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Investigation (Cd + Co) Co-Loading Impact on Physical Properties of Nano-Structured (CuO) Thin Films

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Abstract

Pure CuO and (Cd+Co) double doping CuO thin films were produced using the sol- gel method and the spin coating approach, with various (Cd+Co) co-doping concentrations ((1+1), (3+3), (5+5), and (7+7) wt.%) of (Cd+Co). XRD results showed that all prepared pure and metals co-doped CuO nanostructured thin films are polycrystalline and have a monoclinic structure with preferred planes on (002) and (111) without additional peaks related to Cd and Co. The surface morphology and layer thickness of synthesized thin films were analyzed by field emission Scanning Electron Microscopy. The SEM images showed Agglomerated spherical grains form at high co-doping concentrations. The existence of Cu, Cd, Co, and O elements was confirmed by EDS measurements., The energy gap decreased from 2.139eV to 2.02 eV was investigated by the Tauc's and Davis-Mott relations.

Keywords: Hydrated copper acetate, Cadmium Acetate, cobalt acetate, Sol Gel Method, Spin coating technique, annealing.

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دراسة تأثير التطعيم المشترك (Cd + Co) على الخصائص الفيزيائية للأغشية الرقيقة ذات البنية النانوية (CuO) المحضرة بطريقة Gel-Sol

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الخلاصة

تم تحضير أغشية رقيقة من CuO ذات تطعيم مزدوجة نقي من CuO و (Cd + Co) تم إنتاجها باستخدام طريقة sol-gel وطريقة طلاء الدوران، بتركيزات مختلفة (Cd + Co) في المنشطات المشتركة ((1 + 1)، (3 + 3)، (5 + 5) و (7 + 7) بالوزن٪) من (Cd + Co). أظهرت نتائج XRD أن جميع الأغشية الرقيقة ذات البنية النانوية النقية المحضرة والمغطاة بالمواد المعدنية هي متعددة البلورات ولها هيكل أحادي الميل مع مستويات مفضلة على (002) و (111) دون أي قمم إضافية متعلقة بـ Cd and Co. تم تحليل الأغشية الرقيقة المركبة بواسطة "الفحص المجهري الإلكتروني لمسح الانبعاث ". أظهرت صور SEM شكل حبيبات كروية متكتلة بتركيزات عالية من التطعيم المشترك. تم تأكيد وجود عناصر Cu و Cd و Co و O من خلال قياسات "EDS". وانخفضت فجوة الطاقة من eV2.139 إلى 2.02 eV بواسطة علاقات Tauc;s and Davis-Mott relations

كلمات مفتاحية: خلات النحاس المائية و خلات الكادميوم وخلات الكوبلت، طريقة السول جل، تقنية الطلاء البرمي، التلدين، دراسة تأثير التطعيم اغشية، CuO تاثير التشويب بـ (Cd، Co) XRD، UV-VIS، FE-SEM،

Introduction

Among the nanostructured oxides of transition metals thin films, the Nano crystallized CuO has attracted much attention and interest related to its structural, optical, morphological, electrical, and chemical properties. Copper oxide (CuO), has a monoclinic structure and energy band gap range between (1.2 eV to 2.1 eV) and shows p-type electrical conductivity resulting in the existence of excess oxygen (O) or copper (Cu) vacancies in its crystal structure, also CuO has direct energy gap, and has high optical absorption in visible light area and NIR region. In addition, CuO is a non-toxicity semiconductor and low-cost production. These CuO properties lead to the use and applied application of nanostructured CuO thin films in different potential applications such as solar cells, photodiode, gas sensing medium and semiconductor applications. Nanostructured CuO thin films have been deposited and prepared by several methods, such as Sol-Gel (SG) dip coating or spin coating, thermal evaporation technique , Pulse Laser Deposition, chemical bath deposition, and magnetron sputtering technique. The spin coating process is one of the most efficient methods for producing transition metal oxide films among these several manufacturing procedures[1].

The spin coating technology has several benefits, including the ability to change the deposition rate, fabrication at high oxygen pressure, formation of oriented crystalline films, and the ability to adjust the temperature of the add There have been some studies that have been carried out to investigate the effect of introducing various dopants into the CuO structure. Some examples of these studies include "Mn, Fe, In, and Sn" doped CuO[2].

As mentioned above, the presence of an excessive amount of oxygen (O) or copper (Cu) vacancies in the lattice of cupric oxide causes it to show p-type conductivity and results in a band gap that ranges from (1.2 to 2.1 eV). On the other hand, the presence of oxygen vacancies and/or Cu phase may result in n-type behavior for the CuO compound[3].

Researchers have used many different metals doped CuO thin film to change its semiconducting type from n-type to p-type such as Co doped CuO [4] and Cd doped [5]. In this paper, we use the sol-gel processto introduce Cd-Co ions dual-doped into CuO thin films [6]. Thisresearch aims to determine the influence of different concentrations of Cd-Co on the features of cupric oxide CuO thin films. Using the weight method

Materials and methods

On glass substrates, pure and dual doped CuO thin films were produced using the sol-gel spin-coating process. Gold seal Micro Slides Cat. No. 3010 commercial glass slides were used.

$Cu(CH_3COO)_2.H_2O$ a copper(II) monohydrate, was utilized and dissolved in 2-methoxyethanol to make a 0.6M solution. Both cadmium acetate $Cd(CH_3COO)_2.H_2O$ and cobalt acetate $Co(CH_3COO)_2.H_2O$ with an equal Add s of (Cd+Co), This doping concentration varied (1 + 1, 3 + 3, 5 + 5, 7 + 7 wt%) all weights were mixed in solution into one solution. To achieve the appropriate viscosity and stability of the mixture solution mono ethanolamine (MEA) was added to the agitated mixture. A temperature of 75°C was used to heat the stirred solutions for 1.5 hours. After this step, we get the clear dark green color solution, and it leaves at room temperature for 24 hours.

Previous research has found that solution anesthetics improve the morphology, crystallization, pore structure, and other properties of spin-coated thin-film electrodes. [7]. Before deposition the solution on the glass substrates by spin coating, the glass substrates were cleaned with diluted detergents, acetone, 99 percent pure ethanol, and deionized water inside ultra-sonication water bath for 20 minutes. and before being dried with nitrogen gas and placed in an oven at 80°C. The aged solutions were filtered using 0.1 micrometer filter to remove any agglomerated particle that may be found in the solution that can affect Standardization of thin-film deposition by spin coating. All prepared samples were deposited on soda lime glass substrates by spin coating at 3300 rpm for 40 s. A solution of 200μm is placed on the precipitation base until it is completely covered and after each layer, the sample is dried for 15 minutes on a hot plate with a temperature set at 195°C. Spin Paint Steps to drying step were repeated four times. Finally, in an oven at 475°C, the samples were annealed under air for 1 hour. the sample was gradually cooled to room temperature. Samples (Cu-1, Cu-2, Cu-3, Cu-4, Cu-5) were labeled for each CuO membrane, as well as the doped samples (0+0, 1+1, 3+3, 5+5, 7+7 wt.%), respectively. The structural and morphological features of the pure and metals co-doped CuO thin films were investigated using XRD, UV-visible, and SEM. Table (1) shows the quantities and proportions used to prepare undoped and duplex (CuO) films in equal proportions with cadmium and cobalt.

Table 1: Quantities and percentages used to prepare undoped and duplex (CuO) films in equal proportions with cadmium and cobalt

SAMPLES	(CD+ CO) WT%	MASS OF CU ACETATE DI-HYDRATE (G)	MASS OF CD ACETATE DI-HYDRATE (G)	MASS OF CO ACETATE DI-HYDRATE (G)	2- VOLUME OF METHOXY ETHANOL (ML)	MOLARITY (M)	ANNEALING TEMPERATURE (°C)
Cu-1	0+0	1.1979	0	0	10	0.6	475
Cu-2	1+1	1.173942	0.0159918	0.0149454	10	0.6	475
Cu-3	3+3	1.149984	0.0479754	0.0448362	10	0.6	475
Cu-4	5+5	1.07811	0.079959	0.074727	10	0.6	475
Cu-5	7+7	1.030194	0.1119426	0.1046178	10	0.6	475

Results and Discussions

Structural analysis

Using XRD with the parameters "Cu-K radiation; wavelength: 1.5400 Å ; scan rate: 0.01 degree per second", researchers were able to examine the structure and crystallinity of pure and dual-doped CuO films that had been formed on soda lime glass substrates by the spin coating method., are shown in figure (1). XRD results showed all prepared films are polycrystalline, with a monoclinic structure

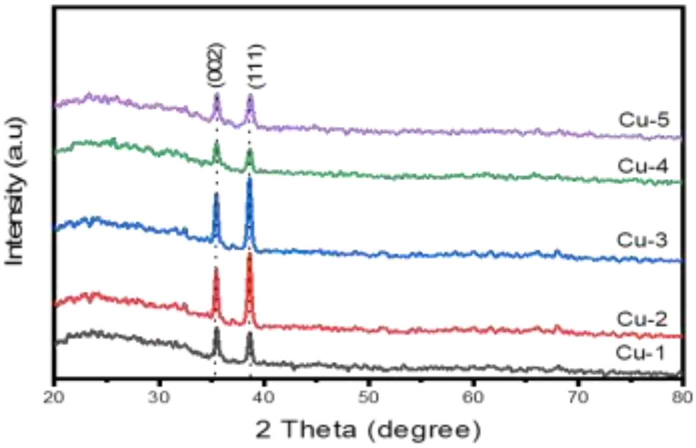


Figure 1: XRD patterns of (Cu-1, Cu-2, Cu-3, Cu-4, Cu-5) thin films.

The XRD patterns of undoped and various levels (1+1, 3+3, 5+5, and 7+7 w t %) of cobalt and cadmium doped CuO nanostructures are shown in Fig. 1a. The products have successfully crystallized, as evidenced by the spectra, which features sharp peaks. All of the diffraction features can be indexed to the monoclinic system (JCPDS Card No. 01-080-0076) of CuO, which has a space group of C2/c, and there are no distinctive evident peaks of Cd and Co, or any other impurity phases that can be identified. This suggests that the manufactured samples have a high level of purity. As a result, the presence of Cd does not affect the monoclinic structure, but it does have an effect on the intensity of the samples. On the other hand, if we increase the amount of doping, the intensity of the (111) plane of diffraction will eventually reach its maximum, in contrast to the intensity of the (002) plane The cadmium and cobalt grafting does not affect the monoclinic structure, while affecting the intensity of the samples[8]. The strength of the diffraction peaks was seen to gradually change by 0.03 due to the increasing concentration of cobalt and cadmium dopants. The fact that the intensity of (002) and (111) reflections increased as a result of Co doping is suggestive of an improvement in the crystal quality of CuO films [2]. With an increase in the doping ratios of (3 + 3), the intensity of the peaks of the samples decreases. The reason may be due to the occurrence of deformation in the membranes as a result of the increase in the rates of grafting with cadmium, as the ionic drop is greater than the ionic diameter of copper. Using Scherrer's [3] formula, we were able to determine the crystalline size, denoted by the letter D, of the Cd-Co dual-doped CuO thin films by calculating the full peak width at “half maximum (FWHM)” of both (002) and (111)[1]:

$$\mathbf{D}=\frac{n\lambda}{\beta cos\theta} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(1)}$$

where D represents the size of the crystallite, λ represents the wavelength of the incident radiation, n represents a shape factor, β represents the "Full Width Half Maximum value (FWHM)", and θ represents the Bragg diffraction angle[1][6]. These values may be found in Table (2). The particle crystallite size increased withthe increases the concentration of cadmium and cobalt. In the ratios (1+1 and 3+3), then the size of the particles decreased at the ratios (5+5 and 7+7). The high ionic mobility and small radius (0.72 Å)[15] of Co ions in the solution are thought to be responsible for the increase in the volume of crystallite size that occurred as a result of Co-doping in the CuO films, as seen in figure (2). Because of the lower activation energy, it is simpler to move these ions throughout the crystal growth process from the trap sites to the nucleation sites, which indicates a bigger crystal size [5] while the crystallite size with increasing cadmium concentration due to high ionic radius of Cd^{++} (0.95 Å) compared to ionic radius of Cu^{++} (0.73 Å). size reduction determines that cadmium doping on copper Nano membranes is known to influence membranes growth behavior [8]. The variations of lattice constants are due to the larger ionic radius of Cd^{++} (0.95 Ǻ) to be substituted Cu^{++} ions of smaller ionic radius (0.73 Ǻ).

The values of the lattice spacing, denoted by "d," for each film were determined by applying Bragg's equation:

$$\mathbf{d} = \frac{n\lambda}{2sin\theta} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(2)}$$

where n represents the degree of diffraction, represents the wavelength of the X-ray pattern, and represents the angle of X-ray diffraction.

The dislocation density (δ), which reflects the density of defects in the CuO films, was determined through the use of the following expression in the calculation process.:

$$\boldsymbol{\delta = \frac{1}{D^2}} \text{...} \mathbf{(3)}$$

where D represents the typical size of a crystallite. The following equation was used to get the strain (ε) in both the undoped and Cd-Co dual doped CuO films:

$$\varepsilon = \boldsymbol{\frac{\beta}{4tan\theta}} \text{...} \mathbf{(4)}$$

Table 2: Parameters of CuO and Cd-Co dual-doping of CuO thin films

Sample	2 theta peaks (Degree)	FWHM (radians)	Average crystallite size(D) (nm)	d-Spacing (Å)	Dislocation (δ)*10^{11} (cm^{-2})	Strain (ε) (10^{-6})
CU-1	35.498	0.484	18.28	2.52680	3.0958	2.01361
	38.642	0.472		2.32811	2.8897	1.94543
CU-2	35.445	0.432	19.12	2.53047	2.46785	1.79783
	38.615	0.485		2.32973	3.04841	1.99814
CU-3	35.445	0.432	19.12	2.53047	2.46785	1.79783
	38.615	0.485		2.32973	3.04841	1.99814
CU-4	35.488	0.479	17.62	2.52747	3.02659	1.99097
	38.626	0.514		2.32908	3.43197	2.12012
CU-5	35.509	0.470	17.32	2.52604	2.92155	1.95612
	38.681	0.544		2.32589	3.83311	2.2406

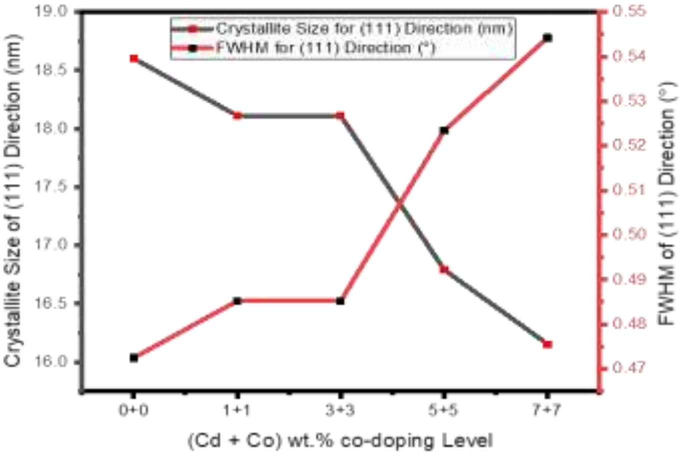


Figure 2: Relationship between graft ratios and crystalline body, FWHM

Doping leads to a reduction in the amount of dislocation density inside the crystal structure. A reduction in the dislocation density is indicative of a crystal structure that is becoming more regular. As the quantity of co-doping increases, there is a corresponding decrease in the number of defects found in CuO films. Furthermore, if the amount of doping is raised, we observe an increase in the dislocation density inside the crystal structure. This suggests that there is an increase in the total number of defects present in the CuO films. Table 2 contains a listing of the structural parameters that were computed based on the XRD spectra.

Surface morphology studies

The scanning field-emission electron microscopy (FE-SEM) technique was used to study the nature of the surfaces of thin films (CuO) Grafted or doped with cadmium and cobalt in equal proportions due to their ability to magnify and accurately describe the surface structure. And cobalt, where (Image J) program was used for the purpose of calculating the average grain size and average grain area and knowing the effect of grafting on the formation of copper oxide films as shown in Table (3) where the diameter of the grains was calculated in each image with several (100-200) grains.

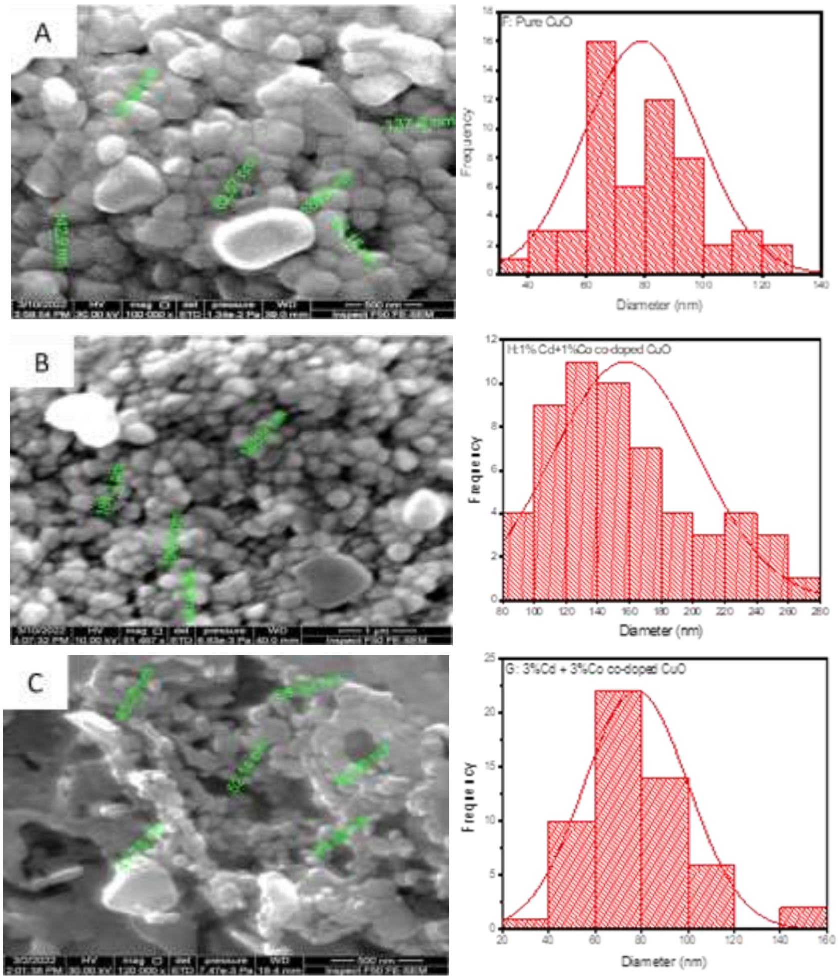
To calculate the largest, mean and smallest granule size as well as the standard deviation, a distribution plot for the granule size ratios was drawn as shown in Figure (3). It was observed that the increase in CuO bi-doped membrane with cadmium and cobalt leads to an increase in particle size.Due to the decrease in the values of the micro-strain at low ratios to reach (45.02533nm) at (3 + 3) grafting ratio, the grain size begins to decrease with the increase of the doping ratios in a greater amount as a result. because of the high micro-strain values, and the cause can be attributed to Crystal growth is hampered due to the ionic element cadmium. diameter (95Å) [16], whereas the diameter of copper is $(0{,}69A°)$[17], resulting in is the same as the results of X-ray diffraction (XRD).

The cross-section SEM photographs of pure CuO and (7%Cd+7%Co) are shown in figure (4). Images of figure (4) showed that average of cross section thickness of deposited CuO thin film was (440) nm and for (7%Cd+7%Co) dual-doped CuO thin film was (425)nm. These results showed that the height concentration ratio of doping has almost no effect on the thickness deposition of CuO thin film.

Table 3: Values of smallest and largest grain size, mean, average grain size and standard deviation of CuO films grafted with cadmium-cobalt binary grafting

Sample	Maxim um Grain Size (nm)	Median Grain Size (nm)	Minimum Grain Size (nm)	Average Grain Size (nm)	Standard Deviation (SD)(nm)
Cu-1	128.959	78.148	35.306	78.91241	19.7441
Cu-2	242.535	171.662	97.719	170.16662	36.35336
Cu-3	248.885	138.86	65.86	140.49893	45.02533
Cu-4	169.308	89.418	49.857	93.28077	26.68611
Cu-5	142.05	88.971	47.667	89.40571	21.69232

the materials that are part of the composition of the thin films (Cu, Cd, Co, O) have undergone slight alterations, and that other materials, such as (Na Al, Ca, Cl, k, S, O). (SI, C, Mg), which represent the components of the bases of the substrate (glass) on which the CuO film was deposited, and this explains the high value of oxygen in the apparent proportions; the majority of that proportion belongs to the components of the glass, which are referred to as the deposition bases. As shown in Figure (5)



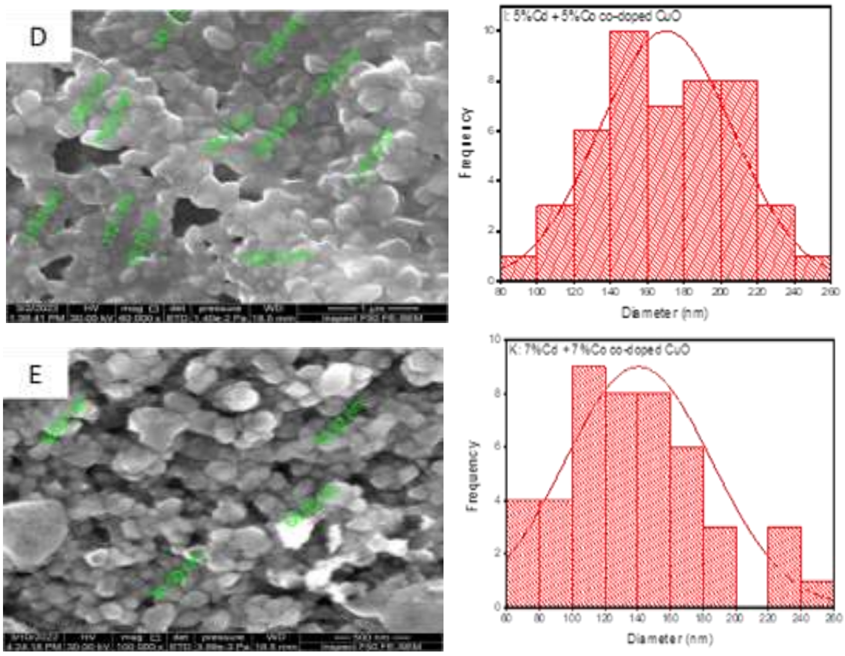


Figure 3: XRD patterns of (Cu-1, Cu-2, Cu-3, Cu-4, Cu-5) thin films.

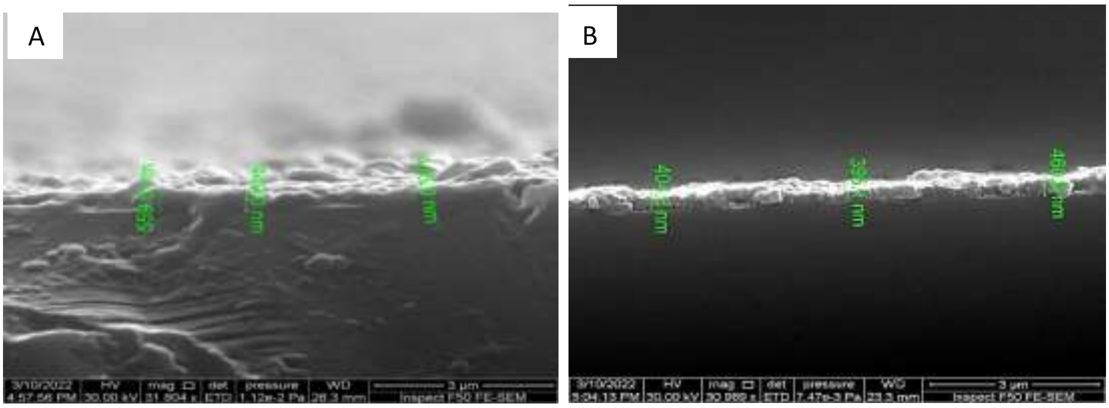


Figure 4: The cross-sectional FE-SEM photographs of (a) the unloaded and (b) (7%Cd +7%Co) co-doped CuO thin films

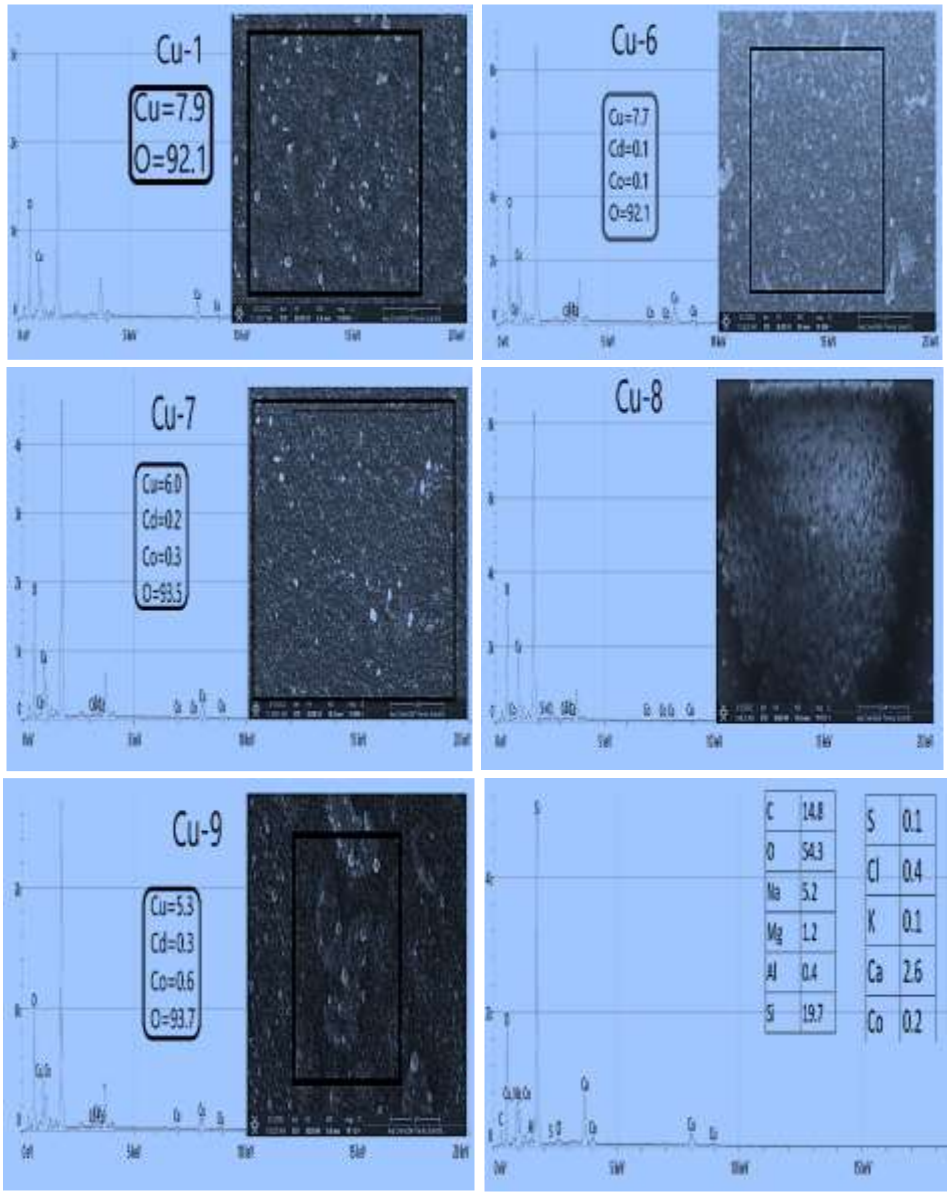


Figure 5: EDS images with Electron Images of prepared CuO films

Optical studies

(UV– Vis) spectroscopy spanning the wavelength range of (300–1100 nm) at room temperature was employed for these studies. To evaluate the influence of doping on the energy band gap Eg, the optical characteristics of the un-doped and (Co + Cd) co-doped CuO films were compared. Figure (4-a) shows that the absorbance takes on an exponential decay with the increase in the wavelength. This is because the energy of the photon is not sufficient to transfer electrons from the valence bands to the conduction bands, Since the relationship between wavelength and photon energy is inverse, The explanation for this is that the photon energy is less than the band gap of the CuO film, so the absorbance decreases with increasing wavelength [9].

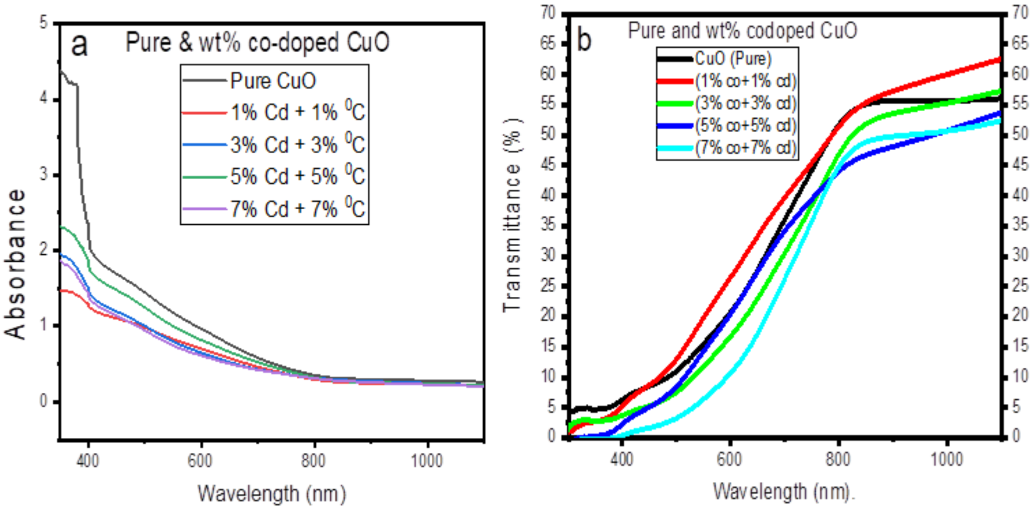
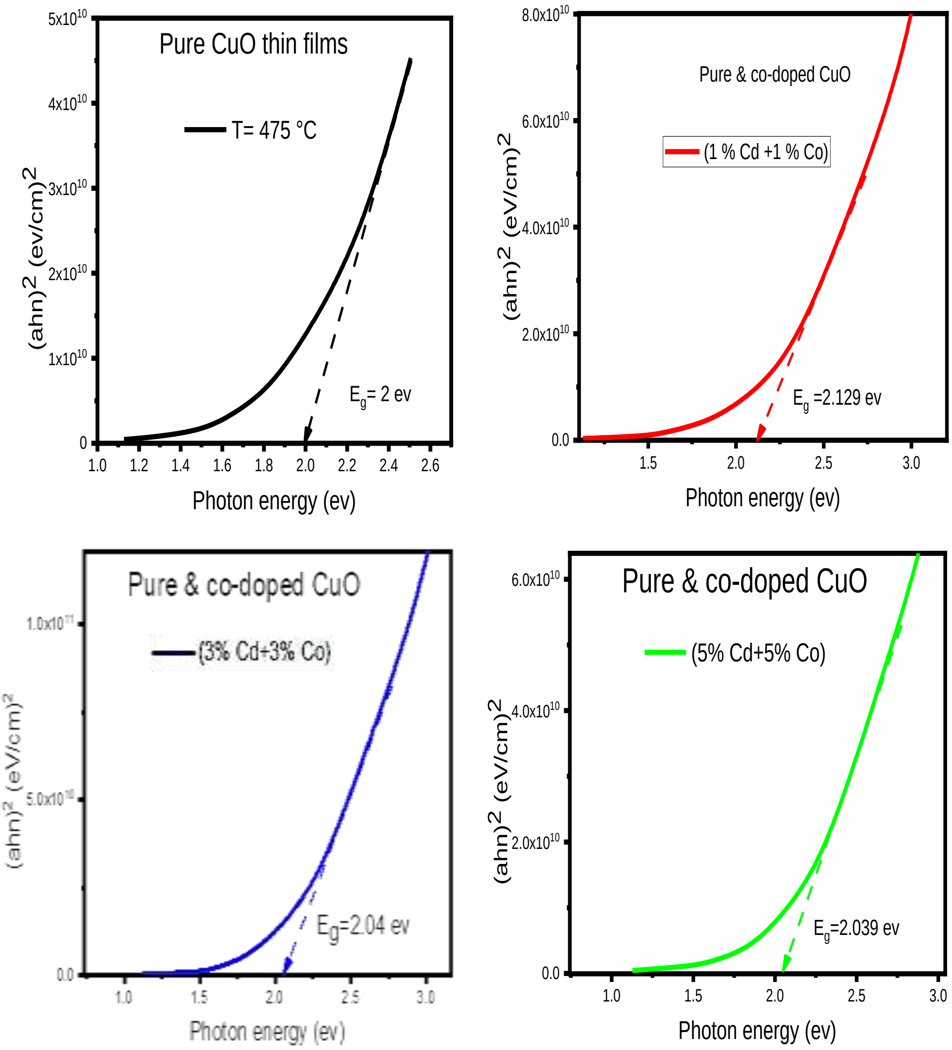


Figure 4: (a) Absorption spectrum (b) Transmittance spectrum of undoped and doped (CuO) films double-grafted in equal proportions with cadmium, cobalt and annealed at 475 °C

.It was noticed that the lowest absorbance is at the ratio of grafting (1 + 1) and then it starts to increase with increasing grafting rates to reach the highest absorbance for grafting at the ratio (5 + 5), but the highest absorbance value remains for the pure films free of grafting. The reason could be due to a decrease in photon scattering due to crystal defects or an increase in optical transmission[10]. Also, the transmittance spectra shown in Figure (4-b) showed the opposite behavior of the absorption spectra of the ungrafted (CuO) films grafted with cadmium and cobalt in equal proportions. The transmittance value was (57%), and the increase in transmittance is attributed to the decrease in photon scattering due to crystal defects or an increase in optical transmission[10]. Then the transmittance begins to decrease with an increase in the grafting concentrations to reach the transmittance at the ratio (7 + 7) to reach a value of (55%), which has many applications in electronic devices[4, 10]. A decrease in transmittance may be due to an increase in photon scattering by crystal defects. Or, the free absorption of photons may also reduce the optical transmission of thin films grafted with high percentages of metals [4, 11]. However, the optical burst gap was determined by plotting $(\alpha h\upsilon)^2$ versus photon energy (hυ) for the films; As shown in Figure (5). It was found that the optical band gap increased from 2.00 to 2.139 eV with an increase in the (1+1) concentrations of both cadmium and cobalt ions. Then, a decrease in the optical power gap was observed as the grafting ratios increased to reach 2.02 at the ratio (7 + 7), as it is well known that the effective change of the optical band gap by many factors such as oxygen voids, interstitial, impurities and substitution defects [12]. The optical band gap of thin films (CuO) is altered by substitution and interstitial defects. Because these defects occur within the CuO lattice matrix which are mentioned in the structural properties examination. Importantly, these defects always induce a sub-band above the valence band (VB) or below the conduction band (CB)[13]. Or it may be that the increase in the optical band gap of the CuO-doped thin film (Cd + Co) could be related to the filling with a smaller density of states and the enhancement of the carrier concentration, which is known as the (Mohs-borstein) effect [14].


Pure CuO thin films
T= 475 °C
E_g= 2 ev
(ahn)2 (ev/cm)2
5x10^10
4x10^10
3x10^10
2x10^10
1x10^10
0
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Photon energy (ev)
Pure & co-doped CuO
(1 % Cd +1 % Co)
E_g =2.129 ev
(ahn)2 (eV/cm)2
8.0x10^10
6.0x10^10
4.0x10^10
2.0x10^10
0.0
1.5
2.0
2.5
3.0
Photon energy (ev)
Pure & co-doped CuO
(3% Cd+3% Co)
E_g=2.04 ev
(ahn)2 (eV/cm)2
1.0x10^11
5.0x10^10
0.0
1.0
1.5
2.0
2.5
3.0
Photon energy (ev)
Pure & co-doped CuO
(5% Cd+5% Co)
E_g=2.039 ev
(ahn)2 (eV/cm)2
6.0x10^10
4.0x10^10
2.0x10^10
0.0
1.0
1.5
2.0
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3.0
Photon energy (ev)

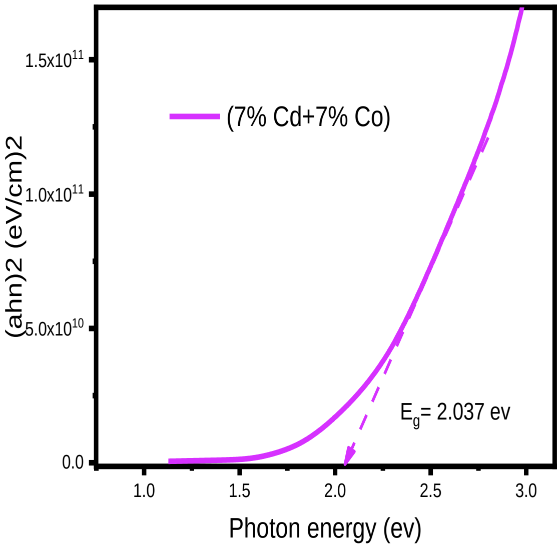

Figure 5: The optical band gap of undoped (CuO) films dotted with cadmium and cobalt ions in equal proportions and at annealing temperature of 475°C

Conclusions

Doped CuO thin films with equal concentrations of (Cd + Co) were prepared using liquid gel method with spin coating technique. From FESEM analysis,The shape of a spherical surface resembling a petal and a flower is observed. In addition, the presence of O, Cu, and Co atoms is traced firmly via EDX. Investigation. Structural analysis was performed by XRD and proposed That the deposited CCO thin films belong to monoclinic structure With the mixed phase and 2+Co2+/Cd has a great influence in the CuO . network lattice, resulting in the control of crystal size, dissociation density and torsion. The surface nature of the sample p was verified. Moreover, the The experimental optical band gap was found and it was noticed that the gap increased when doped with cadmium and cobalt, then it started decreasing with increasing dotting up to 2.037eV,

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