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ORIGINAL ARTICLE

Effects of concentration on CdO films grown by electrodeposition

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Abstract Thin films of CdO were synthesized by electrodeposition via chronoamperometry. The concentrations of aqueous solutions of $Cd(NO_3)_2$ were chosen between 0.005 and 0.08 M. It was thought that the reaction rate would reach saturation at 0.02 M of concentration and it was measured as the concentration increased, the thicknesses of the films increased from the 452 nm to the 798 nm. The well-crystallized film was observed to be at 0.01 M of concentration. It was also found that the band gap increased at low concentrations and surface morphology of the films did not change much with concentration.

Keywords CdO · Electrodeposition · Concentration · Thin film

Introduction

Transparent oxides have been extensively investigated because of their applications in semiconductor optoelectronic device technology. One of these oxides is cadmium oxide (CdO) (Zialbari and Ghodsi 2011) which is used for optoelectronic applications such as transparent electrodes, solar cells, phototransistors, photodiodes, and gas sensors (Fan 2009). CdO is an n-type semiconductor of a cubic structure with a direct band gap of 2.3 eV (Karim et al. 2016).

At present, CdO films have been prepared by a large range of techniques including molecular beam epitaxy, electrodeposition, sol–gel, sputter deposition, PLD, MOCVD, spray pyrolysis, and activated reactive evaporation (Liu et al. 2012). Among these techniques, electrodeposition is an inherently simple and inexpensive method for preparing semiconductor thin films and has been widely deployed for the preparation of oxide semiconductor thin films (Yogeeswaran et al. 2006).

When $Cd(NO_3)_2$ is used, the possible formation mechanism of CdO is suggested as follows (Singh et al. 2011a).

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2 \quad (2)$$

The conversion of $Cd(OH)_2$ to CdO takes place above 280 °C by the following reactions (Singh et al. 2011a).

$$Cd(OH)_2 \rightarrow CdO + H_2O \quad (3)$$

In the literature, there are no studies about the effect of concentration on CdO films but there are studies carried out at various concentrations such as 0.025 M (Jayakrishnan and Hodes 2003), 0.02 M (Baykul and Orhan 2014), 0.005 M (Henríquez et al. 2010), 0.001 M (Singh et al. 2011b) aqueous solutions of $CdCl_2$, 0.005 M aqueous solution of $CdSO_4$, (Ganjiani et al. 2016), 0.05 M aqueous solution of $Cd(C_2H_3O_2)_2$ (Sarma et al. 2012) and 1 M aqueous solution of $Cd(NO_3)_2$ (Singh et al. 2011a).

Experimental details

In this work, CdO thin films were deposited onto ITO-coated glass substrates using electrodeposition at various concentrations. An Ivium Vertex potentiostat/galvanostat

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Table 1 The deposition conditions in the experiments

Experiments	A1	A2	A3	A4	A5
Concentration (M)	0.005	0.01	0.02	0.04	0.08
Deposition time (s)	2700	2700	2700	2700	2700
Cathodic potential (V)	−0.71	−0.71	−0.71	−0.71	−0.71
Temperature (°C)	71 ± 2	71 ± 2	71 ± 2	71 ± 2	71 ± 2

was used for chronoamperometry method of electrodeposition. Three electrodes which are the reference electrode, the counter electrode (platinum wire) and the working electrode (ITO, 25 Ω/sq) were used in the experiments. The concentrations were chosen as to be 0.005, 0.01, 0.02, 0.04 and 0.08 M of aqueous solutions of $Cd(NO_3)_2$ and named as A1, A2, A3, A4 and A5, respectively. The experiment conditions are given in Table 1. 0.1 M KCl (Potassium Chloride) was used as supporting electrolyte and depositions were completed in 45 min. The deposition temperatures were kept at 72 ± 2 °C using a digital heater and stirrer. After the depositions, the obtained samples were annealed in an oven at 420 °C for $Cd(OH)_2$ turning to CdO.

A JASCO V–530 double-beam UV–Vis spectrophotometer was used for analyses of optical properties of the films. The XRD (X-ray diffraction) patterns of the CdO films were obtained by a PANalytical Empyrean X-ray diffractometer. The surface images of the CdO films were taken by a Zeiss Supra 40VP SEM (scanning electron microscope).

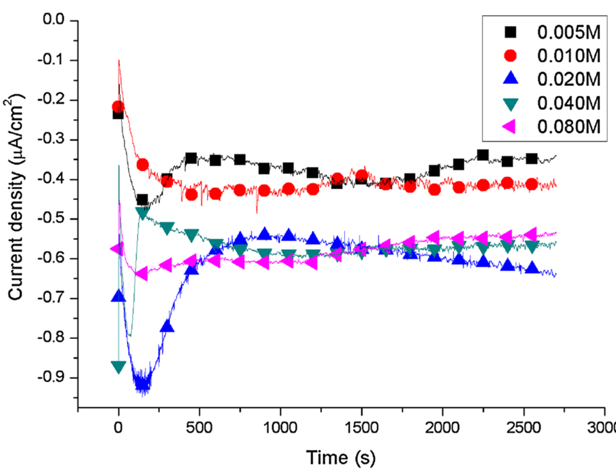


Fig. 1 Current density versus time graphs at various molarities of $Cd(NO_3)_2$

Table 2 The calculated film thicknesses, crystallite sizes and the optical band gaps

Experiments	A1	A2	A3	A4	A5
Thickness (nm)	452	501	784	796	798
Crystallite size (nm)	38	41	59	64	63
Band gap (eV)	2.63	2.59	2.54	2.44	2.49

Results and discussion

XRD studies of CdO films

The current densities versus time plots are given in Fig. 1. The current densities of the films obtained at 0.005 and 0.01 M concentrations demonstrate −0.4 μm/cm^2 while the others demonstrate −0.6 μm/cm^2 at average. These results show that the reaction rates of the films obtained at 0.005 and 0.01 M are relatively lower than that of the other

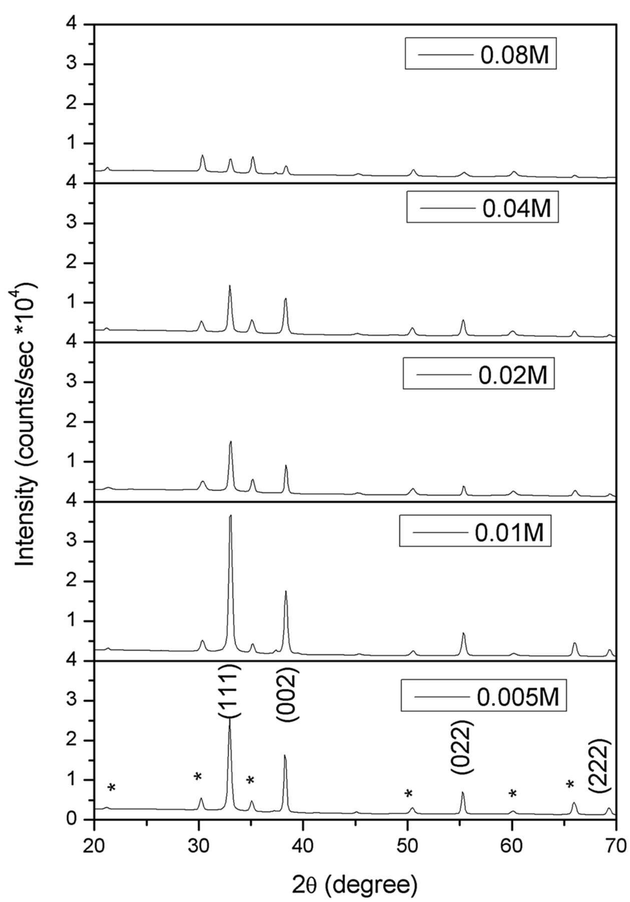


Fig. 2 X-ray diffraction pattern of CdO thin films obtained at various molarities of $Cd(NO_3)_2$

films. It was concluded that in a previous study (Altıokka 2015), the reaction rate affected thickness, crystallite size, band gap and morphology of the thin films.

The film thicknesses of the CdO films were calculated using the gravimetric method and are given in Table 2. As expected, the film thicknesses of the films obtained at 0.005 and 0.01 M are lower than that of the others films. Thicknesses of the films obtained at 0.005 and 0.01 M are average 475 nm while that of the other films are average 790 nm.

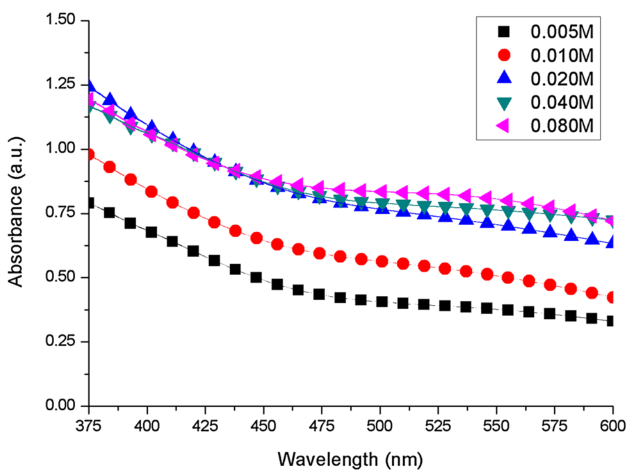


Fig. 3 Absorbance spectra of CdO thin films obtained at various molarities of $Cd(NO_3)_2$

The XRD patterns are shown in Fig. 2 and they show the cubic structure of the CdO. There are the two intense diffraction peaks of the CdO located (111) and (002) planes. Although the thicknesses of the films obtained in 0.005 and 0.01 M are thinner than that of the other films, the peak intensities are higher than that of the other films. This shows that the crystallizations of the films obtained at 0.005 and 0.01 M are relatively very good and it also shows that crystallization strongly depends on the reaction rate.

The crystallite sizes of the CdO films from the prominent (111) XRD peaks were calculated using Debye–Scherrer formula which is given in Eq. 4.

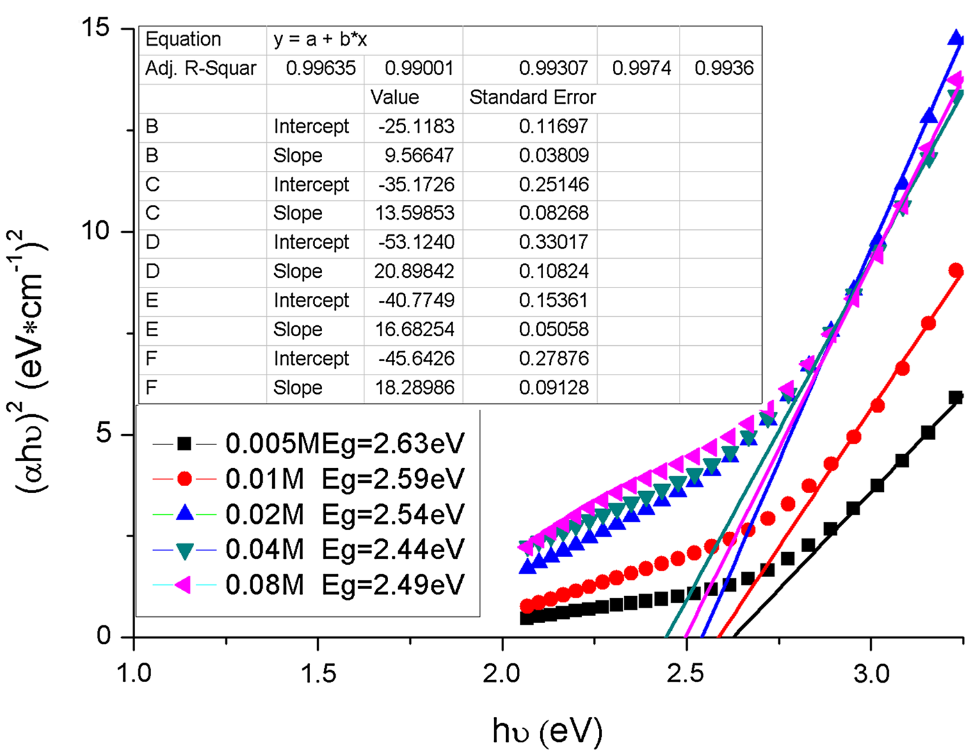
$$\mathrm{cs} = \frac{0.089 * 180 * \lambda}{314 * \beta * cos\theta_C} \mathrm{nm} \quad (4)$$

where cs is the crystallite size, λ is the wavelength of X-ray radiation (1.54056 Å), $2\theta_C$ is the position of peak center, and β is the full width at the half maximum of peak height (in degrees) (Bhowmik et al. 2008). The calculated crystallite sizes are given in Table 2. Crystallite sizes are analyzed in Table 2, and it is found that crystallite size depends on reaction rate which is affected by the concentration of the solutions.

Optical properties of CdO films

Absorbances versus wavelength graphs are given in Fig. 3. Absorbance values of the films obtained at 0.005 and

Fig. 4 Plots of $(\alpha h\nu)^2$ versus $h\nu$ of CdO thin films for the five different molarities of $Cd(NO_3)_2$



0.01 M are lower than that of the other films. It is concluded that film thicknesses and good crystallization cause this result. The absorbance values of the films obtained at 0.02, 0.04 and 0.08 M are nearly same and the thicknesses of these films are also nearly same. This result supports that reaction rate reaches saturation at 0.02 M concentration and this is important because of the fact that there are no works on the reaction rate and the concentration.

For estimating the band gaps of the films Tauc plot is used in general. The dependence of α (absorption coefficient) with the photon energy $h\nu$ can be given by the following equation for the allowed direct transition.

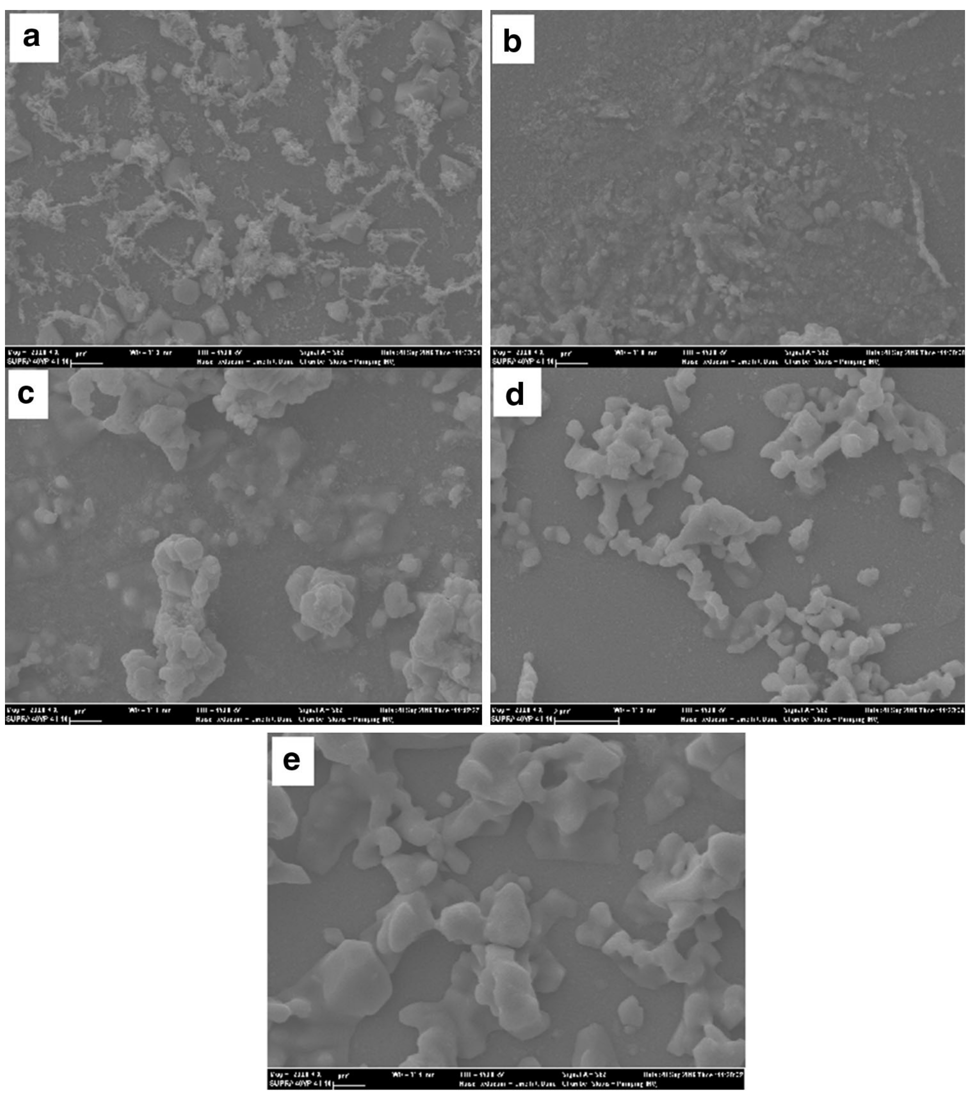
$$h = A\left(h - E_{\mathrm{g}}\right)^{1/2} \quad (5)$$

where A is the band edge constant and E_{g} is the optical band gap (Ziabari and Ghodsi 2011; Mkawi et al. 2015; Vishakha et al. 2013). The E_{g} values were estimated by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ vs $h\nu$ to $\alpha = 0$ (Ziabari and Ghodsi 2011). For this study, the $(\alpha h\nu)^2$ vs $h\nu$ plots are given in Fig. 4 and estimated band gaps of the films are given in Table 2. The band gaps of the films obtained at 0.005 and 0.01 M are 2.63 and 2.59 eV, respectively, whereas the band gap of the bulk CdO is 2.3 eV. It is well known that there is a relation between the band gap and the crystallite size as seen in this work. Due to the fact that concentration affects reaction rate and, therefore, crystallite size, it can be said that there is a relation between the concentration and the band gap.

SEM analysis of CdO films

SEM photographs were used for analyzing the surface morphology of the CdO films. Figure 5 shows 20,000 magnification SEM images of the CdO thin films. There are no cracks, pinholes or voids on the surfaces of the films and CdO covers the substrate well. It is observed that there are

Fig. 5 SEM photographs of the CdO thin films for **a** 0.005 M, **b** 0.01 M, **c** 0.02 M, **d** 0.04 M and **e** 0.08 M of $Cd(NO_3)_2$



polymorphic particles on the surfaces. When the concentration of $Cd(NO_3)_2$ is increased, the size of these particles is also increased. The surfaces of which are seen in Fig. 5a, b are nearly the same. On the other hand, the surfaces in Fig. 5c, d, e are also nearly the same. These results show that when the reaction rate reaches the saturation, the surfaces do not become different. But when the concentration of $Cd(NO_3)_2$ is lower than 0.02 M, filament-like structures appear on the surfaces.

Conclusion

In this work, thin films of CdO were deposited by electrodeposition technique onto ITO-coated glass substrates. For the first time, various concentrations such as 0.01, 0.04 and 0.08 M aqueous solutions of $Cd(NO_3)_2$ were used and effects of concentration were investigated in detail. It was found out from the current densities and film thicknesses that reaction rate reached the saturation at about 0.02 M of concentration. It was understood from the XRD patterns that good crystallization formed at 0.01 M of concentration. Crystallite sizes of the CdO films were calculated using Debye–Scherrer formula. Below 0.02 M of concentration, the crystallite size decreased from about 60 to 38 nm as the concentration decreased. As a result of this, the optical band gap of the CdO increased up to 2.63 eV. It was clearly seen on the SEM images that CdO covered substrate well and there were no pinholes, voids and cracks.

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