



Original article

Effect of annealing temperature and doping with Cu on physical properties of cadmium oxide thin films

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ABSTRACT

In this research, pure and copper doped cadmium oxide thin films were prepared by Successive Ionic Layer Adsorption and reaction (SILAR) method using cadmium acetate as the Cd source (cation) and hydrogen peroxide (anion). Optical transmittance is measured by UV-visible spectrophotometer, it is revealed that the copper doping and annealing at 300 °C improves the transmittance of these films. The optical band gap of CdO increased to (2.8 eV) with Cu doping, but it is decreased to (2.4 eV) with annealing. The results show that the pure and doped CdO thin films at annealing temperature of 300 °C have grain size in the range of 19.1 nm and 44.4 nm, respectively.

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1. Introduction

The rapidly growing development of nanotechnology is due to the unique properties of nanocrystalline materials in comparison with their large-grained analogs. Cadmium oxide (CdO) is an important semiconductor material for the development of various technologies of solid-state devices [1] (panel display, optoelectronic components, thermally insulating glass, etc.) [2]. Recently CdO has attracted attention as a transparent conducting oxide because of its (i) band gap (~2.5 eV), (ii) high conductivity, (iii) ease in doping, (iv) chemical stability in hydrogen plasma, (v) abundance in nature and no toxicity [3]. Some physical properties of this oxide have been investigated by several authors. Various techniques such as thermal evaporation [4], sputtering [5], solution growth [6], pulsed laser sputtering [7], activated reactive evaporation [8],

spray pyrolysis deposition (SPD) [9] and (SILAR) method were employed to prepare thin films of CdO. It was experimentally found that the structural, electrical and optical properties of copper doped cadmium oxide strongly depend on the preparation method and deposition conditions [10]. Transparent conducting oxides (TCOs) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices been successfully used for many applications, including phototransistors [11], gas sensor [12], solar cells [13], liquid crystal displays, IR detectors and anti-reflection coatings [14]. Doping of CdO thin films incorporating various elements such as Sn [15], in [16] F [17] and Al [18] have already been studied.

This paper describes the deposition of pure and copper doped CdO thin films by (SILAR) method. Then investigate the influence of the doping with Cu and annealing at 300 °C on the structural and optical properties of these films.

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2. Experimental details

CdO thin films have been deposited on glass substrates using Successive Ionic Layer Adsorption and reaction (SILAR) method in an aqueous solution of cadmium acetate $[(\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}) 99.99\%]$ (cation) with molarities (0.03 M) and 100 mL (14 M) aqueous ammonia solution. The complexing agent ammonium hydroxide was used to stabilize the crystallite size. The pH of the prepared solution was maintained as 8.5 throughout the deposition process. Other solution was 0.003 M of hydrogen peroxide (anion), as well as double distilled water.

- (1) Immersed first in cadmium acetate (0.03 M) and ammonium hydroxide solution for 40 s.
- (2) Immersed in quantitative amount of double distilled water in 10 s at 90 °C.
- (3) Immersed in 0.003 M of hydrogen peroxide (anion) solution for 30 s.
- (4) Cu was prepared by a chemical technique for doping CdO thin film.

1% Cu was added drop by drop until the homogeneous and clear solution was obtained, then the stirring continued for 1 h. This cycle was repeated several times in order to increase the overall film thickness of CdO. The deposited film was

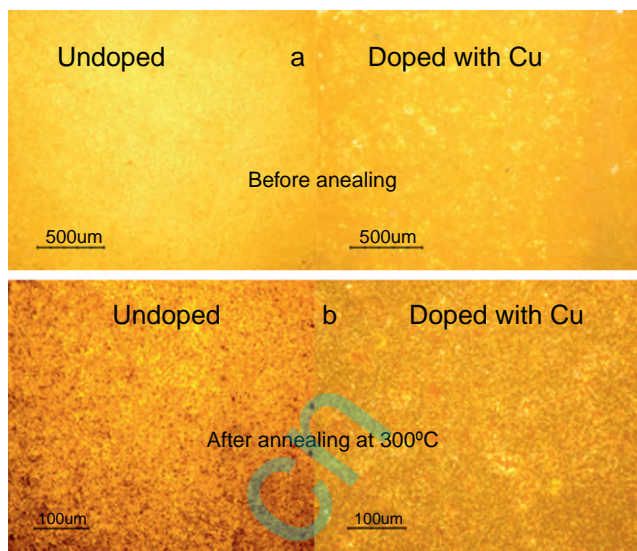


Fig. 1 – Images for CdO (undoped) and CdO: Cu films, before and after annealing at 300 °C.

subsequently annealed in air at 300 °C for 50 min. The structural measurements were done using optical microscope type (NIKON, ECLIPSE, ME600). For measuring the optical absorption and transmittance of thin films, a double beam (OPTIMA

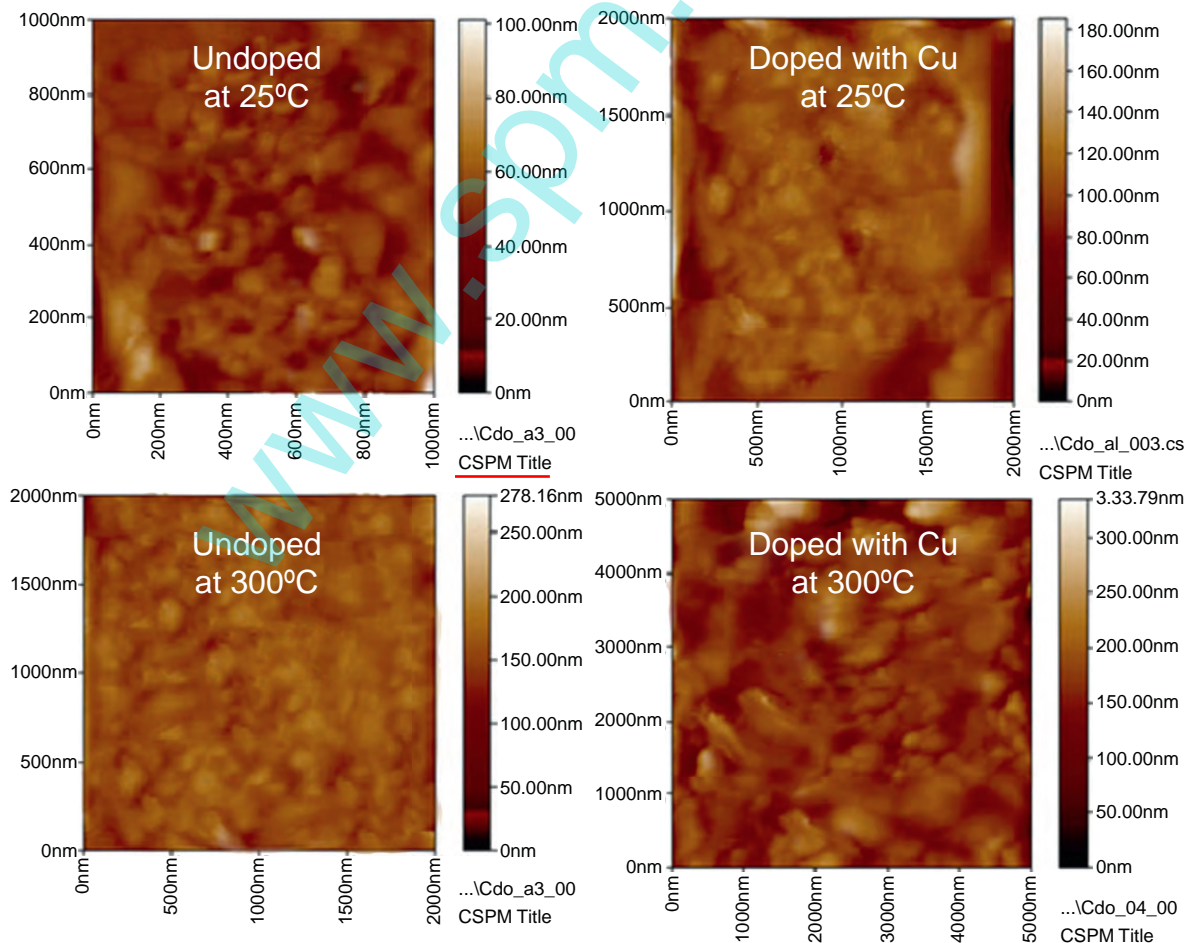


Fig. 2 – AFM images for CdO (undoped) and CdO: Cu films, before and after annealing at 300 °C.

Table 1 – X-rays results of pure and copper doped CdO at 25 °C.

Sample	2θ (°) undoped	2θ (°) with Cu	I (a.u.)	I (a.u.) with Cu	(hkl)	Angle shift Δ(2θ) (°)	Grain size (nm)
CdO & CdO:Cu at 25 °C	33.05	32.94	100	100	(111)	0.37	19.2071
	38.27	38.03	63	61	(200)	0.24	19.529
	55.3	55.2	26	21	(220)	0.1	19.112

SP3000) UV/VIS/NIR spectrophotometer was used. The XRD measurements were carried out using (SHIMADZU XRD-6000) X-ray diffractometer.

3. Results and discussion

3.1. The results of optical microscopic examination

We noted the occurrence of homogeneous and smooth surfaces at the microscopic examination light of undoped CdO thin film and doped with Cu before and after annealing, as shown in Fig. 1. It can be observed that the annealing temperature appreciably affected both the nanostructures and crystallite sizes of the films. This modifies the grain boundaries of films and consequently increases the crystal size. Also the doping with Cu led to increase of the band gap and the absorption is slightly changed depending on the change in the crystalline nature. For these reasons we observe dots with different color intensities in Fig. 1.

3.2. Atomic force microscope (AFM)

Typical AFM images for CdO (undoped) and CdO:Cu films, before and after annealing at 300 °C for 50 min are shown in Fig. 2. It is seen that films display similar surface morphologies, comprising of image nanostructures, which provide evidence for its growth features [19]. In general, the grain size depends on the chemical composition of the starting solution and the post annealing process. The grain size of as-grown films is around 19.1 nm, which increases to 44.4 nm after the annealing process.

3.3. X-ray diffraction (XRD)

The X-ray diffraction (XRD) of pure and Cu doped CdO thin film is displayed in Fig. 3. All the peaks of CdO corresponding to (111), (200) and (220) reflections are observed. The shift in the CdO peak positions was observed, which indicated that Cu does react with CdO. Considering the results above, it can be concluded that the deposition of a very thin Cu layer on a CdO film has a noticeable influence on the crystalline structure. One can observe shift in the position of the (111), (200) and (220) peaks, as shown in Tables 1 and 2. The intense and sharp peaks in the X-ray diffraction pattern reveal the crystalline of the films which also confirm the stoichiometric nature of the CdO films. The degree of crystallization in the film was improved by a sufficient thermal crystallization (300 °C) and the grain size become 44.4 nm instead of 19.1 nm. The intensity of the peaks is found to decrease with Cu doping which means that the crystalline nature of the film is decreased. Grain size was calculated by compensation values that were

obtained from the X-ray diffraction results of the previous figures in the equation of Sherrer [20],

$$G.S. = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

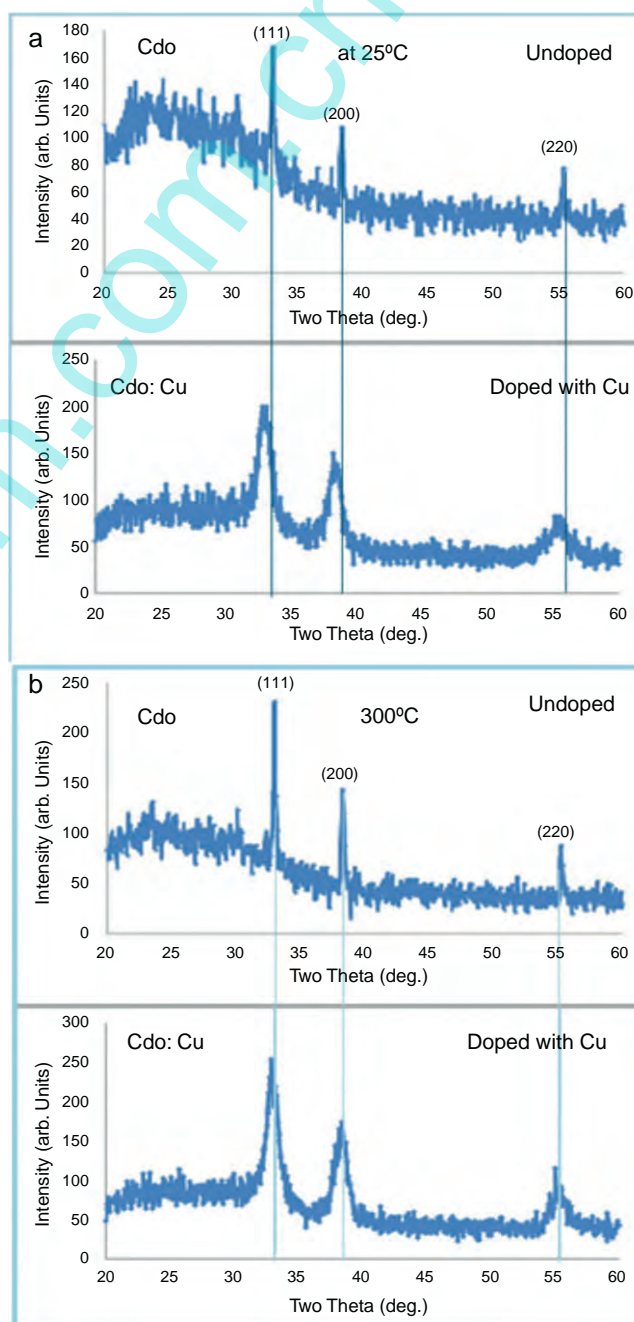


Fig. 3 – XRD patterns of deposited and annealed CdO thin films with and without Cu impurity.

Table 2 – X-rays results of pure and copper doped CdO at 300 °C.

Sample	2 θ (°) undoped	2 θ (°) with Cu	I (arb. units)	I (arb. units) with Cu	(h k l)	Angle shift $\Delta(2\theta)$ (°)	Grain size (nm)
CdO & CdO:Cu at 300 °C	33.32	32.92	100	100	(1 1 1)	0.4	38.704
	38.34	38.18	65	64	(2 0 0)	0.24	32.236
	55.47	55.12	28	24	(2 2 0)	0.35	44.413

Table 3 – (h k l) plane, FWHM value, D grain size, dislocation density (δ) and texture coefficient ($T_{c(hkl)}$) values of the pure thin films at 25 °C.

(h k l) CdO	FWHM	Grain size D (nm)	(δ) = $1/5.0696^2$ (nm^{-2})	$T_{c(hkl)}$	(h k l) CdO with Cu	FWHM	Grain size (nm)	(δ) = $1/D^2$ (nm^{-2}) D	$T_{c(hkl)}$
(1 1 1)	0.45080	19.207	0.00271	1.3	(1 1 1)	1.29	6.68	0.02295	1
(2 0 0)	0.450	19.529	0.00262	1.1	(2 0 0)	1.06	8.1745	0.1496	0.989
(2 2 0)	0.4510	19.112	0.00274	1.14	(2 2 0)	26	6.35	0.2477	1.01

where G.S. is the grain, K is a constant (0.94), λ is the wavelength of Cu $K\alpha$, θ is the Bragg's angle, and β is the Full Width at Half Maximum (FWHM).

The X-rays pattern reveals that all investigated coated films are polycrystalline of cubic CdO structure and Bragg position for strong reflections like (1 1 1) direction was 33.31° and 32.94°, respectively, for pure and doped (1% Cu) at 25 °C of CdO coated films. A slight angle shift, estimated at 0.37–0.24°, was carefully detected as sketched in Fig. 3. Others reflection positions (2 θ) and their angle shifts are listed in Tables 1 and 2.

The value of the dislocation density (δ) which gives the number of defects in the film was calculated from the average values of the crystallite size D by the relationship [21]:

$$\delta = \frac{1}{D^2} \quad (2)$$

Texture coefficient (T_c) is used to quantify the preferential orientation of the film deposited at different substrate temperature using the following relation [22]. It is found that the T_c

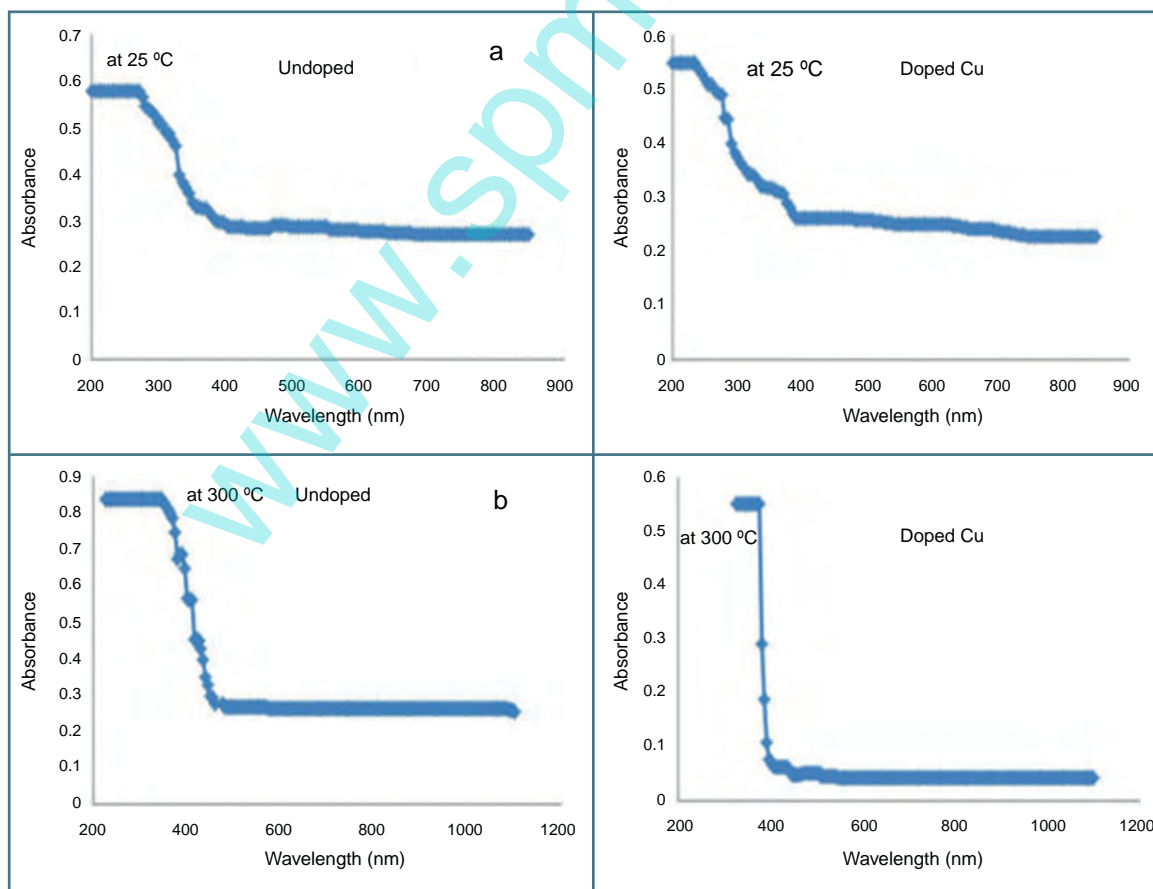


Fig. 4 – (a) Optical absorption spectrum of CdO thin films deposited at 25 °C undoped and with doped Cu. (b) Optical absorption spectrum of CdO thin films deposited at 300 °C undoped and with doped Cu.

Table 4 – (h k l) plane, FWHM value, D grain size, dislocation density (δ) and texture coefficient ($T_{c(hkl)}$) values of the pure thin films at 300 °C.

(h k l) CdO	FWHM	Grain size D (nm)	(δ) = 1/D ² (nm ⁻²)	T _{c(hkl)}	(h k l) CdO with Cu	FWHM	Grain size D (nm)	(δ) = 1/D ² (nm ⁻²)	T _{c(hkl)}
(111)	0.22380	38.704	6.699	0.97	(111)	1.13	7.66	58.6756	0.94
(200)	0.27240	32.236	9.62	1.2	(200)	1.258	6.98	48.72	1
(220)	0.15000	44.413	5.069	1.23	(220)	1.283	7.03	53.358	1

is maximum for (111) plane for all the films deposited at different temperature. This indicates no orientation and phase change in the CdO film.

$$T_{c(hkl)} = \frac{I_{(hkl)}/I_{o(hkl)}}{N^{-1} \sum n I_{(hkl)}/I_{o(hkl)}} \quad (3)$$

where I is the measured intensity, I_o is the standard intensity and N is the number of diffraction peaks. The results of T_c and grain sizes for 25 °C and 300 °C are shown in Tables 3 and 4, respectively.

4. Optical properties

The optical absorption of CdO films deposited onto a glass substrate was studied in the range 200–900 nm. Fig. 4 shows the variation of absorption with wavelength. The absorption of the film is found to increase after annealing at 300 °C. This is possibly due to increase in crystalline nature and decrease

in the number of defects in the localized state [23]. Also, we found after doping with 1% Cu that the absorption is slightly changed depending on the change in the crystalline nature. It is clearly seen from the optical spectrum that the absorption edge is red shifted for annealed films, this indicates a decrease of the optical band gap. The optical band gap was calculated using the following relation [24]:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (4)$$

where A is a constant and n is a constant equal to $\frac{1}{2}$ for direct band gap semiconductors. The estimated band gap from plots of $(\alpha h\nu)^2$ versus $(h\nu)$ are shown in Fig. 5 as as deposited and annealed CdO films. The linear nature of the plot indicates the existence of direct transition. The band gap was determined by extrapolating the straight portion to the energy axis at $\alpha = 0$. It was found to be 2.5 eV for as deposited CdO films and show "red shifts" by 2.4 eV after annealing for temperatures of 300 °C and 2.8 eV when doped with Cu. The decrease in band gap

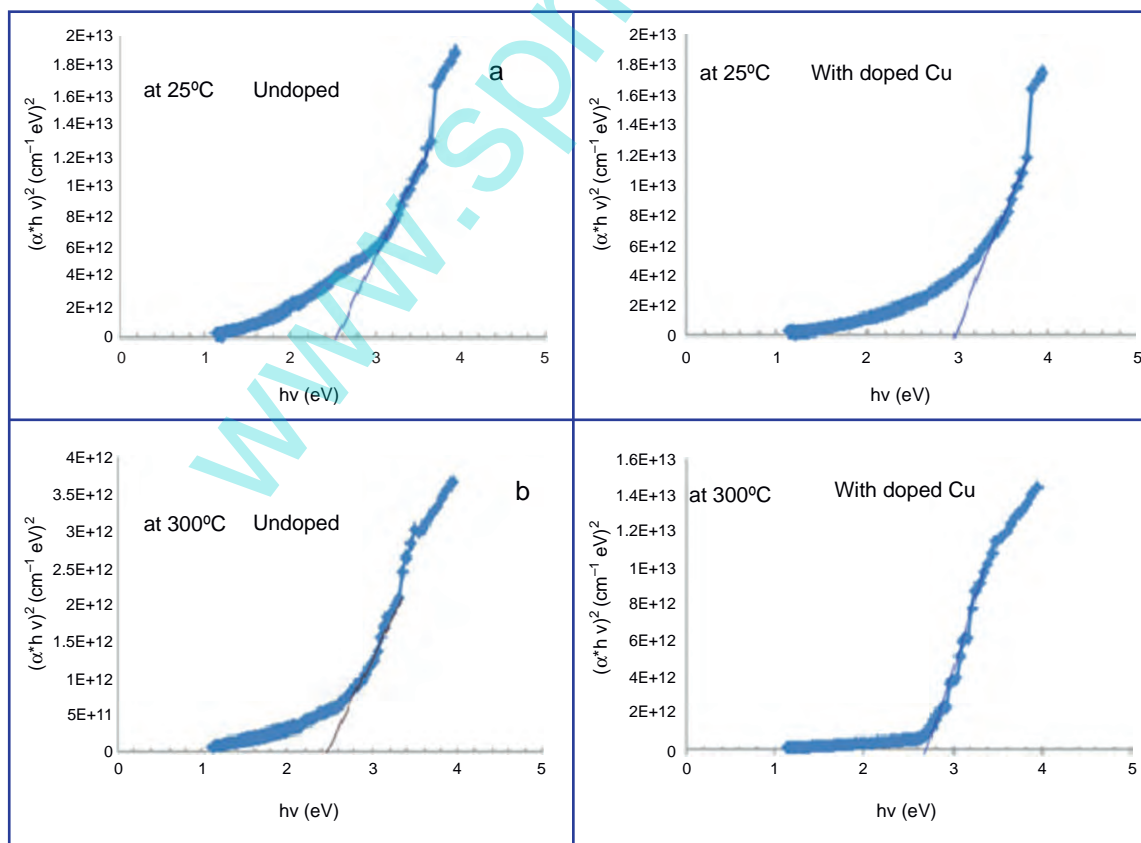


Fig. 5 – (a) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdO thin films deposited at 25 °C undoped and with doped Cu. (b) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdO thin films deposited at 300 °C undoped and with doped Cu.

