**Influence of Temperature and Thickness on Optical Properties of Sulphide (ZnS, CdS, and PbS) Thin Films Prepared by Chemical Bath Deposition**

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**1 CHALCOGENIDES**

Materials labelled as chalcogenides (CG) include several chalcogen elements as core components. Sixteenth group of the periodic table are oxygen (O), sulphur (S), selenium (Se), tellurium (Te), and polonium (Po) have two ions and six valence electrons and their compounds are referred as chalcogenides. The metal content of these elements increases as the atomic number rises. In which O and S are nonmetals, whereas the Po, Se and Te are metals. These elements' bonding properties coincide with their metal properties. These substances are covalently bound and can be crystalline or amorphous. These substances are covalently bound and can be crystalline or amorphous. Depending on composition, CG are basically semiconductors of band gap ranges from 1-2 eV, depending on composition. Chalcogenides are photosensitive, they also have glassy semiconductor features, which give them fascinating electrical characteristics. Due to its versatile features in optoelectronics and energy devices, metal chalcogenide semiconductors have actively participated in the development of thin film photovoltaic systems as absorber layers. The chalcogenides ZnS, CdS, and PbS are also. These three resources are primarily used to advance research [1,2].

**1.1 ZINC SULFIDE**

Zinc Sulphide (ZnS) is indeed a CG semiconductor material with a vast direct band gap of 3.7 eV at 300 K (room temperature). Additionally, it possesses a high refractive index of 2.35 at a wavelength of 632 nm. These properties make ZnS a significant material in various optical and semiconductor applications especially the most probable important role in the photovoltaic technology [3]. ZnS is identified by a single bond between each zinc and sulphide atom and maintaining a 1:1 zinc to sulphur ratio [4].

Table 1.1 Fundamental properties of zinc sulphide CG semiconductor.

|  |  |
| --- | --- |
| Molecular Weight | 97.44 g/mol |
| Density‎ | 4.090 g/cm3 |
| Melting point | 1. 1,850 °C (or) 2. 3,360 °F (or) 3. 2,120 K |
| Crystal structure | 1. Wurtzite (Hexagonal structure) 2. Zinc Blended (or) Sphalerite (Cubic structure) |

Zinc blende is characterized as a cubic closet packing (CCP), also known as face-cantered cubic (fcc), structure [5].  This crystal lattice structure is shown in Fig. 1.1 and listed in the table 1.1. [5, 6].

ZnS has a huge band gap, as a result it is a potentially key material to be used as an antireflection coating for heterojunction solar cells. It is a chief material used for fabrication detection device, in the region of visible and UV-visible region.



**Fig. 1.1 The molecular structures of the ZnS (a) Sphalerite (b) Wurtzite [5].**

**1.2 CADMIUM SULFIDE**

Cadmium sulphide is an II-IV group semiconductor with the strong direct band gap around 2.4 eV and is a highly potential candidate for recent research in science and technology. The crystal structure and fundament properties of cadmium sulphide semiconductor were labelled in Fig. 1.2 and Table 1.2, respectively [7].

Table 1.2. Fundamental properties of cadmium sulphide CG semiconductor.

|  |  |
| --- | --- |
| Molecular Formula | CdS |
| Molecular Weight | 144.46 g/mol |
| Density‎ | 4.826 g/cm3 |
| Melting point | 1. 1,750 °C (or) 2. 3,180 °F (or) 3. 2,020 K |
| Crystal structure | 1. Wurtzite (Hexagonal structure) 2. Zinc Blended (Cubic structure) |

CdS thin film is extensively studied in many optoelectronics devices such as solar cells, Field effect transistors, photo-dectors and light emitting diodes [7].



**Fig. 1.2 The molecular structure of cadmium sulphide (c)** [**Greenockite**](https://en.wikipedia.org/wiki/Greenockite) **(d)** [**Hawleyite**](https://en.wikipedia.org/wiki/Hawleyite) **[7]**

**1.3 LEAD SULFIDE**

Lead Sulfide (PbS) is a p-type material of IV-VI group compound semiconductors with the direct band gap of 0.4 eV at 300 K, which is an important one has a rock salt crystal structure face centered cubic (FCC), the atomic position of PbS is shown in Fig. 1.3 and Table 1.3 [9].

**Table 1.3. Fundamental properties of cadmium sulphide CG semiconductor [9].**

|  |  |
| --- | --- |
| Molecular Formula | PbS |
| Molecular Weight | 239.3 g/mol |
| Density‎ | 7.60 g/cm3 |
| Melting point | 1. 1,118 °C (or) 2. 2,044 °F (or) 3. 1,391 K |
| Crystal structure | 1. Rock salt (face cantered cubic) |
| Excitation Bohr radius | 1. 18 nm |



**Fig.1.3 LEAD SULFIDE (PbS) [9]**

These unique structural and optical properties make PbS more strongly acceptable for infrared detection application and also been used in many fields such as photography, Pb2+ ions elective sensors and solar absorption. In inclusion, PbS has been direct as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings. To derive from a variety of physical mechanisms, when they are excited by photons with energy greater than energy of the materials. The free carrier absorption and multiphoton absorption are idea to the fundamental physical mechanism behind nonlinear absorption [9].

**2. EXPERIMENTS**

**2.1 CHEMICAL BATH DEPOSITION**

Chemical bath deposition (CBD) is a method for deposition of thin films and nanomaterials that can be used for continuous or continuous deposition of large quantities of material. In 1933, Bruckman deposited a thin film of lead (II) sulphur (PbS) in a chemical bath deposition or solution growth method. This technology is systematically used to deposit buffer layers in thin film photovoltaic cells. Chemical bath storage CBD is a solution growth process that is used to deposit thin films of composite materials such as ZnS, CdS, and PbS. The approach of chemical bath deposit requires direct precipitation of a compound from a solution to an acceptable substrate. The scope of this technology in the field of photovoltaics is enormous. This method is ideal for producing large-scale thin films for solar energy applications [10].

**2.2 SUBSTRATE CLEANING**

Substrate cleaning is a process that breaks down the bonds between a substrate and a contaminant without damaging the substrate. In the thin film processing process, the cleaning of the substrate is an important factor in the production of reproducible films, as it affects the smoothness, uniformity, conformity and porosity of the films. The cleaning process of the substrate depends on the nature of the substrate; the required cleanliness and the nature of the contaminants to be removed. Common contaminants include grease, water absorption, airborne dust, lint, oil particles, etc. Micro slides supplied by Riviera, 25.4 x 76.2 mm, are used as substrate.

The following process has been adopted for cleaning the substrates.

1. 1. The substrate is washed with double-distilled water.
2. The substrate immersed KOH solution for one hour.
3. These substrates KOH solution for about ten minutes ultrasonic.
4. Substrates were cleaned with double distilled water.
5. These substrates were kept in isopropanol solution to remove the impurity contaminations for 10 min of ultrasonic.
6. The substrates were again washed with distilled water and then substrate immersed acetone for ten minutes cleaned ultrasonically.
7. Finally, substrates were dried in hot air oven at 90 °C (1 hour).

**2.3 PRECURSOR OF MATERIAL**

**2.4 EXPERIMENTAL SETUP**

It consists of two parts, namely

* Magnetic stirrer with thermostat
* Chemical bath

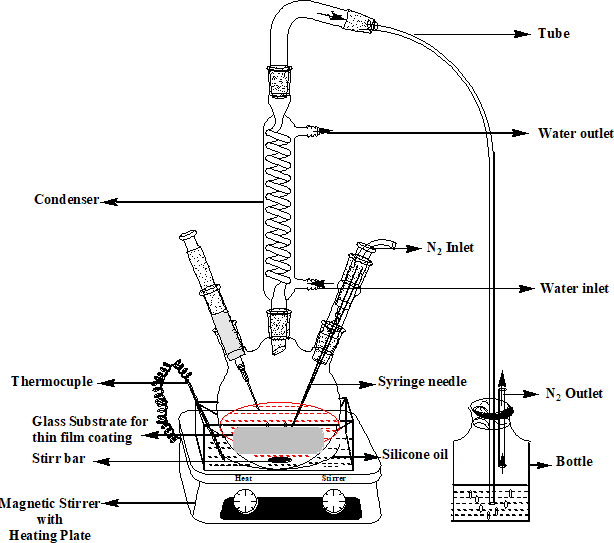
**Table 4.2 The precursors used for synthesis of ZnS and CdS.**

|  |  |  |
| --- | --- | --- |
| **ZnS** | **CdS** | **PbS** |
| Zinc Chloride (ZnCl2) | Cadmium Chloride (CdCl2) | Lead nitrate (Pb (NO3)2) |
| Thiourea (CS (NH2)2) | Thiourea (CS (NH2)2) | Thiourea (CS (NH2)2) |
| Hydrazine hydrate (N2H4) |  | Sodium hydroxide (NaOH) |
| Ammonia (NH3) | Ammonia (NH3) |  |

**2.5 MAGNETIC STIRRER WITH THERMOSTAT**

The reaction mixture is continuously stirred using a magnetic stirrer with hot plate. The temperature of the solution can be controlled by the thermostat.

**2.6 THE CHEMICAL BATH**

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**Fig. 2.1. Experimental setup of Chemical bath deposition**

It consists of three neck bottles, containing the reaction mixture of the required ratios of the precursor and the complex agent solution. The reaction started with the N2 gas condition. The input of the N2 gas is placed in the neck, the syringe is placed in the other neck of the bottle, and the solution drops in dropwise. The condenser is located in the middle of the three-leaf flange. Cool the hot vapours and condensate them into liquids for the separate collection. Lastly, the substrate is placed horizontally in a 3-neck glass as shown in Fig 2.1.

**2.7 DEPOSITION OF ZnS**

The thin film of ZnS was prepared from a solution of 0.2 mol of zinc chloride (ZnCl2), 0.2 mol of thoracia (CS(NH2)2), 18 mol of hydrogen hydrate and 5.5 mol of ammonia. First, a 50 ml bottle of distilled water mixed with zinc chloride, and a drop of hydrogen hydrogen hydrate was added to the barrel. Add the ammonia solution at the drop to achieve a clear solution and keep it at a pH of 10.5 [11]. Then add a thiourea solution to the solution. Finally, the pre-cleaned glass substrate is placed horizontally in the three-headed pot and the N2 gas is allowed to enter the pot for 30 minutes during the process. The deposition temperature was 90°C for 12 hours. During this process, the colour of the solution turns from clear to milky white after 45 minutes. At the end of the reaction, ZnS is deposited on the substrate. After depositing, remove the substrate from the container and clean the surface with distilled water to remove loose adhesion ZnS particles, resulting in very thin and uniform thin layers of ZnS with good adhesion properties. Finally, the thin film is dried in a 90-degree oven for one hour. Subsequently, thin ZnS films were exposed to different temperatures (350 °C and 200 °C) annealing process.

**2.8 DEPOSITION OF CdS**

CdS thin films are prepared from a solution of 0.2 mole cadmium chloride (CdCl2), 0.2 mole of thiourea (CS (NH2)2) and 0.6M ammonia (NH3) of as precursor. First cadmium chloride is mixed with 25ml of distilled water. Then ammonia chloride added to the solution. Then, ammonia solution is added drop wise to maintain a PH value of 10.5 and allowed continuous stirring. Then, pre-cleaned glass substrate is vertically placed into the beaker and thiourea is added into the beaker. During the process 15 minutes later the solution colour changed into yellow colour to form the CdS. The deposition temperature was maintained at 50 °C for 2 hours. At the end of the reaction CdS is deposited on the substrate in yellow colour. The substrate is removed from the beaker and cleaned with distilled water in order to remove loosely adherent CdS particles from the surface which results the very thin and uniform layer is obtained having good adherent property. Finally, the film is dried in the hot air oven at 90°C for one hour. After the CdS thin films were subjected to annealing with different temperature 350 °C and 200 °C [12].

**2.9 DEPOSITION OF PbS**

PbS thin film is made of 0.1M lead nitrate (Pb (NO3)2), 0.1M thiorea (CS (NH2)2), and 0.6M sodium hydroxide (NaOH) as precursors. The first lead nitrate is mixed with 25 ml of distilled water. The solution of sodium hydroxide is added in dropwise to get a black color solution and maintained at a PH value of 10.5 and continuous stirring. Then the pre-cleared glass substrate is placed vertically in the beer. And thethiourea is added to the beaker. The deposition temperature is 50 °C and maintained for various deposition processes (5, 10, 20, 60 minutes). At the end of the reaction, PbS is deposited on the substrate. The substrate is removed from the bucket and cleaned with distilled water to remove the loosely adherent PbS particles from the surface. A very thin and uniform layer with good adhesion property is obtained. Finally, the film is dried for an hour in a hot air oven at 90 oC [13].

**Table 2.1. PbS CONCENTRATION**

|  |  |  |
| --- | --- | --- |
| **REAGENTS** | **CONCENTRATION (mole)** | **QUANTITY REQUIRED/ g** |
| Pb(NO3)2 | 0.1 | 1.6560 |
| CS(NH2)2 | 0.1 | 0.3806 |
| NaOH | 0.6 | 1.19991 |

**3 RESULTS AND DISCUSSION**

**3.1 FILM THICKNESS**

The thickness of the thin films of zinc sulfide and cadmium sulfide was measured with a style profiler. The thickness of ZnS and CdS is measured at about 360 nm and 436 nm respectively. The prepared thin films were attached to a vacuum medium at different temperatures, such as 200 oC and 350 oC. It was observed that the thickness changed little due to the annealing effect.

**3.2 OPTICAL STUDIES OF ZnS**

The transmission vs. the wavelength of prepared and bound ZnS samples is measured in the range of 300 - 2500 nm, as shown in Figure 3.1 (a). Then various ZnS annealing films measured the transmittance range (65 % - 80 %). The films prepared and annealed show a high and almost uniform transmittance in the visible and near infrared area. This high transmission of the ZnS material is effective both as prepared and annealed films show a strong absorption.

**Fig. 3.1. (a) the wavelength dependence transmittance (%) spectra and (b)(c)(d) the Tauc’s plot of the band gap of ZnS thin films prepared by Chemical Bath Deposition at different deposition condition in room temperature annealing 200oC and 350oC.**

The direct energy of the band gap is determined using the Tauc relation diagram. According to this equation (h) 2, the corresponding plot for the prepared and annealed film depend linearly on the photon energy, h and Fig. 4.1. The band gap (Eg) values were determined by extrapolating the linear part of each curve to (αhυ)2 = 0. Calculated band gap film prepared (2.61 eV) is less than 200 oC (2.48 eV) and 350 oC (2.48 eV). When the annealing temperature rises, the band gap decreases.

**Table 3. 1. Bandgap of the ZnS thin films depends on Annealing temperature**

|  |  |  |
| --- | --- | --- |
| **Sample** | **Temperature(**0C) | **Bandgap(eV)** |
| ZnS (Pristine) | 80 | 2.61 |
| ZnS (Annealing 200oC) | 80 | 2.48 |
| ZnS (Annealing 350oC) | 80 | 2.37 |

**Fig. 3.2 Plot of (a) reflection spectra, (b) refractive index and (c) extinction coefficient of Zinc Sulfide films as a function of annealing temperature.**

Fig. 3.2 (a) shows that the reflectivity spectrum of thin ZnS films is synthesized by various precursors. The reflection of ZnS films and 200- and 350-degree annealing films is within the range of 8 to 20%. The refractive index semiconductor material is very important to determine the optical properties of thin films. The refractive index (n)of the film is calculated by equation [14].

Fig. 3.2 (b) shows that the refractive index depends mainly on the density of the voids and their volume fractions related to the packing density of the material. This indicates that the variations in the refractive index do not follow normal dispersion. The refractive index evaluated varied from 1.2 to 2.6.

Figure 3.2(c) shows that the extinction coefficient (k) is evaluated directly from the absorption coefficient (α). The extinction coefficient is calculated using the equation [15]. The variations in the wavelength of the extinction coefficient for ZnS films and heating films at 200°C and 350°C. The maximum value of the extinction coefficient is at the edge of absorption. The observed value of the extinction coefficient is slightly high for all films. The extinction coefficient (k) is ZnS film, and the annealing temperature of 200°C and 350°C is 0.3 - 0.55.

**3.3 OPTICAL PROPERTIES OF CdS**

The optical transmission spectrum of the thin cadmium sulphate film shows that Figure 3.3 (a) The wavelength range of the spectrum varies from 300 nm to 3000 nm at ambient temperature. The average optical transmission is between 50 and 60 % [14].



**Fig. 3.3 (a) the wavelength dependence transmittance (%) spectra and (b) the Tauc’s plot of the bandgap of CdS thin films prepared by Chemical Bath Deposition at different deposition condition in room temperature, annealing 200 oC and 350 oC.**

The as prepared and annealing films are exhibiting high and nearly uniform Transmittance in the visible and near infrared region. This high transmission of CdS material is effective of both as prepared and annealed films exhibited a sharp absorption. The direct band gap energy is determined using Tauc’s relation plot. According to this equation (αhυ)2 linearly depends upon the photon energy, hυ and the corresponding plot for as prepared and annealed films is depicted in Fig. 3.3 (b). The values of band gap (Eg) have been determined by extrapolating the linear portions of the respective curves to (αhυ) 2 = 0. The optical band gap is inversely proportional to the film thickness. The obtained direct band gap for pristine and annealed CdS thin film were 2.37 eV, 2.35 eV and 2.34 eV respectively.

**Table 3.2 Bandgap of the CdS thin films depends on Annealing temperature.**

|  |  |  |
| --- | --- | --- |
| **Sample** | **Temperature(**0C) | **Bandgap(eV)** |
| CdS (Pristine) | 80 | 2.37 |
| CdS (Annealing 200oC) | 80 | 2.33 |
| CdS(Annealing 350oC) | 80 | 2.30 |

Fig. 3.4 (a) Reflectivity spectrum of CdS thin films synthesized with different precursors. The reflection of CdS films and 200 oC and 350 oC annealing films is in the range of 2.2-19.3%. The reflective spectrum of CdS annealed decreased gradually in the wavelength range from 850 nm to 2000 nm. The purity was gradually increased at a wavelength range of 647 nm. The refractive index (n) of the film is calculated using the equation (14, 15).





**Fig. 3.4 Plot of (a) reflection spectra, (b) refractive index and (c) extinction coefficient of Cadmium Sulfide films as a function of annealing temperature**

The refractive index depends mainly on the density of the space and its volume ratio, which are related to the packing density of the material. This indicates that the change in the refractive index does not follow the normal diffusion. The refractive index compared varied from 1.14 to 2.66. The refractive index increases in the wavelength range of 400 to 800 nm and is approximately constant. The extinction coefficient is a measurement of the fraction of light lost by radiation and absorption per unit distance of the penetration medium. The extinction coefficient (K) is calculated with the equation [15]. The spectrum of extinction coefficients in the wavelength ranges from 400 to 2000 nm. The three peak decreases gradually in the wavelength range from 600 to 2000 nm. The observed value of the extinction coefficient is slightly high for all films. The range of extinction coefficients is between 1 and 8.

**3.4 SCANNING ELECTRON MICROSCOPE (SEM)**

The surface morphology of ZnS thin films was studied with a scanning electron microscope. Figure (3.4) shows the SEM image of the ZnS thin film at two different magnifications. The surface of the ZnS film compact and well covered with a smooth surface, irregular sphere grains of random sizes. The average size of these nanograins is between 200 and 300 nm.

The high-resolution image (160.39 kx) clearly shows that the grains are composed of ZnS cubics. Lower-level micrographs (127.57 kx) showed that the substrate was well covered with many sphere grains and that the film surface was uniform in compact growth. The grain is relatively smooth and distributed randomly.



**Fig. 3.4 SEM image of ZnS thin film at magnification (a)160.39kx and (b)127.57kx**

The surface shape of the CdS thin film was studied using a scanning electron microscope. Figure (3.4) shows the SEM image of CdS thin film at two different enlargements. This CdS film surface is compact, well coated with a smooth AZD surface, and has an irregular shape of a random-sized sphere grain. The average size of these nanograins is between 200 and 1000 nm. High-resolution images (173.05 kx) clearly show that the grain is composed of cubic CdS. The lower magnified microscope (34.14kx) shows that the substrate is well covered with many sphere grains and the film surface is uniform in compact growth. The grain is relatively soft with a random distribution.



**Fig. 3.5 SEM image of CdS thin film at magnification (a) 173.05kx and (b) 37.14kx**

**3.5 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDAX)**

The film composition analysis is done using the EDAX connection of the SEM image. The representative EDAX spectrum of the sample ZnS. The film is composed of Zn, S, and silicon, and other impurities are oxidized in the spectrum. The dependence of the ratio of sulphur to zinc by atom proportion as measured by EDAX. Quantitative EDAX analysis of ZnS films shows a high atomic composition with 18.93% zinc and 8.63% sulphur. The ZnS film EDAX spectrum is shown in Fig. 3.6.



**Fig. 3.6 EDAX spectrum of ZnS film**

The film's composition analysis is performed with the EDAX attached to the SEM image. A representative EDAX spectrum of CdS samples. Film consists of other peaks of Cd, S, and silicon. The dependence of the ratio of the atomic percentage of sulphur to cadmium, obtained from the EDAX measurement. Quantitative EDAX analysis of CdS films yielded highly atomic compositions, 49.35% cadmium and 36.50% sulphur. The EDAX spectrum of CdS film Figure 3.7.



**Fig. 3.7 EDAX spectrum of CdS film**

**3.7 THICKNESS MEASUREMENT**

The thin film of PbS developed by chemical bath deposition under different ambient deposition conditions has been measured by a stylo profilometer for thickness. The properties of the thin film depend greatly on the thickness of the film. Due to surface phenomenon, the properties of the thin film vary depending on thickness. Table 3.3 shows the thickness changes with the deposition time, which shows the thickness of the thin film increased with the deposition time.

**3.8 OPTICAL STUDY**

In the present study, a selected wavelength photon is directed at the sample, a relative transmission of different photons is observed, and a 500 UV-VIS NIR spectrum spectrometer is used to determine the optical band gap energy of a PbS thin film at ambient temperature. Figure (3.8) shows the optical transmission spectra and Tauc curves of PbS thin films prepared by chemical bath deposition at different times of deposition at room temperature. All films are highly transmitted in the NIR region and absorbed in the visible region.



**Fig. 3.8. shows the wavelength dependence transmittance (%) spectra.**



**Fig. 3.9 The Tauc’s plot of the PbS thin films prepared by Chemical Bath Deposition at different deposition condition in room temperature.**

The optical band gap energy (Eg) of the PbS thin films have been determined by extrapolating the linear portion of the curves of (αhν) 2 Vs (hν) as shown in Fig. (3.8). 

**Fig. 3.9 shows the deposition time dependent thickness and band gap of the PbS thin films prepared by chemical bath deposition.**

From Fig. 3.9, the band gap decreases, and thickness increases with the time of deposition, the value used for these samples and the concentration of thin films is shown in the following table.

**Table 3.3. Thickness and band gap of the PbS thin films depends on deposition time**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **SAMPLE** | **CONCENTRATION**  **(mol)** | **TIME**  **(min)** | **THICKNESS (nm)** | **BAND GAP**  **(eV)** |
| PbS1 | 0.1 | 5 | 36 | 1.58 |
| PbS2 | 0.1 | 10 | 100 | 1.48 |
| PbS3 | 0.1 | 20 | 150 | 1.15 |
| PbS4 | 0.1 | 60 | 180 | 1.05 |

**3.10 HALL EFFECT MEASUREMENT**

The voltage between the two ends of the path is the total energy required to move a small charge along the path and is divided by the load. Mathematically, this is expressed as the linear integral of the electric field and the speed at which the magnetic field changes along this path. In general, both static (invariable) and dynamic (invariable) electromagnetic fields must be included in the determination of the voltage between the two points. The Hall effect is the generation of a voltage difference in a conductor that crosses the current of the conductor to the electric current and produces a magnetic field perpendicular to the current. Thus, electrical characteristics are another important factor in the development of materials for the manufacture of solar cells. In this study, the input current is maintained at 110-5A, and in all cases the magnetic field is applied at 5.110-1. The conductivity, mobility, and carrier concentration of thin films determined by the experiment were determined. Conductivity is caused by the majority of the movements of the carriers that are either electrons or holes. So the type of carrier is defined by the sign of Hall mobility. Hall coefficients are the characteristics of materials made by conductors. In addition, the Hall coefficient depends on the type of charge carrier that constitutes the current. Therefore, the Hall coefficient of the film is used to determine the type of charge carrier [5]. The sign is positive and the load carrier is caused by electrons. The result showed that the prepared PbS thin film had a positive conductivity (type p).

The mobility is the speed at which the drift speed per electric file unit is generated. The mobility of semiconductor materials depends on the concentration of impurities, temperature and load carrier. The mobility of the PbS thin film is calculated from measurements of the Hall effect. The sample is connected to the Hall Effect's current and voltage terminals and the film's mobility is estimated to be 11.78 cm2/Vs.

The Hall coefficient of semiconductor film is used to describe the materials from which it is manufactured, because its value depends on the current charge carrier. The value of Rh in ammonia concentrations is found by examining the relationship between Hall voltage and current. The necessary theory for calculating the carrier concentration (n). This is estimated by calculating the Rh value. The carrier concentration of the PbS4 film shows a range of approximately 3.1847 x 1017 cm-3, which is comparable to the literature reported [5].

**3.11 HOT PROBE METHOD**

The type of conductivity of the film is determined by the hot probe method. In this method, the thermal emf or Seebeck voltage signals generated by the temperature gradient determine the type of conductivity.



**Fig. 3.10 HOT PROBE SETUP**



**Fig 3.11 Hot-Probe characteristic of PbS4 thin film, measured at 350 oC.**

Two probes—one hot and the other cold according to the established method—were used to make contact with the sample surface. The direction of current flow can be used to evaluate conductivity [6]. The electron current for a p-type conductor will move from the hot probe to the cold probe [7]. Similar behaviour is displayed by the PbS4 sample in Fig. 3.11. They have the same outcome and are p-type conductivity-related to the Hall Effect.

**3.12 SCANNING ELECTRON MICROSCOPE (SEM)**

SEM analysis of the surface morphology of PbS thin films was done. The SEM picture of a PbS thin film is shown in Fig. 3.12 at two different magnifications. The PbS film surface is compact and completely coated with smooth, spherical grains of varying sizes and odd shapes. These nanograins range in size from 300 to 1000 nm on average.

The highly magnified image (127.57 kx) demonstrates unmistakably that the grains are made of cubic PbS. The lower magnified (94.03 kx) micrograph showed that the film surface is homogeneous with compact growth, and the substrate is well coated with a significant number of spherical grains. The distribution of the grain is variable, yet reasonably smooth.

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1. **(b)**

**Fig. 3.12 SEM image of PbS thin film at magnification (a) 127.57kx and (b) 94.03kx.**

**3.13 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDAX)**

Using EDAX connected to a SEM image, the film's composition is examined. A typical EDAX spectrum of the PbS sample. PbS makes up the film; there are no additional spectral impurity peaks. The relationship between the atomic percentages of lead and sulphur as determined by EDAX measurements. According to quantitative EDAX analysis of PbS film, the atomic composition is extremely stoichiometric, consisting of 59.81% lead and 40.19% sulfur. The PbS film's EDAX spectrum.



**Fig. 3.13 EDAX Spectrum of PbS film**

**4. SUMMARY AND CONCLUSION**

ZnS, CdS, and PbS thin films were created in the current work using chemical bath deposition. The films were annealed in a vacuum system at two distinct temperatures, 350 0C and 200 0C. The profilometer's stylus was used to measure the thickness of the ZnS and CdS materials. With the help of an LC 500 UV-Visible Spectrometer, the following properties of the deposition thin films are measured: transmittance, band gap, reflectance, refractive index, and extinction coefficient.

The optical transmission spectra of ZnS range from 70 to 90%, while those of CdS range from 40 to 60%. The annealing temperature of the thin ZnS and CdS films is rising even as the optical band gap narrows. Pure ZnS and CdS have a wider optical band gap. Therefore, the optical band gap is affected by the annealing temperature. ZnS has a band gap of 2.61 eV before annealing, 2.48 eV after annealing, and 2.37 eV after annealing. 2.35 eV and 2.34 eV are the measured direct band gaps for annealed CdS thin films. Without annealing, a 2. 37eV straight band gap is produced.These ZnS and CdS band gap values are suitable for photovoltaic applications.

The ZnS film surface and the CdS film surface are both compact and thoroughly covered in the SEM picture, with a smooth surface and irregularly formed, randomly sized spherical grains. ZnS nanograins typically range in size from 200 to 300 nm, while CdS nanograins typically range in size from 200 to 1000 nm. ZnS thin films had 18.93% zinc and 8.63% sulfur, while CdS thin films contained 49.35% cadmium and 36.50% sulfur, according to quantitative EDAX analysis.

Either Pb2+ and S2- ions condense one by one on the substrate surface to form a PbS film, or PbS colloidal particles are absorbed to form a PbS film. The glass substrates were properly cleaned before being placed in the deposition chamber with the necessary quantity of prepared solution. PbS layers are black in colour and have a smooth surface as-grown.

During the film deposition process, the growth rate in the chemical path deposition time was maximized. The transmittance and band gap of the optimized film were measured by the UV-VIS-NIR Spectrometer in the 400-2500 nm range, and the electrical investigations were measured with the Hall effect and Hot probe. It was found that as deposition time increases, the band gap narrows and thickness rises.

The PbS used to make the conductor has a property called the Hall Effect. The sort of charge carriers that make up the current also affects the Hall coefficient. As a result, the type of charge carriers is determined by the films' Hall coefficient. For the PbS sample, the Hall coefficient was computed. Charge carriers are present because of holes, and the indication is positive. The outcomes demonstrated that the PbS thin films that were created have positive (P-type) conductivity. According to the observations, the Hall coefficient is 19.65 cm3/C. The films' mobility is 11.78 cm2/Vs. The Hall experiment was used to determine the carrier concentration of the PbS thin films with regard to 3.1847 x 1017 cm-3. The positive Hall coefficient of the formed PbS sheets validates the p-type conductivity.

Using the hot probe approach, a negative voltage measurement that is correlated with the Hall effect is used to confirm the presence of P-type semiconductors. Additionally, PbS thin films must be deposited and characterized via chemical bath deposition.

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