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Study of the optical proprieties of copper oxide nanoparticles prepared by PLD method

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Abstract

Nano CuO thin films on glass substrates were prepared at a constant temperature of (300°C), by pulsed laser deposition (PLD) using Nd:YAG laser at 1064 nm wavelength and five deposition energies (400, 500, 600, 700 and 800 mJ) with fixed pulses (300 pulse and 6 Hz) was used on the properties of CuO films. CuO nanoparticles were deposited on glass substrates to study optical properties and formed thin films of thickness (200 nm).CuO thin flims were characterized by X-ray diffraction (XRD) measurements have shown that the polycrystalline CuO prepared at laser energies , includes optical transmittance and absorption measurements and energy gap of these films.

Introduction

Nano materials, like nanoparticles, nanotubes, nanowires and thin films, are defined as very small aggregate of atoms with less than 100 nm dimension. The importance of nanoparticles is due to the unique different physical, chemical and biological characteristics compared to the bulk scale, due to their high surface-to-volume ratio[1]. Copper oxides are important semiconductors because they are chemical compounds of copper. They are not dissolved in water or bases and can be obtained from oxidation of copper. It is characterized by its mono crystalline synthesis [2]. Copper oxide is dark brown, which is the antiquity of the plate. Copper is a relatively large energy gap and high absorption coefficient in the visible region. It is used in solar applications, especially photovoltaic solar thermal cells, which require high efficiency absorption and a good degree of stability and also require high absorption in visible wavelength range .With good specifications that enable us to use them in applications of solar cells and reagents[3].

The Nd:YAG laser is one of the solid state lasers used in deposition technology [4]. The Nd:YAG laser generates high-energy laser pulses which is caused by the chronological age of electrons in the volatile energy level. The active medium, here, is a great reservoir of energy [5]. In order for the laser to have an effect on the material, there must be an absorption of the laser beam. This absorption is highly important for the interaction between the laser and the material. The absorption process is an essential source of energy within the material. This source shows that the laser beam emitted determines the material Laser irradiation. The falling pulse of the laser quickly heats the target material, causing a phase shift and, thus, generates waves of stress in the irradiated target. The useful range of the wavelengths in the laser deposition technique is (200-1100) nm [6,7].

Materials and methods

copper oxide nanoparticles were synthesized by pulsed laser deposition of copper oxide target in ethanol. The copper oxide target (purity of 99%) was fixed at bottom of glass vessel containing of 4 ml of ethanol, the level of the ethanol up to the target surface is 5 mm, the high of laser source is 17 cm, The deposition was achieved using focused output of pulsed Nd:YAG laser operating with a repetition rate of 6Hz. Deposition is carried out with laser operating at (1064 nm) wavelengths with (400,500,600,700,and 800) mJ by (300) pulses. (CuO) nanoparticles were deposited on glass substrate at (300 °C) to study optical properties and formed thin films of thickness (200 nm) The grain size of the copper oxide nanoparticles measured by X-ray diffraction. The

optical properties of copper oxide nanoparticles measured by UV-Vis spectrophotometer.

Results and Discussion

XRD technique was used to determine the structure and grain size of the CuO nanoparticles, using the following equation (Scherrer formula) to calculate grain size (G.S) [2]:

$G.S = 0.94\ \lambda / \beta \cos\theta$ ….(1)

Where λ= 1.54 Å is the wavelength of the X-ray radiation, θ is the angle of diffraction and β is the FWHM in radians of the XRD peak.

The figure (1) shows the results of the XRD tests showing that all prepared thin films have a polycrystalline structure with differing values and different preferential directions, CuO was monocrystalline. It was noted that the increase in deposition energy, causes increase in the Intensity, grain size , Improves crystallization. It was noted that there is a small displacement of some peaks may be due to mechanical stress and high laser energy [2]

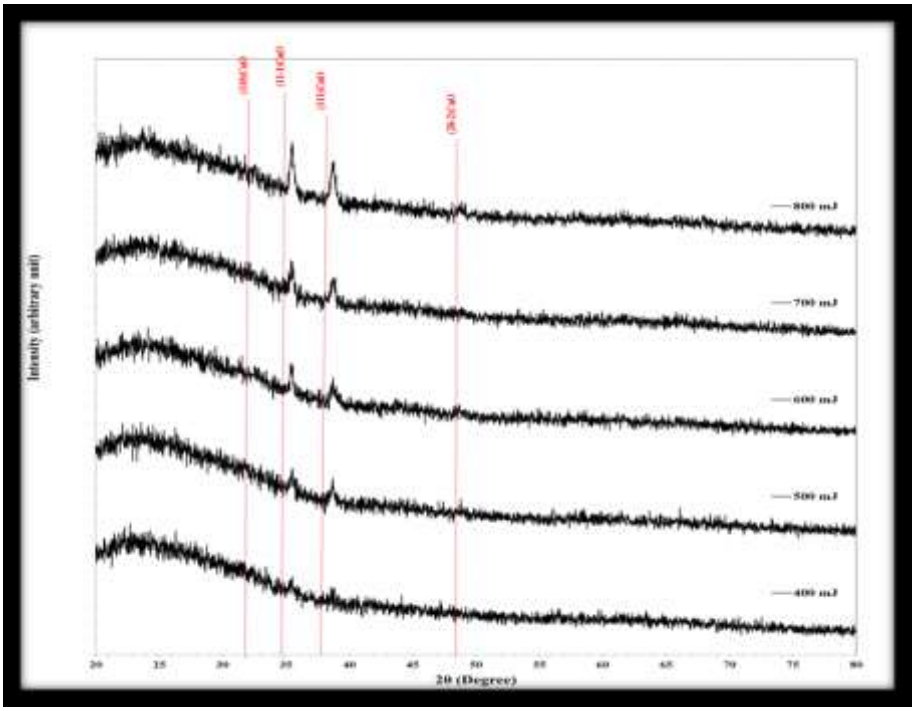

Fig.1: The (XRD) of CuO Thin Films

Table.1: The result of the (XRD) of copper oxide thin films

Laser Energy(mJ)	2θ(Deg)	FWHM (Deg)	d_{hkl} Exp.(Å)	G.S(nm)	d_{hkl} Std.(Å)	Phase	hkl	Card No
400	35.4773	0.4772	2.5283	17.5	2.5216	CuO	$(11^{-}1)$	96-410-5686
500	35.4773	0.4773	2.5283	17.5	2.5216	CuO	$(11^{-}1)$	96-410-5686
	38.6818	0.5454	2.3278	15.4	2.3158	CuO	(111)	96-410-5686
600	35.3750	0.4091	2.5283	20.4	2.5216	CuO	$(11^{-}1)$	96-410-5686
	38.6477	0.5113	2.3259	16.5	2.3158	CuO	(111)	96-410-5686
	48.6364	0.6136	1.8632	14.2	1.8679	CuO	$(20^{-}2)$	96-410-5686
700	35.4432	0.3409	2.5306	24.5	2.5216	CuO	$(11^{-}1)$	96-410-5686
	38.7500	0.4090	2.3219	20.6	2.3158	CuO	(111)	96-410-5686
800	32.5455	0.4432	2.7490	18.7	2.7460	CuO	(110)	96-410-5686
	35.4773	0.3068	2.5353	27.2	2.5216	CuO	$(11^{-}1)$	96-410-5686
	38.7841	0.4091	2.3200	20.6	2.3158	CuO	(111)	96-410-5686
	48.8409	0.4432	1.8706	19.7	1.8679	CuO	$(20^{-}2)$	96-410-5686

Absorption and Transmittance measurements were performed within wavelength range (300-1100) nm for all samples of different energies. Fig.(2) shows the absorption change as a function of the wavelength of the CuO sample in energies (400, 500, 600, 700, and 800)mJ. Absorption (Å) calculate using the following equation [8]:

$A=I_A/I_o$ ……(2)

Where I_A is absorbed intensity, I_o is incident intensity.

It shows that the increase in energy leads to a clear increase in the values of absorption. It is noticed that the absorption decreases by increasing the wavelength in the wavelength range (450-700) nm and then is almost stabilized. Physically this means that the fallen photons could not irritate electrons to move from the band valance to the conduction band because the energy of the falling photons is less than the value of semiconductor energy gap [8].

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Figure (3) shows that the increase in energy leads to a clear decrease in the values of transmittance (T) which calculate using the following equation [8]:

$$T = \frac{I_T}{I_o} \quad \ldots\ldots (3)$$

Where I_T is transmitted intensity .

This is due to the increase in the growth rate which is caused by increasing the deposition energy and the particle size, thus aggregates the material content and crystalline growth[2].

Figure (4) shows that the values of the absorption coefficient increase with increase of energy deposition , absorption coefficient (α) calculate using the following equation [3]:

$$\alpha = \frac{2.303\ A}{t} \quad \ldots\ldots (4)$$

Where A is absorption and t is film thickness.

This is due to the fact that the increase in energy led to an increase in the number of collisions with the material. This indicates that the models prepared for copper oxides are polycrystalline[9].

The figure (5) shows that increasing deposition energy leads to a clear decrease in the values of the forbidden energy gap which calculate using the following equation[10]:

$\alpha h\upsilon = A\,(h\upsilon - Eg)^r$ .. (5)

where hυ is photon energy, A is constant , Eg is forbidden energy gap ,and r coefficient depends on the transition type when r value is 1/2 for allowed direct transition , 3/2 for forbidden direct transition , 2 for allowed indirect transition , and 3 for forbidden indirect transition.

This decrease can be explained by the fact that the increase in energy has led to a clear increase in the number of photon collisions with the material and thus the matter will absorb more photons and this will increase the number of electrons and gaps leading to a decrease in the energy gap. This decrease in the value of the energy gap is also due to the regulation of the distribution of atoms within matter and the change of crystalline phases, as well as the type of material by changing the deposition energy[2] .

Table (2) shows the values of the forbidden energy gap and the optical constants of copper oxide at λ=(500)nm.

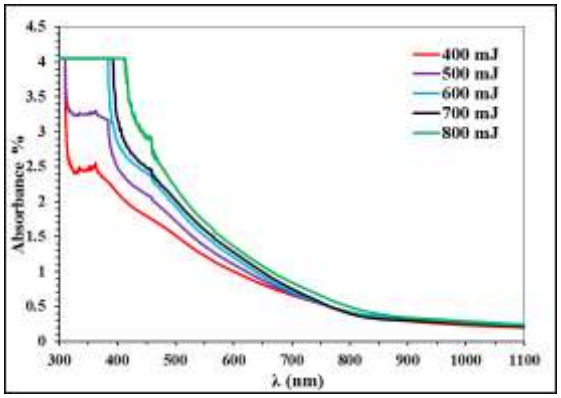

Fig.2: The absorption of CuO Thin Films

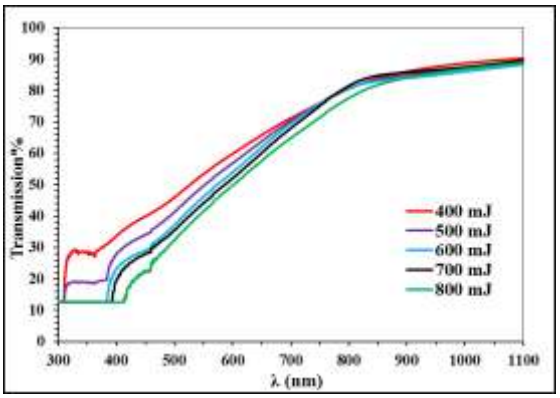

Fig.3: The transmission of CuO Thin Films

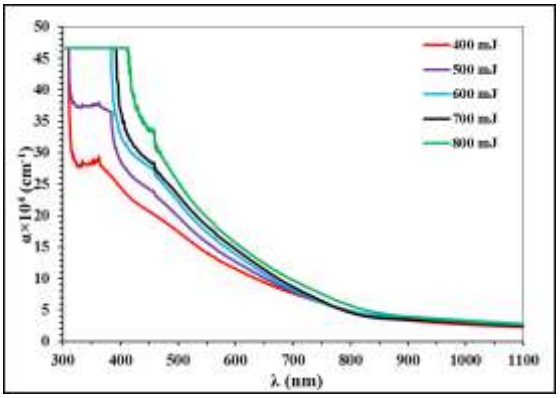

Fig.4: The absorption coefficient of CuO Thin Films

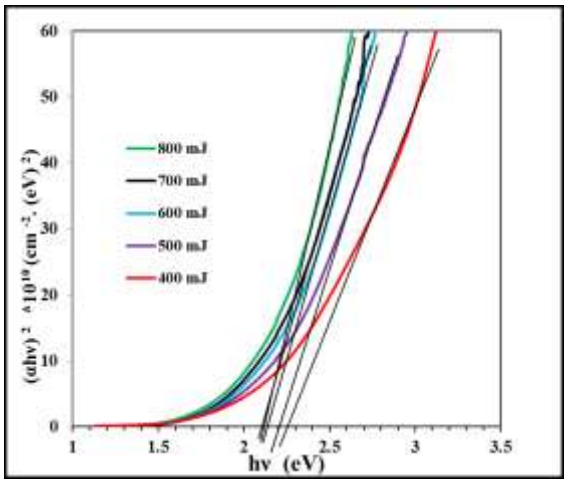

Fig.5: The forbidden energy gap of CuO Thin Films

Table.2: The values of the forbidden energy gap and the optical constants of copper oxide at λ=(500)nm

Laser Energy mJ	A %	T %	α (cm^{-1})	Eg (eV)
400	1.52	45.96	174905	2.25
500	1.73	41.33	198813	2.2
600	1.93	37.16	222722	2.12
700	2.02	35.56	232629	2.11
800	2.20	32.35	253895	2.1

Conclusion

1- The value of the forbidden energy gap decreases with increased pulse laser deposition energy, thereby reducing the structural defects of the Thin films.

2- The inverse relationship between transmission and absorption was demonstrated. Absorption increased

with the increase of pulse laser deposition energy while the transmission decreased with increased pulsed laser deposition energy.

3-The possibility of using pulsed laser to control thin film properties and by changing the values of optical parameters.

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دراسة الخصائص البصرية لجسيمات (CuO) النانوية المحضر بطريقة الترسيب بالليزر النبضي

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الملخص

تم تحضير اغشية اوكسيد النحاس النانوية الرقيقة على قواعد زجاجية عند درجة حرارة ثابتة تساوي (300 °C) باستعمال تقنية الترسيب بالليزر النبضي حيث تم استعمال ليزر النديميوم ياك واستعملت خمس طاقات للترسيب mJ (800، 700، 600، 500، 400) وبعدد نبضات ثابت (300) نبضة وبتردد (6)Hz وبطول موجي (1064)nm.

رُسبت محاليل جسيمات (CuO) النانوية على أرضيات زجاجية لدراسة الخصائص البصرية وتكونت أغشية بسمك (200)nm، وتمت دراسة تأثير اختلاف طاقة الليزر ما بين mJ (400-800) على خصائص اغشية اوكسيد النحاس، أظهر فحص حيود الأشعة السينية أن أغشية أوكسيد النحاس المحضرة بمختلف طاقات الليزر كانت متعددة التبلور ، شملت القياسات النفاذية البصرية و الامتصاصية وفجوة الطاقة لهذه الاغشية.