Influence of magnetic field on CdO thin films obtained by electrodeposition

A. KIYAK YILDIRIM
Bilecik Şeyh Edebali University, Bilecik 11210, Turkey

In the current study, the effects of external magnetic field on CdO (cadmium oxide) thin films were investigated in detail. The XRD results showed that the magnetic field has good effects on crystallization. To estimate energy band gap, absorbance measurements were used by employing an UV-vis spectrophotometer. While the band gaps of the films obtained under magnetic field varied between 2.48 eV and 2.57 eV, the band gap of the film obtained without magnetic field was 2.05 eV. It was deduced from the SEM images that surface areas of the films obtained under magnetic field might increase because of the fact that roughness are seen high.

(Received July 11, 2018; accepted February 12, 2019)

Keywords: CdO, Cadmium oxide, Electrodeposition, Magnetic field, Reaction rate

1. Introduction

Over the last years, the nanostructured form of semiconductor nanowires, nanorods, nanobelts and nanotubes has attracted much attention due to their potential applications in various fields and their special physical properties [1]. In these semiconductors, cadmium oxide (CdO) has been used for applications including phototransistors, transparent electrodes, photovoltaic cells, photodiodes, liquid crystal displays, IR detectors, and anti-reflection coats [2].

CdO is a well-known II–VI semiconductor with a direct band gap of 2.2 eV [3] and it exhibits a very high electrical conductivity without doping due to the existence of shallow donors caused by intrinsic interstitial cadmium atoms and oxygen vacancies [1]. Recently, CdO or CdO-based compounds have been prepared by various techniques such as sol–gel, MOCVD, molecular beam epitaxy, spray pyrolysis, PLD, sputter deposition and activated reactive evaporation [4]. Among these methods, electrodeposition is becoming more prominentbecause of the fact that it is used for the growth of metal oxide films from aqueous or non-aqueous solutions. Moreover, the advantages of electrodeposition method also include inexpensiveness, low process temperature, capability of controlling film thickness and morphology of the films [5].

The process of electrodeposition of CdO nanostructures on the ITO (indium tin oxide) coated glass substrate mainly involves the following chemical reactions [6].

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

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

Thermal annealing processes after deposition cause cadmium oxide formation from the cadmium hydroxide [6].

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

Regarding the literature, the effects of the magnetic field on the electrodeposition of ZnO films have been investigated [7] but currently, there are no studies on the effects of the magnetic field on electrodeposition of CdO thin films.

In this study, the external magnetic field was applied during the deposition of the films. It was understood that the magnetic field affected crystallite size, reaction rate and morphologies of the films.

2. Experimental procedure

In this work, we examined the effects of magnetic field on CdO thin films obtained by an IVIUM-vertex electrodeposition device. Electro-deposition cell was utilized for the production of $Cd(OH)_2$ and their composite using a platinum wire as the cathode, a saturated calomel electrode as the reference electrode and an ITO as the anode. The mechanism shown in Fig. 1 was applied in the depositions [7]. Before depositions, both the container and the ITO coated substrates were cleaned with acetone and after then, they were additionally washed with deionized water. The magnetic field was applied perpendicular to the surface of the substrates in the depositions. One deposition was carried out without magnetic field and four depositions were carried out under magnetic field. The frequencies of the magnetic field were adjusted to 25Hz and 50Hz. The depositions were completed in 2700s and the bath temperatures were kept at 70±1ºC. The pH values of the final solutions were adjusted to 5 by decreasing 5%ww hydrochloric acid (HCl). The final solutions were stirred at 600rpm by a stirrer and a heater. After the $Cd(OH)_2$ depositions were readied, samples were annealed by using an oven at 420°C for converting to CdO and then, they were left to cool in air. The summarized conditions of depositions are given in Table 1.

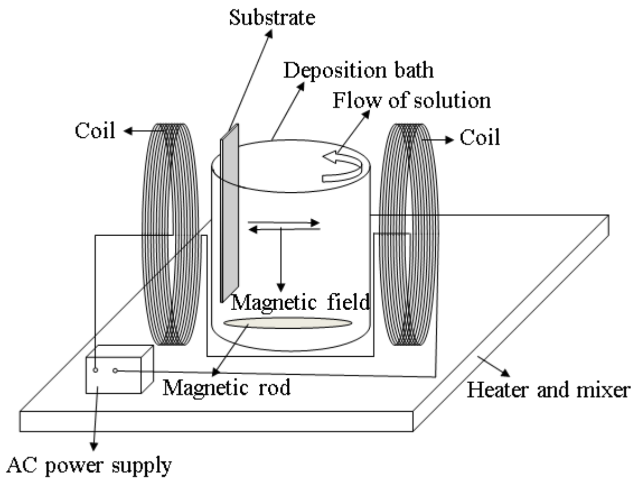

Fig. 1 Shematic illustration of modified electrodeposition system

Table 1. Experimental condition

Experiments	**M0**	**M1**	**M2**	**M3**	**M4**
Concentration (M)	0.01	0.01	0.01	0.01	0.01
Deposition time (sec)	2700	2700	2700	2700	2700
Cathodic potential (V)	-0.71	-0.71	-0.71	-0.71	-0.71
Temperature (°C)	72±1	72±1	72±1	72±1	72±1
Frequency (Hz)	0	25	50	25	50
Magnitude of (mT) Magnetic field	0	3.25	3.25	6.50	6.50

An Unilabteslameter and a PANalytical Empyrean XRD (X-ray diffractometer) were employed for the analysis of the magnitude of the magnetic field and the structural analysis, respectively. JASCO V–530 UV-vis and Zeiss SUPRA 40VP SEM were used for analysing the optical properties and the surface morphologies of the CdO films.

3. Results and discussions

3.1. XRD analysis of the CdO thin films

The current draws were recorded during the depositions and current densities vs. time are given in Fig. 2. The current density of the deposition without magnetic field was nearly $-1.5(\frac{mA}{cm^2})$ while that of the others was nearly $-1.0(\frac{mA}{cm^2})$. The current density decreased as the frequency and the magnitude of the magnetic field were increased. Magnetic field caused magnetic force due to the fact that the final solutions were stirred. It might be stated that the magnetic force caused the ions to scatter and therefore, reaction rate might be decreased.

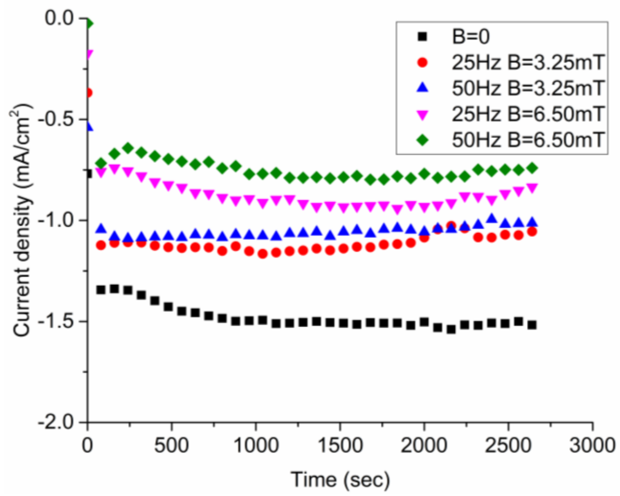

Fig. 2 Current density as a function of magnetic field

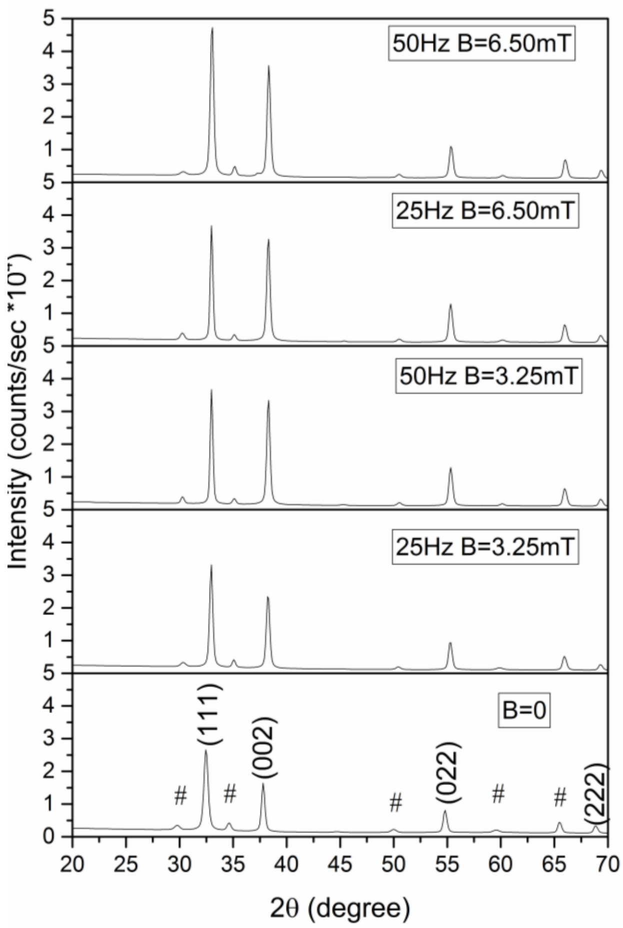

Fig. 3. XRD for CdO thin films

The film thicknesses were calculated by employing the gravimetric method and they are given in Table 2. The thickness of the film obtained without magnetic field was greater than that of the other films. It was concluded that the magnetic field decreased the reaction rate and therefore, the film thicknesses.

Fig. 3 shows the patterns of the XRD and it is seen in Fig 3. that there are two intense peaks of (111) and (002) planes related to cubic CdO. It also attracted attention that although the thicknesses of the films obtained under the magnetic field were lower than that of the film obtained without magnetic field; the peak intensities of the films obtained under the magnetic field were higher than that of the other. This might be due to good crystallization.

The Scherrer equation given in Eq. 4 is used to calculate the crystallite sizes.

$$cs = \frac{0.089 \times 180 \times \lambda}{314 \times \beta \times \cos\theta_C} nm \qquad (4)$$

where β is the (FWHM) full width at the half maximum of peak height (in degrees), λ is the wavelength of X-ray radiation (1.54056 Å) and $2\theta_C$ is the position of the peak centre. The values of β and $2\theta_C$ were calculated by fitting the XRD peak profile to Lorentzian shape [8]. The calculated crystallite sizes are demonstrated in Table 2.

Table 2. Thicknesses, crystallite sizes and band gaps for obtained CdO films

Experiment	M0	M1	M2	M3	M4
Thickness (nm)	983	712	705	686	679
Crystallite size	93nm	64nm	63nm	59nm	57nm
Band gap (eV)	2.05	2.48	2.49	2.55	2.57

As the reaction rate increased, the crystallite size increased. This was an expected result because of the fact that increasing crystal forming rate increases the crystallite size. When the crystallite size of the film obtained without magnetic field was 93nm, the crystallite sizes of the others films varied between 57nm and 64nm. When crystal was growth rapidly, the crystallite sizes were also increased. But, this situation might not be supported by the grain sizes. The only difference of the surfaces could be observed regarding the grain shapes.

3.2. Optical properties of the CdO thin films

UV-VIS spectra of CdO thin films are shown in Fig. 4. The absorbance measurement was performed in a wavelength range between 350nm and 550nm because of the fact that the ITO substrates have a very strong absorbance at wavelength <300 nm [9].

It can be seen in Fig. 4 that when the film was obtained without a magnetic field, it demonstrated absorbance two times higher than that of the other films, on average.

The optical absorption of the film obtained without a magnetic field started to rise at a wavelength of nearly 475nm. On the other hand, the optical absorption spectra of the films obtained under magnetic field started to rise at a wavelength of nearly 440nm. These results indicated that band gaps were shifted by applying a magnetic field.

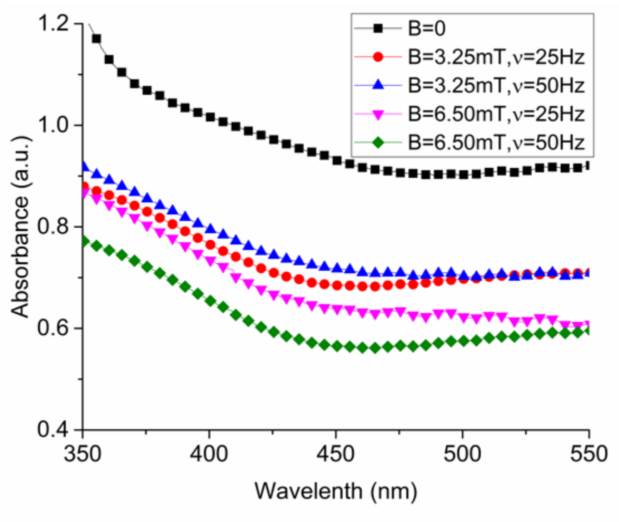

Fig. 4. Absorbance measurements for CdO films

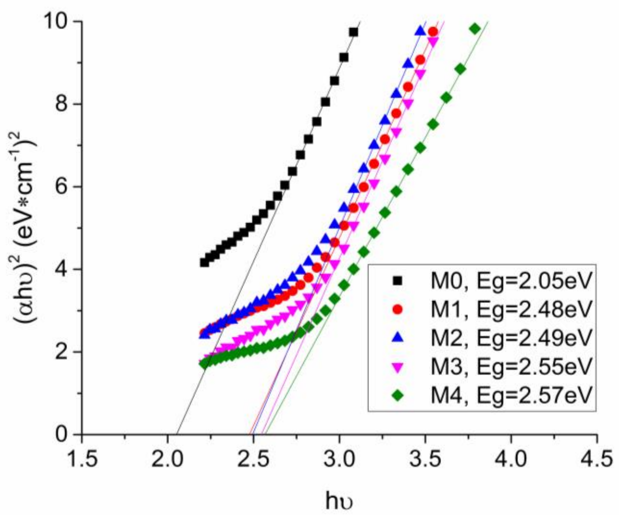

Fig. 5 Direct band gap energy determinations for CdO samples

The optical band gap of the thin films of CdO was estimated by extrapolation of the linear portions of the $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) plots based on the relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (5)$$

where α is the optical absorption coefficient, $h\upsilon$ is the photon energy, A is a constant for a direct transition, and $Eg$is the optical band gap [10-11]. Calculated $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots are given in Fig. 5 and estimated optical energy gaps are given in Table 2. The band gap of the CdO film obtained without magnetic field was 2.05eV. In addition to this, the band gaps of the CdO films obtained under magnetic field varied between 2.48eV and 2.57eV. The most obvious result was that the band gap increased as the magnitude and the frequency of the magnetic field increased. It was concluded that when the magnetic force caused the ions to scatter, reaction rate decreased, and therefore, crystallite size also decreased as expected. The band gap depended on crystallite size strongly.

In the matter, the energy levels of the atom split if the atoms merge for bulk formation. If the crystallite size increases, the number of overlapping of energy levels increases and therefore, conduction and valence bands get larger. When bands get larger, the gap between conduction and valence band gets narrower. Therefore, band gap decreases [12].

3.3. Surface morphology of the CdO thin films

Fig. 6 shows the 50000 times magnified top view SEM images of the cadmium oxide films. Fig. 6a is the SEM image of the film obtained without magnetic field. This surface is the common morphology of the CdO [13]. There are sparse particles on the surface and sizes of these particles are about 400nm. The surfaces are seen in Fig. 6b and 6c resemble each other.

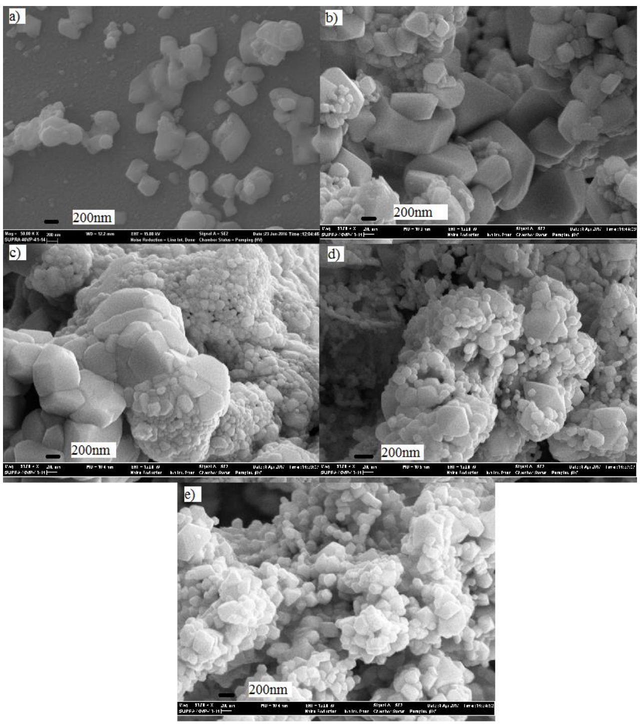

Fig. 6. SEM images of produced CdO films

6b and 6c resemble each other. The surfaces consist of both relatively large particles and relatively small particles having sizes about 800nm and 50nm, respectively. It is shown in Fig. 6d and 6e that the surfaces are formed in grains and the sizes of these grains are nearly 50nm. There is a difference between the surface of the film obtained without magnetic field and the surfaces of the films obtained under magnetic field: The surfaces of the films obtained under magnetic field look cloud-like. This finding may be important due to the fact that the surface area looks increased. It may be useful for anti-reflection coats.

4. Conclusion

In the presented paper, CdO thin films were produced by using the chronoamperometry method of electrodeposition and the effects of the magnetic field were investigated in detail. It was understood from the current densities and the film thicknesses that the magnetic field decreased the reaction rate. Decreasing reaction rate led to good crystallization and reduced the crystallite size from 93nm to 57nm. There was a strong relationship between the crystallite size and the optical band gap. The band gap increased as the crystallite size decreased. Because if the number of atoms increases, the band width increases, and therefore, the band gap decreases. In this study, while the band gap of the film obtained without magnetic field was 2.05 eV which is nearly same with the literature data[14, 15], that of the others varied between 2.48 eV and 2.57 eV. The morphologies of the films were analyzed by the investigation of SEM images. It was concluded that when CdO films were obtained under the magnetic field, it can be reported that the surface area increased. This result might be useful for anti-reflection coats.

References

[1] R. Henríquez, P. Grez, E. Muñoz, E. A. Dalchiele, R. E. Marotti, H. Gómez. Thin Solid Films **520**, 41 (2011).
[2] S. Kondawar, R. Mahore, A. Dahegaonkar, S. Agrawal, Adv. Appl. Sci. Research **2**, 401 (2011).
[3] Z. N. Abdul-Ameer, I. R. Agool, Int. Lett. Chem. Phys. Astron. **63**, 127 (2016).
[4] Z. Q. Liu, R. Guo, G. R. Li, Q. Bu, W. X. Zhao, Y. X. Tong, Electrochim. Acta **59**, 449 (2012).
[5] T. Singh, D. K. Pandya, R. Singh, Mat. Sci. Eng. B **176**, 945 (2011a).
[6] T. Singh, D. K. Pandya, R. Singh, Mater. Chem. Phys. **130**, 1366 (2011b).
[7] B. Altiokka, A. Kiyak Yildirim, Arab. J. Sci. Eng. **41**, 2345 (2016).
[8] R. N. Bhowmik, Nrisimha M. Murty, E. Sekhar Srinadhu, PMC Phys. B **1**, 20 (2008).
[9] W. Y. Gan, K. Chiang, M. Brungs, R. Ama, Int. J. Nanotechnol. **4**, 574 (2007).
[10] J. Rahul, A. K. Verma, R. S. N. Tripathi, S. R. Vishwakarma, Natl. Acad. Sci. Lett., (2012).
[11] S. R. Vishwakarma, R. S. N. Tripathi, A. K. Verma Rahul, Proc. Natl. Acad. Sci. India Sect. A Phy. Sci. **82**, 245 (2012).

[12] A. Kiyak Yildirim, B. Altiokka, Appl. Nanosci. **7**, 513 (2017).
[13] K. Giribabu, R. Suresh, R. Manigandan, A. Stephen, V. Narayanan, J. Iran. Chem. Soc. **10**, 771 (2013).
[14] A. Purohit, S. Chander, M. S. Dhaka, Opt. Mater. **66**, 512 (2017).
[15] A. Purohit, S. Chander, S. L. Patel, K. J. Rangra, M. S. Dhaka, Phys. Lett. A **381**, 1910 (2017).

____

*Corresponding author: ayca.kiyak@bilecik.edu.tr