Effects of pH on CdO films deposited onto ITO coated glass substrates by electrodeposition

Barış Altıokka* and Ayça Kıyak Yıldırım

Bilecik Vocational School of Higher Education,
Bilecik Şeyh Edebali University,
Bilecik 11210, Turkey
Fax: +90 228 214 1332
Email: baltiokka@gmail.com
Email: ayca.kiyak@bilecik.edu.tr
*Corresponding author

Abstract: Thin films of CdO were deposited onto indium tin oxide (ITO) coated glass substrates using electrodeposition method. The pH of the final solutions was adjusted from 4 to 8 and effects of pH on the films were investigated. The maximum film thickness was reached at pH 5 and XRD studies showed that this film had relatively high peak intensities. Optical studies showed that band gap varies between 2.04 and 2.41 eV and depend on pH. The surface morphologies were analysed by SEM images and they revealed that films were deposited compact and there were no voids, cracks or pinholes.

Keywords: CdO; thin films; electrodeposition; pH.


Biographical notes: Barış Altıokka is an Assistant Professor in the Department of Vocational School of Higher Education, Bilecik Şey Edebali University, Turkey. He is experienced on chemical bath deposition, electrodeposition and thin films.

Ayça Kıyak Yıldırım is an Assistant Professor of Vocational School of Higher Education, Bilecik Şey Edebali University, Turkey. She is interested in electrodeposition and thin films.

1 Introduction

Metal-oxide semiconductors have been investigated by researchers due to remarkable advantages such as non-toxicity, high transparency, high energy band gap and good electrical conductivity (Ganjiani et al., 2016). One of these materials, cadmium oxide (CdO) is a transparent conducting oxide material which possesses high electrical conductivity and high optical transparency (> 80%) in the visible region of the light (Abdulridha, 2016) however CdO thin films show relatively low electrical resistivity (Ziabari and Ghodsi, 2011). Among the various nanostructured metal oxides, CdO is an
n-type semiconductor metal oxide, which belongs to the II–VI group (Giribabu et al., 2013) with a direct band gap at approximately 2.3 eV (Karim et al., 2016).

Cadmium oxide has been widely used in applications such as transparent electrodes, photodiodes (Abdul-Ameer and Agool, 2016), liquid crystal displays, photovoltaic cells, IR detectors, phototransistors and antireflection coatings (Kondawar et al., 2011). CdO films can be deposited by many techniques such as chemical vapour deposition (CVD), sputtering, thermal evaporation, spray pyrolysis, sol-gel and electrochemical (Abdulridha, 2016). Among these methods, the electrochemical method is a kind of effective method for produced CdO nanostructures using aqueous solutions (Singh et al., 2011) because of the low deposition temperature, inexpensiveness and capability of controlling the morphology of the films (Singh et al., 2011).

The electrodeposition processes take place on the surface of indium-doped tin oxide (ITO) and the possible formation mechanism of CdO is suggested as follows (Singh et al., 2011):

\[
NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)
\]
\[
CD^{2+} + 2OH^- \rightarrow CD(OH)_2 \quad (2)
\]

After deposition, thermal annealing in the air causes cadmium hydroxide to convert to cadmium oxide (Singh et al., 2011a).

\[
CD(OH)_2 \rightarrow CDO + H_2O \quad (3)
\]

So far plenty of electrodepositions of CdO have been reported. However, there has been no study on pH. In this work, effects of pH would be investigated in detail.

## 2 Experimental section

In this work, chronoamperometry method of electrodeposition was employed to deposit CdO thin films on ITO-coated glass substrates. ITO-coated glass substrates, platinum wire and saturated calomel electrode were served as the working, counter and reference electrodes, respectively. Before the depositions, ITO-coated glass substrates were washed with acetone and deionised water in order and then were left to dry in air condition. The final solution contained 0.01 M Cd(NO_3)_2 and 0.1 M KCl as the supporting electrolyte and depositions were completed in 2700 seconds. Depositions temperatures of the final solutions were kept at 72 ± 2°C during the deposition. After the Cd(OH)_2 samples were deposited on the surface of the substrate, they annealed by an oven at 420°C. The conditions of the depositions are summarised in Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Conditions of the deposition in the experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments</td>
<td>p1</td>
</tr>
<tr>
<td>Concentration of Cd(NO_3)_2 (M)</td>
<td>0.01</td>
</tr>
<tr>
<td>Deposition time (sec)</td>
<td>2,700</td>
</tr>
<tr>
<td>Cathodic potential (V)</td>
<td>–0.71</td>
</tr>
<tr>
<td>Deposition temperature (°C)</td>
<td>72 ± 2</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
</tr>
</tbody>
</table>
In this study, effects of pH were investigated from 4 to 8. The pH of the final solution was measured as 7 without any additives. The pH of the final solution was increased from 7 to 8 by adding diluted NaOH but when NaOH was added, the colour of the solution turned to turbid white. It was concluded that this resulted from precipitation of Cd(OH)$_2$. For this reason, pH of the solution was not increased above 8. The pH values of the final solutions were decreased by adding ww 5% HCl to 6, 5 and 4. When pH was decreased below 4, CdO thin film was not coated.

The absorbance measurements were obtained by using a JASCO V–530 double beam UV-Vis spectrophotometer. The crystal structures of the CdO thin films were studied by a PANalytical Empyrean x-ray diffractometer. The surface morphologies of the films were performed by a Zeiss Supra 40VP SEM (scanning electron microscope).

3 Results and discussion

3.1 XRD studies

The current densities versus time were recorded during the deposition and are given in Figure 1. It attracted attention that when pH values of the solutions were decreased from 8 to 5, the current densities of the experiments increased. It can be said that the pH value of the solution affected the reaction rate. In a previous study (Wu et al., 2015), it had been found that there was a strong relation between pH value and reaction rate in electrodeposition. On the other hand, when pH was 4, current densities decreased. Therefore, it may be said that HCl dissolves Cd(OH)$_2$ at low pH such as 4.

The film thicknesses were obtained by using the gravimetric method and they are given in Table 2. When pH values of the final solutions were decreased to 5, film thicknesses increased from 385 nm to 681 nm. This result demonstrated the pH affecting the reaction
rate. On the other hand, when pH was 4, the film thickness decreased from 681 nm to 515 nm.

The structural properties can be characterised by using XRD diffractions (Sin et al., 2014). The XRD patterns are given in Figure 2 and they revealed that all CdO films formed were in cubic structure. The film obtained at pH 5 showed the highest peak intensities. This result manifested that good crystallisation and thick film could be obtained if pH equalled to 5. It was important because of the fact that natural pH value of the final solution was 7. The peak intensities of the films obtained at pH 8 and 4 were relatively low.

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

<table>
<thead>
<tr>
<th>Experiment</th>
<th>p1</th>
<th>p2</th>
<th>p3</th>
<th>p4</th>
<th>p5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>385</td>
<td>512</td>
<td>574</td>
<td>681</td>
<td>515</td>
</tr>
<tr>
<td>Crystallite size</td>
<td>61 nm</td>
<td>72 nm</td>
<td>85 nm</td>
<td>92 nm</td>
<td>78 nm</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>2.41</td>
<td>2.37</td>
<td>2.18</td>
<td>2.04</td>
<td>2.23</td>
</tr>
</tbody>
</table>

The crystallite sizes of samples can be calculated by using Debye-Scherrer equation which is given in equation (4) (Bhowmik et al., 2008; Kumar et al., 2014).

\[
cs = \frac{0.089 \times 180 \lambda}{314 \times \beta \times \cos \theta_c} \text{nm}
\]

where \( \lambda \) is the wavelength of x-ray radiation (1.54056 Å), \( 2\theta_c \) is the position of peak centre, \( \beta \) is the full width at the half maximum of peak height (in degrees). Values of \( \beta \) and \( 2\theta_c \) are calculated by fitting the XRD peak profile to Lorentzian shape (Bhowmik et al., 2008; Solookinejad et al., 2016). The calculated crystallite sizes of the samples are given in Table 2. The crystallite sizes varied between 61 and 92, depending on the decreasing pH but, when pH was 4, crystallite size decreased to 78 nm. It was understood from a previous study (Altıokka, 2015) that crystallite sizes were affected by reaction rate. This study showed that the reaction rates and therefore, the crystallite sizes were strongly affected by pH.

The crystallisation begins with random nucleation for materials (Yu et al., 2017). Reaction rate affects crystallite size and thus, boundary defects (Altıokka, 2015). The good crystallisation is important for the semiconductor. In semiconducting materials, grain boundary defects cause trap within the band gap. The coexistence of different phases, textures and polymorphs can cause this problem, creating barriers to charge transport and causing charge recombination, with important detrimental effects on the optoelectronic properties of the semiconductor (Yu et al., 2017). This work showed us that good crystallisation could be grown at pH 5 and thus, it could be said that there were fewer defects.
Effects of pH on CdO films deposited onto ITO coated glass

3.2 Optical studies

The optical properties of the CdO thin films were investigated by using absorbance measurement which is given in Figure 3. When the photon beam passes through the sample, a certain amount of photon beam is absorbed and some photon beam is reflected by the sample (and in some samples, some photon beam is also scattered by the film layers) and the remaining power of the incident photon beam is captured as transmitted.
light for spectral analysis (Alam et al., 2014) The absorbance increased as the pH was decreased from 8 to 5. This result might be due to the increasing thicknesses of the films.

**Figure 3** Absorption spectra of CdO thin films obtained at various pH values (see online version for colours)

![Absorption spectra](image)

**Figure 4** Tauc plots and band gaps of CdO thin films at various pH values (see online version for colours)

![Tauc plots and band gaps](image)

The energy band gap can be estimated by the fundamental absorption, which is due to the electron excitation from the valence band to conduction band. Thus, the energy band gap $E_g$ can be calculated using the equation by Bardeen as shown in equation (5) (Mkawi et al., 2015).
\[ \alpha h = A(hv - Eg)^m \]  

(5)

where \( m = 1/2 \) or \( 3/2 \) for direct allowable transmission, \( A \) is a constant, \( hv \) the photon energy, \( A \) is the absorption coefficient (Mkawi et al., 2015). The energy band gap \( Eg \) values were estimated by extrapolating the linear portion of the plots of \( (\alpha hv)^2 \) vs. \( hv \) (Hu et al., 2014) which is shown in Figure 4 and given in Table 2. The energy band gaps were between 2.41 and 2.04 eV. The pH affected reaction rate and thus reaction rate affected crystallite size. Energy band gap depends on crystallite size. The band gap of the bulk CdO was approximately 2.3 eV (Karim et al., 2016). In this work, CdO thin films whose energy band gaps were below and above 2.3 eV could be produced. Besides, it was discovered that the band gap depended on pH.

**Figure 5** SEM images of the CdO thin films for (a) pH = 8 (b) pH = 7 (c) pH = 6 (d) pH = 5 and (e) pH = 4
The band gap of the n-type layer of thin film solar cells varies from the 1.71 eV to 2.08 eV (Zhang et al., 2017). In this work, when pH of the final solution was decreased from the 7 to the 5, the band gap of the film decreased from the 2.37 eV to 2.04 eV. Therefore, it can be said that by decreasing pH to 5, the samples became more suitable for thin films solar cells.

3.3 Surface studies

Surface images were magnified 20,000 times by a SEM. The surface images of the CdO thin films synthesised at various pH values are given in Figure 5. There are no cracks, voids or pinholes seen on the surface of the films and surfaces are covered well with CdO crystals. There are nearly same morphologies in Figures 5(a), 5(b) and 5(c) which are surface images of the films obtained at pH values equal to 8, 7 and 6 respectively. The surfaces consist of polymorphic CdO crystals and under this, there is sheet-like structure. Figure 5(d) and 5(e) show the surfaces of the films obtained at pH 5 and 4 respectively. These two surfaces resemble each other. There are pyramidal forms of CdO crystals on these two surfaces. As a result, Figure 5 demonstrates that surface morphology depends on the pH value of the solution.

When the light beam hits on thin film semiconductor, a part of the light beam passes throughout materials and another part of the light beam is absorbed or is scattered by semiconductor materials. This depends on the band gap and the morphology of the semiconductor. In this work, surface morphologies of the films varied depending on the pH value of the solution. In this way, it was concluded that absorbance was affected by band gap and morphology of the films such as surface area.

4 Conclusions

In this study, CdO thin films were obtained by using electrodeposition. Effects of solution pH were investigated in detail and for the first time. Natural pH of the final solution was measured as to be 7. When pH increased above 7, the Cd(OH)$_2$ precipitated. Therefore relatively high pH was not investigated. It was already shown in the XRD patterns that good crystallisation formed in relatively low pH values such as 6 and 5. Optical studies have revealed very interesting results such as band gap depending on the pH value. When pH of the solutions decreased from 8 to 5, the energy band gap also decreased from 2.41 eV to 2.04 eV proportionally. When the band gap of the n-type layer varies between 1.7 and 2.08 eV, it is suitable for thin films solar cells. In this study, the band gap of the film was decreased up to 2.04 eV. Therefore, it was thought that obtained CdO thin film was made more suitable for thin films solar cells. Surface morphologies were investigated by SEM images. SEM images revealed that surface morphology depended on solution pH. When pH was relatively low such as 5 and 4, pyramidal form of CdO appeared on the surface of the films. It might be said that morphologies of the films varied depending on pH of the final solutions such as surface area. It is well known that the band gap and the transmittance were affected with structure and morphology.
Effects of pH on CdO films deposited onto ITO coated glass

References


