

CHAPTER - I
INTRODUCTION

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1.1 Thin Film:General

Thin film can be defined mathematically as a surface bounded by two parallel planes extending infinitely in two directions and restricted in the third direction known as thickness 't' of the film. The thickness 't' of the film can be changed from two to several times the wavelength of light but always remains much less than the other two dimensions. According to the nature of distribution of the deposited material on the substrate, thin films can be classified mainly into the two groups (1) Continuous thin films and (2) Discontinuous thin films.

The thin film technology has wide spread applications as it is easy to reproduce the film. Very few material is required to deposit the film on given substrate. With the help of thin film various properties of the bulk materials can be studied; which prevents the wastage of material and is economically cheap. Thin film technology has important role in the development of various fields such as microelectronics, optical coatings, integrated optics, thin film metallurgical coating, amorphous materials, surface engineering and solar energy conversion devices. New fields are also emerging for the thin films. The materials with micrometric and nanometric, and the industrial applications of microscience and microtechnology for the development of synthetic materials of tailored properties for VLSI/GSI, communication, informatics and solar energy conversion with decreasing size of active electronic devices, a higher packing density, higher speed performance and lower costs are obtained. (1).

Depending on the photoconductivity of the thin films, the films have been used in various solid state devices such as solar cells (2), photoelectric cells, photoconductors (3), thin film transistors (3,4), gamma ray detectors (5), light amplifiers, electrophotographic copying processes, television camera tube etc. (6).

1.2 Cadmium Sulphide Thin Films :

Polycrystalline thin films of CdS have received considerable attention during the recent years because of their actual and potential applications in variety of semiconductor devices such as photoconductors, photoresistors, transistors, image magnification and recently in solar cells and light activated valves for large screen liquid crystal displays (7-12).

The CdS thin films have been prepared by physical methods and chemical methods. Due to simplicity, economics and input energy, large area thin films have been deposited by various chemical methods. Electrodeposition, anodization, electroconversion, electrophoresis, electroless, spray pyrolysis, dip growth and chemical deposition etc., are some of the chemical techniques for the growth of thin films from the liquid phase (8,9). Out of these techniques, chemical deposition, which is also known as solution growth, controlled precipitation, electroless plating or chemical bath deposition, is now attracting considerable attention as it is relatively inexpensive, simple and convenient for large area depositions. It does not require sophisticated instrumentation like

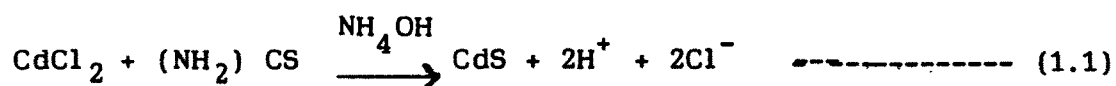
vacuum systems and other expensive equipments. The starting chemicals are commonly available and cheap materials. With proper adjustment, large number of substrates can be coated in a single run. Like electrodeposition, electrical conductivity of the substrate is not necessary. Any insoluble surface can be used as a substrate to which the solution has free access. The preparative parameters are easily controllable and better orientation and improved grain structure can be obtained. Chemical deposition results in pinhole free and uniform deposits as solution from which these are deposited always remains in to touch with the substrates. Stiochiometric deposits are easily obtained since the basic building blocks are ions instead of atoms.

Depending on the deposition conditions, such as the bath temperature, stirring, rate, pH, solution concentration etc, the film growth can take place by ion-by-ion condensation of the materials or by adsorption of colloidal particles from the solution on the substrate.

1.2.1 Experimental reports on CdS prepared by chemical methods :

Most of the CdS films have been deposited by using Cadmium salt and Thiourea in hot (80° - 90° C) alkaline medium bath by a number of workers (13-35). In general, equimolar Cadmium salt and Thiourea and NaOH solutions in the appropriate volume ratio are mixed together. The substrates are suspended from a shaft in a reaction bath and rotated continuously by a motor at constant

temperature of 80° to 90°C. After 30-40 minutes, yellow-reddish CdS films have been obtained. The overall chemical reaction, for example, is as follows :-



Cadmium ions have been complexed with $\text{Cd}(\text{NH}_3)^{+2}$

(13-15, 33-36); $[\text{Cd}(\text{CN})_4]^{+2}$ (36), and $[\text{Cd}(\text{TEA})^{+2}]$ (16,17).

Pavaskar et al (13) reported that as - deposited CdS films exist as a mixed phase (Wurtzite and Zinc Blende) and films are polycrystalline in nature. Thermoelectric power measurement showed that CdS films are n-type. The optical band gap is 2.4 eV. Kaur et al (14) have studied the kinetics of growth of CdS from alkaline solution and reported that the films in the presence of $\text{Cd}(\text{OH})_2$ in the solution were very adherent, physically coherent and specularly reflecting. Vigorous stirring of the solution decreases the powdery nature and increases adhesion. In general, the higher the deposition rate, lower is the terminal thickness. Mondal et al (16) using TEA complexed Cd^{+2} ions, have reported film growth at room temperature (30°C). After 18 hours, the substrates were covered with orange-yellow CdS deposits. At 30°C, the rate of growth was slow and the terminal thickness was 3 microns after 18 hours. It was found that the increase in temperature, increased the rate of growth of CdS but decreased terminal thickness. Nair et al (18) have been prepared very high photoconducting ($P/d > 9$) and low resistive (10^{-1} ohm⁻¹cm) CdS films by adjusting molar ratios

of Cd^{+2} to Thiourea between 1:0.5 : to 0.25 at 75°C . They reported that the films with equimolar ratios found to be inferior. The thickness on glass substrate was in the 0.3 to 0.4 micron range. The dark conductivity was $2 \times 10^9 \text{ ohm cm}^{-1}$ and activation energy was $> 1 \text{ eV}$.

Sahu and Chandra (20) added Li_2O_3 (10^{-5} M) in to bath. The optical band gap of CdS:Li films was 2.35 eV and the resistivity of the films was lower. Pavaskar et al (13) prepared CdS:Cu films by addition of copper salt (CuI , 0.1 wt%) to the bath. They reported that the addition of cations like Cu, AS, In, Zn, etc., to the bath makes the films amorphous. The field effect measurement showed that, the density of states was of the order of $10^{19} - 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$. The carrier density was 10^{14} cm^{-3} and mobility was $5 \text{ cm}^2 \text{ V}^{-1} \text{ Sec}^{-1}$. The Lithium doped CdS films by adding Lithium salt (0.1 wt%) to the bath were prepared by Shikalgar and Pawar (22). The XRD study showed that CdS:Li films are polycrystalline and contain a mixture of 90% of β cubic and 10% hexagonal forms of CdS . The optical properties of these films were also studied. Bargale et al (23) prepared Na doped CdS films by adding Sodium Sulphate - (1 wt%) to bath. They reported that Na doped films become less crystalline. The thermoelectric power and conductivity experiments showed that the films are n-type and Na acts as an acceptor. Warad et al (25) prepared CdS:Bi films by addition of Bismuth Nitrate (0.1 to 5 wt%) to the bath. They have reported that the thickness of the film increased with doping levels and attains maximum at

2wt% Bi doping. The band gap decreased to 2.2 eV from 2.4 eV. The thermoelectric power, mobility and conductivity were higher for Bi doped CdS films. The Al doped CdS films by adding $\text{Al}_2(\text{SO}_4)_3$ (0.1 wt%) to bath were prepared by Lokhande and Pawar (27-29). They have reported that, the crystallinity was improved with CdS:Al films. The surface state density was $10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$. Pawar et al (30) prepared CdS:In films. The Indium doping was reported to be 0.01 wt% They reported the structural and electrical characterization of the films. Pawar and Deshmukh (32) prepared Indium doped CdS photoanodes and reported that Indium doping has lowered the band gap energy. The absorption coefficient ' α ' was found to be increased with increased doping concentration from 0.005 wt% to 0.01 wt%. Deshmukh et al (33) have prepared Antimony doped CdS films. The doping range was from 0.005 to 1 wt%. They have reported that the films were polycrystalline in nature for lower doping and becomes less crystalline beyond 0.075 wt%. All the samples were n-type and carrier concentration was of the order of 10^{19} cm^{-3} . The optical band gap was decreased with increased doping concentration. Hernandez et al (34) have prepared Sulphur-Annealed CdS films. They reported that the films were yellowish and with a good adherent on the substrate. They have studied the influence of open tube Sulphur annealing on the structural and optical properties of CdS films.

Lokhande (37) has reported on CdS film deposition

from an acidic bath using sodium thiosulphate as a sulphide source. The films were prepared by mixing equimolar solutions of CdSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ and the bath was heated to 85°C for 15-20 minutes. The films were yellowish. Film thickness was between 0.1 - 0.15 micron. Room temperature resistivity was $10^3 - 10^4 \text{ ohm cm}^{-1}$. The optical band gap was 2.25 eV. Photoelectrochemical characterization showed that the films were of n-type and photoactive.

1.3 Statement of the problem :

The Cadmium Sulphide claims amongst few of the best photoconducting materials. It has received considerable attention during recent years because it is the most widely used visible - light photoconductor, with high photoconductive gain. The CdS has created interest due to their feasibility in fabrication of economical heterojunction solar cells. It has proven applications such as transistors and recently in light activated valves for large screen liquid crystal displays. It is thus clear that CdS films used in different applications should yield films of desirable photoelectric properties.

Many investigations on the films of CdS have been carried out concerning its photoconductivity properties. Many attempts have been made to increase the photoconducting properties of CdS films by adding the different impurities. Many workers have reported that photoconductivity of CdS film increased with

doping trivalent impurities. However, the photoconductivity decreased with doping of monovalent impurities. It has been reported that the trivalent impurities act as donors while monovalent impurities act as acceptors. A very few work has been carried out by variation of Cd:S ratio. Nair and Nair have reported on highly photosensitive CdS thin films prepared by molar ratios of Cd⁺² to thiourea as 1:0.5 and deposition time of 90 minutes; by solar assisted chemical deposition method (21).

In the present investigation, CdS films will be prepared by adjusting the volume ratios of Cd⁺² to Thiourea as 1, 1.25, 1.66, 2.5 and 5. The films will be prepared from aqueous bath by Chemical bath deposition method, as it offers many more advantages over other methods. Thiourea will be used as a sulphide ion source. The CdS films prepared for various Cd:S volume ratios, will be characterized by means of XRD, optical absorption and SEM techniques to study the effect of Cd:S ratio on the particle size, optical band gap and microstructure. The effect of annealing in nitrogen atmosphere on optical band gap, particle size and surface structure will also be studied.

As CdS is one of the best photoconducting material, the Cd:S volume ratio will be optimized to get maximum photoconducting CdS film. The photoconductivity property will be studied in detail by measuring dark and light conductivity, intensity response of photocurrent, spectral response, rise and decay time in air at room temperature. The photoconductivity of the

optimised film will be studied in vacuum in order to study the effect of surface adsorbed oxygen on photoconductivity property.

It has been reported that 0.1 wt% Al doping increases the photoconductivity and 0.1 wt% Cu doping decreases the photoconductivity of CdS film. The optimized Cd:S volume ratio CdS film will be further doped separately by 0.1 wt% Al and Cu each. The effect of Al and Cu doping on the photoconductivity properties of the optimized Cd:S volume ratio CdS thin film will be studied in air as well as in vacuum at room temperature. The doped samples will be characterized by XRD, optical absorption and SEM to study the effect of Al and Cu doping on the particle size, optical band gap and surface structure. The results obtained will be presented.

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