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Effect of annealing temperature on the Structural, Morphological and Optical properties of PbS Films deposited using spray pyrolysis Technique

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ABSTRACT

Lead sulphide (PbS) semiconductor material has attracted a great deal of attention because of its applications in optoelectronics, solar control coatings, gas and humidity sensor and photo electrochemical solar cells. PbS polycrystalline thin films prepared by the spray pyrolysis technique was deposited onto glass substrates at a substrate temperature of 300°C and was annealed at 300°C and 400°C. The solution containing Pb precursors was used to obtain good quality film deposits at optimized parameters. The characterization of these films was performed using X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Ultraviolet-visible spectrophotometer (UV-VIS) to explore the structural, morphological and optical properties of the PbS films respectively. The prepared films are crystalline in nature and well adhered to the substrates. The films are polycrystalline with preferred orientation along the 200 cubic phase. The optical properties were determined from ultraviolet-visible spectroscopy measurements in the absorbance energy range 200–800 nm. The UV-visible analysis shows the band gap value of the annealed PbS thin films as 3.6 eV which makes it suitable for window layer in photovoltaic devices. The micrographs revealed that PbS thin films are polycrystalline and uniformly distributed.

Keywords: PbS thin films, semiconductor, spray pyrolysis, material characterization, Annealing

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 have direct optical bandgap that can be varied from 0.39 up to 5.20eV (Koao *et al.*, 2014).

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).

Gao et al. (2013) explored the effect of post-deposition thermal annealing on PbS quantum dot (QD) solar cells, observing an optimal annealing temperature that increased power conversion efficiency by 1.5 times for QDs with bandgaps of 1.65 eV and 1.27 eV. Annealing at 120°C improved carrier

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transport without altering QD size or bandgap significantly. Furthermore, a decrease in the activation energy of shallow traps was noted, contributing to the enhanced solar cell efficiency.

Akhtar et al. (2022) fabricated and characterized lead sulfide (PbS) thin films on soda lime glass substrates using electron beam evaporation. After annealing at temperatures from 200°C to 450°C, the films were analyzed for structural, optical, and electrical properties. X-ray diffraction (XRD) confirmed crystalline structure, while field emission scanning electron microscopy (FESEM) showed uniform deposition.Energy dispersive spectroscopy (EDS) confirmed lead and sulfur presence. Ultraviolet-Visible-Near-Infrared (UV-Vis-NIR) spectroscopy revealed increased transmittance post-annealing and a band gap range of 2.12–2.78 eV. Hall-effect measurements indicated p-type carriers and decreased conductivity due to lead oxide presence.

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 (Thangaraju and Kaliannan, 2000).

In the present study, the authors investigated the effect of annealing temperature on the lead sulphide (PbS) thin films deposited on glass slide substrates via spray pyrolysis technique.

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) and the morphology of the films were studied using JOEL-JSM 7600F Scanning Electron Microscope.

EXPERIMENTAL PROCEDURE

Lead sulphide thin films were deposited on glass substrate by the spray pyrolysis method. The materials used were lead acetate hydrate $(CH_3COO)_2$ Pb:3H_2 O, thiourea [$(NH_2)_2CS$)], spray pyrolysis machine, the solvent used was methanol while the substrate used was a commercial glass slides.

The PbS deposition electrolyte was prepared from a non-aqueous methanol solution containing 0.1M of lead acetate (Purity = 98%), 0.1M Thiourea [(NH2)2CS)] (Purity = 99.0%), and 0.3M acetylacetone.

Two sets of PbS samples were prepared from the above-prepared solution with each set having two samples. In the first set, the films were deposited at two different substrate temperatures of 300°C and 400°C. In the second set, the films were deposited at a temperature of 300°C and were annealed at

300°C and 400°C. 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. The precursor flow rate was 20 ml/hr, and the volume dispensed was 2 ml.

RESULTS AND DISCUSSION

This section discussed the various techniques used in the characterisation of the sprayed films and the results obtained.

Structural Studies

Figure 1(a) shows the XRD patterns of PbS thin films deposited at a substrate temperature of 300°C. It can be observed that the diffraction pattern exhibited by the films showed a very low intensity diffraction peaks, this might be attributed to the temperature used in the deposition process. Figure 1(b) shows XRD pattern for the annealed PbS thin films at a temperature of 300°C. In this material it can be observed that there are 3 noticeable peaks. The diffraction peaks were found at 2θ equal to 25.98°, 30.24° and 43.00° which are preferentially orientated along (111), (200), and (220) cubic phases respectively. This correspond to standard X-ray diffraction data files with reference No.03-065-0692.The values are in good agreement with the work of Ezekoye *et al.,* (2015).

It can be observed that, from the XRD patterns of all the three samples figure 1(b) (which was annelead at 300°) show the most intense peak which could be due to the annealing temperature used in the annealing process. This is in line with the work of Azadi and Azim (2015) that increase in annealing temperature leads to increase in the crystallinity of the material.

Fig. 1(c)] has a hump like shape on the pattern which might be due to the annealing temperature used in the annealing of the films in this sample. The temperature of 400^{o}C may be on the high side for the films which could have let to it deterioration and hence the amorphous behaviour shown by the film.

Morphological Studies

This 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 were scanned using JOEL-JSM 7600F Scanning Electron Microscope.

Figure 2(a) shows the morphology of the as-deposited PbS sample. This sample shows a mixture of cubic and rectangular grains shapes. The films show a sparsely arrange grains with many gaps in between. This films are not suitable for the development of electronic devices due to their shorting paths nature.

Figure 2(b) shows surface morphology of PbS thin film annealed at 300°C. This material show a denser and compact morphology with no or less gaps when compared with one of sample shown in Figure 1 (a). This could be attributed to the annealing carried out on this sample. It is known that annealing of thin films materials improve the crystallinity thereby resulting in increase in grain size thereby filling the gaps. This is in agreement with the work of Azadi and Azim (2015) which revealed that crystallite arrangement is improved by increasing annealing temperature up to 250°C.

Figure 2(c) shows the morphology of the thin film of PbS annealed at a temperature of 400°C. In this sample, the morphology show a melted like surface with the gaps shown in

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Figures 2 (a) and (b) completely eliminated. The exhibited a cemented surface free from pinholes and voids which could be due to the high annealing temperature (400^{o}C) which cause a phase transition in the films.

The SEM result of all the three PbS samples are in good agreement with the XRD results shown in Figure 1.

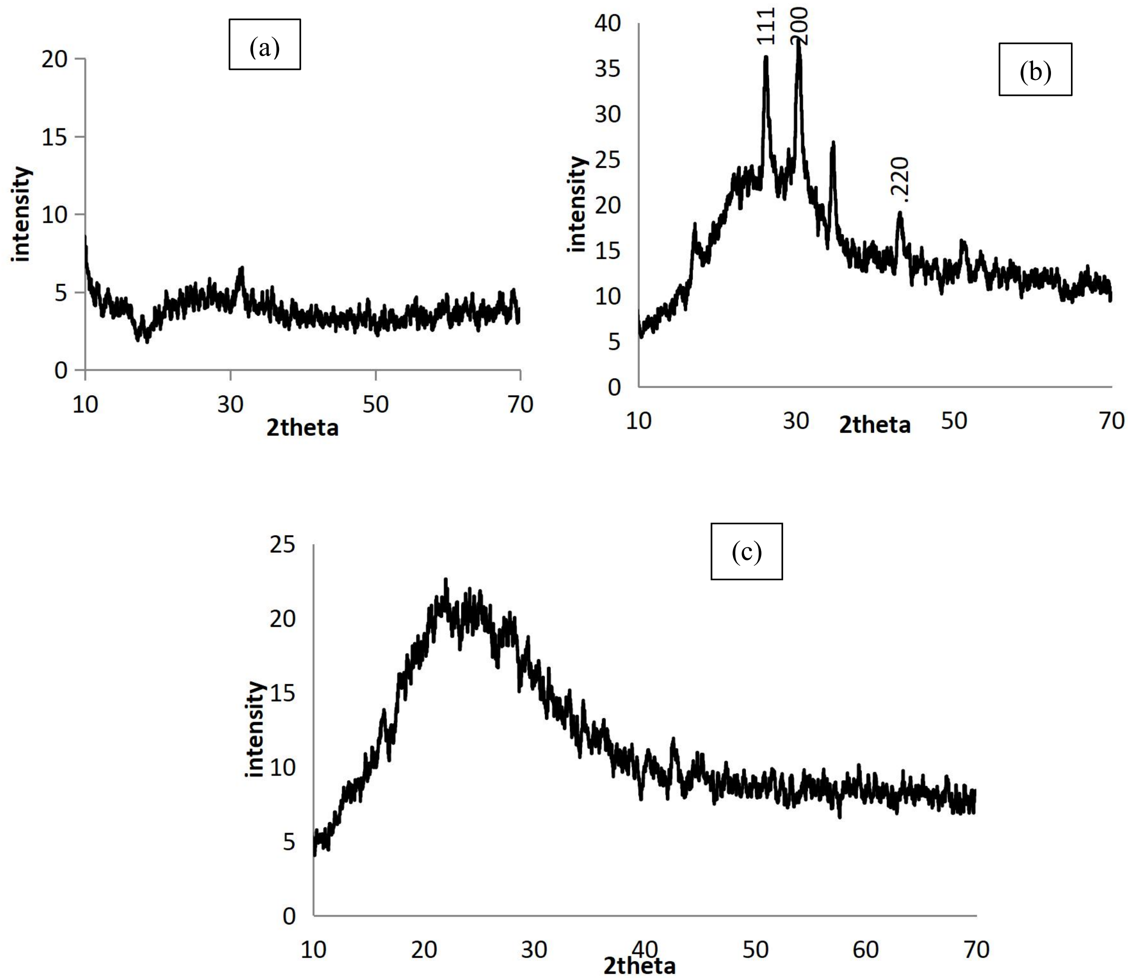

Figure 1: XRD patterns of PbS (a) deposited at 300° celcius, (b) annealed at 300°celcius and (c) annealed at 400°

The micrographs were also analyzed using IMAGEJ software to obtain the average size of the grains. The average thickness of the grains shown in figure 2(a), (b), and (c) were estimated to be 14.16µm, 17.55µm and 1.17µm respectively. It can be seen that PbS annealed at temperature of 300°C has larger grain size than the other samples. This may be due to rearrangement of atoms into larger or more regular crystal structures during the annealing process.

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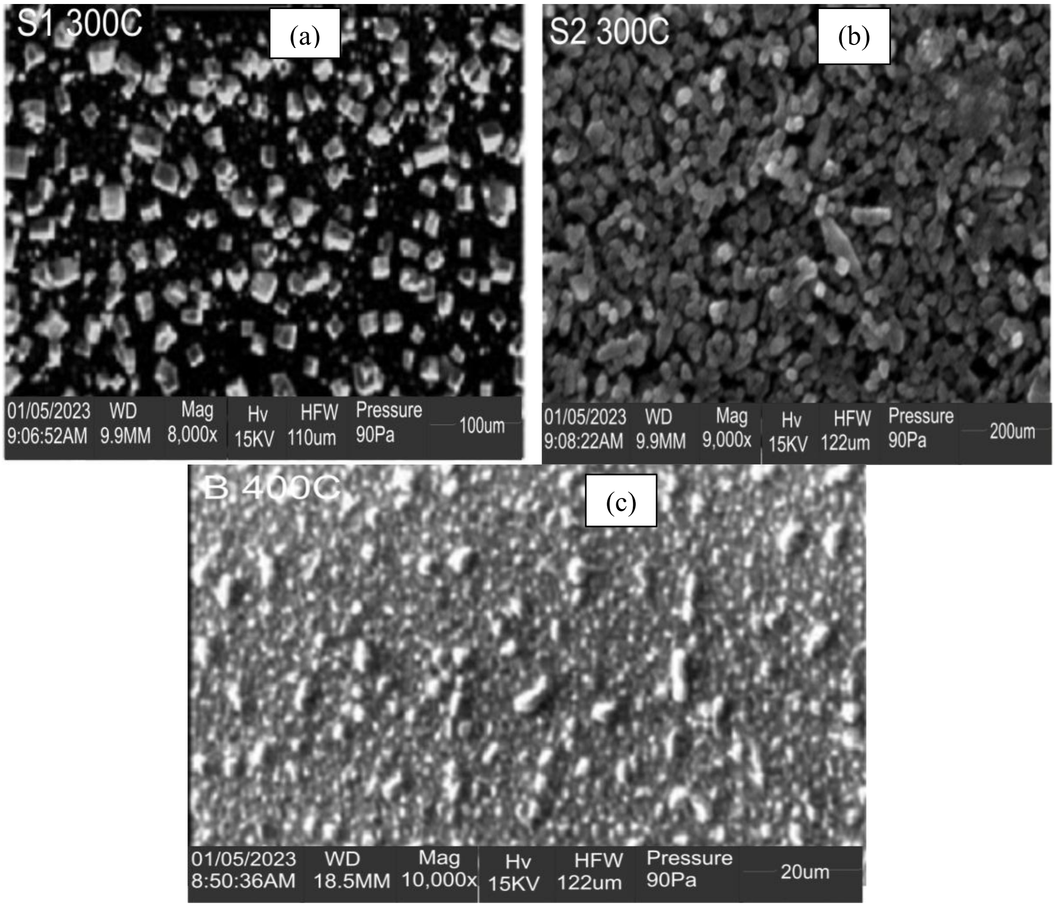

Figure 2: PbS films morphology (a) deposited at 300°C (b) annealed at 300°C and (c) annealed at 400°C.

Optical Studies

The optical properties of the films were investigated majorly to study the absorption and Bandgaps of the semiconductor films under different processing conditions. It can be observe from Figure 3(a) that the deposited lead sulphide thin film starts absorbing at wavelength of 412 nm which then increases untill it reaches a maximum at 603 nm before it starts to decrease. Fig 3(b) shows that leadsulphide deposited at 300°C has an optical bandgap of about 0.95eV which is in close agreement with the work of Faremi et al., (2021), in which a band gap of 0.78 eV was obtained at 300°C.

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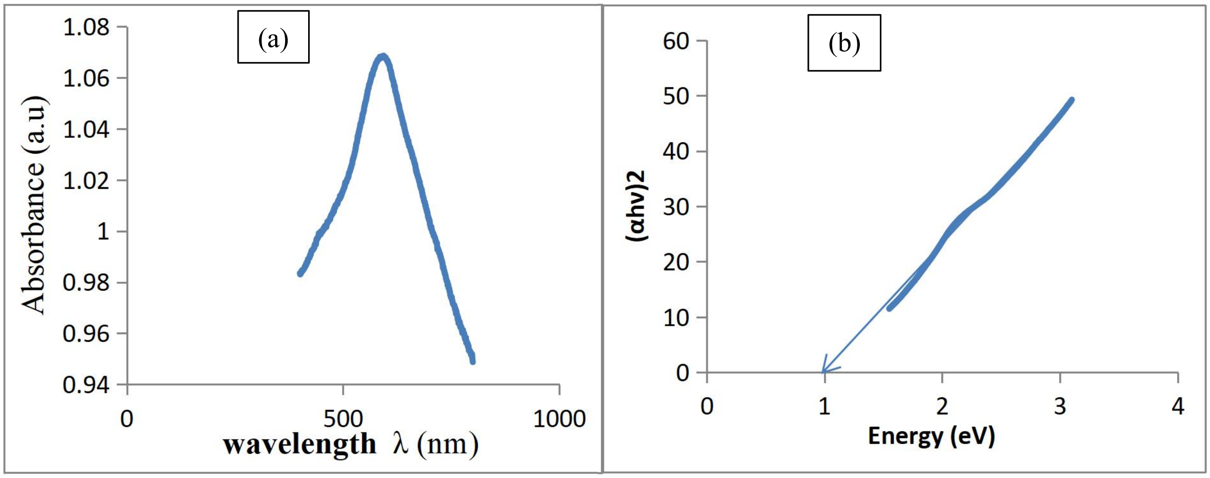

Figure 3: (a) Absorbance against Wavelength of PbS deposited at 300°C Thin Film and (b) $(ahv)^2$against Energy of PbS deposited at 300°C Thin Film.

Figures 4 (a) and (b) show the film absorbance and the energy bandgap graphs respectively. The graph of $(ahv)^2$ versus photon Energy (*eV*) is shown in Figure 4(b). The extrapolation of the linear region of the curve to X-axis (x=0) gives the value of energy band gap of the thin films. Energy band gap for the annealed lead sulphide is found to be 3.6eV in this film. This shows a considerable increase in the band gap of PbS without annealing as shown in Figure 4(b), this is in line with the report of akhtar *et al.,* (2022) that " band gap of PbS increases with increase in temperature". And it was also reported by seghaier *et al.,*(2006) that "The PbS direct band gap can be varied up to 3eV".

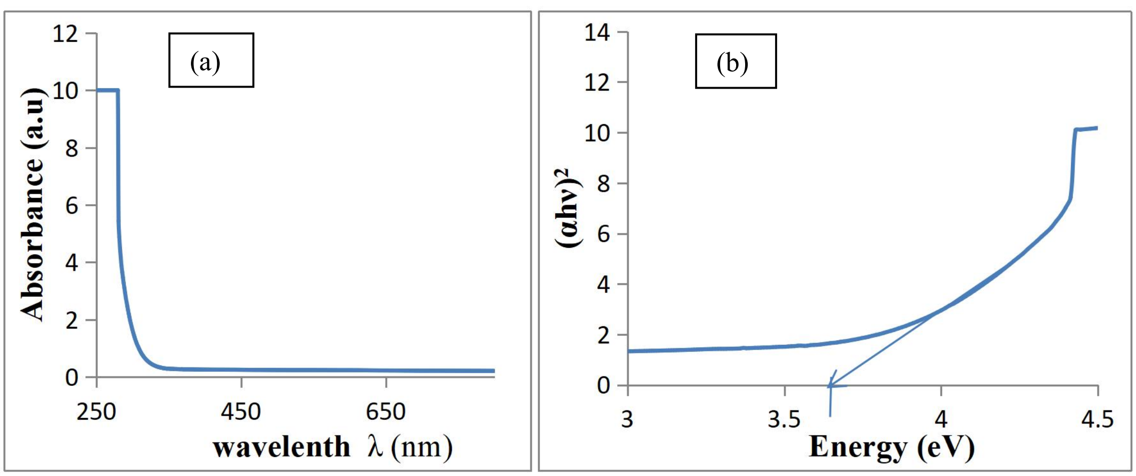

Figure 4: (a) Absorbance against Wavelength of PbS Thin annealed at Film 300°C and Figure 4(b) $(\mathrm{ahv})^2$against Energy (eV) of PbS annealed at 300°C Thin Film.

CONCLUSION

Lead sulphide (PbS) thin films were successfully prepared using spray pyrolysis method and characterised using material characterization techniques such as XRD, SEM and UV-visible machines. The surface micrographs revealed that 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. Lead sulphide exhibits

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face-centred cubic structure with preferential orientation along (200) plane. UV-Visible analysis revealed that the Lead sulphide thin film has its absorption edges at UV-Vis region. The optical absorption measurement indicates a material with optical energy band gap of 3.6 eV.

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