CHAPTER - 5

**Concluding remarks*

**Proposed future work*

In this present work, we have reported two techniques for the deposition of thin films. They are the DIP TECHNIQUE and the OPEN AIR CHEMICAL VAPOUR DEPOSITION (OACVD) TECHNIQUE. Using the DIP technique, we have prepared a few oxide (SnO_2 & CuO) and sulphide ($Zn_xCd_{1-x}S$, SnS, SnS_2, MoS_2 & Cu_2S) thin films, while the OACVD technique has been used for the deposition of SnO_2 films only. The films were characterised by various standard methods. The major observations and conclusions drawn from the work reported in this thesis are presented along with suggestions for future work.

I. THE DIP TECHNIQUE

The dip technique has been developed as a simple and inexpensive process for the deposition of oxide and sulphide films. For both types of films, the film-forming process consists of dipping and withdrawal of the substrate from a suitable starting solution and its subsequent baking at a high temperature. The starting solution has methanol as the solvent, in which the corresponding metallic chlorides are disolved for the preparation of oxide films. For sulphide films, it also contains a suitable sulphur containing compound such as thiourea or ammonium thiocyanate in addition to the corresponding metallic chloride or nitrates. These films were smooth, highly uniform and strongly adherent to the substrate.

Undoped and F-doped transparent semiconducting films with tin dioxide (SnO_2) as the active material as also copper oxide (CuO) films have been prepared. The transparent conductor with SnO_2 as the active material film is formed in situ by the hydrolysis of stannous chloride (with NH_4F added for F-doped films) which takes place when the substrate is withdrawn from a methanol solution of $SnCl_2.2H_2O$ and baked at a high temperature as described above. The maximum film thickness obtainable per dipping cycle is about 0.58 μm, but can be increased by multiple dipping. The film consist of a mixed phase consisting of small amount of SnO_2 crystallites over an amorphous background, probably of Sn(OH)Cl. The films have a featureless microstructure and a high resistivity. The high resistivity is thought to be due to the presence of Sn(OH)Cl along with small amounts of crystalline SnO_2. But as the film thickness is increased by repeating the number of dipping, these crystallites increase in number and finally merge into a continuous layer after 15-20 dippings. However, even at this stage there is a large amorphous background present, as shown by the high value of resistivity. viz, 2.4×10^{-2} Ω cm compared to 2.4×10^{-4} Ω cm for CVD SnO_2 films. In spite of the presence of the amorphous background the films are quite transparent and have a high optical transmission. These are suitable for those display application where the current requirment is low, e.g. liquid crystal or electrochromic displays.

The copper oxide films were prepared at different baking temperatures using methanolic solution of $CuCl_2$. The films have the crystalline CuO structure and its optical band gap as determined from the optical absorption data is 1.85 eV.

$Zn_xCd_{1-x}S$ ($0 \leq x \leq 1$) alloy thin films prepared at 500° C using an alcoholic solution of the corresponding metal nitrates and thiourea. $Zn_xCd_{1-x}S$ ($0 \leq x \leq 0.6$) were hexagonal in structure, whose lattice parameter c and a are found to decrease with increase in x. An increase in x also produces a similar drop in the thickness of the film, the total number of (Cd + Zn) moles in the starting solution being kept constant. This agrees well with the fact that the Zn atoms have a relatively smaller size compared to Cd atoms.

The bandgaps obtained from optical absorption and spectral response of photoconductivity measurements are in good agreement with each other and vary from 2.30 eV (CdS) to 2.69 eV ($Zn_{0.6}Cd_{0.4}S$). Beyond this range (x>0.6) the films are amorphous and the bandgaps obtained from optical absorption measurements (optical bandgap) are much less than that obtained from photoconductive measurements due to a change from crystalline to amorphous structure. Surface morphology study by SEM as well as XRD data also confirm that good crystallinity is obtained upto a zinc atomic fraction of 0.6 only.

Tin mono- and disulphide (SnS & SnS_2) were prepared using an alcoholic solution of the corresponding chloride and thiourea. SnS & SnS_2 thin film show good crystalline structure when prepared at a baking temperature of 300° C for SnS and 360° C for SnS_2 films. Bandgaps obtained from photoconductivity measurements are 1.4 eV and 2.4 eV for SnS and SnS_2 films respectively. Optical absorption measurements on SnS_2 films also yield a bandgap value of 2.4 eV. Antimony-doping of SnS_2 films produces an increase in bandgap along with a sharp reduction in crystallinity. Annealing in atmospheric condition at 400° C both SnS and SnS_2 films convert them to transparent conducting tin dioxide, thus providing an alternative route for its preparation.

For MoS_2 and Cu_2S thin films, methanolic solution of ammonium molybdate and copper nitrate respectively along with ammonium thiocyanate as a starting solution were used. MoS_2 and Cu_2S films with good crystallinity were obtained for baking temperature of 360° C, 450° C and 500° C respectively. Optical absorption data shows the films are uniform and homogeneous. The optical bandgaps are 1.80 eV and 1.4 eV for MoS_2 and Cu_2S respectively which were calculated from optical absorption data.

II. OACVD TECHNIQUE

A simple and low-cost technique has been developed in our laboratory for the preparation of transparent conducting tin dioxide films. Using this technique,

transparent conducting undoped and doped (Mo, Sb & F) tin dioxide films have been prepared on glass substrates at 400° C. Here the substrate was placed vertically in the central region of a long tube heated from outside by winding a heater coil on its outer surface. The starting material in the form of $SnCl_2$ paste was heated at the bottom of an open-ended glass tube inside which the substrate was placed. On heating, the $SnCl_2$ decomposed into $SnCl_4$ and H_2O, the former getting hydrolyzed on the heated substrate and depositing SnO_2 film. The films were of a very high quality and showed long term stability with respect to their optical, electrical and mechanical properties. Doping of the films by F, Mo and Sb was achieved by mixing Ammonium fluoride, Ammonium molybdate and Antimoni trichloride respectively. The films were characterised by XRD & SEM as also measurement of electrical and optical properties. The films were deposited on glass and mica substrates. The grain size of the films 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 showed the lowest resistivity ~ 4 X 10^{-4} Ω cm and average optical transmission of 80% at a thickness of 3500 A°.

IV. SUGGESTION FOR FUTURE WORK

(a) To assess the usefulness of the dip technique, it is necessary to prepare films of different materials under various deposition conditions and their subsequent characterisation. For example, Tin sulphide films described here have only SnS & SnS_2 phase, but the same technique may be used to prepare SnS_x ($1 \leq x \leq 2$) films, and even films with composition Sn_2S_3, Sn_3S_4. Other dopants like Cu could also be used for tin sulphide films.

(b) The simple OACVD technique for deposition of SnO_2 film could be used for the deposition and study of films using other dopants, such as Cl, In, Cd, P. In addition,

preparation and characterisation of cadmium-tin-oxide ($CdSnO_2$) or ZnO films in this method could also be used.

It is evident that for the future well-being of nations, a supply of energy, based on a renewable source which is economically and environmentally acceptable need to be developed. Direct conversion of solar energy electric power by thin film PV devices appears to be the ideal solution. In the present work, the films which were prepared are suitable as materials for the above purpose. The above techniques which can be adopted for the preparation of solar photovoltaic energy conversion thin film materials are very simple and low-cost and can be carried out in virtually any laboratory.

We hope that in future these techniques will be found to be useful for long-term success of PV technology as a way of effectively utilizing our solar income due to its simplicity and low-cost.