Influence of substrate temperature and deposition time in energy band gap characteristic of lead sulfide thin film

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Abstract. Ion by ion mechanism as a principle of chemical bath deposition (CBD) was employed in the synthesis of Lead Sulfide (PbS) film to characterize the influence of substrate temperature. The deposited films were annealed at varied temperature (200 °C, 250 °C and 300 °C) in 20 minutes and characterized for optical, morphology properties and elemental composition. The average crystalline size of PbS thin film size was estimated to be 28.249 nm. The energy band gaps of the films decreased (2.2 - 0.78 eV) as the time of deposition increases. Equivalent bulk energy band gap (0.78 eV) was achieved at 300 °C. The Scanning Electron Microscopy (SEM) micrograph revealed the level of agglomeration with faceted edge. Energy Dispersive X-ray Spectroscopy (EDX) also revealed the predominance of lead in the film elemental composition. Realization of less than 1.0 eV PbS energy band gap has posed a major challenge to the application of PbS films in photovoltaic fabrication. However, optimized synthesis of PbS breaks the challenge. The various results obtained indicate the suitability of the material in optoelectronics applications.

Keywords: Thin films; Tuned energy band gap; Annealing; Microstructural Properties, Chemical Bath Deposition (CBD)

1. Introduction
Recently, the potential applications of compound semiconductor thin films in device fabrication have received many researchers’ attentions in the field of material science. Especially, group IV–VI elements of the periodic table are focused for study because of their narrow energy gap, ease of production and photon absorption capability which hold potentiality for solar cells and sensors applications[1], [2]. Such a narrow
energy band gap has been associated with lead sulfide (PbS) thin film which place the film above commonly used photovoltaic materials [3]. The PbS thin films energy band gap falls between 0.37 and 0.4 eV [4]. Recent researchers has reported PbS based solar cells as a good photovoltaic (PV) solar conversion capable of absorbing photon energy at the tail of infrared of the solar spectrum, which make the film to be more advantageous over other commonly used PV materials [3]. Despite the potential of PbS in both science and industry, reduction in cost of production as a primary aim of producing optoelectronic material and fine-tuning of the film energy band gap below the optical band gap of other absorber layer compound semiconductors are subjects of debate in the field of material science. However, many groups of researchers had reported previously that variation of preparative parameters could lower the material energy band gap to make a best alternative to other absorber layers but cost of production is still area of concern. Scaling down semiconductor material from bulk to nano-range has been attributed to two factors which are quantum effect and surface to volume ratio. These factors have played a vital role in the tunability of semiconductor’s energy band gap. Among the various semiconductor materials, PbS has shown a strong quantum size effect even below the excitonic Bohr radius [2], [5]. Different deposition techniques have been employed in literatures to investigate the synthesis of PbS thin films [6]–[15]. However, among the various methods, Chemical bath deposition (CBD) has gotten a lot of interest as being a promising deposition technique in the synthesis of PbS thin films. This growing technique, apart from its cost effective, it enables the stoichiometry of the bath solution and allow easy control of the preparative parameters [1], [16]–[18]. CBD has several significant advantages in the compound semiconductor formation on the glass substrate. This include; proper adhesion of the film resulting to free pinholes, fewer carrier trapping, chemical stability and high transparent layer [19]–[21]. In this work, CBD is employed to synthesis PbS thin films on glass substrate in which time of deposition and the substrate temperature are varied from 1 to 3 hours and 200º C to 300º C respectively. The variation of time of deposition and substrate temperature have observable effect on the optical properties, structural, morphological and, elemental composition of the synthesized samples.

2.0 Materials and Methods
Lead sulfide (PbS) thin films were synthesized on a well degreased glass substrate through chemical bath deposition route. PbS aqueous solution was prepared using lead chloride (PbCl) as a lead (Pb2+) ions source and thiourea (SC(NH2)2) as a sulfur (S2-) ions source, respectively. The 5.69 grams of lead chloride was dispensed into 500 ml beaker containing 300 ml of deionized water to form 0.05 M of lead chloride. The 0.05 M of thiourea which was formed by adding 1.14 grams to 300ml of deionized water was added to the solution of lead chloride and the admixed solution was magnetically stirred for 2 hours to ensure thorough dissolution of the solute. The pH (9.00) of the solution was adjusted using ammonium solution to control the stoichiometry of the solution to assure a slow nucleation of the ions that formed PbS thin films. Coloration change precipitated from dark brown at bath temperature of 50º C to dark colour at 80º C resulting to deposition of the films on the substrate at varied time of deposition (1, 2 and 3 hours) without any complexing agent as against the conventional route.
X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX), and UV-Vis spectrometer at wavelengths ranging from 200 nm to 1000 nm, were used to investigate the influence of such treatment on the elemental composition, morphology and optical properties of the polycrystalline PbS thin films. The thickness of the films was estimated using gravimetric method through weight difference. The weight of the film is denoted as \( W_{film} \), the weight of the substrate used is denoted as \( W_{sb} \) and the weight of substrate after deposition is denoted as \( W_{sa} \).

\[
W_{film} = W_{sa} - W_{sb}
\]  
(1)
where “t” is the PbS film thickness, “A” is the area covered by the deposited PbS film on the substrate and “ρ” is the density of the PbS whose numeric value is 7.45 g cm\(^{-3}\). The optical property of the films was obtained using Tauc. J formulation \[2\], \[22\].

\[ \alpha h\nu = A(h\nu - E_g)^n \]

where \(\alpha\) = 1 is a constant, \(E_g\) = energy band gap and \(n = 0.5\) and 2 for direct and indirect transitions between valence band and conduction band.

3.0 Results and Discussion
3.1 Sample Characterization
The average crystalline size of the films (PbS thin films) was determined by XRD. Fig. 1 shows the XRD pattern of the films. The pattern contained six prominent peaks that are clearly defined. The peak values of 21.016°, 25.0767°, 27.5131°, 29.1373°, 35.1266° and 42.0803°, correspond to the crystal planes of (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), and (2 2 2). The dominant and sharp peaks of the thin films indicate highly crystalline nature of PbS.

The average crystalline size (D) of the PbS thin film was calculated using Scherer’s equation, \(D = \frac{k\lambda}{\beta\cos\theta}\), where \(k = 0.9\) (constant), \(\lambda = 1.5418\) Å (X-ray wavelength) and \(\beta\) is the full width at half maximum (FWHM) of the diffraction peaks \[23,\,24\]. The average crystalline size of the thin film size was estimated as 28.249 nm.

The SEM micrograph of the deposited PbS thin film revealed relatively low level of agglomeration as shown in Figure 2.

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**Figure 1:** X-ray Diffraction (XRD) of deposited PbS thin films
The film was evenly distributed on the entire surface of the substrate without a pinhole with faceted edge despite the film spherical shape.

The film as predominantly covered by relatively low agglomeration indicated improvement in the nucleation of the material with its suitability in solar cell application. The micrograph as depicted shows good agreement with the previous work on the PbS thin film [18], [25]–[28]. The qualitative and quantitative elemental composition of the chemically deposited material (Fig 3) revealed the success in the synthesis of none complexing PbS nucleation. The EDX showed the presence of lead (Pb), carbon (C), sulfur (S) and, oxygen (O). Lead and sulfur are the main constituents of the bath. However, the presence of carbon and oxygen have been reported to have resulted from the EDX machine used and hydroxyl nature of the bath[16], [28]. Despite the presence of carbon and oxygen, Pb is predominant as given as an insert of the figure 3. The result is evidence that PbS can be fabricated without necessarily using a complex agent.

### 3.2 Sample Analysis

The energy band gap of the deposited PbS thin films as depicted in figure 4a, 4b and 4c revealed the influence of the various substrate temperatures adopted during the curing of the material to ensure proper adherent to the substrate. Figures showed the energy band gap of the sample deposited for 1hr, 2hrs and 3hrs at substrate temperature of 200 °C, 250 °C and 300 °C respectively.
There is a noticeable reduction in the deposited material’s energy bandgap from 2.2 eV to 1.9 eV with increase in the time of deposition and further reduction when subjected to substrate temperature at 20 minutes. The reduction in the energy band gap has been reported to be as a result of quantum confinement effect and surface density regularity. The material assumed its bulk energy band gap at 300°C indicating the optimum substrate temperature to achieve less than 1 eV of PbS.

The energy band gap (0.78 eV) is an improvement made to realize a low-cost photon absorber layer material capable of perfectly forming heterojunction with any window layer material [29], [30]. Figure 5 revealed the reduction in energy band gap of PbS thin films with increase in substrate temperature. The lowest value of energy band gap achieved can be attributed to relative low agglomeration, chemical purity and minima lattice defect in the constituent of PbS nanocrystal resulting to an improved optical conductivity which perhaps suggest the material a good absorber material in solar cells applications [27], [31].

4.0 Conclusion

The potential of ion by ion mechanism in the chemical bath deposition has been realized in the growth of PbS thin films. The material was deposited on well treated glass substrate to avoid possible impurity on the surface of the glass at various substrate temperatures. The influence of the substrate temperature adopted was investigated on the morphology and optical properties of the material using SEM coupled with EDX and UV-s spectroscopy. The SEM revealed evenly distributed film with relatively low level of agglomeration resulting to proper adhesion of the film on the substrate. The different elements as depicted in EDX plot revealed the primary constituent of the film as Pb and S indicating PbS thin film. The UV-V revealed the potential of annealing in the optical characteristics of the material as the band gap energy decreases with increase in substrate temperature. However, the various investigations carried out showed success in the synthesis of none complexing PbS thin films which hold potentiality for a best absorber layer capable of preventing front surface recombination of electron-hole in solar cell device.

5.0 References

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