ABSTRACT

During the past decade there has been a large amount of research activity in the field of thin film technology for its different practical and commercial applications. Realising its importance in technology, academic institutions, national laboratories and industries have entered this activity. The interests are varied and encompass both fundmental amd applied aspects for use in space, defence, industry and other areas. Many organisations have installed automatic as well as manually operated deposition systems.

In this work, a number of oxide and sulphide thin solid films have been prepared and their properties have been studied in relation to their practical and commercial applications. These films were prepared by (1) Dip technique and (2) Open air chemical vapour deposition technique (OACVD). The first has been used for deposition of oxide (SnO_2, CuO) and sulphide ($Zn_xCd_{1-x}S$, SnS, SnS_2, MoS_2 & Cu_2S) films, while the second, for transparent conducting tin oxide (SnO_2) films only.

In the first chapter, an introduction to thin film technology, its different applications in science and technology and a brief review of different techniques for deposition of thin films have been discussed.

In chapter two, details of the DIP TECHNIQUE are given and preparation of oxide (SnO_2 & CuO) films using this technique and their characterization have been discussed. In the dip technique as used for oxide films the substrate is withdrawn vertically at a controlled speed from a starting solution containing a suitable metal nitrate or chloride and alcohol, when a liquid layer adheres to the substrate surface. It is then baked in a furnace under atmospheric conditions, when the liquid film reacts on the substrate inside the furnace and is converted to a solid film. Undoped and F-doped transparent semiconducting films with tin dioxide as the active material have been prepared by the hydrolysis of stannous chloride which takes place when a substrate is

withdrawn from a methanol solution of $SnCl_2$. $2H_2O$ and baked at a high temperature as described. F-doping is achieved by adding NH_4F to the starting solution. The maximum film thickness obtainable per dipping (dip-withdrawal-bakecycle) is about 0.58 μm, but can be increased by multiple dipping. The films appear to be a mixed phase consisting of crystalline tin dioxide over an amorphous background, probably of Sn(OH)Cl. The film produced by a single dipping consists of a small number of isolated SnO_2 crystallites. But as the film thickness is increased these crystallites increase in number and finally merge into a continuous layer. Typical values of resistivity of F-doped films produced by this method is 2.4×10^{-2} Ω cm, with an average transmission of 85% at a thickness of 2.96 μm. This work has been published in the ***"Surface and coating technology"*** Vol. 102 (1998) Page 73-80.

For the preparation of copper oxide (CuO) films, a methanolic solution of cupric chloride ($CuCl_2.2H_2O$) was used. These films were prepared at three different baking temperatures. ASTM data confirms that the films are of CuO phase. The optical band gap of the films calculated from optical absorption measurements is 1.85 eV which is quite comparable with the reported in the literature.

The third chapter describes the deposition and study of various properties of sulphide films. For the preparation of sulphide films, the starting solution contains a suitable compound of sulphur like thiourea or amonium thiocyanate in adddition to a metallic chloride or nitrate. The films prepared were of $Zn_xCd_{1-x}S$, SnS & SnS_2, MoS_2 and Cu_2S.

For preparation of $Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) alloy thin films by this technique, an alcoholic solution of the corresponding metal nitrates and thiourea was taken as a starting solution from which the substrate was withdrawn and baked at 400^o C - 600^o C. X-ray diffractometric study suggests that for zinc atomic fraction $x \leq 0.6$ films prepared at a baking temperature of 500^o C are homogeneous with a hexagonal (wurtzite) structure. Increase in the proportion of zinc in the starting solution is found to produce a decrease in the lattice parameter. SEM studies reveal an increase in grain size with Zn atomic fraction x upto a value of 0.6. For $x > 0.6$, the films appear to have an amorphous character, as no distinguishable peaks can be seen in the X-ray diffractograms. The SEM micrographs also do not show any clearly defined grains over this range. Values of bandgap obtained from optical absorption measurements as well as from spectral response of photoconductivity, are in good agreement with each other and vary monotonically from 2.30 eV (CdS) to 2.69 eV ($Zn_{0.6}Cd_{0.4}S$) over the range $0 \leq x \leq 0.6$. For $x > 0.6$, the films appear to develop an amorphous nature and the optical band gaps obtained from optical absorption measurement are much less than those obtained from photoconductive measurements. This work has been published in the ***"Thin Solid Films"*** Vol. 322/1-2 (1998) Page 117-122.

For the preparation of SnS and SnS_2 films the starting solution was prepared by dissolving $SnCl_2$ and thiourea in methanol. The structure and photoconductive properties of these films and their conversion to tin dioxide by annealing in atmospheric condition have been studied. XRD and SEM data suggest that good quality SnS and SnS_2 films are obtained at a baking temperature of 300^o C and 360^o C respectively. Values of bandgap for SnS and SnS_2 obtained from spectral response of photoconductivity are 1.4 eV and 2.4 eV respectively. The bandgap values for SnS_2 also agree with that obtained from optical absorption measurements. Optical absorption data for SnS_2 and Sb-doped SnS_2 films shows an increase in bandgap with increasing dopant concentration. However, increasing dopant concentration is accompanied by a loss in crystallinity as observed from XRD data. Annealing in atmospheric condition both of SnS and SnS_2 films at 400^o C converts them to transparent conducting SnO_2.

In the last two sections of this chapter, preparation of MoS_2 and Cu_2S thin film and their optical & structural properties have been discussed briefly.

In chapter four we discuss a new technique developed by us, which is very simple and cost effective. This is the Open Air Chemical Vapour

Deposition (OACVD) technique. This technique was used for the preparation of transparent conducting undoped and doped (Mo, Sb & F) tin dioxide films. In OACVD technique, the substrate was placed vertically in the central region of a long tube heated from outside of the tube in atmospheric condition by winding a heater coil on its outer surface. When the substrate attained the desired temperature then the starting material (for SnO_2 film; $SnCl_2.2H_2O$ with few drops of water) kept in another container placed at the bottom of the tube was heated separately. White fumes, which contained $SnCl_4$ vapour, were given off by the paste and deposited SnO_2 films where they came into contact with the hot substrate. The electrical, optical, XRD & SEM properties were studied. Films were deposited on glass and mica substrates. The grain size of the film deposited on mica substrate was larger compared to those prepared on glass substrate. Optimum concentration for each dopant, at which the sheet resistance is a minimum, was determined. 4.5 at% F-doped SnO_2 films show the lowest resistivity ~ 4×10^{-4} Ω cm and average optical transmission of 80% at a thickness of 3500 A°. This work has been published in the ***"Thin Solid Films"*** Vol. 307 (1997) Page 221-227.

The fifth chapter summarizes the work presented in the thesis and future work that may be carried out in the field is suggested.