

Study of Cadmium Doped Lead Sulphide Thin Films Deposited Using Spray Pyrolysis Technique

M.L. Madugu and J.A. Makko

Department of Physics,
Faculty of Science,
Gombe State University

Email: jamalumakko@gmail.com

Abstract

PbS and Cd-doped PbS thin films have attracted a great deal of attention because of their applications in optoelectronics, solar cells. Cadmium doped lead sulphide (PbS:Cd) thin films prepared by the spray pyrolysis technique was deposited onto glass substrates at 300°C while dopant concentration was varied from 0.05M to 0.15M for PbS:Cd. The solution containing Cd^{2+} and Pb^{2+} precursors was used to obtain good quality film deposits at optimized preparative parameters. The characterization of these films was performed using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Ultraviolet-visible spectrophotometer (UV-VIS) and Energy dispersive X-ray spectroscopy (EDX) analyses to explore the properties of PbS and Cd-doped PbS films. The prepared films were adherent to the substrate and well crystallized according to the cubic structure, which displayed a preferred orientation. The optical properties were determined from ultraviolet-visible spectroscopy measurements in the absorbance energy range from 200–800 nm. The UV-visible analysis shows that the band gap value of the PbS thin films increased from 1 eV to 3.3 eV by doping with Cd. The micrographs revealed that PbS and PbS:Cd thin films are polycrystalline and uniformly distributed. The energy dispersive X-ray analysis showed that the film contains Cd, Pb and S elements.

Keywords: Thin films; Spray pyrolysis, Doping, thin films, PbS thin films,

INTRODUCTION

Lead (II) sulphide is an inorganic compound with the formula PbS. Galena is the principal ore and the most important compound of lead. It is an important semi conducting material with numerous applications used in friction industry for enhancing heat conduction and regulating friction coefficient. PbS thin films have been deposited through various deposition processes such as electrodeposition (Olusola *et al.*, 2018; Madugu *et al.*, 2018). 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).

The addition of metal ions can be used in engineering of material band gap, which increases as the size of the particle decreases. This property of PbS makes it an excellent candidate for opto-electronic applications in many fields such as photography, IR detectors, solar absorbers, light emitting devices and solar cells (Nazir *et al.*, 2014; Kaci *et al.*, 2015). Increases in the optical energy band gap (E_g) of the thin films can be attributed to quantum size effects, which are expected from thin films with a nanocrystalline nature (Alex *et al.*, 2008). Ni and Cd doping of PbS thin films can shift the forbidden band gap energy range from 1.4 to 2.4 and 0.15 to 0.5 eV (Castilla *et al.*, 2013). Sn and Sb doping of PbS thin films can significantly change band gap

*Author for Correspondence

values (Das and Kumar, 2012; Kumar *et al.*, 2014). The increases in the electrical conductivity of PbS films are due to interstitially doped Al atoms that act as donor impurities (Preetha and Remadevi, 2012; Preetha and Remadevi, 2014). Mn, Cd and co-doped PbS nanocrystals have also been investigated (Sakthi-Sudar-Saravanan *et al.*, 2015). The optical absorption analysis of Bi-doped PbS thin films (Hernández-Téllez *et al.*, 2013) and Cd-doped PbS nanocrystalline thin films, and the optical band gap has been investigated (Thangavel *et al.*, 2010)

In view of these findings, the significant changes in the energy band gap of the films due to metal ion doping are very useful for solar detector applications.

Spray pyrolysis is an efficient and cost effective method for depositing thin films of high quality materials. Spray pyrolysis allows the precise control of the deposition parameters such as temperature, time and concentration of the precursors. Spray pyrolysis involves spraying an aqueous solution containing soluble salts of the constituent atoms/vapour of the required compound onto a substrate at very high temperatures, such that pyrolytic (endothermic) decomposition is achieved, resulting in the formation of a single crystal or an aggregate of crystallite of the required product. Hence the energy needed for the thermal decomposition and subsequent recombination of the constituent atoms/vapours followed by sintering and recrystallisation of the aggregates of the crystallites to form a coherent film is provided by the thermal energy of the substrate (Chopra and Das, 1983).

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 PbS (Thangaraju and Kaliannan, 2000).

In the present study, the authors investigated the influence of doping concentration on the structural, morphological and optical properties of the deposited cadmium doped lead sulphide thinfilms (PbS: Cd).

METHODOLOGY

EXPERIMENTAL PROCEDURE

The pure and doped PbS thin films were grown onto commercial glass substrates via the spray pyrolysis method. The materials used were lead acetate hydrate $(\text{CH}_3\text{COO})_2\text{Pb}\cdot 3\text{H}_2\text{O}$, thiourea $[(\text{NH}_2)_2\text{CS}]$, and Cadmium acetate $[\text{Cd}(\text{CH}_3\text{COO})_2]$.

The PbS deposition electrolyte was prepared from a non-aqueous methanol solution containing 0.1M of lead acetate (Purity = 98%), 0.1M Thiourea $[(\text{NH}_2)_2\text{CS}]$ (Purity = 99.0%), and 0.3M acetylacetone. The films were deposited at a substrate temperature of 300°C for the undoped lead sulphide sample. Similarly, Cd-doped PbS films were deposited by adding Cadmium acetate $[\text{Cd}(\text{CH}_3\text{COO})_2]$, solution to the reaction mixture. The films were deposited at two (2) different molar concentrations ratios of 1.0:0.05M and 1.0: 0.15M of the dopant respectively. The deposition process started by atomization of the chemical solution into a spray of fine droplets affected by a spray nozzle with the help of compressed air as a carrier gas. The substrate-to-nozzle distance was 15 mm, and the internal and external diameters of the nozzle were 0.7 mm and 0.311 mm, respectively. The precursor flow rate was 20 ml/hr, the volume of the dispenser was 2 ml, and the atomizing voltage was +6kV.

EXPERIMENTAL TECHNIQUES

The sprayed thin films were characterised using a variety of material characterisation techniques. Structural properties of the films were studied using X-ray Diffractometer Thermo

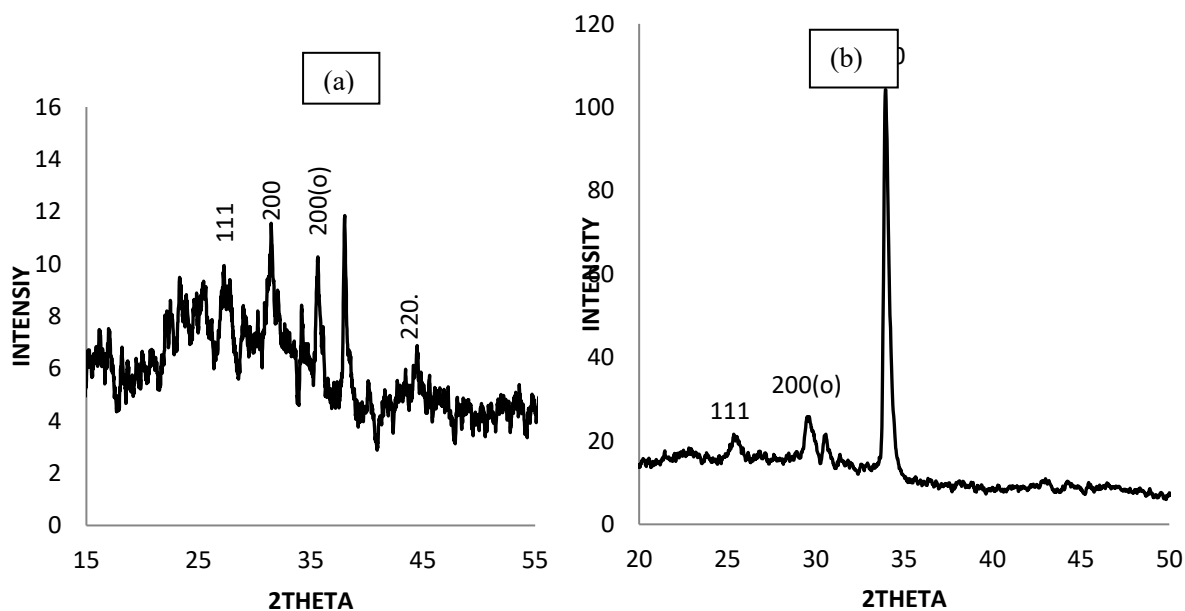
scientific model: ARL'XTRA X-ray and serial number 197492086. Optical properties of the films were investigated using UV-Visible spectrophotometer (Helios Zeta, Model 164617), the morphology of the films were studied using JOEL-JSM 7600F Scanning Electron Microscope and the elemental analysis were carried out using Energy dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

Structural Studies

Figure 1(a) and 2(b) illustrate the x-ray diffraction pattern of the cadmium doped PbS thin film layers deposited at temperature 300° C with different doping concentrations. The XRD Pattern of PbS:Cd has face centered cubic structure as confirmed by JCPDS Data card with reference No.03-065-0692 and the peaks correspond to (111), (200) and (220) crystal planes. It can be observed from Figure 1(a) and figure 2(b) that both samples are polycrystalline in nature. The intensity of the diffraction peaks showed considerable increased on increasing the cadmium doping concentration from 0.05M to 0.15 and is in accordance with the work of Goutom *et al.*, (2021). Diffraction along the (200) plane shows the highest intensity with well define sharp peak indicating the preferred orientation of the deposited lead sulphide thin film. Additionally, there is a very small shift in the 2θ range after Cd doping. This can be attributed to doping induced structural disorder in the films. This marginal shift in the diffraction peaks could be due to the lattice strain, which contributes to the structural disorder generated during films growth (Prathap *et al.*, 2008).

Figure 1(c) shows XRD patterns of PbS thin films deposited at a temperature of 300°C. The pattern exhibit very low intensity diffraction peaks, this might be attributed to the temperature used in the deposition process.



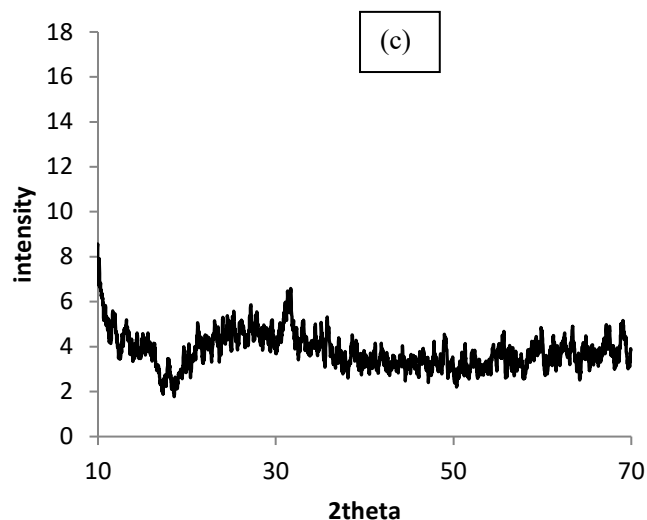


Figure 1. XRD pattern of (a) PbS:Cd, 1:0.05 (b) PbS:Cd, 1:0.15 (c) undoped PbS. All the three samples were deposited at substrate temperature of 300°C.

Morphological Studies

This was carried out to study the surface morphology of the films. Figure 2 show the SEM morphology of the sprayed samples. All the three samples of lead sulphide films were studied using JOEL-JSM 7600F Scanning Electron Microscope.

The SEM micrograph of cadmium doped lead sulphide deposited at ratio of 1:0.05M is shown in Figure 2(a). The micrographs revealed that the PbS:Cd appear to have spherical like and well distributed grains but with gaps and less densely packed grains. Figure 2(b) shows the morphology of the PbS:Cd thin film deposited at 300°C at 1:0.15 Molar ratio. The SEM image shows a highly densified surface morphology of the cadmium-doped PbS material. The grains exhibit a remarkable level of uniformity in both size and shape, forming a densely packed structure that covers the entire substrate. The image revealed a clustered arrangement of crystals in a well-defined, smooth and continuous surface. It can be seen that adding concentration of this dopant ratio gives a better structural and morphological properties, as highlighted above which is in good agreement with the work of Rajashree *et al.* (2015). In contrast, figure 2(c), shows the morphology of undoped PbS sample, which shows that the grains are spherical like with no definite pattern. These results infer that the PbS film morphology could be modified with Cd doping and the film with 0.15M dopant concentration has better morphological properties. The SEM result of all the three PbS samples are in good agreement with the XRD results shown in Figure 1.

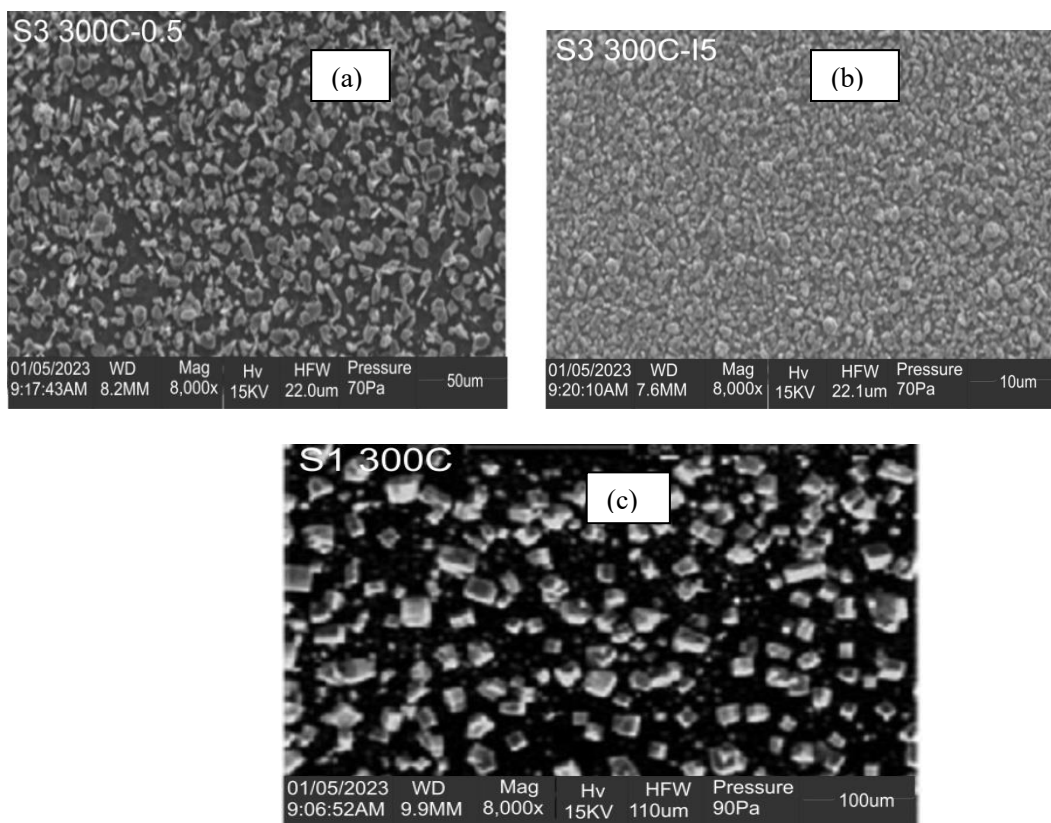


Figure 2: Film morphology of (a) PbS:Cd, 1:0.05 (b) PbS:Cd, 1:0.15 (c) undoped PbS. All the three samples were deposited at substrate temperature of 300°C.

Elemental analysis

Figure 3 shows the elemental analysis of the cadmium doped lead sulphide thin film performed using Energy Dispersive X-ray spectroscopy (EDX). The spectrum confirmed the presence of the expected Cadmium, Pb and S atoms. Other signals in the spectrum are due to the elements in the sodalime glass substrate. The weight percentage of the elements in the prepared films obtained from the EDX was found to be 50.45%, 4.42% and 24.48% for Pb,S and Cd respectively. The result shows that the deposited film is non-stoichiometric in composition and similar trend was reported by Rajathi *et al.*(2017).

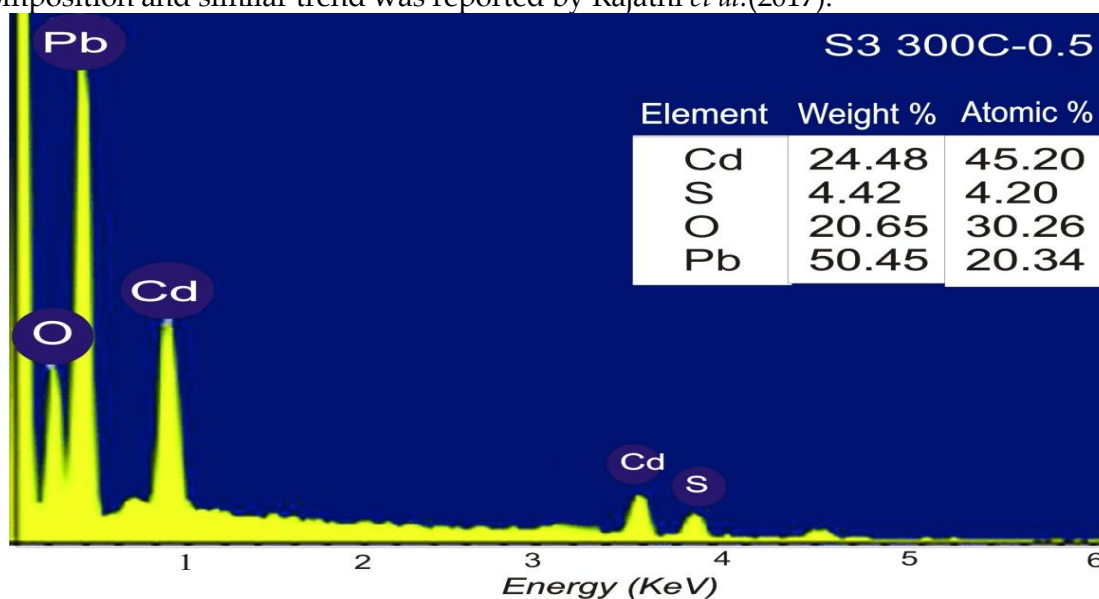


Figure 3: EDX Spectrum of PbS:Cd Thin Film

Optical Studies

The UV-visible spectrums of the deposited Cadmium doped lead sulphide thin film using two different dopants concentrations are shown in Figure 4. The spectrum is a plot of absorbance (a) against wavelength (λ). The spectrum shows that the deposited Cadmium doped lead sulphide thin films start absorbing at wavelength of 200 nm to about 800 nm. The absorption edge lies in the near Infrared region. And α^2 or $(ahv)^2$ versus photon energy ($h\nu$ in electron volts) with extrapolation to zero absorption coefficient ($h\nu$ axis) gives the band gap energy of the materials. A plot of $(ahv)^2$ against energy ($h\nu$) for PbS:Cd thin film for concentration 1:0.15 and 0.05 is shown in Figure 4(b) and 4(d) respectively. The band gap of the material was estimated by extrapolating the linear portion of the absorption edge to the energy axis which gives an optical band gap of 3.50 eV for 1:0.15M and 3.30 eV for 1:0.05M respectively. This is in agreement with the work of Rajashree *et al.*, (2015) this shows increase in band gap with increase in Cd content. Additionally, according to Koao *et al.*, (2014) PbS thin films has direct optical bandgap that can be engineered from 0.39 up to 5.20eV depending on the preparation conditions.

Figure 5 shows that leadsulphide deposited at 300°C has an optical bandgap of about 0.95eV.

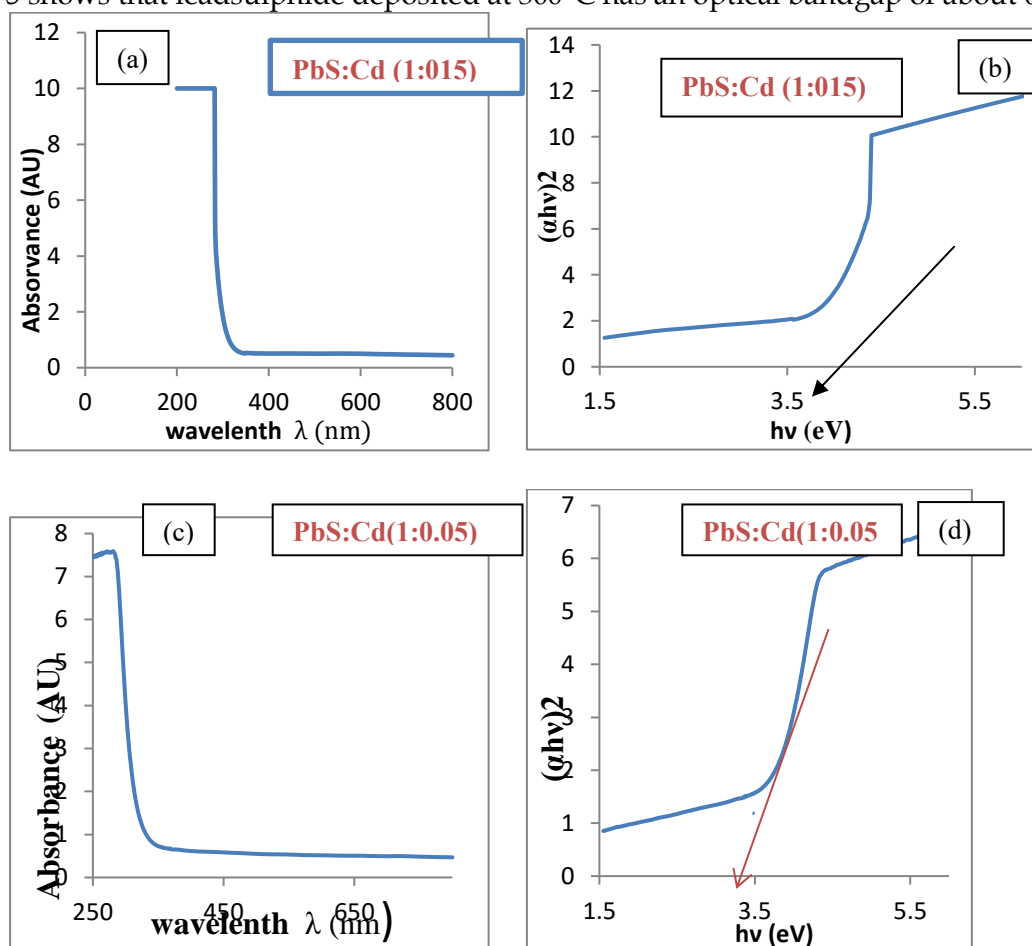
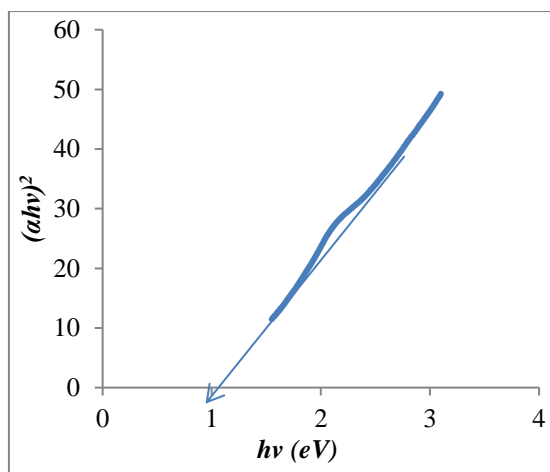


Figure 4:(a) Absorbance against Wavelength of PbS:Cd (1:0.15), (b) $(ahv)^2$ against Energy (eV) of (1:0.15), (c) Absorbance against Wavelength of PbS:Cd (1:0.05) and Figure (d) $(ahv)^2$ against Energy (eV) of PbS:Cd (1:0.05) Thin Films.



. Figure 5: $(\alpha hv)^2$ against Energy (eV) of PbS thin films.

CONCLUSION

In this study, PbS and Cd-doped PbS crystalline thin films were successfully prepared using spray pyrolysis method and characterised using material characterization techniques such as XRD, UV-visible SEM, EDX and machines.

The surface micrographs revealed that PbS and Cd-doped PbS thin films are polycrystalline and uniformly distributed on the glass substrate in different sizes. The structural studies show the polycrystalline nature of the films. Cd-doped PbS exhibits face-centred cubic structure with preferential orientation along (200) plane.

UV-Visible analysis revealed that the Cd-doped PbS thin film has its absorption edges at UV-Vis region. We have successfully tuned the optical band gap of the prepared PbS thin film from 0.95 eV to 3.3 eV and thereby have made it scientifically exciting for superior photovoltaic applications. From the SEM images, the films are homogeneous depending on the deposition parameters. The XRD and EDX analyses confirmed the incorporation of Cd in the PbS: Cd thin films.

Conflict of Interest: The authors declare that there are no conflicts of interest.

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