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EFFECT OF COMPLEXING AGENT ON THE THICKNESS AND TRANSMITTIVITY OF CHEMICAL BATH DEPOSITED LEAD SELENIDE (PbSe+) THIN FILMS

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Abstract
Lead Selenide (PbSe) thin films were successfully deposited on glass substrates using the chemical bath deposition (CBD) method at room temperature (300 K). The study focused on examining the effect of the complexing agent, EDTA, on both the thickness and optical transmittance of the films. Structural characterization was conducted using an X-ray mini diffractometer (MD-10), and the results confirmed that the films were crystalline with a cubic structure, exhibiting a prominent diffraction peak corresponding to the (200) plane of PbSe. The pH of the deposition solutions, measured with a Mac Digital pH meter (MSW-552), was found to be in the alkaline range. It was observed that an increase in film thickness led to a corresponding decrease in transmittance, indicating the potential application of these films as thermal window coatings or in opaque coatings.

***Keywords*:** *Chemical bath, Lead Selenide, thin films, Transmittance, X-ray diffraction*

Introduction

Thin film technology has garnered significant interest in recent years due to its unique size-dependent properties and wide range of applications in optoelectronic devices, solar cells, sensors, and laser materials (Wenran *et al* 2024, Yu *et al* 2023, Isi and Ekwo, 2013). Despite advancements in the synthesis of thin films, the search for low-cost, scalable, and efficient deposition methods remains a central challenge in materials science (Mohammad *et al* 2023, Anuar Kassim *et al* 2024). Various techniques have been developed for thin film deposition, including chemical spray pyrolysis (CSP) (Faraj, 2015, Salim and Hamid, 2001), molecular beam epitaxy (Gautier *et al*, 1997, Hussain *et al*, 2012) chemical vapor deposition (CVD) (Ugwu *et al* 2024) Khan *et al*, 2016), sol-gel spin coating (Jeevitesh *et al*, 2018), successive ionic layer adsorption and reaction (SILAR) (Babasaheb 2000, Md Abdul 2022) and electrochemical atomic layer epitaxy (Ezekoye *et al* 2013). However, many of these methods require sophisticated instrumentation, are costly, or involve high-temperature processes, making them less suitable for large-scale or resource-constrained applications.

In response to these challenges, the chemical bath deposition (CBD**)** method has emerged as a promising alternative. It is currently gaining attention for its cost-effectiveness, ease of operation, minimal material wastage, and compatibility with low-temperature, large-area deposition (Ezekoye *et al*, 2013, Grozdanov *et al*, 1999).

The technique has successfully been applied in the fabrication of various semiconductor thin films such as Cu_4SnS_4 (Anuar *et al*, 2010, Cu_2S (Lu *et al* 2008), FeS_2 (Anuar *et al*, 2009), SnS (Avellaneda *et al* 2009), $CuInS_2$ (Cui *et al*, 2009) PbS (Larramendi *et al* 2001), and BaSe. (Ezenwa 2012), demonstrating its versatility and potential for scalable manufacturing.

Among IV-VI group semiconductors, lead selenide (PbSe) stands out due to its narrow band gap and high carrier mobility, making it highly suitable for infrared detection, photovoltaic applications, and other optoelectronic devices (Prabahar *et al* 2024). PbSe thin films have found applications in infrared sensors, lenses, diffraction gratings, and photo-detecting devices such as photoconductors and photoresistors (Prabahar *et al* 2024). However, despite the

recognized potential of PbSe, there remains a limited understanding of the optimization parameters for high-quality PbSe thin film deposition via CBD, especially with regard to achieving uniform morphology, controlled thickness, and enhanced optical and electrical properties.

This research aims to address this gap by systematically investigating the CBD process for PbSe thin film fabrication. The study seeks to understand how variations in bath composition, deposition time, temperature, and other critical parameters affect the structural, morphological, and optical characteristics of the resulting films.

The objectives of this study are to:

1. To determine the effect of various concentrations of complexing agent (EDTA)
2. Synthesize PbSe thin films using the CBD technique under varied deposition conditions.
3. Characterize the deposited films using appropriate structural, morphological, and optical techniques.
4. Determine the optimal conditions for achieving high-quality PbSe thin films with desired properties for infrared and optoelectronic applications.

By focusing on the cost-effective and scalable CBD method, this study contributes to the broader goal of developing efficient, low-cost fabrication routes for advanced semiconductor materials used in next-generation photonic and electronic devices.

Materials and Method

Lead Selenide thin films were deposited on microscope glass slides using chemical bath deposition method. Prior to deposition, the substrates were degreased in ethanol for 10 mins, and ultrasonically cleaned with distilled water for another 15 mins and finally dried in air. Lead acetate ($(CH_3COO)_2$ Pb. $3H_2O$)) was used as source of lead ion, EDTA Di Sodium salt as the complexing agent, Ammonia (NH_3) as the source of pH, Selenium Sulphate ($SeSO_4$) as the source of selenium ion, distilled water (H_2O) as the solvent and glass slides which were used as the substrates. The basic principle of the CBD technique consists of the controlled generation of the metal and chalcogenide ions in an alkaline medium and their precipitation on the substrate in order to form a film. In this experiment, five chemical reaction baths (50ml beakers) were used. 5ml of lead acetate was measured into a 50ml beaker using burette; 2ml, 4ml, 6ml, 8ml and 10ml of EDTA were added respectively and stirred gently to achieve uniform mixture. The reaction is exothermic. 5ml of selenium sulphate was added, 5ml, of ammonia solution was then added to the mixtures in the reaction baths. The mixtures were then topped with distilled water to 50ml mark and stirred to achieve uniform mixture. A glass substrate was dipped vertically into all of the five reaction baths. The baths were left to stand for 24 hours (as indicated in Table 1) after which the substrates were removed, rinsed with distilled water and dried in clean air. The slides were observed to have been coated with thin films. The optimal parameter was found to be pH of 10.38. The optical characterization of PbSe thin films was done using Janeway 6405 UV-VIS model of spectrophotometer while the X-ray mini-diffraction (MD-10) using Cukα radiation with λ = 1.5406nm was used to study the structural properties. Chemical equations for the deposition are as follows;

$$(CH_3COO)_2Pb.3H_2O + EDTA \leftrightarrow [Pb(EDTA)]^{2+} + 2(CH_3COOH) + 2(OH)^- + H_2O$$
$$Pb(EDTA)^{2+} \leftrightarrow Pb^{2+} + EDTA$$
$$SeSO_4 + 2(OH)^- \leftrightarrow SO^{2-}_4 + (OH)_2Se$$
$$(OH)_2Se + 2(OH)^- \leftrightarrow Se^{2-} + 2H_2O + O_2$$
$$Pb^{2+} + Se^{2-} \leftrightarrow PbSe$$

Results and Discussion

Table 1. Variation of Complexing Agent for 24 hrs.

Volume of reagents (ml)

Reagents used	**Slide 1**	**Slide 2**	**Slide 3**	**Slide 4**	**Slide 5**
$(CH_3COO)_2Pb.3H_2$	5	5	5	5	5
EDTA	2	4	6	8	10
$SeSO_4$	5	5	5	5	5
NH_3	5	5	5	5	5
Distilled H_2O.	33	31	29	27	25

Variation of concentration of complexing agent (edta) for 24 Hours.

By volumetric method: The chemical baths were prepared by putting 5ml of 1.0 molar solution of lead acetate into 50ml beakers and adding various volumes of EDTA as indicated on the table 1. Then 5ml of 1.0 molar solution of selenium sulphate and 5ml of ammonia solution was added in each beaker. Each bath was topped to 50ml mark with distilled water and stirred gently but long enough to ensure uniformity of mixture. Glass slides (substrates) were partially immersed vertically into the baths and left to stand for twenty-four (24) hours and were removed to dry in clean dry air.

Table 2: Variation of film thickness with volume of complexing agent (EDTA) and pH values for 24 hrs.

Slide No	**Thickness ($x10^{-5}$cm)**	**Volume (ml)**	**pH Values**
1	3.81	2	9.34
2	2.93	4	9.37
3	1.69	6	9.96
4	1.13	8	10.14
5	1.11	10	10.38

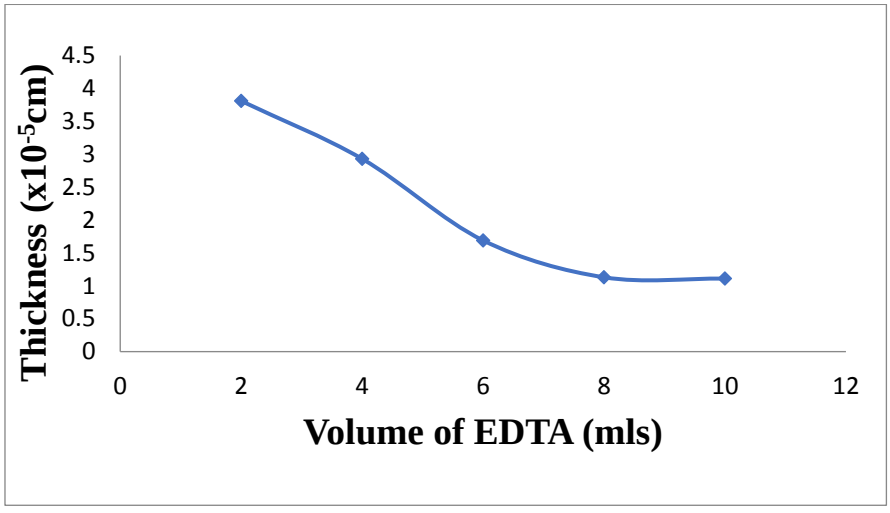

Figure 1: Variation of film thickness with the volume of Complexing agent (EDTA)

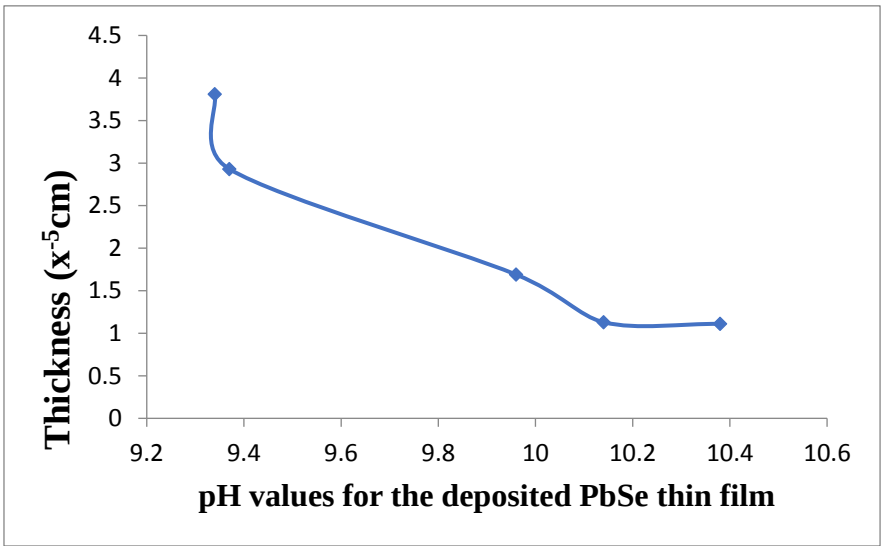

Figure 2: Variation of thickness with pH for 24 hours

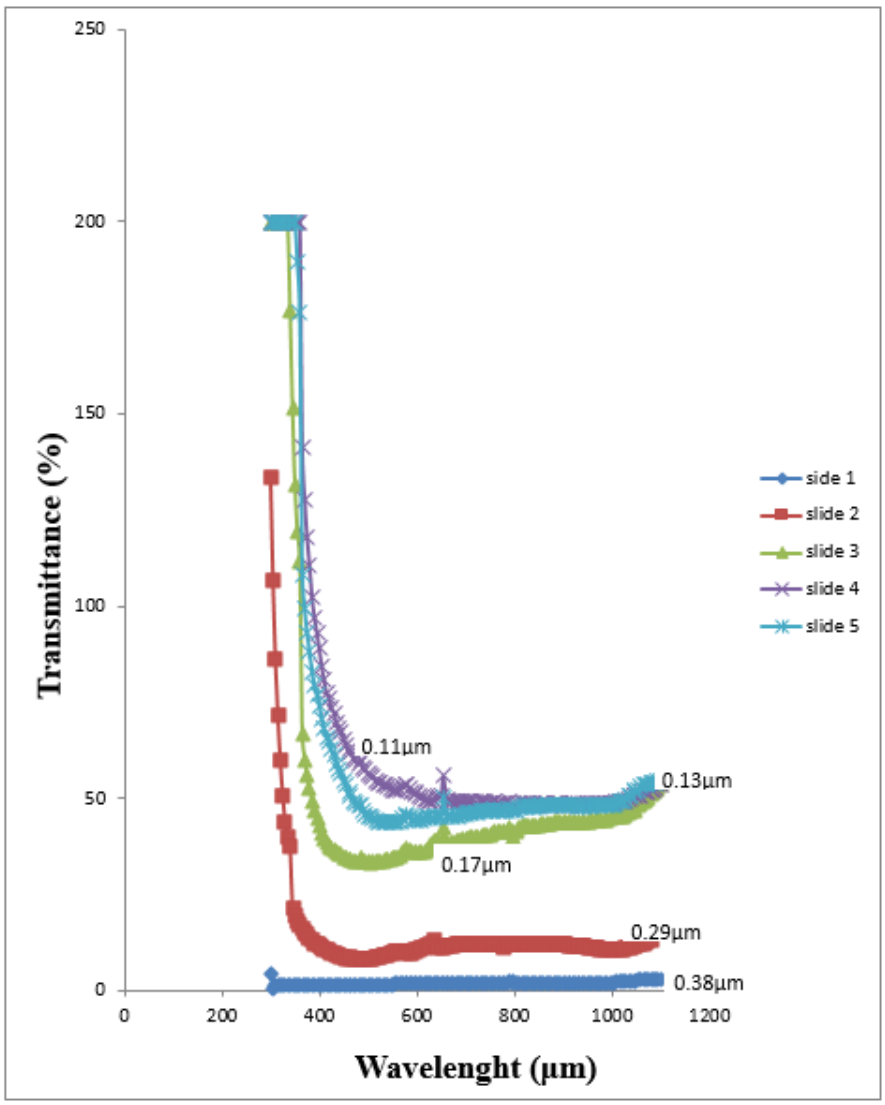

Figure 3: Spectral Transmittance of PbSe thin film.

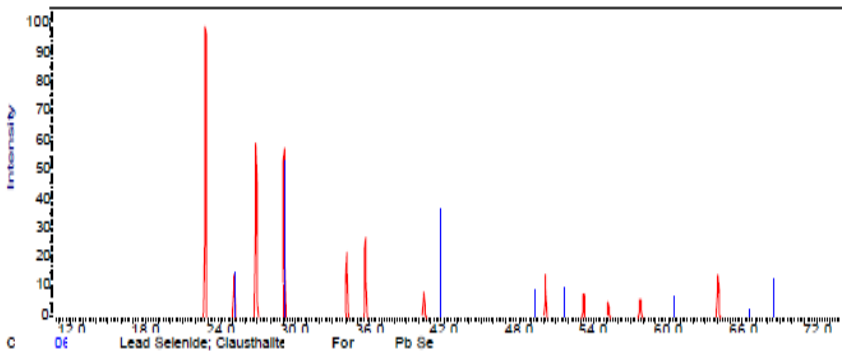

Figure 4: XRD diffraction Pattern for PbSe

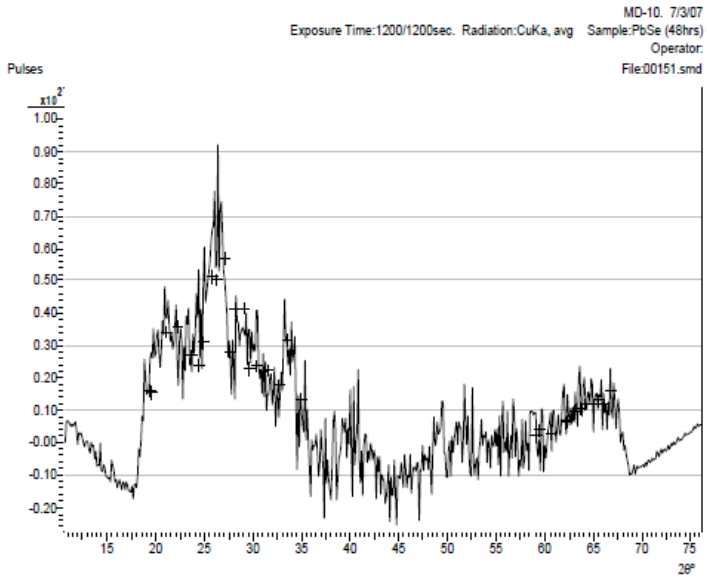

Figure 5: X-ray spectra at 300k

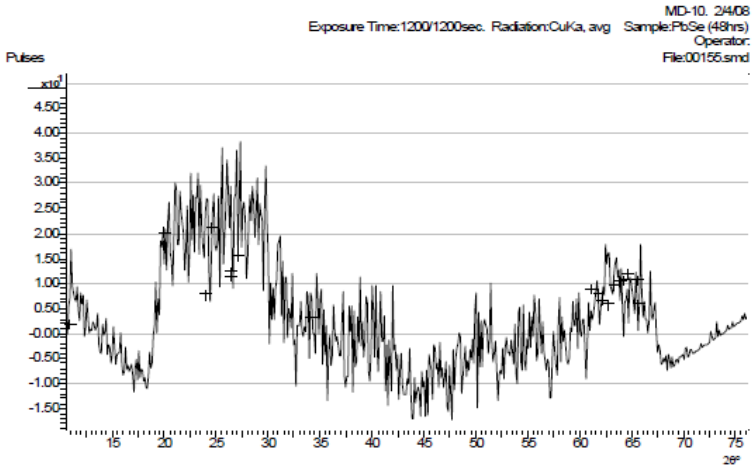

Figure 6: X-ray spectra for slide 5 at 300k

Figure 1 is a plot film thickness versus the volume of complexing agent (EDTA). This shows the relationship between the film thickness and the volume of complexing agent (EDTA) used. From the graph, it can be seen that greater film thickness was obtained with small volume of EDTA than with larger volumes. When excess EDTA was used (say, 10ml) the number of

Pb^{2+} ions decreased, resulting to less number of the Pb^{2+} ions being available for film formation. As a result of this, thinner films of PbSe were obtained. Generally, film thickness was found to be decreasing as volume EDTA increased.

Figure 2 shows the variation of the film thickness with pH. It was observed that as the pH increased in the alkaline range, the film thickness reduced. This implies that the greater the volume of ammonia solution used the less the film thickness.

Figure 3 shows the variation of transmittance with wavelength for slide 1 to 5. It was observed that slide 1 has zero transmittance within the visible and infrared region of the electromagnetic spectrum, and it's as a result less volume of EDTA (2ml). When the volume of EDTA was increased to 4mls, 6mls, 8mls and 10mls, there was drastic change in the transmittance for various volumes of EDTA. This indicates that as the volumes of EDTA were increased, higher transmittance were observed for slide 2, 3, 4 and 5. Hence large volume of EDTA is required for effective transmittance.

Figure 4 shows the XRD diffraction Pattern for PbSe, this indicates the presence of PbSe with various peaks and that the deposited film has no impurity.

Figure 5 shows the variation of pulses against 2θ for slide 1. In this plot it was observed that less volume of EDTA is favorable due to the presence of various peaks as indicated in the figure. Thus, less volume of complexing agent is required for more and pronounced peaks.

Figure 6 displays the variation of pulses against 2θ for slide 5. Here, there is no pronounced peak, because large volume of EDTA (10mls) was used and excess EDTA reduces the rate of deposition.

Conclusion and Summary

Lead Selenide (PbSe) thin films were successfully synthesized using EDTA as a complexing agent, with NH_3 providing the alkaline medium, $SeSO_4$ as the source of selenide (Se^{2-}) ions, and lead acetate [$Pb(CH_3COO)_2 \cdot 3H_2O$] supplying Pb^{2+} ions. The study revealed that the film thickness was influenced by the volume of EDTA used during deposition. Specifically, an increase in the volume of EDTA resulted in thinner films. This indicates that lower volumes of EDTA are more suitable for achieving thicker and more substantial film deposition, while higher volumes are better suited for applications requiring ultra-thin films.

Structural analysis showed that the films were crystalline with a cubic phase, and the most intense diffraction peak corresponded to the (200) plane of PbSe. Optical measurements indicated that films deposited with lower EDTA volumes exhibited negligible transmittance, while those prepared with higher EDTA volumes demonstrated significantly higher transmittance. These findings suggest that PbSe thin films have potential applications in opaque coatings, such as thermal window glass coatings, where controlled transmittance is desirable.

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