Zinc Effect on Quantum Dots Potential of PbI₂ Nanostructures

Y. Al-Douri¹,2,∗, U. Hashim¹, A. Bouhemadou³, and M. Ameri⁴

¹Institutes of Nano Electronic Engineering, University Malaysia Perlis, 01000 Kangar, Perlis, Malaysia
²Physics Department, Faculty of Science, University of Sidi-Bel-Abbes, 22000-Algeria
³Laboratory for Developing New Materials and Their Characterization, University of Setif 1, Setif 19000, Algeria
⁴Laboratoire Physico-Chimie des Matériaux Avancés (LPCMA), Université Djilali Liabès de Sidi Bel-Abbès, Sidi Bel-Abbès, 22000, Algérie

The structural properties of undoped and Zn-doped lead iodide (PbI₂) nanostructures of different dopants weights have been investigated. Undoped and different Zn-doped PbI₂ were grown successfully by thermal evaporation method using substrate of glass at room temperature. The dislocation density and particle size are elaborated in addition to energy band gap. The quantum dots potential, refractive index and optical dielectric constant are calculated, this leads to investigate nanoelectronics of quantum dots for solar cells applications. A careful analysis of the absorption coefficients has indicated the band gap. The obtained results are in good agreement with experimental and theoretical data.

Keywords: ZnPbI₂ Nanostructure, Optical Properties, Quantum Dots Potential.

1. INTRODUCTION

Lead iodide (PbI₂) has average band gap of 2.32 eV for using in solid state X-ray and gamma-ray detectors.¹,² The sequence of I–Pb–I planes defines a molecular layer. The unit cell dimension is a = 4.557 and c = 6.979 Å.³ Due to high-atomic number of its elements (Z Pb = 82, Z I = 53), the mass absorption coefficient for these radiations determines 7 and 1560 μm are sufficient for 90% absorption of 6 and 120 keV radiation, respectively.⁴ It is very important for technological applications that can be used as detectors.⁵

Sun et al.⁶ have prepared PbI₂ polycrystalline thin films by thermally physical vapor phase growth in vacuum. X-ray diffraction measurement and atomic force microscope analysis show that the structural change of the films occurs depending on growth condition. They have found that the films structure is sensitive to growth parameter. A microstructure evolution model with respect to grain orientation is developed to explain the morphological and structural variation process during the films growth. While, Bourret-Courchesne et al.⁷ have studied the doping of In in CdS and Ga in ZnO as donors to generate electrons close to bottom of conduction band. It is thought that additional dopant is responsible for trapping ionization holes and promoting rapid radiative recombination and these compete with native non-radiative centers. Also have explored possibility of introducing dopants as efficient hole traps and radiative centers. And, Gulia et al.⁸ have shown vacuum-evaporated stoichiometric ultrathin discontinuous. PbI₂ films has a linear grain size (4–16 nm) growth with film thickness as revealed by transmission electron microscopy/X-ray diffraction analyses. They have researched the optical spectra for films thicker than 20 nm. Relevant data from similar earlier studies agree quite well with their analysis and show that an appropriate choice of the bulk optical transition concerned is necessary for correctly interpreting the grain size-induced blue shift of optical structures for anisotropic and complex band structure materials like PbI₂. Theoretically, our group⁹,¹⁰ has elaborated quantum dots potential using density functional theory (DFT) of the full potential-linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2K code for different materials. The optical properties are predicted to be applicable for solar cells applications.

This paper goal to grow undoped and Zn-doped PbI₂ nanostructures using thermal evaporation technique to investigate the optical and structural properties depositing on glass substrate. In addition, elaborate the doping effect on quantum dots potential and refractive index. Explanation of experimental process is detailed in Section 2. Section 3 presents both structural and optical properties.

Conclusion is summarized in Section 4.
2. EXPERIMENTAL PROCESS

According to the following experimental steps, lead iodide was prepared by a reaction of potassium iodide (KI) with lead nitrate Pb(NO₃)₂:

(a) Pb(NO₃)₂ solution of 0.01 M by dissolving 3.31 mg in 1000 ml of distilled water.

(b) KI solution preparation with 0.05 M by dissolving 8.31 mg in 1000 ml of distilled water. Adding 50 ml of KI solution to 50 ml of Pb(NO₃)₂ solutions to prepare PbI₂ will appear yellow lead iodide at the bottom of the beaker insoluble by water.

Also, potassium nitrate (KNO₃) is dissolved by water. After that, the water is discarded beyond drying deposited material. Finally, it is removed from the beaker to keep in desiccators.

\[
Pb(NO_3)_2 + KI \rightarrow PbI_2 + KNO_3
\]

PbI₂ nanostructures were grown on glass substrates at room temperature by Electron Beam Evaporation (Auto 306 Vacuum Coater, USA). The main reason of utilising this method is to permit the large area deposition in cost-effective manner. To measure the thickness, the weight method was used. Sensitive electrical balance (Metler AE-160, USA) was utilised, with precision reaching 10⁻⁶ g. The structural properties were investigated via XRD to determine the crystallinity of sample, the diffraction for determining spacing, preferred orientation and the particle size. XRD system (Philips PW 1710 X-ray diffractometer, USA) has been used for the followings: Source radiation of CuKα with 1.54 Å wavelengths, incidence angle: 10–60 degree, and scanning speed: (5 degree/min). The optical properties have been investigated by ultraviolet spectroscopy (UV-vis) at room temperature via Perkin-Elmer Lambda (950 spectrophotometer, USA) in the 300–1100 nm wavelength range.

3. RESULTS AND DISCUSSION

3.1. Structural Properties

Undoped and Zn-doped PbI₂ nanostructures are deduced via XRD patterns and shown in Figure 1. The sharp peaks in (001), (002), (003) and (004) are appeared and indicate that the mentioned nanostructures are polycrystalline, where have strong preferred orientation along c-axis. The inter plane spacing can be measured using diffraction Bragg’s equation:

\[
n \lambda = 2d \sin \theta
\]

where \( n \) is integer, \( \lambda \) is wavelength, \( d \) is inter-planar spacing and \( \theta \) is Bragg’s angle. The rated of impurities have effect on the density peaks, when the dopants rates increase, the peaks intensity increases. This means crystallization increasing as shown in Figure 1. Due to few percentage of doping, there is not distinguished change of crystalline structure. In addition, the mentioned rate will affect the thickness gradually as doping increases. It is obvious the angles are observed at \( 2\theta = 12.69^\circ, 25.52^\circ, 38.71^\circ \) and \( 52.44^\circ \) correspond to (001), (002), (003) and (004), respectively. Table I gives the measured inter-planar spacing (\( d \)) for different dopants weights. The measured results are in good agreement with experimental theoretical data. It can be inferred from the observed data and ASTM data that the strongest peak is observed at \( d = 6.979 \) Å corresponds to (001), as confirmed previously. The lattice constants (\( a \) and \( c \)) of hexagonal crystal structure were measured via:

\[
\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}, \quad \frac{c}{a} = 1.531
\]

where \( d \) is inter planar spacing and \( hkl \) is Miller indices. The measured \( a \) and \( c \) constants for undoped and doped PbI₂ nanostructure give good accordance with experimental and theoretical results. Also, it is found that different doping rates lead to change of lattice constant (\( c \)) for (001) that is bigger than other orientations. Doping percentage effect on lattice constants may be explained as:

(i) Zn-doped dissociates into Zn²⁺ (ionic radius = 0.74 Å) might replace Pb²⁺ (ionic radius = 1.21 Å).
Table I. Variety of structural properties of PbI$_2$ nanostructures for different dopants weights.

| Doped weight Zn (mg) | $2\theta$ | $d_{200}$ (Å) | $d_{002}$ (Å) | $d_{004}$ (Å) | $c_{004}$ (Å) | FWHM | PS particle size (nm) | $\eta$ dislocation density (10$^{20}$ lines/cm$^2$)
|---------------------|---------|-------------|-------------|-------------|-------------|------|-------------------|---------------------
| Zn-0                | 12.67   | 6.979       | 6.985       | 4.562       | 6.985       | 0.2952 | 33.3              | 9                   |
|                     | 25.50   | 3.489       | 3.492       | 4.561       | 6.984       | (002)  | 0.2952            |                     |
|                     | 38.68   | 2.326       | 2.327       | 4.559       | 6.981       | (003)  | 0.1968            |                     |
|                     | 52.40   | 1.744       | 1.746       | 4.561       | 6.984       | (004)  | 0.2952            |                     |
| Zn-0.02             | 12.64   | 6.979       | 6.999       | 4.571       | 6.999       | (001)  | 0.2952            | 25.5 1.5            |
|                     | 25.44   | 3.489       | 3.500       | 4.572       | 7           | (002)  | 0.2952            |                     |
|                     | 38.66   | 2.326       | 2.328       | 4.561       | 6.984       | (003)  | 0.2952            |                     |
|                     | 52.38   | 1.744       | 1.745       | 4.559       | 6.98       | (004)  | 0.3000            |                     |
| Zn-0.04             | 12.64   | 6.979       | 6.999       | 4.571       | 6.999       | (001)  | 0.2952            | 28.7 1.2            |
|                     | 25.46   | 3.489       | 3.497       | 4.568       | 6.994       | (002)  | 0.2952            |                     |
|                     | 38.68   | 2.326       | 2.327       | 4.559       | 6.981       | (003)  | 0.1968            |                     |
|                     | 52.38   | 1.744       | 1.745       | 4.559       | 6.98       | (004)  | 0.3000            |                     |
| Zn-0.06             | 12.69   | 6.979       | 6.975       | 4.555       | 6.975       | (001)  | 0.2952            | 28.8 1.2            |
|                     | 25.53   | 3.489       | 3.488       | 4.556       | 6.976       | (002)  | 0.1968            |                     |
|                     | 38.71   | 2.326       | 2.326       | 4.557       | 6.978       | (003)  | 0.2952            |                     |
|                     | 52.44   | 1.744       | 1.743       | 4.553       | 6.972       | (004)  | 0.3000            |                     |
| Zn-0.08             | 12.68   | 6.979       | 6.979       | 4.558       | 6.979       | (001)  | 0.2952            | 30.1 1.1            |
|                     | 25.52   | 3.489       | 3.490       | 4.559       | 6.98       | (002)  | 0.1968            |                     |
|                     | 38.70   | 2.326       | 2.326       | 4.557       | 6.978       | (003)  | 0.2952            |                     |
|                     | 52.42   | 1.744       | 1.745       | 4.559       | 6.98       | (004)  | 0.2460            |                     |


(ii) For high dopants of Zn, the non-isoelectronic substitution may create the vacancies.

The Zn$^{2+}$ substitution at cation sites aims to create cation vacancies. The vacancies have arisen in the lattice as impurities to increase the lattice constants, especially the c-axis. Table I gives the measured particle size via Scherrer’s formula:

\[ P_S = \frac{0.9 \lambda}{B \cos \theta} \]

where \( P_S \) is particle size (nm) and \( B \) is full-peak width at half maximum (radians). The dislocation density (\( \eta \)) were calculated by Eq. (4) and listed in Table I.

\[ \eta = \frac{1}{D^2} \]

where \( D \) is crystallite size. The \( \eta \) value for the doped PbI$_2$ was less than for undoped one as given in Table I.

3.2. Optical Properties

The optical band gap was determined by extrapolating the straight-line segment of the \((ahv)^2\) versus \((hv)\) graphs to the \(hv\)-axis according to Eq. (5):

\[ ahv = A(hv - E_g)^{1/2} \]

where \( A \) is constant and \( E_g \) is the optical band gap. The optical band gap for doped PbI$_2$ nanostructure increases as Zn-doped decreases as given in Table II. The linear regions of the corresponding plots confirms a band gap as shown in Figure 2. The decreasing can be correlated with the creation of new donor levels in the forbidden zone. The decrement of band gap value may be attributed to the merge of these levels of PbI$_2$ conduction band. Using our recent model\(^{17}\) for quantum dot potential calculation as:

\[ P_{QD} = \frac{h}{a} \cdot E_{STX} \cdot 10^{-3} \cdot \lambda \]

Table II. Energetic values for different dopants weight of PbI$_2$ nanostructures correspond to QDs potential, refractive index, and optical dielectric constant using Ravindra et al.,\(^23\) Herve and Vandamme,\(^24\) Ghosh et al.,\(^25\) models.

| Doping weight Zn (mg) | \( E_g \) (eV) | \( P_{QD} \) (mV) | Reflective index \( n \) | Optical dielectric constant \( (\varepsilon_{\infty}) \)
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<td>1.328</td>
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<td>6.76' 6.60' 6.40'</td>
</tr>
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where $b/a$ is constant (in eV$^{-1}$) [see Table IV in Ref. [17], $E_{\Gamma X}$ is the energy gap along $\Gamma-X$ (in eV) and $\lambda$ is parameter for group-IV ($\lambda = 6$), III–V ($\lambda = 4$) and II–VI ($\lambda = 2$) semiconductors (in V). It is stated a correlation between QDs potential and zinc concentration. If Zn varies, the covalent structure is affected that leads to change QDs potential. This discrepancy at Zn concentration is a consequence of quantum dot potential difference. Table II gives the calculated QDs potential at different doping weight.

The Zn concentration separates the decrease and the increase of the QDs potential. The QDs potential varies non-linearly as Zn increases (Table II) and confirmed by Figure 3. Consequently, fluctuations of the QDs potential observes. The calculated QDs potential agrees other data.\(^{18}\) It is indicated that the QDs potential variation is an indication of the electron tunnels the quantum dot.

It is well known that refractive index $n$ is related to microscopic atomic interactions. There are two different approaches of refractive index related to density, and local polarizability.\(^{19}\) Other side, the crystalline structure is indicated by delocalized picture and closely related to band structure and complicated quantum mechanics. There were many attempts focused on connected the refractive index $n$ and the energy gap $E_g$ through simple relationships.\(^{20–23}\)

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**Fig. 2.** Plot of $(\alpha \nu)^2$ of different doped Zn–PbI₂ nanostructures.
Ravindra et al.\textsuperscript{23} had researched different relationships of band gap and higher frequency refractive index to present linear form of $n$ as a function of $E_g$:

$$n = \alpha + B E_g$$  \hspace{1cm} (7)

where $\alpha = 4.048$ and $B = -0.62$ eV$^{-1}$. While, Herve and Vandamme\textsuperscript{24} had suggested empirical relation given by:

$$n = \sqrt{1 + \left( \frac{A}{E_g + B} \right)^2}$$  \hspace{1cm} (8)

where $A = 13.6$ eV and $B = 3.4$ eV. And, Ghosh et al.\textsuperscript{25} had considered the band structure and quantum-dielectric formulations of Penn\textsuperscript{26} and Van Vechten.\textsuperscript{27} $A$ is the contribution from the valence electrons and $B$ is a constant additive to the lowest band gap $E_g$, the high-frequency refractive index is:

$$n^2 - 1 = \frac{A}{(E_g + B)^2}$$  \hspace{1cm} (9)

where $A = 25E_g + 212$ and $B = 0.21E_g + 4.25$. Thus, the mentioned three models of $n$ have been calculated. Additionally, the optical dielectric constants ($\varepsilon\infty$) were calculated via relation $\varepsilon\infty = n^2$.\textsuperscript{28} The results are displayed in Figure 4. Our calculated refractive index values are in good agreement with experimental value\textsuperscript{29} as given in Table II. This is giving an appropriate model of Ravindra et al. for solar cells applications that is important in enhancing the photo conversion for solar cells. Again, a linear dependence of Zn:PbI$_2$ properties on the QDs potential is observed, where the refractive index for Zn concentrations dependence tends to shift towards the blue–green. It means a high absorption and low reflection spectrum may be attributed to increase solar cells efficiency.

4. CONCLUSION

Zn-doped PbI$_2$ has been grown via thermal evaporation method. XRD peaks have indicated the crystallinity of PbI$_2$ nanostructures. It also has shown that the particle size and dislocation density decrease as doping weight increases. It is noticed that Zn doping has caused important changes in the band gaps. It is proved that Zn\% of 0.08 is more appropriate for QDs and Ravindra et al. model is very suitable for applications of solar cells to expect new trends and realization for other compounds and quantum dots, respectively.

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References and Notes


![Fig. 3. QDs potential versus Zn concentration of Zn–PbI$_2$ nanostructures.](image)

![Fig. 4. Refractive index versus Zn concentration of Zn–PbI$_2$ nanostructures.](image)
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