

OPTICAL AND STRUCTURAL PROPERTIES OF SILAR-GROWN HIGHLY ORIENTED LEAD SULPHIDE (PbS) THIN FILMS

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The lead sulphide (PbS) thin films were deposited on a glass substrate using successive ionic layer absorption and reaction (SILAR) method at different number of cycles at a room temperature using lead nitrate, thiourea, and sodium hydroxide as chemical precursors. The optical and structural studies was performed by UV-VIS spectrophotometry, X-ray diffraction (XRD) and SEM. The XRD showed films of cubic (galena), crystalline in nature with the preferential (111) orientation. The PbS thin films obtained under optimal deposition conditions were found to polycrystalline with face centered cubic structure. The lattice parameter, grain size, were calculated. The values of the average crystalline sizes were found to be in the ranges of (7-15) nm. Optical studies was carried out using UV spectrometer and it revealed the existence of direct band gap values in the ranges of (1.58-1.70) eV.

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1. Introduction

Thin films of metal chalcogenides have received much awareness due to its wide range of applications in manufacturing of large area photodiode arrays, electronic and optoelectronic devices, infrared photography, photo thermal converters, solar absorbers, solar control coatings, photoconductors and sensors. [1-4]. Chalcogenides of IV-VI group materials are considered as interesting narrow band gap 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]. Among them PbS is found to be an interesting narrow band gap semiconductor with an energy gap values of 0.45eV. This band gap can be enhanced by decreasing the sizes of the crystallites [5]. This change in band gap in PbS can be obtained for comparatively larger crystallite sizes as its bohr excitonic radius is comparatively larger than other chalcogenides. [6] Chalcogenide materials have shown to be good candidates for p-type semiconductor [7]. This has been demonstrated using various chemical methods including Chemical bath deposition (CBD). [7], Electrochemical [8], Successive ionic layer absorption and reaction (SILAR) [9], Spray pyrolysis deposition [10, 11]. The aim of this paper is to investigate the effect of nos of cycles on the structure, morphology and optical properties of PbS thin film prepared by Successive ionic layer absorption and reaction (SILAR).

2. Experimental details & materials

Lead sulphide 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 our sulphide ion source and lead nitrate as our lead ion source. Lead sulphide were

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constituted from solution of 15ml of 0.1 M $[Pb(NO_3)_2]$, 30ml of 0.8M thiourea $[SC(NH_2)_2]$, 15ml of 0.8M sodium hydroxide $[NaOH]$ and distilled water for 30 secs in cationic precursor solution, rinsed 5secs in high-purity deionized water, immersed 30secs in the anionic precursor solution, the ions reacted with absorbed lead ions on the active center of the substrate and finally rinse it again in deionized water for 5secs. It was also optimized by 40 cycles, 60 cycles & 80 cycles, during the process of film formation the thickness of the film increases as the cycle increases. The resulting film was homogenous, well adhered to the substrate with darker surface like mirror.

3. Results and discussion

Fig 1 is the XRD pattern for the PbS thin films which shows polycrystalline in nature with cubic structure and lattice constant ($\text{\AA}=5.9380$) with reference nos 03-065-0346. The diffraction peaks of the cubic PbS were found at 2θ values of 26° , 30° , 43° , 51° and 53° for all the samples deposited, these angles correspond to the lattice planes (111), (200) (220), (311), (222) respectively. Different peaks in the diffraction pattern were indexed and the corresponding values of interplanar spacing d , were calculated for cubic PbS [12, 13, 14]. It was observed that all the peaks are from PbS and hence no additional peak corresponding to Pb and S was present.

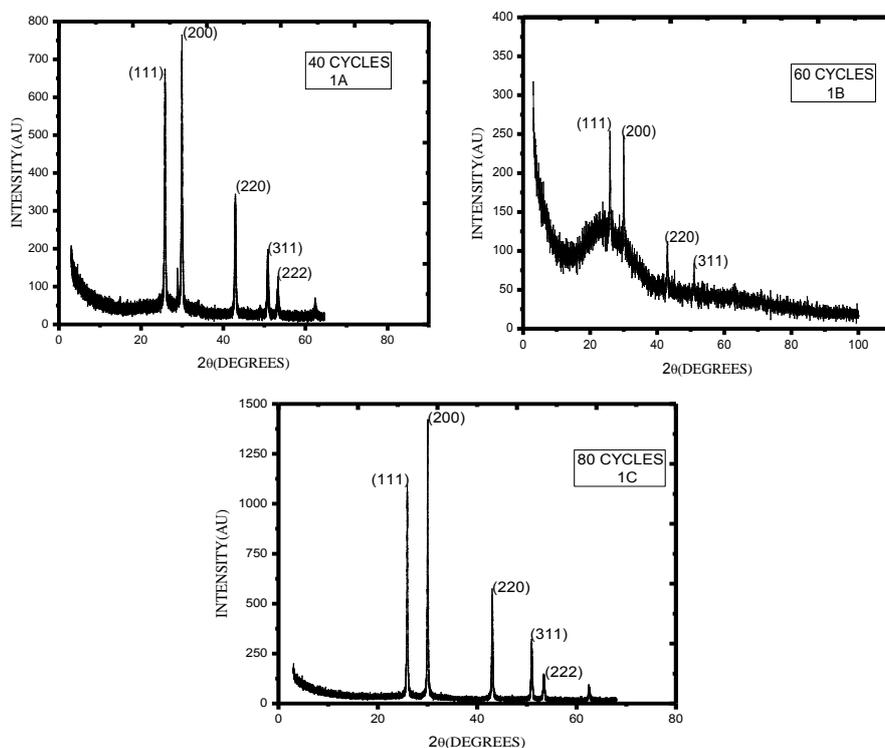


Fig. 1a, b and c Samples, XRD Pattern of PbS Thin Films

The peak corresponding to (200) plane was found to be higher than all other peaks in the diffraction pattern of samples A and C, while in sample B, it corresponds to (111) plane and was found to be the highest peak, this indicates that the plane is preferentially oriented along (200), as reported by [15,16] and also along (111) plane. The crystallite size of the deposited films were calculated using Debye-Scherer formula that is equation (1), their crystal sizes lie within the range of (7-15) nm.

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

Where D = Grain Size, λ = is the wavelength of $\text{CuK}\alpha$ target used, θ = is Bragg's diffraction angle at peak position in degree and β = is Full width at half maximum of the peak in radian. [12].
 Fig 2 shows SEM which revealed the surface morphologies of the PbS film deposited by SILAR method, it shows that the PbS thin films were homogeneous in nature with sparsely packed crystallites which appear to be randomly oriented with irregular and spherical shape of similar sizes distributed for films deposited by silar methods. This agrees with other reports. [10, 12].

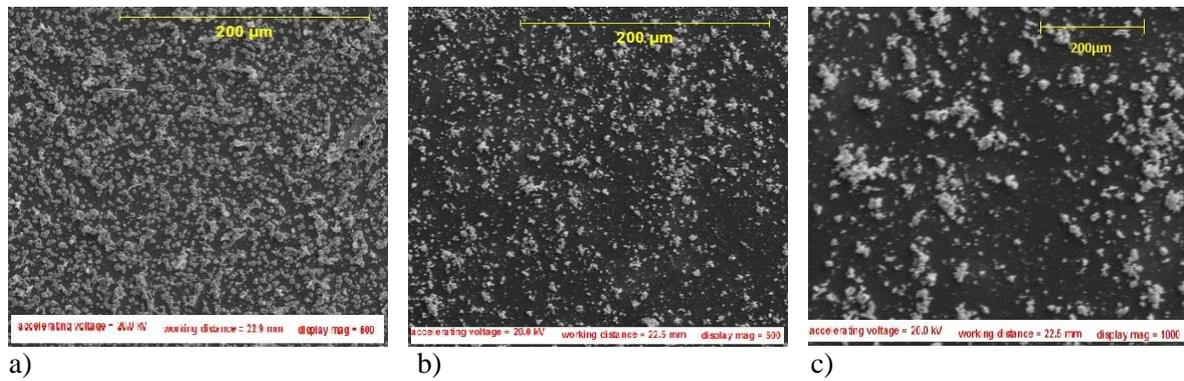


Fig 2 a, b and c SEM images of PbS thin films

Figure 3a, b and c below shows the plots of absorbance vs wavelength, reflectance vs wavelength and transmittance vs wavelength of PbS thin films deposited by SILAR.

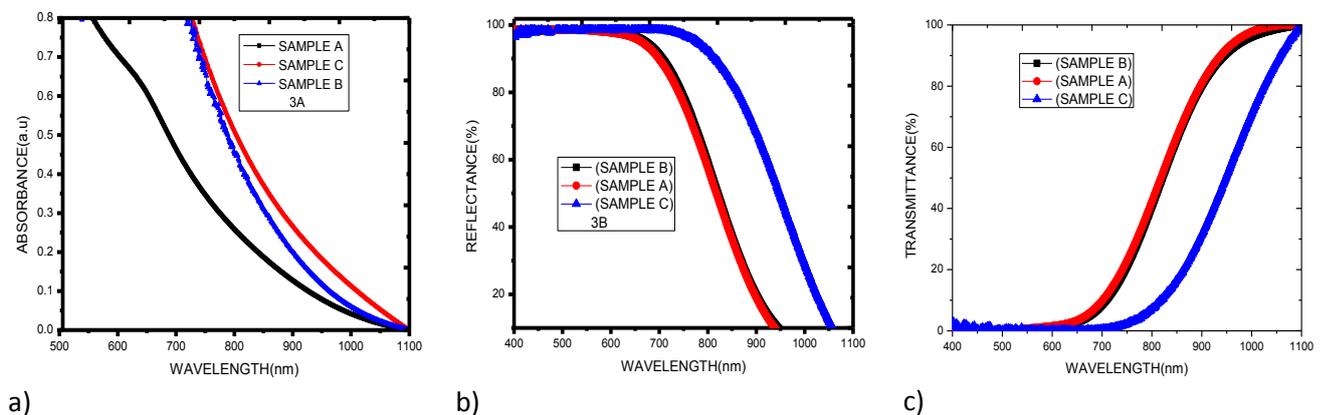


Fig 3a, b and c Absorbance, Reflectance and Transmittance spectra of PbS thin films.

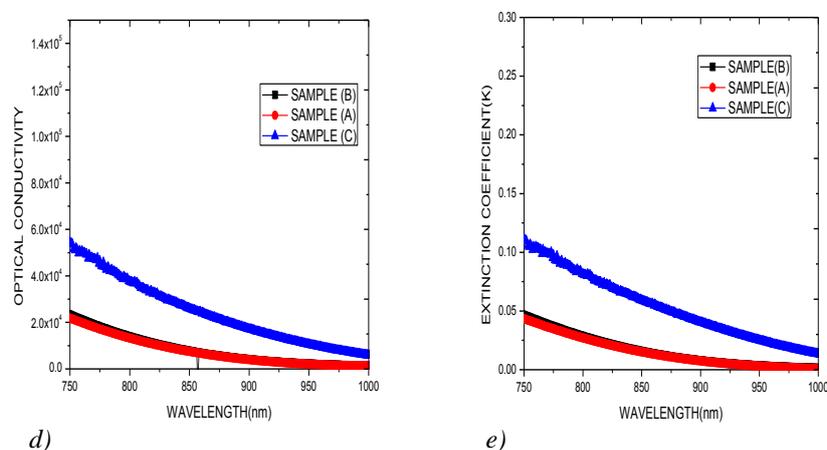


Fig 3d and e: Optical conductivity and extinction co-efficient of SILAR PbS thin films.

Fig 3a above shows the absorption spectra of PbS thin films deposited by silar method of different numbers of cycles. The spectra shows two pattern of absorption, one that is sample A (40 cycles) is high in the visible region from 550nm -700nm and the other two samples B and C (60 & 80) cycles are very high in the infrared region while Fig 3b above shows the reflectance spectra of PbS thin films deposited by silar method of different numbers of cycles. Fig 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 increases in the infrared region. This show that the reflectance spectra is correct because it is opposite of transmittance. This is done using the equation (2). [11, 12, 17, 18].

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

Where t = thickness, λ = wavelength.

Fig 3d is the optical conductivity shows the plot of (σ_{op}) against wavelength, the optical conductivity ranged between (6.0×10^4 and 1.0×10^9) and it decreases as the wavelength increase which is because of the increase in thickness of the samples [15, 16]. Fig 3e which is the extinction coefficient, shows that the three samples increases in the UV- visible region and decreases with increasing thickness. It has been noticed that the increasing K at wavelength below 500nm is due to high absorbance of PbS films in that region as reported in [7].

All the spectra show high reflectance in the visible region and high absorbance in the near infrared region. This high reflectance in the visible and high absorbance in the infrared region make the films good material for anti-reflection coating and for solar thermal application, the films may be employed as a solar control coating, also applied in infrared (IR) detectors. [12, 15, 18, 19]. The optical band gap energy for PbS samples A, B, C deposited were obtained considering a direct transition between the valance and conduction bands when the photon energy falls on the materials. 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 weighting method, using the relation above [13, 14, 20]

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

The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors. [13.14].

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

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

The band gap was determined from the intersection of straight line portion of $(\alpha h\nu)^2$ versus $h\nu$ the nature of the optical transition is confirmed. Extrapolation of these graph to the point where $\alpha = 0$ is known as energy band gap. The values obtained for the direct band gap of PbS thin films by silar method lies within the ranges of (1.59 – 1.70)eV for samples A, B, C. These were obtained by the plot of the $(\alpha h\nu)^2$ as a function of $(h\nu)$ are shown in fig 4a-c below in accordance with equation (4). The values of E_g increased with increasing cycles and this is attributed to the increase in the thicknesses of the density of localized state in the energy gap.

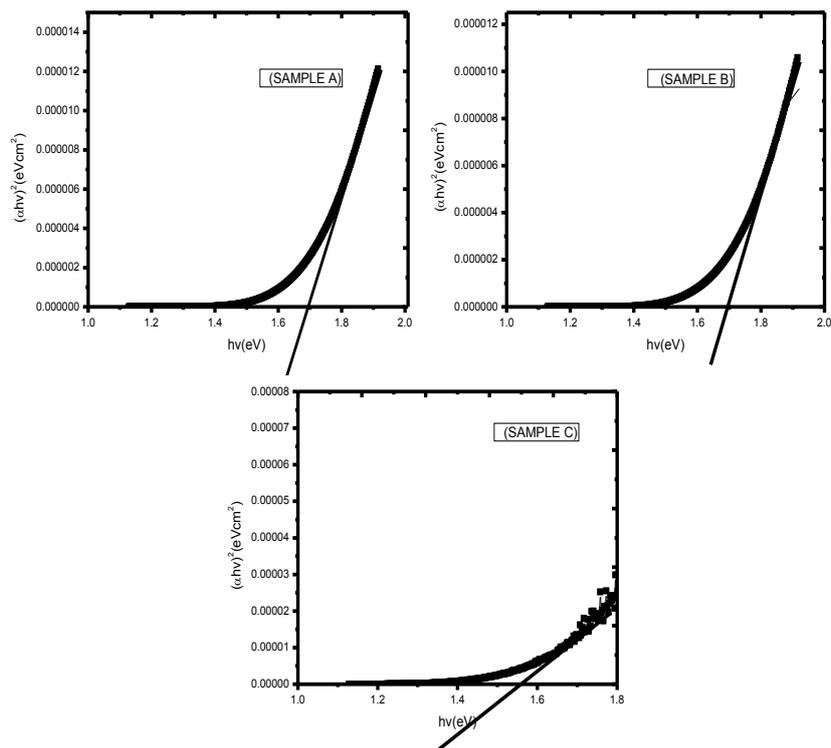


Fig 4a, b & c: Plots of $(ahv)^2$ versus $h\nu$ for PbS thin films for 40, 60 and 80 cycles.

Fig 5, shows the plot of thickness against the number cycles, from the graph it can be seen that as the thickness increases the number of cycles increases and remained almost constant from 100 number of cycles [12, 13 and 14].

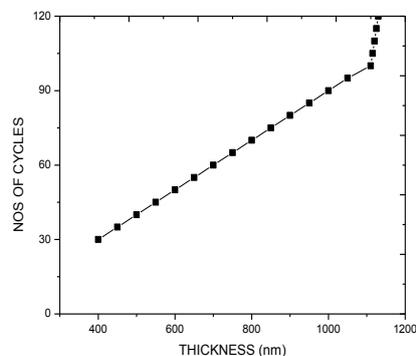


Fig 5: Plot of Number of cycles Vs Thickness of PbS thin films.

4. Conclusion

In this work successive ionic layer absorption and reaction (SILAR) method have been successfully used to deposit PbS thin films. The optical absorption, 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 (7-15nm). The properties of high absorbance and high reflectance in the visible region, low absorbance and high reflectance in the near infrared region makes the film a good material for anti-reflection coating and for solar thermal applications and infrared (IR) sensors.

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