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Results of SILAR Cycles Variation on the Optical, Structural and Electrical Properties of Lead Iodide Thin Films

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Abstract:

Lead iodide (PbI_2) thin films were deposited using the successive ionic later adsorption and reaction (SILAR) method. $Pb(NO_3)_2$ and KI were used as the precursors to produce PbI_2 films of different SILAR cycles on a glass substrate. The structural, electrical and optical properties of the deposited films were examined using the X-ray diffraction (XRD) technique, four-point probe apparatus and 756S UV-VIS spectrophotometer respectively. The structural analysis showed that the films are polycrystalline in nature having a hexagonal structure. Electrical analysis showed that the resistivity of the films ranged between $1.68 \times 10^7\ \Omega cm$ and $7.96 \times 10^7\ \Omega$cm while the electrical conductivity is between $1.26 \times 10^{-8}\ S/cm$ and $5.96 \times 10^{-8}\ S/cm$. The resistivity of the films decreased while the conductivity increased as the number of SILAR cycles increases. This shows that the film tends to be more of a conductor as to an insulator and therefore is a semiconducting thin film. Optical analysis showed that the energy band gap ranged from 2.10 to 2.60 eV and the thickness of the films increased from $38.94\ nm$ to 155.84 nm with increase in the number of SILAR cycles. The deposition technique has good quality and can be used for the development of thin film solar cell for photovoltaic application.

Keywords:

Lead Iodide Thin Film, SILAR Cycle, Optical Properties, Electrical Properties

1. Introduction

Lead iodide is a salt with chemical formula PbI_2. It is an excellent and interesting candidate of high efficiency room temperature detectors working in the medium energy range of 1 keV to 1 MeV [1]. It is an important and promising p-type semiconductor that exists in hexagonal crystalline structure having an intrinsic band gap of 2.3 to 2.6 eV (depending on the deposition method) [2], and can be widely applied in medicine, monitoring ecology, non-destructive defectoscopy and X-ray and

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gamma ray spectroscopy. The peculiarities of this material are high resistivity, ability to work in a wide range of temperature and high chemical stability [3].

Thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin film (a process referred to as deposition) is a fundamental step in many applications. A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface [4]. Thin films have very interesting properties that are quite different from those of the bulk materials which they are made of. As the film becomes thinner, the surface properties become more important than the bulk. The other cause of interest is the miniaturization of elements such as electronic resistors, thin film transistors and capacitors. This is because of the fact that their properties depend on a number of interrelated parameters and also the deposition technique [5]. Therefore, in this work, PbI_2 think films were deposited using the successive ionic later adsorption and reaction (SILAR) technique, and the structural, electrical and optical properties of the film were determined.

2. Experimental Details

Successive Ionic Layer Adsorption and Reaction (SILAR) was used in this work to deposit lead iodide thin films. SILAR growth of PbI_2 thin films was carried out at room temperature using 0.25 M of lead (ii) nitrate as lead precursor and 0.05 M of potassium iodide as precursor of iodine ion. The following procedures were adopted to deposit PbI_2 thin films; one SILAR growth cycle involves four steps with cycle time of 80 seconds.

Step 1: Immersion of the cleaned substrate in first reaction beaker (a) containing cationic precursor solution of 0.25 M of lead nitrate for 30 sec. This process leads to absorption of Pb^{2+} ions on the surface of the substrate.

Step 2: This substrate was rinsed by dipping it into the second beaker (b) which contains high purity distilled water for 10 sec to remove excess Pb^{2+} ions that are loosely adherent to the glass substrate (achieved in the previous step).

Step 3: The substrate was then immersed in the third beaker (c) containing the anionic precursor solution of 0.05 M potassium iodide for the 30 sec. The iodide (I^-) ions reacted with the absorbed Pb^{2+} ions on the active center of the substrate to form yellow colored PbI_2 thin films.

Step 4: Finally, the substrate was rinsed by dipping the substrate in the fourth beaker (d) which contains distilled water for 10 sec to remove loosely bound ions present on the substrate and unreacted Pb^{2+} and I^- ions.

The procedure was repeated for 5 cycles to get a uniform film with good thickness. Four other samples of lead iodide thin films were deposited with different SILAR cycles of 10, 15, 20 and 25 respectively. At the end of each cycle, these thin films were subjected to post-heating treatment at 200 °C for 2 hours. The aim of varying the SILAR cycle was to determine the effect of increase in SILAR cycle on the structural, electrical and optical properties of the deposited PbI_2 thin films. The deposited PbI_2 thin films were examined using the X-ray diffraction technique, four-point probe apparatus and 756S UV-VIS spectrophotometer (in the wavelength range 300 nm to 1100 nm) to obtain the structural, electrical and optical properties of the film respectively.

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3. Results and Discussion

3.1. Structural Characterization

The x – ray diffraction patterns showed that the films are polycrystalline in nature. The result corresponds to standard x – ray pattern of hexagonal of lead iodide belonging to the space group P-3m1 and of JCPDS file number 00-007-0235. Four peaks corresponding to this structural pattern were observed. Figure 1 showed the structural pattern and the peaks with their corresponding miller indices of lead iodide thin films deposited under 5, 15 and 25 SILAR cycles. The diffraction spectra revealed increase in intensity of the diffraction spectra as SILAR cycles increases. Also, shift in peak positions towards larger angles were observed as SILAR cycles increases. The structural parameters as indicated in the result as shown in table 1 include; 2 theta angles and their corresponding d – spacing, crystallite sizes, dislocation density and micro-strain. Values of the d – spacing and the corresponding angles showed that they varied slightly with that of the standard JCPDS file. Crystallite size was found to increase as SILAR cycles increases. This showed an improvement in the crystalline nature of the deposited thin films. Dislocation densities and micro-strains of the deposited lead iodide thin film were found to decrease as SILAR cycles increases. These results are in line with similar variation in the structural properties as number of SILAR cycles increase as obtained by [6].

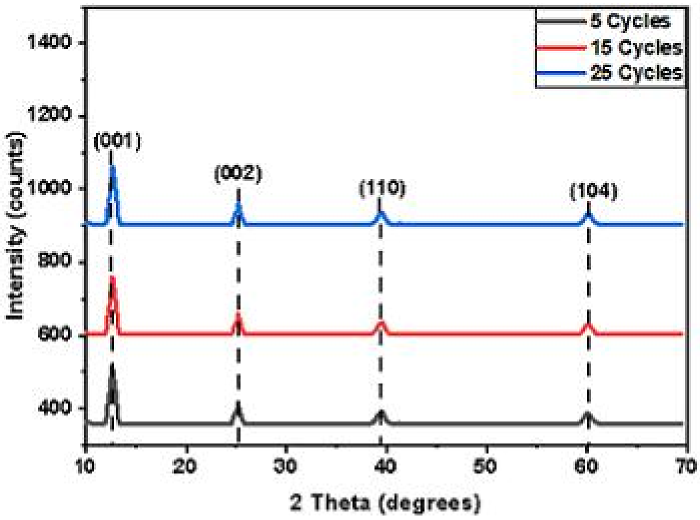

Figure 1. *X – ray diffractogram of Lead Iodide thin films deposited under 5 SILAR cycles.*

Table 1. *Structural parameters of SILAR Deposited Lead Iodide thin films.*

	2 θ (°)		d – spacing (nm)		[hkl]	FWHM (◦)	D (nm)	$\delta \times 10^{15}$ limes/m^2	$\varepsilon x\ 10^{-3}$
Sample	**Observed**	**Standard**	**Observed**	**Standard**					
5 cycles	12.675	12.672	0.698	0.698	001	0.369	22.65	1.95	1.60
	25.140	25.510	0.354	0.349	002	0.298	28.52	1.23	1.27
	39.427	39.528	0.228	0.228	110	0.485	18.18	3.03	1.99
	60.052	61.603	0.154	0.150	203	0.493	19.42	2.65	1.86
	Average						**22.19**	**2.21**	**1.68**
15 cycles	12.695	12.672	0.697	0.698	001	0.359	23.28	1.85	1.56
	25.160	25.510	0.354	0.349	002	0.298	28.52	1.23	1.27
	39.447	39.528	0.228	0.228	110	0.425	20.75	2.32	1.74
	60.072	61.603	0.154	0.150	203	0.42	22.82	1.92	1.59
	Average						**23.84**	**1.83**	**1.54**
25	12.715	12.672	0.696	0.698	001	0.343	24.37	1.68	1.49

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cycles	25.180	25.510	0.353	0.349	002	0.258	32.94	0.92	1.10
	39.467	39.528	0.228	0.228	110	0.418	21.09	2.25	1.72
	60.105	61.603	0.154	0.150	203	0.451	21.25	2.21	1.70
	Average						**24.91**	**1.77**	**1.50**

3.2. Estimation of Film Thickness (t)

The thickness values of the films shown in figure 2 were obtained using gravimetric method as given by [7]. The dimension of the substrates covered by the film (5.0 cm by 2.5 cm) which gave an area of 12.50 cm^2. Density of 6.16g/cm^3 for bulk PbI_2 material was used while the change in mass of the substrates was obtained by measuring the masses of the substrates before and after deposition. Estimated thickness values of the films are presented in table 2 while the variation of obtained thickness with the number of SILAR cycles is presented in figure 2. The thickness values of the deposited films were found to increase from 38.96 nm at 5 SILAR cycles up to a peak value of 155.84 nm at 25 SILAR cycles.

Table 2. *Variation of Film Thickness with number of SILAR Cycles.*

Number of SILAR Cycle	Change in Mass $\Delta m \times 10^{-3}$ (g)	Area (cm^2)	Thickness (nm)
5	3.00	12.50	38.96
10	6.00	12.50	77.92
15	9.00	12.50	116.88
20	10.00	12.50	129.87
25	12.00	12.50	155.84

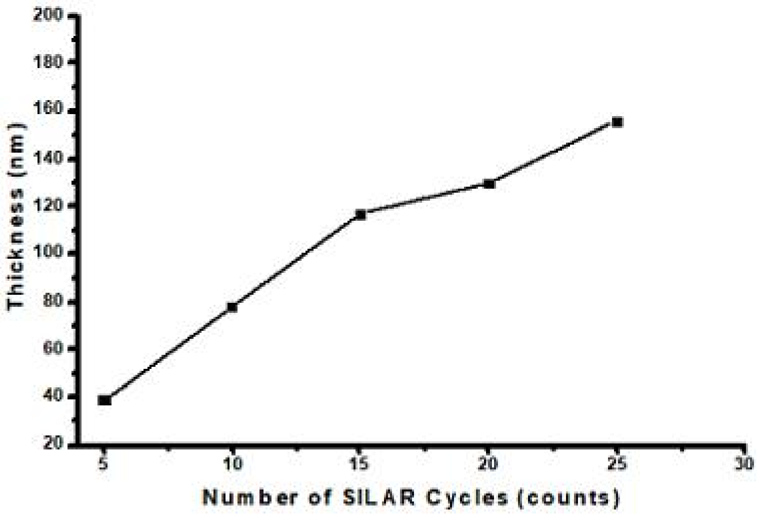

Figure 2. *Graph of thickness plotted against number of SILAR cycles.*

3.3. Electrical Characterization

The results from Table 3 showed that lead iodide is a high electrical resistive material. Electrical resistivity of the films ranged between $1.68\ \Omega\,\text{cm}$ to $7.96\ \Omega\,\text{cm}$ while the electrical conductivity is between $5.96\ \text{S/cm}$ to $1.26\ \text{S/cm}$. The resistivity of the films was found to decrease as number of SILAR cycles increases while conductivity was found to increase as number of SILAR cycles increases. This is to say that with increase in the number of SILAR cycles, the film tends to be more of a conductor as to an insulator and therefore can conduct. The values of resistivity obtained in this work corresponds to great extent the results of [6]. Other researchers such as [1,2,8,9] obtained electrical resistivity values that are higher than the result obtained in this work. Figure 3 showed the variation of electrical resistivity and conductivity of the deposited lead iodide with number of SILAR cycles.

Table 3. *Electrical Properties of SILAR Deposited Lead Iodide thin films.*

Samples	Voltage (mV)	Current (A)	Resistance (Ω)	Thickness (nm)	Sheet Resistance (Ω-cm^2)	Resistivity (Ω cm)	Electrical Conductivity (S/cm)
5	64.47	14.30	45.10	38.94	20.43	7.96	1.26
10	73.72	88.10	8.37	77.92	3.79	2.95	3.39
15	85.86	2.19	3.91	116.88	1.77	2.07	4.83
20	88.87	3.02	2.94	129.87	1.33	1.73	5.78
25	97.51	4.11	2.38	155.84	1.08	1.68	5.96

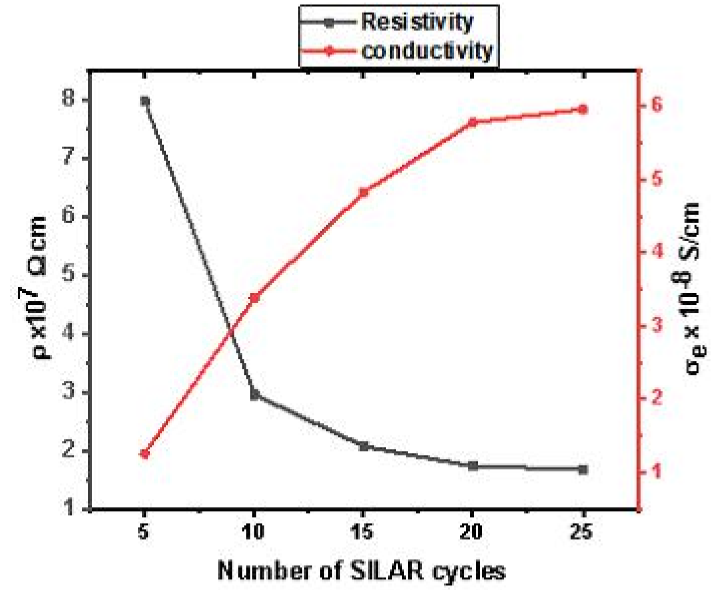

Figure 3. *Variation of electrical properties of Lead iodide thin films with number of SILAR cycles.*

3.4. Optical Characterization

Optical properties such as transmittance, reflectance and energy band gap of the films were evaluated using expressions as presented by [10,11,12,13] while absorbance values were obtained from the spectrophotometer. Figure 4, Figure 5 and Figure 6 illustrate the absorbance, transmittance and reflectance respectively in the wavelength region of 300 to 1100 nm. The absorbance showed that the deposited lead iodide thin films have absorption peak at 310 nm. There was no shift in the absorption peak to either longer or shorter wavelength rather the absorbance of the films increases as number of SILAR cycles increase. The absorbance was found to decrease as wavelength increases with maximum absorbance of 0.56 % obtained at 310 nm for films deposited with 25 SILAR cycles and least absorbance of 0.06 % was obtained within the NIR region. Transmittance results revealed an increase as wavelength increases from 300 nm to 1100 nm. Also, the transmittance decreases as number of SILAR cycles increases. Peak transmittance values of 86.81 %, 81.91 %, 75.97 %, 63.48 % and 53.70 % were obtained at 1100 nm for 5, 10, 15, 20 and 25 SILAR cycles respectively while least transmittance values of 66.69 %, 60.17 %, 45.88 %, 31.93 % and 27.65 % were obtained at 310 nm. The films generally showed high reflectance within UV region for 5, 10 and 15 SILAR cycles and subsequently drop as the wavelength increases. The graph also showed a low reflectance value at 310 nm for 20 and 25 SILAR cycles before increasing to a peak value at 450 nm, then a minimal decrease as the wavelength increases.

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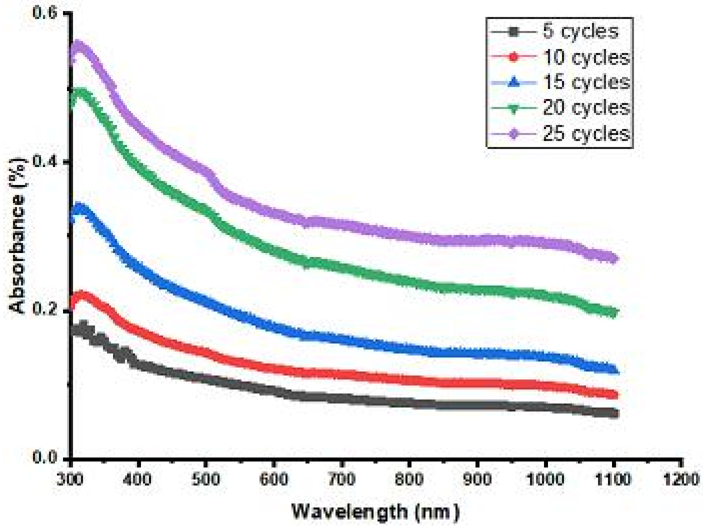

Figure 4. *Graph of absorbance plotted against wavelength for lead iodide thin films deposited at different SILAR cycles.*

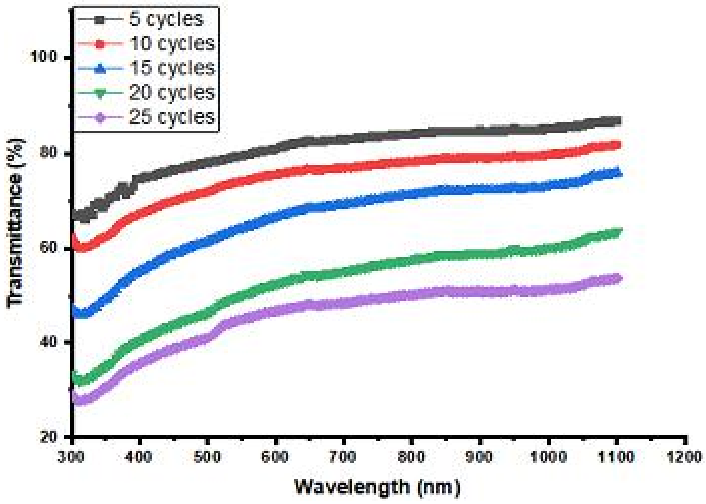

Figure 5. *Graph of transmittance plotted against wavelength for lead iodide thin films deposited at different SILAR cycles.*

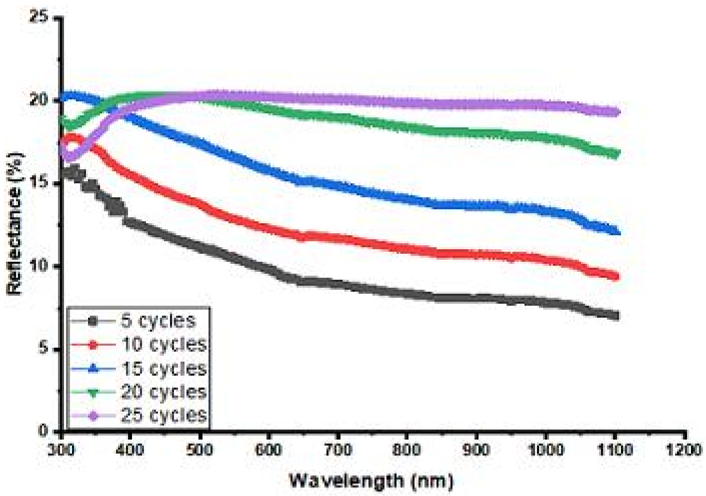

Figure 6. *Graph of reflectance plotted against wavelength for lead iodide thin films deposited at different SILAR cycles.*

Figures 7 and 8 also showed the energy band gap of the deposited films with respect to the number of SILAR cycles. The energy band gap falls between 2.10 and 2.60 eV.

Peak energy band gap was obtained at 10 and 15 SILAR cycles and the least energy band gap at 5 SILAR cycles. The values of the energy band gap obtained in this work slightly corresponds to that of [2,14,15,16]. Energy band gap of the films were found to decrease from 2.60 eV to 2.40 eV as SILAR cycles increased from 15 SILAR cycles to 25 SILAR cycles. Least value of band gap of 2.10 eV was obtained at 5 SILAR cycles.

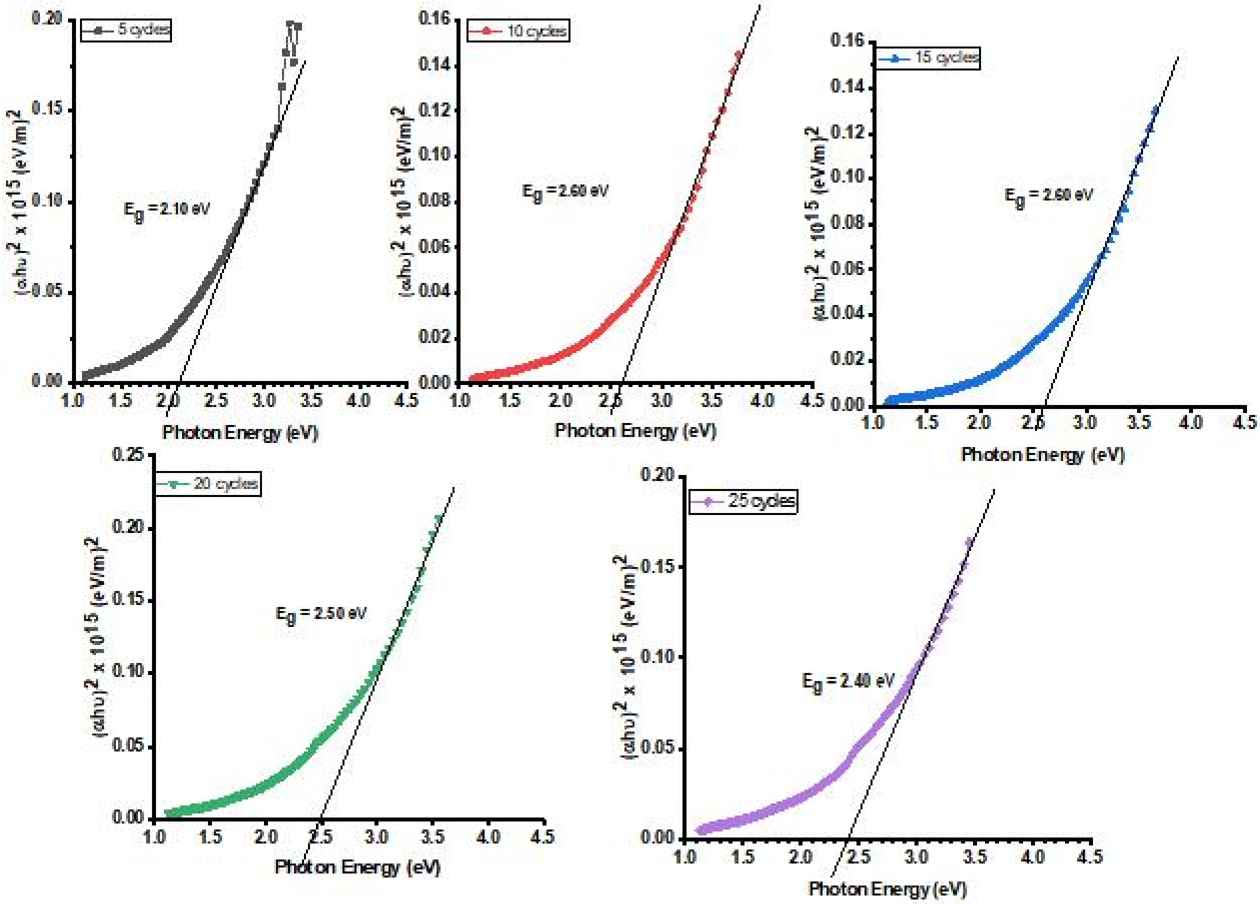

Figure 7. *Graph of $(\alpha h\nu)^2$ plotted against photon energy (eV) for lead iodide thin films deposited at different SILAR cycles.*

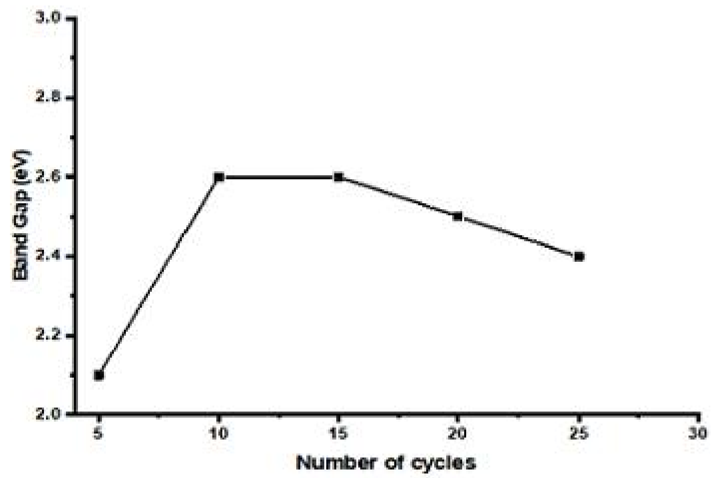

Figure 8. *Graph of energy band gap plotted against number of SILAR cycles.*

4. Conclusions

In this paper, PbI_2 thin films were deposited using the successive ionic later adsorption and reaction (SILAR) method. The effect of the number of SILAR cycles on the structural, electrical, and optical properties of the films was investigated using X-ray diffraction (XRD) analysis, four-point probe apparatus and 756S UV-VIS spectrophotometer respectively. The XRD analysis revealed that the deposited PbI_2 thin films are polycrystalline in nature having a hexagonal structure. The electrical study showed that the resistivity of the films was found to decrease as number of SILAR cycles increases while conductivity was found to increase as number of SILAR cycles increases. The optical analysis showed that the deposited thin films have an energy band gap which ranges from 2.10 to 2.60 eV. The thickness of the films increased from $38.94\ nm$ to 155.84 nm with increase in the number of SILAR cycles. The deposition technique (SILAR) has good quality and can be used for the development of thin films for photovoltaic application.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Author Contributions

Conceptualization: N.C.J., O.N.L.; Methodology: N.C.J., O.N.L., I.D.C.; Software: O.N.L., I.D.C.; Validation: N.C.J., O.N.L.; Formal analysis: N.C.J., O.N.L., I.D; Investigation N.C.J., O.N.L., I.D.C.; Resources: N.C.J., O.N.L., I.D.C.; Data Curation: N.C.J., O.N.L., I.D.C.; Writing – original draft preparation: I.D.C.; Writing – review and editing: N.C.J., O.N.L.; Visualization: N.C.J., O.N.L., I.D.C.; Supervision: N.C.J., O.N.L.; Project administration: N.C.J., O.N.L.; Funding acquisition: N.C.J., O.N.L., I.D.C.

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References

[1] Matuchova, M.; Zdansky, K.; Zavadil, J. Study of the influence of the rare-earth elements on the properties of lead iodide. *Journal of Crystal Growth,* 2009, 311(14), 3557-3562.

[2] Condeles, J.F.; Ando, R.A.; Mulato, M. Optical and structural properties of PbI2 thin films. 2008, *J Mater Sci ,* 43,525-529.

[3] Hanaor, D.A.H., Triani, G. and Sorrell, C.C. Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films. *Surface and Coatings Technology,* 2011, 205(12), 3658-3664.

[4] Nain, C.K.; Maini, K.A. Thin films and their application in military and civil sectors, DRDO, New Delhi, 2010.

[5] Akaltun, Y.; Astam, A.; Cerhan, A.; Çayir, T. Effect of thickness on electrical properties of SILAR deposited SnS thin films. *AIP Conference Proceedings,* 2016, 1722(220001), 1-4.

[6] Acuna, D.; Bindu, K.; Sadasivan, S.; Sepulveda, S.; Jorge, L. M. Growth and properties of lead iodide thin films by spin coating. *Bulletin of material science,* 2016, 39 (6), 1453-1460.

[7] Egwunyenga, N.J.; Onuabuchi, V.C.; Okoli, N.L.; Nwankwo, I.E. Effect of SILAR cycles on the thickness, structural, optical properties of cobalt selenide thin film. *International Research Journal of Multidisciplinary Technovation,* 2021, 10, 1-9.

[8] Khan, M.T., Shkir, M., Almohammedi, A.; Al-Faify, S. Fabrication and characterization of La doped PbI_2 nanostructured thin films for opto-electronic applications. *Solid State Sciences.* 2019, 90, 95-101.

[9] He, Y.; Zhu, S.; Zhao, B.; Jin, Y.; He, Z.; Chen, B. Improved growth of PbI2 single crystals. *Journal of Crystal Growth,* 2007, 300(2), 448-451.

[10] Whyte, G.M.; Awada, C.; Offor, P.O.; Whyte, F.U.; Kanoun, M.B.; Goumri-Said, S.; Alshoaibi, A.; Ekwealor, A.B.C.; Maaza M.; Ezema, F.I. Experimental and theoretical studies of the solid-state performance of electrodeposited Yb_2O_3/As_2Se_3 nanocomposite films. *Journal of Alloys and Compound,* 2021, 855, 157324.

[11] Ezenwaka, L.N.; Umeokwonna, N.S.; Okoli, N.L. Optical, structural, morphological, and compositional properties of cobalt doped tin oxide (CTO) thin films deposited by modified chemical bath method in alkaline medium. *Ceramics International,* 2020, 46(5), 6318-6325.

[12] Augustine, C.; Nnabuchi, M.N.; Chikwenze, R.A.; Anyaegbunam, F.N.C.; Kalu, P.N.; Robert, B.J.; Nwosu, C.N.; Dike, C.O.; Taddy, E.N. Comparative investigation of some selected properties of Mn_3O_4/PbS and CuO/PbS composites thin films. *Material Research Express,* 2019, 6(066416), 1-10.

[13] Egwunyenga, N.J.; Ezenwaka, N.L.; Ezenwa, I.A.; Okoli, N.L. Effect of annealing temperature on the optical properties of electrodeposited ZnO/MgO superlattice. *Materials Research Express,* 2019, 6(10), 105921(1-9).

[14] Khalaph, K.A.; Shanan, Z.J.; Jafar, K.A.; Al-Attar, F.M. Structural and Optical Properties of PbI_2 Thin Films to Fabricate Perovskite Solar Cells. *Defect and Diffusion,* 2020, 398, 140-146

[15] Hassoon, K.I.; Mohammed, M.S.; Salman, G.D. Characterization of PbI2 Thin Films Prepared by Fast Vacuum Thermal Evaporation. *Digest Journal of Nanomaterials and Biostructures*, 2019, 14(2), 401-406.

[16] Abid Alnabi, R.K.; Malek, A.H.; Muhi.; Najim, A.A. Structure and optical properties of pbI2 thin film by thermal evaporation technique. *Journal of University of Anbar For Pure Science*, 2018, 12(2), 37-42.