

GROWTH AND CHARACTERIZATION OF PbS THIN FILMS
A PROJECT REPORT SUBMITTED TO

SAVITRIBAI PHULE PUNE UNIVERSITY, PUNE



FOR THE DEGREE OF
MASTER OF SCIENCE
IN
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UNDER THE FACULTY OF SCIENCE

BY

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SAVITRIBAI PHULE PUNE UNIVERSITY

BONAFIDE CERTIFICATE

This is to certify that the work incorporated in the project report entitled “**Growth and Characterization of PbS Thin Films**” submitted to Savitribai Phule Pune University, Pune, is benefited work of **Miss.Bembale Monali Subhash** of MSc. (Physics) during the academic year 2020-21, who carried out the project work under my supervision



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Date:

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(MSc. Physics)

Chapter-I

Introduction and Literature Survey

1.1 Introduction and material background

PbS is a IV-VI group, direct narrow energy band gap semiconductor. PbS has relatively high Bohr radius (18 nm), therefore, it is easy to prepare particles with size smaller than the Bohr radius that show strong quantum confinement effects. PbS also low-toxicity and cost-effective material. These properties indicate the potential use of PbS in solar cells [1], IR detector materials [2], quantum dots applications [3], photothermal conversion of solar energy [4], For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition [5], spray pyrolysis [6], successive ionic layer adsorption reaction (SILAR) [7], atomic layer deposition (ALD) [8], electro-deposition [9], Solution growth technique [10,11]. SGT method is presently attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films.

Lead sulfide (also spelled *sulphide*) is an inorganic compound with the formula PbS. It finds limited use in electronic devices. PbS, also known as galena, is the principal ore and most important compound of lead. Molecular formula: PbS

Molar mass: 239.30 g/mol

Melting point: 1118 °C

Boiling point : 1281 °C

Crystal structure: cubic

1.2. Applications of Lead Sulphide:-

PbS is one of the oldest and most common detection element materials in various infrared detectors.

As an infrared detector, PbS functions as a photon detector, responding directly to the photons of radiation, as opposed to thermal detectors, which respond to a change in detector element temperature caused by the radiation.

1. PbS element can be used to measure radiation in either of two ways: by measuring the tiny photocurrent the photons cause when they hit the PbS material, or by measuring the change in the material's electrical resistance that the photons cause.
2. Measuring the resistance change is the more commonly used method.

3. At room temperature, PbS is sensitive to radiation at wavelengths between approximately 1 and 2.5 μm .
4. This range corresponds to the shorter wavelengths in the infra-red portion of the spectrum, the so-called short-wavelength infrared (SWIR). Only very hot objects emit radiation in these wavelengths.
5. The combination of such properties makes PbS suitable for efficient electroluminescent devices, such as inorganic-organic bulk hybrid solar cells.
6. Tunable near-infrared detectors.
7. Solid state lasers.
8. biological sensing applications

1.3. Literature Survey

M.M.Abbas et al [12] have reported Nanostructure PbS thin films at low temperatures prepared by a simple bath deposition method. The results of AFM & XRD tests showed that the deposited PbS thin films consist of nanosize grains and the grain size increases with increasing film thickness.

Ezenwa I.A. [13] has studied PbS thin films by chemically deposited on glass substrates from aqueous solutions of lead nitrate $[\text{Pb}(\text{NO}_3)]_2$, and thiourea ($\text{SC}(\text{NH}_2)_2$), using EDTA disodium salt as a complexing agent and ammonia solution as a pH adjuster at 300K. The films also have high transmittance in the visible/ near infrared region of the electromagnetic spectrum. This makes the films excellent glazing material for solar control in warm climate regions.

S. Seghaier et al [14] have reported chemical bath deposition method to elaborate the PbS crystallites. From structural analysis we can conclude that the best crystallinity and the great adhesion of PbS on glass substrate is obtained

UBALE A.U. et al [15] have reported Nanostructured PbS thin films at low temperature were prepared by a simple chemical Bath Deposition method. The results of XRD and SEM show that the deposited PbS film consists of nano-sized grains and the grain size increases with increasing film thickness. An XRD study shows nanocrystalline structure with cubic phase

Tavakkol Tohidi et al [16] have reported PbS thin films from two different baths using the CBD method. The polycrystalline structure of the films was studied by XRD.

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Chapter-II

Thin film Deposition Techniques

2.1 Introduction

There are several methods that can be used for the deposition of thin films. The selection of a specific deposition technology is ultimately determined by the material system used and cost of the process.

The thin layer can be transferred to glass, plastic or other flexible materials, opening a wide range of possibilities for flexible electronics. In addition, the semiconductor film can be flipped as it is transferred to its new substrate, making its other side available for more components. A material is said to be a thin film when it is built up as a thin layer on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a chemical reaction, various processing routes both physical and chemical deposition techniques have been utilized to prepare lead sulphide thin films. Among these, the chemical bath deposition method was chosen as an ideal preparation method for preparing lead sulphide thin film.

2.2 Thin Film

Whenever the growth of material is allowed in only two dimensions such that third dimension is very small or negligible compared to other two dimensions, then it is called thin film. It can be considered as two dimensional materials. Thin films are useful because their properties are much different than the bulk material. The nanostructured materials can be in the form of thin films, multilayer films or nanoparticles. There are several methods in which material of interest is brought in the gaseous phase (atom or molecules) which can form clusters and then deposit on appropriate substrates. It is also possible to obtain very thin (even atomic layers known as monolayers) layers or multilayers (multilayers are layers of two or more materials stacked over each other) forming nanomaterials of wide interest.

2.3 Deposition of thin film

Any thin film deposition process involves three main steps:

1. Production of the appropriate atomic, molecular, or ionic species.
2. Transport of these species to the substrate through a medium or vacuum.
3. Condensation on the substrate (Chemical or electrochemical)

Formation of a thin film takes place via nucleation and growth process. The general picture of the step-by-step growth process emerging out of the various experimental and theoretical studies can be presented as follows:

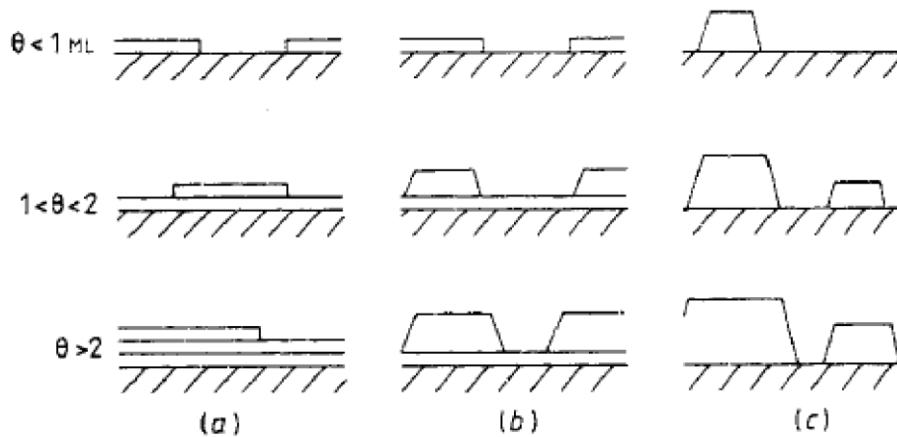
- The unit species, on impacting the substrate, lose their velocity component normal to the substrate and are physically adsorbed on the substrate surface.
- The adsorbed species are not in thermal equilibrium with the substrate surface. In this process they interact among themselves, forming bigger clusters.
- The clusters or the nuclei, as they are called, are thermodynamically unstable and may tend to desorb in time depending on the deposition parameters. If the deposition parameters are such that a cluster collides with other adsorbed species before getting desorbed, it starts growing in size. After reaching a certain critical size, the cluster becomes thermodynamically stable and nucleation barrier is said to have been overcome.
- The critical nuclei grow in number as well as in size until a saturation nucleation density is reached. The nucleation density and the average nucleus size depend on a number of parameters such as chemical nature of the substrate, the activation energies of adsorption, the energy of the impingement species, the rate of the impingement, thermal diffusion, the temperature. The grown nuclei are called islands.
- The next stage in the process of film formation is the coalescence stage, in which the small islands start coalescing with each other in an attempt to reduce the surface area.

- Larger islands grow together, leaving channels and holes of uncovered substrate. The structure of the films at this stage changes from discontinuous island type to porous network type. A completely continuous film is formed by filling of the channels and holes.

2.3.1 Growth modes

It is generally accepted that there are three possible modes of crystal growth on surfaces, which are illustrated schematically in figure 1.1. In the island, or Volmer-Weber mode (figure 2.1 (a)), small clusters are nucleated directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms (or molecules) of the deposit are more strongly bound to each other than to the substrate. This mode is displayed by many systems of metals growing on insulators, including many metals on alkali halides, graphite and other layer compounds such as mica.

The layer, or Frank-van der Merwe mode (figure 2.1(c)), displays the opposite characteristics. Because the atoms are more strongly bound to the substrate than to each other, the first atoms to condense form a complete monolayer on the surface, which becomes covered with a somewhat less tightly bound second layer. Providing the decrease in binding is monotonic, toward the value for a bulk crystal of the deposit, the layer growth mode is obtained. This growth mode is observed in the case of adsorbed gases, such as several rare gases on graphite and on several



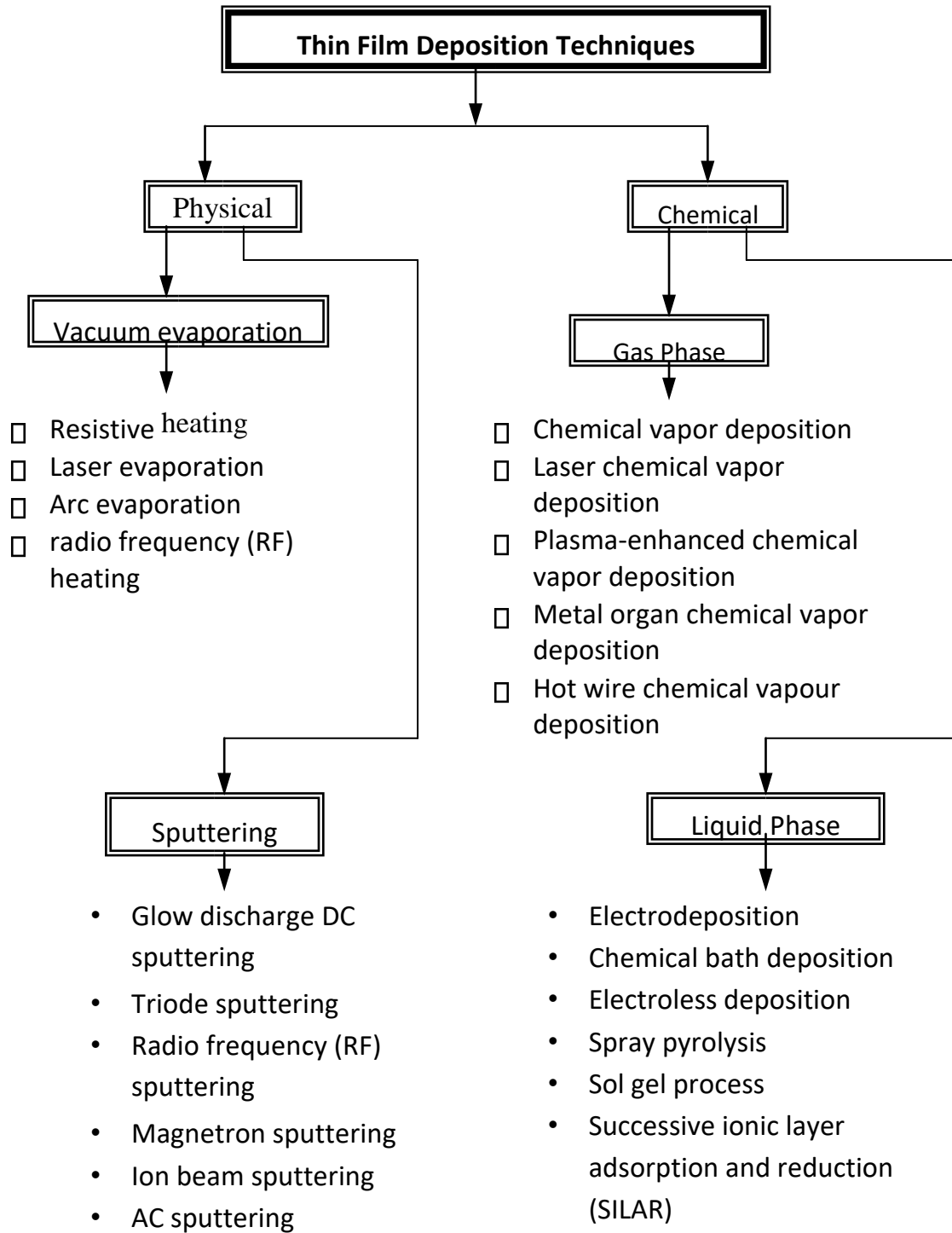
metals, in some metal-metal systems, and in semiconductor growth on semiconductor

s.

Figure 2.1. Schematic representation of the three crystal growth modes: (a) island or Volmer-Weber, (b) layer plus island or Stranski-Krastanov, (c) layer or Frank-van der Merwe mode.

The layer plus island, or Stranski-Krastanov, growth mode (figure 2.1(b)) is an interesting intermediate case. After forming the first monolayer (ML), or a few ML, subsequent layer growth is unfavourable and islands are formed on top of this 'intermediate' layer. There are many possible reasons for this mode to occur, and almost any factor which disturbs the monotonic decrease in binding energy, characteristic of layer growth, may be the cause. For example, the lattice parameter of, or symmetry of, or molecular orientation in, the intermediate layer may not be able to be continued into the bulk crystal of the deposit. This results in a high free energy of the deposit intermediate-layer interface which favours subsequent island formation. As will be seen later, this growth mode is much more common than was thought just few years ago. There are now many examples of its occurrence in metal-metal, metalsemiconductor, gas-metal and gas-layer compound systems.

2.4 Thin film deposition Techniques



Since the physical methods are costly and required sophisticated instruments. For chemical methods in gas phase vacuum is always necessary, so we give our attention to chemical methods in liquid phase.

2.4.1 Electrodeposition

Electrodeposition is widely used in making metallic coatings. Electrodeposition can be understood as a special electrolysis resulting in the deposition of solid material on an electrode. This process involves i) oriented diffusion of charged growth species (typically positively charged ions) through a solution when an external electric field is applied and ii) reduction of the charged growth species at the growth or deposition surface which also serves as an electrode. Electrodeposition is only applicable to electrically conductive substrates. The process is also known as electroplating. When deposition is confined inside the pores of template membranes, if the template membrane is removed, nanorods or nanowires are prepared.

2.4.2 Chemical bath deposition

Chemical bath deposition (CBD) is a method for the deposition of metal chalcogenide thin films. In chemical bath deposition metal chalcogenide thin film occurs due to substrates maintained in contact with dilute chemical baths containing the metal and chalcogenides ions. The film formation takes place when ionic product exceeds solubility product. In chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with dilute chemical bath containing metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product.

2.4.3 Electroless deposition

In the electroless deposition films of metals may be deposited directly without any electrode potentials being involved, by the use of suitable compound in solutions. Such deposition is known as electroless deposition or chemical reduction plating. In electroless deposition films can be grown on substrate by dipping them in appropriate solutions of metal salt and reducing agent without the application of any electric field. Deposition may occur by homogeneous chemical reactions usually reduction of metal ions in solution by a reducing agent. There are three type of reaction takes place, i) Noncatalytic reaction where any type of substrate used, ii) Catalytic reaction where the film formation takes place on metallic substrate and iii) Catalytic reaction using activators where deposition takes place with the help of activators to activate non catalytic surface.

2.4.4 Spray pyrolysis

This is thermally stimulated reaction between the clusters of liquid / vapour atoms of different spraying solutions of the desired compound onto the substrate maintained at elevated temperature. The sprayed droplets on reaching the hot substrate undergo pyrolytic decomposition and form a single crystal or cluster of a crystallite product. The other volatile byproducts and excess solvents escape in the crystallite of the product. The other volatile byproduct and excess

solvents escape in the vapour phase. The thermal energy for decomposition, subsequent combination of the species, sintering and recrystallization of crystallites is provided by hot substrates.

2.4.5 Sol-gel method-

Sol-gel method is commonly useful in formation of metal oxide. Sol-gel process is low temperature process. Sols are solid particles in liquid. Gels are nothing but a continuous network of particles with pores filled with liquid. A sol-gel process involves formation of sols in liquid and then connecting the sol particles to form porous network. By drying the liquid, it is possible to obtain powders, thin films.

2.4.6 Successive ionic layer adsorption and reaction (SILAR)

In SILAR method thin films are obtained by immersing substrate into separately placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water. The rinsing time in ion exchange water is critical for ionic layer formation. Basic mechanism of SILAR involves three most important steps: (i) specific adsorption of the most strongly adsorbed ions of the compound to be grown, by the substrate immersion in a solution of one of its cationic precursor, (ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the most strongly specific adsorbed cations and the less strongly adsorbed anions by the subsequent substrate immersion in the solution.

2.5 Why Chemical bath deposition?

The chemical bath deposition is the chemical liquid phase which is one of the cheapest methods to deposit thin films and nonmaterial's, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. In 1933 Bruckman deposited PbS thin film by chemical bath deposition (CBD) or solution grown method. The major advantage of CBD is that it requires only solution containers and substrate mounting devices.

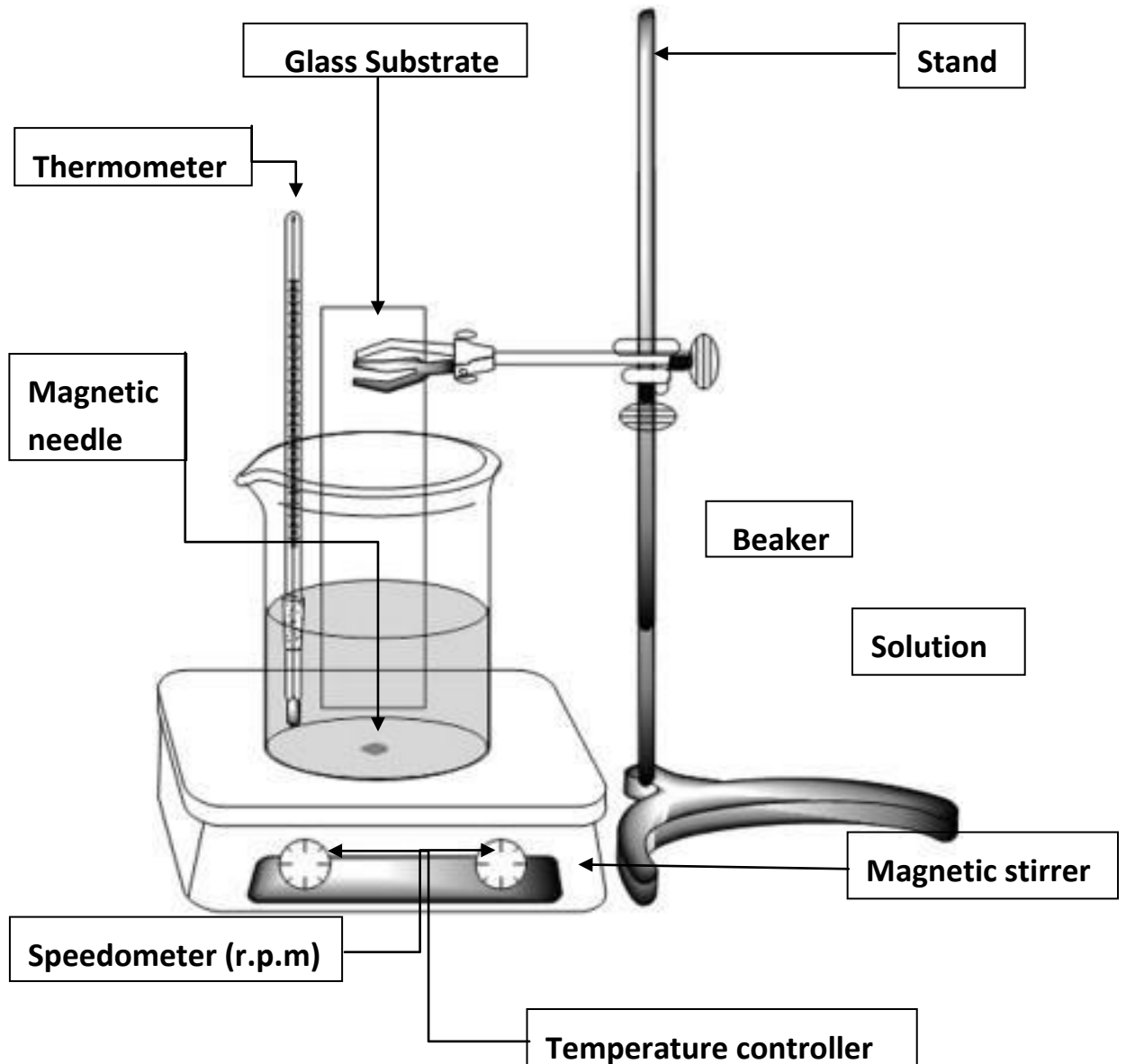


Fig.2.2 Schematic diagram of chemical bath deposition technique

The Chemical bath deposition (CBD) method is one of the cheapest methods to deposit thin films and nanomaterials, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. In 1933 Bruckman deposited Lead (II) sulfide (PbS) thin film by chemical bath deposition (CBD) or solution grown method. The experimental set-up is shown in figure. The substrate is stirred with the help of magnetic stirrer. Water or paraffin baths with constant stirring are used to heat the chemical bath to the desired temperature. In some cases, stirring is continuous from room temperature. In some cases, it is started after attaining the desired temperature. The beaker containing precursor solution and the deionised water are alternately placed as shown in fig

2.6 Advantages of Chemical Bath Deposition Method

This method is presently attracting considerable attention as it does not require any sophisticated instrumentation like vacuum system and other expensive equipment's. Simple equipment's like water bath with temperature indicator, magnetic stirrer with solution beakers are used in this method. The starting chemicals are commonly available and cheap. With this method, a large number of depositions of thin films can be done with number of cycles. Any insoluble surface of any shape can be a suitable substrate for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained. It is low cost and efficient method and easy to scale up for industrial purpose.

Chapter-III Characterization Techniques

3.1 Introduction

This chapter describes various experimental techniques used in the present investigations for the characterization thin films. Thin films are widely used in electronic, optical and magnetic devices; its structure, surface morphology and nature of crystallites/grains have a prime importance in deciding the suitability of the materials for above mentioned applications. In order to study the different properties of these semi conducting materials in the form of thin films, various characterization techniques are used. These techniques include thickness measurement, structural morphology by X-ray diffraction (XRD), Surface morphology by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), Optical absorption and transmission by UV-VIS spectrophotometer, Electrical resistivity measurement, I-V characteristics, TEP etc. Following sections describe these methods.

3.2 Characterization techniques

3.2.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is well known technique to obtain the information of composition, phase and crystallite orientations of the material. Structure identification, determination of lattice parameters and grain size are based on the X-ray diffraction pattern. Improved detection methods for X-ray, the availability of commercial mono-chromators and intense micro focus X-ray sources have made X-ray diffraction method applicable to film as thin as 100Å. The several workers have described X-ray diffraction arrangement, suited to study of thin films. This technique employs a chromate to provide a diffracted beam, which is further diffracted from the film surface oscillating about the mean diffraction position. The X-ray diffraction technique based on monochromatic radiation is more important because the spacing of the planes can be deduced from the observed diffraction angles. The phenomenon of X-ray diffraction can be considered as reflection of X-rays from the crystallographic planes of the material and is governed by the Bragg's equation;

$$2d \sin\theta = n \lambda \quad (7)$$

Where, d is lattice spacing, λ is the wavelength of the monochromatic X-ray, n is the order is diffraction and θ is diffraction angle. The 'd' values are calculated using above relation for known values of θ , λ and n . the X-ray diffraction data thus obtained is compared with American Standards for Testing of material (ASTM) powder diffraction data to identify the unknown material. The sample used may be powder, single crystal or thin film.

The crystallite size (D) of the deposits is estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Scherer's equation as follows.

$$k$$

$$D$$

$$\cos$$

Where, D is crystallite size, λ is wavelength of X-rays used (Cu $K\alpha$ 1.0542 Å), β is full width of half maxima of the peak (FWHM) in radians, θ is Bragg's angle and K is constant. Value of K varies from 0.89 to 1.39, but for most cases it is closer to 1. Though this technique is applicable for determination of crystal structure, lattice parameters, particle size etc, it is not useful for identification of individuals of multilayer or percentage of doping material.

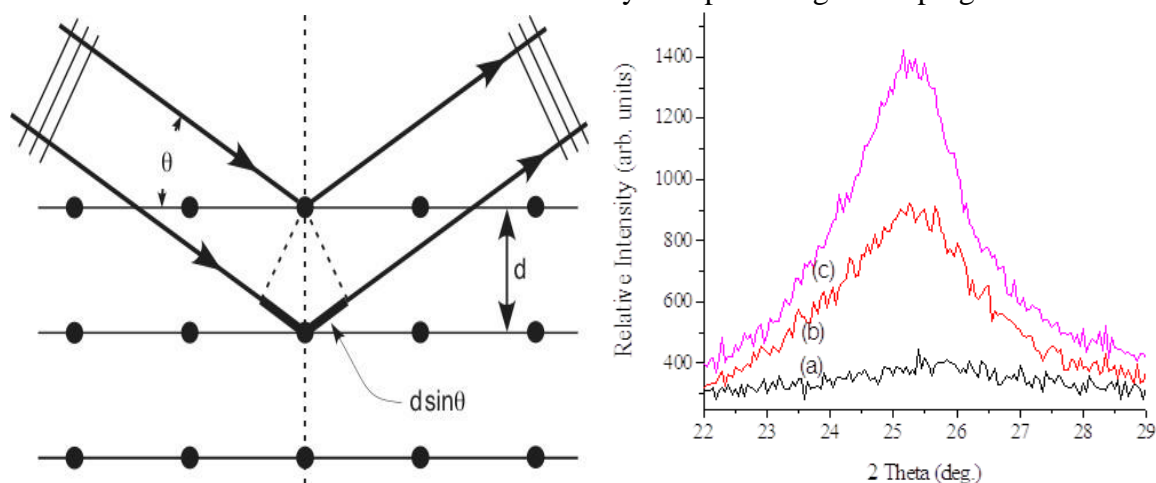


Figure. 3.1 Bragg's diffraction by using X-ray and XRD graph with intensity variation

3.2.2 UV-Vis spectroscopy

It involves the spectroscopy of photons & spectrophotometer. It uses light in the visible & adjacent near ultraviolet & near infrared ranges. In this region of energy molecules of space undergo electrons transitions. UV/Visible spectroscopy is routinely used in the quantitative determination of solution in the transition metal ions & highly conjugated organic compounds.

- 1) Solution of transition metal ions can be colored (i.e. absorb visible light) with 'd' electrons within the metal atoms can be excited from one electronic state to another. The colors of metal ions solution is strongly affected by the other species such as certain anions or ligands.
- 2) Organic compounds also absorb light in the UV or visible regions of the electromagnetic spectrum. Solvents for these determinations are often water for water soluble compounds or ethanol for organic soluble compounds.
- 3) While charge transfer complexes also give rise to color so the colors are often too intense to be used for quantitative measurement.

The **Beer-Lambert law** states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/VIS spectroscopy can be used to determine the concentration of the absorber in a solution.

The method is most often used in a quantitative way to determine concentrations of an absorbing species in solution, using the Beer-Lambert law:

$$A = -\log_{10}(I/I_0) = \epsilon \cdot c \cdot L \quad (9)$$

where A is the measured absorbance, I_0 is the intensity of the incident light at a given wavelength, I is the transmitted intensity, L the path length through the sample, and c the concentration of the absorbing species. For each species and wavelength, ϵ is a constant known as the molar absorptivity or extinction coefficient.

The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The ratio I / I_0 is called the *transmittance*, and is usually expressed as a percentage (%T). The absorbance, A , is based on the transmittance:

$$A = -\log (\%T / 100\%) \quad (10)$$

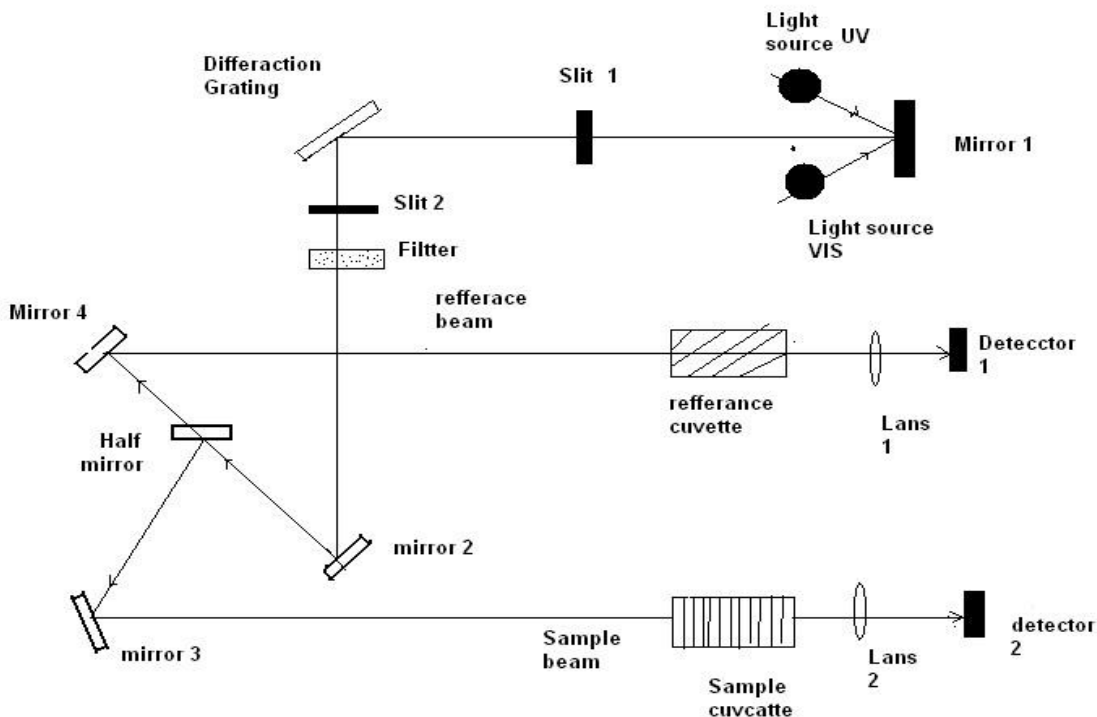


Figure 3.2 Block diagram of UV-Vis spectrophotometer

The spectrophotometer consists of a light source (an incandescent bulb for visible wavelength or a deuterium arc lamp in UV), a sample holder, diffraction grating or monochromator to separate the different wavelengths of light & a detector. The detector is typically photodiode or a CCD. Photodiodes are used with monochromator which filter the light so that only light of single wavelength reaches the sample. Diffraction gratings are used with CCD's which collect light of different wavelengths on different pixels.

Study of the optical properties of the films is necessary for applications of the films in opto-electronic devices. The considerable theoretical and experimental investigations on the optical behaviour of thin films deal primarily with reflection, transmission and absorption properties and their relation to the optical constants of the film. The equilibrium situation in a semiconductor can be distributed by generation of carriers due to optical absorption. An optical photon incident on any material may be reflected, transmitted or absorbed. The phenomenon of radiation absorption in a material is altogether considered to be due to (i) inner shell, (ii) valence band electron, (iii) free carriers including holes as well as electrons, and (iv) electron bound to localized impurity centre or defects of some type. In study of fundamental property of the semiconductors, absorption by the second type of electron is of great importance. In an ideal semiconductor, at absolute zero temperature the valence band would be completely full of electrons, so that an electron could not be excited to a higher energy state from the valence band. Absorption of quanta of sufficient energy tends to transfer of electrons from valence band to conduction band.

For crystalline materials, the transition of electrons from valence band to conduction band can be grouped into direct and indirect processes. In direct inter band optical transition the value of wave vector K for electrons remains unchanged in E-K space and momentum also does not change, while in indirect inter band transition the wave vector K for electrons changes in the E-K space. It is possible to differentiate the nature of optical transition as direct allowed or direct forbidden by classical relation

$$\alpha \propto h \nu - E_g)^{1/2}$$

3.2.3 Electrical study

I-V characteristic curves are generally used as a tool to determine and understand the basic parameters of a component or device and which can also be used to mathematically model its behaviour within an Electronic Circuit. But as with most electronic devices, there are an infinite number of i-v characteristic curves representing the various inputs or parameters and as such we can display a family or group of curves on the same graph to represent the various values.

It is well known that one of the subatomic particles of an atom is the electron. The electrons carry a negative electrostatic charge and under certain conditions can move from atom to atom. The direction of movement between atoms is random unless a force causes the electrons

to move in one direction. This directional movement of electrons due to an electromotive force is known as electricity.

Chapter-IV

Growth of PbS Thin Film

1. Introduction

PbS is a IV-VI group, direct narrow energy band gap semiconductor. PbS has relatively high Bohr radius (18 nm), therefore, it is easy to prepare particles with size smaller than the Bohr radius that show strong quantum confinement effects. PbS also low-toxicity and cost-effective material. These properties indicate the potential use of PbS in solar cells [1], IR detector materials [2], quantum dots applications [3], photothermal conversion of solar energy [4], For these reasons, many research groups have shown a great interest in the development and study of this material by various deposition processes such as electrodeposition [5], spray pyrolysis [6], successive ionic layer adsorption reaction (SILAR) [7], atomic layer deposition (ALD) [8], electro-deposition [9], Chemical Bath technique [10,11]. CBD method is presently attracting considerable attention, as it does not require sophisticated instrumentation. It is relatively inexpensive, easy to handle, convenient for large area deposition and capable of yielding good quality thin films. The characteristics of chemically deposited PbS thin film by SGT strongly depend on the growth conditions.

In this paper, we report optical and surface morphological properties of PbS thin films obtained by SGT method by optimizing different deposition parameters such as precursor concentration, bath pH and deposition time.

2. Experimentales

2.1 Thin film preparation

Thin films of lead sulphide have been grown by chemical bath technique. The substrates used for the deposition of PbS thin film were commercial microscope glass slides with the size of 75mm×25mm×1.35 mm. Before deposition, the substrates were degreased in HNO₃ solution for 24 h, cleaned by commercial detergent. Finally rinsed with deionised water and dried in desiccators. This process is done to ensure a clean surface, which is necessary for formation of

nucleation centers, required for thin film deposition. Aqueous solution of 0.1M lead acetate [Pb(CH₃COO)₂·3H₂O], 0.1M thiourea (SC(NH₂)₂), triethanolamine and 3M sodium hydroxide were used to prepare the PbS thin films. All chemicals used in the present investigation were Analytical reagent (AR) grade. Ten milliliters lead acetate solution was taken in a 50ml glass beaker. Under continuous stirring 4ml NaOH solution were added slowly. 10 ml thiourea solution was then added with constant stirring. The pH of final mixture was about 11. The solution was then transferred to 25 ml glass beaker. Pre-cleaned glass substrates were inserted and inclined at 90° with the walls of the beaker. The bath is allowed to stand for 1 h at room temperature. Thereafter substrate coated with PbS was removed, rinsed with distilled water, and dried in open air at room temperature. Film obtained was uniform, well adherent, reflecting and dark gray in color.

2.2 Characterization Techniques

The as-deposited thin films of PbS were characterized for structural, optical and electrical properties. The PbS film thickness was measured by weight difference method technique. The surface morphology was studied by scanning electron microscopy (SEM, JOEL-JSM-5600). Transmittance and absorbance spectra were recorded in the range 600–1100 nm by means of JASCO V-630 spectrophotometer.

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Results and Discussions

3.1 X- Ray diffraction

Structural characterization was carried out with the help of XRD (D8 ADVANCED Bruker). Figure 5.1 shows the XRD patterns of the as-deposited and annealed PbS thin film deposited by chemical bath deposition. All the diffraction peaks (111), (200), (220), (311), (222), (400), (331), (420), and (422) are exactly matches to standard JCPDF data [1]. So it is confirmed that formation of PbS takes place with cubic structure.

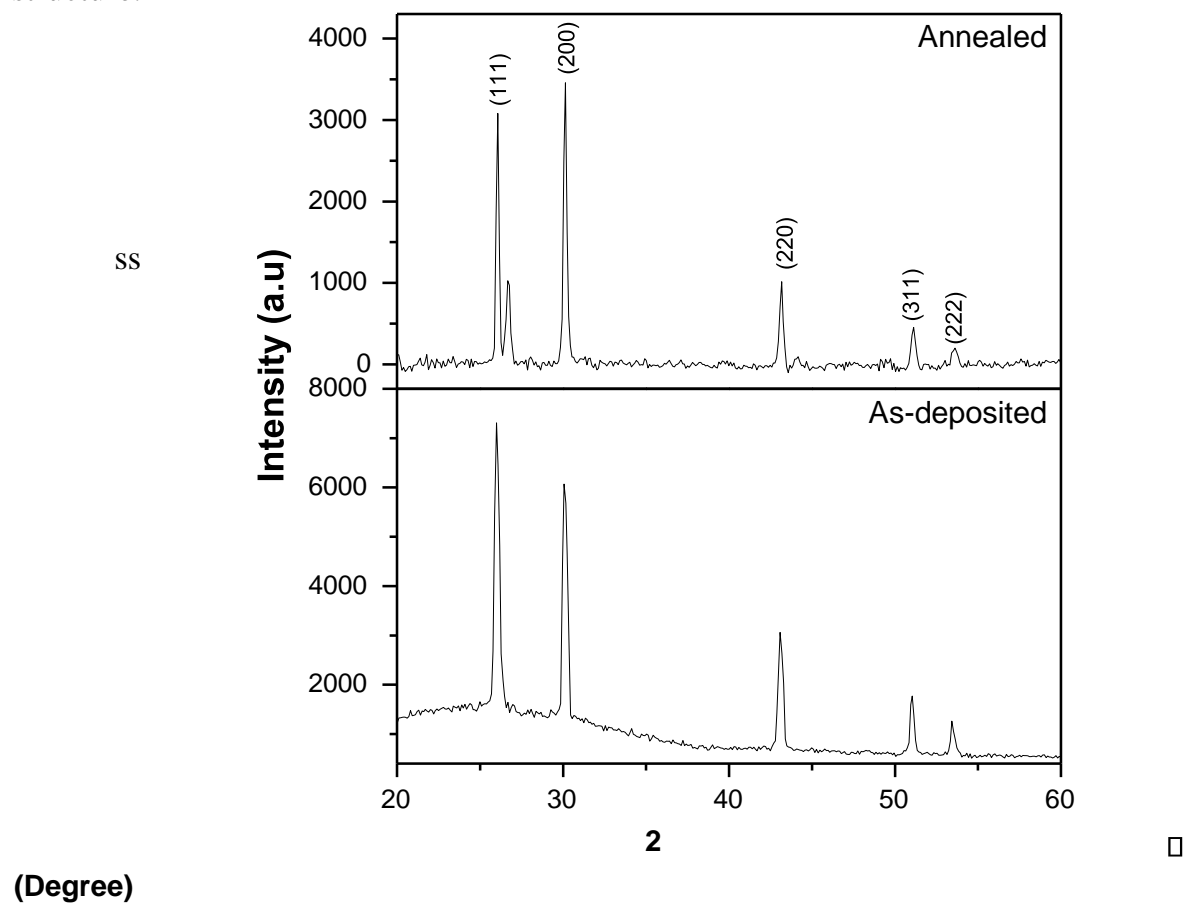


Fig 5.1. XRD pattern of as-deposited and annealed PbS thin films deposited by chemical bath deposition method

The average particle size is calculated from Debye Scherrers formula [2] given below.

$$t = \frac{0.9 \lambda}{\beta \cos \theta}$$

Where, t = Crystallite size (Å).

λ = wavelength of incident X-ray.

B = full width half maxima (FWHM) ,

θ = angle of diffraction,

0.9 = constant

The average crystallites size was estimated around 28.56 nm and 42.75 nm for both asdeposited and annealed PbS thin films using scherrer's formula. After annealing it is observed that the crystallinity of the film increases. The particle size was calculated for each peak and the final size was estimated by averaging all data.

3.2 Scanning Electron Microscopy (SEM)

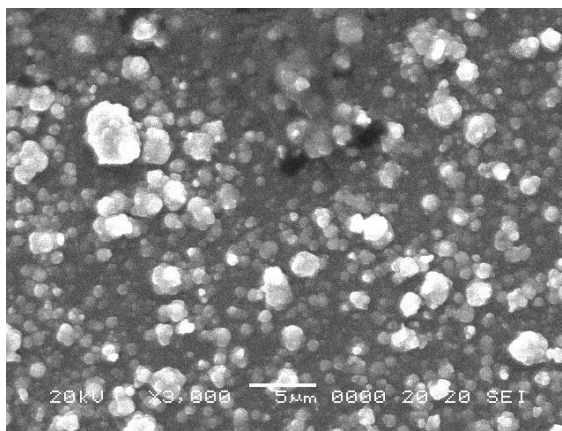


Fig.5.2. SEM micrograph of as-deposited PbS thin film

Fig.5.2 shows SEM image of as-deposited PbS thin film. It is observed that the film is uniform and covers the entire substrate surface. The fine grains were well defined, spherical with different sizes and were uniformly distributed over a smooth homogeneous background corresponding to the nanocrystalline phase of PbS. Some of the grains are seen to be united/fused forming agglomerates and the grain size obtained from SEM is about $\sim 200 \pm 20$ nm.

3.3 Optical Analysis:-

Optical characterization was carried out with the help of UV-VIS absorption spectrophotometer (JASCO-UV-VIS-NIR Spectrophotometer; model V-670). Optical absorption measurements are essential for the understanding of the band gap of any semiconducting material. The optical absorption spectra of the film were recorded in the wavelength range 500-1200 nm. Figure 5.3 shows optical absorption spectra of asdeposited and annealed PbS thin film. Absorption spectra shows that for annealed PbS thin film the absorption edge red shifted as compare to as-deposited sample, which is due to increase in particle size after annealing.

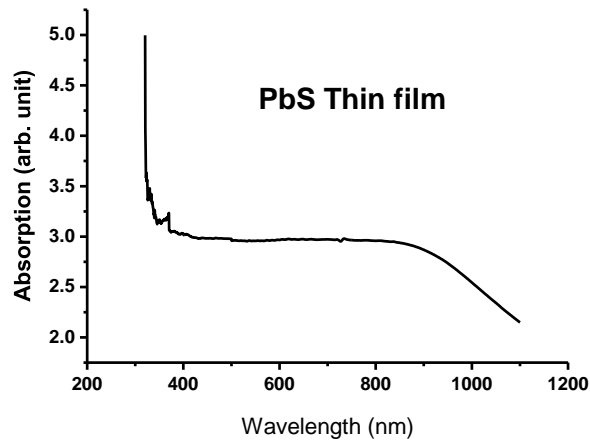


Fig.5.3. Plot of absorbance and transmittance versus wavelength

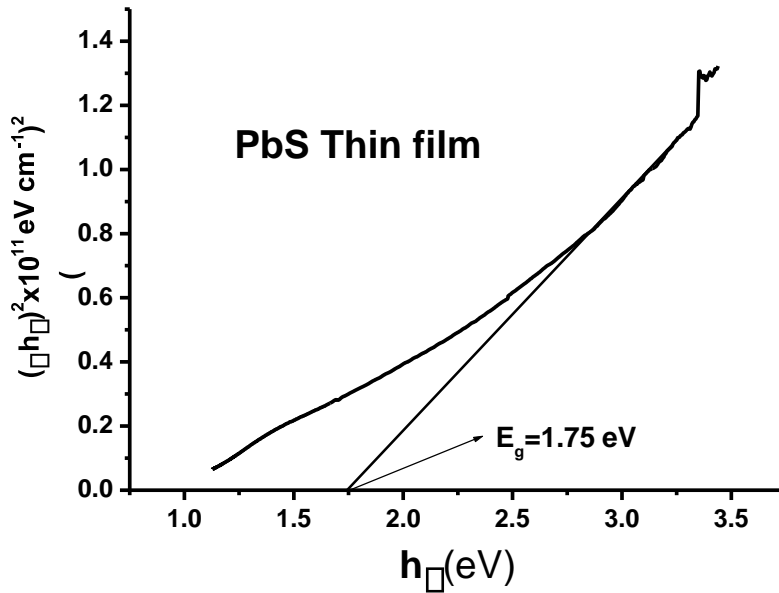


Fig.5.4. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ obtained from as-deposited PbS thin film

The relation between the absorption coefficient α and the incident photon energy ($h\nu$) can be written as [3],

$$\alpha = A(h\nu - E_g)^n \quad (6)$$

where 'A' is constant, $n = \frac{1}{2}$ for direct allowed transition, ' E_g ' is optical band gap of the material. Fig. 5.4 shows the plot of $(\alpha h\nu)^2$ against $(h\nu)$ for PbS thin film derived from the absorbance spectra. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ vs $(h\nu)$ for zero absorption coefficient value gives the band gap, which is found to be 1.75 eV at room temperature.

3.4 Resistivity of as-deposited PbS thin film

The dark electrical resistivity of the thin film was measured using four-probe method in the temperature range 300–500 K. A plot of inverse absolute temperature versus $\log \rho$ for cooling cycle is shown in Fig. 3.5. The dependence is almost linear indicating the presence of only one type of conduction mechanism in the film. It shows as temperature increases resistivity decreases. This is the behavior of semiconductor.

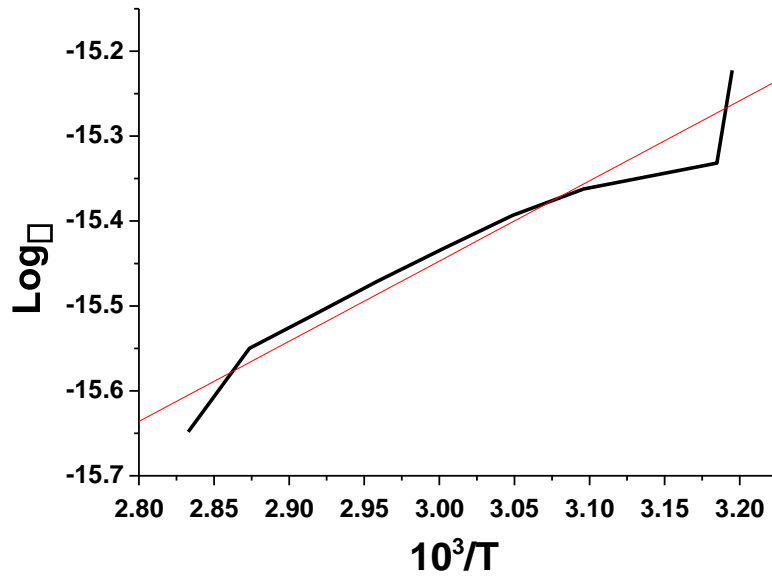


Figure 5.5 Plot of $1000/T$ vs $\text{Log}_{10}\rho$

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Conclusion and Future Scope Conclusion:

- ✓ PbS thin films can be successfully deposited by chemical bath deposition method.
- ✓ XRD confirms the formation of cubic structure of PbS. After annealing crystallinity of the film increases.
- ✓ Optical absorption spectra show the PbS material absorption starts in the IR range. The band-gap values were calculated from Tauc plot are 1.75 eV .
- ✓ It is confirmed from the electrical measurement that the prepared PbS thin films is semiconducting in nature from chemical bath deposition. The film is suitable for photovoltaic applications.

