

Structural and optical properties of CuO thin films prepared via R.F.magnetron sputtering

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ABSTRACT

In this paper, CuO thin films having different thicknesses 20, 100 and 200 nm were deposited onto glass substrates by a radio frequency (R.F.) magnetron sputtering process using copper oxide target under Ar pressure. The sputtering deposition was performed by using R.F. power of 130 W. X-ray diffraction (XRD) results suggested that the deposited CuO films were formed by nanoparticles with average particle size in the range of (4-11) nm. The average surface roughness (Ra) measured with atomic force microscopy (AFM) was ranged between (.03-.3) nm. The optical properties concerning the absorption and transmission spectra were studied for the prepared thin films. The energy band gap were found to be in the range of (2.25 eV to 2.6 eV) When the film thickness varying from 20 nm to 200 nm.

Keywords: CuO: Thin Film; Nanostructure; Optical; Sputtering RF.

1. INTRODUCTION

Magnetron sputtering has developed rapidly over the last decade to the point where it has become established as the process of choice for the deposition of a wide range of industrially important coatings. Consequently, magnetron sputtering now makes a significant impact in application areas including hard, wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings and coatings with specific optical or electrical properties [1]. Thermal oxidation was a most widely used method for the preparation of Cu₂O in the early stage. It gives a low resistive, p-type polycrystalline material with large grains for photovoltaic applications. It was found that Cu₂O grown at high temperature has high leakage-current due to the shorting paths created during the formation of the material, and it causes low conversion efficiencies. Therefore it was focused to prepare Cu₂O at low temperature, which may provide better characteristics in this regard. Among the various Cu₂O deposition techniques [2]. Most of the techniques produce p-type conducting thin films. Many theoretical and experimental studies [3]. CuO has a relatively low band gap (1.3-2.1 eV)[4] and is occasionally considered as an n - type semiconductor with a monoclinic structure, which is of interest on account of its potential uses in many technological fields. CuO and Cu₂O materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as pn junction diodes [5]. Copper oxides have been used as electrode materials for lithium batteries. The earliest studies in this area focused on their potential use as cathodes in lithium primary cells[6,7]. CuO thin film can also be used in p-type field effect transistors and CO gas sensors [8]. A wide range of deposition techniques such as chemical vapor deposition[9] electrodeposition[10], thermal evaporation [11], sol gel techniques[12], spray pyrolysis[13], pulsed laser deposition[14] and plasma based ion implantation and deposition [15]. Many investigations have used magnetron sputtering for preparation of Cu films [16], [17] as well. In this research, reactive radio frequency (RF) magnetron sputtering was used to prepare copper oxide films with different thickness and study the structural, electrical and sensing.

2. EXPERIMENTAL DETAILS

CuO thin films were prepared by RF magnetron sputtering system with a copper oxide target of 99.99% purity on microscope glass slides as substrates. Firstly, the target was pre-sputtered in an argon atmosphere in order to remove oxide layer. The sputtering was performed under Ar (99.999%) atmosphere supplied as working gas through mass-flow controller. The sputtering chamber was evacuated down to 5×10^{-5} mbar by the turbomolecular pump. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally they were rinsed with distilled water and dried. The crystalline properties of the CuO films were analyzed by an X-ray diffractometer (N 1999 JCPDS prevalent) using Cu K α radiations ($\lambda=0.15406$ nm) and operating at an accelerating voltage of 40 kV and an emission current of 40 mA. The XRD method was used to study the change of crystalline structure. For morphological investigations, AFM images were recorded using Nanoscope IIIa scanning probe microscope controller in a tapping mode.

3. Results and discussion:

3.1 Structural Properties

The crystalline properties of the (CuO) films were analyzed by an X-ray diffract meter (N 1999 JCPDS prevalent) using Cu K α radiations ($\lambda=0.15406$ nm) and operating at an accelerating voltage of 40 kV and an emission current of (40) mA. Figure (1) illustrates the (XRD) patterns of (CuO) films which were as-deposited at room temperature for different thicknesses (20,100 and 200) nm. From this figure, it was found that all the films were polycrystalline having anatase phase only. From diffraction patterns, it was observed that the films with different thicknesses exhibited characteristic peaks of anatase crystal planes (111) and (200), at (35.5° and 38.73°) direction, respectively. These results comply with the standard (CuO) for (20,100 and 200) nm thickness XRD] X-ray diffraction data file N 1997 JCPDS prevalent]. It was found that anatase films were deposited and crystallized effectively for unheated substrate using radio frequency plasma (PRF) of 130 W and working pressure of 3 Pa. The reason may be that the kinetic energy of the impinging particle is high enough to initiate crystallization. In general, the peak intensity increases as the film thickness increases and the increase of grain size. This may be due to the improvement of crystallinity in the films [18] as shown in tables (1),(2), (3). It is important to say, that there are two possibilities to improve the crystalline of the films: an increase in grain size to decrease the number of grain boundaries and a decrease in barrier height at the grain boundaries. The comparison of (XRD) data also shows that the full-width at half-maximum (FWHM) values of the (XRD) peaks decrease with increasing film thickness, which indicates that the crystalline of the (CuO) films enhanced as the film thickness increases. This result is consistent with the increase of the grain size with the film thickness as shown in figure (2). Table (4) shows the structural properties of (CuO) thin film at various thicknesses (20,100 and 200) nm. In all samples, the obtained majority peaks are matched with the (111) and (200) directions. The average grain size and crystal size can calculated from application of Scherer's equation $D = \frac{0.94\lambda}{\beta \cos\theta} \dots \dots \dots (1)$

D: is the grain size (G.S), K: is a constant (0.94) λ : is the wavelength of Cu K α , θ : is the Bragg's angle and β is full width half maximum (FWHM) of the preferential plane

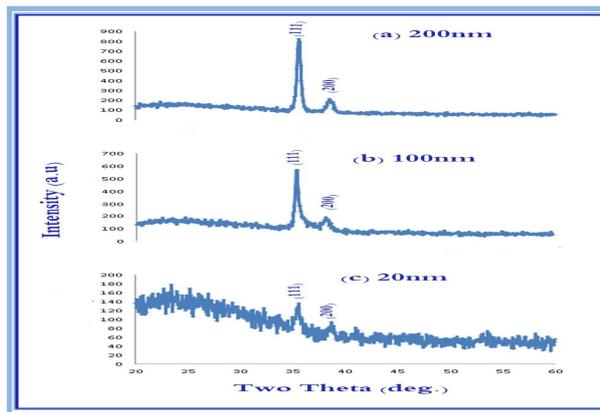


Figure (1):X-ray diffraction pattern of (CuO) thin films with (a) t= (200) nm, (b) t= (100) nm, (c) t= (20) nm.

Table (1): X-rays results of structural (CuO) thin film with thickness (20) nm

2 θ (deg.)	d Exp.(Å)	I(intensity)	FWHM	Grain size (nm)
35.524	2. 7341	100	0.6510	13.41
38.612	2.6140	15	0.6985	12.48

Table (2): X-rays results of structural (CuO) thin film with thickness (100) nm

2 θ (deg.)	d Exp.(Å)	I(intensity)	FWHM	Grain size (nm)
35.524	2. 5180	100	0.5060	17.17
38.612	2. 3349	24	0.6911	12.73

Table (3): X-rays results of structural (CuO) thin film with thickness (200) nm

2θ (deg.)	d Exp.(Å)	I(intensity)	FWHM	Grain size (nm)
35.3204	2.5180	100	0.3813	22.85
38.1664	2.3356	27	0.6459	13.6

The (hkl) plane, dislocation density (δ) and the texture coefficient ($T_{C(hkl)}$) values of thin film are listed in Tables (4), (5) and (6).

Table (4): The (hkl) plane, dislocation density (δ) and the texture coefficient ($T_{C(hkl)}$) values of (CuO) films with thickness (20) nm

Sample	Thickness (nm)	hkl	δ (nm) ⁻²	$T_{C(hkl)}$
(CuO)	20	(111)	$5.56 * 10^{-3}$	1.34
		(200)	$6.42 * 10^{-3}$	0.15

Table (5): The (hkl) plane, dislocation density (δ) and the texture coefficient ($T_{C(hkl)}$) values of (CuO) films with thickness (100) nm.

Sample	Thickness (nm)	hkl	δ (nm) ⁻²	$T_{C(hkl)}$
(CuO)	100	(111)	$3.40 * 10^{-3}$	1.01
		(200)	$6.17 * 10^{-3}$	0.99

Table (6): The (hkl) plane, dislocation density (δ) and the texture coefficient ($T_{C(hkl)}$) values of (CuO) films with thickness (200) nm.

Sample	Thickness (nm)	hkl	δ (nm) ⁻²	$T_{C(hkl)}$
(CuO)	200	(111)	$1.92 * 10^{-3}$	0.89
		(200)	$5.41 * 10^{-3}$	1.1

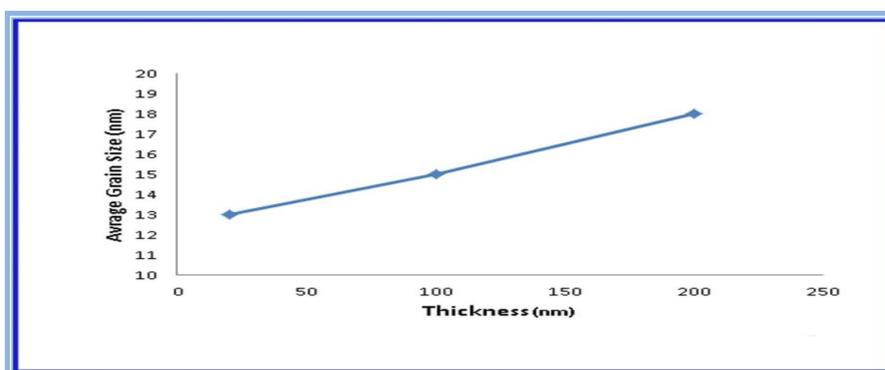


Figure (2) Average grain size variations as a function of thickness for different thickness of (CuO) thin films.

3.2 Morphology

Figure (3) depicts the surface morphology of the copper oxide thin films analyzed by (AFM). The surface of the (CuO) thin films as observed from the (AFM) micrograph confirms that the grains are uniformly distributed within the scanning area (520nm x 520 nm). An initial visual realization of the deposited films on glass substrate have shown that they are compact and have good adherence to the substrate. All the (CuO) films exhibit a smooth surface with uniform grains. In figure (3), the surface morphology reveals the nano-crystalline (CuO) grains, which combine to make denser films significantly with the increased thickness. From the images, it was observed that the surfaces of the films exhibited a certain degree of roughness and the film came rougher when the thickness increases as shown in table (7).

This result indicates that the growth of larger grains with increasing thickness leads to an increase in the surface roughness. It is observed that the average grain size increases with increasing of thickness and the values of the average grain size variable from (4 -11 nm) depending on film thickness as shown in table (7). It is clear from this table, that there are minimum difference between the value of grain size measured by (AFM) and by (XRD) analysis. The former one measure the grain size directly which give the exact value which, the latter measure the grain size through Scherer's equation which needs some corrections. Our results are nearly in agreement with [19].

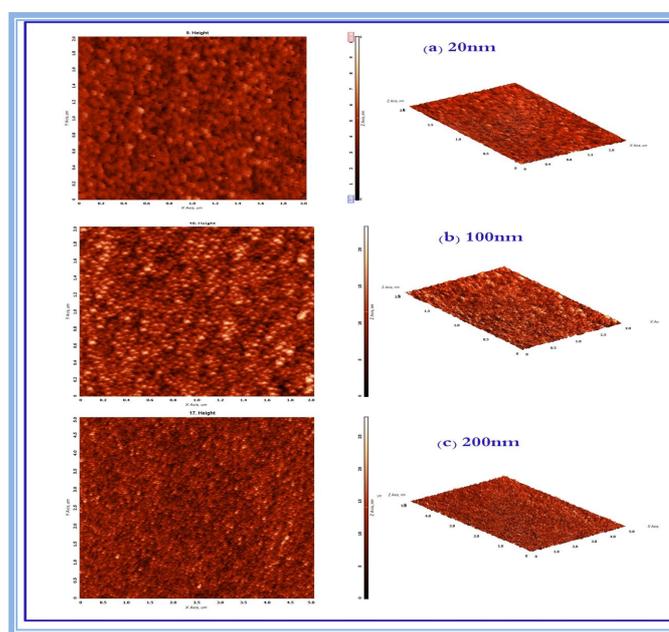


Figure (3) shows the (AFM) images of (CuO) thin films with different thicknesses : (a) 20 nm, (b) 100 nm and (c) 200 nm.

Table (4-7) shows the different thicknesses (20, 100 and 200 nm) and grain size and average roughness for (CuO) thin films obtained from (AFM) and (XRD) analysis.

Thickness (nm)	AFM of plane grain size (nm)	Average roughness(nm)	X-ray of plane grain size (nm)
20	4.12	0.0399	12.48
100	10.16	0.191	12.73
200	11.54	0.307	13.6

The results obtained from the (AFM) of the nanostructure for different thickness as of (CuO) thin film show that the histogram of the percentage of (CuO) as a function of the grain size are shown in figure (4). From this figure, the percentage of minimum grain size were (38% , 18% and 14%) for film thickness of (20,100 and 200) nm respectively. Also, it is clear from the figure, that the average grain size were (28, 36 and 40) nm with percentage of (45%, 30% and 32%) for the previous thickness. This nano structural films are very important for many novel applications such as optoelectronic devices, gas sensors and biological science.

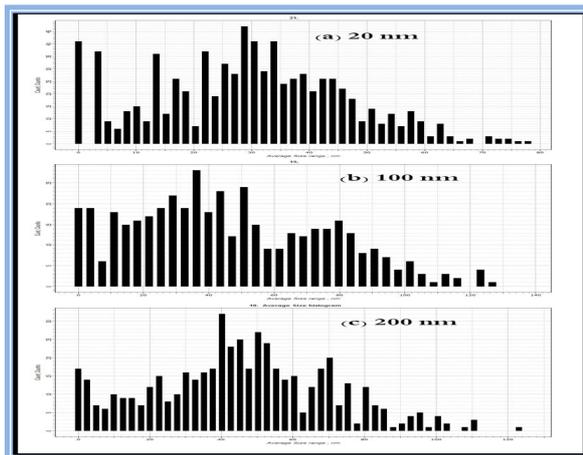


Figure (4): Granularity cumulation distribution report of (CuO) thin films with different thickness :(a) 20nm, (b) 100nm and (c) 200 nm.

3.2 Optical Properties

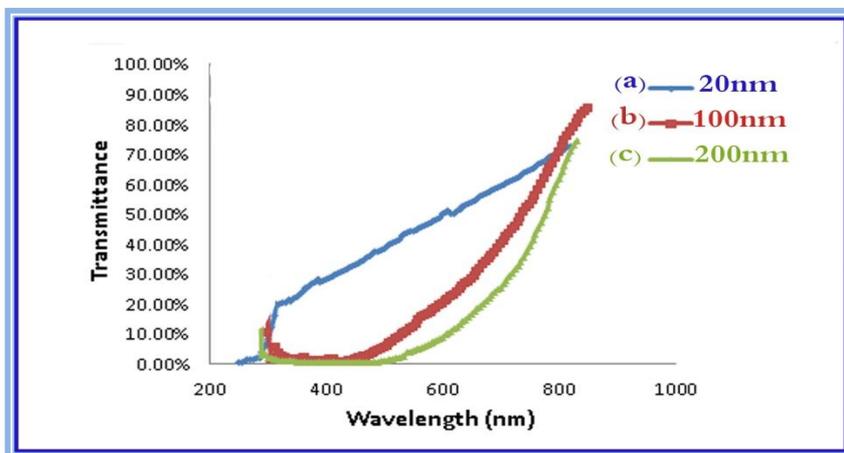


Figure (5) :- illustrates transmittance spectrum of CuO films for different thickness (20,100,200 nm.). It is observed that maximum transmittance at (100 nm) thickness for wavelength (~ 800 nm).

Figure (6) illustrates absorbance spectrum for (CuO) films of 20, 100, 200 nm. When the thickness of the film is increased, absorbance is also increased. At the visible spectrum absorption is minimum, that it is suitable to be antireflection coating.

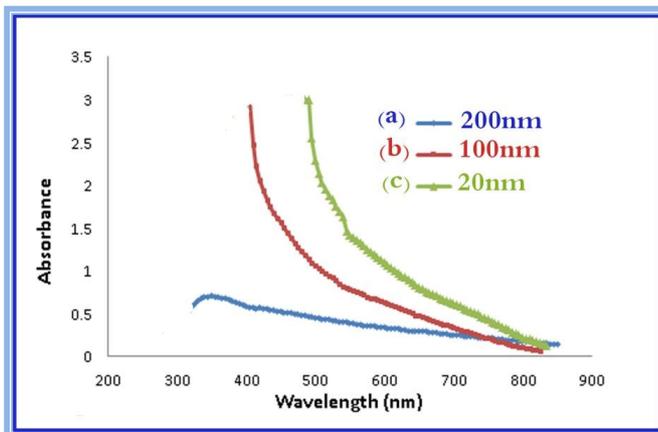


Figure (6) :- The relation between Absorbance and wavelength of TiO₂ thin films

3.3 The Energy gap

The energy gap can be calculated from equation: $(\alpha h\nu)^{1/2} = B (h\nu - E_g)^{1/2}$ (2)

Where : (α) Absorption coefficient, (h) Planck's constant, (ν) the frequency of the photon, ($h\nu$) photon energy, (B) Constant depends on the probability of the transfer of electronic. The relation is drawn between $(\alpha h\nu)^2$ and photon energy ($h\nu$), as shown in figure (7.) which illustrate the allowed direct transition electronic. The optical energy band gap were found to be in the range of (2.25 eV to 2.6 eV) When the film thickness varying from 20 nm to 200 nm.

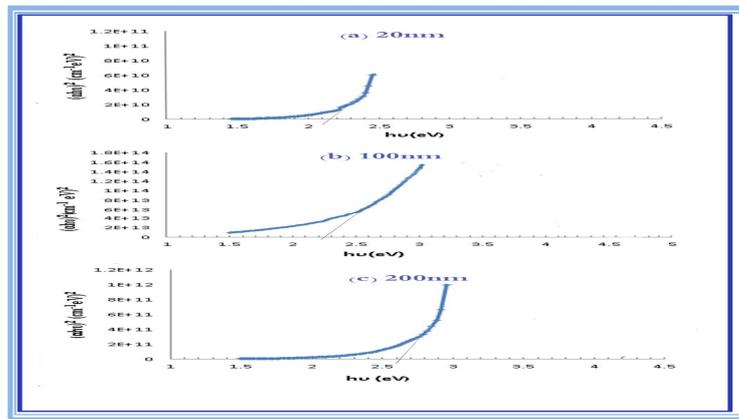


Figure (7):- allowed direct electronic transitions of CuO thin film (20,100,200 nm).

4 CONCLUSION

The anatase phase copper oxide thin films have been produced by RF reactive sputtering method on unheated glass substrates. The crystallization is found to increase slightly in the increased film thickness. AFM images also support the slow growth of crystallite sizes for the as-grown films and increasing thickness. The CuO films are highly resistivity with increasing thickness. The optical properties concerning the absorption and transmission spectra were studied for the prepared thin films. The energy band gap were found to be in the range of (2.25 eV to 2.6 eV) When the film thickness varying from 20 nm to 200 nm.

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