Structural and optical properties of PbI₂ nanostructures obtained using the thermal evaporation method

Safaa I. Mohammed, Y. Al-Douri, U. Hashim, N.M. Ahmed, and R. Al-Gaashani

Abstract: Lead iodide (PbI₂) nanostructures were successfully prepared using the thermal evaporation method on a glass substrate at room temperature. The structural properties were analyzed using X-ray diffraction, which revealed that the crystal size increases as thickness increases. Crystal size was calculated to be in the range 27.3–61.08 nm. In addition, the preferred growth orientation was (001) for all samples. The surface morphologies using scanning electron microscopy have shown an increasing of grain size with increasing thickness. Also, optical properties using ultraviolet–visible spectroscopy were researched as a function of thickness. The absorption data have indicated direct transmission with optical energy band gap that varies continuously from 2.35 to 2.40 eV at room temperature. The refractive index and optical dielectric constant were investigated to verify the suitability of the model for electro-optical systems. The low fluctuation in energy band gap indicates that the grain size is quite small. The obtained results are in good agreement with experimental and theoretical data.

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Résumé : Nous préparons des nanostructures d’iode de plomb par évaporation sur un substrat de verre à la température de la pièce. L’analyse de leurs propriétés structurelles par diffraction X (XRD) révèle que la grosseur des cristaux augmente avec l’épaisseur. Notre calcul indique que les cristaux varient en grosseur de 27.3 à 61.08 nm et l’orientation préférée est (001) pour tous les échantillons. La microscopie électronique à balayage montre des morphologies de surface dont le grain croît en grosseur avec l’épaisseur. La spectroscopie UV permet d’étudier les propriétés optiques en fonction de l’épaisseur. Les données d’absorption indiquent une transmission directe, avec un intervalle de bande d’énergie (gap) variant de façon continue de 2.35 à 2.40 eV à la température de la pièce. Nous étudions l’indice de réfraction et la constante diélectrique optique afin de vérifier la valeur du modèle pour les systèmes électro-optiques. Les faibles variations du gap indiquent que les grains sont très petits. Les résultats obtenus sont en bon accord avec des données expérimentales et théoriques. [Traduit par la Rédaction]

Introduction

Lead iodide (PbI₂) is a direct band gap semiconductor of 2.3–2.4 eV and hexagonal structure. It is a toxic yellowish solid, and displays a range of colors with varying temperatures from bright yellow at room temperature to brick red. PbI₂ has attracted the attention of many researchers because of its potential applications in the areas of radiation detectors, optoelectronic devices, and solar cells [1, 2]. Because of the high atomic number of its elements (ZPb = 82, ZI = 53), the applications of PbI₂ depend on the fabrication technique and growth process [3, 4]. Moreover, it can detect ionizing radiation at room temperature using the direct detection method, which is particularly suitable for low energy [5, 6]. It is used as an ionizing radiation detector of X- and γ-rays [7, 8]. Some researchers have investigated the structural properties of PbI₂ [9, 10]. Because several methods for depositing films require sublimation or evaporation of the material, it should have a temperature for appreciable evaporation or at least a temperature for appreciable sublimation as films that can be grown at temperatures lower than 250 °C, the maximum temperature for the detector stability during deposition. The material must be thick enough to absorb a high percentage of X-rays, taking into consideration its absorption coefficient. The grain size must be less than 100 μm, therefore, small grain size polycrystalline films or epitaxial films are required [11].

Bhavsar and Saraf [12] have studied the growth of PbI₂ crystals using the silica gel method. They have mentioned many observations of the crystals faces that reveal that they have grown by layer as well as by spiral mechanisms. Manol et al. [13] have prepared PbI₂ according to the Bridgman technique by physical vapor transport. They have obtained that electrical conductivity was to be 3 × 10⁻¹² Ω⁻¹ cm⁻¹ and the optical energy band gap is 2.28 eV. Also, Matuchova et al. [14] have synthesized, prepared, and purified PbI₂ using Bridgman zone melting and growth techniques. They have investigated the structural and higher resistively equals to 1.4 × 10⁻¹² Ω⁻¹ cm⁻¹. Derenzo et al. [15] have elaborated the temperature dependence of pulsed X-ray time spectra, wavelengths, and intensities of PbI₂. Increasing the temperature to 165 K leads to a decrease in the luminosity by a factor of 27 and full width at half maximum (FWHM) from 0.52 to 0.15 ns, and improves the efficiency of nonradiative recombination centers. Zhu et al. [16] have grown PbI₂ single crystal samples with dimensions of 10 mm × 10 mm × 1 mm reaching 40% transmittance in the range 400–4000 cm⁻¹. Their measurement of ultraviolet–visible (UV–vis) radiation has indicated a cutoff wavelength equal to 547.6 nm and corresponds to E₆ = 2.27 eV.

This work aims to prepare PbI₂ nanostructures using the thermal evaporation method and to study the structural and optical properties for determining the grain size and energy gap, respectively, in addition to researching the thickness dependence of surface morphology and topography with grain size, microstrain, and energy gap.
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Evacuated to about $5 \times 10^{-5}$ Torr. The PbI$_2$ was heated using a tungsten filament causing PbI$_2$ to sublimate and condense onto and the substrate [13]. PbI$_2$ grew on a 10 cm × 10 cm area up to included separate temperature controllers for the charge (or source) and the cooler surroundings including a specially prepared substrate. The process control and monitoring equipment in this setup includedseparated temperature controllers for the charge (or source) and the substrate. The weight of dissolved material was determined according to the following equation:

$$\text{Pb(NO}_3\text{)}_2 + 2\text{KI} \rightarrow \text{PbI}_2 + 2\text{KNO}_3$$

Adding 50 mL of KI solution to 50 mL of Pb(NO$_3$)$_2$ solution to prepare PbI$_2$ through the following reaction. Soon, a yellow deposit appeared in the bottom of the beaker. This deposit was lead iodide (PbI$_2$), which is not soluble in cold water, while the potassium nitrates (KNO$_3$) are dissolved in cold water. Then, the water is removed from the beaker using a scaled syringe to avoid any disturbance. After the deposited material was dried, it was removed from the bottom of the beaker and kept in a desiccator. Thus, PbI$_2$ was deposited on glass substrates at room temperature using electron beam evaporation (Auto 306 Vacuum Coater). The principle reason for using this technique was to allow deposition of a large area in a cost-effective manner [17]. A tungsten boat was used, with precision reaching 10$^{-4}$ g. Samples were taken of different thicknesses 350, 400, and 1700 nm. Because of technique limitations, XRD (Philips pw 1710 X-ray diffractometer) was used to determine whether the sample was crystalline or not with the following characteristics; the source of the CuK$_\alpha$ radiation with 1.54 Å wavelength, incidence angle is 10$^{-6}$–60$^{-6}$ and scanning speed is 5°/min. The optical properties were studied by UV–vis (Perkin-Elmer Lambda 950 spectrophotometer) in the 300–1100 nm wavelength range. The morphology and topography studies were done using the scanning electron micrographs (SEM; JEOL-JSM-6460 LV) and atomic force micrographs (SII Sciko Instrument INC, SPI 3800N), respectively with probe station scan area 2000 nm and scan speed 2 Hz.

### Experimental process

Glass substrates were provided of thickness 1 mm and dimensions $15 \times 20$ mm prior to the thermal evaporation of PbI$_2$. They were ultrasonically cleaned for 10 min using isopropanol alcohol and deionized water. PbI$_2$ was prepared by reacting potassium iodide (KI) with lead nitrates (Pb(NO$_3$)$_2$) according to the following experimental steps. Preparation of Pb(NO$_3$)$_2$ solution of 0.01 mol/L by dissolving 3.31 g in 1000 mL of distilled water. Setting of KI solution with 0.05 mol/L by dissolving 8.31 g in 1000 mL of distilled water. As well, the weight of dissolved material was determined according to the following formula:

$$\text{PbI}_2$$

where $d$ is the interplanar spacing, and $\theta$ is Bragg’s angle. Table 1 presents the structural properties of PbI$_2$ as a function of different thicknesses. One can see strong peaks at $d = 6.98$, 2.327, and 1.74 Å which correspond to (001), (003), and (004), respectively. For thicker deposits, other peaks at 3.49, 2.56, and 1.92 Å correspond to (002), (102), and (112) planes. The presence of these reflections indicates a high degree of crystallization with preferred orientation perpendicular to the c-axis. These results are in good agreement with the findings of other researchers [19, 20]. Figure 1 shows the increase of thickness that leads to an increase of intensity because of higher orientation and crystallization. This indicates a large number of Bragg planes and hence a higher diffraction intensity of the (001) peak. These findings clearly demonstrate that the size of the crystals increase as the thickness increases. Fig. 2 shows that the layers are made of spherical platelets parallel to the substrate plane. The scanning electron micrograph images are homogenous and the grains take plate shape as thickness increases. One can calculate the average grain size and determine whether the deposited ones suffer from stress or not. The lattice constants, $a$ and $c$, were calculated using the following relationships for hexagonal crystal structure [21]:

$$n\lambda = 2d \sin \theta$$

(1)

where $n$ is a positive integer, $\lambda$ is a wavelength, $d$ is the interplanar spacing, and $\theta$ is Bragg’s angle. Table 1 presents the structural properties of PbI$_2$ for different thicknesses. The process control and monitoring equipment in this setup includedseparate temperature controllers for the charge (or source) and the substrate [13]. PbI$_2$ grew on a 10 cm × 10 cm area up to 250 μm in thickness [17]. The weight method was adopted to measure the thickness. A sensitive electrical balance Metler (AE-160) was used, with precision reaching 10$^{-4}$ g. Samples were taken of different thicknesses 350, 400, and 1700 nm. Because of technique characteristics, XRD (Philips pw 1710 X-ray diffractometer) was used to determine whether the sample was crystalline or not with the following characteristics; the source of the CuK$_\alpha$ radiation with 1.54 Å wavelength, incidence angle is 10$^{-6}$–60$^{-6}$ and scanning speed is 5°/min. The optical properties were studied by UV–vis (Perkin-Elmer Lambda 950 spectrophotometer) in the 300–1100 nm wavelength range. The morphology and topography studies were done using the scanning electron micrographs (SEM; JEOL-JSM-6460 LV) and atomic force micrographs (SII Sciko Instrument INC, SPI 3800N), respectively with probe station scan area 2000 nm and scan speed 2 Hz.

### Results and discussion

Lead iodide (PbI$_2$) has shown crystalline structure using XRD to give the preferred direction (001), the strongly higher than other trends. The interplane spacing can be calculated using Bragg’s diffraction equation [18]:

$$n\lambda = 2d \sin \theta$$

(1)

where $n$ is a positive integer, $\lambda$ is a wavelength, $d$ is the interplanar spacing, and $\theta$ is Bragg’s angle. Table 1 presents the structural properties of PbI$_2$ as a function of different thicknesses. One can see strong peaks at $d = 6.98$, 2.327, and 1.74 Å which correspond to (001), (003), and (004), respectively. For thicker deposits, other peaks at 3.49, 2.56, and 1.92 Å correspond to (002), (102), and (112) planes. The presence of these reflections indicates a high degree of crystallization with preferred orientation perpendicular to the c-axis. These results are in good agreement with the findings of other researchers [19, 20]. Figure 1 shows the increase of thickness that leads to an increase of intensity because of higher orientation and crystallization. This indicates a large number of Bragg planes and hence a higher diffraction intensity of the (001) peak. These findings clearly demonstrate that the size of the crystals increase as the thickness increases. Fig. 2 shows that the layers are made of spherical platelets parallel to the substrate plane. The scanning electron micrograph images are homogenous and the grains take plate shape as thickness increases. One can calculate the average grain size and determine whether the deposited ones suffer from stress or not. The lattice constants, $a$ and $c$, were calculated using the following relationships for hexagonal crystal structure [21]:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

(2)

where $hkl$ are Miller indices belonging to the (001), (002), (003), (004), (102), and (112) planes in the diffraction pattern of PbI$_2$, it is found that the obtained values of lattice parameters are in a good agreement with others [19, 20]. The effect of thickness on lattice
parameters is observed in Table 1. The average grain size is determined from the FWHM for the most intense peak using Scherer’s formula [22]

\[
D = \frac{0.9\lambda}{\beta2\theta \cos \theta} \tag{3}
\]

where \(D\) is the average grain size, and \(\beta2\theta\) is the FWHM. Figure 3 shows the variation of average grain size with different thickness, where the average grain size increases gradually with increasing thickness. The FWHM is an indication of the existence of dislocation in the material [23]. From Table 1, we can conclude that as the FWHM decreases, the thickness increases,
which may be attributed to the good crystallization of the deposited thicker films. The microstrain could be calculated using

\[ \delta = \left( \frac{|C_{\text{ASTM}} - C_{\text{XRD}}|}{C_{\text{ASTM}}} \right) \times 100\% \]

where \( \delta \) is the residual stress. The measured value of micro strain for different thickness of PbI\(_2\) is given in Table 1. It is increasing gradually as shown in Fig. 4. Figure 5 shows atomic force micrographs images to depict very smooth surfaces for both 350 and 1700 nm thicknesses with an average surface roughness of 0.020 and 0.047 \( \mu \)m, respectively. The optical properties of the transmittance spectrum within wavelengths of 500–1100 nm exceeded 75\% for 350 nm thickness with a sharp decrease near the spectrum record transmittance for the other thicknesses, as shown in Fig. 6, while plots of \((\alpha h \nu)^2\) versus the photon energy \((h \nu)\) in the absorption region near the fundamental absorption edge indicates direct allowed transmission, as shown in Fig. 7. It is observed that \( E_g \) decreases as thickness increases, as shown in Fig. 8 and confirmed in Table 2. In general, thickness dependence of optical energy band gap can arise due to one or combined effects of the change in barrier height and grain size in polycrystalline films [22].

The refractive index, \( n \), is an important physical parameter related to microscopic atomic interactions. Theoretically, the two different approaches in viewing this subject are the refractive index (related to density), and the local polarizability of these entities [29]. On the other hand, when the crystalline structure is represented by a delocalized picture, \( n \) will be closely related to the energy band structure of the material, complicated quantum mechanical analysis requirements, and the obtained results. Many attempts have been made to relate the refractive index, \( n \), and the energy gap, \( E_g \), through simple relationships [25, 30–34]. Here, the various relationships be-
between $n$ and $E_g$ will be reviewed. Ravindra et al. [25] had suggested different relationships between the band gap and the high frequency refractive index and presented a linear form of $n$ as a function of $E_g$

$$n = \alpha + \beta E_g$$

(5)

where $\alpha = 4.048$ and $\beta = -0.62$ eV$^{-1}$.

Inspired by the simple physics of light refraction and dispersion, Herve and Vandamme [26] proposed an empirical relation as

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2}$$

(6)

where $A = 13.6$ eV and $B = 3.4$ eV. Ghosh et al. [27] had taken a different approach to the problem by considering the band structural and quantum-dielectric formulations of Penn [35] and Van Vechten [36]. Introducing $A$ as the contribution from the valence electrons and $B$ as a constant additive to the lowest band gap, $E_g$, the expression for the high-frequency refractive index is written as

$$n^2 - 1 = \frac{A}{(E_g + B)^2}$$

(7)
where $A = 25E_g + 212$, $B = 0.21E_g + 4.25$, and $(E_g + B)$ refers to an appropriate average energy gap of the material. Thus, these three models of variation $n$ with energy gap have been calculated. Also, the calculated values of the optical dielectric constant $(\varepsilon_\infty)$ were obtained using the relation $\varepsilon_\infty = n^2$ [37]. Our calculated refractive index values are in good agreement with experimental value [28] as given in Table 2. This gives an appropriate model of Ravindra et al. for electro-optical applications.

### Conclusion

PbI$_2$ was prepared using the thermal evaporation method. PbI$_2$ nanostructures are homogenous with plaque shape. The nearest-neighbor distance and lattice constant are in agreement with experimental and theoretical data. The grain size increases with increasing thickness. The low fluctuation of the XRD pattern is due to the fluctuation in lattice parameters which is attributed to the stress (positive) that accompanies the increasing grain size. The energy band gaps vary from 2.35 to 2.40 eV as the thickness increases. The low fluctuation in energy band gap indicates that the grain size is quite small. The transmission has exceeded 75% for 350 nm thickness in accordance with absorption coefficient. Additionally, the calculated refractive index using the Ravindra et al. model is in accordance with experimental data that recommends PbI$_2$ nanostructures for electro-optical applications.

### Acknowledgements

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### References


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**Table 2.** Energy band gap of PbI$_2$ for different thicknesses corresponding to refractive index $n$ and optical dielectric constant $\varepsilon_\infty$ using Ravindra et al. [25], Herve and Vandamme [26], and Ghosh et al. [27] models.

<table>
<thead>
<tr>
<th>Thickness, $t$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>Reflective index, $n$</th>
<th>Optical dielectric constant, $\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>2.40‡</td>
<td>2.56*</td>
<td>6.55‡</td>
</tr>
<tr>
<td>350</td>
<td>2.38‡</td>
<td>2.54†</td>
<td>6.45†</td>
</tr>
<tr>
<td>350</td>
<td>2.28§</td>
<td>2.50∥</td>
<td>6.25∥</td>
</tr>
<tr>
<td>350</td>
<td>2.27**</td>
<td>2.84††</td>
<td>—</td>
</tr>
<tr>
<td>400</td>
<td>2.38‡</td>
<td>2.57*</td>
<td>6.60*</td>
</tr>
<tr>
<td>400</td>
<td>2.38‡</td>
<td>2.55†</td>
<td>6.50†</td>
</tr>
<tr>
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<td>2.51∥</td>
<td>6.30∥</td>
</tr>
<tr>
<td>1700</td>
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<td>2.59*</td>
<td>6.70*</td>
</tr>
<tr>
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<td>2.56∥</td>
<td>6.35∥</td>
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<tr>
<td>1700</td>
<td>2.35‡</td>
<td>2.52∥</td>
<td>6.35∥</td>
</tr>
</tbody>
</table>

*Ref. 25, using Ravindra et al.
†Ref. 24, exp.
‡Ref. 26, using Herve and Vandamme.
§Ref. 13, exp.
∥Ref. 27, using Ghosh et al.
**Ref. 16, exp.
††Ref. 28, exp.

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