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Effect of deposition time on optical properties of CuO thin film prepared by chemical bath deposition method

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In this paper, thin films of copper oxide (CuO) deposited on glass slides using chemical bath deposition method. Aqueous copper sulfate ($CuSo_4.5H_2O$) used to obtain the required solution. The films prepared during different deposition times (1, 4 and 8) days at room temperature. The effect of deposition time on the optical properties of prepared films was studied. Optical measurements of copper oxide (CuO) thin films calculated from the transmittance and absorbance spectrum in the range (200-1000) nm using a UV-VIS spectrophotometer. The results showed that, in general in the visible region of the electromagnetic spectrum, all optical constants decrease with increasing wavelength and increase with increasing deposition time, except for transmittance, they increase with increasing wavelength and decrease with increasing deposition time. Finally, it was noticed that the value of the energy gap ranges between (1.8 eV - 2 eV) as it decreases with increasing deposition time.

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Keywords: CuO thin films, Chemical bath deposition, Optical properties, Deposition time

1. Introduction

The semiconducting metal oxide nanostructures are attracting the attention of researchers worldwide. The applications of this material are numerous and relate to various fields of technology, including biotechnology, microelectronics, photovoltaic industry, corrosion, etc. [1,2]. Nowadays, most techniques are used to reduce the size of materials to nanoscale, which leads to the emergence of new and unique behaviors of such materials in optical, electrical, optoelectronic, dielectric, and so on [3,4,5]. Copper oxide (CuO) is widely used for many different applications including lithium ion electrodes, sensors, high critical temperature superconductors, field emission, photocatalyst, and resistance switch, and it can also be used as a solar absorbent due to its high absorption coefficient and low thermal emission [6]. Copper oxide (CuO) is a p-type semiconductor material [7] with a direct energy gap of about 2 eV and close enough to the optimum energy gap in the radioactive spectrum (AM1.5) [8]. Copper oxides are usually present in two stable forms, copper oxide (Cu_2O) and copper oxide (CuO) [9]. There are several techniques used to manufacture and synthesize copper oxide (CuO) thin films, including thermal oxidation, atomic layer precipitation, chemical bath deposition, sol-gel method [10], laser pulse deposition, permeable coating method, activated microwave atomization, magnetic spray [11], chemical vapor deposition [12], vacuum evaporation, electro deposition [13,14], in addition to electronic beam evaporation [15]. In this work, we used the chemical bath deposition (CBD) method to prepare a copper oxide (CuO) thin film with nanostructure. Chemical bath deposition (CBD) is a good growth method that has attracted great interest from the global research community due to its simplicity and cost- effectiveness in addition to its ability to expand the deposition area for commercial production [16].

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2. Experimental part

Copper oxide (CuO) thin films prepared by chemical bath deposition (CBD) method shown in the fig. 1 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 mixer at room temperature for 30 minutes to ensure complete dissolution of the solution.

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

$$CuSO_4 + H_2O \longrightarrow CuO + H_2SO_4 \quad (1)$$

Glass slides are placed slightly diagonally in the bathroom without magnetic stirring, after washing them with distilled water and washing powder first, then ethanol alcohol, then acetone. After the required time for deposition has elapsed, the sample is dipped in distilled water for a few seconds to remove the impurities attached to the surface of the film if any and then left in the air to dry. After the preparation of the thin films was completed, Optical measurements of copper oxide (CuO) thin films calculated from the transmittance and absorbance spectrum in the range (200-1000) nm by a UV- Spectrophotometer (Model: Metertech SP 8001).

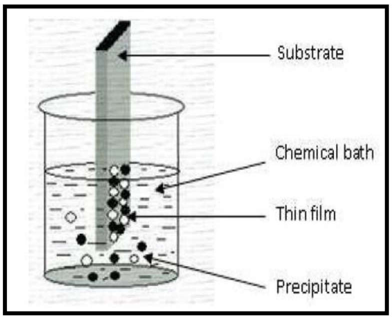

Fig. 1. Schematic of Chemical Bath Deposition [17].

3. Results and discussion

The absorption spectrum of CuO film is as shown in Fig. 2. It can be noticed that the absorbance, in general, decreases with increasing wavelength in the visible region, and the absorbance values increase with increasing deposition time. So the absorption studies were exhibited that the fabricated films were high absorptive at the visible region and is more suitable for many applications such as solar cells.

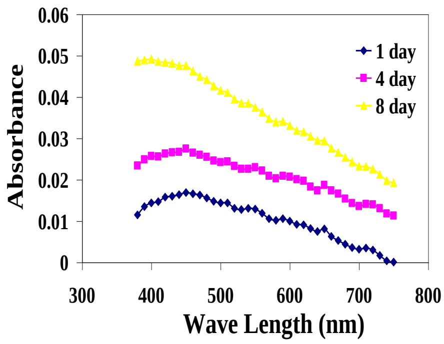

Fig. 2. Absorption spectrum of CuO thin film at different deposition times.

The transmittance spectrum of CuO thin film is as shown in Fig. 3. From this figure, we notice that the transmittance increases with the increase in the wavelength in the visible region of the electromagnetic spectrum, as the transmittance values decrease with the increase in deposition time. We also note that the transmittance values are very high for the prepared films.

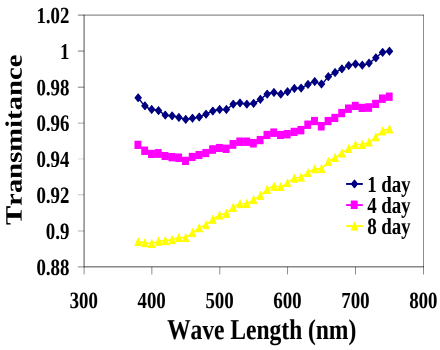

Fig. 3. Transmittance spectrum of CuO thin film at different deposition times.

Fig. 4 shows the reflectance spectrum for CuO thin film. The reflectance (R) has been found by using the relationship [18]:

$$R + A + T = 1 \tag{2}$$

where A is the absorbance and T is the transmittance. It is clear that reflectance decreases with increasing wavelength in the visible region, and the reflectance values increase with increasing deposition time. We notice from the reflectance spectrum that it is very similar to the absorbance spectrum, and this may be due to the high values of the transmittance spectrum.

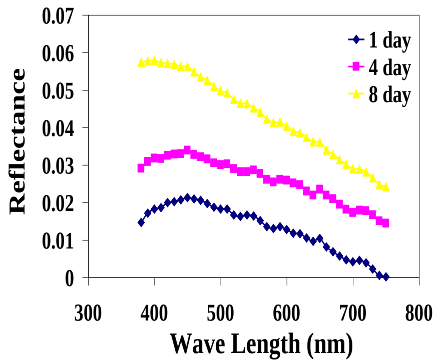

Fig. 4. Reflectance spectrum of CuO film at different deposition times.

Fig. 5 shows the absorption coefficient (α) of CuO film which is determined from Lambert's law [19-22]:

$$\alpha = 2.303\ A / t \tag{3}$$

where t is the film thickness. We note that the absorption coefficient decreases with increasing wavelength and increases with increasing deposition time, as it has high values ($\alpha \geq 10^4$ cm^{-1}) that explain the possibility of direct transitions.

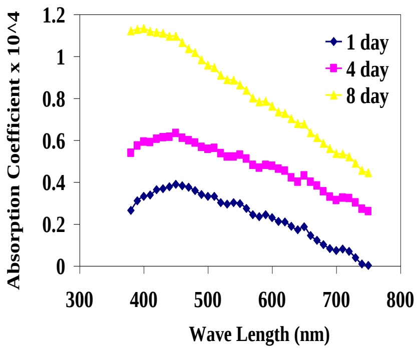

Fig. 5. Absorption coefficient of CuO film at different deposition times.

Extinction coefficient (k) of prepared film is calculated by using the relation [23-25]:

$$k = \alpha \lambda / 4\pi \tag{4}$$

where λ is the wavelength of the incident photon. So the extinction coefficient of CuO film has been shown in Fig.(6). We notice that there is a slight change in the extinction coefficient values with increasing wavelength, while we notice a clear increase in the extinction coefficient values with increasing deposition time.

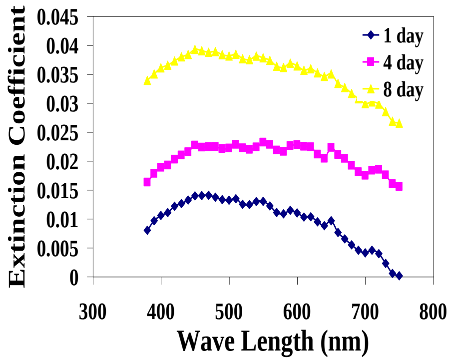

Fig. 6. Extinction coefficient of CuO film at different deposition times.

Now, from the reflectance data, the refractive index (n) is calculated by the following relationship [26]:

$$n = 1+(R)^{1/2} / 1-(R)^{1/2} \tag{5}$$

Fig. 7 shows the variation refractive index of CuO film as a function of the wavelength, the values of the refractive index decrease slightly with increasing wavelength and increase slightly with increasing deposition time.

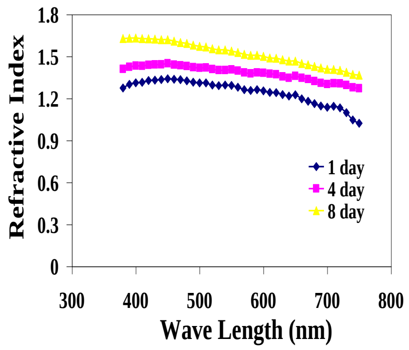

Fig. 7. Refractive index of CuO film at different deposition times.

Fig. 8 shows the variation of optical conductivity for CuO film as a function of wavelength. Optical conductivity (σ) was calculated using the following relationship [27]:

$$\sigma = \alpha n c / 4\pi \quad (6)$$

where c is the velocity of the radiation in the space. It is clear that the optical conductivity decrease with increasing the wavelength. We also note that the optical conductivity increases with increasing deposition time.

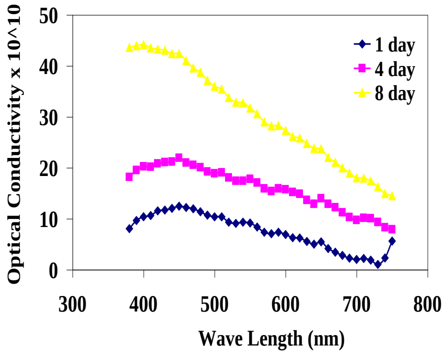

Fig. 8. Optical conductivity of CuO film at different deposition times.

The dielectric constant calculated with its real (ε_r) and imaginary (ε_i) parts using the following relationships [28]:

$$\varepsilon_r = n^2 - k^2 \quad (7)$$

$$\varepsilon_i = 2nk \quad (8)$$

where (ε_r) is the real part of the dielectric constant and (ε_i) is the imaginary part of the dielectric constant**.** We notice from the figures 9and 10 that the values of the dielectric constant, both real and imaginary decrease with increasing in the wavelength and increase with increasing in the deposition time.

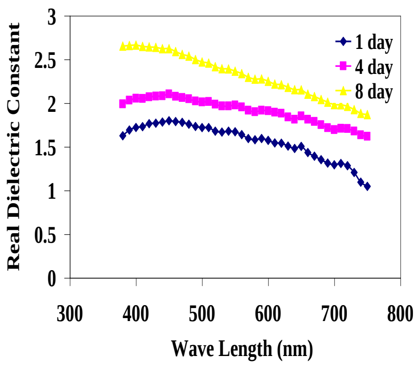

Fig. 9. Real dielectric constant of CuO film at different deposition times.

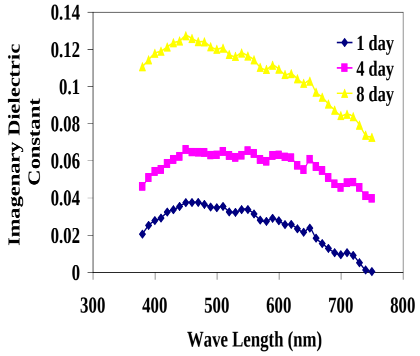

Fig. 10. Imaginary dielectric constant of CuO film at different deposition times.

The nature of transition (direct or indirect) is determined by using the relation [29,30]:

$$\alpha h\upsilon = a\,(h\upsilon - E_g)^r \tag{9}$$

where hυ is the photon energy, Eg is band gap energy, a and r are constants. It is worth to note that for an allowed direct transition, r=1/2 and for an allowed indirect transition, r=3/2. The linear behavior of the plot curve is shown in Fig. 11 indicates the existence of direct transitions. We note from Table (1) that all optical constants increase with increasing deposition time except for the energy gap, so they decrease with increasing deposition time. As we can see from Fig. 12 that the energy gap is inversely proportional with the deposition time of thin film.

Table 1. Maximum values for the optical constants of CuO films.

Deposition time (day)	Eg (eV)	α (cm$^{-1)}$ x 10^4	σ x 10^{10}	k	n	ε_r	ε_i
1	2	0.3892	12.46	0.014	1.341	1.798	0.0374
4	1.86	0.6333	21.92	0.023	1.45	2.102	0.0657
8	1.8	1.1330	44.15	0.039	1.632	2.663	0.1271

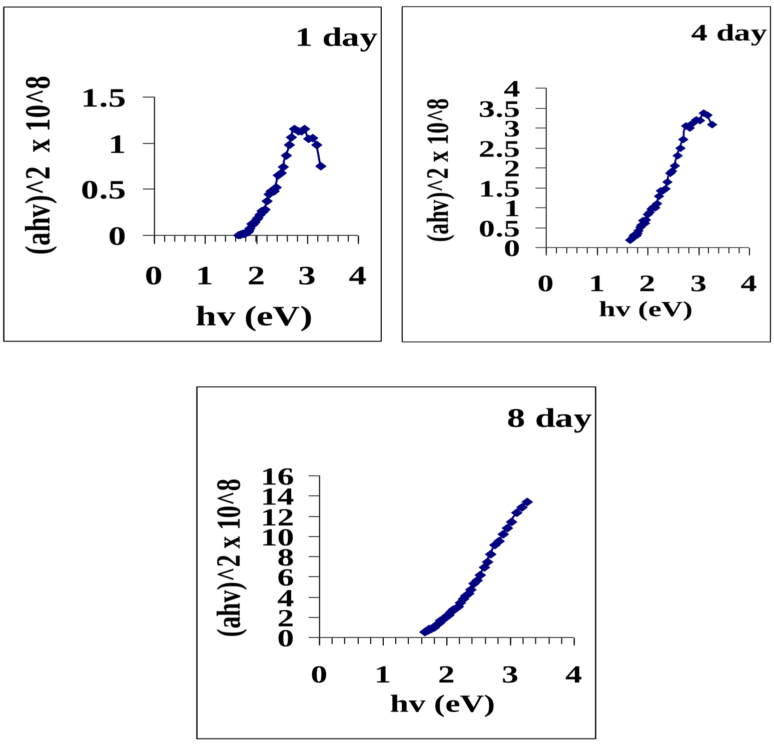

Fig. 11. The plots of $(\alpha h\upsilon)^2$ versus the photon energy for CuO film at deposition time: (a) 1 day (b) 4 day (c) 8 day

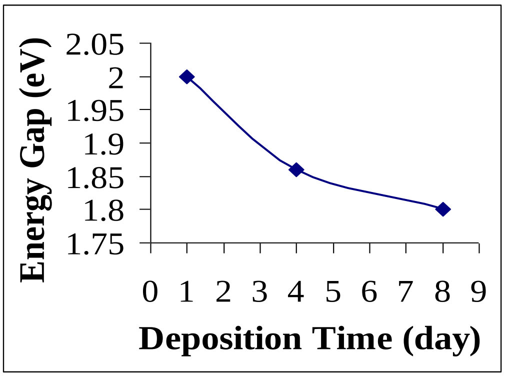

Fig. 12. The relation between energy gap and deposition time of CuO film.

4. Conclusion

The Copper Oxide (CuO) thin film have produced by CBD method on glass substrates of deposition time 1-8 day at room temperature. The effect of deposition time on the optical properties of thin films have determined by using optic transition measurement techniques. Absorption coefficient value was found to be higher than 10^4 cm^{-1} at 200-1000 nm. The energy band gap decrease from 2 eV to 1.8 eV when the deposition time of film increase from 1 day to 8 day. The prepared films with high transmittance and low reflectance are good material for antireflection coatings of solar thermal devices.

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