم فحص شدة خط الانبعاثات ومعلمات البلازما كدالة لطاقة الليزر. تم تحديد كثافة رقم الإلكترون (ne) ودرجة حرارة الإلكترون (Te) باستخدام طريقة مؤامرة Boltzmann ومعيار McWhirter.

الكلمات الدالة: بلازما النانو والنحاس (Cu)، تقنية التحليل الطيفي، التحليل الطيفي.