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RESEARCH ARTICLE

STUDY OF STRUCTURAL AND OPTICAL PROPERTIES OF $CD_{(1-X)}Cr_XO$ THIN FILMS PREPARED BY CHEMICAL SPRAY PYROLYSIS METHOD

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ABSTRACT

In this study, undoped (CdO) films and Cr doped (with 2,4,6 and 8 wt%) were deposited on glass sub strate at (400 ºC) by chemical spray pyrolysis technique using cadmium acetate as the Cd source. The effect of Cr doping on structural and optical properties has been investigated. XRD investigations showed that all the films were polycrystalline in nature and had a cubic structure with preferred orientation along (111) plane for all doping percentages. It was found that doping with (Cr) led to decrease in the intensity of (111) peak and the average grain size decreases as (Cr) doping percentage increases. The optical characterization of the films have good transmittance in the visible region of spectrum and it increases with Cr-doping, with increase in direct band gap (2.4 eV for undoped to 2.63, 2.65, 2.67 and 2.71 eV) for different values of Cr percentage respectively. The absorption coefficient, reflectance, and Urbach tail were calculated also.

INTRODUCTION

Transparent conductive oxide (TCO) films have been extensively studied because of their use in semiconductor device technology. CdO thin films have high transparency in the visible region of the electromagnetic spectrum and show degenerate n-type conductivity mainly due to oxygen vacancies, high carrier concentration contributed by shallow donors resulting from self non-stoichiometry (Sahin *et al.,* 2014; Khan *et al.,* 2010). In recent years, transparent conductive oxide (TCO) layers have attracted much attention due to their high optical transmittance and low resistivity. They have been obtained by different research groups because they have potential applications in photovoltaic solar cells, phototransistors, liquid crystal displays, optical heaters, gas sensors, transparent electrodes, and other optoelectronic devices (Ali Yıldırım and Ates 2009; Zheng *et al.,* 2010). Inherently CdO is an n-type semiconductor with optical band gap varying from 2.2 to 2.9 eV. Currently, nanostructured materials are not only in the forefront of the hottest studies on fundamental materials, but are also gradually entering the daily lives of people. One-dimensional (1D) metal oxide semiconductor nanostructures, such as nanorods and nanowires have attracted wide attention for their potential applications in device and interconnect integrations in nano and molecular electronics (Zaien and Ahmed, Z. Hassan 2012). Different techniques such as sol–gel, spray pyrolysis, ion beam sputtering, magnetic sputtering, and pulsed laser deposition have been used for deposition of pure and doped CdO films (Serbetc *et al.,* 2012). In the present paper, we report the effect of (Cr) doping on the optical and structural properties of CdO films prepared by chemical spray pyrolysis technique.

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Experimental procedure

Chemical spray pyrolysis technique was used to deposit undoped and Cr-doped (CdO) films on glass substrates at temperature of (400 ºC). In the preparation of (CdO) films aqueous solution of (0.3M) cadmium acetate ($Cd(CH_3COO)_2.2H_2O$) was mixed with distilled water by using magnetic stirrer for (15min). To achieve Cr-doping aqueous solution of (0.3M) chromium chloride ($CrCl_3.6H_2O$) with various concentrations of (2, 4, 6, 8) wt% and mixed with precursor solution. The resultant solution was sprayed on glass substrate kept at (400 ºC). Other deposition conditions are as follows: spray nozzle substrate distance (30 cm), spray time (8 s), spray interval (2 min) and pressure of the carrier gas (1.5 bar) were kept constant for each concentration. Optical transmittance spectra in the wavelength of (300-900) nm were recorded by using UV-VIS-NIR spectroscopy (Shimadzu,UV-1800) and the X-ray diffraction patterns were obtained in a (Shimadzu XRD-6000) goniometer using copper target (Cu K_α, 1.5418 Å).

RESULTS AND DISCUSSION

Structural analysis

XRD patterns of the undoped and Cr–doped CdO films are shown in Figure 1.

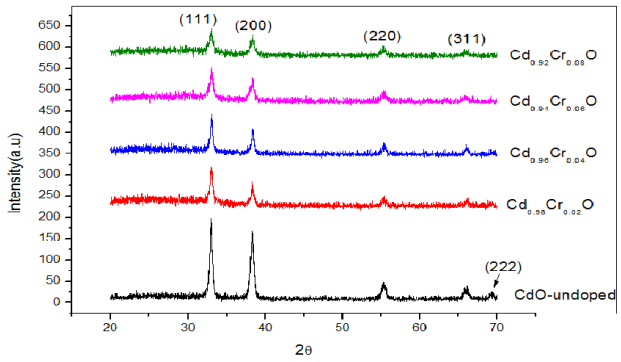

Fig. 1. X–ray diffraction patterns of undoped and Cr-doped CdO films

The patterns indicate that all of the films have a polycrystalline with cubic face centered crystal structure (Dakhel 2010; Yuankun Zhu *et al.,* 2013). For the films, the main characteristic peaks are assigned to the (111), (200), (220) and (311) planes. The relatively stronger peak intensity indicates preferential (111) orientation of the films. Similar behavior has also been reported by other studies (Aydın *et al.,* 2012; Akyuz *et al.,* 2010). The average grain size for the films can be determined using Williamson-Hall formula (Prabhu *et al.,* 2013) shown below:

$$\beta_{hkl}\cos\theta = K\lambda/D + 4S\sin\theta \quad \text{.....(1)}$$

where β_{hkl} is full width of half maximum, D is the average grain size, k is constant and was assumed to be equal to 0.9, λ is wavelength for Cu target for XRD instrument, θ is Bragg's angle for all peaks, and S is the microstrain of the film. The average grain size for all films are also calculated by Scherrer formula according relation (Zaien *et al.,* 2011):

$$D = (0.94\ \lambda) / (\beta\cos\theta) \quad \text{.....(2)}$$

The grain size decreases regularly upon increasing the Cr-concentration and peaks shift towards higher angles were also noted from XRD results which indicate the compression in unit cell. This may be due to the lower ionic radius of Cr^{+3} (0.0615 nm) compared with Cd^{+2} ionic radius (0.095nm) (Dakhel and Hamad 2013). The texture coefficient (T_C) represents the texture of the particular plane; in which greater than unity values imply that there are numerous of grains in that particular direction. The different texture coefficients T_C(hkl) have been calculated from the X-ray data using the well-known formula (Seval Aksoy *et al.,* 2009):

$$TC(hkl) = \frac{I(hkl)/I_o(hkl)}{N^{-1}\sum_n I(hkl)/I_o(hkl)} \quad \text{.....(3)}$$

where I(hkℓ) is the measured relative intensity of a plane (hkℓ), I_o(hkℓ) is the standard intensity of the plane (hkℓ) taken from the JCPDS data, N is the reflection number and n is the number of diffraction peaks. The results indicate that (Tc) decreases with increasing the doping percentage and the calculated values of T_C(hkℓ) are greater than unity, especially those corresponding to (111) plane. This indicates that the respective films have the largest preferred crystallographic orientation along the (111) diffraction planes. All these results are shown in Table 1.

Table 1. Structural parameters of the undoped and Cr-doped CdO films

Sample	CdO pure	$Cd_{0.98}Cr_{0.02}O$	$Cd_{0.96}Cr_{0.04}O$	$Cd_{0.94}Cr_{0.06}O$	$Cd_{0.92}Cr_{0.08}O$
hkl	111	111	111	111	111
2Θ	32.9958	33.0253	33.0481	33.0203	33.0298
d	2.71251	2.71016	2.70834	2.71056	2.70980
FWHM	0.4032	0.4500	0.4767	0.5110	0.5800
D_{av} Scherrer	21	18	17	16	14
D_{av} W-H	13	11	10	9	7
Lattice constant	4.6982	4.6941	4.6909	4.6948	4.6935
T_c	1.47	1.41	1.31	1.30	1.16

Optical analysis

Optical absorption spectra of the films in spectral range of (300-900 nm) were determined by using UV–visible spectrophotometer. The analysis of the dependence of absorption coefficient on photon energy in the high absorption regions is performed to obtain the detailed information about the energy band gaps of the films (Sahin *et al.,* 2014). The transmittance spectra of the films are shown in Figure (2). These spectra show that adding (Cr) to (CdO) improves the transmittance for all deposited samples. The transmittance of undoped films was (51%) at (550 nm) and after doping, the transmittance increases up to (80%) at (550 nm).

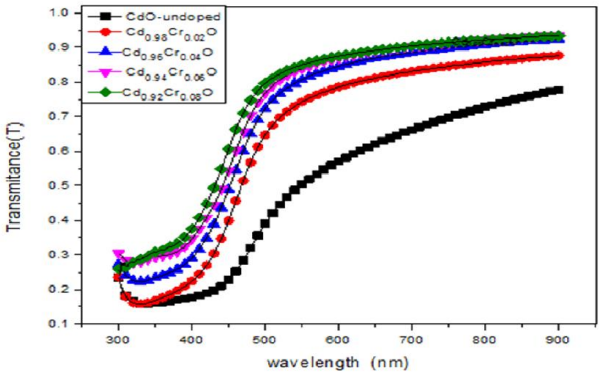

Fig. 2. Transmittance spectra of the undoped and Cr–doped CdO films

The optical transition involved in the absorption process and the absorption coefficient (α) of a film of thickness t can be calculated from the transmission spectra by the relation (Khan *et al.,* 2010)

$$\alpha = \frac{1}{t} \ln \left[\frac{1}{T}\right] \qquad \text{.....(4)}$$

Fig (3) shows the relation between (α) and photon energy. The variation of the optical absorbance with wavelength is shown in Fig (4). Calculated values of absorption coefficient are in the order of (10^4) cm^{-1} which can be attributed to the direct electronic transition. From Fig (4) it is shown that absorbance decreases with increasing Cr doping concentration and a sharp decrease is observed near the band edge.

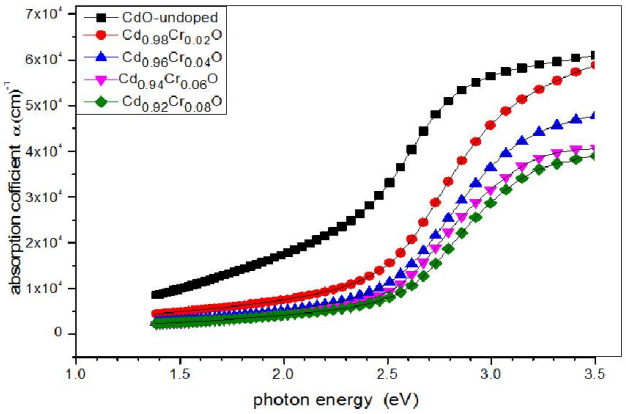

Fig. 3. Absorption coefficient of the undoped and Cr–doped CdO films

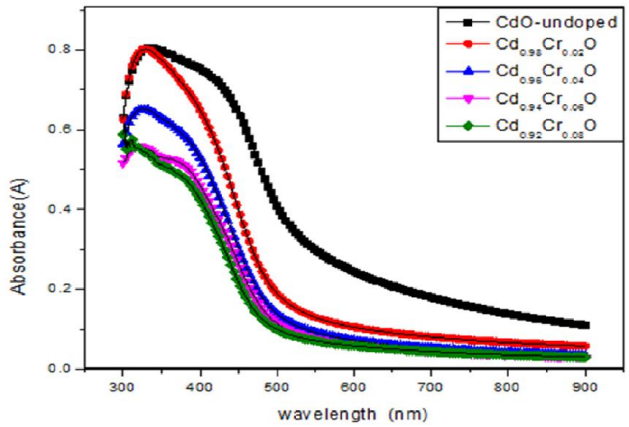

Fig. 4. Absorbance spectra of the undoped and Cr–doped CdO films

The optical energy band gap (Eg) is given by the classical relation (Tauc 1974):

$$\alpha h\nu = A(h\nu - E_g)^r \qquad \text{.....(5)}$$

Where α is the absorption coefficient, hν is the photon energy, Eg is the optical band gap, A is a constant which does not depend on photon energy and r has four numeric values (1/2) for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions. In this work, direct band gap was determined by plotting $(\alpha h\nu)^2$ vs. hν curves, with the extrapolation of the linear region to low energies.

From Figure (5), it was observed that the undoped films exhibit a band gap values of (2.40 eV) and the band gap value increases with increase in Cr-doping concentration (2, 4, 6, and 8) wt% and it is (2.63, 2.65, 2.67 and 2.71) eV respectively. The increase in the band gap energy is due to increase in free electron concentration in the films. The shift of the band gap with change in the carrier concentration can be explained by the Burstein-Moss shift (Fan *et al.,* 2007). Reflectance curves of undoped and Cr-doped films are shown in Fig (6).

It can be seen that the reflectance of the films increases with increase in photon energy and begins to go down near the energies corresponding to the band gap. However the reflectance is higher in the undoped films compared to the Cr-doped films. The shift is related to the changes in the films characteristics. The width of the localized states available in the optical band gap of the films affects the optical band gap structure and optical transitions and it is called as Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges. The Urbach tail of the films can be determined by the following relation (Ilican *et al.,* 2009):

$$\alpha - \alpha_o \exp(E / E_U) \qquad \text{.....(6)}$$

where E is the photon energy, α_o is constant, and E_u is the Urbach energy which refers to the width of the exponential absorption edge.

Figure (7) shows the variation of (lnα) vs .photon energy for the films. This behavior corresponds primarily to optical transitions between occupied states in the valance band tail to unoccupied states at the conduction band edge. The E_U value was calculated from the slope of Figure (7) using relationship:

$$E_U = \left(\frac{d(\ln \alpha)}{d(h\nu)}\right)^{-1} \qquad \text{.....(7)}$$

The obtained E_U values are given in Table (2). Urbach energy values of the films decrease with increasing Cr-dopant. The E_U values change inversely with optical band gaps of films.

Table 2. Values of Urbach energy of the undoped and Cr-doped CdO films

Samples	*E_u(meV)*
CdO-undoped	553
$Cd_{0.98}Cr_{0.02}O$	382
$Cd_{0.96}Cr_{0.04}O$	365
$Cd_{0.94}Cr_{0.06}O$	324
$Cd_{0.92}Cr_{0.08}O$	315

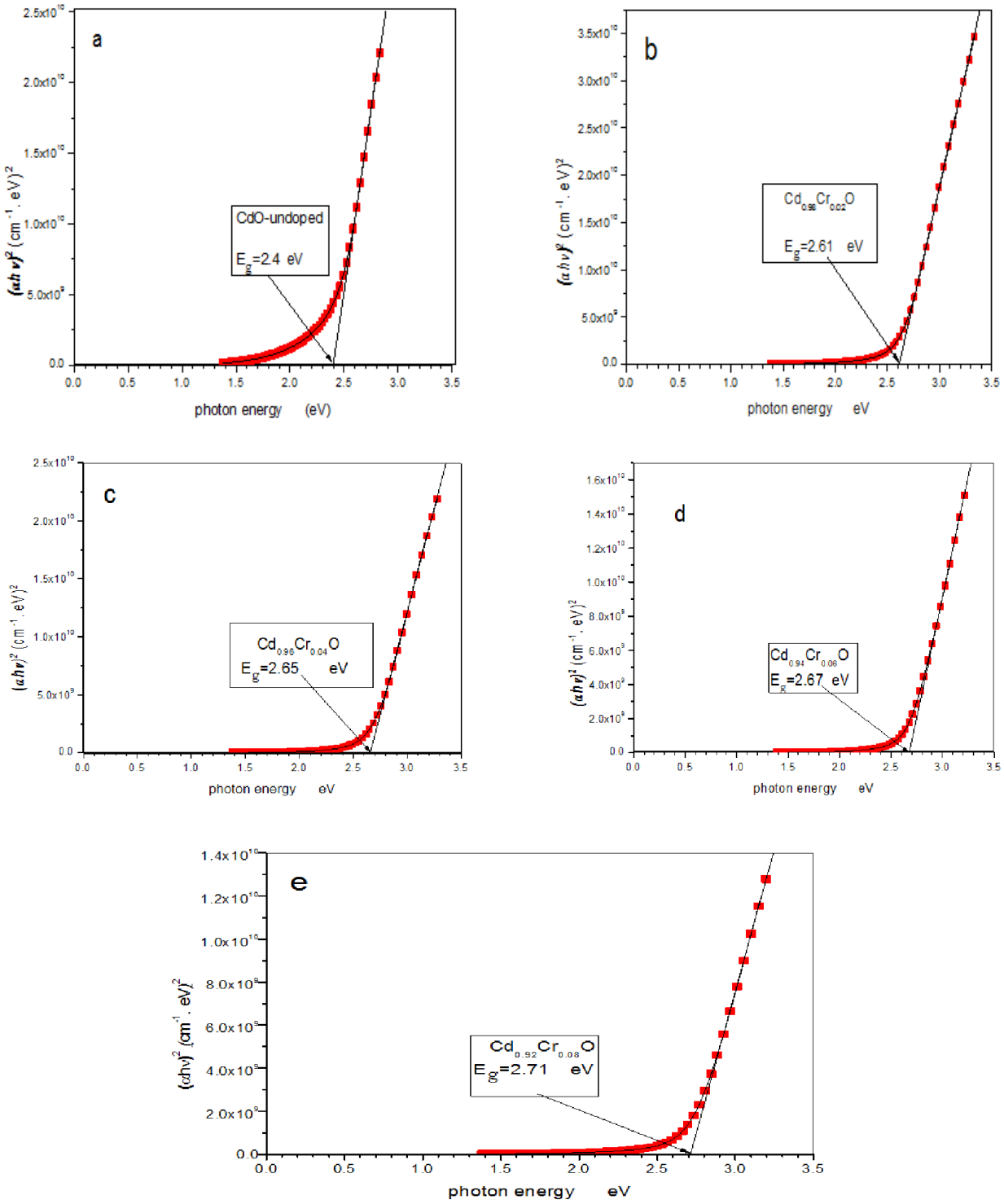

Fig. 5. Energy gap of the undoped and Cr–doped CdO films

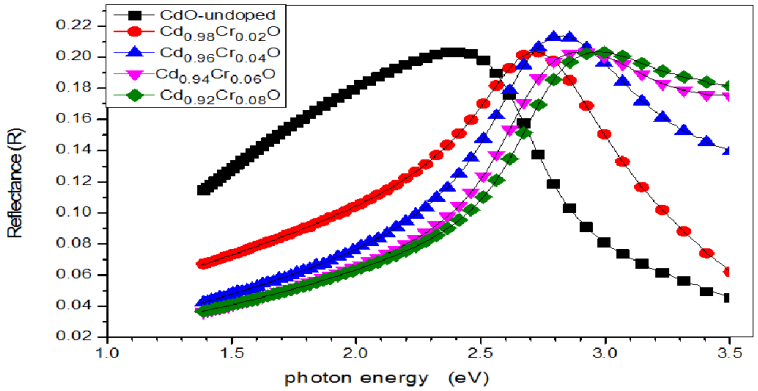

Fig. 6. Reflectance spectra of the undoped and Cr–doped CdO films

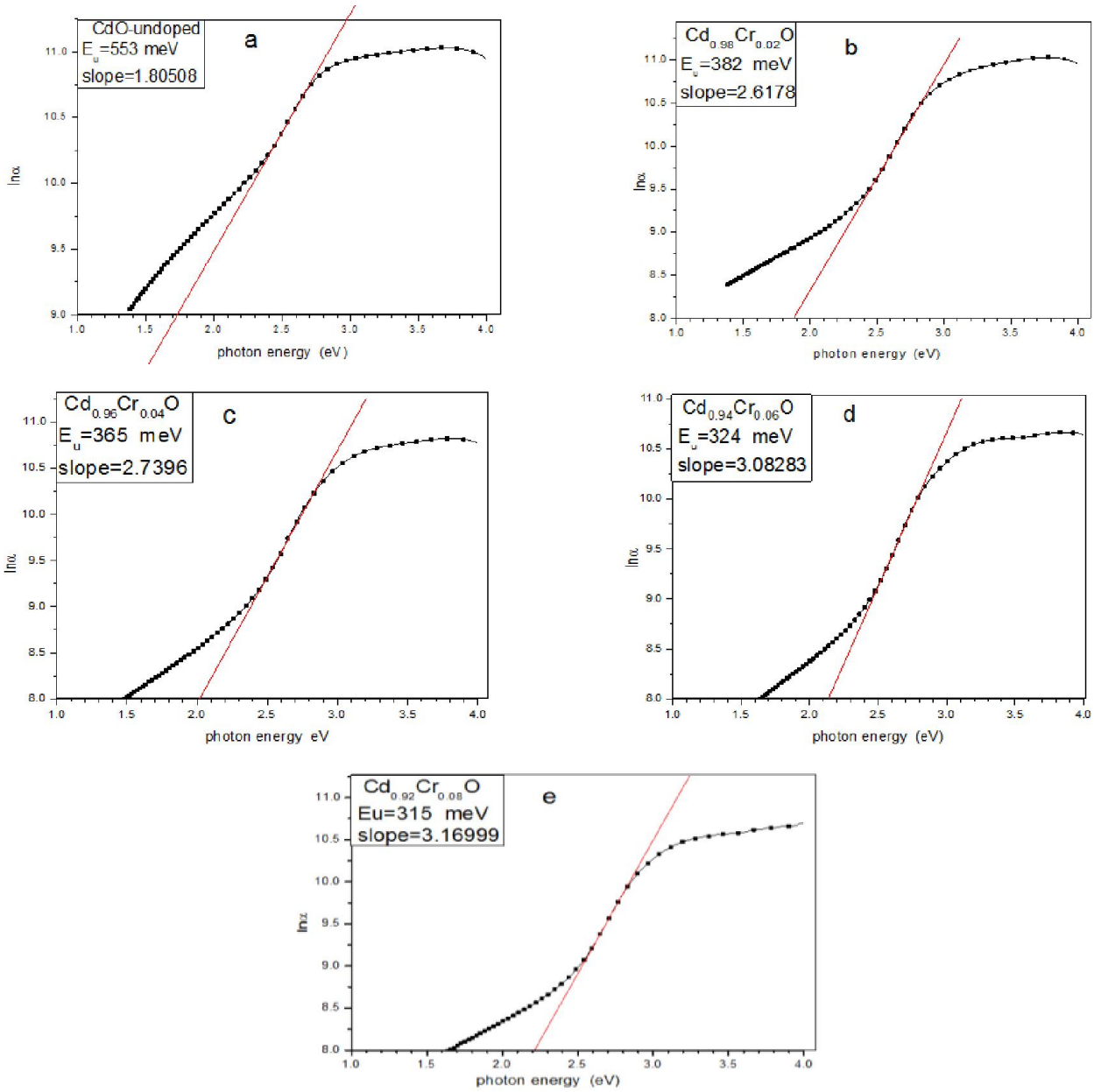

Fig. 7. Urbach energy of the undoped and Cr–doped CdO films

Conclusions

In this study, undoped (CdO) films and Cr doped (with 2,4,6 and 8 wt%) were successfully deposited on glass substrates at (400 ºC) by chemical spray pyrolysis technique using cadmium acetate as the Cd source. XRD patterns of the undoped and Cr–doped CdO films indicate that all of the films are polycrystalline with cubic face centered crystal structure. The main characteristic peaks are assigned to the (111), (200), (220) and (311) planes. The grain size decreases regularly upon increasing the Cr-concentration and peaks shift towards higher angles were also noted from XRD results which indicate the compression in unit cell. This may be due to the lower ionic radius of Cr^{+3} (0.0615 nm) compared with Cd^{+2} ionic radius (0.095nm). The transmittance spectra of the films show that adding (Cr) to (CdO) improves the transmittance for all deposited samples. The transmittance of undoped films was (51%) at (550 nm) and after doping the transmittance increases up to (80%) at (550 nm). It was observed that the undoped films exhibit a band gap values of (2.40 eV) and the band gap value increases with increase in Cr-doping concentration (2, 4, 6, and 8) wt% and it is (2.63, 2.65, 2.67 and 2.71) eV respectively. The increase in the band gap energy was attributed to the increase in free electron concentration in the films. The shift of the band gap with change in the carrier concentration could be explained by the Burstein-Moss shift.

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