Optical, Morphological and Electrical Properties of PBS Thin Films Prepared by Chemical Bath Deposition (CBD) Technique at Different Deposition Time

Author's Details:
A.M. Ramalan[1*], A.S Yusuf[3],D.O. Samson[1,2], A.D.A. Buba[1]
[1] Department of Physics, University of Abuja, P.M.B 117, Abuja, Nigeria.
[2] School of Physics, Universiti Sains Malaysia, P.M.B 11800, Gelugor, Pinang, Malaysia.
[3] Federal University of Technology Minna, P.M.B 65, Minna, Nigeria.
E-mail of the Corresponding Author: abubakar.ramalan@uniabuja.edu.ng ramalan86@yahoo.com

Abstract
Lead sulphide (PBS) thin films have been investigated in this present work by using chemical bath deposition (CBD) technique onto glass substrates with different deposition times (20, 40 and 60 min.) at 70^{o}C (158^{o}F) exploiting lead nitrate and thiourea as lead and sulphide ions sources. The effect of the deposition time on the optical, morphological and electrical properties of the as-deposited PBS films were studied. The thin films exhibit a strong optical absorption in the ultraviolet (UV) and visible regions but low absorption over the longer wavelength region towards near infrared (NIR) of the electromagnetic spectrum. In contrast, the films transmit very low at the UV and visible regions while NIR region exhibit a good optical transmission. The optical band gap energy of the films decreases with increase in deposition time (t_D), ascribing larger particle size. The extinction coefficient (k) of the films increased with deposition time increment which corresponds to greater attenuation of light and also the higher probability of raising the electron transfer across the mobility gap with the photon energy. The image obtained shows almost dense spherical and uniform grains with an increase in time of dipping the glass slides into the solution. The electrical conductivity was observed to be inversely related to the optical band gap energy of the films.

Keywords: *PbS, CBD, UV, NIR, Thin films*

1. Introduction

There is a growing interest globally in the study of lead sulphide (PbS) owing to its unique optical, morphological and electrical properties with a wide range of applications in the field of photovoltaic technology, optoelectronic devices, photoconductors, sensors and infrared detectors (Ezekoye *et al.*, 2015; Preetha *et al.*, 2015; Aadim *et al.*, 2017). PbS is an IV-VI group of periodic table semiconductor with a narrow direct band gap energy of 0.41eV at room temperature and a relatively large excitation Bohr radius of 18nm (Thirumavalavan *et al.*, 2015; Uhuegbu, 2011; Ahmed *et al.*, 2013; Aadim *et al.*, 2017). It has a controllable conductivity by exploiting different dopants such as Al, Cl, and Ag with a very high absorption coefficient approximately $10^5 cm^{-1}$ than other semiconductor materials. PbS has a p-type conductivity which makes it vital materials in the application of the absorber layer in photovoltaic devices (Cheng et al., 2006). PbS thin films have been prepared using different synthesis routes such as electro-deposition, spray pyrolysis, photo-accelerated chemical deposition, microwave-heating, pulsed laser deposition (PLD), successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods (Aadim *et al.*, 2017; Osherov *et al.*, 2007; Rajashree *et al.*, 2014; Gülen, 2014; Pawar *et al.*, 2013). Among the various deposition techniques, CBD is gaining a widespread attention in the recent years due to its simplicity, easier composition control, better homogeneity, low processing temperature, cost effectiveness, potential for large-scale production of thin films and capable of yielding good quality thin films which does not require any sophisticated instrument (Ezekoye *et al.*, 2015; Thirumavalavan *et al.*, 2015; Jana *et al.*, 2008). Due to this superior advantages, CBD method has established highly attractive by researchers aiming to obtain thin films (Göde and Gümüs, 2009). In this present work, CBD technique was used to prepare PbS thin films on soda lime glass substrate with different deposition time using lead nitrate [$Pb(NO_3)_2$] and thiourea [$SC(NH_2)_2$] as lead and sulphide ion sources respectively. The effect of deposition time on the optical, morphological and electrical properties was investigated.

2. Experimental details

2.1. Preparation of PbS thin films

PbS thin films were deposited on ultrasonically prepared soda lime glass substrates by CBD using lead nitrate [$Pb(NO_3)_2$], thiourea [H_2NCSNH_2] and sodium hydroxide [NaOH] as a lead ion source, sulphide ion source, and a base medium respectively. The glass substrates were degreased and washed ultrasonically in a cleaning solution containing sodium lauryl sulfate [$CH_3(CH_2)_{11}SO_4Na$] detergent and subsequently rinsed with methanol and then thoroughly with double distilled water. The deposition was done in a reactive solution containing 20ml each of lead nitrate, thiourea and NaOH solutions with concentrations of 0.07M, 0.4M, and 0.4M respectively, and distilled water of 20ml was added to the solution to achieve a total volume of 80ml. The ultrasonically prepared glass substrate was vertically immersed into the prepared reactive solution at the center of the reaction deposition bath, the solution was stirred with a magnetic stirrer for 10 minutes in order to achieve a homogeneous concentration of the mixture throughout the deposition process and was maintained at room temperature with a final pH value of 12.52. The deposited films were subsequently taken out of the chemical bath after different deposition (dipping) time, t_D, of 20, 40 and 60 minutes, rinsed with double distilled water and dried on a hotplate for 30 minutes at 70^{o}C (158^{o}F). The deposited PbS thin films were homogeneous and well adhered to the soda lime glass substrate. The thickness of each deposited film was determined by Surface Profiler obtaining 100, 000 and 000nm for samples with t_D of 20, 40 and 60 minutes respectively. The effective chemical reaction mechanism in the formation on a substrate of PbS thin films is given as:

$$Pb(NO_3)_2 + 4NaOH \rightarrow [Pb(OH)_4]^{2-} + 4Na^+ + 2NO^{3-} \quad (1)$$

$$[Pb(OH)_4]^{2-} + SC(NH_2)_2 \rightarrow PbS + 2OH^- + CN_2H_2 + 2H_2O \quad (2)$$

The $[Pb(OH)_4]^{2-}$ complex divided into fragments to make bonds with Pb^{2-} ions which led to the formation of PbS.

2.2. Characterization of PbS thin films

The absorbance data of the chemically deposited PbS thin films were obtained using Axiom Medicals UV 752 spectrophotometer at room temperature in the wavelength range of 250nm to 1100nm. The optical properties of the as-deposited PbS thin films were determined from the UV/Vis absorbance data. The absorbance data were then used to evaluate the transmittance, absorption coefficient (α), optical band gap energy and extinction coefficient of the thin films. The optical absorption coefficient (α) was calculated for each PbS films from the absorption spectra using the relation (Rajashree *et al.*, 2014).

$$\alpha = \frac{2.303A}{t} \quad (3)$$

Where t is the thickness, and A is the absorbance of the as-deposited PbS films. As a direct bandgap material, Tauc's relation was used to evaluate the optical band gap energy (E_g) using (Thirumavalavan *et al.*, 2015):

$$(\alpha h\nu)^2 = K(h\nu - E_g) \quad (4)$$

Where E_g is the optical band gap energy of the PbS thin films, and K is a coefficient. A four-point probe method (QUADPRO-301-6) was used to determine the resistivity of the as-deposited PbS films from which the conductivity was evaluated.

3. Results and discussion

3.1. Optical Properties

The effect of the deposition time (t_D) on the optical properties of chemically deposited PbS thin films were studied in this section using Axiom Medicals UV 752 spectrophotometer at room temperature in the wavelength range of 250nm to 1100nm..

3.1.1. Absorbance

The optical absorption spectra of the PbS films at different deposition time (t_D) of 20, 40 and 60 minutes at 70°C (158°) were recorded in the wavelength ranges of 250nm to 1100nm as illustrated in figure 1.

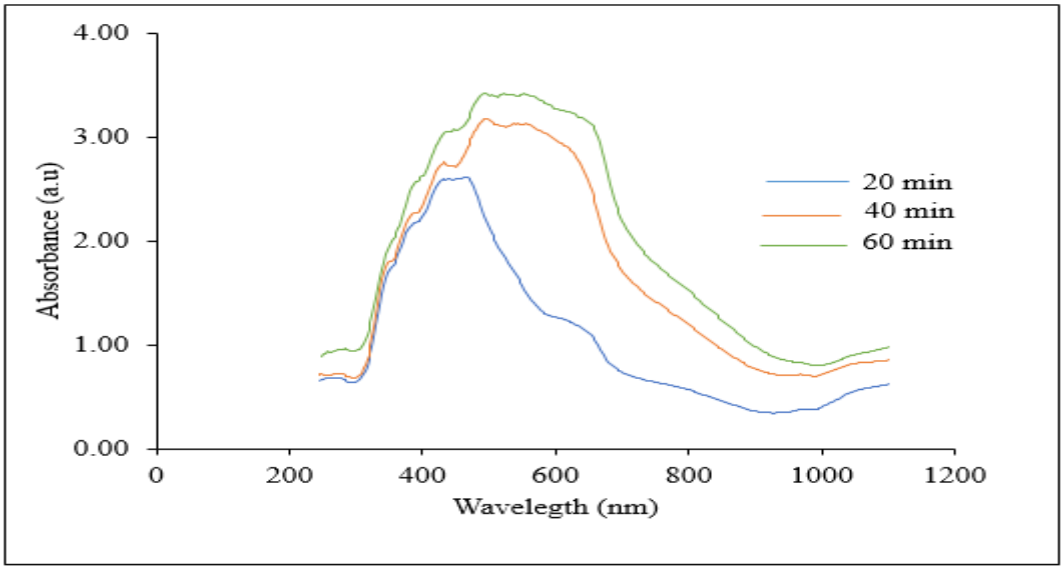

Fig. 1: Absorption spectra of PbS thin films prepared by CBD at a deposition time of 20, 40 and 60 minutes.

Figure 1 shows that the PbS thin films exhibit a strong optical absorption in the wavelength range of about 320nm to 700nm covering most UV and visible regions of the electromagnetic spectrum. It is observed that the shapes of the curves are similar, but there are differences in the absorbency. The absorbance of the films increases with the deposition time (t_D) owing to the increase of the film's thickness, where the thicker films have more atoms present, hence more states are available for the photon energy to be absorbed (Obaid *et al.*, 2013; Ezema *et al.*, 2007). It can be clearly stated from the above figure that PbS thin films exhibit high absorbing nature in the UV-visible regions but low absorption over the longer wavelength region towards near infrared.

3.1.2. Transmittance (T)

The transmission spectra of PbS thin films deposited with different deposition time (t_D) at 70°C (158°) in the wavelength ranges of 250nm to 1100nm as shown in figure 2.

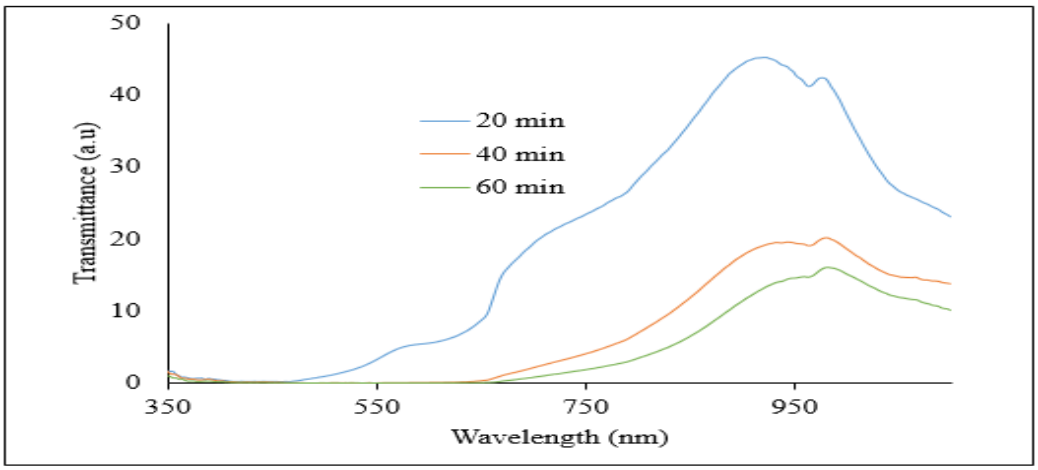

Fig. 2: Transmission spectra of PbS thin films prepared by CBD at deposition time (t_D) of 20, 40 and 60 minutes.

It is observed from the above figure that all the films transmit very low in the UV and visible regions between 300nm to about 700nm. This phenomenon is attributed to the strong absorbance in this regions with similar characteristics observed by Obaid *et al.* (2013). The transmission increases with increasing wavelength towards the NIR regions indicated that the transparency window decreases as the deposition time increases which may be ascribed to the decrease of thickness as the deposition time increases. It also observed that the high transmission in the film could be related with the low thickness and the abundance of porosity in the films.

3.1.3. Optical Bandgap Energy

Optical band gap or energy gap (E_g) is the separation between valance and conduction bands of semiconductor materials (Aadim *et al.*, 2017). The optical band gaps of the PbS thin films were estimated graphically by applying the Tauc's model (see equation 4), the band gap of the sample material with sharp falloff can be deduced from a plot of the squared absorption coefficient $(\alpha hv)^2$ versus photon energy (hv) by extrapolating the straight line of the plot to intersect the energy axis (Aadim *et al.*, 2017). The E_g of the PbS thin films were obtained by extrapolating the straight line portion of the graph to zero absorption coefficient with different deposition time (t_D) of 20, 40, and 60 minutes as indicated in Figure 3(a-c).

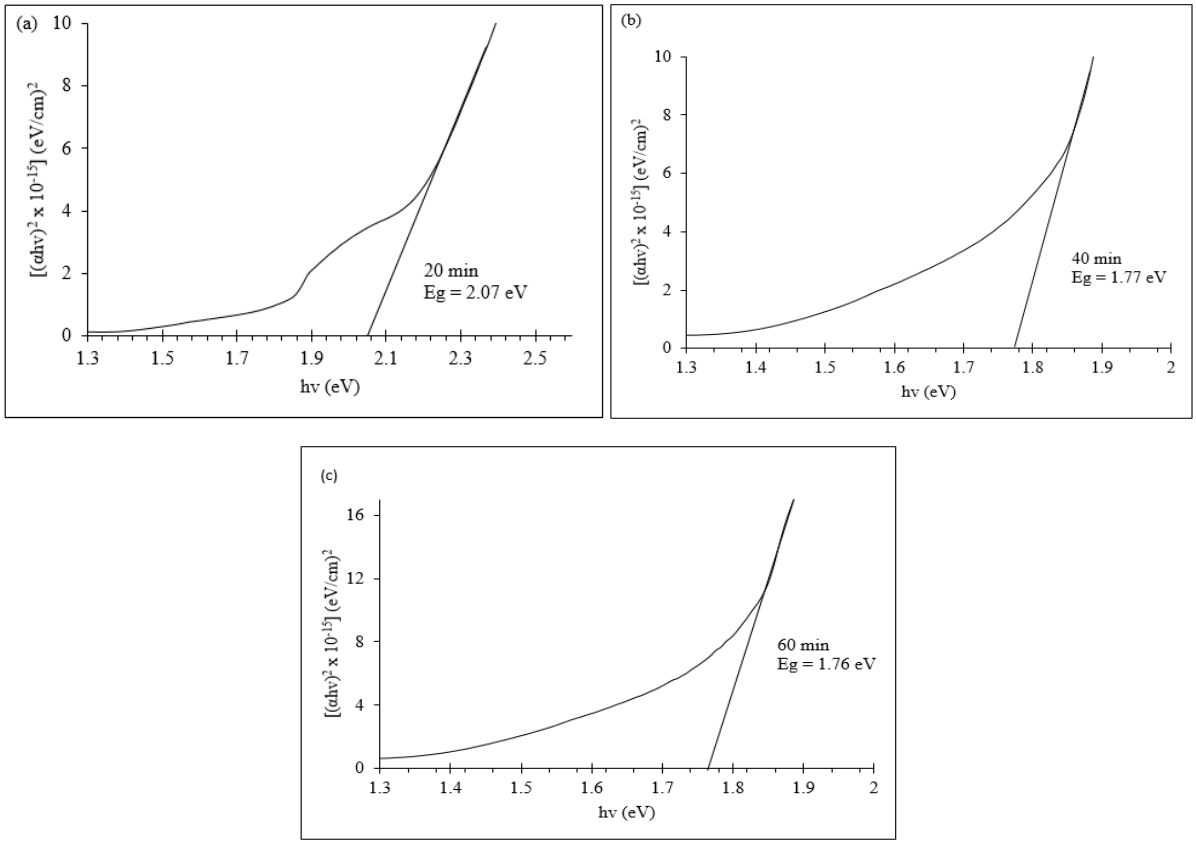

Fig. 3: Tauc plots of chemically deposited PbS thin films at different deposition time (t_D) of (a) 20 (b) 40, and (c) 60 minutes.

The E_g values of the PbS thin films are found be 2.07eV, 1.77eV and 1.76 eV for the films at a deposition time of 20, 40 and 60 minutes respectively. It is observed from the plots that E_g values decrease with increase in deposition time (t_D) due to the increase of the thickness of the film resulting to agglomeration of the nanocrystallites into larger crystallites (i.e., increase in particle sizes). This finding is in good agreement with the results obtained in the literature (Obaid *et al.*, 2012; Göde *et al.*, 2014; Jana *et al.*, 2008; Aadim *et al.*, 2017; Rafa and Rousdy, 2010; Kumara *et al.*, 2009). This value of energy band gap is higher than the value of the direct band gap energy of the PbS thin film which might occur due to poor crystallization because PbS films are polycrystalline.

3.1.4. Extinction Coefficient (k)

Extinction coefficient describes the attenuation of light in a medium and increase of k with the increase of *hv* indicates the probability of raising the electron transfers across the mobility gap with photon energy (Kamal, 2010). Figure 4 shows the extinction coefficient as a function of wavelength for chemically deposited PbS thin films with different deposition time.

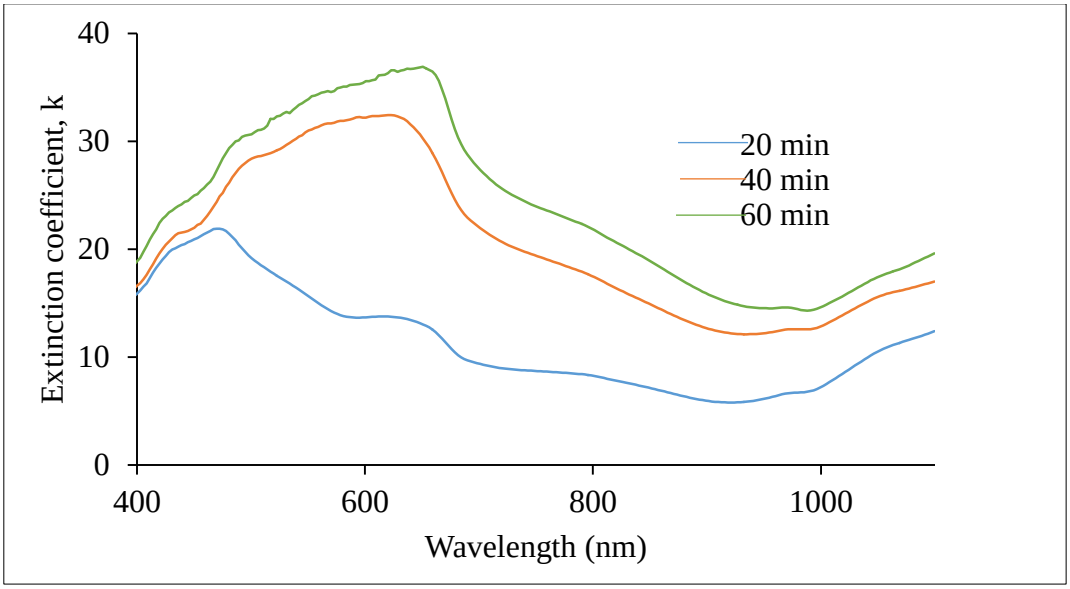

Fig. 4: Extinction Coefficient of chemically deposited PbS thin films with different deposition times of 20, 40 and 60 minutes.

It is observed that the extinction coefficient (k) in general, increased with the increases in deposition times for all films. Hence, the higher values of k are the representation of greater attenuation of light in a thin film and also the higher probability of raising the electron transfer across the mobility gap with the photon energy (Kamal, 2010). The observed increment in extinction coefficient (k) values is attributed to the increase of the thickness of the films as a function of deposition times, as well decreases the optical energy gap as a result of absorbance increment. This finding agrees well with the literature (Aadim *et al.*, 2017; Abbas, Shehab, *et al.*, 2011).

3.2. Morphological properties

The obtained surface morphology of the PbS films with different deposition times of 20, 40 and 60 minutes at 70^{o}C (158^{o}F) was measured by using Carl Zeiss Evo M10 Scanning Electron Microscopy (SEM). SEM was used to show the growth surface and surface roughness of the deposited thin films layers as shown in figure 5. The image shows almost dense spherical and uniform grains, with an increase in time of dipping the glass slides in the solution. The average particle size was found to be 18.2 nm.

Fig. 5: SEM images of PbS thin films at different deposition time.

3.4. Energy Dispersive X-ray (EDX) analysis of PbS thin films

The dispersive energy X-ray (EDX) analysis patterns of the sample in this study shows that the sample comprises only Pb and S elements in the starting solution present in the solid film with little impurities and better quality with an increase in time of dipping.

Fig. 6: EDX images of PbS thin films at different deposition time.

3.5. Electrical Properties

The measured electrical resistivity and the corresponding conductivity of the chemically deposited PbS thin films at different deposition time which are the distinctive quantities of the electrical properties are shown in Figure 7.

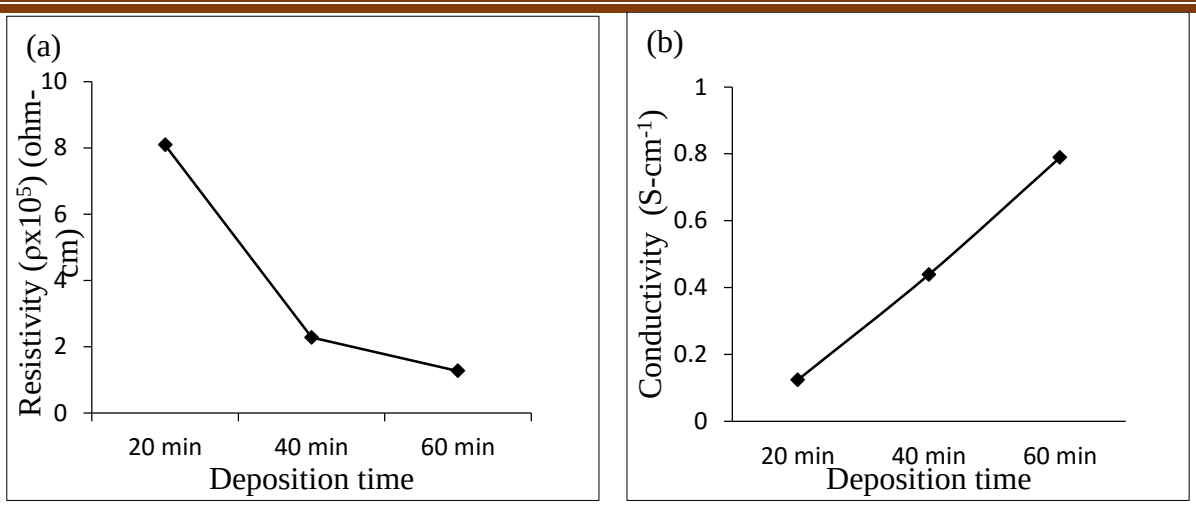

Fig. 7: Graph of electrical (a) resistivity (b) conductivity of chemically deposited PbS films at different deposition time

It is observed from the figure (7a) that resistivity decreased from 8.146**Ω**cm to 1.026**Ω**cm with increasing deposition time from 20min to 60min which implies increasing grain size of the films. The electrical conductivity linearly increases with the increase of deposition time as shown in figure (7b), this observation can be attributed to large levels of scattering (Mosiori *et al.*, 2014). The electrical conductivity is also observed to be inversely related to the optical band gap of the films with minimum optical band gap having the maximum electrical conductivity. This is in agreement with result gotten by Preetha *et al.* (2015).

4. Conclusion

Lead sulphide (PbS) thin films have been successfully prepared by chemical bath deposition method on soda lime glass substrate with different deposition time using lead nitrate [$Pb(NO_3)_2$] and thiourea [$SC(NH_2)_2$] as lead and sulphide ion sources respectively. The study on the optical and electrical properties of the films was carried out to determine the effect of deposition time properties. It was found that the as-deposited films exhibit a strong optical absorption in UV and visible regions but low absorption over the longer wavelength region towards near infrared (NIR) of the electromagnetic spectrum. In contrast, the films transmit very low at the UV and visible regions while NIR region exhibit a good optical transmission.

The optical bandgap (E_g) of the films decreases with increase in deposition time (t_D) was ascribed to agglomeration of the nanocrystallites into larger crystallites. The extinction coefficient (k) of the films increased with the increase in deposition time. Hence, the higher values of k have a greater attenuation of light and also the higher probability of raising the electron transfer across the mobility gap with the photon energy. The electrical conductivity is inversely related to the optical band gap of the films.

References

i. *Aadim, K. A., Ibrahim, A. -M., & Marie, J. M. (2017). Structural and Optical Properties of PbS Thin Films Deposited by Pulsed Laser Deposited (PLD) Technique at Different AnnealingTemperature. International Journal of Physics, 5(1), 1-8. doi:10.12691/ijp-5-1-1*

ii. *Abbas, M. M., Shehab, A. A.-M., Hassan, N.-A., & Al-Samuraee, A.-K. (2011). Effect of temperature and deposition time on the optical properties of chemically deposited nanostructure PbS thin films. Thin Solid Films, 519, 4917–4922.*

iii. *Ahmed, S. S., Hassan, E. K., & Emad, F. (2013). PbS nano thin film photoconductor. International Journal of Physics and Research (IJPR), 3(3), 21-26.*

iv. *Cheng, S., Chen, Y., Huang, C., Chen, G. (2006). Characterization of SnS films prepared by constant-current electro-deposition. Thin Solid Films, 500, 96–100.*

v. *Ezekoye, B. A., Emeakaroha, T. M., Ezekoye, V. A., Ighodalo, K. O., & Offor, P. O. (2015). Optical and structural properties of lead sulphide (PbS) thin films synthesized by chemical method. International Journal of Physical Sciences, 10(13), 385-390.*

vi. *Ezema, F. I., Ekwealor, A. B., & Osuji, R. U. (2007). Optical properties of chemical bath deposited nickel oxide (NiO)thin films. Journal of Optoelectronics and Advanced Materials, 9, 898–1903.*

vii. *Göde, F., Gümüs, C. (2009). Influences of copper and manganese concentrations on the properties of polycrystalline ZnS:Cu and ZnS:Mn thin films. Journal of Optoelectronics and Advanced Materials, 11(4), 429 - 436.*

viii. *Göde, F., Güneri, E., Emen, F. M., EmirKafadar, V., & Ünlü, S. (2014). Synthesis, structural, optical, electrical and thermoluminescence properties of chemically deposited PbS thin films. Journal of Luminescence, 147, 41–48.*

ix. *Gülen, Y. (2014). Characteristics of Ba-Doped PbS Thin Films Prepared by the SILAR Method. Acta Physica Polonica A, 126, 763-767. doi:10.12693/APhysPolA.126.763*

x. *Jana, S., Thapa, R., Maity, R., & Chattopadhyay, K. K. (2008). Optical and dielectric properties of PVA capped nanocrystalline PbS thin films synthesized by chemical bath deposition. Physica E, 40, 3121– 3126.*

xi. *Kamal, U. A. (2010). Preparation and Characterization of II-VI SemiconductorThin Film by Spray Pyrolysis. Dhaka, Bangladesh: Bangladesh University of Engineering & Technology.*

xii. *Kumara, D., Agarwal, G., Tripathi, B., Vyas, D., & Kulshrestha, V. (2009). Characterization of PbS nanoparticles synthesized by chemical bathdeposition. Journal of Alloys and Compounds, 484, 463-466.*

xiii. *Mosiori, C. O., Njoroge, W. N., & Okumu, J. (2014). Optical and Electrical Properties of Pbs Thin Films Grown by Chemically Bath Deposition [CBD] at Different Lead Concentrations. International Journal of Advanced Research in Physical Science, 1(1), 25-32.*

xiv. *Obaid, A. S., Mahdi, M. A., Dihe, A. A., & Hassan, Z. (2012). Effect of Deposition Time on the PbS Thinfilms Prepared using Microwave-Assisted Chemical Bath Deposition: Structure andOptical Characterization. International Conference on Education, Applied Sciences and Management (oju ewe 86 - 89). Dubai, UAE: ICEASM.*

xv. *Obaid, A. S., Mahdi, M. A., Yusof, Y., Bououdina, M., & Hassan, Z. (2013). Structural and optical properties of nanocrystalline lead sulfide thin films prepared by microwave-assisted chemical bath deposition. Materials Science in Semiconductor Processing, 16, 971–979.*

xvi. *Osherov, A., Ezersky, V., & Golan, Y. (2007). The role of solutioncomposition in chemical bath deposition of epitaxial thin films of PbSon GaAs (100). Journal Crystal Growth, 308, 334–339. doi:10.1016/j.jcrysgro.2007.07.046*

xvii. *Pawar, S. B., Pawar, S. A., Patil, P. S., & Bhosale, P. N. (2013). Chemosynthesis ofPbS thin film by SILAR technique. AIP Conf. Proc., 1536, 483-484. doi:10.1063/1.4810311*

xviii. *Preetha, K. C., Deepa, K., Dhanya, A. C., & Remadevi, T. L. (2015). Role ofcomplexing agents on chemical bath deposited PbS thin filmcharacterization. Material Science and Engineering, 73(012086), 1-5. doi:10.1088/1757-899X/73/1/012086*

xix. *Rafa, M. A., & Rousdy, N. (2010). Study of optical properties of nanostructuredPbS films. Journal of Philosophical Magazine Letters, 90(2), 113-120.*

xx. *Rajashree, C., Balu, A. R., & Nagarethinam, V. S. (2014). Substrate temperatureeffect on the Physical properties of Spray deposited Lead sulfide thinfilms suitable for solar control coatings. International Journal of ChemTech Research, 6, 347-360.*

xxi. *Thirumavalavan, S., Mani, K., & Suresh, S. (2015). Investigation on Structural, Optical, Morphological and Electrical Properties of Lead Sulphide (PbS) Thin Films. Journal of Ovonic Research, 11(3), 123 - 130.*

xxii. *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 - 240.*