CHAPTER II
REVIEW OF LITERATURE

2. INTRODUCTION

Devices made in the form of thin film had many advantages over the bulk materials because of superior performance, high reliability, and extreme compactness, reduction in size and weight and lower power consumption. Due to these, materials in thin film are preferred much for fabricating devices.

Preparation of the nanocrystalline thin film materials are of great interest due to their electrical, optical and mechanical properties being superior to those of conventional coarse granular structures [1-4]. In the following section, a brief literature survey relating to the methods of preparation of sulphide of lead are described.

2.1. SOL GEL METHOD

Sol Gel method found to be popular in recent timed for the preparation of inorganic materials. This method has a various advantage like (i) ambient temperature (ii) high purity of precursors (iii) product homogeneity (iv) low temperature of sintering and (v) good control of particle size [5].

Thin film of lead sulfide Nanoparticle was formed by sol gel method [6]. Doped hybrid films with lead sulphide particles were prepared by mixing a colloidal solution of lead sulphide
nanoparticles with solutions of polymerizable silanes and zirconium alkoxides. The matrix solution was synthesized by reacting 3- (trimethoxysilil) propylmethacrylate, Meta acrylic acid, and zirconium n- propoxide. Sulphide particles were produced by reaction of lead acetate in methanol with thioacetamide and control of particle size was achieved by using 3-mercaptopropyltrimethoxy-silane. The methanolic solution containing the lead sulphide colloids was added to the matrix solution, nanocrystallites were fabricated. The sol was filtered and single layer films were deposited on glass by dip coating method and cured for one hour at 70°C or 130°C. The x-ray studies showed the presence of spherically shaped particles with nanometric diameter.

2.2. SILAR METHOD

In SILAR the substrate is treated separately with each precursor and rinsing separates these treatments. As the rinsing isolates the individual steps, the adsorbed species on the substrate surface control the reactions and the growth takes place layer by layer.

Lead Sulphide thin film was grown on soda lime glass by successive Ionic Layer Adsorption and Reaction method [7] and studied structural and topographical developments of thin films. The aqueous solutions were Pb (CH3COO)2, trimethonlamene [N(CH2CH2OH)3] and thioacetamide (CH3CSNH2) respectively.
The growth cycle consists of four steps; adsorption of lead precursor solution for 20ns, rinsing with purified water for 80ns, reaction with sulfide precursor solution for 40s and rinsing with purified water for 80s. By the repetition of the above process, different thickness of lead sulfide film were formed. XRD shows the polycrystalline in nature. The nucleation and the development of the roughness of the grown Lead Sulphide thin films were studied by using Atomic Force Microscopy. As the film grow thicker, the increase in roughness continued, but more slowly than in the initial phase of the growth. The roughness development of the lead Sulphide thin films is different from that of SILAR grown ZnS thin film on a glass substrate [8]. The roughness development of the lead Sulphide thin film was parabolic.

Lead sulphide thin films were prepared on silicon substrates using different precursor solutions such as Pb (CH₃COO)₂ + C₆H₁₅NO₃ + CH₃CSCH₂, Pb (CH₃COO)₂ + CH₃CSCH₂, Pb (NO₃)₂ + CH₃CSCH₂ using SILAR method at room temperature [9-11]. The highest growth was found when triethanolamine complexed lead was used as precursor. The lowest growth rate was detected when lead acetate used as a precursor. Properties of the film grown were compared with different precursor solutions. The thickness of the film was calculated by dissolving the film into con HNO₃ and found the lead concentration in the solution using
Techtron Atomic Absorption Spectrometer. XRD shows the films were polycrystalline cubic and a high preferred orientation was observed in films. The roughness of the grown Lead Sulphide thin films was measured by Atomic Force Microscopy presented the roughness depends on the film thickness. From the SEM images it was observed that, the grains were smaller when lead Acetate was used as a precursor.

2.3. CHEMICAL DEPOSITION METHOD

This method depends on the deposition of the film from aqueous solution by passing a current with the appropriate control over the deposition parameter such as bath composition, temperature, ph, and current density.

Polycrystalline thin films of lead sulphide were chemically deposited on titanium, aluminum and stainless steel substrate [12]. Aqueous solution of analytical reagent grade Pb (NaO3) 2 and Na2S02O3 were used as a Lead and sulphur sources respectively. The ph of the solution were controlled by adding a few drops of dilute Hno3 in the case of Pb (NaO3) 2 and Na2S02O3. Lead Sulphide films were prepared at room temperature by employing a potentiostat on the three substrates. It was observed that the deposition would occur pH were between 2.7 – 2.9. From the XRD studies it was found that higher degree of crystallinity for the films on a Aluminum substrate than films on Titanium substrate. On the other hand pure, Lead Sulphide
formation observed for Stainless Steel substrates. SEM analysis show polycrystalline in nature and their average grain size was in micrometers. Thickness determined to be 0.5 micrometers thick by the Atomic Force Microscopy.

Nanocrystalline Lead Sulphide thin films were prepared by using chemical bath deposition technique and made a comparative study with the standard Lead Sulphide were performed [13]. The nano crystalline film was obtained at a shorter reaction from reducing bath without doping element. The parameters such as ph, temperature and concentration of the reactant were kept constant. The morphological properties of the film were studied from SEM analysis. It showed a continuous layer with grain size around 50 nano meter and less. This film is also very adherent to the glass substrate and has brown color. Both the nanocrystalline and standard Lead Sulphide films presented the p-type conductivity, determined by the hot probe method. Spectral distribution measurements of photoconductive signal revealed a shift of the maximum sensitivity towards shorter wavelengths for nanocrystalline films.

Nanoparticle films of Lead Sulphide were grown on p-type silicon substrates from an alkaline chemical bath containing equal proportions of lead acetate and Thiourea [14]. The temperature of the bath was maintained at 35c and ph of the solution = 10.25 and was stirred continuously. Thin films of Lead Sulphide were
grown on p-si substrates and studied the change of majority carrier
type from p to n in Lead Sulphide semiconductor nanoparticle. From
the Hall effect studies Lead Sulphide semiconductor
nanoparticle films show a change in majority carrier type. Films
are found to be p-type for the DC-bias of more than 24V whereas
grown as n-type for a Dc bias of 36, 48 and 68V respectively. The
 grain Size estimated by the TEM studies clearly shows the
decrease in the average grain size with a decrease of DC bias
applied to the substrate and the peak broadening in X-ray
diffraction patterns for films show a decrease with decrease of
DC-bias from positive to negative through zero applied to the
substrate.

Effects on surface structure on photosensitivity of the film
were studied during film preparation they added small quantities
of Br-1 ions were introduced into the bath in the form of a KBr
solution [15]. The films showed good stoichiometry in all their
thickness. The electron microscopy and the atomic force
microscopy showed that the mean grain size of the lead Sulphide
formed on the substrate increased with KBr concentration in the
bath by the linear dependence. The photoelectric and electrical
properties of these polycrystalline samples are mainly determined
by the surface and not by the bulk characteristics of the film.

Lead Sulphide was grown on the glass substrate previously
coated with Lead Sulphide colloidal particles on a poly vinyl
alcohol solution. The Lead Sulphide films obtained with the inclusion of the polymer showed non-oxygen-containing organic contamination [16]. The amount of effective nucleation centers and the mean grain size have being controlled by the substrate colloidal coating. For the study of surface composition of the Lead Sulphide films XPS spectra were taken and the BE curves were analyzed. Roughness measured using the AFM images and XRD analysis showed galena type cubic structure for all the samples.

Structural, optical and photoelectrical properties of the prepared film were studied [17, 18]. The main characteristic of the film was when the thickness range lies between 0.12 – 0.54 micro meter it had photosensitivity, this parameter is mainly influenced by many factors such as film thickness, grain and crystallite size, faults probability, number of layers, thermal treatment and the presence of impurities. When increasing the film thickness transmission and the reflectivity decreases, this phenomenon is observed in the lead Sulphide films [19]. The surface roughness increases with increasing grain size, which leads to the decreases of the reflectivity [20]. Depending on the deposition time film of different thickness and films of different colours appearance has been obtained.

Films were obtained for different bath temperatures and their structural and optical properties were studied. It was
observed that the intensity of the peaks increases with the temperature deposition of the films [21]. It was found that the spectra of the film differ from that of single crystal, in both absolute values and energy position of the critical points. The low values of e for the films are due to empty space between the aggregates that comprising the films.

Nanoparticle films of Lead Sulphide were deposited on glass, quartz and n-type silicon substrates respectively from the alkaline solution [22-27]. It showed films found to be crystalline both by TEM and XRD studies. The grain size measured by TEM is very much similar to the size calculated from the XRD peaks width. Absorption Coefficient for the films was calculated using the reflectance and the transmission. The (ahn) m Vs hn show linear behavior indicating presence of direct optical band gap in the nanoparticle films. The resistivity of the films is found to be increased with decrease in grain size.

2.4. ATOMIC LAYER DEPOSITION

PbS nanocrystals have demonstrated highly efficient multiple exciton generation (MEG), making it a potentially attractive material for next generation solar cells [28]. Deposition of PbS thin-films has been demonstrated by a variety of techniques, including Chemical Bath Deposition (CBD) [29], Successive Ionic Layer Adsorption and Reaction (SILAR) [30], Electrochemical Atomic Layer Epitaxy (EC-ALE) [31] and Atomic
Layer Deposition (ALD) [32]. The sub-nm precision in film thickness of ALD at low vacuum pressures (10.2 torr) and temperatures (100-350 °C) suggest that it could provide an effective means of mass production of nano-structured materials.

Films of PbS were grown on silicon (100) and soda-lime glass substrates by ALD[33] using Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)lead(II), (Strem Chemicals, inc.) and 3.5% H₂S in N₂ (Accurate Gas Co.) as precursors. The substrate temperature was varied from 140–220 °C. The lead precursor was volatilized at temperatures ranging from 140-175 °C. Reactions were carried out in a Cambridge NanoTech Savannah 200 reactor with no carrier gas.

Film thicknesses were measured using X-ray reflectivity (XRR) and confirmed with ellipsometry. A linear growth rate of 0.18 nm/cycle was measured for film thickness varying from 9-72 nm. Previous reports of ALD PbS using Pb(tmhd)₂ reported a maximum growth rate of 0.6 nm/cycle with a precursor sublimation temperature of 120 °C. In this study, an elevated source temperature is compared to the previous reports, suggesting that a partial decomposition of the precursor may have led to enhanced reactivity of the ALD reaction. However, X-ray photoelectron spectroscopy (XPS) analysis of the PbS film showed no traces of carbon or oxygen contamination in the film, and film growth. X-ray diffraction (XRD) analysis of
the films indicated a polycrystalline cubic structure of PbS. A coarse grain structure was revealed in AFM and TEM measurements of the film, with film roughness increasing with number of cycles, corresponding to grain growth. While elevated growth rates are achieved at higher precursor sublimation temperatures, the precursor also degrades at a faster rate. Optimization of the ALD reaction with respect to sublimation temperature will be presented.

2.5. FLASH EVAPORATION

Because of the higher temperature the material has tendency to decompose or dissociate during evaporation without leaving any residue. On condensations the deposit will retain the composition of the evaporant.

Amorphous thin films of alloys of Arsenic tri sulphide and lead sulphide were prepared by the flash evaporation [34]. The optical transmission and reflection spectra of the compositions were recorded at room temperature in the spectral range 200-2500nm, which covers the fundamental absorption edge and the interband transition regions of the semiconductor. Because of the wide difference in the values of the refractive index of the semiconductor thin film and that of the glass substrate, interfaces fringes in all the transmission and the reflection spectra. At higher photon energies in the interband transition region, there is appreciable modification of the photon energy dependence of the
refractive index with addition of Pb to the alloy system. The broad peak in the refractive index increases with intensity and shifts towards a low energy in compositions that contain higher concentrations of Pb. The optical energy band gap for the films continues to decrease with the concentration of PbS.

2.6. CHEMICAL VAPOR DEPOSITION

Mixed thin films of Lead Sulphide were prepared on the glass substrate by spray pyrolysis technique for various substrate temperatures 300, 320 and 340°C. Structural and Optical properties were studied [35]. The XRD patterns reveal that the film prepared at 300°C has CdO phases only except the low intensity PbO phases start to develop. From these results it is realized that 340°C is the critical temperature for the growth of PbO phases. The resistivity and the sheet resistance of the films increase with increase in the substrate temperature. This may be attributed to the development PbO phases with increase in substrate temperature. The direct band gap value of mixed films is about 2.6 and 2.37 eV respectively. The reduction of lead concentration in the mixed films may improve the optical resistance.

2.7. Langmuir – Blodgett Technique

Pervoskite type thin films are constructed on hydrophilic quartz substrates from monolayers of long chain alkyl ammonium chloride on the sub phase containing the mixture of Pb2+ and CH3Nh3+ ions via Langmuir – Blodgett technique [36]. The
nanoparticles were prepared by reacting the LB film with H2S gas. The film exhibits a absorption band at 331nm, characteristic of the perovskite excitation transition [37], which confirms the formation of perovskite LB films. Reaction with H2S gas will cause a gradual disappearance of this band indicating the production of the PbS nanoparticles. Morphology of the PbS nanoparticle is observed by TEM it showed square nanoparticles with average diameters of 10-30nm from layered perovskite thin films are formed.

2.7. VACUUM DEPOSITION

Nanostructures thin films were prepared by vacuum evaporation of metal on textolyte, glass and alumina at 80k. After annealing to room temperature and exposure to air an oxide shell was formed on particles. A series of experiments involved the injection of dry air or hydrogen sulfide, right after the Pb condensation the chemiresistive properties was studied. For the lead on poly (p-xylene) films the sensitivity to ammonia and humidity were investigated it found the films were sensitive only to the humid ammonia. For the lead on glass and alumina substrates dry air was injected into the chamber just after lead deposition. After the introduction of oxygen the conductance decreased much faster than in vacuum [38].

When the films were annealed to room temperature the condensates were found to be more conductive. The fact arises
due to smaller energy band gap of lead sulphide in comparison to the lead oxide and is promising from the point of view of practical use. The recovery times were several minutes, which is larger than the corresponding values found for oxidized films.

The good quality polycrystalline thin films were grown on ultra clean glass substrates by the vacuum evaporation technique keeping the substrate at the room temperature in a vacuum of $10^{-6}$ Torr [39]. The deposited films were annealed in the same vacuum chamber at about 80°C for two hours. The films were kept at vacuum chamber attained metastable equilibrium as suggested. [40]. The deposited films were characterized. The presence of sharp structural peaks in the XRD pattern confirmed the polycrystalline nature of the films. The absorbance and transmittance spectra of thin films of Lead Sulphide were measured by using the Fourier Infrared Transform Spectrophometer. The band gap found to be 0.42 eV.

**2.8. DIP COATING**

The Lead Sulphide nanocrystals were subsequently, transformed in the form of thin films by dip coating. In this method 0.2 ml solution of carbon tetrachloride saturated with hydrogen sulphide was spread initially with the help of syringe on a water surface containing 10-4M lead nitrates in polypropylene tray. The reaction occurs at the interface resulting in an nanocrystalline lead sulphide thin film [41]. After all the carbon
tetrachloride had evaporated, an oleic acid piston was used to compress the film slowly. The film was transferred onto a glass substrate by immersing vertically in the solution at a constant rate of 0.5cm/min and lifting it vertically at the same rate so that the film covers the dipped area. This operation was repeated many times to get the desired film thickness.

Pyramids with a square base and a triangular top were clearly observed even in the low magnification TEM image. Relatively high magnification TEM image endorse the formation of pyramids of much smaller size presumably indicating the initial generation of large numbers of primary nuclei.

Lead sulphide was confirmed by EDAX. The formation of lead sulphide has been unambiguously ascertained by XPS analysis of the samples. XP spectra revealed doublet structure of s-2p with the peaks centered around 161.4 and 168.3eV and two peaks related to Pb-4f centered around 138.37 and 143.21eV. These binding energy values are in close agreement with the values reported earlier for lead sulphide.

2.9. PULSED LASER DEPOSITION METHOD

The lead sulphide was deposited by pulse laser deposition method on a fused quartz substrate having an active area of 1*1cm2 and a thickness of approximately 1 micrometer and studied the structural stability of lead sulphide films as a function of temperature [42]. At the two edges of the substrate, gold films
were deposited for achieving good electrical and thermal contacts. High resolution X-ray generator with copper target operated at 50kv and 200ma. The angular resolution of the diffractometer is 0.0010. Measurements were done at five temperatures. Measurements were also carried out after the samples were brought back from high temperature to 300k. Temperature measurement was done using a chromel – alumel thermocouple micro welded to the gold film and by coupling an omega inc. controller to a miniature heater, temperature was controlled. From the analysis of the x-ray diffraction data nine peaks are identified for the lead sulphide and four for the gold films. Above the 375k, lead sulphide film undergoes a subtle transition from b1-phase to b3-phase as manifested by a reversal in the intensities of (200) and (220) peaks. The high temperature b3-phase of lead sulphide is retained at room temperature.

The films are highly defective and their structural properties are mainly linked to the growth processes used for the layer deposition [43, 44]. Among the new and up to date techniques used for thin film deposition, pulsed laser ablation (PLA) is one of the most versatile methods to obtain layers of several materials that can be processed into a pellet target. One of the important features of this method is based on the possibility of maintaining the stoichiometry of the ablated target in the deposited layer [45-47]. The target ablated by laser can create a highly energetic
growth precursor, leading to non equilibrium growth conditions. Therefore high quality films can be obtained at a fairly low substrate temperature. Furthermore, PLD is more flexible than other conventional techniques, and it is feasible to control the thickness of films [48,49]. With this aim, in the current work, we study the influence of the laser flux density on the crystalline quality, the surface morphology, PbS thin films on glass substrate grown by pulsed laser deposition.

The UV-PLD is performed with a KrF laser operating at 248nm with a repetition rate of 10 Hz. PbS films were deposited on corning glass substrates by ablating stoichiometric homemade targets. During the film deposition the substrate temperature and ambient pressure were kept at 400°C and 10.5 torr respectively. In order to investigate the effect of laser flux density on the surface morphology and structural properties of PbS thin film, a series of samples were deposited using the laser flux density of 2.5 J/cm², 3.5 J/cm² and 4.16 J/cm². X-ray analysis was performed by using a Bruker D8 Advance diffractometer using CuKα (λ = 1.54 Å) radiation. Surface morphology of the deposited films was studied using atomic force microscopy (NT-MDT Ntegra). Room temperature reflectance spectra were measured in the spectral range from 1500 to 2500 nm using a UV-Vis-NIR spectrophotometer (Varian Cary 5000). Microstructural investigations were carried out by scanning electron microscopy.
by using the FESEM- FEI Quanta 200. The results prove that the crystallinity, the surface quality and the optical properties of PbS thin film is dependent on the laser flux density and the optimal incident energy is around 3.33 J/cm². Surface morphology of the PbS thin films is strongly dependent on the laser incident flux density and is confirmed via R value curve in addition to AFM micrographs. A slight decrease in reflectance is observed with increase in laser flux density.

2.10. MAGNETRON SPUTTERING

Precursor films were deposited on piranha etch-cleaned glass slides by magnetron sputtering at an argon plasma pressure of 667 mPa. The uhv thin film deposition system has a base pressure of 10-6 – 10-7 Pa [50]. The layered precursor films were obtained from continuous 100 w RF –sputtering of an sb2s3 target and cycled 10 w dc sputtering of Pb with different on and off times to achieve target Sb: Pb ratios. Precursor films with 15 repeat units were prepared. Once deposited, precursor films were annealed under sulfur vapor in a two-zone tube furnace. Films were centered in an evacuated tube were heated to temperature of about 400°C for 50 min while the elemental sulfur was maintained at approximately 180°C at one end of the tube, whereas the other end of the tube maintained at room temperature, creating a sulfur flux through the tube. The morphology of as deposited and annealed films were
systematically evaluated with a field emission scanning microscope. The surface of the SEM images shows dense film morphology and that the film was composed of small crystal grains. The cross sectional image shows that the film was completely dense and homogeneous throughout its thickness with no evidence of the layered precursor structure. A preferred crystal growth orientation normal to the substrate was observed. Optical measurements indicated a direct band gap of 1.93eV and a strong absorption coefficient observed for this semseyite thin film.

2.11. ELECTRON BEAM EVAPORATION

Lead sulphide layers were prepared by thermal evaporation of lead sulphide in vacuum (10^-5 - 10^-6 Pa) and deposition onto KCL substrates at 570k. EuS layers were prepared by electron beam evaporation [51]. The thickness of lead sulphide layers was varied in the range of d=2-200nm, and the EuS layer thickness was 25 -30nm. For the prepared film effect of thickness on the thermoelectric properties of lead sulphide were studied. The thermoelectric properties of lead sulphide epitaxial thin films grown on KCL substrates if the thickness in the range d=2-2-nm, oscillations in the electrical conductivity, charge carrier concentration, hall mobility and seebeck coefficient at room temperature. This existence of oscillations is attributed to the manifestation of quantum size phenomena. If the thickness in the
range \( d = 2 - 15 \text{nm} \) it showed stage of a transition from films with channel structure to continues epitaxial films.

2.12. SPRAY PYROLYSIS TECHNIQUE

Spray pyrolysis is simple and inexpensive and requires lesser amount to produce thin films of large area than other conventional techniques [52]. Spray pyrolysis was used as early as 1910 to obtain films. Chamberlin et al [53-55] developed the technique to deposit sulphide and selenide films. Spray pyrolysis [56, 57] involves spraying a solution usually aqueous containing soluble salts of the constituent atoms onto a heated substrate. Various geometric of the spray set-up are employed [58-62] including an inverted arrangement in which large droplets and precipitates are prevented from reaching the substrate resulting in films of better quality. Better quality doped tin oxide films were prepared by spraying appropriate combinations of respective compounds [63, 64].

The control parameters in the Spray pyrolysis method are the temperature of the substrate, the solution composition, the carrier gas, solution flow rate, the deposition time and the substrate to nozzle distance and angle. Viguie and Spitz [65] have investigated the role of substrate temperature in determining the exact mechanism of film formation, which in turn affects the microstructure of the film. Films grown at low
temperature show amorphous nature and those at higher temperatures are polycrystalline [66, 67].

Review of literature shows that there has been very little work done on the preparation of lead sulphide compounds in thin form by spray pyrolysis method. However this simple and inexpensive method has been employed to produce many oxide [68-72] materials. In the present work this method is adopted.

REFERENCES

42. Sanjee Kumar*, Ramesh Chandra, Chalcogenide Letters Vol. 6, No. 6, June 2009, p. 273-278.