Original Article

Structural, optical and porosity properties of CdI$_2$ thin film

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ABSTRACT

Cadmium iodide (CdI$_2$) crystalline thin film was produced via chemical bath deposition on substrates (commercial glass). Transmittance, absorption, optical band gap and refractive index of the film were examined by UV/vis spectrum. The hexagonal form was observed in the structural properties. The structural and optical properties of CdI$_2$ thin films, produced at different pH levels were analyzed by SEM; EDX analysis was performed for analyzing the surface properties and determining elemental ratio of the films. It has been found that some properties of the films have been changed with the pH and they were analyzed according to pH variations. The tested pH values were between 5.65 and 7.20. Optical band gap varied between 3.30 and 3.82 eV with the change of pH. Film thickness was also changed according to pH, varied from 450 to 1444 nm. Refractive index was not correlated with deposition pH, it has been found to be 1.93, 2.27, 2.19 and 2.10 for 5.65, 5.90, 6.75 and 7.20 pH levels. Extinction coefficient has behaved as refractive index, which was 0.011, 0.018, 0.016 and 0.015 at 5.65, 5.90, 6.75 and 7.20 pH levels, respectively (in 550 nm). Also, porosity was found to be negatively correlated with refractive index and reflectivity of the films, whereas it is positively correlated with transmittance and extinction coefficient.

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1. Introduction

Cadmium iodide unit cell is hexagonal and it typically dihalides as MX$_2$ [1]. Cadmium ions’ layer is sandwiched and tightened by the iodine layers. The bonding between cadmium and iodine is ionic. However, iodine ions are bonded with van der Waals bonds. Some researchers have studied optical properties of amorphous cadmium iodide, which is a metal halide, and have achieved to produce amorphous form of cadmium iodide. The optical band gap of cadmium iodide is 3.8 eV [2,3].

Tiyagi and Vedeshwar [4] have conducted the most comprehensive study on CdI$_2$ thin films until today. They observed XRD peaks, indexed hexagonal structure and indicated at (001), (101), (111). In their study, they identified a parabolic curve on the plot of CdI$_2$ grain size versus film thickness. They found that optical band gap was decreasing with grain size and film thickness.

The aim of this paper is to produce CdI$_2$ thin film via chemical bath deposition and examine its structural and optical properties according to porosity properties seen on CdI$_2$ thin films. The crystalline structure and optical properties of CdI$_2$...
can be controlled by changing the pH of the chemical bath. Nobody has worked on CdI₂ thin film produced by chemical bath deposition method yet, so we had no idea about how the pH of the bath would change CdI₂ film’s structure and its optical properties. It should be noted that the production of CdI₂ thin film via chemical bath deposition is a very difficult process.

2. Experimental

The components of the bath were 1% (w/v) potassium hydroxide, 0.005 M cadmium nitrate and 0.010 M potassium iodide. First, 10 ml of 0.005 M cadmium nitrate and 10 ml of 0.010 M potassium iodide were put into the baker, which was containing 20 ml of deionized water. Potassium hydroxide was used to adjust the pH of the bath; 150, 200, 250 and 350 µl of potassium hydroxide (KOH) were added to obtain solutions with 5.65, 5.90, 6.75 and 7.20 pH. Chemical baths’ pH values were measured by using a pH meter (Lenso mark 6230). The crystalline structure of CdI₂ was confirmed by X-ray diffraction (XRD) with a Cu Kα1 radiation source (Rikagu RadB model, λ = 1.5406 Å) at the range 10° < 2θ < 90° at a speed of 3° min⁻¹ with a step size of 0.02°. Surface properties of the films were examined using an EVO40-LEO computer controlled digital scanning electron microscope (SEM). Chemical analysis by EDX was performed with an EDX spectrometer attached to SEM. The optical measurements were performed by a Hach Lange 500 Spectrophotometer at room temperature by placing an uncoated identical commercial glass substrate to the reference beam. The optical spectrum of thin films was recorded at the range of 300–1100 nm wavelengths. Film thicknesses were measured by a Veeco Multi Mode AFM (Controller = NanoScope 3D). Thicknesses were measured in a 10 µm x 10 µm area with tapping mode.

3. Results and discussion

The chemical reactions occurred in the bath during the deposition of cadmium iodide film are summarized below. Cadmium ions (Cd²⁺) were combined with iodine (I⁻) to form an insoluble CdI₂ in the bath.

\[ \text{H}_3\text{O}^+ + \text{I}^- \rightarrow \text{H}_2\text{O} + \text{HI(aq)} \]  
(1)

\[ \text{Cd}^{2+} + 2\text{I}^- \rightarrow \text{CdI}_2(s) \]  
(2)

XRD patterns of CdI₂ films deposited via CBD at different pH levels are shown in Fig. 1 and hkl values are displayed in Table 1. Scherrer formula was used to calculate structural properties, which are grain size (D), dislocation density (δ), number of crystallites per unit area (N), lattice parameters along the (1 0 0), (1 0 2), (1 0 2), (1 0 1) plane, as below [5–9]:

\[ D = \frac{0.991}{B \cos \theta} \]  
(3)

![Fig. 1 - XRD spectrum of CdI₂ at different pH levels, (a) pH 5.65, (b) pH 5.90, (c) pH 6.75, (d) pH 7.20.](image)

\[ \delta = \frac{1}{D^2} \]  
(4)

\[ N = \frac{t}{D^3} \]  
(5)

where t is the film thickness, \( \lambda \) is wavelength of the X-ray used (1.5406 Å), \( \beta \) is FWHM of the peak, \( \theta \) is Bragg angle, \( \delta \) is dislocation density, which is defined as the length of dislocation lines per unit volume of the crystal. It has been found that average grain size has varied with the pH of the bath. The changes of dislocation density and the number of crystallites per unit area are presented in Fig. 2.

XRD analysis shows that the nature of the films deposited at neutral pH (pH 5.65, 7.20) were crystalline. XRD patterns of CdI₂ films deposited at pH 5.65–7.20 indicate hexagonal structure with a preferential orientation along (1 0 0), (1 0 2), (1 0 2), (1 0 1) directions (\( a = b = 4.24, c = 13.72 \)). With the increase

<table>
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<th>pH</th>
<th>(hkl)</th>
<th>2θ (Observed)</th>
<th>2θ (Calculated)</th>
<th>1/λa</th>
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</thead>
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</tr>
<tr>
<td></td>
<td>111</td>
<td>32.040</td>
<td>32.026</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Table 1 – XRD values of CdI₂ at different pH.
of pH, dislocation density (δ) and number of crystallites per unit area (N) have been increased, whereas grain size (D) has been decreased. The best crystalline structure and the highest grain size have been obtained at pH 5.65. The grain size was inversely proportional to dislocation density and number of crystallites per unit area. This may be due to the increase of the defects and empty spaces in the structure as grain size decreases. Mohammed [10], who studied on CdI₂, reported the peaks that they have found from XRD pattern of CdI₂ as following: 13°, 25.7°, 39.2° (150 nm film thickness); 13.1°, 25.6°, 39.1° (250 nm film thickness); 12.95°, 25.97°, 27.55°, 39.4°, 42.6°, 44.7° (450 nm film thickness); 12.95°, 25.97°, 27.55°, 39.4°, 24.6° (600 nm film thickness). It should be noted that the peaks that he has observed at 39°, 42° and 44° were not observed in this study. He has produced films via thermal evaporation technique. Also, he has not observed peaks at 21.058° and 32.026°. These peaks may be related to the peaks at 19.891 and 32.220 in ASTM file, belonging to CdI(OH) with ASTM code: 025–0107. In our study, we observed these peaks in the film produced at pH 7.20.

![Fig. 2 – Grain size (D), dislocation density (δ) and number of crystallites per unit area (N) of CdI₂ thin film at different pH.](image1)

![Fig. 3 – Film thickness of CdI₂ thin film at different pH.](image2)

It should be also noted that thickness and grain directions of the films obtained in this study were different than the literature. Film thickness is shown in Fig. 3. Since nobody has produced CdI₂ thin film via chemical bath deposition before, we could only compare our results with the results of the other methods. Film thickness, which was in line with grain size, has been decreased with pH; taking values 1444, 794, 771, 499 nm. This result was also reported by Tyagi and Mohammed; they observed that film thickness increases with grain size [4,10]. These results are in agreement with the literature; however, nobody has investigated dislocation density and the number of crystallites per unit area of CdI₂ thin films.

The transmittance (T) of CdI₂ thin film can be calculated by using reflectivity (R) and absorbance (A) spectra from the expression [11]:

\[
T = (1 - R)^2e^{-A} \quad (7)
\]

Transmission measurements were performed at room temperature at the range of 300–1100 nm, as shown in Fig. 4. Films

![Fig. 4 – Transmittance (T) and reflectivity (R) of CdI₂ thin films produced at different pH.](image3)
were deposited in the baths having different pH. Transmission varied with the pH of the deposition bath. The bath with pH 5.65 had the highest transmission whereas the bath with pH 5.90 had the lowest. On the other hand, reflectivity was opposite to transmission. Optical transmission of the film produced at pH 5.65 was 68.39%, whereas the one obtained at pH 5.90 was 55.97% (550 nm wavelength). Reflectivity of the film produced at pH 5.65, was 10.18% however the reflectivity of the one produced at pH 7.20, was 12.72% (550 nm wavelength). Transmission was almost in line with film thickness. Mohammed [10] found that transmissions were below 20% for 450 and 600 nm film thicknesses. This result is quite different from the results obtained in our study, however it should be noted that the methods used were different. Tyagi and Vedeshwar [4] observed that transmission varied between 60 and 80%, for 160–250 nm film thickness. The review of the literature shows that this kind of optical properties vary according to the method used by the researcher. Refractive index and extinction coefficient of the films are derived from the following formulas [11]:

\[
n = \frac{(1 + R)}{(1 + R)} + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \tag{8}
\]

\[
k = \frac{\alpha \lambda}{4\pi} \tag{9}
\]

As presented in Fig. 5, refractive index, which were 1.93, 2.27, 2.19 and 2.10, was not in line with deposition pH. However, extinction coefficients, which were 0.011, 0.018, 0.016 and 0.015 for pH 5.65, 5.90, 6.75 and 7.20, have behaved similarly to refractive index (550 nm). Refractive index jumped to 2.27 at pH 5.90 then slowly decreased up to pH 6.75. Tyagi and Vedeshwar [4] calculated refractive index as 2.20 for 250 nm film thickness. This result is in accordance with the literature. The results obtained by Greenaway and Nitsche [3] were similar to the results of our study. Absorbance curves are displayed in Fig. 6.

Absorbance of the films has not varied much with respect to pH level. Absorbance of the films was around 0.2–0.3 (550 nm wavelength). The curve behaved as the curve of refractive index. Rawat et al. [12] have also calculated absorbance of CdI₂ thin film around 0.3, at 500 nm wavelength. In their study, they examined optical properties of CdI₂ at 300–500 nm wavelengths. This is in line with this study [13]. Optic band gap energy (E_g) was derived from absorption spectra of the films by using the following relation [14,15]:

\[(\alpha h\nu) = A(h\nu - E_g)^n\] \tag{10}

where A is a constant, \(\alpha\) is absorption coefficient, \(h\nu\) is the photon energy and \(n\) is a constant that is equal to \(1/2\) for direct band gap semiconductor.

Band gap (E_g) of the films has been varied as 3.82, 3.74, 3.70 and 3.30, according to film thickness in Fig. 7. Film thickness has been decreased for pH 5.65–7.20, similarly optic band gap
of the films has been decreased too. Grain size and film thickness had an impact on optic band gap, which has behaved similar to these properties. Mohammed, Tyagi, Vedeshwar and Tyagi reported that optic band gap was inversely proportional to film thickness and grain size [4,10,16]. Results of this study were in line with the literature.

Scanning electron microscopy (SEM) was used for examining the effects of the deposition pH on the film’s surface properties, as the surface properties directly affect the electrical and optical properties of the films. SEM images of CdI$_2$ thin films produced at different pH are presented in Fig. 8. SEM analysis can provide information about the layout and location of the particles within the structure. As can be seen from Fig. 8a–h, the size of the crystallites was decreased with the increase of solution’s pH. All films had insular structure (island) and strong adherence to the substrates. In Fig. 8g and h, an accumulation of CdI$_2$ nanoparticles can be observed, which reveals how the films was produced at different pH levels. These data are in line with XRD analysis.

These surface properties strongly affect optical properties of the films, such as transmittance, absorbance and reflection. Thus, it seems that CdI$_2$ film showed a better and steady growth at pH 5.65. The best crystallite was obtained from the bath with pH 5.65. Moreover, the highest transmittance and the lowest refractive index were also observed in the film obtained from the bath with pH 5.65, which was formed by regular grains [17,18].

EDX technique was used to estimate the composition of CdI$_2$ thin films. Fig. 9 shows the average atomic ratio of I/Cd as a function of pH. It can be seen that I/Cd ratio decreases from 2.241 to 1.155 with the increase of pH. EDX results indicated that the average atomic ratio of I/Cd was nearly stoichiometric (I/Cd = 2.257) at pH 5.65. But due to the formation of CdI(OH), I/Cd ratio remained at 1.155. The theoretical stoichiometric ratio of I/Cd in CdI(OH) compound was calculated as 1.128. EDX results were in line with XRD and SEM measurements.

Films’ porosities (P) can be calculated on the basis of the following simplified approximation, mentioned in the literature [19]:

\[
\frac{n^2 - 1}{n^2 + 2} = (1 - P) \frac{n_{\text{bulk}}^2 - 1}{n_{\text{bulk}}^2 - 2}
\]

(11)

$n_{\text{bulk}}$ presents the refractive index of bulk CdI$_2$, where $n_{\text{bulk}} = 2.40$ according to literature (550 nm wavelength) [20]. The refractive index of CdI$_2$ thin films was measured by UV–vis and calculated using these data at equal (7) and (8). Table 2 presents the comparison of several optical parameters of the films in terms of porosity. It has been found that porosity does
Fig. 8 – SEM images of CdI₂ thin films (a) pH 5.65 (2 μm), (b) pH 5.65 (10 μm), (c) pH 5.90 (2 μm), (d) pH 5.90 (10 μm), (e) pH 6.75 (2 μm), (f) pH 6.75 (10 μm), (g) pH 7.20 (2 μm), (h) pH 7.20 (10 μm).

not affect optical band gap of these films. Refractive index and reflectivity of the films are negatively correlated with porosity while transmittance and extinction coefficient are positively correlated. Charles et al. have found that refractive index was inversely correlated with porosity; however, they could not identify a similar relation with transmittance. They mostly examined the anisotropy effect impacting the diffusion of adatoms in the surface [21]. Therefore, the reflectivity and extinction coefficient of the films are correlated with the porosity as shown in Eqs. (7) and (8). It seems that adatoms increase the porosity and consequently they affect refractive index. Porosity also causes different refraction indexes, which
allow the utilization of such materials as gratings in the optical devices.

4. Conclusion

This study, where CdI₂ thin films were successfully deposited, is featuring the production of CdI₂ thin films via chemical bath deposition method, which may be useful for researchers who are working in this area. Film thickness and average grain size have decreased with the increase of deposition pH. The best crystalline structure and the highest grain size have been obtained at pH 5.65. XRD pattern and calculations were in line with SEM analysis. From XRD analysis and SEM images, we deduced that optical properties of the films were affected by structural properties. In addition, refractive index and reflectivity of the films were negatively correlated with porosity while transmittance and extinction coefficient of the films are positively correlated, which may be useful for characterization of thin films’ transmittance, reflectivity, refractive index and extinction coefficient. It has been found that the porosity of the films did not affect their optical band gap. This result is in agreement with the literature.

Conflicts of interest

The author declares no conflicts of interest.

References