

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

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ABSTRACT

In this study, thin films of copper oxide (CuO) prepared using a chemical bath deposition (CBD) method on glass substrate. Aqueous copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) 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) mm³, where aqueous copper sulfate (CuSO₄·5H₂O) 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:



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]:

$$t = (m_2 - m_1) / \rho A \dots\dots\dots(2)$$

where t is the thickness of the film, m₁ is weight the sample before deposition, m₂ is weight the sample after deposition, ρ is the density of copper oxide (6.31 gm/cm³), 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]:

$$D = 0.9 \lambda / \beta \cos \theta \dots\dots\dots(3)$$

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]:

$$d = \lambda / 2 \sin \theta \dots\dots\dots(4)$$

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).

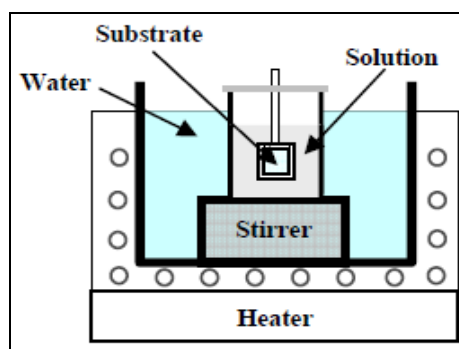


Fig. 1: The schematic diagram of the CBD set up [26].

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

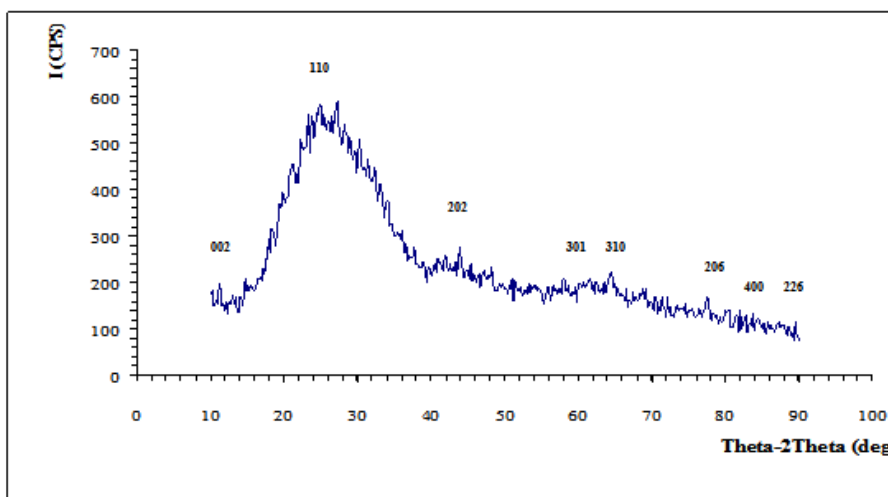


Fig. 2: XRD patterns of CuO thin film at deposition time (8 days).

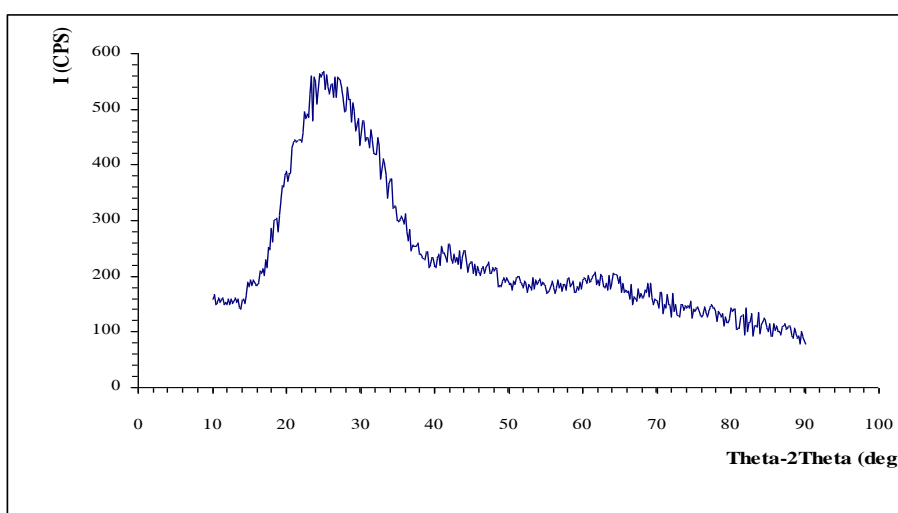


Fig. 3: XRD patterns of CuO thin film at deposition time (1 day).

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

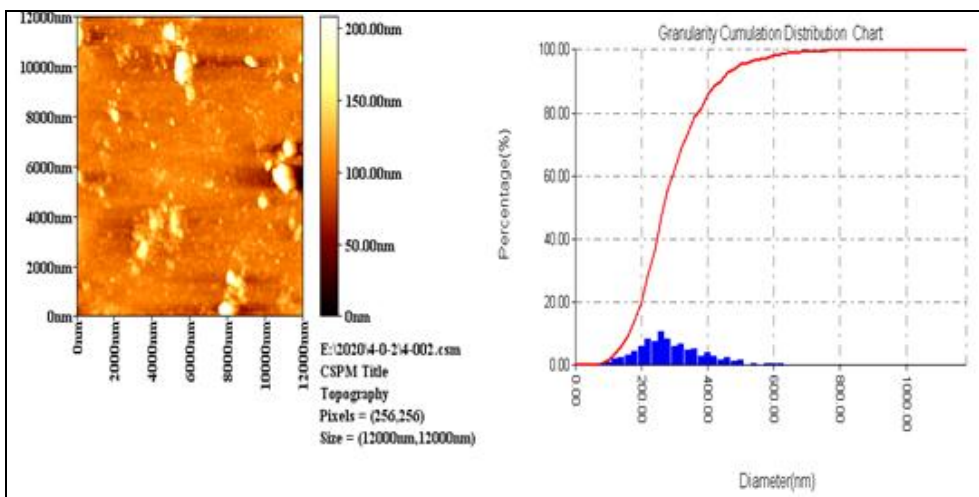


Fig. 4: AFM topography of CuO thin film at deposition time 1 day.

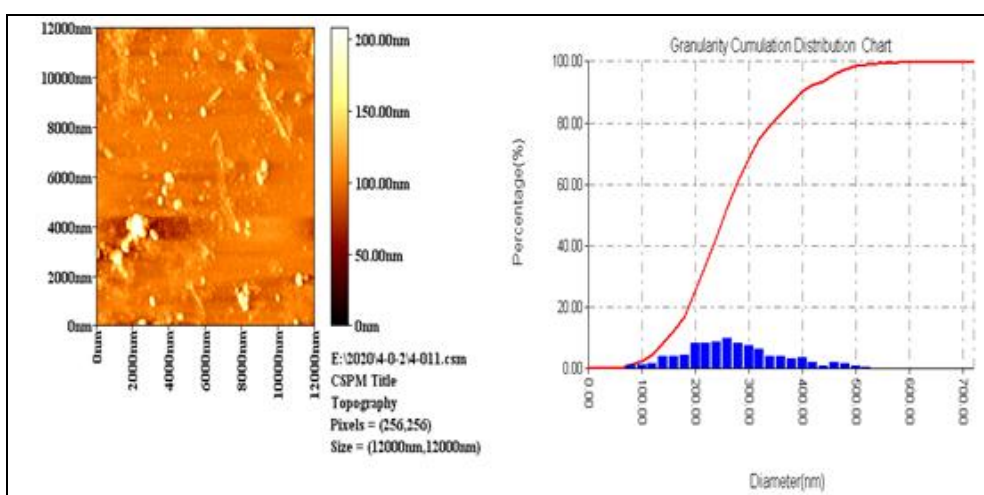


Fig. 5: AFM topography of CuO thin film at deposition time 4 days.

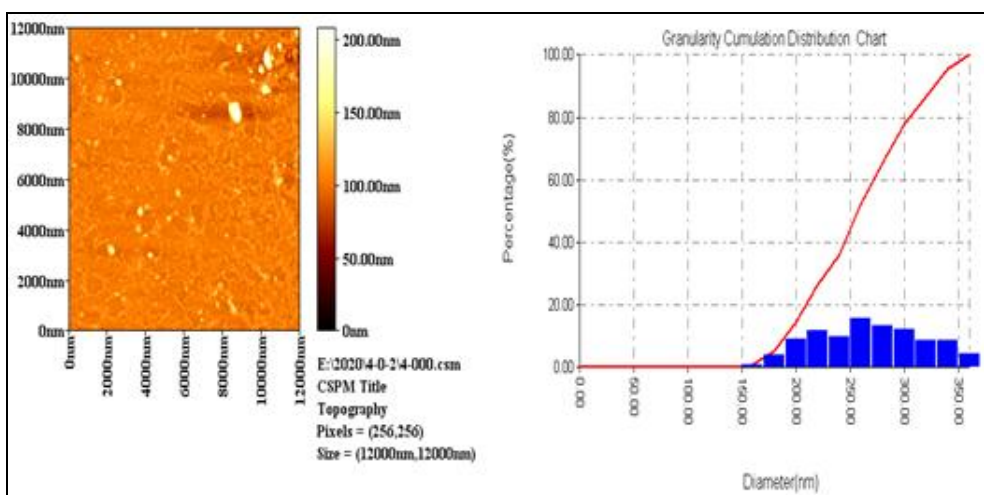


Fig. 6: AFM topography of CuO thin film at deposition time 8 days.

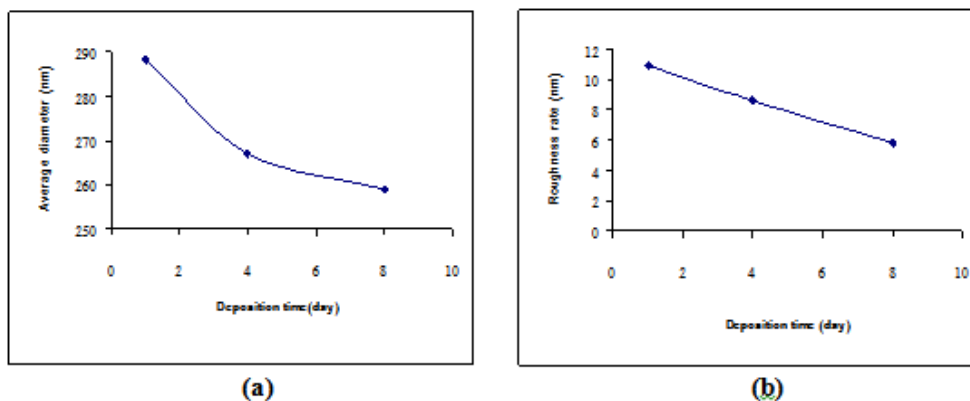


Fig. 7: Relationship between deposition time with : (a) average diameter (b) roughness rate.

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].

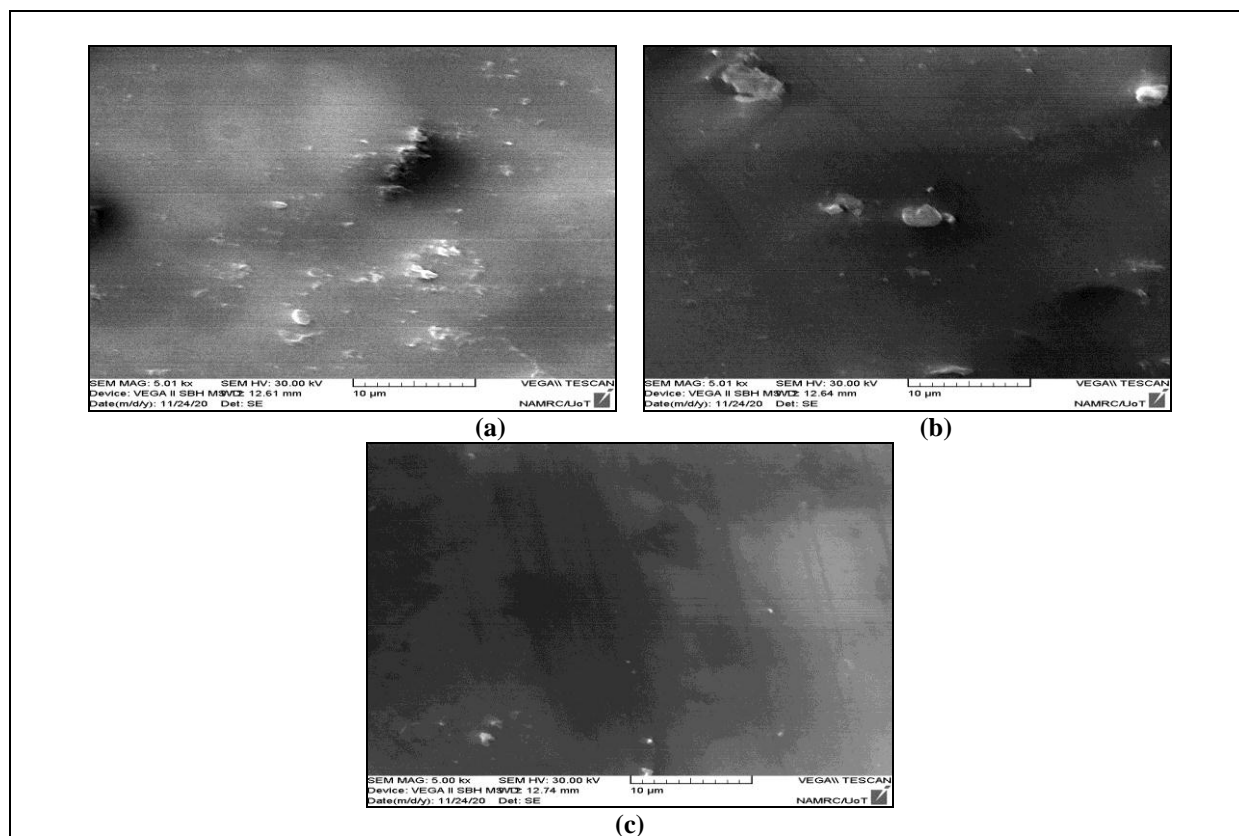


Fig. 8: SEM images of CuO thin film with scale bar (10µm) at deposition time: (a) 1 day (b) 4 day (c) 8 day

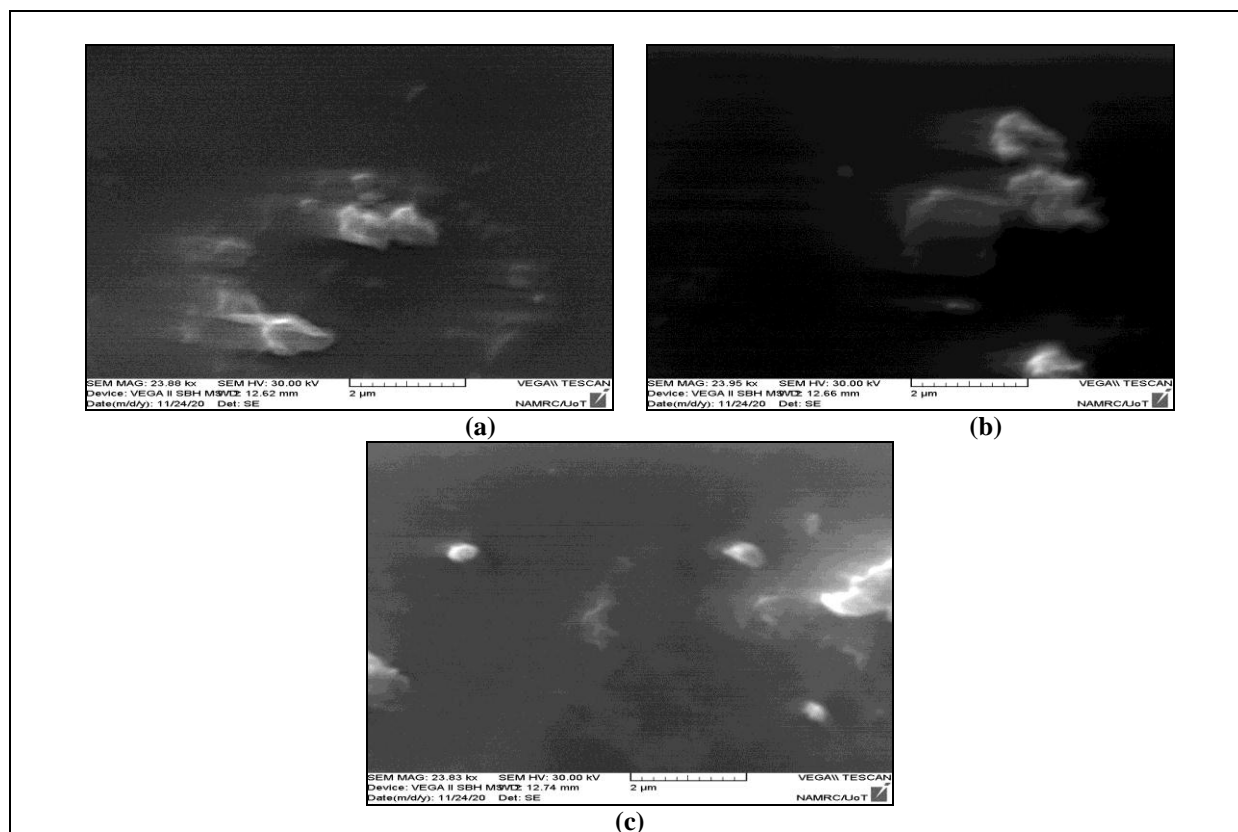


Fig. 9: SEM images of CuO thin film with scale bar (2 μ m) at deposition time:
(a) 1 day (b) 4 day (c) 8 day

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

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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. استخدمت مادة كبريتات النحاس المائية ($CuSO_4 \cdot 5H_2O$) للحصول على الأغشية المطلوبة. تم تحضير الأغشية خلال أزمان ترسيب مختلفة (1 ، 4 ، 8) أيام عند درجة حرارة الغرفة وبتراكيز 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 الإلكتروني الماسح (SEM) أن سطوح الأغشية المحضرة تظهر تجانس أفضل عند زيادة زمن الترسيب من 1 يوم إلى 8 أيام حيث لوحظ تناقص متوسط القطر ومعدل الخشونة والجذر التربيعي لمتوسط الخشونة مع زيادة زمن الترسيب.