Abstract
Lead Sulphide (PbS) thin film was deposited by chemical bath deposition (CBD) process on the glass substrate at room temperature for various time intervals. The precursors used for this deposition are lead acetate since as a supply of lead ions (Pb^2+) and thiourea the same as the supply of sulfide ions (S^2-) with 0.1M concentration. The pH of the mixed precursor's solution was maintained at 9.5-10 by addition of drop by drop ammonia very slowly. The cause of deposition time for different hours studied. The influence of deposition time on properties of PbS film was investigated. The color of films appears black-gray after taking out of the bath. The thickness of the film is increased with increase in deposition time. The electrical resistance and resistivity were 500MΩ and 18.75 MΩ-cm and band gap measured as a function of temperature using D.C. four probe methods was 0.3742 eV. The Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Chronoamperometry were studied by using potentiostat.

Introduction
CBD method is a method due to which we can deposit metal Chalcogenide thin films is receiving a great importance because of its reduction in low cost and production of high-quality material. Lead Chalcogenide is important materials with the wide variety of application including spectrometer detector, IR detector and pollution monitor. PbS is a significant direct narrow bandgap semiconductor material with an estimated energy band gap of 0.37-0.4eV at 300K. PbS thin films have been widely used in a variety of fields such as a light emitting diode, solar energy panel, gas sensors, infrared detector and mid-infrared lasers. The huge excitation Bohr radius of PbS (about 0.18 nm) results in strong quantum confinement of both hole and electron in nano-size structure so that the band gap size can be control by modifying the size of the particle according to effective mass model. This property of PbS makes it desirable for new application such as solar cells. PbS thin films deposited by SILAR method and effect of pH and transport, optical properties can be obtained by several methods such as electrodeposition and PbS...
sensitized photoanodes were studied by the different groups\textsuperscript{10}, solvothermal\textsuperscript{11}, SILAR\textsuperscript{12} and CBD\textsuperscript{13}, etc. Among them, CBD is an economical and simple technique enables for large-scale deposition\textsuperscript{14}. In this method, growth can be easily controlled by controlling concentration of ions, bath temperature, pH, etc. Compared to other deposition methods, CBD offers different advantages such as it is the very simple method for deposition, reproducibility, harmless, cost effectiveness etc. In CBD method various preparative parameter as a temperature of deposition, concentration of precursor, bath pH, time of deposition etc\textsuperscript{15} was optimized to get uniform and well adherent PbS thin films.

**Materials and Methods**

Glass slides with the size of 75 $\times$ 25 $\times$2 mm are used as the substrate. In the CBD process, clean-up of the substrate surface is significant due to the surface effect on different adherent properties of the thin film. First, the substrates were cleaned with hot distilled water after it was washed with acetone. Finally, the glass slide is dried under Infrared (IR) lamp for 10 minutes. 0.1M of Lead acetate (PbAs$_2$) [Pb(CH$_3$(COO)$_2$] and 0.1M of thiourea, SC (NH$_2$)$_2$ were used as sources of Pb$^{+2}$ and S$^{-2}$ ions in the solution to form nano-crystalline PbS thin films. Molar concentrations of Pb$^{+2}$ and S$^{-2}$ ion sources with the proportion of Pb:S (1:1) were used to form the thin film. The pH in all solutions was measured by digital pH meter and it was fixed at 10.5 using ammonia, and the total solution volume was 60mL at room temperature\textsuperscript{3}. In this way, many films are immersed in different bath containing precursors of lead and sulphyde electrolyte whose pH is 10.5 for 2hrs-24hrs and each slide was placed in beaker with 45 degree angle. From observations and testing of the film growth with multimeter, we get the uniform well adherent film at 22 hr. Hence a film was deposited for 22 hr in solution. At the end of deposition time, the substrate coated with PbS on both sides are taken out from the solution and rinsed in double distilled water. Mirror-like thin film surface was obtain with gray-black color\textsuperscript{3}. The electrical resistivity and band gap are by obtained by using four probe methods. The study of CV, LSV, and Chronoamperometry is done by using potentiostatic. Figure 1(a) shows the experimental set up for CBD method and Figure 1(b) shows the well adherent films obtained at different deposition time durations.

**Characterization**

The UV–Vis. absorbance spectra of the samples are recorded using a spectrophotometer (JASCO V-670). The electrical resistivity was measured by four probe apparatus and I-V characterization was done with the static gas sensing unit and all the electrochemical measurements was done with K-LYTE 1.2 Kanopy Techno solutions software designed to control the potentiostat unit with Ag/Agcl as a reference electrode (RE) and Platinum (Pt) as working electrode (WE) and Platinum (Pt) mesh as counter electrode (CE) for a bath.

**Result and Discussion**

The formation reaction mechanism and Electrical, optical and electrochemical characterizations of the films obtained are discussed below.

**Reaction Mechanism**

The result for formation of PbS thin film is also explained by various groups as\textsuperscript{16},

\[
\text{Pb(CH}_3\text{COO)}_2\cdot3\text{H}_2\text{O} \rightarrow \text{Pb}^{+2} + 3\text{H}_2\text{O} + 2\text{CH}_3\text{COO}^- \\
\text{Pb}^{+2} + 4\text{NH}_3 \rightarrow \text{Pb(NH)}_3\text{4}^{+2}
\]
SC(NH\textsubscript{2})\textsubscript{2} + 2OH \rightarrow S\textsuperscript{2-} + CH\textsubscript{2}N\textsubscript{2} + 2H\textsubscript{2}O

Pb(NH\textsubscript{3})\textsuperscript{4+} + SC(NH\textsubscript{2})\textsubscript{2} + 2OH \rightarrow PbS + 4NH\textsubscript{3} + CH\textsubscript{2}N\textsubscript{2} + 2H\textsubscript{2}O

The color of solution changes on addition of dropwise ammonia. This means the formation of reaction begins. The PbS films were deposited for various time durations and the deposition temperature is 300K\textsuperscript{17}. At room temperature, the ions will get sufficient time to condense on the glass substrate surface so that we get a large amount of material is deposited on the substrate.

Electrical properties

I-V Characteristics’ of Film

In the present study, the four-point probe technique was used for the study electrical behavior of PbS films. The resistivity measurement of PbS films deposited onto glass substrate was carried with four probe apparatus and film gives the Ohmic behavior.

Variation of the voltage (mV) and current in (μA) for deposited film is as shown in Figure 2. The behavior of the film was linear in nature and it shows the resistance of 500MΩ at room temperature.

dc Electrical Resistivity

The dc electrical resistivity of the films are measured by various groups\textsuperscript{18} and hence same is used for PbS thin film was measured as a function of temperature (1000/T). Figure 3. Shows the variation of resistivity against temperature for PbS thin film was measured as a function of temperature in the range 300 to 500 K\textsuperscript{19}. The variation of log ρ with reciprocal of temperature, it is observed that the resistivity is decreased with increase with temperature\textsuperscript{20}, suggesting the semiconductor performance of PbS thin film. Resistivity decreases with increase in temperature which is one of the common observations in semiconducting thin films\textsuperscript{21}. A room temperature electrical resistivity of metal oxides and metal Chalcogenide are determined\textsuperscript{22} for PbS thin film was obtained 18.75 Ω cm.

Band Gap

For finding the band gap of a semiconducting material the four probe method is used. Firstly the current and voltage is measured across the lead acetate thin film at different value of temperature. From resistivity be obtained by using relation ρ = (V/I)\textsuperscript{2πs/(w/s)} in which V is the floating potential difference between different inner probes while I is current through outer two probe and S is the spacing between two probe\textsuperscript{23}. The variation of semiconductor resistivity with temperature is inferred by plotting a graph between log of resistivity, log 10 ρ and reciprocal of temperature 10\textsuperscript{3}/T . From readings a plot is obtained. From this plot a slope is obtained
and by this a band gap of PbS film is calculated the formula for band gap is

\[ E_g = 2.3026 \times 10^3 \times 2 \times k \times \text{slope} \]

Where, \( K = \text{Boltzmann constant} = 8.617 \times 10^{-5} \text{eV}^{-1} \)

\[ E_g = \text{Band gap} = 0.3742 \text{ eV (from calculation).} \]

**UV Visible Spectroscopy**

The UV–Vis. absorbance spectra of the samples are recorded using a spectrophotometer(JASCO V-670)as shown in figure 4. and absorbance against wavelength is plotted and we get the sharp peak at the 1150nm region which gives the bulk gap of material formed as PbS.

**Electrochemical Measurements**

Electrochemical measurements was done with K-LYTE 1.2 Kanopy Techno solutions software designed to control the potentiostat unit with Ag/Agcl as RE and Pt as WE and Pt mesh as CE for an bath

**Cyclic Voltammetry**

In CV the voltage is changes between two values with fix rate. When voltage reaches highest value then the scan is reversed and voltage is swept back to lowest value. CV of Pb\(^{2+}\) and S\(^2-\) was carried out from maximum voltage 0.6V to minimum voltage -0.6V with respect to Pt as working electrode and Pt(mesh) as counter electrode. All the potential were measured against Ag/AgCl electrode, which served as reference electrode. All the experiments were carried out at room temperature. The concentration of solution which is used for CVwas 0.1M.CV was taken at sweep rate of 50.00mV/s. The starting and returning potential were 0.00V and 0.00V respectively.CV shows oxidation of S\(^2-\) at 0.3V and reduction of Pb\(^{2+}\) at 0.58V. The gap between irreversible cathodic and anodic peak increases with decreases in size indicates the quantum confinement effect .Hence it is being revealed that quantum confinement effect can be observed in the as synthesized PbS films.

The reaction is,

\[ \text{Pb}^{4+} + 2e^- \rightarrow \text{Pb}^{2+} \quad E^\circ=-0.13V \]
\[ S + 2e^- \rightarrow S^{2-} \quad E^\circ=0.48V \]

**Linear Sweep Voltammetry (LSV)**

The current at a working electrode is measured and potential between working electrode and reference electrode is swept linearly with time in LSV method and the voltage is scanned from a lower limit to an upper limit. The studies of Pb\(^{2+}\) and S\(^2-\) was carried out from starting voltage at 0.00V and ending voltage at 1.0V with sweep rate 50.00mV/s. The scan starts from left hand side of current plot where no current flows through the solution. As the voltage is swept further to right value means more reduction of ions in the solution that is a current begins to flow and reaches a highest peak value before dropping. There is reduction of Pb\(^{4+}\) to Pb\(^{2+}\).

**Chronoamperometry**

In certain electrochemical technique where potential of working electrode is stepped to a constant value and results the current in a faradic process happening at substrate electrode is monitored as a time
function for the process taking place at the electrode. For experiment carried out reference electrode was Ag/Agcl and working electrode was Pt. The potential of working electrode in three electrode configurations was prescribed by k-lyte 1.2 software and current was follower with rise of time. It is a single potential step in which only current resulting from forward step. In Chronoamperometry current is usually monitored vs. time. In this expt charge is monitored at working electrode. The voltage was fixed during experiment at 0.200V.

Conclusions

Nano-crystalline PbS film is produced by using CBD method on cleaned glass substrate at 22hrs at room temperature. During research it is observed CBD method is a cost effective method for the synthesis of the thin film. The organize way to add the reactants of precursor’s solutions is important. The films show the ohmic nature and the obtained band gap is 0.3742eV. The selection of precursor solution also plays a great role in formation of the films. The resistance values of PbS films can be measured using four probe method it means that the films are conductive in nature. The resistivity is found to be 18.75Ω.cm. The band gap is obtained at room temperature about 0.37eV. The good quality results are obtained of CV, LSV, and Chronoamperometry by using k-lyte potentiostatic.

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