IASJ المجلات الاكاديمية العراقية

Tikrit Journal of Pure Science

ISSN: 1813 – 1662 (Print) --- E-ISSN: 2415 – 1726 (Online)

Journal Homepage: http://tjps.tu.edu.iq/index.php/j

Study of Topographical Properties of CuO thin film prepared by CBD method at various deposition times

Tahseen Ali Aswad

General Directorate of Education Saladin, Iraq.

https://doi.org/10.25130/tjps.v26i3.144

ARTICLE INFO.

Article history:

-Received: 10 / 3 / 2021

-Accepted: 26 / 5 / 2021

-Available online: / / 2021

Keywords: CuO, thin films, chemical bath deposition, topographical properties, deposition time.

Corresponding Author:

Name: Tahseen Ali Aswad

E-mail:

tahseenphysics84@gmail.com

Tel:

ABSTRACT

In this study, thin films of copper oxide (CuO) prepared using a chemical bath deposition (CBD) method on glass substrate. Aqueous copper sulfate ($CuSo_4.5H_2O$) used to obtain the required thin films and in concentration 0.1M. The films prepared during different deposition times (1, 4 and 8) days at room temperature. The XRD studies showed that the thin film prepared at deposition time (8 days) has polycrystalline structure (monoclinic structure). Morphological studies by using AFM measurements and topographical studies by using SEM measurements revealed that the surfaces of the prepared thin films show better uniformity when increasing deposition time from 1 day to 8 days, where the average diameter, roughness rate and root mean square (RMS) decreased with increasing deposition time.

1. Introduction

Thin film is a layer of material that is a few nanometers thick. In the past two decades, a large number of researches have been carried out on thin semiconductor films and for various applications [1]. Thin films are generally used to improve the surface properties of solids. Permeability, reflection, absorption, hardness, wear resistance, penetration and electrical behavior are just some of the characteristics of the macroscopic material surface that can be improved with the use of thin film. Nanotechnology relies heavily on thin film technology [2]. In recent years, reducing the metal oxide size has become of great importance due to the fact that the Nano-size particles greatly improve the properties of the metal oxide compared to the macroscopic form [3].

Copper oxide (CuO) is abundant on Earth and is non-toxic, exhibiting relatively high minority carrier diffusion lengths, high absorption coefficient in the visible area, and large exaction binding energy [4] with low-cost manufacturing processes [5]. Copper oxide (CuO) can be synthesized as nanoparticles [6], nanorods [7], nanoflowers [8], nanowires [9], nanofilms [10] and nanoplates [11,12]. Copper oxide is a p-type semiconductor having an energy gap of 1.2 to 1.9 eV with a black color and partial transparency in the visible region [13]. Copper oxide (CuO) is one of the most important compound semiconductors (I – IV) and has many applications such as diodes, cathodes in lithium batteries [14,15], catalyst [16-20], lithium-copper oxide electrochemical cells, field emission device in addition to its use as a gas sensor [13], it is also used in the manufacture of solar photovoltaic cells [5]. Thin copper oxide films can be manufactured with different techniques such as thermal evaporation, DC sputtering [21], magnetron sputtering [22], spray pyrolysis [23], laser pulse evaporation, chemical vapor deposition [4,5], sol-gel [13], etc.

The aim of this work is to deposit thin films of copper oxide (CuO) on glass substrates using the chemical bath deposition method and then study the topographic properties of these thin films at different deposition times.

2. Experimental details

In this work, we used a chemical bath deposition (CBD) method shown in figure (1) to fabricate a copper oxide (CuO) thin film with a nanostructure. The chemical bath method is a thin film deposition method that has many advantages including simple preparation, low-cost equipment, large-scale production, easy parameter setting, in addition to the fact that the manufacturing process is carried out at a

relatively low temperature compared to other deposition methods [3].

Copper oxide (CuO) thin films prepared by chemical bath deposition method on glass slides with dimensions of (25.4 × 76.2 × 1) mm^3, where aqueous copper sulfate ($CuSo_4.5H_2O$) used to obtain copper ions in the solution. The solutions prepared at room temperature with different deposition times (1, 4, 8) days, with fixing the concentration of the solution at 0.1 M. The process done by dissolving the required weight of the substance (1.2484) g in 50 ml of distilled water gradually dissolving using a magnetic stirrer at room temperature for 30 minutes to ensure complete dissolving of the solution.

The basic reaction for formation the CuO thin film is given by:

$$CuSO_4 + H_2O \longrightarrow CuO + H_2SO_4 \quad \text{..... (1)}$$

Glass slides were placed vertically inside the chemical bath without magnetic stirring, after washing them well with distilled water and washing powder first, then with ethanol alcohol, then acetone. After completing the deposition of the film, the sample is immersion in the distilled water for a few seconds to get rid of the plankton if any on the surface of the film, then it is left in the air to dry. The thickness of the prepared thin films was measured by gravimetric method, using an electronic balance with a sensitivity (10^{-4} gm) where the floor was weighed before and after the deposition process, and by finding the weight difference and knowing the density and area of the film material, the thickness (t) can be found according to the following equation [24]:

$$t = (m_2 - m_1) / \rho A \text{ .....(2)}$$

where t is the thickness of the film, m_1 is weight the sample before deposition, m_2 is weight the sample after deposition, ρ is the density of copper oxide ($6.31 gm/cm^3$), A is the area of the film.

After the preparation of the thin films was completed, we performed the structural measurements with an X-ray diffraction device (Model: XRD 6000/ Shimadzu/ Japan) with Objective (Cu), wavelength (1.5406Å), voltage (40kV) and current (30mA). The average grain size was calculated using the Scherer equation shown in the following equation [14]:

$$D = 0.9 \lambda / \beta \cos \theta \text{.....(3)}$$

where D is the average grain size, λ is the X-ray wavelength, β is the full width at half maximum of the peaks, θ is the diffracting angle.

The inter-planar distance (d) is calculated by using the following equation [25]:

$$d = \lambda / 2 \sin \theta \text{.....(4)}$$

Morphological measurements were examined with an atomic force microscope (AFM) (Model: SPM-AA3000/USA) and topographic measurements were examined by using scanning electron microscope (SEM) (Model: TESCAN-VEGA/USA).

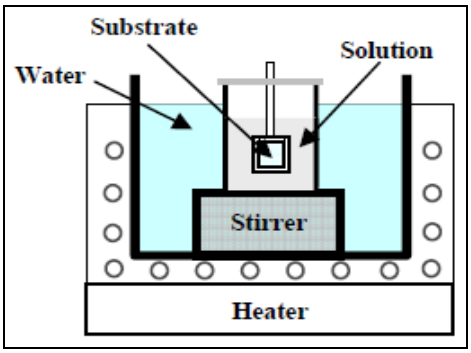


Fig. 1: The schematic diagram of the CBD set up [26].

3. Results and Discussion

3.1. Structural characterization

The XRD patterns of copper oxide (CuO) thin film deposited at deposition time (8 days) are given in Fig. 2 since no clear crystallization was obtained at the other deposition times as illustrated in Fig 3. The appearance of more than one peak in fig. 2 indicates that the prepared thin film is polycrystalline (monoclinic structure). The diffraction pattern showed three strongest peaks at 2Θ values of 25.7497°, 43.9400°, and 61.1340° at planes (110), (202) and (301) respectively with other peaks at 2Θ values of 13.1314°, 62.8234°, 75.3448°, 82.4123° and 87.4166° at planes (002), (310), (206), (400) and (226) respectively as illustrated in table 1 and this corresponds to standard x-ray diffraction powder patterns [27]. It was generally observed from the results of X-ray diffraction that the peaks were not high and not sharp; the reason is that the manufactured films prepared at low temperature (room temperature).

Table 1: The peaks data for CuO thin film deposited at deposition time (8 days).

Peak no.	2Theta (deg)	I / I_1	d (Å)	hkl	FWHM (deg)	Grain Size (nm)
1	13.1314	4	6.73678	002	0.3	26.65
2	25.7497	100	3.45702	110	10.175	0.801
3	43.94	17	2.05896	202	0.8397	10.203
4	61.134	10	1.51471	301	1.78	5.183
5	62.8234	7	1.47798	310	0.24	38.79
6	75.3448	3	1.26042	206	0.35	28.67
7	82.4123	5	1.1693	400	0.2111	50.02
8	87.4166	5	1.11478	226	1	10.99

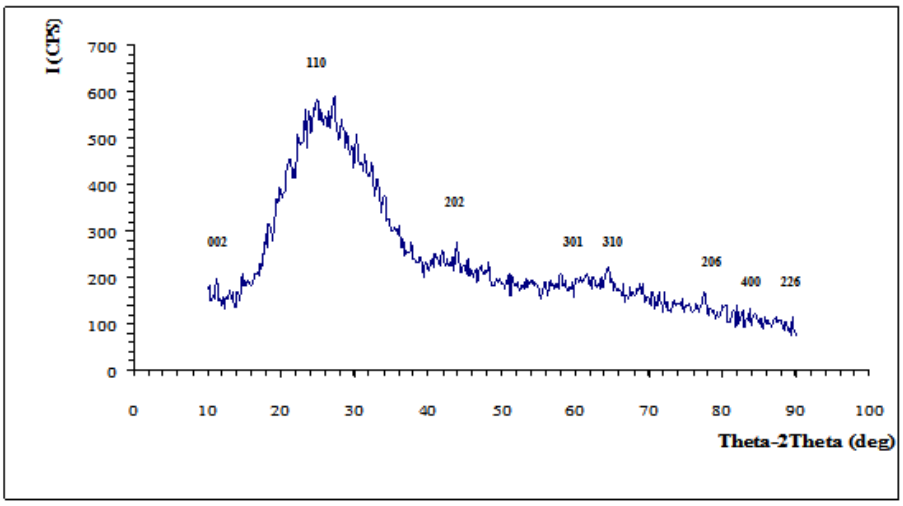


Fig. 2: XRD patterns of CuO thin film at deposition time (8 days).

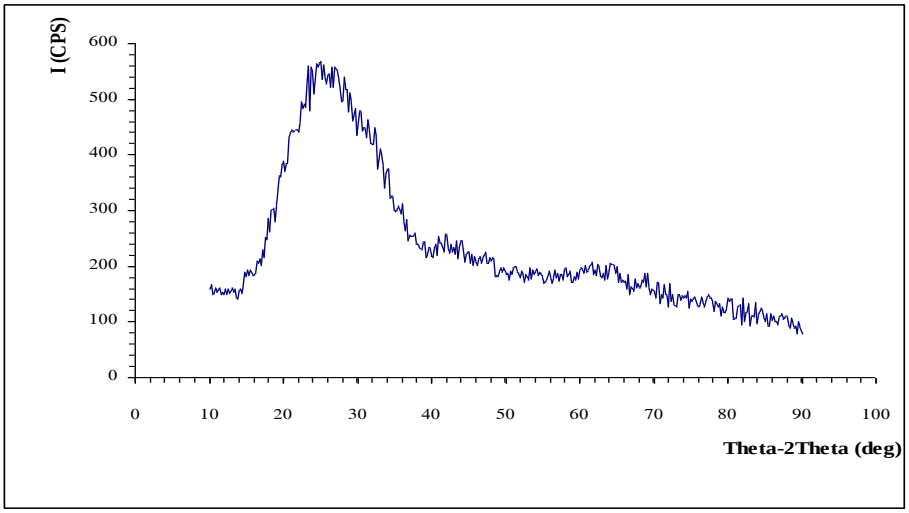


Fig. 3: XRD patterns of CuO thin film at deposition time (1 day).

3.2. Morphologic and Topographic characterization

3.2.1. AFM measurements

The figures (4, 5 and 6) show atomic force microscope images with image size (12000nm × 12000nm). It is evident from the figures that the particle sizes of all samples are located in the nanometer area. It has also been observed that the grains appear smooth and uniform, and there are some luminous areas appearing on the surface depending on the reflex of the laser beam, which determines and maps the topography of the scanned surface. These areas decrease as the deposition time increases from 1 day to 8 days, which indicates an increase in the smoothness of the upper surface of the thin films. It also confirms this decrease of average diameter, roughness rate and root mean square with increased deposition time, as shown in table 2.

Fig. 7 illustrates the inverse proportion of the average diameter and roughness rate with deposition time. The large values of the average diameter of the grains may be due to the fact that the deposition time used is relatively long and this corresponds to [28].

Table 2: The average diameter, roughness rate and root mean square for CuO thin films deposited at different deposition times.

Deposition time (day)	Average diameter (nm)	Roughness rate (nm)	Root Mean Square (nm)
1	288.36	10.9	18.7
4	266.98	8.58	14.9
8	258.88	5.79	10

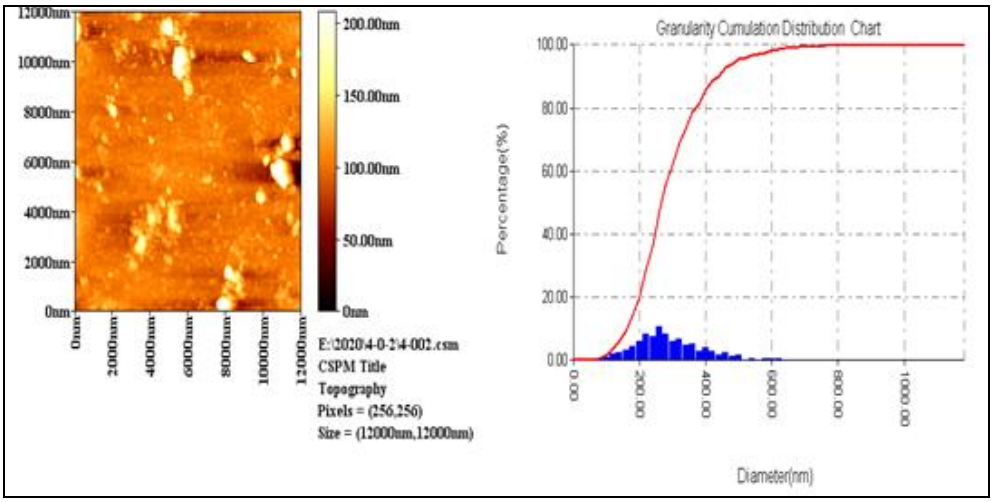


Fig. 4: AFM topography of CuO thin film at deposition time 1 day.

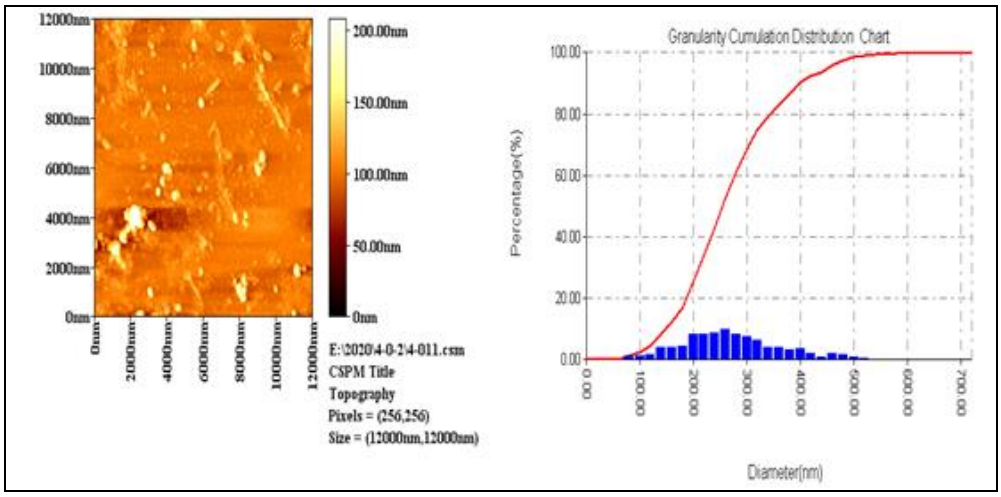


Fig. 5: AFM topography of CuO thin film at deposition time 4 days.

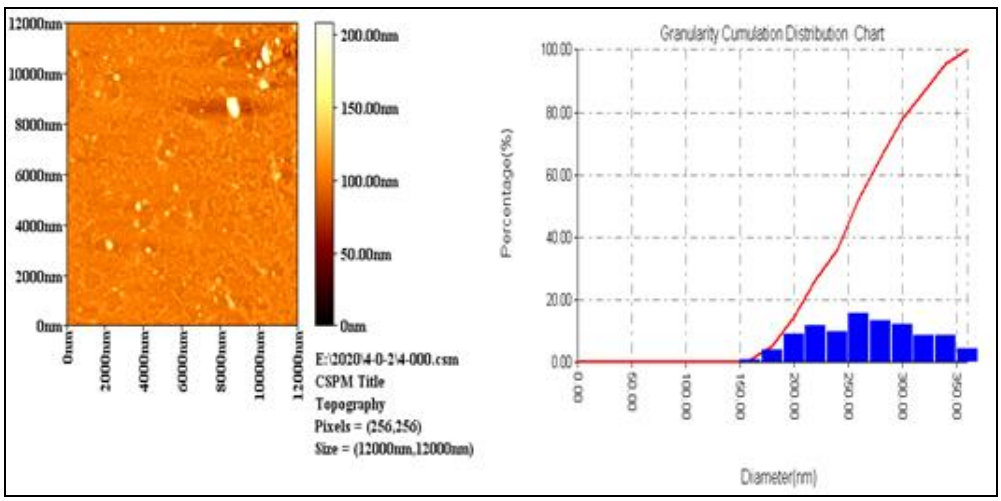
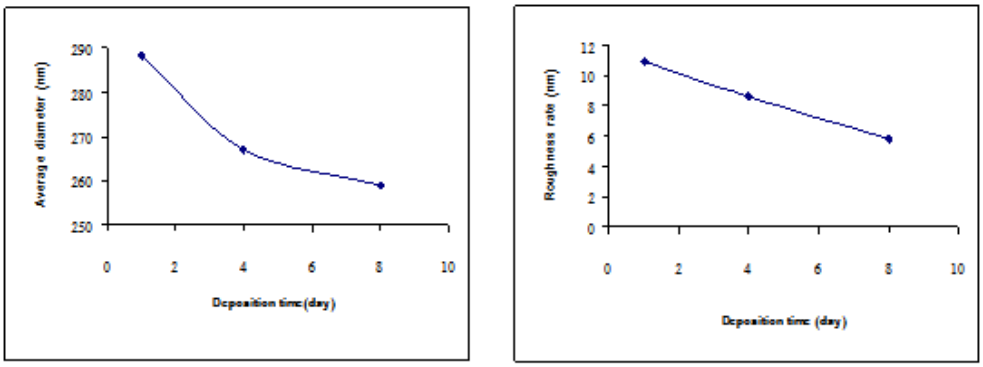


Fig. 6: AFM topography of CuO thin film at deposition time 8 days.



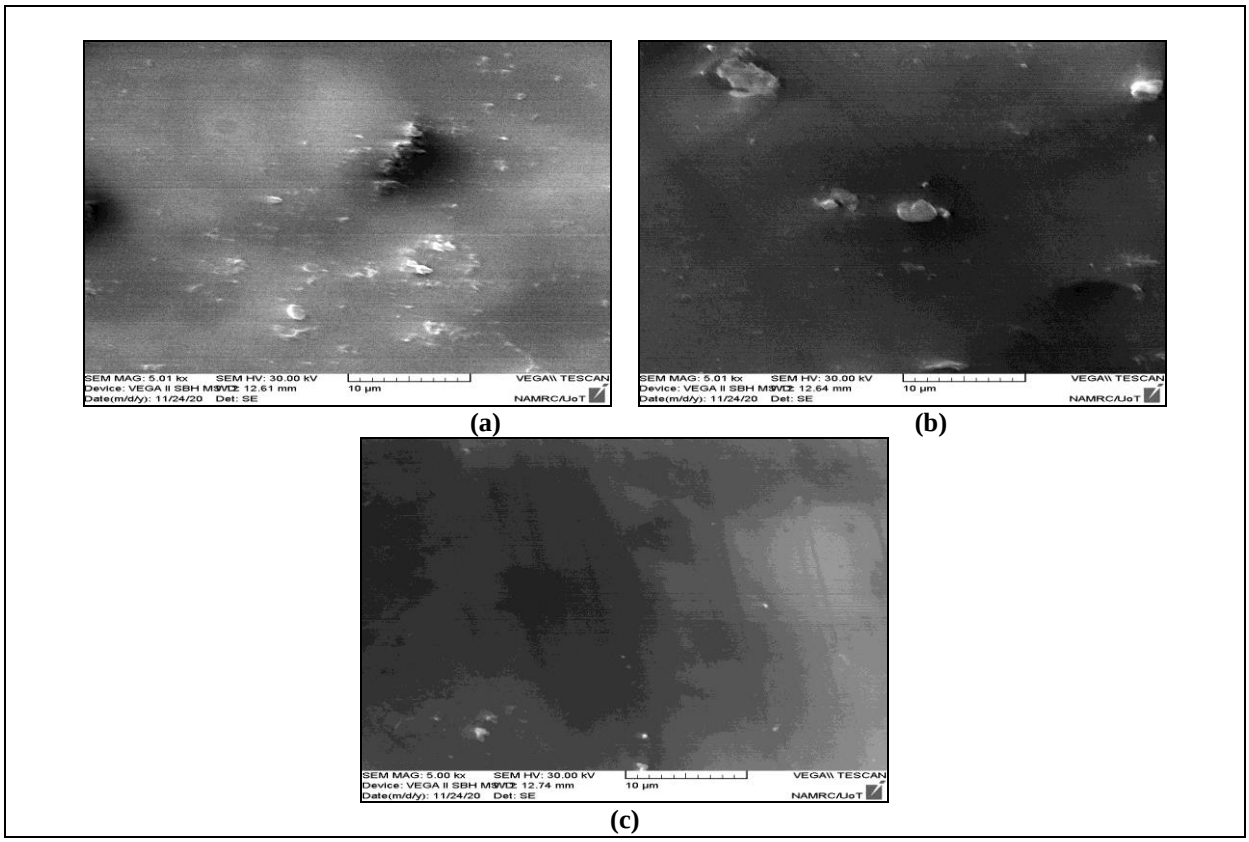
(a) **(b)**

Fig. 7: Relationship between deposition time with : (a) average diameter (b) roughness rate.

3.2.2. SEM measurements

The topographic of (CuO) thin films with nanostructures were studied using a scanning electron microscope (SEM) with voltage (30kV), magnification (5.01kx), tape measure (10µm) as shown in Figure (8), and with magnification (23.83kx - 23.95kx), tape measure (2µm) as shown in Figure (9).

It was observed from the figures that the size of clusters begins to decrease with increasing deposition time from 1 day to 8 days, as homogeneity becomes more pronounced within 8 days and this corresponds to the results of (AFM) shown in table (2), as the average diameter decreases with increasing deposition time. It also observed from the figures that there are no clear cracks and discontinuities on the surface of the films, indicating that the precipitated films have taken sufficient time for the chemical reaction in order to obtain the appropriate deposition and this corresponds with [13].



(a) **(b)**

(c)

Fig. 8: SEM images of CuO thin film with scale bar (10µm) at deposition time:
(a) 1 day (b) 4 day (c) 8 day

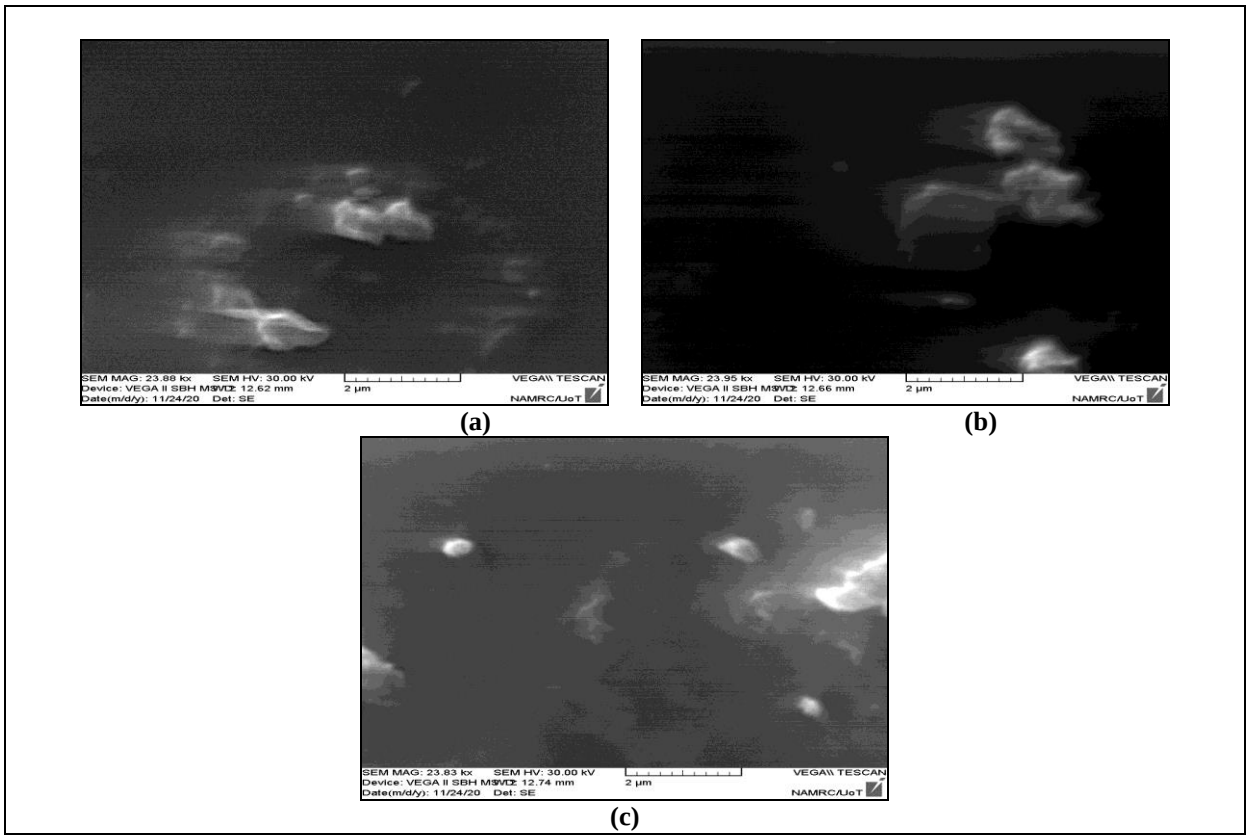


Fig. 9: SEM images of CuO thin film with scale bar (2µm) at deposition time: (a) 1 day (b) 4 day (c) 8 day

Conclusions

The CuO thin films were successfully deposited on glass substrates by chemical bath deposition method in deposition time range (1, 4 and 8) days at room temperature. X-ray diffraction results showed that the deposited thin films at deposition time (8 days) have a polycrystalline structure. The effect of deposition time on the surface morphology and topography of prepared thin films was determined by using AFM and SEM measurements respectively. As a result of the calculations, it was found that the average diameter decreased from 288.36 nm to 258.88 nm and the roughness rate decreased from 10.9 nm to 5.79 nm with increasing deposition time (1, 4 and 8) days. It was noticed that there are no clear cracks and discontinuities on the surface of the prepared films and that the increase in deposition time led to an increase in the homogeneity between the atoms and to the improvement of the topographical properties of the films. The lack of clumps visible on the surface of the films through SEM images confirms the success of the method of preparing these films.

References

[1] Hussian, S.K. (2017). Study of Optical properties of Copper Oxide (CuO) thin film prepared by SPD technique. *AL-Muthanna Journal of pure sciences*, **4(1)**: 144-152.

[2] Frey, H. and Khan, H.R. (2015). Handbook of Thin-Film Technology. *Springer-Verlag Berlin Heidelberg*, 1-3 .

[3] Yuliarto, B.; Suyatman; Septiani, N.L.W.; Nugraha and Rafa, G. (2016). Preparation of Copper Oxide nanostructure thin film for Carbon Monoxide Gas Sensor. *Molekul*, **11(2)**: 202 – 207.

[4] Mugwang'a, F.K.; Karimi, P.K.; Njoroge, W.K.; Omayio, O. and Waita, S.M. (2013). Optical characterization of Copper Oxide thin films prepared by reactive dc magnetron sputtering for solar cell applications. *International Journal of Thin Films Science and Technology*, **2(1)**: 15-24.

[5] Dahrul, M.; Alatas, H. and Irzaman (2016). Preparation and optical properties study of CuO thin film as applied solar cell on LAPAN-IPB Satellite. *Procedia Environmental Sciences*, **33**: 661–667.

[6] Etefagh, R.; Azhir, E. and Shahtahmasebi, N. (2013). Synthesis of CuO nanoparticles and fabrication of nanostructural layer biosensors for detecting Aspergillus niger fungi. *Scientia iranica F*, **20(3)**: 1055–1058.

[7] Shrestha, K.M.; Sorensen, C.M. and Klabunde, K.J. (2010). Synthesis of CuO nanorods, reduction of CuO into Cu nanorods, and diffuse reflectance measurements of CuO and Cu nanomaterials in the near infrared region. *The Journal of Physical Chemistry C*, **114(34)**: 14368–14376.

[8] Duan, Y. et al. (2014). Optically active chiral CuO nanoflowers, *Journal of the American Chemical Society*, **136(20)**: 7193–7196.

[9] Hoa, N.D. et al. (2010). Synthesis of porous CuO nanowires and its application to hydrogen detection, *Sensors and Actuators B: Chemical*, **146(1)**: 266–272 .
[10] Dhanasekaran, V.; Mahalingam, T. and Ganesan, V. (2013). SEM and AFM studies of dip-coated CuO nanofilms, *Microscopy Research and Technique*, **76(1)**: 58–65.
[11] Li, R. et al. (2012). Ionic liquid precursor-based synthesis of CuO nanoplates for gas sensing and amperometric sensing applications, *Sensors and Actuators B: Chemical*, **168**: 156–164.
[12] Moumen, A.; Hartiti, B.; Thevenin, P. and Siadat, M. (2017). Synthesis and character-ization of CuO thin films grown by chemical spray pyrolysis, *Optical and Quantum Electronics*, **49(70)**: 1-12.
[13] Kumar, D.A.; Xavier, F.P. and Shyla, J.M. (2012). Investigation on the variation of conductivity and photoconductivity of CuO thin films as a function of layers of coating, *Archives of Applied Science Research*, **4(5)**: 2174-2183.
[14] Sultana, J. et al. (2017). Chemical bath deposited (CBD) CuO thin films on n-silicon substrate for electronic and optical applications: Impact of growth time, *Applied Surface Science*, **418(Part A)**: 380-387.
[15] Fu, L.J. et al. (2007). Effect of Cu_2O coating on graphite as anode material of lithium ion battery in PC-based electrolyte, *Journal of Power Sources*, **171(2)**: 904–907 .
[16] Hashim, H.; Shariffudin, S.S.; Saad, P.S. M. and Ridah, H.A. M. (2015). Electrical and Optical Properties of Copper Oxide Thin Films by Sol-Gel Technique, *IOP Conference Series: Materials Science and Engineering*, **99(1)**: 1-8.
[17] Ibrahim, F.T. (2017), Characterization of Pulsed-Laser Deposited CuO-Doped MgO Thin Films for Gas Sensing Applications, *Iraqi Journal of Applied Physics*, **13(3)**: 13-17.
[18] Tamaekong, N.; Liewhiran, C. and Phanichphant, S. (2014).Synthesis of thermally spherical CuO nanoparticles, *Journal of Nanomaterials*, **(2014)**, 1-5.
[19] Hammadi, O.A. (2015). Photovoltaic Properties of Thermally-Grown Selenium-Doped Silicon Photodiodes for Infrared Detection Applications, *Photonic Sensors*, **5(2)**: 152-158.
[20] Hammadi, O.A. and Naji, N.E. (2016). Electrical and Spectral Characterization of CdS/Si Heterojunction Prepared by Plasma-Induced Bonding, *Optical and Quantum Electronics*, **48(8)**.
[21] Tripathy, S.K.; Kumar, S. and Narava, D.A. (2019). Effect of Grain Size on Strain in a Copper Oxide Nano film for Gas Sensing Applications. *Journal of nano and electronic physics*, **11(5)**: 1-4.
[22] Zeng, X.; Zhukova, M.; Faniel, S.; Proost, J. and Flandre, D. (2020). Structural and Opto‐electronic characterization of CuO thin films prepared by DC reactive magnetron sputtering. *Journal of Materials Science: Materials in Electronics*, **31(6)**: 4563-4573.
[23] Fasasi, A.Y. et al. (2018). Effect of Precursor Solvents on the Optical Properties of Copper Oxide Thin Films Deposited Using Spray Pyrolysis for Optoelectronic Applications. *American Journal of Materials Synthesis and Processing*, **3(2)**: 12-22.
[24] Naser, G.Y. et al. (2013). Some optical properties of CdO thin films. *Energy Procedia*, **36**: 42 – 49.
[25] Ahmed, A.M.; Rabia, M. and Shaban, M. (2020). The structure and photoelectrochem-ical activity of Cr-doped PbS thin films grown by chemical bath deposition, *The Royal Society of Chemistry*, **10**: 14458–14470.
[26] Busarin, N.; Panita, C.; Intira, S. and Chanwit, C. (2008). The Influence of Growth Conditions on the Chemical Bath Deposited ZnS Thin Films. *Journal of Metals, Materials and Minerals*, **18(2)**: 49-52.
[27] Swanson, H. E.; McMurdie, H. F.; Morris, M. C. and Evans, E. H. (1967). Standard X-ray Diffraction Powder Patterns, *National Bureau of Standards Monograph 25* - Section 5, Issued August 31.
[28] Abdallah, B.; Ismail, A.; Kashoua, H. and Zetoun, W. (2018). Effects of Deposition Time on the Morphology, Structure, and Optical Properties of PbS Thin Films Prepared by Chemical Bath Deposition, *Journal of Nanomaterials*, **(2018)**, 8 pages.

دراسة الخواص الطبوغرافية لغشاء أوكسيد النحاس (CuO) الرقيق والمحضر بطريقة الترسيب بالحمام الكيميائي عند أزمان ترسيب مختلفة

تحسين علي أسود

المديرية العامة لتربية صلاح الدين

الملخص

تم في هذه الدراسة تحضير أغشية رقيقة من أوكسيد النحاس (CuO) باستخدام طريقة الترسيب بالحمام الكيميائي (CBD) على شرائح زجاجية. أستخدمت مادة كبريتات النحاس المائية ($CuSo_4.5H_2O$) للحصول على الأغشية المطلوبة. تم تحضير الأغشية خلال أزمان ترسيب مختلفة (1 ، 4 ، 8) أيام عند درجة حرارة الغرفة وبتركيز 0.1 مولاري. أظهرت دراسات حيود الأشعة السينية (XRD) أن الغشاء الرقيق المحضر في زمن ترسيب (8 أيام) يمتلك بنية بلورية متعددة التبلور. كشفت الدراسات الطبوغرافية باستخدام صور مجهر القوة الذرية (AFM) وصور المجهر الالكتروني الماسح (SEM) أن سطوح الأغشية المحضرة تظهر تجانس أفضل عند زيادة زمن الترسيب من 1 يوم الى 8 أيام حيث لوحظ تناقص متوسط القطر ومعدل الخشونة والجذر التربيعي لمربع متوسط الخشونة مع زيادة زمن الترسيب.