Effect of annealing temperature and laser pulse energy on the optical properties of CuO films prepared by pulsed laser deposition

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Abstract

In this work; copper oxide films (CuO) were fabricated by PLD. The films were analyzed by UV-VIS absorption spectra and their thickness by using profilometer. Pulsed Nd:YAG laser was used for prepared CuO thin films under O_2 gas environment with varying both pulse energy and annealing temperature. The optical properties of as-grown film such as optical transmittance spectrum, refractive index and energy gap has been measured experimentally and the effects of laser pulse energy and annealing temperature on it were studied. An inverse relationship between energy gap and both annealing temperature and pulse energy was observed.

Key words
Thin films, Pulsed laser deposition, CuO, Optical properties of thin films, Energy band gap, spectroscopy.

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تأثير درجة حرارة التلدين وطاقة الليزر على الخصائص البصرية لاغشية CuO المحضرة بترسيب الليزر النبضي

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الخلاصة

في هذا البحث تم تحضير اغشية CuO بواسطة تقنية PLD، وتم تحليلها ودراسة خصائصها باستخدام مطياف الامتصاص UV-VIS. اما اسماكها فقد قيست بجهاز profilometer. استخدم ليزر Nd:YAG النبضي لتحضير اغشية CuO بوجود غاز الاوكسجين مع تغيير كل من درجة حرارة التلدين وطاقة الليزر. اما الخصائص البصرية للاغشية المتكونة مثل طيف النفاذية البصرية ومعامل الانكسار وفجوة الطاقة فقد درست هي الاخرى. لوحظ ان هناك علاقة عكسية بين فجوة الطاقة وكل من درجة حرارة التلدين وطاقة الليزر.

Introduction

Pulsed laser deposition (PLD) is now increasingly being used to prepare a wide variety of materials in thin-film firm. In the most basic configuration of PLD, the flux of the material to be deposited is generated by irradiating an appropriate target with a high-intensity beam of pulsed laser light, and a film is grown by collecting this flux on a nearby substrate [1]. Since the advent of high-temperature ceramic superconductors, a worldwide effort to produce high-quality thin layers of these materials has led to a wide spectrum of investigations of viable techniques. Among these, PLD ranks as one of the most successful, due to its high controllability, relatively modest costs, and flexibility [2,3]. Nature yields copper oxides Cu_2O and CuO as cuprite and tenorite, respectively[4]. CuO is a black semiconductor with a monoclinic structure [4]. Cupric has attracted more interest as a promising material for solar energy devices due to the matching optical and electrical properties and due to its low thermal emittance. It has an indirect band gap semiconductor with about 1.2-1.5 eV [5,6], The smallest direct transition starts at 1.7 eV. Furthermore, it is expected that it would be an inexpensive cell as the constituent materials are abundantly available on earth crust. CuO is known to be p-type semiconductor mainly due to the presence of negatively charged copper vacancies in the structure which act as acceptors. It has been utilized in photovoltaic devices, pn junction diodes, power sources, microwave dielectrics, solid state gas sensor, and catalysts for several environmental processes. CuO thin films have been grown by a variety of preparation techniques like thermal oxidation, electrodeposition, molecular beam epitaxy, induced physical vapor deposition, radio frequency magnetron sputtering, and pulsed laser deposition [5,6]. CuO has a complex monoclinic crystallographic structure (a = 0.4684 nm, b = 0.3425 nm, c = 0.5129 nm, β = 99.471) [6]. The PLD of CuO can yield films with improved qualities; however, there is no straightforward theoretical or experimental model for the deposition processes or the resulting film properties. Hence, optimizing the surface film quality, investigating the governing parameters, and understanding the causal mechanisms are of great importance [6]. The influence of PLD process parameters on optical properties of CuO films are mainly investigated in this work such as annealing temperature and laser pulse energy.

Experimental

The target of the deposition was Cu bulk with purity 99.999%, shaped liked disc with a diameter of 3cm and the target surface was smoothed by using coarse sand paper. PLD experiment was carried out under O_2 pressure (0.1mbar by using Varian DS219 Rotary pump) for this pressure sufficiency to oxidize pure Cu and product CuO. The beam of Nd:YAG laser with fundamental harmonic frequency (λ=1064nm, 10ns, 6Hz) was focused onto Cu target with quartz lens (f=10cm), the target was kept onto rotating holder (speed 4 rev/min) to prevent fast drilling. The substrate distance from the target was fixed at 1cm. The PLD experiment was performed at room temperature and the as-grown samples were annealed after deposition. PLD setup scheme has been shown in Fig.1 [7]. Optical properties (UV/VIS absorption spectrum) of the CuO films were performed using Cary 100 Conc. (UV-Visible spectrometer). All CuO films were deposited on glass microscope slides which cleaned well with ultrasonic bath. The Cu target was ablated by 1000 pulses (time of deposition =2.77 minutes). The laser pulse energy was varied from (400-1000)mJ with increment 200 mJ in each step, also the annealing temperature was altered from (400-600 ^{0}C) to study their effects on the optical properties of the deposited films.

Results and discussion

Optical transmittance measurements depend strongly on the annealing temperature of CuO thin films prepared by PLD method. For the purpose of measuring the optical transmittance laser pulse energy has been set constant at 500mJ and oxygen gas pressure has been fixed at 0.1mbar. UV-VIS optical properties with range of 400nm to 800nm for different temperatures (400^{0}C-600^{0}C) using Nd: YAG laser have been

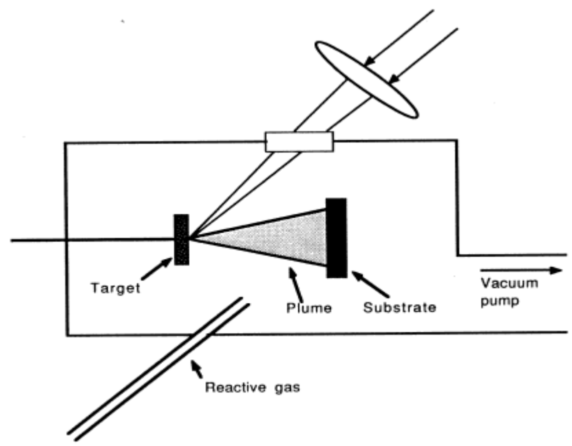

Fig.1:Schematic diagram of the PLD experimental setup [1].

illustrated in Fig.2 with oxygen as a background gas.

It is clear from the above figure that for each analyzed thin film it has been noticed that the optical transmittance decreased with increasing annealing temperature. This is probably due to the improvement in the size of the crystal. It is clear that the annealing temperature has a clear impact on the transmittance decreasing, this is a result of increasing roughness of the surface of the thin film surface and increase the scattering of light. The CuO films annealed at higher temperatures show less transmittance. Because of the heat treatment annealing causes thin film surface to be more roughness, which in turn makes light to be scattered. Fig.2 shows also that the greatest rate of transmittance is in the visible range of the spectrum 400-800nm almost 75% for temperature annealing 400^0C and be less transmittance rate for temperature annealing 600^0C is 55%. Also the optical transmittance depends on the thickness of the film. As the thickness of the thin film increases the transmittance decreases i.e. inverse proportionality between them. It is noted in all CuO films prepared by PLD technology that higher optical transmittance can be achieved at longer wavelengths. Fig.3 shows optical transmittance of the CuO thin films prepared by PLD method at different laser pulse energies.

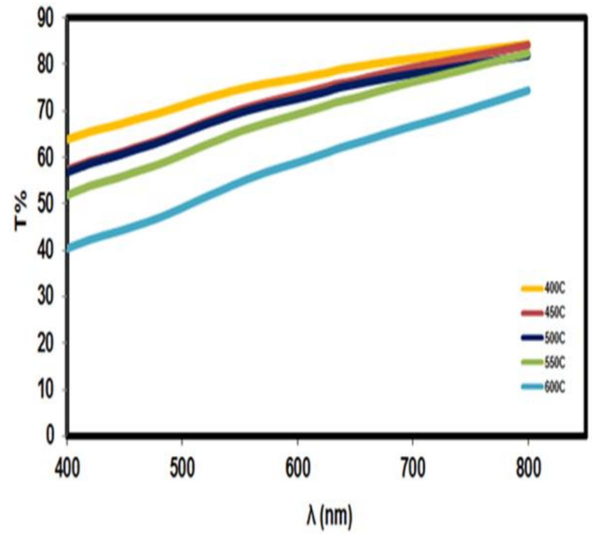

Fig.2:Optical transmittance spectra of CuO/glass thin films at different annealing temperature by using Nd:YAG laser wavelength 1064nm, laser pulse energy 500mJ, and O_2 background gas pressure 0.1 mbar.

It is obvious from the figure that at certain wavelength the transmittance decreases with increasing the incident laser pulse energy. When the incident laser energy increased the amount of energy absorbed in the target increased, which in turn leads to an increase of particles ejected toward the substrate.

These ejected particles have high kinetic energy when it absorbs the high energy laser and ultimately the density of particles deposited on the substrate increases, and the thickness of the film will increase and thus the transmittance will decrease with increasing thickness. Fig.4 shows the variations in the refractive index (n) with wavelength 400-800nm of CuO thin films deposited on a glass substrate at different annealing temperatures 400-600^0C.

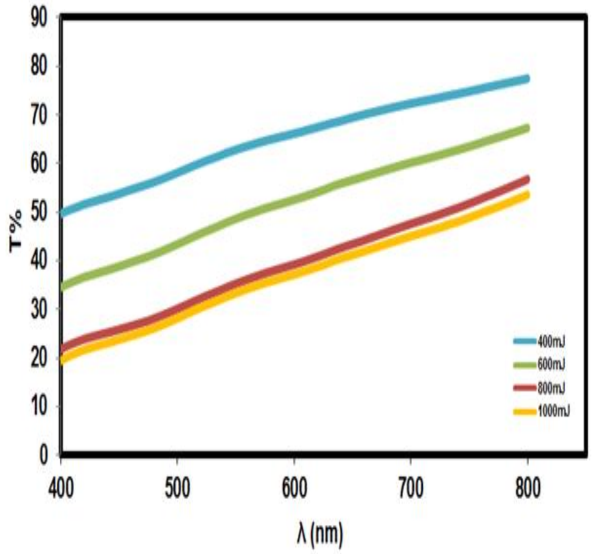

Fig.3: Optical transmittance spectra of CuO/glass thin films at different laser pulse energy by using Nd:YAG laser wavelength 1064nm , annealing temperature 500^{0}C, and O_2 background gas pressure 0.1 mbar.

Fig.4 indicates that the refractive index (n) increases with increasing annealing temperature and the reason for this, first the compactness after heat treatment increases along with increasing the size of the crystal. Secondly, due to the high packing density and the effect of annealing temperature on the morphology of the film, thereby causing a change in the refractive index. The values of the refractive index of CuO the thin films for different annealing temperatures are ranging from 1.8-2.62. Fig.5 shows refractive index of the CuO thin films prepared by PLD method as a function of laser pulse energy.

It is clear from the figure that the refractive index increases with increasing laser pulse energy. The reason for this is due to the improvement in the CuO crystallization with increasing laser pulse energy, as well as the effect of laser pulse energy on the morphology of the thin film surface and increase the reflectivity.

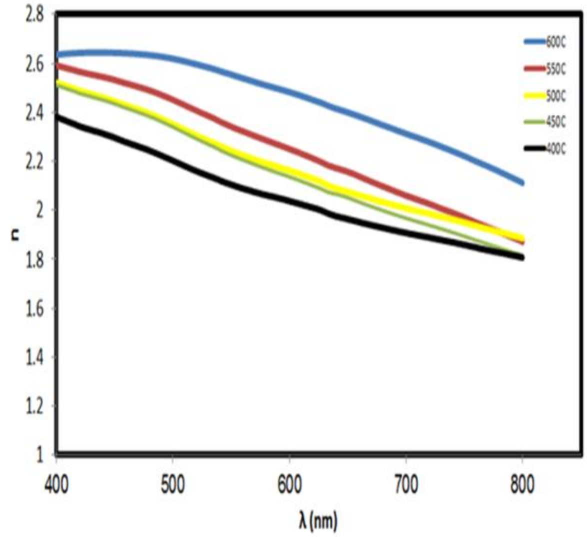

Fig. 4: Refractive index of CuO/glass thin films at different annealing temperature by using Nd:YAG laser wavelength 1064nm , laser pulse energy 500mJ, and O_2 background gas pressure 0.1 mbar.

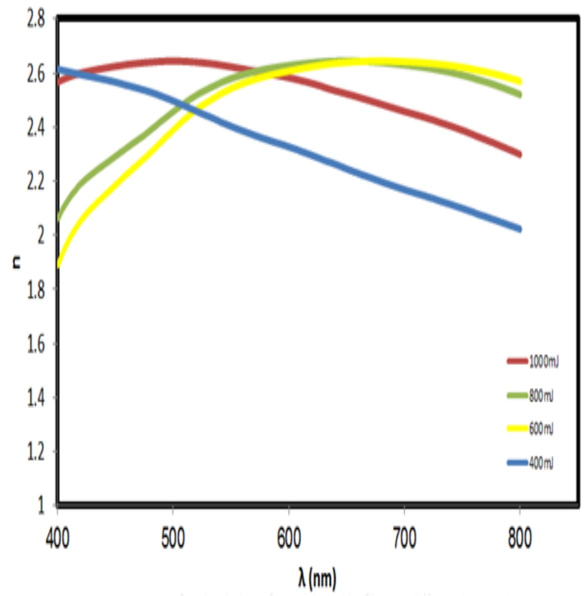

Fig. 5: Refractive index of CuO/glass thin films at different laser pulse energy by using Nd:YAG laser wavelength 1064nm , annealing temperature 500^{0}C, and O_2 background gas pressure 0.1 mbar.

The n values of the CuO films as a function of laser pulse energy are ranging from 1.9 to 2.64 and these values are reasonable and close to the theoretical value of 2.63. The plot of $(\alpha h\nu)^{1/2}$ versus (hν) for CuO films with different temperature annealing is shown in the Fig.6.

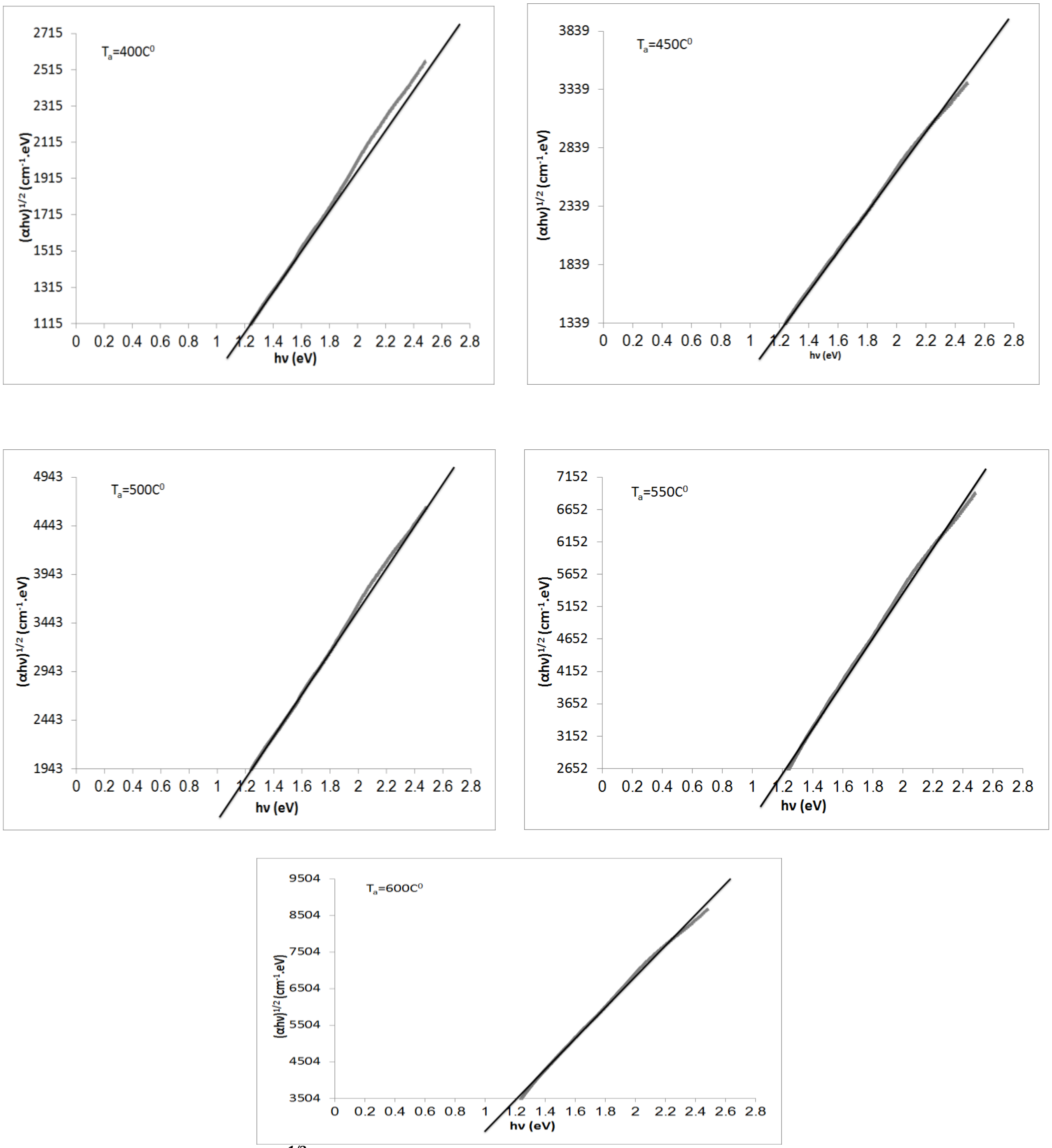

Fig. 6: Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) of CuO thin films as a function of annealing temperatur

The figure refers to indirect allowed transition for CuO thin films. Band gap energies values decreases with increasing annealing temperatures for each CuO film prepared by PLD technique. The explanation for this is due to the growth of Crystallization. Values of energy band gap E_g for CuO films has been calculated using Tauc equation used to find the type of optical transition by drawing a relationship between $(\alpha h\nu)^{1/n}$ versus photon energy hν and choosing optimal linear part where α is the absorption coefficient, h is Planck constant, ν is photon frequency and n is integer takes the values 1,2,1/2,1/3. It has been found that the relationship for n = 2 achieves linear dependence. Annealing leads to increase the local levels near the valence band and conduction band and these levels are ready to receive electrons and generate tails in the optical energy gap and tails works towards reducing the energy gap and probably the reducing in the energy gap is due to the increasing size of the nanoparticles in the CuO thin films as a result of increasing annealing temperature. These results are compatible with and close to the theoretical value of the energy gap of the CuO films which is 1.2. It has been found that the band gap energy affected extremely with incident laser pulse energy as shown in Fig.7.

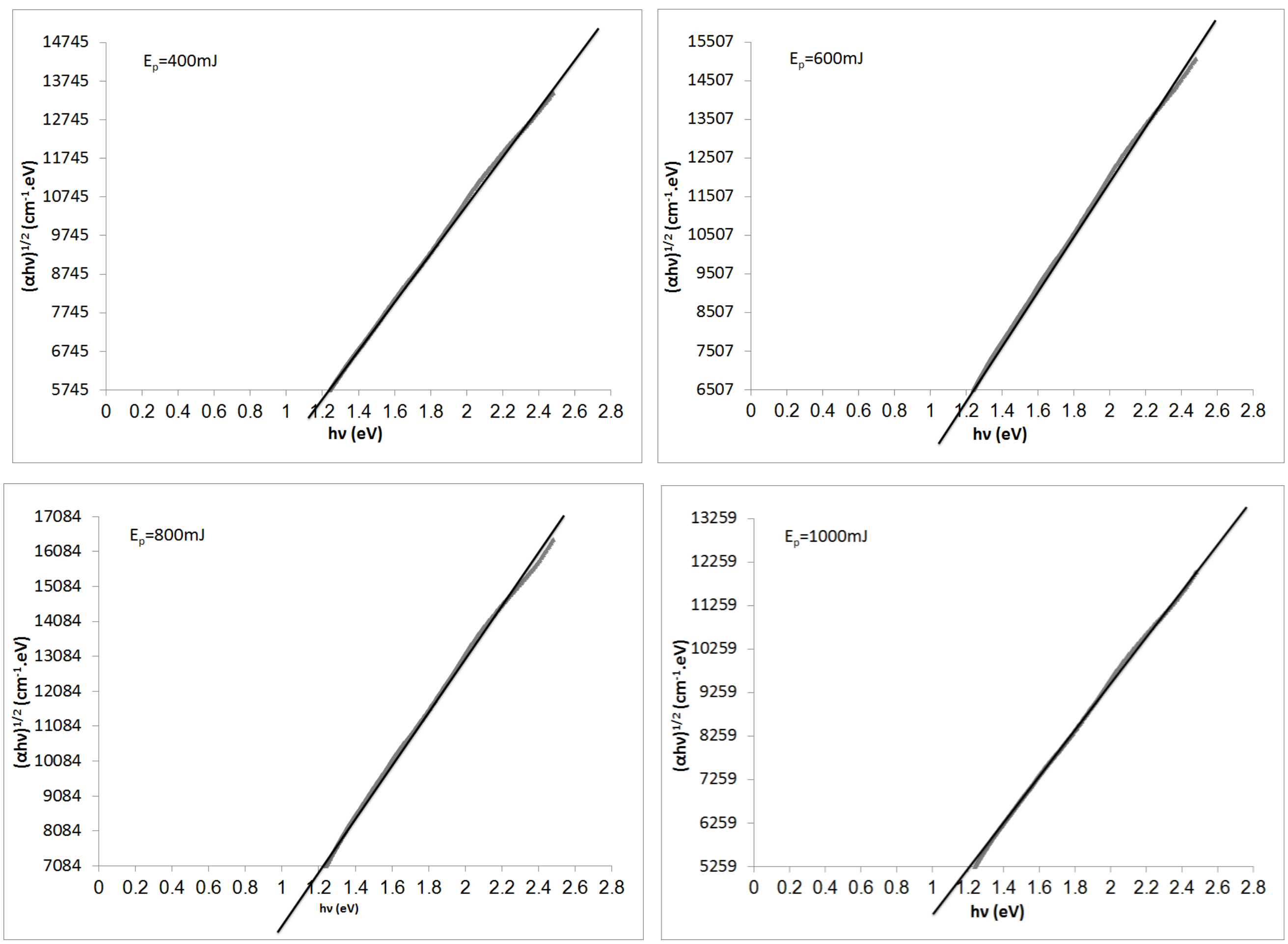

Fig. 7: Variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν) of CuO thin films as a function of laser pulse energy.

When the low laser pulse falls on the copper target, a small number of CuO nanoparticles with large-size is ablated from the target and the band gap energy is 1.24. Additional increase in laser pulse energy leads to increasing in laser power density and thus increase the number of large nanoparticles and thus band gap energy. This band gap is up to 1.2 at high energy of laser pulse and the possibility of high shift observed in the band gap energy can be attributed to the decrease in the particle size according to the quantum confinement effect. It is noted that the band gap decreases with increasing laser pulse energy as a result of the size reduction. Band gap increases as the confined dimension decreases. This probability corresponds to the micron sized ablated particles. The crystalline defects also have a direct effect and as a result, and in turn, it reduces the value of E_g. Figs.8 and 9 show the influence of the annealing temperature and laser pulse energy on band gap energy of the CuO thin films produced by PLD technique respectively.

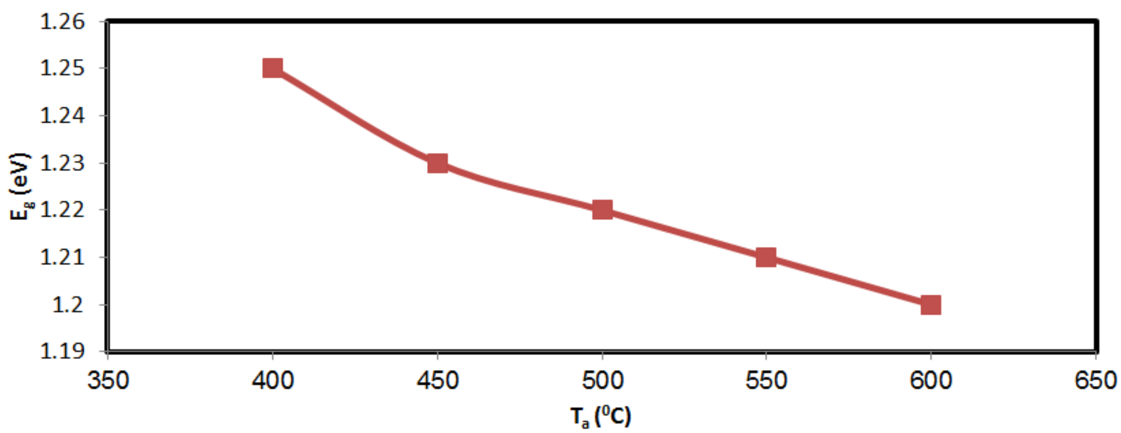

Fig.8: Band gap energy as a function of annealing temperature for different laser wavelengths of CuO thin films.

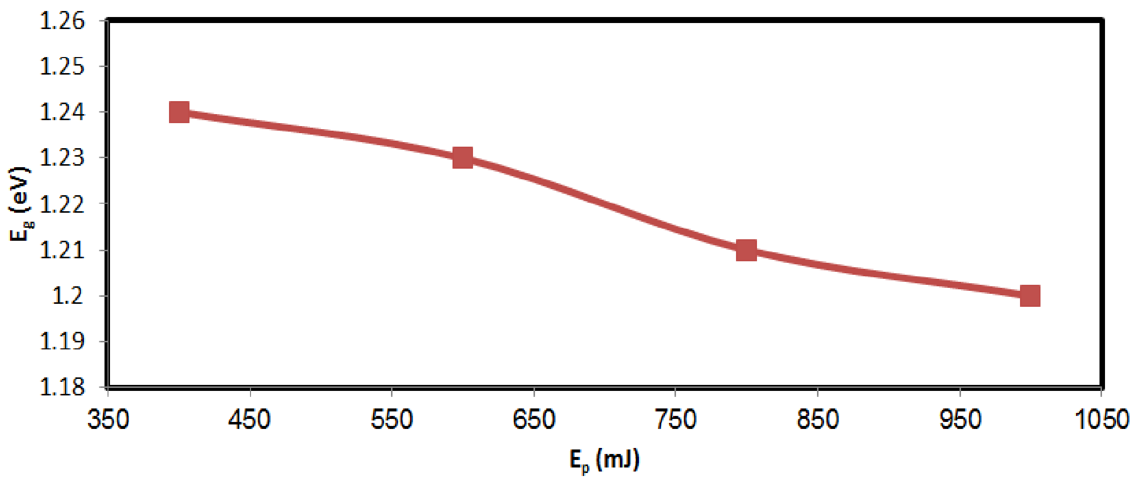

Fig. 9: Band gap energy as a function of laser pulse energy for different laser wavelengths of CuO thin films.

Generally there are several possible mechanisms that cause the observed shift in the energy gap, such as:- i)Improvement or crystallinity degradation.

ii) Modifications in the height of the barrier as a result of a change in the dimensions of crystallite.

iii) The quantum size effect.

iv) Variations in the density of impurities and compressive or tensile strains.

Conclusions

The optical properties of CuO thin film prepared by pulsed laser deposition technique depends strongly on the deposition conditions such as annealing temperature and laser pulse energy. The optical transmittance decreased with increasing annealing temperature. This is probably due to the improvement in the size of the crystal. The transmittance decreases with increasing the incident laser pulse energy due to increase the amount of energy absorbed in the target which in turn leads to an increase of particles ejected toward the substrate. The refractive index increases with increasing annealing temperature because of the compactness after heat treatment increases along with increasing the size of the crystal and due to the high packing density and the effect of annealing temperature on the morphology of the film. The refractive index increases with increasing laser pulse energy due to the improvement in the CuO crystallization with increasing laser pulse energy, as well as the effect of laser pulse energy on the morphology of the thin film surface and increase the reflectivity. The results refer to indirect allowed transition for CuO thin films. Band gap energies values decreases with increasing annealing temperatures for each CuO film prepared by PLD technique due to the growth of Crystallization. Increase in laser pulse energy leads to increasing in laser power density and thus increase the number of nanoparticles and thus band gap energy.

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