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Research Article

The Effect of Thickness Difference on the Structural Morphological and Optical Properties of CdO Films Produced with the SILAR Method at Room Temperature

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Abstract

In this study, CdO thin films were grown on glass substrates with SILAR technique at different thicknesses at room temperature. The thin films were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV vis spectrophotometer. SEM images showed that the surface morphology of CdO thin films changed with the change in thickness. XRD results showed that all the samples had a cubic structure and the intensity of the peaks changed with the change in the number of cycles. Optical absorption measurements showed that the increase in thickness caused by the varied number of deposition cycles enlarged the band gap, and these values changed from 2.2 eV to 2.7 eV.

Keywords: SILAR, thickness effect, CdO, thin film

Oda Sıcaklığında SILAR Tekniği İle Üretilen CdO Filmlerinin Kalınlık Farkının Optik Yapısal ve Morfolojik Özellikleri Üzerindeki Etkisi

Öz

Bu çalışmada CdO ince filmleri cam altlıklar üzerine SILAR tekniği ile oda sıcaklığında farklı kalınlıklarda büyütüldü. Elde edilen ince filmlerin taramalı elektron mikroskobu (SEM), X-ışını difraksiyonu (XRD) ve UV vis spektrofotometrede ölçümleri alınarak incelendi. SEM görüntüleri CdO ince filmlerinin yüzey morfolojisinin kalınlık değişimi ile değiştiğini göstermiştir. XRD sonuçları büyütülen tüm numunelerin kübik yapıya sahip olduğunu ve tur sayısının değişimi ile piklerin şiddetlerinin değişim sergilediğini göstermiştir. Alınan optik soğurma ölçümleri ise tur sayısının artmasına bağlı olarak artan kalınlık miktarının band aralığını arttırdığını ve bu değerlerin 2.2 eV'den 2.7 eV'e kadar değiştiğini göstermiştir.

Anahtar kelimler: SILAR, kalınlık etkisi, ince film,CdO

1. Introduction

Researchers have focused their efforts in recent years on semiconductor thin films due to their capacity to exhibit a variety of structural morphologies and an electronic structure that can act as an insulator, metal, or semiconductor. Zinc oxide (ZnO), copper oxide (CuO), tin oxide (SnO_2), and cadmium oxide (CdO_2) are some well-known transparent conductive oxide films (CdO). (Kabir et al., 2021)

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Transparent conductive oxide films have high-tech applications in the field of optoelectronics and other solid-state devices (Balu et al., 2012). Due to the nature of electrical conductivity and optical transmission, transparent conductive oxides (TCO's) have been used in many technological applications, such as photovoltaic devices, flat panel display and smart windows (Şakar et al., 2021).

SnO_2, ZnO, InO_2, ITO, FTO and CdO oxide varieties are used as transparent electrodes in solar cells and other electronic components (Gurumurugan et al., 1994).CdO, which is one of the II-VI group semiconductors, is one of the most promising transparent conductive oxides, which has a high absorption and radiation emission capacity with a forbidden energy range of 2.2-2.7 eV (Roy, 1969). In the past few years, researchers have focused on CdO semiconductor materials, especially in the field of optoelectronic devices such as solar cells (Carballeda-Galicia et al., 2000; Hameş and San, 2004).However, most of its physical properties have been found to depend on preparation methods and conditions (Chug et al., 2015).

Many techniques such as DC magnetron reactive sputtering (Subramaniyam et al., 1997), Metal-Organic Chemical Vapor Deposition (Li et al., 2004; Ellis and Irvine, 2004), vacuum evaporation (Dakhel, 2009), electrochemical deposition (Chang et al.,2007), Pulsed Laser Deposition (Gupta et al.,2008), spray pyrolysis (Salunkhe et al.,2009), electron beam evaporation (Ali et al.,2009), Chemical Vapor Deposition (Cullity, 1956), sol-gel technique (Aksoy et al.,2009), Chemical Bath Deposition (de León-Gutiérrez et al.,2006; Ocampo et al.,1993) and Sequential Ionic Layer Adsorption and Reaction (SILAR) (Salunkhe et al.,2009) have been used in order to prepare CdO thin films.SILAR has a number of advantages over the other techniques, including low cost, simplicity, and repeatability. It also supports controlling deposition parameters including pH, temperature, and time. The only drawback of this method is the generation of hydroxide during oxide growth and the slow pace of growth (Gokul et al., 2013).

In this study, CdO thin films with different thicknesses in different cycles were prepared by the SILAR method and the structural, morphological and optical properties of CdO thin films were investigated according to the changes in the thickness values of the thin films.

2. Materials and Methods

The SILAR approach was utilized to manufacture a pure CdO thin film at room temperature and in an atmospheric environment using a glass lamella substrate as the basis material. The glass lamella were soaked in a 5 percent sulfuric acid solution for 5 minutes before being cleaned in an ultrasonic bath, then repeated for 5 minutes with deionized water (DI). It was left to dry at room temperature after ultrasonic cleaning. As shown in figure 1, two different solutions, anionic and cationic, were prepared in accordance with the SILAR technique (Albayrak et al., 2019). In the anionic solution, a DI solution adjusted to pH 11.5 with ammonium hydroxide (NH_4OH) was used. In the cationic solution, 0.1 M cadmium nitrate ($Cd(NO_3)_2 + 4H_2O$) solution in DI was used as Cd^{+2} source.

In order to examine the effect of the number of SILAR cycles, 6 50 ml ammonium hydroxide solutions at pH 11.5 were prepared. These prepared solutions were mixed with a magnetic stirrer and homogenized. In order to obtain CdO semiconductor thin films of different thicknesses, the experiment was carried out with 5-10-15-25-30-35 cycles of SILAR cycles.

In order to ensure the accumulation of Cd^{+2} ions on the surface, glass substrates were immersed in the cationic solution for 30 seconds. Afterwards, the substrates were immersed in the anionic solution for 30 seconds to allow Cd^{+2} ions and OH^{-1} ions to come together and form $Cd(OH)_2$. In the experiment, CdO thin films were enlarged in cycles of 5-15-20-25-30-35 at room temperature.

The obtained samples were annealed at 200 ^{0}C for 1 hour to transform the Cd(OH)2 structure into CdO thin films. Then, in order to examine the surface properties of these samples, SEM measurement with Zeiss-Sigma300 device, XRD measurement with PANalytical Empyrean X-Ray diffractometer and permeability and absorption results with Shimadzu UV-1800 Spectrophotometer device were observed.

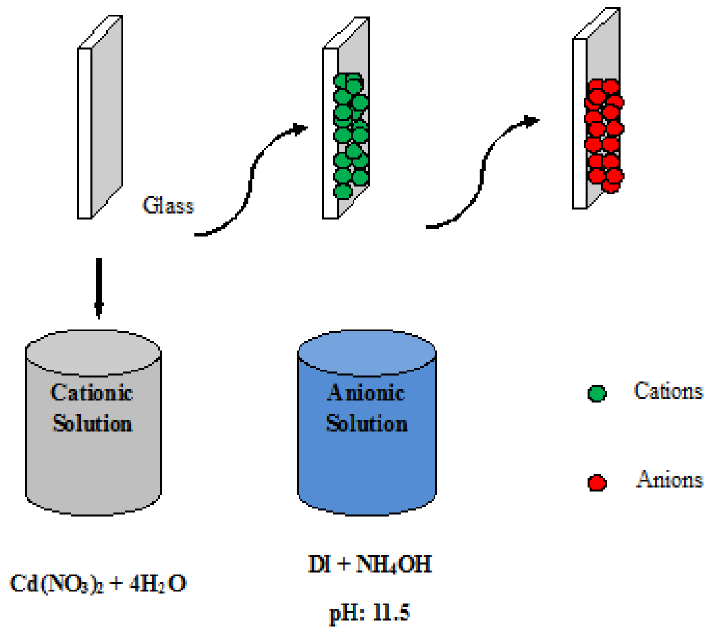

Figure 1. Representative experimental setup of the SILAR technique

3. Results and Discussion

The SILAR method was used to deposit CdO thin films of various cycles and thicknesses on a glass substrate at a pH of 11.5 in the tests. The thickness of the CdO thin films obtained with 5-15-20-25-30-35 cycles grew in direct proportion to the number of cycles in the experiment, especially in the solution. Figure 2 shows the pictures of the grown samples after annealing.

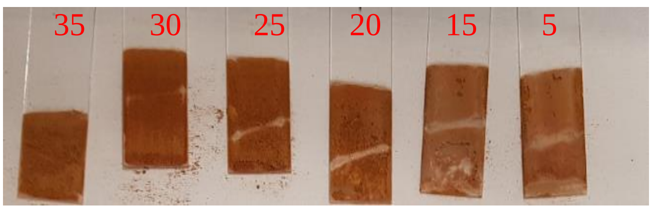

Figure 2. CdO thin films obtained in different thicknesses with different cycles

After using Equation 1 to compute the thickness of the CdO thin films, the calculated thickness values are listed in Table 1. (Bulakhe et al., 2013).

$$T = \frac{M}{\rho\, A} \quad (1)$$

In this equation, ρ is density and the unit is gr/cm^3, M is mass and the unit is g, and A is the surface area of the base material, with its unit being cm^2.

Table 1. Thicknesses of CdO thin films obtained at pH 11.5

Sample	Number of cycles	Thickness (nm)
1	5	182
2	15	585
3	20	950
4	25	1183
5	30	1504
6	35	2655

The number of cycles grew in direct proportion to the thickness of the CdO thin films produced on the glass substrate at pH 11.5, as shown in Table 1. Figure 3 illustrates the results of XRD measurements on CdO thin films. The peaks in the XRD patterns obtained after annealing are consistent with the conventional CdO cubic structural pattern. The peaks in the XRD patterns demonstrate that annealing causes changes in the plane peak intensities in the crystal structure of the films (Astam, 2017; Aydin and Sahin, 2017).

XRD Analysis

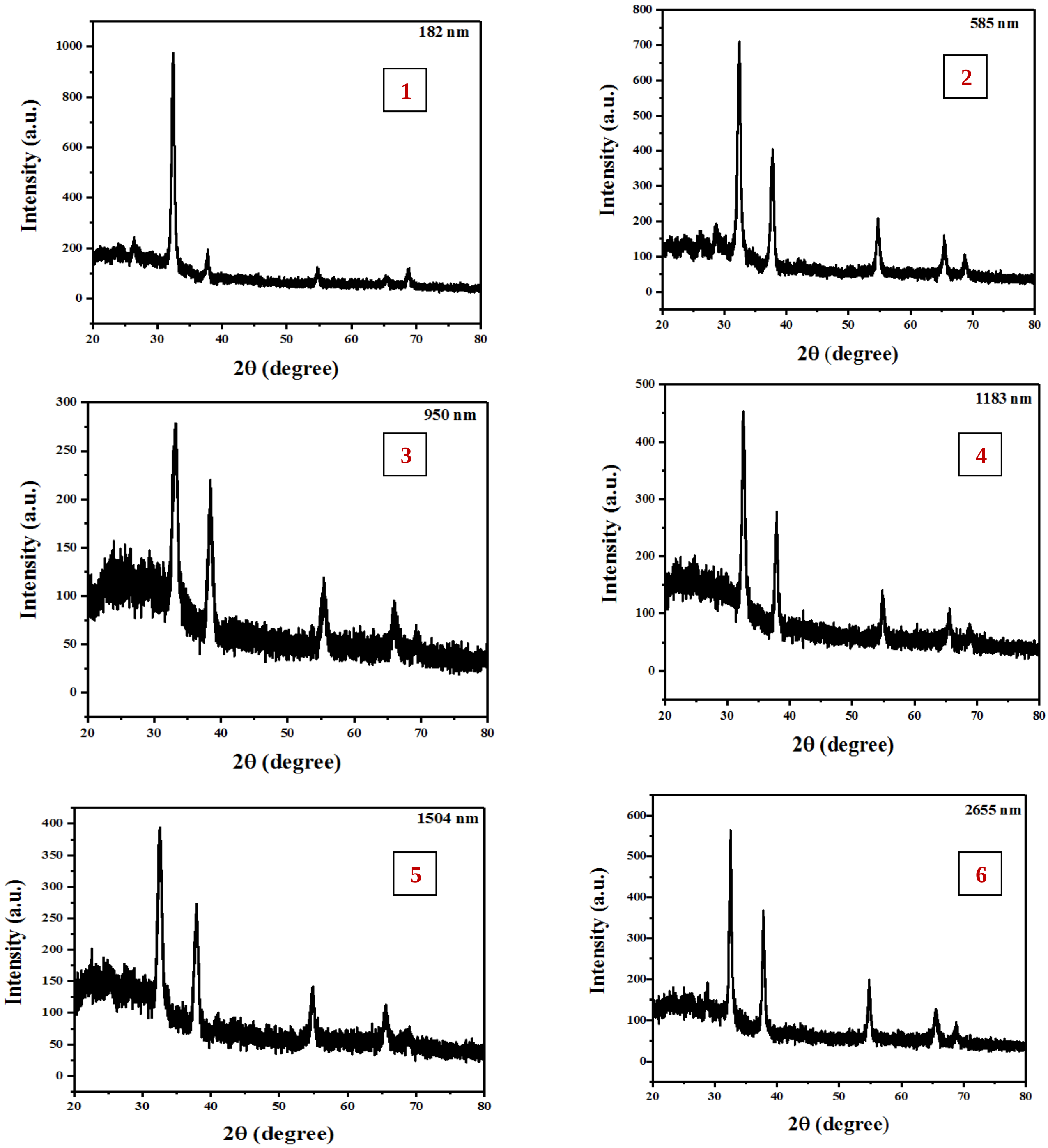

Figure 3. XRD plots of CdO thin films obtained with variable number of turns at pH 11.5

The crystal orientations of the samples had angles of approximately 33˚, 38˚, 55˚, 66˚, and planes of (111), (200), (220), and (311), as seen in the graphs in figure 3. According to the JCPDS Card no: 05-0640, the CdO thin films obtained with these data exhibited a polycrystalline cubic structure (Çavuşoglu, 2018, Çavuşoğlu et al., 2019).

It was calculated how the average particle size of the CdO thin films formed after annealing changed using Scherer's equation and XRD measurements indicated in Equation 2. Scherrer's relationship is as follows (Aydin et al., 2016):

$$D = \frac{0{,}94\,\lambda}{\beta\,\cos\theta} \tag{2}$$

D is the particle size, λ is the X ray wavelength (1.5405), β represents half the width of the maximum peak value in the XRD pattern (FWHM), and θ is half the angle value of the abrupt increase in the XRD pattern in this equation (Anwar and Mishra, 2015). The grain size values of the samples were computed using Equation 2 for the main peak, the (111) plane, and are listed in Table 2.

Table 2. Calculated thickness, and the observed 2θ, FWHM and D values in the (111) plane for the obtained CdO thin films.

Sample	**Number of Cycles**	**Thickness (nm)**	**FWHM**	**Observed D(nm)**	**Observed 2θ (^{O})**
1	5	182	0.612	24.66	32.44
2	15	585	0.700	21.55	32.32
3	20	950	1.226	12.30	33.16
4	25	1183	1.116	13.52	32.60
5	30	1504	0.974	15.50	32.54
6	35	2655	0.563	26.80	32.54

Table 2 shows how the D values of thin films fluctuate as the number of cycles increases. This variation was due to the change in thickness values as the number of cycles increased. This shows that the thickness difference in the samples had an effect on the surface morphology of the CdO films (Güney and İskenderoğlu, 2017).

SEM Images

SEM images were acquired to see the effect of the thickness values of the obtained CdO thin films on the surface changes, as well as to observe the importance of surface morphology, which has an effect on the optical, electronic, sensory, and other properties of a material. From the SEM images, it was noticed that the surface morphology had changed. The CdO thin film surfaces of various thicknesses were rough, and agglomeration occured as a result of small particles colliding in spots, as seen in SEM pictures. The small particle size and high surface energy are thought to be the cause of these agglomerations (Li et al., 1999).

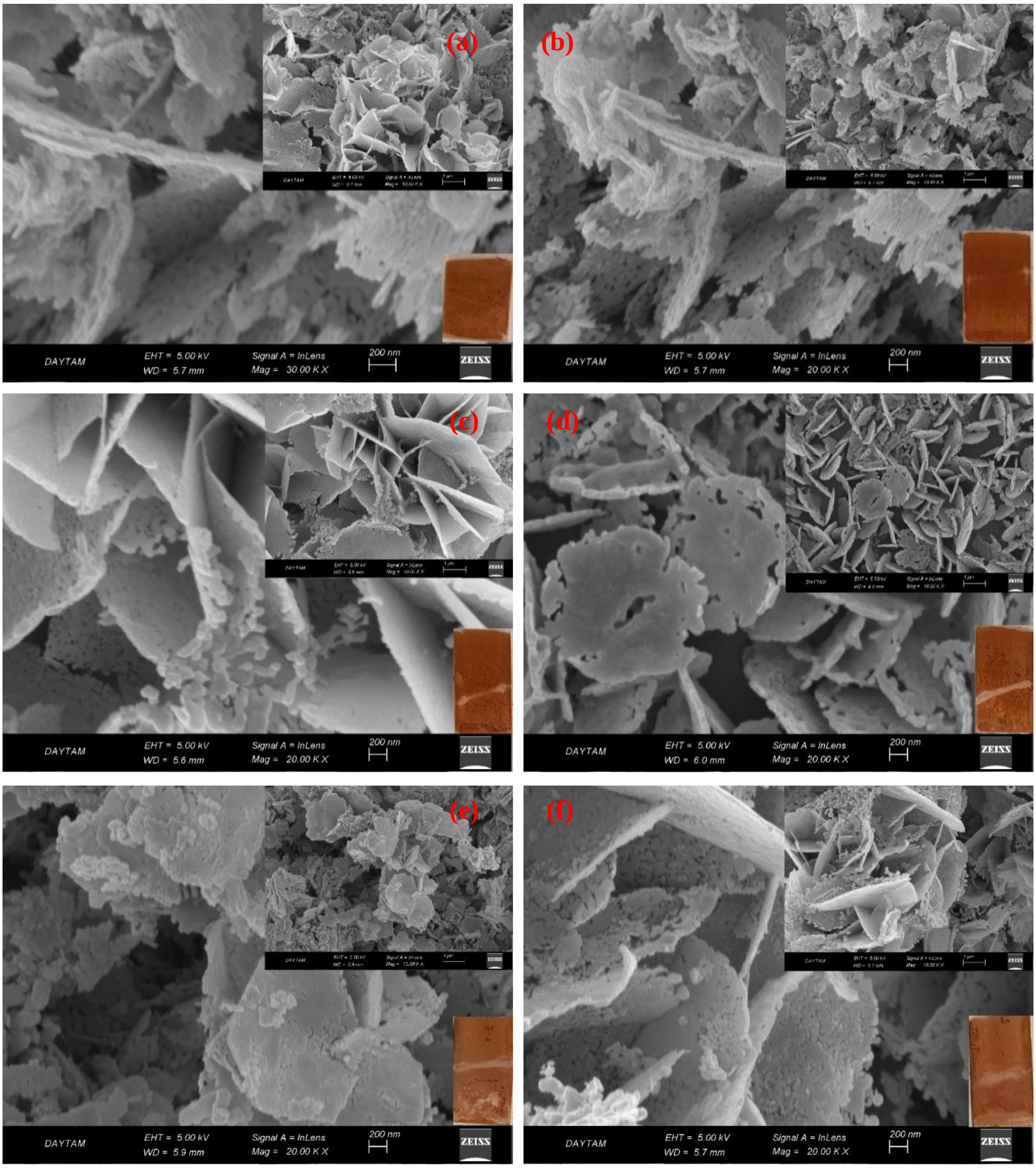

Figure 4. SEM images of CdO thin films obtained with a varying number of cycles

Optical Properties

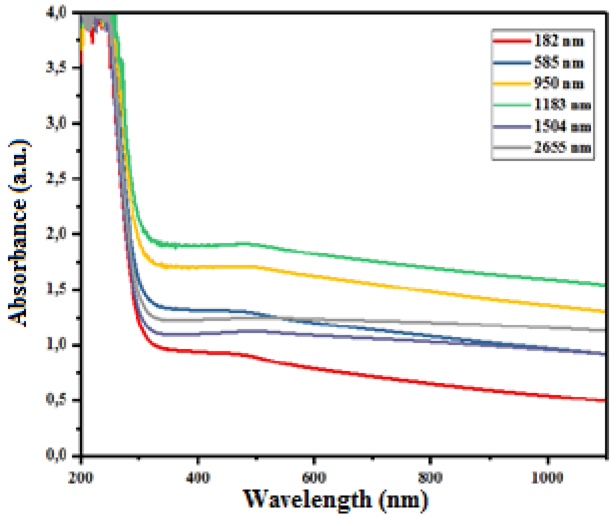

Figure 5. Absorption plots of CdO thin films obtained with variable number of cycles

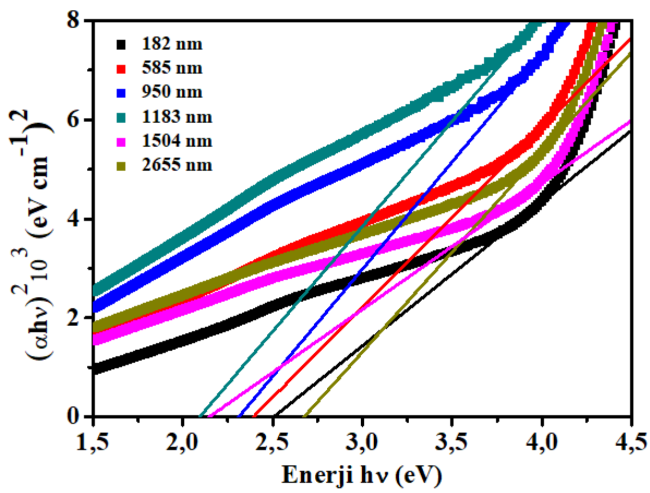

Figure 6. Band gap graphs of CdO thin films obtained with variable number of cycles

The absorption measurements of the samples were taken and presented in Figure 5. The absorption band edges of the samples grew substantially, as shown in the absorption graph. This demonstrated that the samples crystal structures were good. The graphs of the band gaps were drawn based on the absorption measurements in order to see how the band gaps changed with the variation in sample thickness.

Relationship between forbidden energy gaps (Eg) and absorption coefficients (α) of materials are given as follows (Pankove,1971);

$$\alpha = \frac{A\left(h\nu - E_g\right)^{1/2}}{h\nu} \tag{3}$$

For direct transitions, A is an independent constant, hν is the photon energy, and n is ½ in this equation. The direct forbidden energy gap of the materials may be calculated by extending the linear region of the graph $(\alpha h\nu)^2$–hν to the x-axis at α=0, according to this expression. Figure 6 displays $(\alpha h\nu)^2$–hν graphs for the CdO thin films that were formed, which were drawn from optical absorption measurements after annealing. The band gaps tend to decrease from 2.5 eV to 2.2 eV as the thin film thickness grows and then increase after the thin film thickness of 1504 nm.

4. Conclusion

In this study, undoped CdO samples were grown on the glass substrate with gradually increasing 5-10-15-25-30-35 cycles numbers. It was examined how the change in thickness values of these grown samples affected the structural, morphological and optical properties of the CdO thin film. The angles exhibited in the XRD patterns that correspond to their orientation in the planes (111), (200), (220), (311), (222) are generally compatible with CdO in the cubic structure. As a result of this outcome, the band gaps of the samples can be modified to the desired values depending on the application's purpose. However, this can only be done within certain limits. Furthermore, the surface shape was shown to alter with the number of cycles. Thin films have been discovered to have strong physical properties with their band gaps, making them ideal for solar cells and other opto-electronic applications.

Ethics in Publishing

There are no ethical issues regarding the publication of this study

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