

INVESTIGATION ON OPTICAL PROPERTIES OF SILAR-GROWN HIGHLY ORIENTED LEAD SULPHIDE (PbS) THIN FILMS

Chandrashekhar L Gamit¹, Vikas Kumar Bhavsar^{2*}, Trupti Patel³

Lecturer in Physics, Applied Science & Humanities, Government polytechnic, Waghai-Dang, Gujarat Technological university, Ahmedabad, Chandkheda, Gujarat-India. (E-mail: gamit.chandu@gmail.com)¹

Assistant Professor in applied Science & Humanities, Sankalchand Patel University, Visnagar, Gujarat-India.

(E-mail: India@vikasbhavsar@gmail.com)^{*,2}

Assistant Professor, SRICT-ISR, UPL University of Sustainable Technology, Ankleshwar, Gujarat-India.

(E-mail: p.trupti9@gmail.com)³

Abstract: Using lead nitrate, thiourea, as well as sodium hydroxide as chemical precursors, the lead sulphide powder was formed at room temperatures and (PbS), at a given room temperature thin film were deposited on a glass substrate using the (SILAR) method at varying numbers of cycles. The optical studies for powder form and thin films were performed by UV-VI diffuse reflectance spectrophotometer-3600 SHIMADZU and UV-VIS-NIR Spectrophotometry. It was discovered that the PbS powder form as well as thin films produced under ideal deposition circumstances were polycrystalline with a face-centered cubic structure. Optical studies for powder form and thin films were carried out using a UV-VI spectrometer and it revealed the existence of direct bandgap for powder form is 1.69 eV and for thin films values in the ranges of (1.45-2.32) eV.

Keywords: Lead Sulphide, thin films, SILAR, UV-VIS spectrophotometry-bandgap.

I. Introduction

Metal chalcogenide thin films have garnered significant attention because of their numerous uses in the manufacturing of large-area photodiode arrays, electronic and optoelectronic devices, infrared photography, photothermal converters, solar absorbers, solar control coatings, photoconductors and sensors. [1-4]. Chalcogenides of IV-VI group materials are considered as interesting narrow bandgap semiconductors with an energy gap value in the range of 0.26 and 0.45eV which makes them interesting for infrared (IR) detectors [1,3,4]. With an energy gap value of 0.45 eV, PbS is discovered to be the most interesting narrow bandgap semiconductor among them. The decreasing of crystallite sizes can improve this bandgap [5]. Because PbS has a greater Bohr excitonic radius than other chalcogenides, a change in bandgap can be attained for relatively larger crystallite sizes. [6] It has been demonstrated that chalcogenide materials make good p-type semiconductor candidates [7]. Several chemical techniques, such as (CBD) Chemical Bath Deposition method used to illustrate this. [7], Electrochemical [8], Spray pyrolysis deposition [10, 11], and (SILAR) Successive Ionic Layer Absorption and Reaction method [9]. Here Purpose of this work is to examine how the number of cycles affects the electrical and optical characteristics of Lead Sulphide thin film made by (SILAR) Successive Ionic Layer Absorption and Reaction method.

II. Experimental details & materials

Lead Sulphide (PbS) Thin films were grown by the method of silar (Successive Ionic Layer Absorption and Reaction using glass substrate (microscopic slide), lead nitrate [$Pb(NO_3)_2$] solution, thiourea solution and sodium hydroxide solution as the complexing agent. Thiourea is used as a Sulphide ion source while a Lead Nitrate source was an ion source.

Sulphide was constituted from a given solution of 15ml of 0.1M [$Pb(NO_3)_2$], 30ml of 0.8M thiourea [$SC(NH_2)_2$], 15ml of 0.8M sodium hydroxide [$NaOH$] and distilled water for 30 secs in the cationic precursor solution, rinsed 5secs in high-purify deionized water, immersed 30secs in the anionic precursor solution, the ions which reacted with absorbed lead ions on the active center of the given Substrate and finally rinse it again in deionized water for 5secs. It was also optimized by various cycles such as 40 Cycles, 50 Cycles, 60 Cycles & 70 Cycles, during the process of thin film formation the Thickness of the thin film increases as the cycle goes on increases. The resulting film was homogenous, well Adhered to the substrate with a darker surface like a mirror annealed at 150°C and cooled at room temperature.

III. UV-VIS-NIR Spectrophotometer

A UV-VIS-NIR Spectrophotometer (Make: SPECTROPHOTOMETER-3600 SHIMADZU), is the most recently device, as illustrated in Fig.1, is used to determine the absorbance value with wavelength maxima in the UV-VIS-NIR region for a

variety of chemicals.

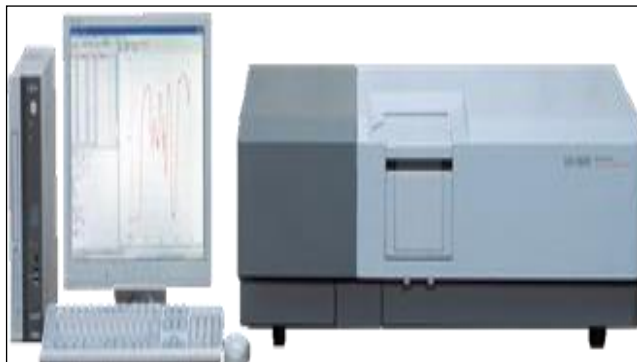


Fig. 1. UV-VI Diffuse Reflectance Spectrophotometer-3600 Shimadzu

Among other things, the approach is used to discover and develop new compounds, new chemicals, dyes, electro-optic properties of single films, thickness, and other types of filters. Mostly in the reflectance method of operation, the accessories "Integrating Sphere" to be used on the Lambda-19 spectrometer simplifies sample analysis. This accessory can be used to analyse a variety of samples, including fabric, lather, films, due-products, as well as colour products, among others. The instrument could be used to look at how a chemical reaction's kinetic behaviour changes over time. It can be utilised for a variety of biological samples as well as reaction investigations, among other things. The equipment consists of a double-beam double monochromator having UV-VIS spectrometer ratio recording and microcomputer electronics controlled by a personal computer. When utilising a UV-VIS-NIR spectrophotometer, thin flakes of as formed crystals are required to get absorption spectra using single-crystal specimens. These flakes are placed on such a thick black piece of paper that has been sliced to expose the crystal flake to the incident light. A replica of a black paper was used as a reference, with a cut made just at the same spot as that of the crystal flake just on the paper's surface. Because now the crystal size is less than the specimen compartment, this arrangement is essential. In addition to real slides, blank glass slides can be used as copies. A common aluminium-coated mirror can also be used as a reference when measuring reflectance.

IV. Results and discussion

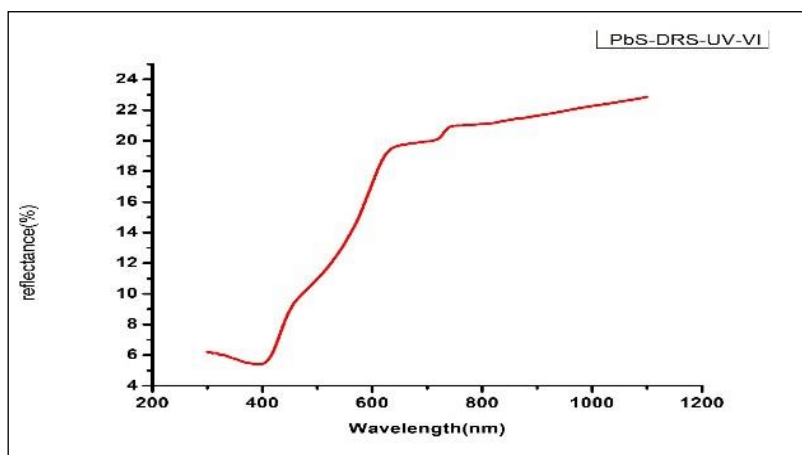


Fig.2. Reflectance (R%) versus wavelength for PbS powder

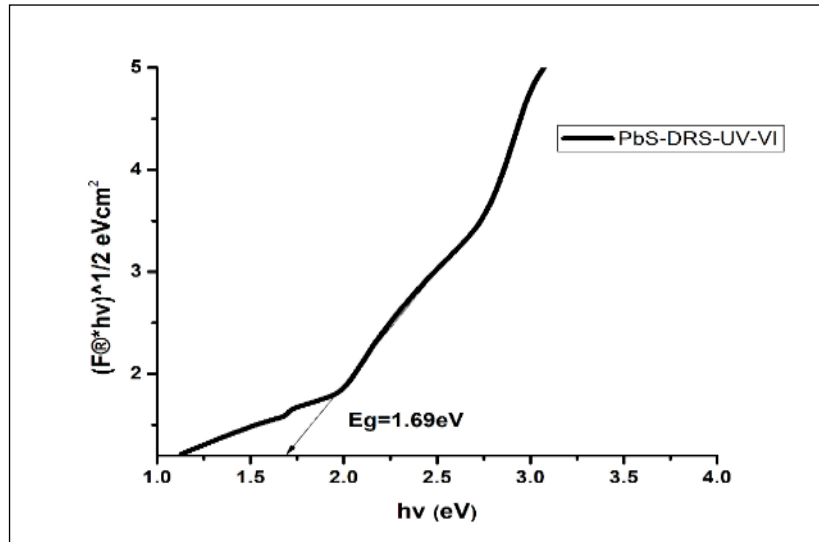


Fig. 3. Optical diffuse reflectance spectra for PbS powder

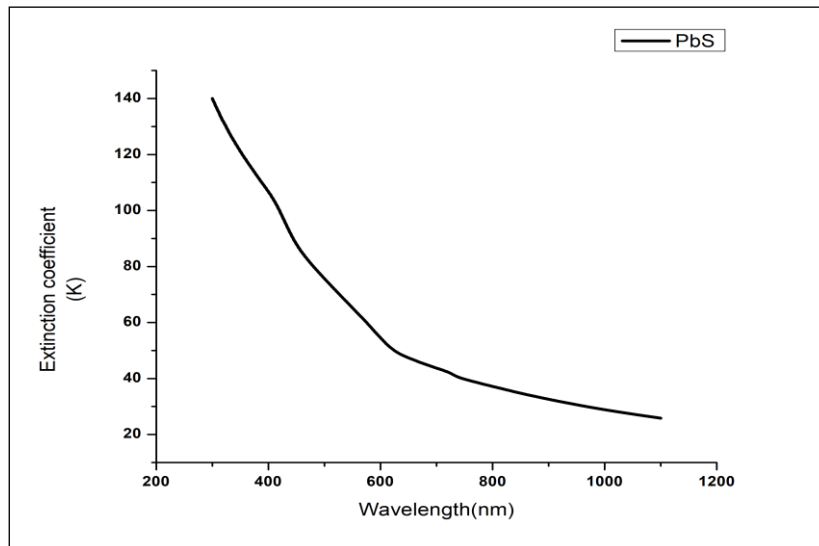


Fig. 4. Extinction coefficient k versus wavelength for PbS powder

V. UV-VI analysis for optical Diffuse reflectance for Powder form

The optical Diffuse reflectance (R per cent) spectra for the nanocrystalline PbS powder form measured with an UV-VI spectrophotometer at room temperature are shown in fig.2. The graph demonstrates that it has a high reflectance and very high absorption in the visible range of Reflectance. Due to this feature, PbS is an interesting option for the absorber layer in solar cells.

The optical diffuse reflectance spectra for PbS powder form deposited at room temperature are shown in fig.3. A graph of the diffuse reflectance spectra in UV-VIS revealed the direct band-gap of approximately 1.69 eV.

It's also applicable from fig.4. In the UV-VIS Diffuse Reflectance graph, the extinction coefficient decreases with wavelength. The Refractive Index (n) and Extinction Co-efficient are related to a reflectance values. For nanostructured PbS powder, the average extinction coefficients in the 300–1100 nm range are calculated to be 57.18.

VI. Optical analysis for thin films



Fig.5. UV-VIS-NIR Spectrophotometer

The most straightforward way to examine a semiconductor's band structure is through its absorption spectrum as shown in fig.5. The process of absorption uses a photon with a known energy to excite an electron to a lower-energy state towards a higher-energy state. By placing a semiconductor slab near an output monochromator and observing the variations of the transmitted radiation that occur, it is possible to find every possible transition an electron can make as well as to learn a great deal about the distribution of states. The coefficient ($\alpha h\nu$), which is the relative rate of decreasing in light intensity, can be used to express absorption. The propagation path's length determines $L(h\nu)$ is

$$\alpha = \frac{1}{L(h\nu)} \frac{d[L(h\nu)]}{dx} \dots\dots\dots 1(a)$$

The phenomenon known as the excitons transition, which happens when an electron passes from Valence band to Conduction band, is referred as a fundamental absorption. Fundamental absorption of the Semiconductor, which shows up as a sharp rise in absorption, must be identified before Energy Gap of the Semiconductor can be calculated. Therefore, even when competing absorption processes are considered into account, measuring the energy gap resulting from the "absorption edge" isn't a simple task because the transition is susceptible to certain selection concepts. Because the momentum of a photon, h/λ (where λ is the wavelength of light), is extremely small when compared to the momentum of a crystal, h/a (where a is the lattice constant), the photon-absorption process should result in the conservation of the electron's momentum (h/a). For every given photon energy ($h\nu$), it is necessary to assume that the absorption coefficient $\alpha(h\nu)$ correlates to the density of available (empty) final states (n_f), and the probability (P_{if}) of transferring from an initial state (n_i). This process is required to occur for all possible transitions between the states separated by an energy difference that is equal to the photon energy to

$$\alpha(h\nu) = A \sum p_{if} n_i n_f \dots\dots\dots 1(b)$$

The lower states will be filled and the upper states will be empty in this case, which is the case for an undoped semiconductor at 0o K. this will make things easier to understand.

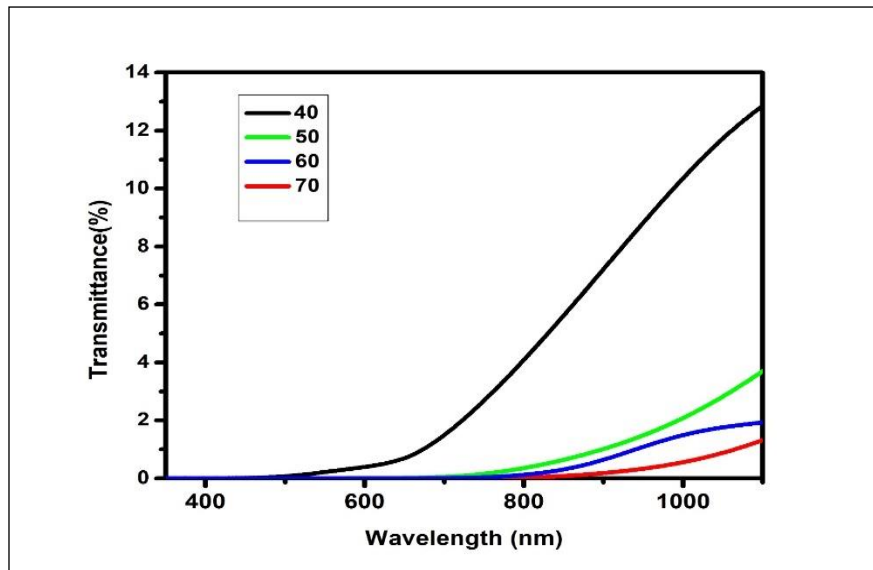


Fig.6.Shows the plot of transmittance vs wavelength.

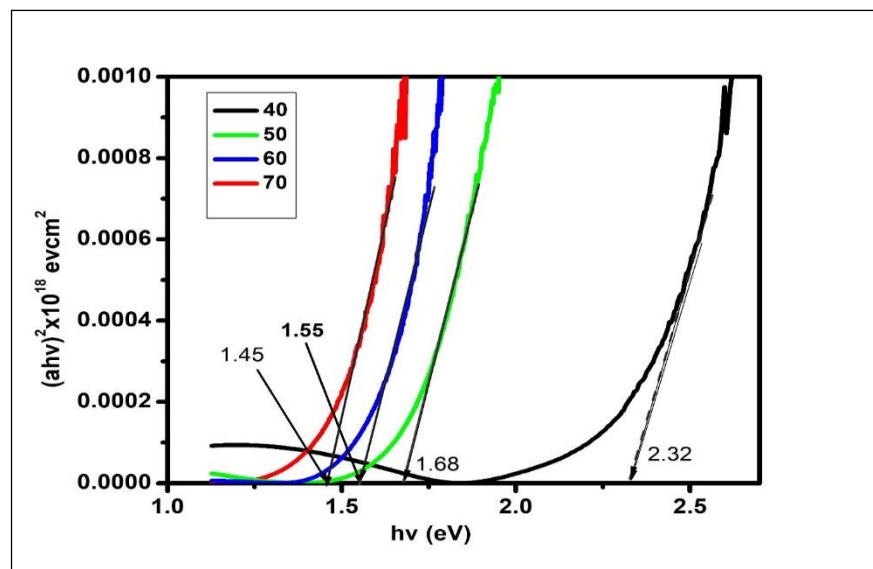


Fig.7. Shows the plot of $\alpha(h\nu)^2$ versus photon energy ($h\nu$).

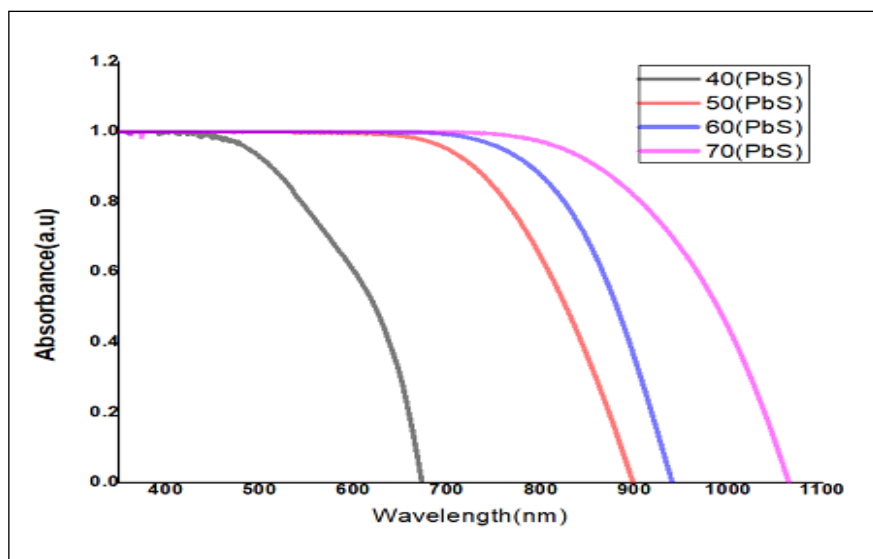


Fig.8. optical absorbance (a.u.) versus wavelength (λ) spectra of Lead Sulphide thin films.

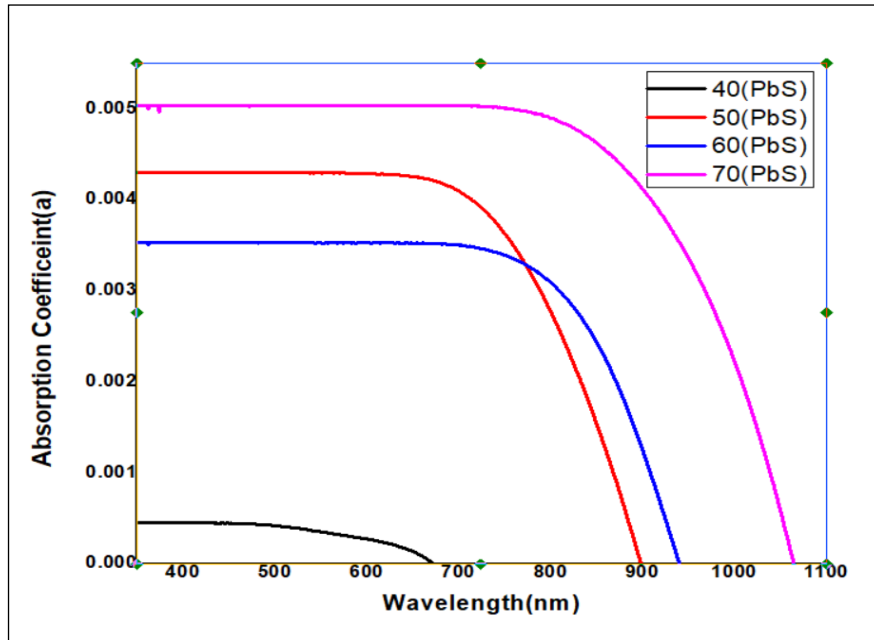


Fig.9. Extinction coefficient (k) versus wavelength (Lambda) Spectra of Lead Sulphide thin films.

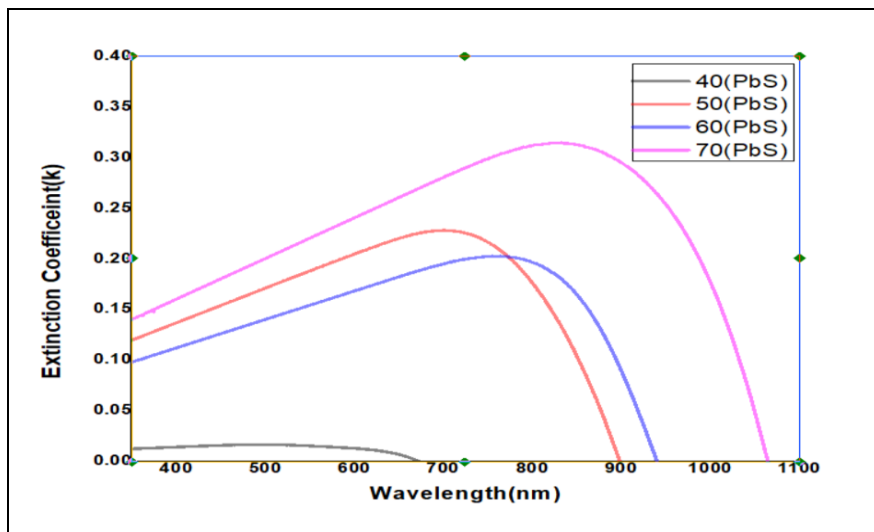


Fig.10. Shows the Absorption Coefficient (a) Versus Wavelength Spectra of Lead sulphide thin films.

Plots of transmittance vs wavelength and $(\alpha h)^2$ versus energy $(h\nu)$ of Lead Sulphide thin films produced by SILAR are displayed in Fig.6. and Fig.7. The Absorption Spectra of Lead Sulphide thin films produced using the silar technique across varying cycle counts are displayed in Fig.8 above. The spectra display two distinct absorption patterns: sample A (40 cycles) exhibits a significant absorption in the visible range of 450–700 nm, whereas samples B, C, and D (50, 60, and 70 cycles) exhibit a large absorption in the infrared area. The Transmittance Spectra of Lead Sulphide thin films at various dipping times are displayed in Fig.6. In the visible spectrum, all of the samples exhibit poor transmittance, which increases quickly in the infrared spectrum. Since reflectance is the opposite of transmittance, this demonstrates that the reflectance spectra are accurate. To do this, apply equation (2). [11, 12, 17, 18].

$$T = (1 - R^2) \exp(-4\pi t \lambda) - R^2 \exp(-8\pi t \lambda) \dots\dots\dots (2)$$

Where, t = thickness, λ = wavelength.

The extinction coefficient, in fig.9., indicates that all samples grow in the UV-visible area and decrease as thickness increases. As noted in [7], it has been observed that the High Absorbance of Lead Sulphide films in a graphical region causes to increased K at a wavelength shorter than 500 nm. High Absorbance near-Infrared regions and High Reflectance

near visible regions are seen in all of the spectra. The films are suitable for solar thermal applications and anti-reflection coatings because to their high absorption in the infrared and high reflectivity in the visible spectrum. They can also be used in infrared (IR) detectors as well as in solar control coating [12, 15, 18, 19]. PbS samples A, B, C, and D (40, 50, 60, and 70 cycles) had their optical band gap energies determined by taking into account a direct transition between the bands of valance and conduction when photon energy strikes the materials. The absorbance coefficient against wavelength spectra of Lead Sulphide thin films are displayed in Fig.10. The relationship below was used to compute the Absorption Coefficient (α) is associated with the strong Absorption region of the thin film from Absorbance (A) and Thickness (t), was derived using the weighting approach [13, 14, 20].

$$\alpha = 2.3026A/t \dots \dots \dots (3)$$

The following equation for semiconductor optical absorption was used to analyze the absorption Coefficient (α) [13,14].

$$(\alpha hv) = K (hv - Eg)^{n^2} \dots \dots \dots (4)$$

Where, K = constant, For a semiconductor with an authorized direct band gap, $n = 1$ and Eg = energy band gap. The straight-line component of $(\alpha hv)^2$ versus (hv) was used to Calculate the Band gap, confirming the Optical transition's nature. Energy band gap is the result of extrapolating these graphs to the point where $\alpha = 0$. For samples A, B, C, and D, the direct band gap values obtained using the silar technique fall between 2.32 and 1.45 eV (40, 50, 60, and 70 cycles). Plotting the $(\alpha hv)^2$ as a function of (hv) yielded these, is displayed in fig.7. above equation (4). While increasing the thicknesses of localized State density in the Energy gap is responsible for the drop in Eg values as the number of cycles increased.

VII. Acknowledgement

The authors are grateful to the R & D Laboratory Changa University for permission to use facilities, laboratories and the cleanroom. Lastly, we would like to express our gratitude to Uka tarsadia University Maliba Campus, Bardoli-Surat provided the facility for their kindly support in material characterization.

REFERENCES

- [1] Thanikaikarasan, S., Mahalingam, T., Veeramuthumari, S., & Ixtlilco, L. (2013). Electrochemical Growth and Characterization of Lead Sulphide Thin Films. *Journal of New Materials for Electrochemical Systems*, 16(2).
- [2] Li, K., Meng, X., Liang, X., Wang, H., & Yan, H. (2006). Electrodeposition and characterization of PbSe films on indium tin oxide glass substrates. *Journal of solid-state electrochemistry*, 10, 48-53.
- [3] Preetha, K. C., Murali, K. V., Ragina, A. J., Deepa, K., & Remadevi, T. L. (2012). Effect of cationic precursor pH on optical and transport properties of SILAR deposited nano crystalline PbS thin films. *Current Applied Physics*, 12(1), 53-59.
- [4] Valenzuela-Jauregui, J. J., Ramirez-Bon, R., Mendoza-Galvan, A., & Sotelo-Lerma, M. (2003). Optical properties of PbS thin films chemically deposited at different temperatures. *Thin Solid Films*, 441(1-2), 104-110.
- [5] Choudhury, N., & Sarma, B. K. (2008). Condensed Matter: Structural, Mechanical and Thermal Properties-Structural characterization of nanocrystalline PbS thin films synthesized by CBD method. *Indian Journal Of Pure & Applied Physics*, 46(4), 261.
- [6] S Choudhury; S.K Dolui; D.K Avasthi; A. Choudhury; *Indian J of Physics*.79, 1019 (2005).
- [7] Carrillo-Castillo, A., Aguirre-Tostado, F. S., Salas-Villasenor, A., Mejia, I., Gnade, B. E., Sotelo-Lerma, M., & Quevedo-Lopez, M. A. (2013). Effect of chemical bath deposition parameters on the growth of PbS thin films for TFTs applications. *Chalcogenide letters*, 10(3), 105-111.
- [8] Seghaier, S., Kamoun, N., Brini, R., & Amara, A. B. (2006). Structural and optical properties of PbS thin films deposited by chemical bath deposition. *Materials Chemistry and Physics*, 97(1), 71-80.
- [9] Pawar, S. B., Pawar, S. A., Patil, P. S., & Bhosale, P. N. (2013, June). Chemosynthesis of PbS thin film by SILAR technique. In *AIP Conference Proceedings* (Vol. 1536, No. 1, pp. 483-484). American Institute of Physics.
- [10] K. Wasa; M. Kitabatake; H. Adachi; *Thin Film Material Technology*. William Andrew Pub, Springer: New York, NY, USA. 183-198, 2004.
- [11] B. Thangaraju; P. Kaliannan; Semiconductors. *Sci. Techn.*15, 849 (2000).
- [12] Rajashree, C., Balu, A. R., & Nagarethinam, V. S. (2016). Enhancement in the physical properties of spray deposited nanostructured ternary PbMgS thin films towards optoelectronic applications. *Journal of Materials Science: Materials in Electronics*, 27, 5070-5078.
- [13] Leach, M., Reddy, K. R., Reddy, M. V., Tan, J. K., Jang, D. Y., & Miles, R. W. (2012). Tin sulphide thin films synthesized using a twostep process. *Energy Procedia*, 15, 371-378.
- [14] Uhuegbu, C. C. (2011). Growth and characterization of lead sulphide thin film for solar cell fabrication. *Canadian Journal on Scientific and industrial research*, 2(6), 230.
- [15] Pop, I., Nascu, C., Ionescu, V., Andrea, E., & Bratu, I. (1997). Structural and optical properties of PbS thin films obtained by chemical deposition. *Thin Solid Films*, 307(1-2), 240-244.
- [16] Emeakaroha, T. M., Ezekoye, B. A., Ezekoye, V. A., & Ighodalo, K. O. (2016). Optical and structural properties of silar-grown highly oriented lead sulphide (PbS) thin films. *Chalcogenide Lett*, 13, 91-96.

- [17] Ubale, A. U., Junghare, A. R., Wadibhasme, N. A., Daryapurkar, A. S., Mankar, R. B., & Sangawar, V. S. (2007). Thickness dependent structural, electrical and optical properties of chemically deposited nanoparticulate PbS thin films. *Turkish Journal of Physics*, *31*(5), 279-286.
- [18] Abbas, M. M., Shehab, A. A. M., Al-Samuraee, A. K., & Hassan, N. A. (2011). Effect of deposition time on the optical characteristics of chemically deposited nanostructure PbS thin films. *Energy Procedia*, *6*, 241-250.
- [19] Preetha, K. C., & Remadevi, T. L. (2014). Band gap engineering in PbSe thin films from near-infrared to visible region by photochemical deposition method. *Journal of Materials Science: Materials in Electronics*, *25*, 1783-1791.
- [20] Ezekoye, B. A., Ighodalo, K. O., Ezekoye, V. A., Emeakaroha, T. M., Ezema, J. I., & Offor, P. O. (2015). Nanocrystalline Cadmium sulfide (CdS) thin film synthesized at different dip times by chemical bath deposition technique.