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Growth and Characterizes of PbI_2 Films by Vacuum Evaporation Method

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Abstract

In this work, thin films of lead iodide (PbI_2) were deposited on glass substrates with different thicknesses by vacuum thermal evaporation method. The structural, chemical, electrical and optical characteristics of the thin films were studied. XRD analysis showed that lead iodide film is polycrystalline having hexagonal structure. A particle size was estimated by Williamson - Hall of technique (13) nm and strain ($4.90*10^{-3}$) is found from the intercept with y-axis and slope for PbI_2. The UV-VIS measurements illustrated that the lead iodide has a direct optical band gap and Urbach energy to be 0.677 eV. Raman peaks are detected at 70, 96, 99.5, 188 and 202 cm^{-1} which corresponding to the characteristic of PbI_2 at (E_{21}, A_{11}, $2E_{11}$ and A_{1g}). The FTIR spectrum of PbI_2 thin film showed six bands at 1650, 1900, 3100, 3400, 3600 and 3800 cm^{-1}. Mechanism of dc transport was also analyzed in the temperature range 315–395 K. However the variation of reflectivity in the range near infrared is conductive which attributed to thin film nature, where this film contains light scattering and large surface area, which enhance the optical absorption and hence, a low reflectivity is obtained.

Keywords: PbI_2 thin films, Vacuum evaporation, direct band gap, Raman scattering, Urbach energy and Reflectivity.

الخلاصة

في هذا العمل، ترسبت أغشية رقيقة من يوديد الرصاص (PbI_2) على ركائز زجاجية بأسماك مختلفة بواسطة طريقة التبخير الحراري بالفراغ. تمت دراسة الخصائص التركيبية والكيميائية والكهربائية والبصرية للأغشية الرقيقة. أظهر تحليل XRD أن غشاء يوديد الرصاص عبارة عن غشاء متعدد البلورات له بنية سداسية. تم تقدير حجم الجسيم (13 nm) بواسطة تقنية Williamson-Hall و المطاوعة ($4.90*10^{-3}$) من التقاطع مع المحور y والميل لـ PbI_2. توضح قياسات الأشعة فوق البنفسجية UV-VIS أن يوديد الرصاص له فجوة طاقة بصرية مباشرة وأن طاقة أورباخ هي (0.677 eV). تم الكشف عن قمم رامان في 70, 96, 99.5, 188و 202 cm^{-1} والتي تتوافق مع خصائص PbI_2 في (E_{21}، A_{11}، $2E_{11}$ و A_{1g}). أظهر الطيف FTIR لغشاء PbI_2 الرقيق ستة اواصر في cm^{-} 1650, 1900, 3100 , 3400 , 3600 و 3800 cm^{-1}. كما تم تحليل آلية نقل التيار المستمر في نطاق درجة الحرارة 315–395 K. ومع ذلك ، فإن تغيّر الانعكاسية في المدى القريب من الأشعة تحت الحمراء موصلٌ إلى الطبيعة الغشاء الرقيقة ، حيث يحتوي هذا الفيلم على تشتت الضوء ومساحة سطح كبيرة ، مما يعزز الامتصاص وبالتالي ، يتم الحصول على انعكاسية قليلة.

Introduction

Lead Iodide (PbI2) is a yellow and toxic, solid, as from powder material, having boiling point at 1,226 K and melting point at 675 K [1]. At high temperature the yellow color of PbI2 converts to orange and red, but when cooling its color returns to yellow [2]. PbI2 is a semiconductor material with direct optical band gap about (2.45 eV) [3]. Lead Iodide has some application such as medical imaging [4] and X-ray and gamma-ray detectors [5] and photo-sensitivity semiconductor applications [6]. It has also used in manufacturing of solar cell for obtaining the methylammonium lead iodide (CH3NH3PbI3) perovskite solar cell [7]. The fundamental structure of PbI2 is starting from the layer of Pb atoms as sandwiched between two layers of I atoms. This structure is a nearly-octahedral [PbI6] unit, in which each atom of lead is surrounded by six atoms of iodide. Interactions between layers are weak Van der Waals kind; so, there are many methods of stacking layers and consequently for this compound exist many poly types [8]. Large atomic number of PbI2 (ZPb=82, ZI=53) and high density (D=6.2 g/cm3) [1]. PbI2 thin films can be grown with different method such as solution, vapor and gel [3]. The aim of this work is to prepare PbI2 films with different thickness by evaporation technique, and studying the optical, electrical, and some properties of this material.

Materials and Methodology

Lead iodide (PbI2) films were grown by vacuum thermal evaporation technique on glass substrate. The high purity (99.9 %) of PbI2 from Sigma- Aldrich was palletized for evaporation. All the films were grown in a base vacuum about 10-5 Torr. The deposition rate was improved at 1-2 nm/s to grow uniform and good quality films. The thickness of PbI2 films was calculated using the formula [9].

$$t = \frac{m}{\pi \rho h2} \qquad (1)$$

Where;

t is thickness of film, m is the mass of material, ρ is density of material, h is the density between substrate and boat.

The structural properties of PbI2 films were analyzed by Shimadzu XRD Model-6000. The optical properties were recorded by using UV-vis spectrophotometer (Metertech SP8001). Phase identification was confirmed by Raman spectra of PbI2 films using Raman microscope (Bruker Sentera) with excitation wavelength at 532 nm. The electrical properties were measure by using FTO substrate to evaporate PbI2 and then deposition of aluminum electrodes on these films. The electrode with length equal to 0.3 cm and width equal to 0.4 cm. Electrical measurements were performed by using the heater, the PbI2 film was heated and the resistance was measured ratio to temperature change by use the ovometer and then the resistivity was calculated and hence calculate the electric conductivity of the film. The transmittance spectra for PbI2 films were recorded using Fourier transform infrared spectrophotometer FTIR (SHIMADZU 8400S spectrophotometer) as a function of wavelength ranging from 1000 to 4000 nm. The diffused reflectance spectra analyzed by (AvaLight-DH-S-BAL- 2048).

Results and Discussion

Figure (1) illustrates XRD of lead iodide film with thickness equal to (602 nm) prepared by thermal evaporation technique with a range registered for 2 from 10o to 80o. Table (1) displays the grain size, the (h k l) planes, the inter-planer distance of lead iodide film by Scherer equation [8].

$$Dave = \frac{K\lambda}{\beta \cos\theta B} \qquad (2)$$

Where:

K: is a constant and, usually equals to (0.9).

λ: is the, wavelength, of, incident radiation equal to (0.15406nm for (CuKα).

β: is the full width half maximum of the peak (in radians).

θ: is angle of Bragg diffraction of the XRD peak.

PbI2 film is polycrystalline, 2θ° having hexagonal structure confirmed by XRD analysis. The main diffraction peaks of PbI2 thin film were (001), (002), (003), (004) and (202).

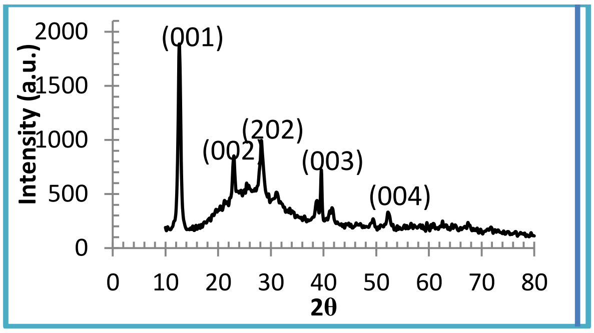

Figure (1): XRD and Miller indices of PbI_2 film.

Table (2): Scherrer analysis of PbI_2 film.

$\delta=1/D^2$ (lines/nm^2)	D(nm)	(hkl)	2θ(deg)
0.00433	15.198	001	12.724
0.01555	8.017	202	28.263
0.01453	8.221	003	38.635

Crystallite size by Williamson - Hall presented a technique strain broadening and for DE convoluting size via looking at the peak width versus 2θ. W-H plot is shown in Fig 2, for PbI2 by sketched the (sinθ) versus with (βcosθ). A particle size was estimated from the data is (13 nm) and strain (4.90*10-3) are found from the intercept with y-axis and slope for PbI2. The particle size found by Scherer equation equal to (10.47 nm) and the particle size found by Williamson – Hall technique equal to (13 nm). The Williamson – Hall technique is the most accurate in calculating particle size because it is the result of strain and particle size the reverse of the Scherer equation depend only on the particle size. The results of lead iodide were compared with ASTM data of Lead Iodide (Card No.7/235).

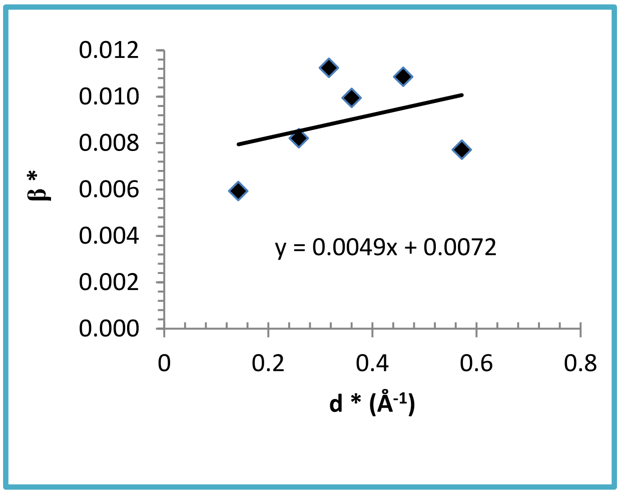

Figure (2): Williamson Hall plot of PbI2 film.

Absorbance measurements were carried out within the wavelength range (300-1300) for PbI2 film with thickness so thin (about 200 nm) prepared by vacuum thermal evaporation method. Figure 3 demonstrates high transmittance as high as 75% in the infrared spectrum. The optical band gap of the thin film was calculated from the following equation is called Tauc relation [10].

$(\alpha h\upsilon)n = A(h\upsilon - Eg)$

Where hν and α photon energy and absorption coefficient, respectively, Eg is an optical band gap, A is a constant. This equation used to determine type of electron transitions (The direct or the indirect) and to estimate value of optical band gap (Eg) [11]. The optical absorption data indicate an allowed direct transmission with optical energy gap equal to 2.4 eV for thin film as show in Figure 4.

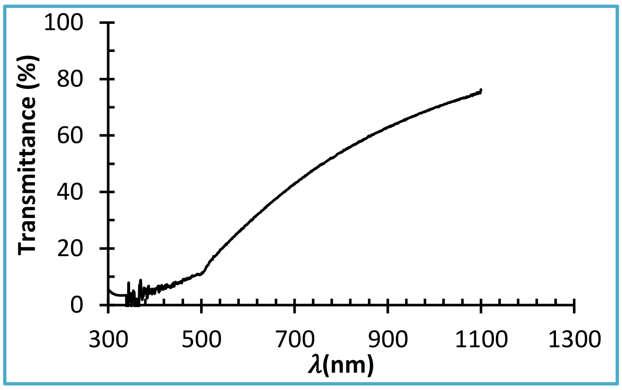

Figure 3: Transmittance spectra of PbI_2 film.

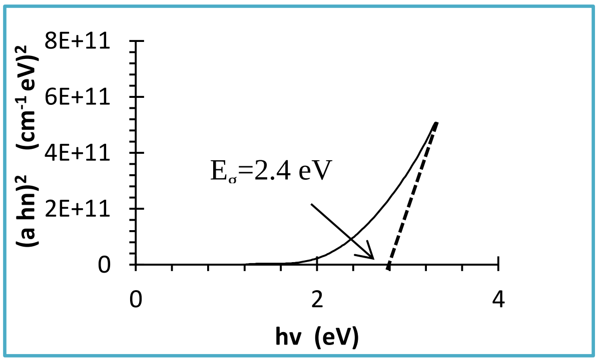

Figure 4: The relationship between $(\alpha\ h\upsilon)^n$ and (hυ) photon energy for PbI2 film.

The Urbach tails energy was calculated for (PbI2) film from the following relationship [12].

$$\alpha = \alpha o \exp\left(\frac{hv}{Eu}\right) \quad (4)$$

Where;
αo: proportionality constant.
Eu: The tail width for the topical levels in the optical gap region (Urbach tails energy) and
(3) (3)
are equal to the inverted slope resulting from drawing the graphical relationship between (hv) and (Ln α).

Figure (5) shows the relationship between (Lnα) and photon energy (hυ), the energy of the Urbach tails represents the presentation of the allowed local cases within the allowed optical energy gap and their calculation is taken by reversing the slope of the straight line of the exponential region, and we found Eu equal to 0.677 eV. Where the energy of the Urbach tails is backward proportional to the energy gap, this means the optical behavior of the Urbach energy is opposite to the optical behavior of the energy gap [22].

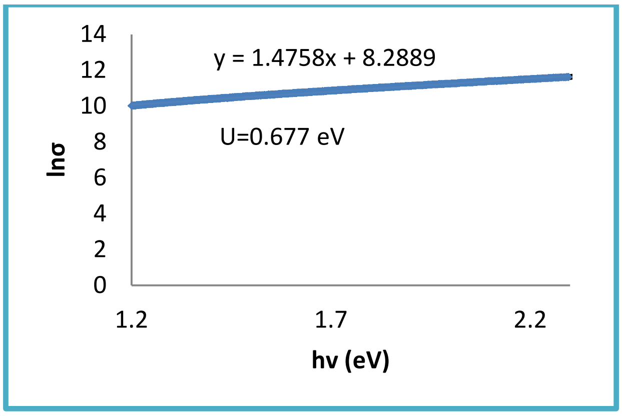

Figure 5: Urbach tails energy for PbI_2 film.

The dc conductivity of lead iodide (PbI2) film is provided in Fig 6. The resistivity of film was calculated using the following equation [8].

$$\rho = Rt\ \frac{w}{l} \quad (5)$$

Where;

R is the resistance of the film, (b, l) are width and length of the electrodes respectively, and t is the thickness of the film.

The conductivity of the material was calculated by taking the inverse of the resistivity. The film exhibited resistivity of 1.34*10-3 versus conductivity 7.46*102 S cm−1. The conductivity of PbI2 film was found an increase with increasing temperature. This result is an agreement with the electronic properties of semiconductor material. In a semiconductor material at low temperature most of the free carriers can't jump from one level to another level because don't have sufficient energy. But the carrier concentration increases in conduction band when the temperature increases, the resultant increase in the dc conductivity [13]. The activation energy equal to 0.05614 eV has been determined by using the following equation [14].

$$Ea = \frac{kB}{q} * 1000 \quad (6)$$

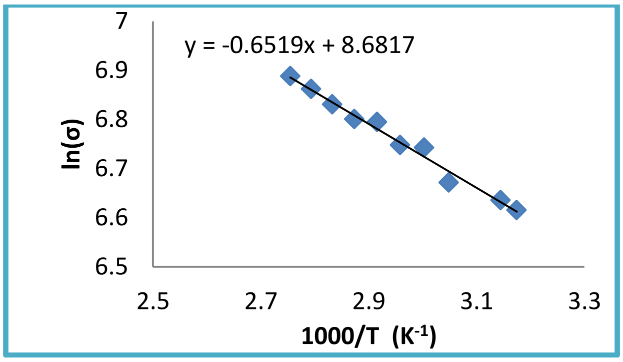

Figure 6: dc Conductivity of PbI_2 film.

Raman spectrum of PbI2 film as shown in Fig 7, with a range 200-1000 cm-1 and were appeared different peaks at 70, 96, 99.5, 188 and 202 cm-1.

The unit cell of 2H contains three atoms, in which there are nine normal modes of vibration of the PbI2 2H poly type. Which can be represented in the irreducible D3d point group: equal to Alg+Eg+ 2A2u+ 2E where Eu, Eg are doubly degenerate and A represent wave functions are singly degenerate, u is ungerade (odd), g is gerade (even) [15]. The peaks at 70, 96, and 202 cm−1, which can be attributed the vibration modes E21, A11, and A1g, respectively [16]. The peak 96 cm-1 is the signature of PbI2 [17]. The peak at 188 cm-1 is probably due to multi-phonon interactions (they correspond to the sum and difference sets of two or more photons) [18].

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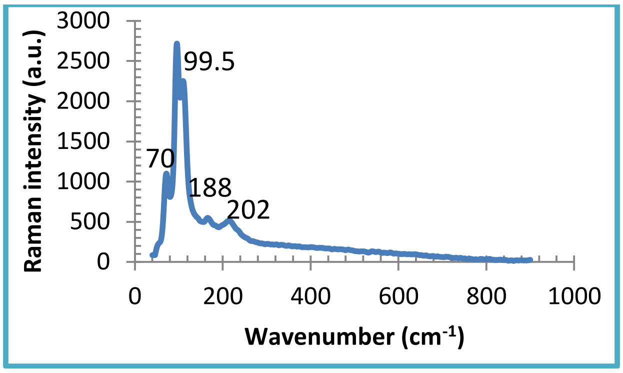

Figure 7: Raman spectra at λ_{exc} = 532 nm for PbI_2 film.

The reflectance of PbI2 in range (200-1400 nm) shows in Figure 8. By reflectance measurement, the band gap energy was calculated and equal to 2.8 eV and hence this result is an agreement with result of optical measurement. From Figure 8, we note high value of reflectance at 550 nm and after then begin to decrease gradually with. The refractive index as shown in Figure 9, we observe less value of refractive index when high value of wavelength as there is an inverse relationship between them and can be calculated using [19].

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (7)$$

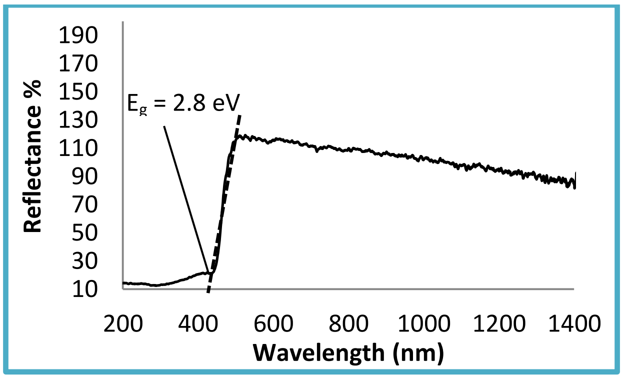

Figure 8: Reflectance versus incident wavelength.

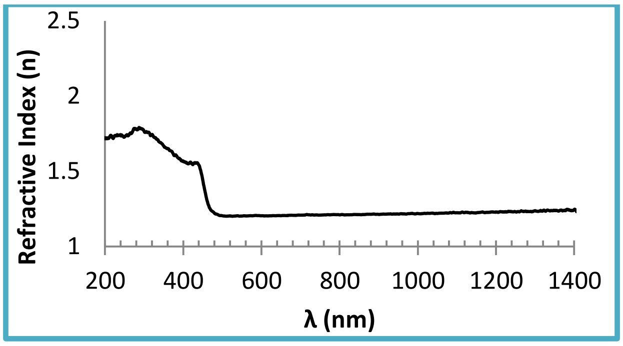

Figure 9: Refractive index for.PbI_2 film.

The FTIR spectrum for PbI2 is shown in Fig 10. Different vibration modes of Oxygen–hydrogen group of absorbed water molecules in which lines at 3400 and 1650 cm-1 can be appointed. From the Fourier transform infra-red noted strong interactions between Pb and I molecules. Two modes Asymmetric near 3700 cm-1 and symmetric near 3600 cm-1 stretching vibrations generally happen [20, 21].

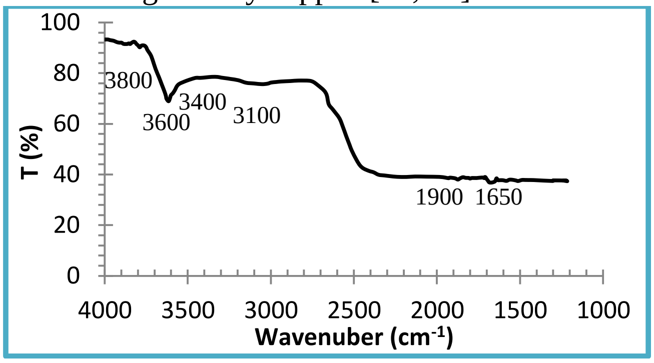

Figure 10: FTIR spectra for PbI_2 film.

Conclusions

In the present work, lead iodide (PbI2) film is prepared by vacuum thermal evaporation method. The structural properties of lead iodide film demonstrated polycrystalline and hexagonal structure. The optical properties exhibited high transmission equal to 75% with optical band gap equal to 2.4 eV. The electric studies showed high conductivity at room temperatures. The Raman intensity illustrated different peaks, but the signature of lead iodide is 96 cm-1. The reflectance with a wavelength range from 200 to 1400 nm, showed high reflectance in 550 nm and after this wavelength decrease gradually. The three emission bands at 1650, 1900, 3100, 3400, 3600, 3800 cm-1 were analyzed by FTIR studies.

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