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Structural And Resistivity Study Of PbS Thin Film Prepared By CBD Method

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Abstract:

Lead sulfide (PbS) thin films have garnered significant interest due to their potential applications in optoelectronic devices, infrared detectors, and photovoltaic systems. In this study, PbS thin films were deposited on glass substrates using the Chemical Bath Deposition (CBD) technique. The structural properties were analyzed using X-ray diffraction (XRD), confirming the cubic galena phase of PbS with well-defined crystallinity. Electrical resistivity measurements were carried out using the experimental set up designed and fabricated in the departmental workshop, showing a dependency on film thickness and deposition parameters. The influence of deposition time, temperature, and precursor concentration on the structural and resistivity properties was systematically investigated. The findings demonstrate that CBD is a cost-effective and efficient method for fabricating PbS thin films with tunable properties for potential electronic applications.

Keywords:* *PbS thin film, Chemical Bath Deposition, resistivity, X-ray diffraction, surface morphology

Introduction:

Modern day Technology is proceeding towards the field of thin films for a variety of applications. The pivotal role of Thin Film Technology in the development of diverse and challenging frontiers as microelectronics, optical coating and integrated optics, thin film super - conductivity and quantum engineering and amorphous material, surface engineering and solar energy conversion devices is all to well-known and is now recognized as frontier area of micro science and micro technology. New and even most exciting fields are also emerging. The driving forces behind the exploration of new frontiers are: the exciting phenomena of micro science associated with low dimensional micro and nanomaterial and the industrial applications of micro science and micro technology. Lead sulfide (PbS) is a narrow-band gap semiconductor (Eg ≈ 0.41 eV at room temperature) with unique electrical and optical properties, making it suitable for applications in infrared photo detectors, solar cells, and gas sensors.

Thin films form the basic for today's electronic components. Even complicated device structures are constructed from films, deposited one by one. Thin films can be fabricated in various ways. These techniques can be divided into physical and chemical methods. In physical methods, the film material is moved from a target source with some form of energy to the substrate. This technique is widely used in one-component films, like metal films. Chemical film fabrication methods involve chemical reactions and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Chemical method for making this film can further be divided into gas phase and solution methods. The ability to tailor its properties through controlled synthesis techniques has led to extensive research on different deposition methods, including physical vapor deposition, electrochemical deposition, and chemical bath deposition (CBD) [1]. Among these, CBD has emerged as a widely used technique due to its low cost, simplicity, and ability to produce uniform films over large areas without requiring sophisticated equipment [2].

The CBD method involves a controlled reaction between lead and sulfur precursors in an aqueous solution, allowing PbS to nucleate and grow on a substrate. Parameters such as deposition time, bath temperature, precursor concentration, and pH play a crucial role in determining the final film characteristics [3]. Previous studies have demonstrated that optimizing these parameters can enhance the structural quality, surface morphology, and electrical properties of PbS thin films [4, 5]. Every technique has its own advantages and disadvantages, chemical bath deposition (CBD) has attracted great deal of attention of numerous investigators because it is simple relatively inexpensive and convenient for large area deposition of any configuration (6).

The film materials can be prepared by different techniques. These methods can be broadly classified into two main categories as physical and chemical techniques. With this chemical bath deposition (CBD) method, different metal sulphide thin films can be carried out using different S^{2-} ion sources such as sodium thiosulphate ($Na_2S_2O_3$ TS), thiourea (NH_2 -CS-NH_2,TU), thioacetamide (CH_3 -CS -NH_2,TAM) and its higher ethoxy and methoxy derivatives etc. (7) The rate of release of sulfide ions changes from source to source and accordingly thin film morphology and crystallinity is affected. Further the deposition can be carried out using complxing agents for controlled supply of metallic ions in the bath during metal sulphide film formation (8). Lead and cadmium chalcogenides such as CdS, CdSe ZnS, CdTe are important materials as photoanodes for photolectro chemical solar cells. Several preparation techniques have been used to prepare polycrystalline thin films of PbS, CdS, CdSe for PEC application viz. elemental evaporation (9), Cold pressing (10), painting (11) chemical growth (12) spray pyrolysis (13,14). In this paper, we investigate the structural and resistivity properties of PbS thin films synthesized via the CBD method. The structural analysis is conducted using X-ray diffraction (XRD) to determine the crystallographic phase and grain size. The electrical resistivity is measured to understand the influence of deposition parameters on the film's conductive behavior. The objective is to provide insights into optimizing the CBD technique for high-quality PbS thin films, contributing to their potential integration into optoelectronic applications.

Experimental:

Experimental Setup:

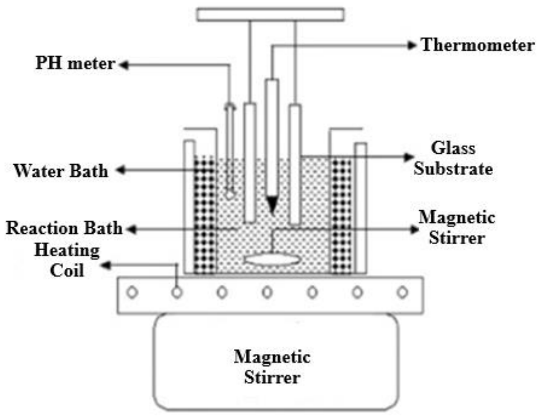

Figure 1: Experimental set up of CBD [15]

The experimental setup used for the film deposition is shown schematically in figure 1 as used earlier by researcher C.D. Lokhande [15]. The substrates are immersed vertically in the reaction bath which can be stirred continuously with a magnetic stirrer. The temperature of bath is monitored by a contact thermometer that form a part of feedback circuit to maintain constant temperature. The complete synthesis process of PbS thin film preparation is given in following steps

Preparation of PbS Film:

The preparation of PbS thin films involved multiple steps, including substrate selection, cleaning, solution preparation, and deposition optimization. The substrates used for deposition were primarily **amorphous glass microslides**, though **stainless steel** was occasionally utilized for **photoelectrochemical studies**. For film characterization, glass substrates were preferred. These glass slides, obtained from Blue Star, Bombay, originally measured **72 × 25 × 1 mm** and were carefully cut to **72 × 8 × 1 mm** using a **diamond point cutter** for further processing. Before deposition, proper **substrate cleaning** was essential to ensure good film adherence. The cleaning process began with **washing the slides with water**, followed by **boiling them in 0.5 M concentrated chromic acid for 1 hour** and further soaking them in the acid for **48 hours**. Afterward, the substrates were **rinsed with distilled water**, dried using **AR-grade acetone**, and stored in a **dust-free chamber** to maintain cleanliness. For the **chemical bath deposition of PbS films**, all chemicals were dissolved in **fresh doubly distilled water** to obtain their **ionic forms**. The primary reagents used were **lead acetate (AR Grade), sodium thiourea (NH_2CSNH_2, AR Grade), ammonia solution, concentrated nitric acid (HNO_3, AR Grade)**, and **disodium salt of ethylene diamine tetraacetic acid (EDTA, AR Grade)**. In an **alkaline bath (P^H = 8)**, lead acetate and thiourea solutions served as sources of **Pb^{2+} and S^{2-} ions**, respectively. PbS films could be deposited **with or without a complexing agent**.

In the present investigation, PbS films were deposited from an alkaline thiourea solution (TS) bath. The deposition process was carried out under the following conditions:

Bath Composition are as follows

45 ml of lead acetate (0.05 M)

45 ml of thiourea (0.05 M)

pH of the solution: 8 (alkaline medium)

Initially at room temperature, but the deposition time was reduced by increasing the temperature to 65°C using a constant-temperature water bath. To study thickness-dependent properties, film with a thickness of 713 nm were prepared by varying the deposition time from 9 hours to 24 hours.

To optimize the **sulfide ion source**, the **P^H = 8 and deposition time** were kept constant while varying the volume of **thiourea solution (TS)** added to **10 ml of lead acetate solution** in **50 ml beakers**. The mixture was stirred briefly, and **glass substrates were immersed vertically** in the solution. The beakers were kept at **room temperature for 2.45 hours**, after which the films were removed, washed with **distilled water**, and air-dried. The **thickness of each film** was measured using the **gravimetric weight difference method**, allowing the optimal **sulfide ion concentration** to be determined. Similarly, to optimize **deposition time**, the **P^H = 8 and reactant volume** were kept constant, and films were extracted at **30-minute intervals**, dried, and analyzed for thickness variations. PbS films deposited at **room temperature** required an extended deposition time, which could be significantly reduced by increasing the **reaction temperature**. By maintaining the **bath at 65 ^{0}C for 30 minutes** using a **constant-temperature water bath**, deposition efficiency improved, reducing the required time while ensuring proper film formation.

Result and Discussion:

Measurement of Thickness:

Thickness is defined as distance perpendicular to the surface from a point on the boundary surface through the film to the other boundary surface. Amongst the different methods for measuring the thickness the weight difference method is simple & convenient. The film thickness, measured as 713 nm,is related to mass, area & density of the materials as

$$t = m / A.d$$

Where

m = weight in grams of the sample

A = Area in cm^2 of the sample

d = density of the material is the bulk form

Structural Analysis:

The X-ray diffraction (XRD) pattern shown in Figure 2 corresponds to a PbS thin film deposited at a bath temperature of 60 ± 2°C. The presence of well-defined diffraction peaks

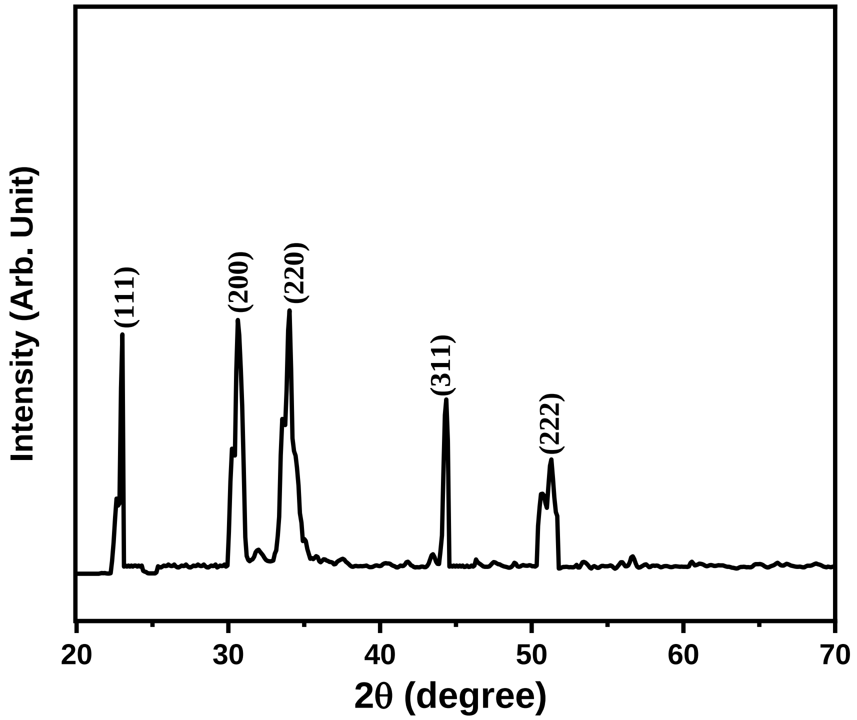

Figure 1 - X-ray diffraction (XRD) pattern of 713 nm PbS thin film

indicates that the film is crystalline, rather than amorphous, and exhibits a polycrystalline nature. The peaks observed in the XRD spectrum correspond to various crystal planes of PbS, specifically (111), (200), (220), (311), and (222), confirming that the film adopts a cubic (galena) phase. These peaks align well with the standard reference data for PbS, such as JCPDS 05-0592, verifying the correct phase formation. Additionally, the measured interplanar spacing (d-values) closely matches the standard values, further confirming the composition as PbS.

A notable feature in the XRD pattern is the presence of a broad hump, which is attributed to the amorphous glass substrate used for film deposition. Despite this, the sharp and intense diffraction peaks suggest that the PbS film possesses a nanocrystalline or microcrystalline structure with well-formed grains. The results obtained in this study are consistent with previously reported findings by L.F. Koao [4], who also identified the cubic phase structure of PbS thin films. This confirms that PbS films deposited under similar conditions tend to develop a polycrystalline structure with dominant (111), (200), and (220) orientations. In conclusion, the XRD analysis verifies the successful deposition of a polycrystalline PbS thin film with a cubic galena phase, demonstrating good crystallinity while also showing some influence from the underlying glass substrate.

Electrical Resistivity:

The variation of **dc-electrical resistivity** log (ρ) with temperature for the PbS thin film is studied using the **two-point dc probe method**. The plot of **log** (ρ) **vs. 1/T** (Figure 3) exhibits a **decreasing resistivity with increasing temperature**, which is a characteristic feature of **semiconducting materials**. The film was heated gradually in the temperature range **300 K to 666 K**, and resistivity measurements were taken at different temperatures. The experimental setup utilized a **glass substrate of 1 cm², silver paste for ohmic contacts**, and a **brass block as a sample holder and heater.** A **Chromel-Alumel thermocouple** (24 gauge) was used for temperature measurement, while current measurements were carried out using a **nanoammeter**. From the graph, it is observed that **log** (ρ) **decreases almost linearly with increasing temperature**, suggesting that the conduction mechanism follows an **Arrhenius-type behavior** given by the equation

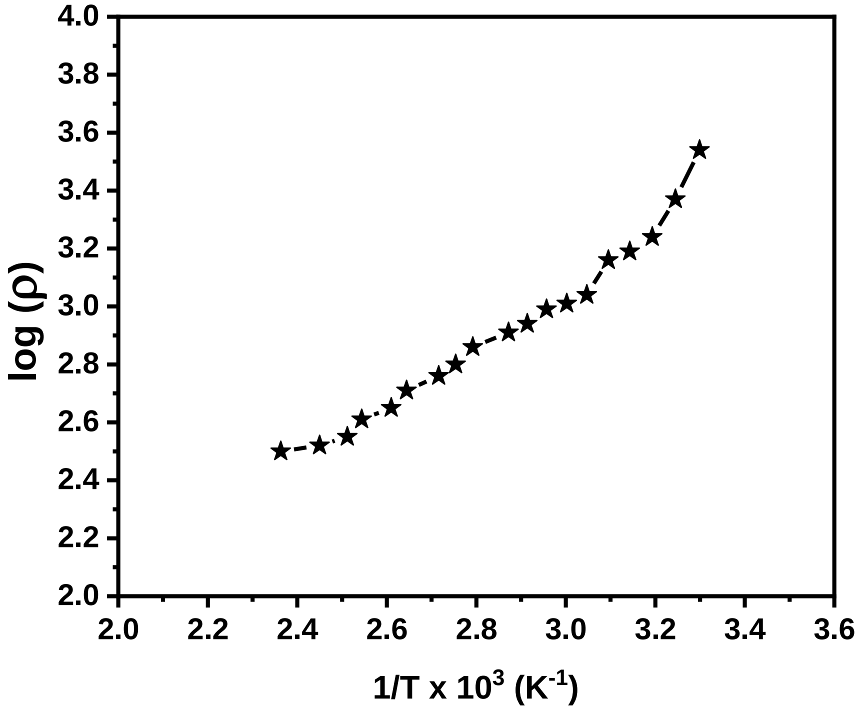

Figure 3 : Variation of electrical resistively log (ρ) with (1/T) x 10^3 Pbs thin film of 713 nm thickness

$$\rho = \rho_o \exp\left(\frac{E_0}{kT}\right)$$

where ρ_o is a constant, E_0 is the activation energy required for conduction, k is **Boltzmann's constant**, and T is the absolute temperature. The linear trend in the **log** (ρ) **vs 1/T** plot indicates **thermally activated conduction**, confirming the semiconducting nature of the PbS film

The study of **dc-electrical resistivity** reveals that the PbS thin film exhibits **semiconducting behavior**, as evidenced by the decrease in resistivity with increasing temperature. The resistivity follows an **exponential temperature**

dependence, which conforms to the Arrhenius equation, indicating that conduction occurs via a **thermally activated process**. The activation energy (EoE_oEo) can be determined from the slope of the **log (**ρ) **vs 1/T** graph. The observed behavior confirms that PbS is a **temperature-dependent semiconductor**, and its electrical properties can be tuned by controlling factors such as **film thickness and deposition conditions**.

Conclusions:

This study confirms that **PbS thin films** deposited via the **CBD method** exhibit **a cubic galena phase** with good **crystallinity** and **polycrystalline nature**, as verified by XRD analysis. The electrical resistivity measurements show a **semiconducting behavior**, where resistivity decreases with increasing temperature, following **Arrhenius-type conduction**. The influence of **deposition parameters** such as **temperature, time, and precursor concentration** was systematically studied. The results demonstrate that **CBD is a cost-effective method** for fabricating **PbS thin film** with tunable properties. These findings make PbS film promising for **optoelectronic, infrared, and photovoltaic applications**.

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