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Effect of Molar Concentration on Structural, Morphological and Optical Properties of CdO Thin Films Prepared by Chemical Bath Deposition Method

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ABSTRACT: Cadmium Oxide (CdO) thin films were grown on Indium Tin Oxide (ITO) coated glasses by Chemical Bath Deposition (CBD) technique. The concentration of aqueous bath was varied between 0.03 M and 0.05 M. The films were annealed at 400 °C for 2 h. Structural, morphological and optical properties of the CdO thin films were investigated with XRD, SEM and Uv-Vis measurements. Additionally, the hydrophobic and hydrophilic nature of the films were studied with the water contact angle (WCA) measurements. The CdO thin films showed cubic crystal phase diffraction peaks in the spectra. The surface of CdO thin films changed from prism-like morphology to network-like (nano-fibrous) morphology with increasing concentration. The optical band gaps of thin films were calculated between 3.816-3.857 eV by Uv-Vis spectra. The Prisma- like morphology exhibited maximum transmittance above 65%. Nature of the CdO thin film surface changed from hydrophobic to hydrophilic, depending on changing morphology with increasing the precursor concentration.

Keywords: Cadmium Oxide, Chemical Bath Deposition, the Effect of Concentration.

Kimyasal Banyo Biriktirme Metodu ile hazırlanmış CdO İnce Filmlerin Yapısal, Morfolojik ve Optik Özellikleri Üzerinde Molar Konsantrasyonu Etkisi

ÖZET: Kadmiyum Oksit (CdO) ince filmler, farklı konsantrasyonlardaki solüsyonlar kullanılarak İndiyum Kalay Oksit (ITO) kaplamalı camlar üzerine Kimyasal Banyo Biriktirme (CBD) yöntemi ile sentezlenmiştir. $CdCl_2$'nin sulu banyosunun konsantrasyonu 0.03 M ile 0.05 M arasında değişmektedir. Filmler 400 °C 'de 2 saat tavlanmıştır. CdO ince filmlerin yapısal, morfolojik ve optik özellikleri araştırılmıştır. Ek olarak, filmlerin hidrofobik ve hidrofilik yapısı, su temas açısı (WCA) ölçümleriyle çalışılmıştır. Bütün filmler kübik kristal yapıdan elde edilmiş, ancak ince filmlerin yüzey morfolojisi artan konsantrasyon ile, prizma benzeri yapılardan ağsı (nano lifli) yapılara dönüşmüştür. Optik bant boşluğu Uv-Vis spektrumları kullanılarak değerleri 3.816-3.857 eV aralığında hesaplanmıştır. Prizma benzeri morfoloji %65 üzerinde maximum geçirgenlik göstermiştir. Konsantrasyonun artmasıyla, CdO ince filmlerin yüzey doğası, morfolojide meydana gelen değişikliklere bağlı olarak hidrofobik yapıdan hidrofilik yapıya dönüşmüştür.

Anahtar Kelimeler: Kadmiyum Oksit, Kimyasal Banyo Biriktirme, Konsantrasyon Etkisi

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INTRODUCTION

CdO has used some applications due to having unique electrical and optical properties depending on vacancies and crystal structure such as wide bandgap (2.5 eV direct and 1.98 eV indirect), high transparency in the visible and near infrared rays (NIR) (Jung et al., 2014; Ahmed, 2017). It is one of TCO, II-IV group metal oxide semiconductor with FCC Bravais lattice cubic crystal structure which makes it similar to the NaCl crystal structure (Ahmed, 2017). CdO structures can be synthesized by several methods such as spin coating (Thambidurai et al., 2015), solvothermal synthesis (Ghosh and Rao, 2004), spray pyrolysis (Usharani et al., 2015), chemical bath deposition (Bulakhe and Lokhande, 2014). Among them, the CBD method is very easy, low cost, large area and repeatable technique (Morkoç Karadeniz et al., 2016).

In this paper, it was reported that thin films in form of CdO were synthesized by using simple CBD method at different precursor concentrations. Effect of the precursor concentration on structural, morphological and optical properties of the CdO thin films was investigated.

MATERIALS AND METHODS

In the present study, CdO thin films were grown on clean ITO substrates in the bath with 0.03, 0.04 and 0.05 M concentration. The bath was prepared using Cadmium Chloride ($CdCl_2$), Ammonia Hydroxide (NH_4OH- 26% NH_3 in H_2O) chemical compounds and distilled water. After mixing $CdCl_2$ and distilled water (50 ml) for ten minutes, NH_4OH was dropped slowly in the bath until getting a clear solution (9-10 pH). The ITO substrates were cleaned with methanol and deionized water in an ultrasonic cleaner for ten minutes respectively. Then, the substrates were dried at 100 °C for 1 hour in an air oven. The clean ITOs were immersed in the bath for 4 days at the room temperature. The as-deposited $Cd(OH)_2$ films were dried at 100 °C for 15-20 min. The reaction of CBD synthesis was given as follow;

$$CdCl_2 + 2NH_4OH \longrightarrow Cd(OH)_2 + 2NH_4Cl \quad (1)$$

Then, the samples were annealed at 400 °C for 2 hours to obtain the CdO thin films. The white $Cd(OH)_2$ thin films converted to brown CdO thin films with an annealing process. The crystal structures of the films were studied using a Panalytical Empyrean X-Ray diffractometers (XRD) measurements operated at 45 kV, 40 mA with CuKα radiation (λ = 1.5406 Å). The morphological properties of the films were studied using an FEI Inspect S50 Model Scanning Electron Microscopy (SEM). The optical properties of the thin films were studied using a PerkinElmer Lambda-35 Ultraviolet-Visible Spectrophotometer (Uv-Vis) and the water contact angles of the thin films were observed using an Optical Tensiometer (Attension, Theta Lite) method.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of the CdO thin films. The XRD peaks were in good agreement with the cubic CdO crystal system with (111) preferential orientation (Morkoç Karadeniz et al., 2016; Güney and İskenderoğlu, 2019).

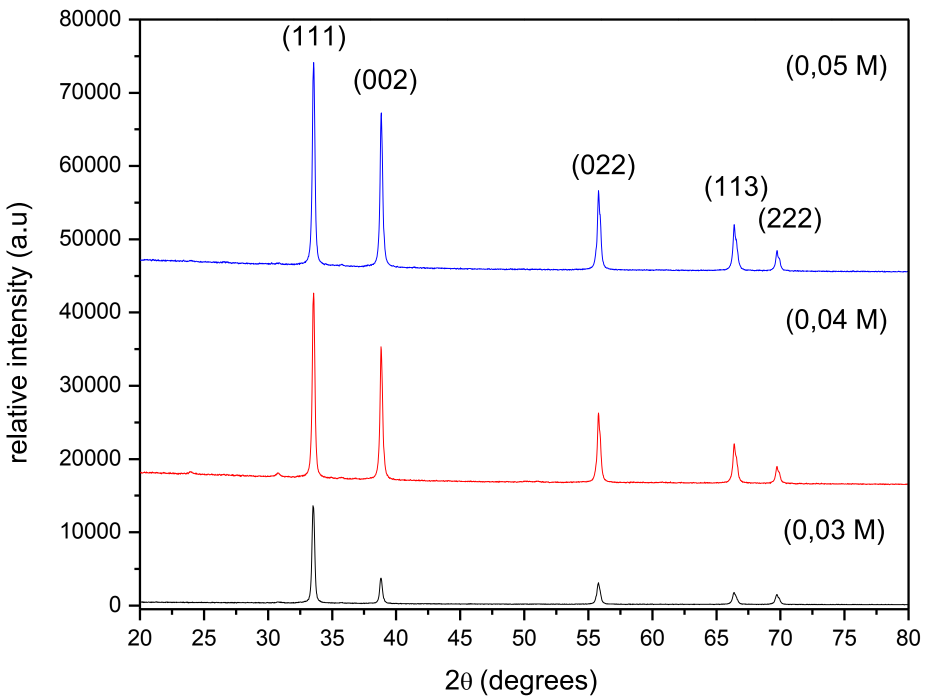

Figure 1. XRD spectra of the CdO thin films

The (002), (022), (113), (222) peaks also emerged in the fig.1 (JCPDS file No. 05-0640). The crystallinity of the thin film was improved with increasing concentration. The quantitative improvement in the crystallinity can be understood from the calculation of the grain size (*D*) using Scherrer's formula is given as Equation 1;

$$D = 0.9\lambda \,/\, \beta cos\theta \qquad (1)$$

where λ is the x-ray wavelength (1.5406 Å for CuKα), θ is the diffraction angle and β is the full width half maximum (FWHM). XRD parameters of the films are given in Table 1.

Table 1. XRD parameters of the CdO thin films

Concentration (M)	2 θ°	d-spacing Å	a (Å)	FWHM	D (nm)
0.03	33.2224	2.69675	4.67077	0.205	42
0.04	33.5141	2.67174	4.62745	0.183	47
0.05	33.5185	2.67139	4.62648	0.178	48

Figure 2 shows SEM images of the CdO thin films. In previous studies, it was obtained CdO nanoplates for 0.1 M concentration with 12 pH on glass substrates (Bulakhe and Lokhande, 2014) and CdO nanolayers for 0.03 M concentration with 9-10 pH on ITO substrates (Morkoç Karadeniz et al., 2016) in the same bath for different conditions. In the present study, prism-like morphology with porous was obtained for 0.03 M concentration in the bath. Then, network-like (nano-fibrous) structures were grown on the prism-like structures with increasing precursor concentration (0.04 M). Distribution density of the CdO network-like (nano-fibrous) structures on the surface increased for 0.05 M concentration. Although the morphology of the thin films changed with increasing solution concentration, preferential orientation of the crystal structure didn't change.

$Cd(OH)_2$ ions get closer to each other to start the nucleation process in the bath, after nucleation of $Cd(OH)_2$ molecules are aligned in one direction. Then, aggregated $Cd(OH)_2$ ions merge into each other and finally, in stacking process, a collection of $Cd(OH)_2$ molecules aggregates form prism-like morphology (Bulakhe and Lokhande, 2014). With increasing precursor concentration, the cadmium content in solution increases and saturate over the surface. Since the higher concentration causes higher viscosity and more complex structures, network-like (nano-fibrous) agglomeration is formed.

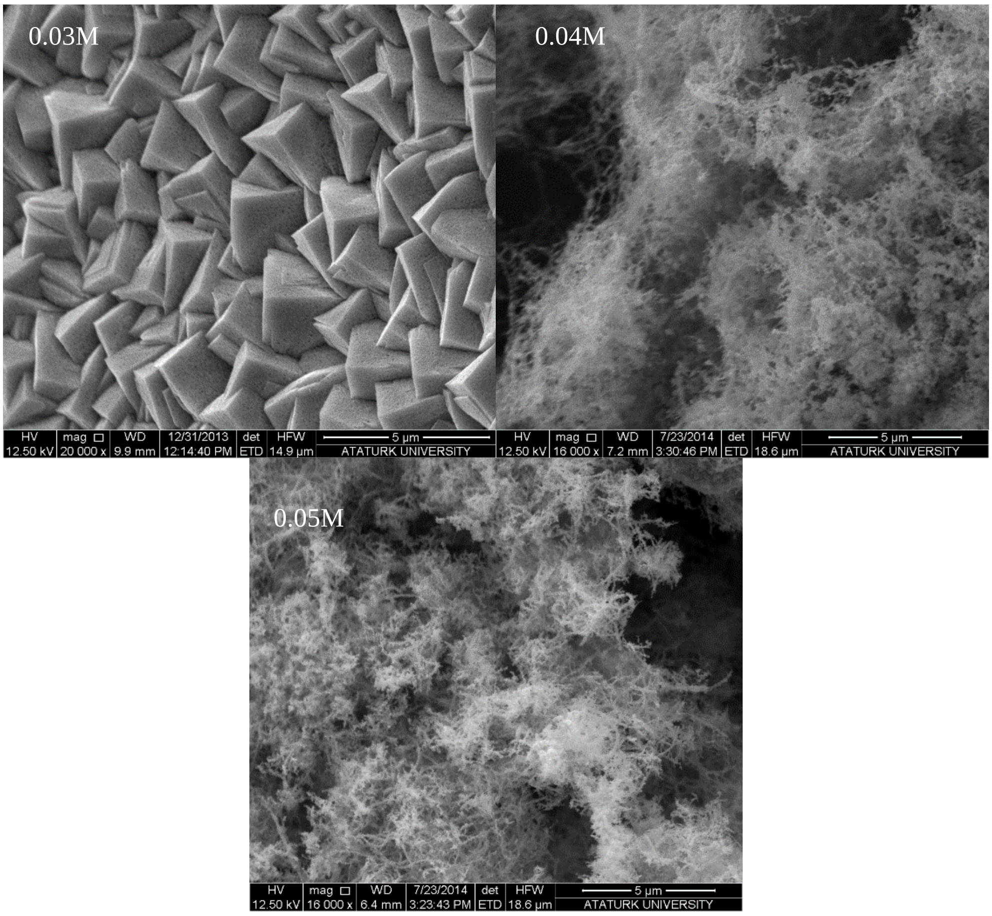

Figure 2. SEM images of the CdO thin films

Prism-like CdO thin films can be used for solar cell applications as a TCO film if it has high transmittance value (Chala et al., 2015). Also, It is known that prism-like and network-like (nano-fibrous) CdO thin films can be used for gas sensor applications (Bulakhe and Lokhande, 2014; Salunkhe et al., 2008). It is reported that if the thickness of the film increases, gas sensor performance of the films increases (Chandiramouli and Jeyaprakash, 2013).

Figure 3 shows UV-Vis Transmittance (%T) and Absorbance (A) spectra (Wavelength range in 300–700 nm) of the CdO thin films. It was determined that the optical transmittance decreases, due to the increased film thickness of thin films. In the present study, CdO thin film which was grown on TCO substrate in the bath with 0.03 M concentration, shows high transmittance (69 %). Therefore, it can be used solar cell applications (Chala et al., 2015).

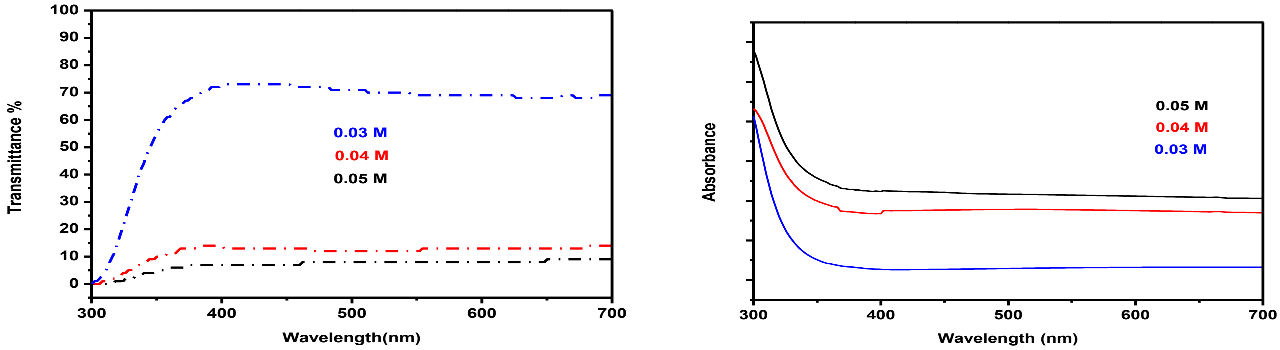

Figure 3. Transmittance (T %) and Absorbance (A) spectra of the CdO thin films

Figure 4 shows $(\alpha h\nu)^2$ versus $h\nu$ diagrams of the CdO thin films plotted by using Eqs. 2 and 3. Tauc Equation is given as Equation 2;

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where $h\nu$ is photon energy, it has been given as Equation 3;

$$h\nu = 1240 / \lambda \quad (3)$$

The optical band gap (E_g) was obtained using the linear part of the graph in figure 4. The point which cuts x-axis, that belongs to the linear part gives the E_g values.

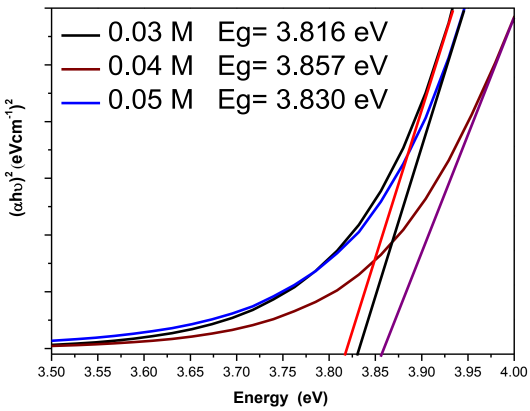

Figure 4. $(\alpha h\nu)^2$ vs. $h\nu$) spectra of the CdO thin films

In this study, it was obtained higher optical band gaps than the bulk CdO band gap due to Burstein - Moss effects in the semiconductors (Yousefi et al., 2012). Approximate T % and E_g (eV) values of the CdO thin films were given in Table 2.

Table 2. Transmittances (T %) and Optical band gaps (E_g) of the CdO thin films

Concentration (M)	T (%) (λ~600 nm)	E_g (eV)
0.03	69	3.816
0.04	13	3.857
0.05	8	3.830

Figure 5 shows WCA images of the CdO thin films. The chemical composition of the surface determines its surface energy: whereas surfaces rich in non-polar groups have low surface energies and, thus, are hydrophobic, surfaces with a high density of polar groups exhibit high surface energies and are hydrophilic. If the thin film has a hydrophobic nature, it shows less wettable. With regard to surface topography, an increase in the surface roughness enhances the surface hydrophobicity for the thin films (Jakaria et al., 2014).

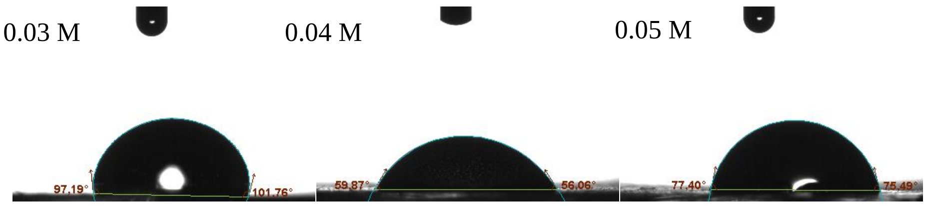

Figure 5. WCA images of the CdO thin films

If WCA of the film is larger than 90°, the structure becomes hydrophobic nature and if WCA of the film is smaller than 90°, the structure becomes hydrophilic nature (Myint et al., 2013). Also, the highly hydrophilic (WCA < 10°) coating can be desirable for some applications (Kenanakis et al., 2008).

It is known that thin films give a larger contact angle if they have a higher surface to volume ratio, smaller WCA indicates larger particles or the absence of a nanostructures on the surface of the substrate, the asymmetry exhibited by the angles is attributed to the irregular distribution of nanoparticles on the surface (Rashidzadeh et al., 2016). The Prisma-like CdO structures had a larger contact angle because of their higher surface to volume ratio and the increasing concentration decreased their contact angle and lotus effect. The hydrophilic nature for network-like (nano-fibrous) structure is attributed to the irregular distribution of nanoparticles (agglomeration) on the surface of the substrate with increasing concentration. So, the CdO thin films lost hydrophobic nature with losing Prisma –like shapes of the nanostructures. Left, right, mean WCAs of the CdO thin films were given in Table 3.

Table 3. WCAs of the CdO thin films

Concentration (M)	Contact Angles (CA°)		
	Left	Right	Mean
0.03	96.91	101.56	99.24
0.04	62.12	59.28	60.70
0.05	77.84	76.10	76.97

CONCLUSION

In this study, CdO thin films were grown by the CBD method at different precursor concentration. All of the CdO thin films showed a cubic crystal structure. The (111) peak intensity of the patterns increased with increasing concentration. As a function of increasing concentration, the prism-like morphology structures of the CdO thin films were coated with network-like (nano-fibrous) structures. The hydrophobic CdO prism-like structures with high transmittance (69%) and wide optical band gap (3.81 eV) is desirable as a TCO metal oxide for solar cell and gas sensor applications. Additionally, CdO thin films with nano-fibrous morphology can be used for LPG gas sensors due to high thickness.

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