Optical Properties,Structure,and Morphology of CuO Grown by Thermal Oxidation of Cu thin film on Glass Substrate

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Abstract:

Oxidation method was used to prepare nanostructure of cupric oxide (CuO) film. Thin film of Copper metal were deposited on substrate (quartz) in a thermal vacuum evaporator. The thickness of the film was measured to about 20 µm. The thermal oxidation of this evaporated film was done in a horizontally heated quartz furnace at temperature (400°C) in air for 4 hour. The product was tested by X-ray diffraction pattern (XRD), Fourier transfer infrared (FTIR) spectrometer, The surface properties was characterized using scanning electron microscopy(SEM),UV–vis spectrometer ,the average crystal diameter derived from the XRD data analysis is found to be 27nm and completely converts this Cu film to tenorite structure with composition of CuO with peak appeared at 2θ equal to 35.5˚, 38.7˚.

The conversion was also confirmed by the FTIR spectrometer measurement. The UV–vis spectrum of the material shows significant amount of blue-shift in the band gap energy(Eg) and is found to be 3.82eV due to the quantum confinement effect exerted by the nanocrystals.

Keywords: cupric oxide (CuO), Oxidation method, Thin films, Morphology analysis, optical properties.

الخواص البصرية والطبوغرافية لأوكسيد النحاس المحضر بطريقة الأكسدة الحرارية على الزجاج

عمار هادي

الخلاصة :

تم تحضير غشاء من اوكسيد النحاس ذا تراكيب نانوية بطريقة الاكسدة ، تم ترسيب معدن النحاس على قاعدة من زجاج الكوارتز بطريقة التبخير الحراري بالفراغ .سمك الغشاء كان حوالي 20 ميكرومتر . تم الاكسدة الحرارية للغشاء بواسطة تسخين زجاج كوارتز في فرن افقيا بدرجة حرارة 400 سيليزية في الهواء لمدة اربعة ساعات . تم دراسة الخواص التركيبة بواسطة حيود الاشعة السينية ، ومطيافية الاشعة تحت الحمراء ، والخواص السطحية بواسطة المجهر الالكتروني الماسح ، والخواص البصرية بواسطة مطيافية الاشعة المرئية وفوق البنفسجية ، معدل قياس حجم البلورة 27 نانومتر مع تحول كامل لغشاء النحاس الى لاوكسيد النحاس بقمة ظهرت بزوايا 38.7˚ ,35.5˚ .

تم تاكيد التحول بواسطة مطيافية الاشعة تحت الحمراء وبمقياس مطيافية الاشعة المرئية وفوق البنفسجية اظهرت زاحة في فجوة الطاقة نحو اللون الازرق من الطيف الكهرومغناطيسي وقد وجدت 3.82الكترون-فولت وذلك بسبب تاثير الحصر الكمي للبلورات النانوية .

كلمات مفتاحية: الخواص البصرية ،اوكسيد النحاس (CuO)، اغشية رقيقة ، طريقة الأكسدة ، طبوغرافية السطح

1.Introduction:

Cupric oxide (CuO) is a p-type semiconductor having a band gap of 1.21–1.51 eV and monoclinic crystal structure[1] . These materials have several advantages: (i) availability and abundance of the starting materials, (ii) non-toxic nature, (iii) low production cost, (iv) band gaps lie in an acceptable range for solar energy conversion, and (v) and p-type conductivity [2,3]. Copper oxides have found numerous applications in diverse fields such as solar cells and photovoltaic materials [4], electrochromic coatings [5], catalytic applications [6], and gas sensors [7]. Doped copper oxide thin films have found applications such as in the fabrication of p-type transparent conductors [8].Several methods have been used to prepare copper oxide thin films. These include electrochemical deposition [9]; chemical conversion [10]; sol–gel synthesis [11]; spraying [12]; reactive sputtering [13]: molecular beam epitaxy [14]; pulsed laser deposition[15] thermal evaporation [16]; This method is direct, simple, and has less incorporation of impurities since it was carried out under vacuum. Moreover, it is a low-temperature technique, and films can be deposited on a variety of conducting or insulating substrates .Thermally evaporated copper oxide thin films were mainly carried out by evaporating pure copper in an oxygen atmosphere [17]. Only in one report was CuO powder directly evaporated [18]. Moreover, copper oxide thin films grown by oxidation of metal layers [16,19,20].

In the present study, we have synthesized CuO nanostructures by thermal oxidation method to calculate the optical properties, structure and morphology of the growth product.

2.Experimental details

2.1 Synthesis of cupric oxide (CuO)

The quartz substrate used in this work , was cleaned with acetone ,washed with deionized water , ultrasonically cleaned in alcohol for about 15 minutes ,washed with deionized water ,then dried with nitrogen gas .Pure copper metal powder (commercial grade) was thermally evaporated using PVD technique on quartz substrate with sizes of 1cmx2cm each. .The thickness of the deposited film was measured by weighting method found to be 20μm. The substrate was loaded onto alumina boat and then inserted through the center of one meter quartz tube within electrical tube furnace. The oxidation experiment last for 4h in air atmosphere attemperature 400°C The heating rate was 25°C/min. At the final of the oxidation experiments, the furnace was switched off and left to cool down. The rate of cooling was5 °C/min. The samples were then tested by XRD, SEM, FTIR spectrophotometer.

2.2 Film thicknesses

The evaporated copper film on glass substrate was calculated by weight difference method(BALANCE MODEL KERN ALJ220-4NM) using formula:

$$t = m/A.\rho \quad \ldots\ldots\ldots (1)$$

Where t is film thickness of the evaporated copper film on substrate, m is actual mass of copper deposited on substrate, *A* is area of the film (ρ = 8.92 g/ cm^3) [21] . The calculated thickness of the deposited Cu film was 20 μ m.

2.3 Characterization:

Powder X-ray diffraction (XRD) of the product was carried out on Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm),employing a scanning speed of 12° min^{-1} and 2θ ranges from 20° to 60° . The morphology of the produced films was investigated using Scanning Electron Microscope – SEM (Tescan Vega II- Cheek). Fourier Transform Infrared –FTIR Spectrophotometer (Shimadzu / ARAffinity-1)was used , optical properties was carried out on UV-VIS spectrophotometer (metertech sp8001) .

3.Results and Discussion:

3.1 XRD Analysis:

Figure 1. shows the XRD pattern of the prepared CuO sample annealed at 400°C for 4h in air . All the peaks were indexed to a monoclinic phase CuO ((JCPDS File No. 5-661). No other phases was detected , indicated that the CuO film obtained was a pure phase .

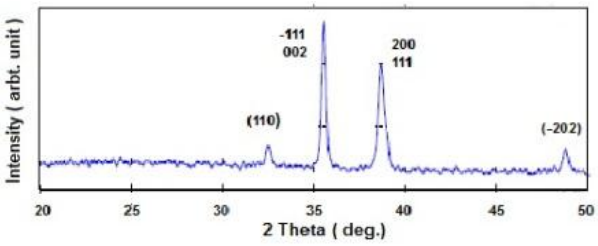

Fig. 1. The XRD pattern of the as prepared CuO film.

The mean crystallite sizes of CuO grown on glass substrate was calculated using Debye-Scherrer eq.2 [22].

$$L = 0.9\lambda / \beta.\cos\theta \qquad \ldots\ldots.(2)$$

Where, L is the mean crystallite size (nm) , λ is the wavelength of Cu Kα (0.15406 nm) , β is the full width half maximum (FWHMXπ/ 180 rad.), and θ is the Bragg angle .The average crystallite size of CuO nanoparticales was calculated using sherrer = 27nm as shown in table (1) .

Table 1. XRD analysis results for CuO thin film .

2θ (deg.)	d (nm)	FWHM	Relative.Int.	L (nm)	Refl.Plane
35.5651	0.252222	0.2689	100%	31	(-111)(002)
38.7198	0.232367	0.3700	72%	23	(200)(111)

4.2 FTIR Analysis :

The two broad absorption bands at 601, 529 and 489 cm^{-1} areassociated with Cu–O stretching modes [18]. Thus, the FTIR resultsuggests the presence ofCu–Obonds. Thus, the formation ofcopper oxide compound is confirmed from FTIR study the Table 2 . FTIR results of our work compare with previous reports, from the table obvious that our work approximately match with ref. [24]

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No.	Band cm^{-1}			Ref.
1	480	517	650	23
2	480	529	---	24
3	437	503	606	25
4	489	529	601	Our work

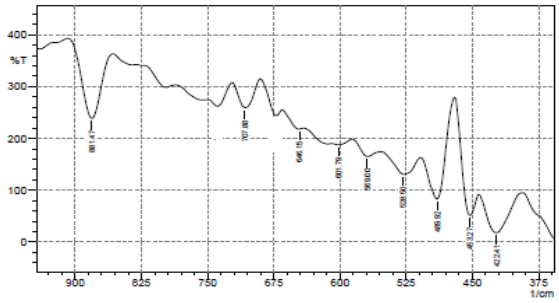

Fig. 2. FTIR spectrum of CuO thin film on glass as prepared by oxidation at 400°C for 4h in air

3.2 Morphology analysis:

The morphology of CuO nanoparticales is shown in Figure 3. This figure shows the SEM images of CuO as prepared at 400°C for 4h in air in different magnifications(5kx,12kx,29kx,57kx),the images show that the grains are not highly homogeneous in shape and size there are shape cubic , spherical and others.The average grain diameter,as determined from Fig. 3 is about 50nm,which is to some extent higher than the value of the crystallite diameter (27nm) as obtain fromXRD pattern analysis,whichisobvious,since,the crystallites Clustered together to form grains with larger size.

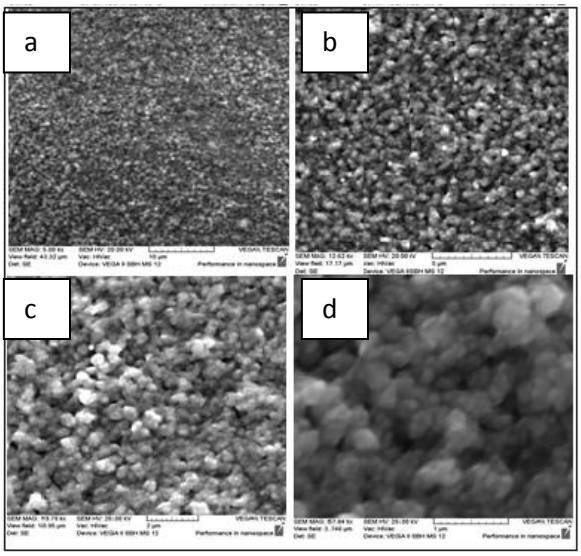

Fig. 3.SEM of CuO thin film on glass as prepared by thermal oxidation at 400C for 4h in air , at different magnifications (5kx,12kx, 29kx, 57kx), (a,b,c,d) respectively .

3.3 Optical properties calculations:

Fig.(4) shows the absorption coefficient spectrum of CuO thin film recorded in UV-VIS spectrophotometer.This figure shows spectrum in the wavelength range o-1500 nm. The band gap energy (E_g) was ≈ 3.82eV. This was calculated from the relation: Eg=hc/ λ, where h = $4.13566x10^{-15}$eV.s is the Plank's constant, c=$3X10^3$m/s is the light velocity, and λ is the cut-off wavelength. Extrapolation of the line to the base, where the value of absorption coefficient α is zero, gives the cut-off wavelength 325 nm.

The theory of optical absorption gives the relationship between the absorption coefficient and the photon energy hν for direct allowed transition as:

$$\alpha = (h\nu - E_g)^{1/2}/h\nu \quad \ldots.(3)$$

This equation gives the band gap energy Eg when straight portion of $(\alpha h\nu)^{1/2}$ against hν plot extrapolated to the point α=0. Fig. 4c shows plot of $(\alpha h\nu)^2$ versus hν for the CuO thin film . From this Fig. , The CuO sample show higher direct band gap (3.82eV) as compared to the bulk value (1.21–1.51 eV) [1] and still comparable to the value of other worker (3.57eV) Our band gap value is due to the quantum confinement effect [26,27,28].Table 3 compare of our work with previous report , from table obvious our work approximately match with Ref. 28

Table 3 compare of our work with previous report

No.	Optical band gap eV	Grain size nm	Ref.
1	3.57	26	26
2	2.9	27	27
	4	28	28
3	3.72	28	28
4	3.82	27	Our work

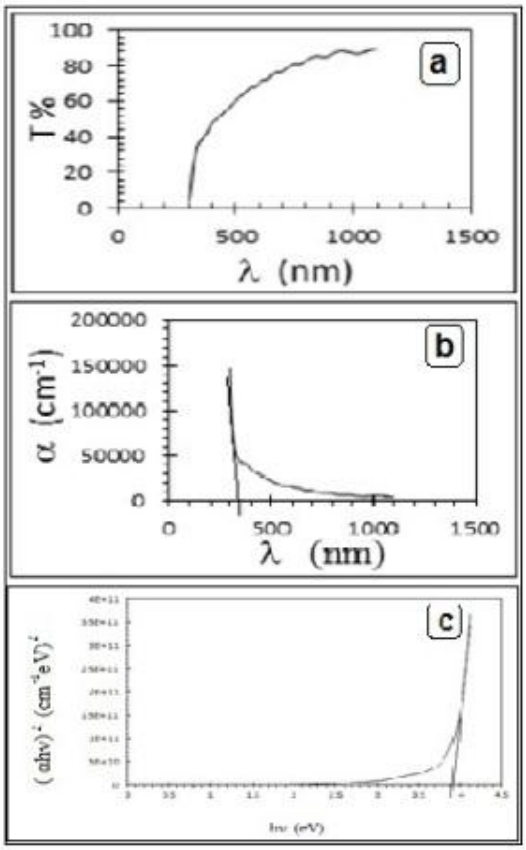

Fig. 4 UV-VIS transmittance of CuO nanoparticles grown on glass (a), calculated absorption coefficient (b) and energy band gap(c).

4.Conclusion

Thin film of copper oxide was prepared through oxidization of the metallic Cu films deposited on glass substrates by thermally evaporation . At temperature to 400˚C, The XRD measurements showed that the CuO nanostructures have a high crystal quality with monoclinic crystal structure, the average crystal diameter derived from the XRD data analysis is found to be 27nm, The direct allowed band gap is 3.82eV.

5. References

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