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EFFECTS OF TEMPERATURE ON CDO FILMS GROWTH BY ELECTRODEPOSITION

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ABSTRACT

This study investigated some physical effects of bath temperature on electrodeposited cadmium oxide thin films. Bath temperatures in the study were 60, 70, and 80 °C. Structural analysis was investigated by using XRD patterns and the analysis revealed that all films were formed in cubic structure. Optical and surface properties of the cadmium oxide thin films were determined by using absorbance measurements and SEM images, respectively. It was understood from the optical properties that the energy band gap of the films were strongly related to bath temperature.

Keywords: CdO, Cadmium oxide, Electrodeposition, Temperature

1. INTRODUCTION

Transparent metal oxide films are important materials for solar cells, chemical sensors, liquid crystal displays, and nano-porous films [1]. Among various metal oxides, cadmium oxide (CdO) is an important n-type semiconductor metal oxide, which belongs to the II–VI group with large energy band gap, high transmission in the visible region, and low electrical resistivity. Due to these properties, it has been widely investigated in various fields such as photovoltaic cells and transparent electrodes [2]. CdO films can be fabricated by using many techniques such as spray pyrolysis, chemical vapor deposition (CVD), thermal evaporation, sputtering and electrodeposition, andsol gel. Among these techniques, the electrodeposition presents a simple, cheap, and quick method for the synthesis of CdO nanostructure [3].

The electrodeposition takes place on the surface of indium tin oxide (ITO) and the possible formation mechanism of CdO is suggested as follows [4, 5].

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{1}$$
$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2 \tag{2}$$

When the samples are annealed and the annealing temperature exceeds 280°C, the Eq. 3 takes place [4].

$$Cd(OH)_2 \rightarrow CdO + H_2O \tag{3}$$

Various techniques have been carried out so far [6, 7].Besides, there is one study related to the electrodeposition of CdO film at a relatively high temperature such as 90°C [8]. But there is no study conducted at 80 °C.

In this study, effects of bath temperature on structural, optical, and morphological properties of the CdO thin films were researched. The temperature varied between 60 and 80 °C. The good crystalline film was obtained at 70 and especially 80 °C. When the film was obtained at 80 °C, the transmittance increased about two times more than the other films. The expected value of the band gaps of the films obtained at 60 and 70 °C were 2,25 and 2,33 eV, respectively, but when the film was produced at 80

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°C, the band gap increased significantly. When SEM images were investigated, it was found out that there were no cracks, voids, and pinholes.

2. EXPERIMENTAL PROCEDURE

Thin films of CdO were produced by electrodeposition. Chronoamperometry method of electrodeposition was used for depositing films. The three electrodes used for electrodeposition were; calomel reference electrodes, platinum wire, and ITO as the working electrode. Before the depositions, ITO coated glass substrates and electrochemical cell was washed by using acetone, and thereafter, deionized water. After the washing, they were left to dry at room conditions. The bath temperatures varied from 60 °C to 80 °C and the effects of the temperature were investigated. 100 mL 0,02M $Cd(NO_3)_2$ were prepared and $Cd(OH)_2$ was precipitated to ITO coated glass substrates from this electrolyte. After the depositions, Cd(OH)2 films were annealed at 400 °C by using an oven to obtain CdO thin films. All depositions were completed in 2500 s.

Crystallographic properties of the samples were examined by an X-ray diffractometer named PANalytical empyrean. Optical properties were analyzed by using absorbance measurement obtained witha UV-VIS spectrophotometer named JASCO V–530. A Zeiss supra 40VP SEM device was employed to search surface properties.

3. RESULTS AND DISCUSSIONS

3.1. Structural Analysis of the CdO Thin Films

The thicknesses of the films were measured by using gravimetric method. The thicknesses of all films were measured as about 400 nm.

Figure 1 shows the XRD patterns of the thin films of CdO. The XRD patterns, which were investigated to determine crystal properties, showed that all films were formed in the structure of cubic shape. There were two peaks, namely (111) and (002) plane according to card no 98-062-0205. The peak intensity increased parallel to the increase in bath temperature. This result might have two reasons: First, the film thickness might have been bigger than that of the others. But the film thickness for each sample was nearly the same. Hence, this rules out the first option. Second, the reason may be good crystallization effect.

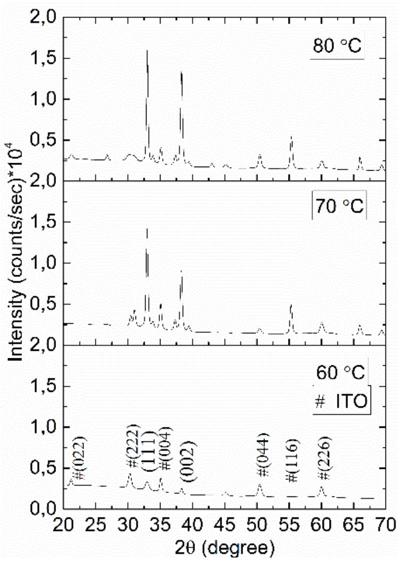

Figure 1. The XRD patterns of the CdO samples

The texture coefficient (TC) was used to determine preferred orientation which is given in Equation 4.

$$TC = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N}\sum_N\left(\frac{I_{(hkl)}}{I_{0(hkl)}}\right)} \quad (4)$$

where I(hkl) is the relative intensity of a plane (hkl), I_0(hkl) is the standard intensity of the plane (hkl) which is given in ASTM card [9]. The calculated texture coefficients were given in Table 1. When Table 1 is analyzed, it is observed that preferred orientation of the films obtained at 60 and 70 °C are (111) plane. On the other hand, there are two preferred orientation of the film obtained at 80 °C.

Table 1. Texture coefficients of the CdO films

Experiments	60°C	70°C	80°C
T.C.(111)	1,41	1,49	1,23
T.C.(002)	0,87	0,92	1,02

Crystallite sizes of the samples were calculated referring to the equation of Debye Scherrer given in Eq. 5.

$$cs = \frac{0.089*180*\lambda}{314*\beta*cos\theta_C}nm \quad (5)$$

Where λis the wavelength of radiation of X-ray (1.54056 Å), cs is the crystallite size, $2\theta_C$ is the position of peak center, β is the full width at the half maximum of peak height (in degrees) [10, 11]. The calculated crystallite sizes of the films obtained at 60, 70, and 80 °C are 65, 59, and 37 nm, respectively. It is concluded that the crystallite sizes might be affected by varying reaction rate.

3.2. Optical properties of the samples

The absorbance measurements are given in Fig.2. According to Fig.2, absorbance decreases as the bath temperature increases. This might be the result of good crystallization or low surface roughness.

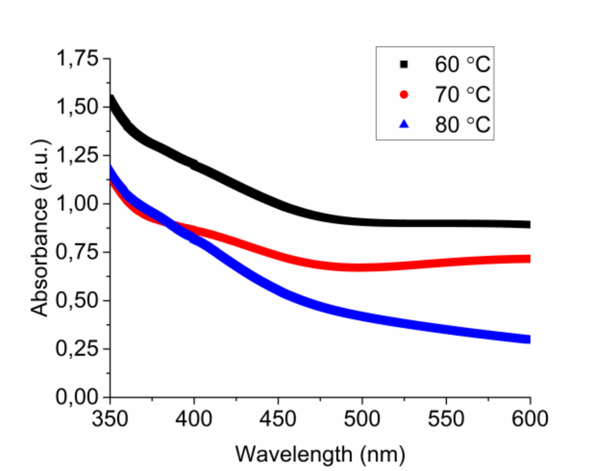

Figure 2. Absorbance values of the CdO films

The transmittance values were calculated from absorbance measurements and they are given in Fig. 3. It is clearly seen from Fig. 3 that transmittance increases in line with the increase in bath temperature.

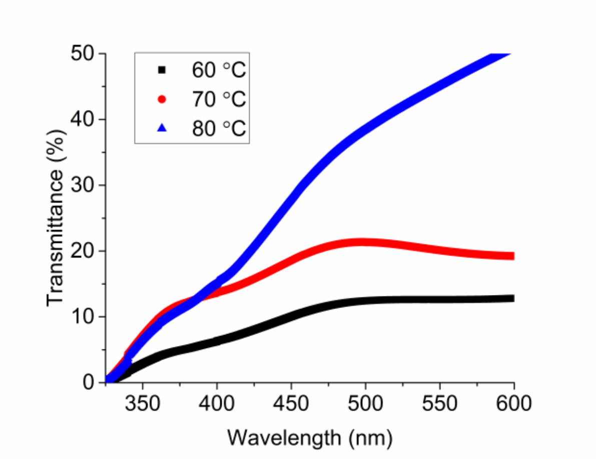

Figure 3. Transmittance values of the CdO films

The energy band gaps were estimated by using Tauc plots given in Equation 6.

$$(\boldsymbol{\alpha h \nu})^2 = \mathbf{A}(\mathbf{h\nu} - \mathbf{E_g}) \qquad (6)$$

where hν is photon energy and A is a constant. The straight-line portion of the curve extrapolates to zero and this and this enables us to guess the band gap energy [12, 13].

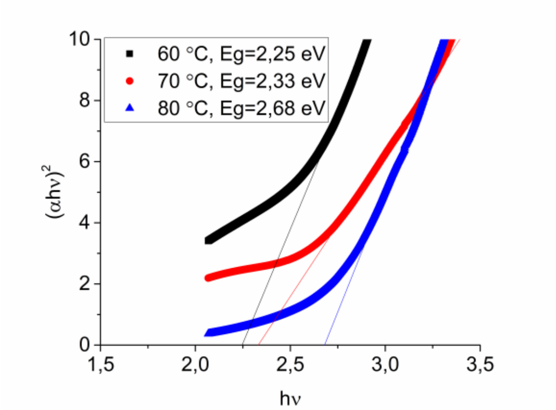

Figure 4. Tauc plots and estimated band gaps of the CdO samples

The band gaps varied between 2,25 and 2,68 eV depending on the bath temperature. The bath temperature affects the crystallite size. And these results are observed as a consequence of the effect of crystallite size on band gap.

3.3. Morphologic properties of the samples

Fig. 5 shows the surface images of the CdO thin films. It is clearly seen from Fig. 5 that there are no voids, cracks, and pinholes. Besides, all surfaces seem compact and dense. On the surface of the film obtained at 60 °C, there are plenty of polymorphic particles, and therefore, there is high surface roughness. This image explains high absorbance and low transmittance. On the other hand, there are pyramidal forms of CdO on the surface of the film obtained at 80 °C.

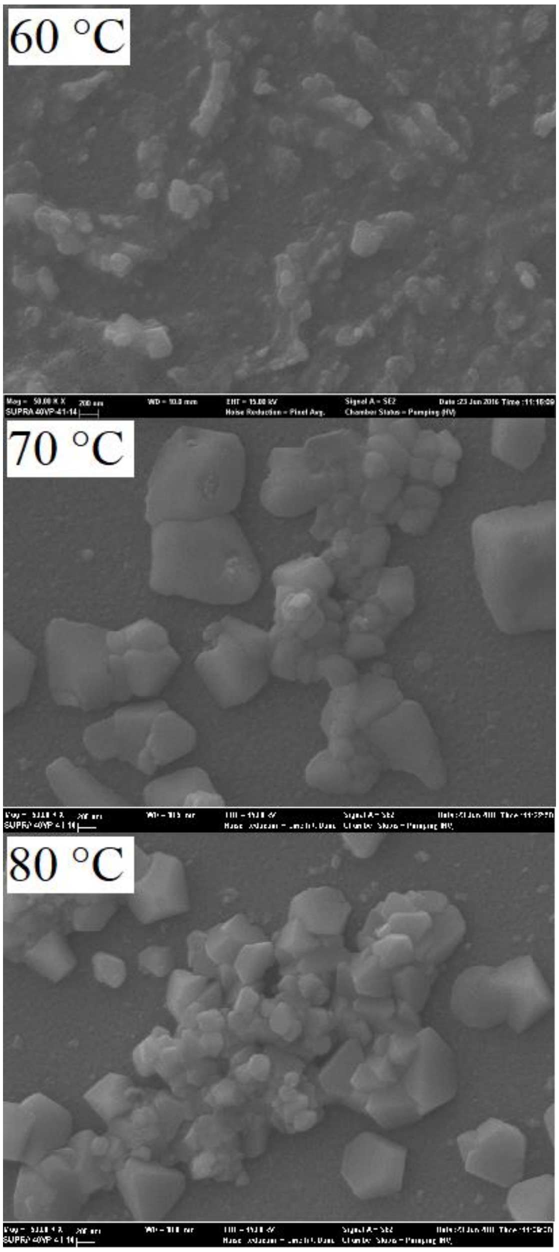

Figure 5. Magnified 50000 times surface images.

4. CONCLUSIONS

This study presents the effects of bath temperature, which varied between 60 and 80 °C, on electrodeposited CdO thin films. It is observed that when the bath temperature increases, the crystallization also increases. While the thicknesses are nearly the same, the peak intensities are relatively high. It is concluded that this outcome have resulted from good crystallization. It is exposed that the optical band gap depends on the solution temperature. It is also concluded that the bath temperature may affect the crystal forming rate, and therefore, the crystallite size. The band gaps of the films varied between 2,25 and 2,68 eV. The band gap and the crystallite size are strongly associated with each other. The surfaces of the films are investigated by SEM images and the SEM images showed no pinholes, voids, and cracks.

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