

Growth, Characterization of Cu Nanoparticles Thin Film by Nd: YAG Laser Pulses Deposition

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Abstract

We report the growth and characterization of Cu nanoparticles thin film of on glass substrate by pulse laser deposition method. The Cu thin film prepared with different energy 50, 60, 70, and 80 mJ. The energy effect on the morphological, structural and optical properties were studied by AFM, XRD and UV-Visible spectrophotometer. Surface topography studied by atomic force microscopy revealed narrowed size distributions, with particle sizes ranging from 65.8 to 90.09 nm. The results showed the Average Gran Size increased with increasing energy and RMS roughness increased with increasing energy. X-ray diffraction showed nanostructure phase With ($2\theta = 43.297, 50.433$ degree). The results show that by increasing thickness, the copper films crystallinity in (111) direction increases. Optical properties measurements showed transformation from metallic properties of bulk Cu to semiconductor properties when formed by sort of nanostructure evidenced by the formation of optical energy gap about (3.45 to 3.89 eV) with different conditions. When the thickness of samples is increased the crystallinity and the mean grain size improved.

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1. Introduction

Thin-film growth by means of pulsed-laser deposition (PLD) has been extensively studied in the past few years.[1] When the laser energy is absorbed by a target, electromagnetic energy is converted

initially into the electronic excitation and then into chemical, thermal and even mechanical energy to cause excitation, ablation, exfoliation, evaporation and plasma formation. The ablated material forms the plume that consists of a mixture of energetic species

like atoms, molecules, cluster, ions, molten globules and micron sized solid particulates. Inside the plume the collision mean free path between different species is very short [2] Pulsed laser deposition technique is popular in the research community for the deposition of thin film due to numerous advantages; including low contamination level, high deposition rate and stoichiometry of the target is preserved in the deposited films[3].

The studies on physical properties of Cu thin films have been the object of investigations for many years. Copper, because of its high thermal and electrical conductivity, has various applications in electronic industries. The electrical conductivity of commercially pure copper is second only to silver, but lower costs and accessibility causes that Cu is the metal used most often in electronic applications.

Cu thin films with nanostructural dimensions have widely applications in electronic devices because of both high electromigration resistance and high electrical conductivity [4,5]. Due to these characteristics; Cu thin films are widely used for many applications alike diodes[6], solar cells [7] and high-speed integrated circuits (IC)[8,9].

In PLD technique the energy source, which creates the plasma plume of the target material, the laser, is independent of the deposition setup [10]. The fundamental laser emission of Nd:YAG laser is at 1064 nm which is well outside the desired range for pulsed laser deposition of most of the materials. The fundamental emission of Nd:YAG can be frequency doubled to 532 nm wavelength using a suitable nonlinear optical crystal at the cost of nearly half the laser energy at fundamental[11]

The ablation rate is strongly influenced by the characteristics of the laser beam (e.g., pulse duration, number of pulses, energy, fluence, wavelength) [12, 13, 14, 15, 16] processed material (e.g., mass density, surface reflectivity, optical absorptivity, thermal

conductance) [12,14,17,18]and by ambient conditions [12,18].

In this work, we report on the results of initial experiments exploring the possibility of preparation of Copper thin films by Pulsed Laser Deposition (PLD). The optical properties have been investigated.

2. Experimental procedure

To preparation Cu Nanoparticles, we used the PLD system it consist of two main parts shows in figure (1).**First**, vacuum chamber includes multiple accessory, target holder, substrate holder, laser window, thermocouple, vacuum gage, substrate heater use IR. Lamp that easily field replaceable, substrate can heated to 300 °C The substrates are placed on substrate holder at distance (4cm) from the rotated target. The pressure in the stainless steel vacuum chamber having many viewing ports chamber be can decreased under 10^{-6} mbar by use two stages rotary and diffusion pump .

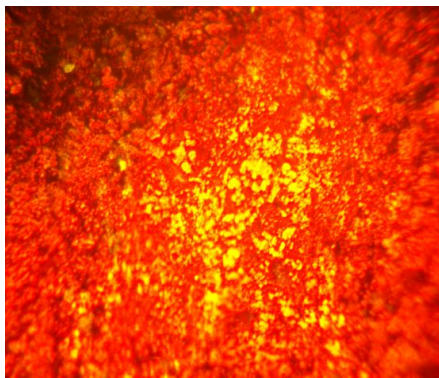
Second, Q-switched Nd:YAG laser system that works in the TEM₀₀ mode and generates fundamental pulse at wavelength of 1064 nm and doubled frequency 532 nm by a second harmonic generation. The laser pulse characterized by duration 10 ns with repetition rate of 6 HZ and energies (400-1000) mJ/pulse. The PLD thin films were analyzed by AFM (Atomic Force Microscope), XRD (X-Ray Diffraction)and UV-Visible spectrophotometer.



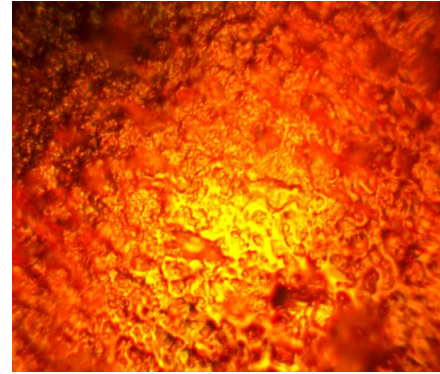
Fig. 1. PLD system Set-Up

3. Materials and methods

In this work, Cu thin films with different energy have been deposited on glass substrate by PLD system technique. The substrate was fixed directly above the Cu target (99.9% in purity) of 2cm in diameter with a target-to-substrate distance of 4 cm. The laser beam is focused on the target surface by using lens with focal length (30) cm at the incident angle of approximately 45° . When focused on the surface of a solid target, pulsed-laser radiation can be absorbed, leading to thermal and non-thermal heating, melting, and finally ablation of the target. The substrate is heated to improve the adhesion of deposited material.



(a) Cu target before ablation



(b) Cu target after ablation

Fig. 2 Cu target before and after ablation

4. Results and discussion

Three-dimensional surface morphology of thin films prepared in different energy is shown in Figs. 3(a-d). AFM examination of the Cu samples illustrated clearly that their surface morphologies are strongly affected by energy. Figure 4(a) show that the grain sizes of the films clearly increase as the energy rises. Investigation of the AFM images revealed that at the beginning of growth, the grain sizes are small (Fig. 3a) and Columnar structures for thin film were observed, which were tiny, dense, and vertical. By increasing energy, these small grains gradually combine and make bigger grains (Figs. 3b, 3c). Finally, with increasing the energy to 80mJ, the grains become bigger and at last it can cause to create clusters, which these clusters combine and create big grains which are shown in Fig. 3d. Also surface roughness of Cu films has been studied by AFM. As can be seen from Figure 4(b) when the film energy increases from 50 to 80mJ, surface roughness increases from 0.0231 to 0.694 nm, which results from an increase of grain size from 65.80 to 90.09 nm. It can be considered that the surface roughness of film originates significant from the surface morphology of the glass substrate.

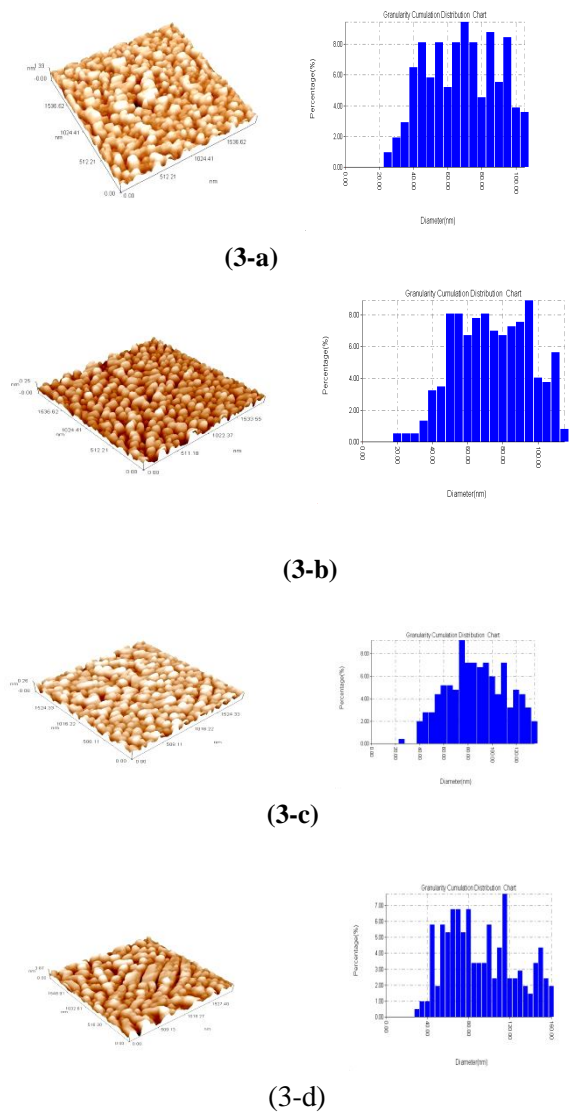
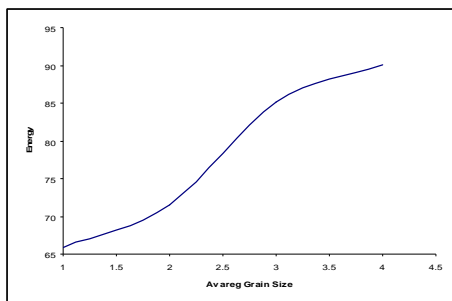
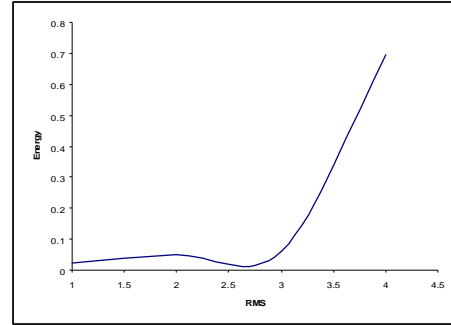


Fig. 3. AFM images of Cu films on SiO₂ and diameter percentage of nano particle at vacuum chamber pressure (1*10E-5) mbar ,4000 pulses/sec, at pulses energy (a) 50mJ, (b) 60mJ, (c) 70mJ, (d) 80mJ.

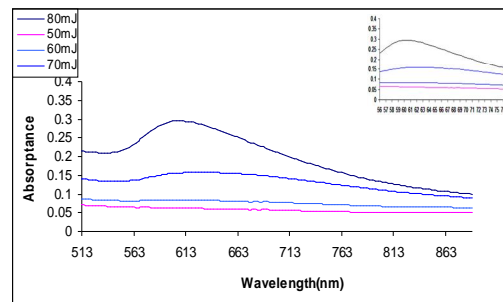


(a)

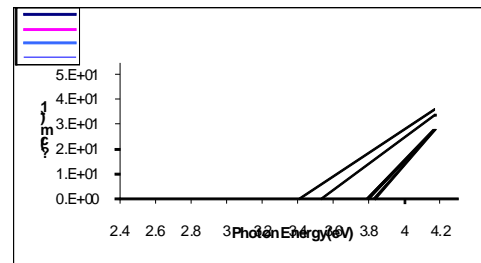


(b)

Fig. 4. Cu thin films deposited in different pulses energy (50mJ, 60mJ, 70mJ, and 80mJ). (a) The Average Gran Size increased with increasing substrate Energy. (b) The RMS roughness increased with increasing substrate Energy.



(a)



(b)

Fig. 5. UV-Visible spectrum of Cu films for different pulses energy (50mJ, 60mJ, 70mJ, and 80mJ). (a) Absorption spectrum, (b) band gab spectrum.

Figure 5, progressive 1064 nm ablation of the target 4000 shots causes growth of the blue absorption of the sample, which is related with interband transitions of metallic copper, and formation of a Plasmon band

peaked at 588 nm, According to Mie theory[19]. A characteristic peak of absorbance near 580 nm grew progressively by increasing laser energy. After initial irradiation, the copper Plasmon bands near 600nm show broadening and tailing toward longer wavelengths .The Peak appeared in the visible wavelength region can be attributed to the Plasmon peak, which is the characteristic absorption of metals. Size effects may shift the Plasmon resonance to longer wavelength values when the cluster size is increased. In metal Nanoparticles this leads to a localized surface Plasmon resonance (LSPR), which is an effect that produces strong peaks in extinction spectra [20,21]. Previous work has demonstrated that the position of the LSPR extinction maximum, λ_{max} , is sensitive to the size, shape, interparticle spacing and dielectric environment of the Nanoparticles [22,23]. It is well-established that Cu Nanoparticles support surface Plasmon resonances that can be tuned throughout the UV-Vis spectrum [24,25].

Table1. Calculation of grain size and roughness with energy at pulse numbers (4000), Temperature (300°C)

Sample	Energy	Average	Roughness
Cu	mJ	Grain size nm	nm
3-a	50	65.80	0.0231
3-b	60	71.56	0.0515
3-c	70	85.09	0.0624
3-d	80	90.09	0.694

The influence of the thickness on XRD pattern of Cu thin films deposited on glass substrates at 100mJ, 10^{-5} mbar ,are shown in Fig. 6a,b. In figures (6a,b), a diffraction peak attributed to the Cu (111) phase is observed at $2\theta=43.297^\circ$, which the diffraction patterns of the samples were similar except the variation of the peak intensities due to the differences in thickness. Also, Cu has the face centered cubic

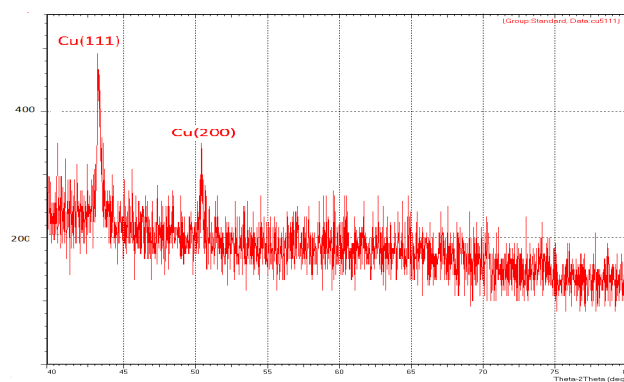
(FCC) crystal structure and for this structure (111) face has the lowest surface energy[26].

When the thickness of samples is increased the crystallinity and the mean grain size improved.

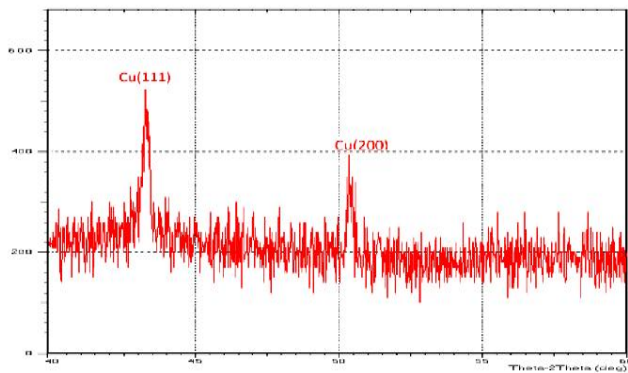
The mean size G of the Cu grains has been estimated by Scherrer's formula [27]:

$$G = \frac{0.9 \cdot \lambda}{FWHM_{hkl} \cdot \cos \theta_{hkl}}$$

Where λ is the X-Ray wavelength and $FWHM_{hkl}$ (Full Width at Half Maximum)and θ_{hkl} are the broadening and the bragg angle of diffraction peak. Two peaks at 2θ values of 43.297and 50.433 deg corresponding to (111)and (200) planes of copper have been observed and compared with the JCPDS, copper file No. 04–0836 and ASTM 03-1005- face-centered cubic copper phase - standard diffraction card. [28]. the said 2θ values of two peaks are in accordance with the standard of both JCPDS & ASTM. The XRD Study confirms / indicates that the resultant particles are (FCC) Copper Nanopartical.



(a)



(b)

Fig. 6. XRD Patterns of Cu Nanoparticles Samples. at 10000Pulsed/sec.(b)at15000Pulsed/sec

5. Conclusion

The surface morphological study with AFM generally shows the enhanced nanostructure, while the XRD patterns reveal the improve crystalline quality for the thicker films. The RMS roughness was found to increase with increasing energy, which is associated with the increase in the crystal size.

A characteristic peak of absorbance near 580 nm grew progressively by increasing laser energy. The Peak appeared in the visible wavelength region can be

Table 2. Analysis of X-Ray Pattern

2θ	(hkl)	FWHM	Grain size
43.297	(111)	0.009454444	15.548
50.433	(200)	0.004363323	35.124

Attributed to the Plasmon peak, which is the characteristic absorption of metals. diffraction peak attributed to the Cu (111) phase is observed at $2\theta=43.297^\circ$, which the diffraction patterns of the samples were similar except the variation of the peak intensities due to the differences in thickness. When the thickness of samples is increased the crystallinity and the mean grain size improved.

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