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Optical and structural properties of lead sulphide (PbS) thin films synthesized by chemical method

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The influence of dip times on the lead sulphide (PbS) thin films deposited on glass slide substrates via chemical bath deposition (CBD) technique using chemical precursors, nitrate $Pb(NO_3)_2$, and thiourea, $(SC(NH_2)_2)$ in alkaline medium at 300 K was investigated. The optical, structural and morphological studies were performed by UV-vis spectophotometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. The XRD showed films of cubic (galena), crystalline in nature with the preferential (111) orientation. The optical studies showed films of direct band gaps in the range of 1.59-1.65 eV.

Key words: Lead sulphide, thin films, lead sulphide (PbS), X-Ray diffraction, scanning electron microscope (SEM), bandgap.

INTRODUCTION

Lead sulphide (PbS) is an important IV-VI group chalcogenides semiconductor that has attracted considerable attention in the recent times due to its numerous optical and opto-electronic properties and useful applications in solar cells, optoelectronic devices, photoconductors, sensors and infrared detector devices (Chattarki et al., 2012; Koao et al., 2014; Preetha et al., 2015). PbS thin films has direct optical bandgap that can be changed from 0.39 up to 5.20eV (Koao et al., 2014). PbS thin films have been deposited through various deposition processes such as electrodeposition (Osherov et al., 2007), spray pyrolysis (Rajashree et al., 2014; Thangaraju and Kaliannan, 2000), chemical bath deposition (Koao et al., 2014; Preetha et al., 2015; Garcia-Valenzuela et al., 2013; Fernandez-Lima et al., 2007), and successive ionic layer adsorption and reaction (Puiso et al., 2003; Gulen, 2014; Pawar et al., 2013).

Chemical bath method is a very simple, relatively cost effective, convenient for large area scaling and is used in the deposition of good quality thin films with physical and chemical properties comparable to other methods. In the last decade, there has been a renewed interest in this method, mainly associated with its remarkable success in depositing semiconductor layers in thin film photovoltaic cells. By chemical bath deposition (CBD), the crystallites can be varied by controlling deposition parameters (Abbas et al., 2011). Researchers observed that thermal treating process has effect on the rate of absorptivity of PbS thin films and consequently influence the optical characterization of chemically deposited (Thangaraju and

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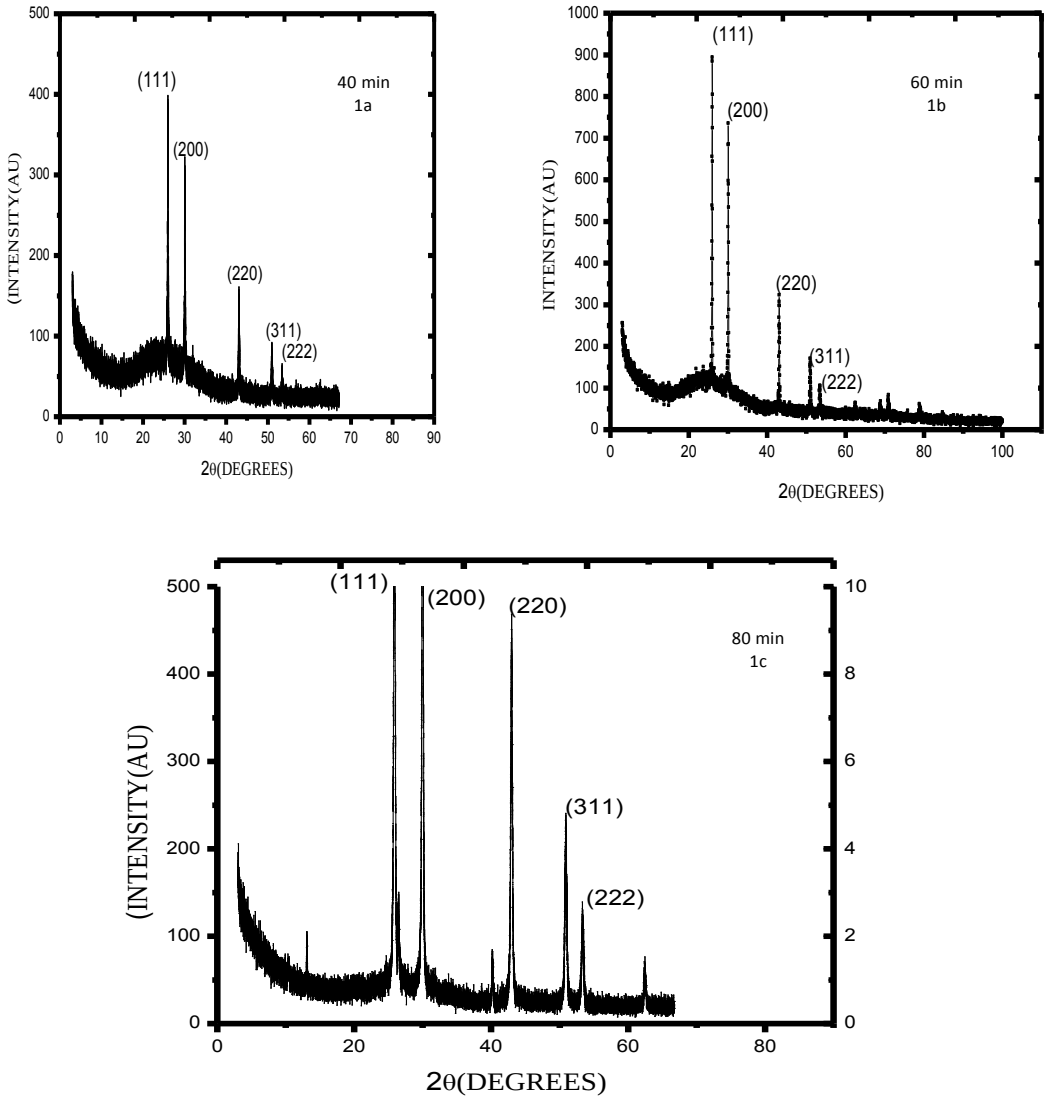

Figure 1. XRD Pattern of CBD PbS Thin Films for (A) 40 min deep time, (B) 60 min and (C) 80 min.

Kaliannan, 2000).

In the present study, the authors investigated the influence of dip times on the lead sulphide (PbS) thin films deposited on glass slide substrates via CBD technique using chemical precursors, nitrate $Pb(NO_3)_2$], and thiourea,$(SC(NH_2)_2)$ in alkaline medium at 300K.

MATERIALS AND METHODS

Lead sulphide thin films were deposited on glass substrate by the chemical bath method. The precursor chemicals were lead nitrate ($Pb(NO_3)_2$), thiourea $(SC(NH_2)_2)$ and sodium hydroxide $NaOH$. Thiourea is used as our sulphide ion source and leads nitrate as our lead ion source. The deposition process is based on slow release of Pb^{2+} and S^{2-} ions in the solution which condensed on the substrate. Lead sulphide were constituted from a solution of 10 ml of 0.1 M lead nitrate ($Pb(NO_3)_2$), 10 ml of 0.8 M thiourea $(SC(NH_2)_2)$, 10 ml of 0.8 M sodium hydroxide ($NaOH$) and distilled water of 40 ml were added to the solution making it total of 70 ml. Cleaned substrates were vertically immersed into the solution and was maintained at room temperature. The substrates were subsequently taken out of the chemical bath after 40, 60 and 80 min dip time, rinsed with distilled water and dried. The resulting films were uniform, homogeneous and well adhered to the substrate with dark surface. The suggested reactions are as follows (Tohidi et al., 2014; Osherov et al., 2007).

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

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

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns for PbS thin

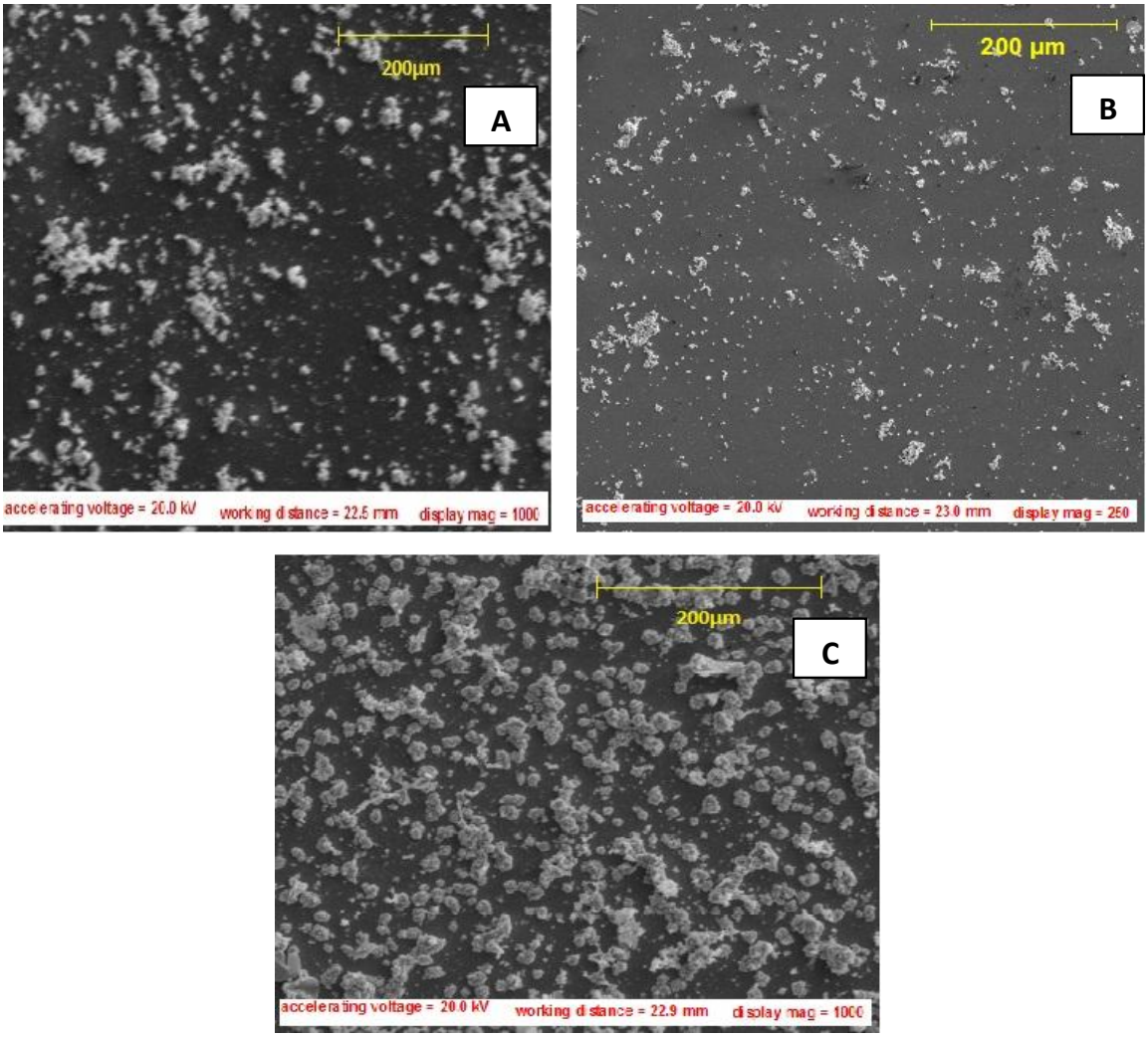

Figure 2. SEM images for PbS deposited thin films for (A) 40 min deep time, (B) 60 min and (C) 80 min.

films according to the standard X-ray diffraction data files with reference No.03-065-0692. The diffraction peaks of the cubic PbS thin films were found at peaks (111), (200), (220), (311), (222), which corresponds to 2θ angles ranging from 25.98-70.95 for all the samples. The as-prepared films have (111) preferential orientation, cubic and polycrystalline in nature and lattice constant 5.9360 Å, with CuKα irradiation (λ=1.5443Å).

The crystalline size of the deposited films for all the samples were calculated using Full Width Half Maximum data (FWHM) and Debye-Scherer formula and their grain size are in within the ranges of (12-27) nm (Chaudhuri et al., 2005; Abbas et al., 2011).

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad (1)$$

Where D=Grain Size, λ=is the wavelength of CuKα used, θ=is Bragg's diffraction angle in degrees and β=is Full width at half maximum of the peak in radians.

Figure 2 shows the SEM PbS thin films using CBD method. It shows that the PbS thin films were homogeneous in nature and sparsely packed crystallites which appear to be randomly oriented with irregular and spherical shape of similar sizes distribution for film deposited by CBD. This agrees with other reports of Castillo et al. (2014) and Jana et al. (2008).

Figure 3 shows the plots from optical studies for the absorption measurements carried out in the wavelength range of 200 to 1100 nm. Figure 3a shows the variation of absorbance with wavelength for the deposited PbS thin films at different dip times from 450 to 100 nm. The sample A (40 min) exhibited absorbance with peak of about 0.98 (a.u) corresponding to wavelength of about 480 nm which is in the near infrared region. Sample B (60 min) shows maximum absorbance of about 750 nm at

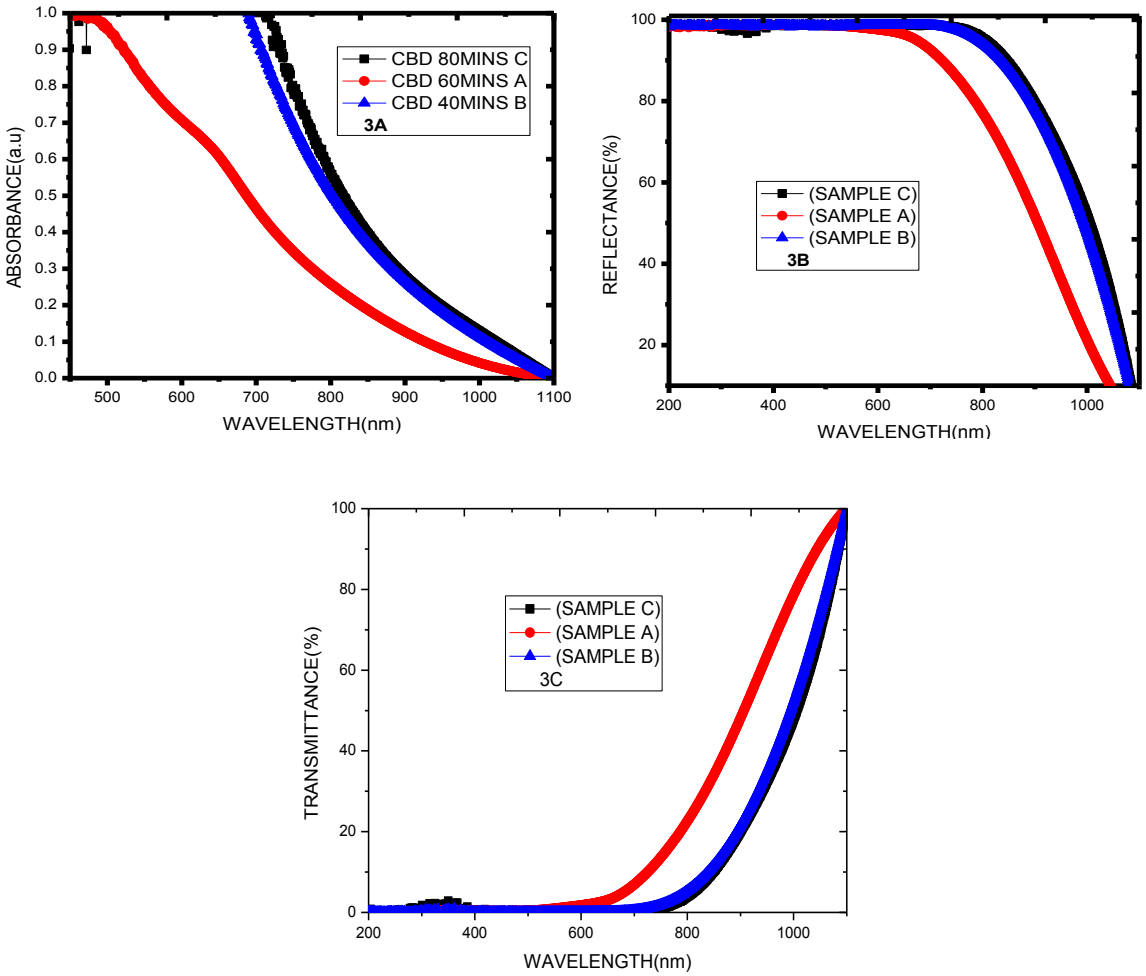

Figure 3. Absorbance, reflectance and transmittance spectra (200-1100 nm) of the PbS CBD deposited thin films.

0.99 (au) in the visible region. Sample C (80 min) shows maximum absorbance with peak of about 0.98 (au) corresponding to wavelength of 760 nm which is also in the near infrared region. The absorbance of the entire sample is about the same (au); this is because of the complexing agent employed during the deposition (Castillo et al., 2014; Abbas et al., 2011; Jana et al., 2008).

Figure 3b shows the reflectance spectra of PbS thin films at different dip times. All the samples show high reflectance in the visible region which rapidly decreased in the near infrared region. This high reflectance and absorbance in the visible region make the thin film good material for anti-reflection coating and also for solar thermal applications, the films can be employed as a solar control coating, also applied in infrared (IR) detectors (Castillo et al., 2014; Abbas et al., 2011; Jana et al., 2008; Larramendi et al., 2001).

Figure 3c shows the transmittance spectra of PbS thin films at different dip times. All the samples show low transmittance in the visible region which rapidly increased in the infrared region. This shows that the reflectance spectra is correct because it is opposite of transmittance. This is done using Equation (2) (Castillo et al., 2014; Abbas et al., 2011).

$$T = \frac{(1-R^2),\exp(-4\pi t/\lambda)}{1-R^2\ \exp(-8\pi t/\lambda)} \quad (2)$$

Where t = thickness and **λ** = wavelength.

The absorption coefficient α associated with the strong absorption region of the film was calculated from absorbance (A) and the thin film thickness (t) which was calculated using the relation below (Manouchehri et al., 2014):

$$\alpha = 2.3026\,A/t \quad (3)$$

The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors (Manouchehri et al., 2014):

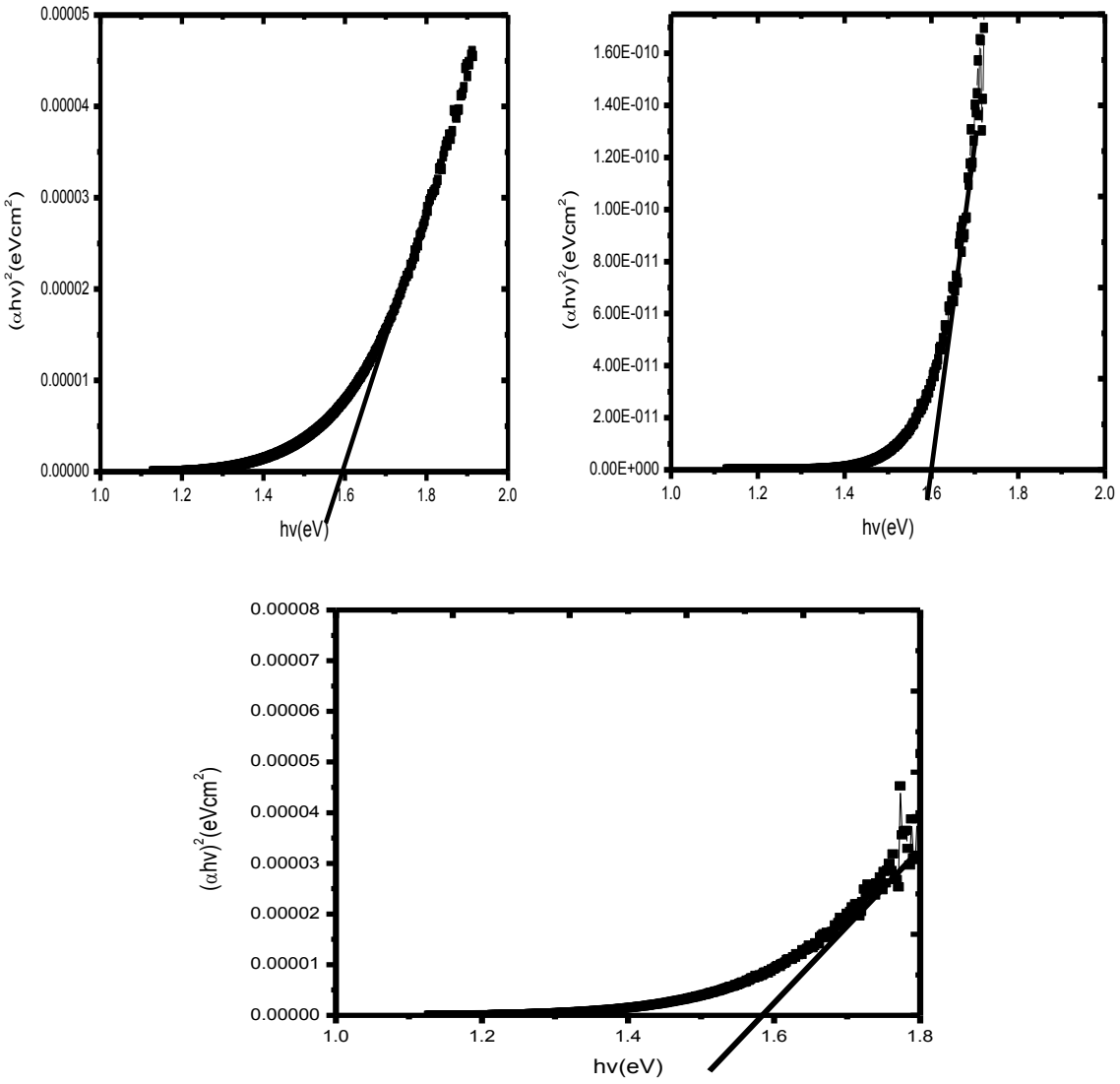

Figure 4. Plots of $(\alpha hv)^2$ versus $h\nu$ for PbS thin films for (A) 40 min deep time, (B) 60 min and (C) 80 min.

$$(\alpha hv) = K(hv - E_g)^{n/2} \quad (4)$$

where K = constant, E_g = energy band gap and n = 1 for allowed direct band gap semiconductor.

Figure 4 shows, Plots of $(\alpha hv)^2$ versus $h\nu$ for PbS thin films at different dip times.

The values obtained for the direct band gap of PbS thin films deposited by chemical bath lies within the range of 1.59-1.65eV. A close observation of the band gap range shows that increase in deposition time increases the band gap.

Figure 5 shows the plot of thickness against the deposition time. The thickness increased with the deposition; time increases (Manouchehri et al., 2014; Abbas et al., 2011), until after 1100 nm and remained almost constant.

Conclusion

Chemical bath deposition (CBD) method has been successfully used to deposit PbS thin films. The optical adsorption, morphological and structural studies of the thin films were carried out. The results obtained from the XRD for the PbS thin films was found to be polycrystalline in nature and grown in cubic crystal structure (galena), with grain sizes of (12 to 27 nm). The properties of high absorbance and high reflectance in the visible region, low absorbance and high reflectance in the near infrared region make the film a good material for anti-reflection coating and for solar thermal applications and infrared (IR) sensors.

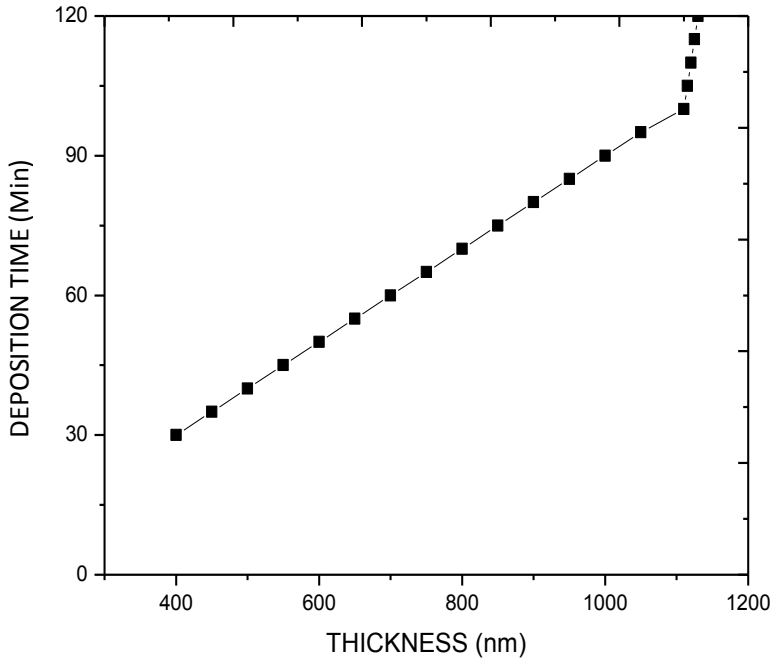

Figure 5. Plot of Deposition time Vs Thickness of PbS thin films.

Conflict of Interest

The authors declare no conflict of interests.

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