Study of the Optical and Structural Properties of PbI₂ Thin Films Prepared by Spin Coating Technique at Room Temperature

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Abstract: Lead iodide thin films were deposited on a glass substrate using a spin coating technique. Powder of PbI₂ with a concentration (0.2M) was dissolved in a solution of Dimethylformamide (DMF). The thickness of the prepared films was controlled through the time of deposition and the spinning speed. The X-ray patterns show that the PbI₂ thin films have hexagonal structures. The bandgap of the thin films was measured optically and found to be about 2.45 eV. The FTIR measurements depicted the vibration modes from 1650 to 700 cm⁻¹; the energy bandgap from the diffused reflectivity measurements was 2.4 eV; which is in a good agreement with energy gap from Tauc plot. (FESEM) images shows the nano rod shape of particles with large pores and non uniform distribution of particles.

Keywords: PbI₂ thin films, bandgap, spin coating, morphology

1. Introduction
Lead iodide (PbI₂) one of the semiconductor family; it has been Commonly studied in many applications, like medical imaging [1], X-ray detectors [2], photosensitivity semiconductor-metal applications [3], and nuclear detection [4]. It is also used as a precursor to obtaining a solar cell depending on methylammonium lead iodide perovskite [5]. Yet, one of the most efficient thin films produced by solar cells[6]

As one of semiconductor family, p-type lead iodide has (2.3-2.6 eV) energy band gap value. The atomic number of lead is 52, and for iodine is 82 which is considered as the high atomic number[7] with a hexagonal structure, PbI₂ is working efficiently at room temperatures[8] PbI₂ is considered as a precursor for perovskite solar cells, but in ambient air, the PbI₂ thin films are unstable. Also, the thin films are damaged when exposed to the electron microscopy device. A range of easy and inexpensive techniques can produce thin films of lead iodide. One of these methods is adding the iodine crystals in a dark chamber containing a chemical bath with PbS thin films deposited in it. The spin coating method considered as an easy and low-cost method to get thin films with excellent quality along with many other methods[9].

The thin films thickness can be controlled by adjusting the variables of spin including spinning time and speed, controlling the thin films quality by controlling the parameters of the precursor such as the concentration, the temperature and the solvent properties [10]. However, a methodical study is still to be carried out on the PbI₂ thin films properties deposited by this technique. The aim of this study is to deposit the PbI₂ thin films on a glass substrate by the spin coating process and studying the optical and morphological properties of these films.
2. Experimental work
PbI₂ powder (sigma Aldrich purity 99.0 %) (0.46mg) was dissolved with 5ml of DMF (sigma Aldrich purity 99.0%) using magnetic stirrer for 20 min. Prior the deposition, glass substrates were cut and cleaned in an ultrasonic bath with ethanol and DI water for 15min for each one. Samples then dried by air and stored in special containers. Drops of PbI₂ solution were spun on the glass substrate using a spin coater to form PbI₂ thin film. The spinning time was 15s, while the spinning rotational speeds were, 1500 r.p.m. Afterward, the films were aneled at 50°C for 4min.

![Figure 1. PbI₂ thin film prepared by spin coating technique with 1500 rpm at 15 s and (2 cm *2cm) daimention.](image)

3. Characterization
The optical properties were determined using Metertech SP8001 UV-VIS spectrophotometer. The structural properties were analyzed by Shimadzu XRD Model 6000. The thickness of the thin films was calculated using the gravimetric method\cite{11}.

\[ t = m_2 - m_1 (A \times \rho)^{-1} \]  \hspace{1cm} (1)

Where \( t \) is the thickness, \( m_1 \) is the weight of the sample before deposition, \( m_2 \) is the weight of the sample after deposition, \( A \) is the area of the sensitive thin film, \( \rho \) is the lead iodide density (6.16 gm/cm³).

The FTIR measurements were carried out by using BRUKER ALPHA (platinum-ART) with wavelength ranging from (500-3500 cm⁻¹), the diffused reflectance were carried out by using Avalight-DH-S-BAL2048 analysis, the FESEM spectrograph was taken by MIRA 3 Tescan Energy Dispersive Spectroscopy, and (EDS) analysis was taken by ARYA Electron Optic (Maxtek AP1.3). For Raman Spectroscopy, Raman (SENTERRA : Burker) Raman Spectrometer with (532 nm) laser for excitation using digital balance with 10⁻⁴ gm type (BL210S).

4. Results and discussion
The thickness of the resulted thin films were measured with the gravimetric method and it found to be equal to 243.5nm at 1500 r.p.m and 15s. This measurement is proved also by the FESEM analysis for the cross section of the resulted sample. Fig. (2) reveals that near the 500nm region the lead iodide thin film starts to absorb strongly and the absorption coefficient as in Fig. (3) is about \( 10^5 \) cm⁻¹, this is enough value for optoelectronic applications \cite{10}. 

\[ \text{t} = \text{m}_2 - \text{m}_1 (A \times \rho)^{-1} \]
Figure 2. Absorbance of lead iodide thin films versus wavelength for 243.5 nm thickness.

Figure 3. The relation between the absorption coefficient and wavelength of PbI₂ thin films.

Figure 4. Transmission of the PbI₂ thin-film deposited by spin coating with 1500 rpm.

Fig. (4) shows transmission of PbI₂ thin film versus wavelength, transmission at 300nm is about 40% and starts to increase then levels off in the range (600-1000nm) reaching to more than 80%, which means that the lead iodide thin films show high transmittance more than 75% as average in the visible range spectrum.

The energy bandgap of the thin film was determined using Tauc formula:

\[ \alpha h\nu = A(h\nu - E_g)^n \]  

where \( E_g \) is the optical band gap for allowed or forbidden transition, \( h\nu \) photon energy in eV, \( \alpha \) is the absorption coefficient, and \( A \) is constant Fig. (5).

The Urbach tails energy as in Fig. (6) for PbI₂ thin films was calculated from the equation below [11].

\[ \alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right) \]  

\( \alpha_0 \) is the proportionality constant, \( E_u \) the tails width for the optical gap region (Urbach tails energy) and it is equal to the inverted slope resulting from drawing the graphic relation between \( h\nu \) and ln(\( \alpha \)).
Figure 5. Tauc plot for energy gap for PbI$_2$ thin film prepared by spin coating.

Figure 6. Urbach energy tail for PbI$_2$ thin films deposited with a spin coating process.

To obtain the direct transition of the film by taking $n=2$ as the best fit, the bandgap value was 2.4 eV. The relation between $\alpha$ and photon energy for the PbI$_2$ thin film with the direct transition is given by:

$$\alpha = \alpha_0 (h \nu - E_g)^{-1/2}$$

(4)

where $h \nu$ the photon energy in eV, and $E_g$ is the bandgap energy in eV.

The direct transition is given by[12]:

$$(\alpha \Delta d)^2 = (\ln (T)^{1/2})^2$$

(5)

where $\Delta d$ is the thickness difference of the film before and after deposition.

The extinction coefficient ($k$) relation is observed as in Fig. (7). Clearly, the extinction coefficient linearly proportional with wavelength for PbI$_2$ thin films followed by a slight increased at wavelengths more than 400nm.

$$K = \ln \frac{(1/T)\lambda}{4\pi\tau}$$

(6)

$$\alpha = \frac{4\pi K}{\lambda} = \ln \frac{(1/T)}{\tau}$$

(7)

$T$ is thickness.

Figure 7. The extinction coefficient spectrum for PbI$_2$ thin film.
The results of the X-ray diffraction pattern for lead iodide films showed a polycrystalline structure with a hexagonal type. There are three peaks at $2\theta=25.66^\circ$, 38.81$^\circ$, and 52.53$^\circ$ assigned to diffraction patterns (002),(003),(004), respectively, fig. (8), and show the hexagonal crystal structure [6].

![XRD analysis for PbI$_2$ thin film prepared by spin coating process at (1500 rpm, 15s.).](image)

The average grain size (D) for PbI$_2$ thin film was calculated by [12].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{8}$$

Where $\theta$ is Bragg angle (rad), $B$ is the full width at half maximum (FWHM) (in rad) and $\lambda$ is the wavelength of the X-ray (0.1nm).

The dislocation density (S) of the PbI$_2$ thin film was calculated by.

$$S = \frac{1}{D^2} \tag{9}$$

Where $D$ is the average grain size of PbI$_2$ thin film. All these parameters tabulated in the table (1).

| 2\theta  (deg) | Plane | D (nm) | S (line/nm$^2$) |
|----------------|-------|--------|-----------------|
| 25.6678        | 002   | 14.989 | 0.00445         |
| 38.8192        | 003   | 14.541 | 0.00472         |
| 52.5307        | 004   | 12.503 | 0.00639         |

FTIR spectrum for PbI$_2$ thin films, shown in Fig. (9), exhibits different vibration modes at 3400 and 1650 cm$^{-1}$ of the O-H group. At 3525-3210 cm$^{-1}$ symmetric stretching and asymmetric stretching vibration modes can be observed as a strong IR broadband. In the 1400 – 1700 cm$^{-1}$ there is asymmetric bending vibration mode and at 1500 cm$^{-1}$ there is a strong absorption in IR region [13].
Figure 9. FTIR spectrum of PbI₂ thin film prepared by spin coating technique.

Figure 10: Energy bandgap from DRS spectrum and reflectivity of PbI₂ thin film prepared by the spin coating process.

By using Kubelka – Munk function the energy bandgap from the diffused reflectivity measurements were determined as in the following equation [14].

\[
F = \frac{K}{S}
\]

where \( K = (1-R)^2 \), \( S = 2R \), where \( R \) is the reflectance.

If we compare the energy gap value determining from the transmission measurements, Fig. (6) and the other one from diffused reflectance measurements, Fig. (10) we find it the same value which it’s equal to 2.45eV.
Figure 11. FESEM top view for coating for different scale (500nm , 5µm) with Histogram for the particle size distribution of PbI₂ thin films

PbI₂ thin films Structural properties viewed by field emission electron microscopy (FESEM) are shown in Fig. (11 & 12) it is clear from top view image for the surface of PbI₂ thin film, that the thin film is inhomogeneous, highly porous and dense, Images shows pores with a size of tenth of nm, the grain size range from 24.26nm to 30.77nm with nanorods shape and the cross section shows that the thin film is deposited as layers over the substrate[15].

Figure 12. FESEM side view (cross-section) for PbI₂ thin film prepared by spin coating
By measuring EDS for the thin films, the spectrum showed good peaks for Pb and I beside the glass substrate material components as explained in Fig. (13) There is a small amount of iodine, maybe because of removing an amount of it during the measurements process[16].

| ELT | W%  | A%  |
|-----|-----|-----|
| Pb  | 17.18 | 2.52 |
| I   | 14.77 | 3.53 |

**Figure 13.** EDS spectrum of PbI₂ thin film prepared by the spin coating process.

Raman spectra of PbI₂ with DMF display three modes at (74, 95,110 cm⁻¹), those modes could be referred to the bending of (I-Pb-I) atoms Fig. (14), and symmetric and a symmetric stretching for I-Pb. So these three peaks belong to the solved PbI₂ in DMF solution [17].

**Figure 14.** Raman spectroscopy PbI₂ thin films. (b) A histogram of intensity frequency

**Conclusion**

This work presents a successful method to prepare lead iodide film by spin coating process and studies its optical and structural properties to use this thin film in optoelectronic applications. The film was smooth and light yellow colored. By taking the UV-Vis measurements to calculate the transmittance range with more than 75% in the visible range, absorption coefficient (10⁵ cm⁻¹) with band gap (2.45eV), the diffused reflectance measurement gives the same value of the UV-VIS spectrum energy bandgap (2.45eV).

The XRD measurements show that the PbI₂ thin films have a hexagonal phase type structure with polycrystalline type. The FESEM & EDS measurement shows that the thin film was inhomogeneous, denser with little amount of iodine elements. Uniform, and good coverage thin film could be produced for lead iodide. Fourier transform Infrared Spectroscopy reveals a strong bending between the molecular of Pb and I at 3500-3200 cm⁻¹.
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