

CHARACTERIZATION OF PbI_2 THIN FILMS PREPARED BY FAST VACUUM THERMAL EVAPORATION

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In this work, XRD and some optical parameters of porous PbI_2 thin films were investigated. Various thicknesses of lead iodide thin films were prepared by fast thermal evaporation technique (TET). X-ray diffraction patterns showed diffraction peaks before and after annealing at the orientations (001), (002), (202), (003) and (220) at $2\theta=12.6^\circ$, 25.4° , 38.8° , 41.6° and 52.2° , respectively. Scherrer analysis indicated that grain size extends from about 8 to 18 nm. Scan electron microscopy (SEM) revealed high porosity of PbI_2 thin films. UV-vis spectroscopy and diffusive reflectivity have been used to calculate the optical bandgap. The two methods indicate that the PbI_2 prepared by TET has a direct optical bandgap (about 2.5 eV) with Urbach tail width of the order 0.76 eV.

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1. Introduction

Recently, there has been a need to fabricate efficient and low cost solar cells adapted to simple possessing methods. In that respect, solar cells have been developed in several stages and the most important one is what is called “the third generation solar cells” or (3G-SC). The definition of 3G-SC is most commonly referred to quantum dot, organic and perovskite solar cells [1]. PbI_2 has been proven to be important precursors in the synthesis of efficient perovskite solar cells [2]. In this work, we will study the physical properties of PbI_2 which is used in perovskite solar cells. In 1999, Somma et al [3] prepared of CsI-PbI_2 films with different thicknesses by TET and studied some structural and optical properties of PbI_2 . Nominal thickness of the films was 0.5 mm. X-ray diffraction with different grazing angles (0.1° - 2°) showed the formation of ternary phases, i.e, CsPbI_3 and Cs_4PbI_6 . Warren-Aberbach method was used to estimate the sizes of aggregates which was around 20-40 nm. In 2008, Ghosh et al [4] investigated some structural and optical properties of PbI_2 thin films deposited by TET. The analysis of X-ray diffraction for PbI_2 thin films showed that the lead iodide films are almost polycrystalline with quite hexagonal structure. The optical bandgap for 300 nm thickness was about 2.58 eV. In 2011, Jamil et al [5] prepared lead iodide thin films with various thicknesses by thermal evaporation. The analysis of the optical parameters revealed a dominant allowed direct-transition with optical bandgap varies from 2.15 to 2.33 eV. Agrawal et al [6] in 2013 studied the growth of PbI_2 films, morphology and optical properties of the films. The results showed that PbI_2 seemed to have a strong affinity to grow in the orientation (001). The d-spacing of that peak matches ASTM data for 2H poly type PbI_2 . As a compound, PbI_2 consists of two element with high atomic number ($Z_{\text{Pb}}=82$, $Z_{\text{I}}=53$). Lead iodide is a bright yellow, toxic solid, with boiling point at 953°C and melting point at 402°C . When heated, lead iodide convert color from bright yellow to becomes orange and red colors [7]. Because of its wide bandgap and high density (6.2 g/cm^3), PbI_2 can be used to manufacture gamma and X-ray detectors with low noise operation [8]. Previously, the thin film of PbI_2 were prepared from solutions, melts and gels [6]. The aim of this work is to prepare PbI_2 thin films by TET and to study some of their structural and optical properties.

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2. Experimental part

PbI₂ films were deposited on glass substrates by TET. PbI₂ powder with high purity (99.99 %) from Sigma-Aldrich was evaporated onto glass slides which were used as substrates for PbI₂ thin films. The substrates were cleaned with ethanol solution and distilled water. Then they were immersed for 30 min. in a basin of ultrasound device to avoid unwanted dirties. The films were deposited inside a chamber with a low pressure of 10⁻⁵ Torr with deposition rate about 100 Å/s. The final films were annealed inside an oven with temperature of 100 °C for 30 min. and then lowered to room temperature. XRD measurements were implemented using Shimadzu XRD Model-6000. The absorption spectra were measured via a spectrophotometer (Metertech SP8001) at room temperature and Tauc plot was utilized to calculate the bandgap. The morphological studies were carried out using a scanning electron microscope (SEM). The film thickness was calculated using the formula [9].

$$s = \frac{m}{\pi\rho h^2} \quad (1)$$

where s and m are the thickness and the mass of the film, respectively, ρ is the density of the evaporated material, h is the distance from the boat to the substrate.

3. Result and discussion

Fig. 1 shows XRD patterns for PbI₂ thin films prepared by TET before and after annealing at 100°C. For as-deposited PbI₂ films, the intensity of diffracted x-ray was recorded for a range of 2θ from 10° to 80°. The main diffraction peaks of PbI₂ thin film before annealing were (001), (110), (002), (003), (004), (202) and (220). The film after annealing showed the same peaks of PbI₂ but with a missing of two peaks. The strongest peaks of pbI₂ films were observed for the planes: (001), (002) and (003) with values of inter-planer distance of ($d= 6.972, 3.863$ and 2.273 Å) respectively. These results have good agreement with references [4-6]. Table (2) and (3): display the grain size and the inter-planer distances of PbI₂ films before and after annealing at 100 °C.

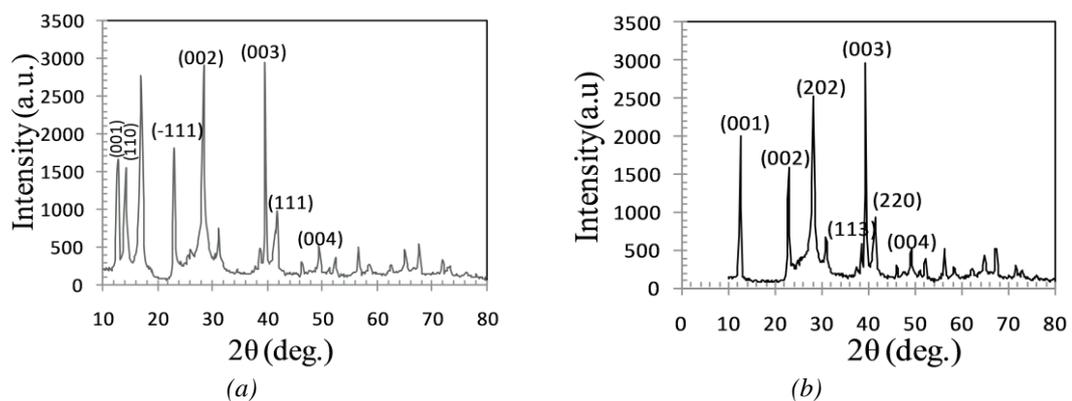


Fig. 1. XRD and Miller indices of PbI₂ film (a) before annealing (b) after annealing at 100 °C.

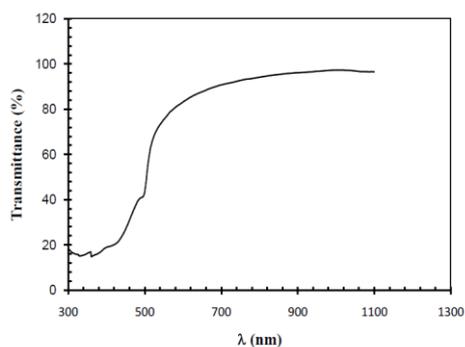
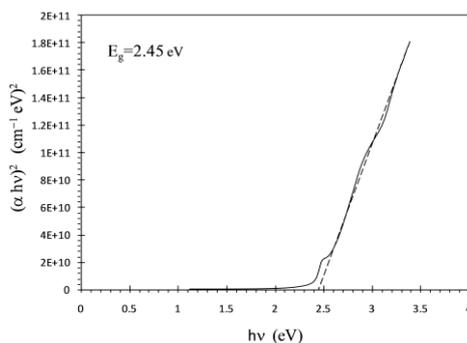
Table 1. Scherrer analysis of PbI_2 film before annealing.

Plane	$2\theta(\text{deg.})$	$D(\text{nm})=0.9\lambda/\beta\cos\theta$	$s=1/D^2(\text{lines}/\text{nm}^2)$
(001)	12.69	13.76	0.0053
(110)	14.16	10.26	0.0095
(002)	23	13.89	0.0052
(202)	28.32	10.80	0.0086
(003)	39.61	17.25	0.0034
(220)	41.6	08.34	0.0140
(004)	52.31	14.95	0.0045

Table 2. Scherrer analysis for PbI_2 film after annealing at 100°C .

Plane	$2\theta(\text{deg.})$	$D(\text{nm})=0.9\lambda/\beta\cos\theta$	$s=1/D^2(\text{lines}/\text{nm}^2)$
(001)	12.70	14.84	0.0045
(202)	28.29	10.52	0.0090
(003)	39.58	17.23	0.0034
(220)	41.49	9.30	0.0116
(004)	52.31	16.21	0.0038

The transmission spectrum of PbI_2 films as a function of wavelength (300-1100 nm) is shown in Fig. 2. The thickness of PbI_2 was so thin (about 150 nm) so that the average transmission over the range (575-1100) nm could exceed 80% with a sharp fall near the fundamental absorption of PbI_2 .

Fig. 2. Transmittance spectrum for PbI_2 film prepared by thermal evaporation.Fig. 3. $(\alpha h\nu)^2$ vs photon energy for a PbI_2 thin film.

The optical bandgap has been analyzed using Tauc plot [10] in which there is a quadratic relationship between the absorption coefficient and the photon energy:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (3)$$

where A is a constant. This equation is frequently used to elicit the type of the optical transition and to calculate the value of the optical bandgap energy (E_g) from UV-vis data [11]. Fig. 3 shows a linear variation between $(\alpha h\nu)^2$ and the photon energy. This behavior indicates a direct allowed transition in the PbI_2 thin film. The optical bandgap can be extracted from the linear part of the curve to the photon energy axis [12]. The extrapolation gave a bandgap value of 2.45 eV for our PbI_2 thin film. This result has a good agreement with the findings of Agrawal et al [6].

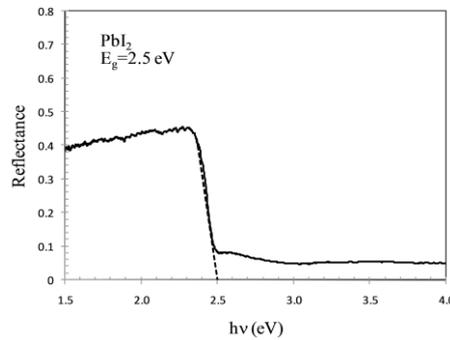


Fig. 4. Determination the energy bandgap of PbI_2 thin films using reflectance data.

Reflectance spectra can also be used to calculate the absorption edge of PbI_2 . Figure 4 shows the reflectance of PbI_2 against the photon energy in the range (1.5 - 4 eV). The sharp fall of reflectance determines where the sample starts to absorb near the band edge. The intersection point between the extrapolation line and the $h\nu$ -axis gives the value of energy bandgap (E_g). The result gives a bandgap of ($E_g = 2.5$ eV) which is in good agreement with result extracted from Tauc plot.

In general, in addition to the fundamental band-to-band absorption, we can observe two types of sub-bandgap absorption. The first one is band-to-defect transition [13] and it shows up a very low value of absorption coefficient compared with that for the fundamental band-to-band absorption. The second one is band-to-tail transition and it is normally described by Urbach rule [13] which is for a constant temperature given by

$$\alpha = \alpha_0 \exp(h\nu / E_u) \quad (4)$$

where α_0 and E_u are material dependant constant and Urbach energy; respectively [14]. This equation describes that the absorption coefficient has an exponential dependence on photon energy below the absorption edge. Fig. 5 shows Urbach tails for PbI_2 thin films prepared by TET. The figure reveals a straight line relationship between $h\nu$ and $\ln \alpha$ given by the equation $y=1.320x+8.597$. The value of Urbach energy ($E_u = 0.757$ eV) is calculated from the reciprocal of the slope.

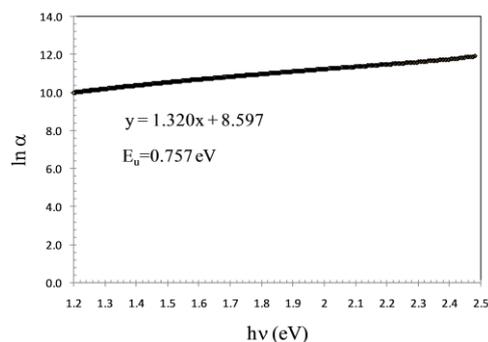


Fig. 5. Urbach tails for PbI_2 thin films prepared by TET.

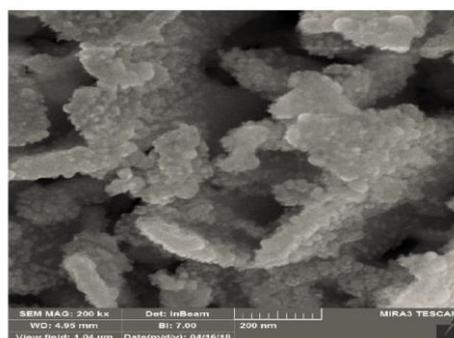


Fig. 6. SEM of PbI_2 thin film prepared by thermal evaporation technique.

Fig. 6 reveals the morphology of PbI_2 imaged by SEM. No regular nano-shape (such as nanotubes or nanorods) can be identified from this image and the figure shows only a sponge-like structure with a great number of pores. Most of the crystallite sizes are in the range from 10 nm to 20 nm and this confirms the results of XRD presented in Tables 3 and 4.

4. Conclusions

The predominant orientations for lead iodide thin films prepared by physical thermal evaporation technique are (001), (002) and (003) as confirmed by X-ray diffraction analysis. The crystallite size of PbI_2 thin films synthesized by thermal evaporation ranges from 8 to 18 nm. The energy bandgap value of PbI_2 determined by the reflectance measurements has good agreement with that calculated from Tauc plot using UV-vis measurements. The lead iodide thin films prepared by fast deposition rate are porous in nature; they showed a direct optical bandgap and an obvious Urbach tail.

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