

### ABSTRACT

In this work, two new techniques for thin film deposition has been described. The first has been used for the deposition of oxide and sulphide films, while the second one is utilised for transparent conducting tin dioxide film only. Two type of solid state devices were fabricated using these films, and their performance evaluated.

The dip technique has been used for the deposition of oxide ( $\text{Al}_2\text{O}_3$  and  $\text{SnO}_2$ ) and sulphide ( $\text{CdS}$ ,  $\text{ZnS}$  and  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ ) thin films. In this technique, as used for oxides, the substrate is withdrawn vertically at a speed of the order of 1 mm/sec from a solution containing metal nitrate and alcohol, when a liquid layer adheres to the substrate surface. It is then subjected to a heat treatment, when the liquid film is converted to a solid one.

For aluminium oxide ( $\text{Al}_2\text{O}_3$ ), the starting material was aluminium nitrate [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] and t-butanol. For alumina films, a two-step pre-baking at temperatures of  $65^\circ\text{C}$  and  $120^\circ\text{C}$  successively for few minutes was necessary before final baking at a temperature of  $550^\circ\text{C}$ . The alumina ( $\text{Al}_2\text{O}_3$ ) films seemed to be amorphous in nature as indicated by the x-ray diffractometric study.

Deposition of tin dioxide ( $\text{SnO}_2$ ) films were also carried out using the dip technique, where the starting solution was stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) and ethanol. After withdrawing the substrate from the starting solution, the substrate with the liquid layer adhering to it was first dried in a desiccator containing sulphuric acid, and then baked at a temperature of  $400^\circ\text{C}$ . Dip deposited  $\text{SnO}_2$  films are uniform, smooth, hard and highly transparent. Unlike  $\text{SnO}_2$  films deposited by other conventional methods, dip deposited  $\text{SnO}_2$  films had a high resistivity. X-ray diffractometric study shows that the films are only poorly crystalline. It is known that in the presence of air and water,  $\text{SnCl}_2$  is converted into  $\text{SnCl}_4$  and stannous oxychloride. On heating most of the  $\text{SnCl}_4$  evaporates, some is hydrolysed to  $\text{SnO}_2$ , while the oxychloride is converted to hydrates of tin oxide. The latter being insulating in nature lead to the high resistivity of the final film.

A novel technique for depositing transparent conducting  $\text{SnO}_2$  films has also been developed and studied. Here a paste of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in a few drops of distilled water was prepared. It was then painted near the bottom end of the substrate which was then heated under atmospheric conditions in a vertical position. The  $\text{SnCl}_4$  produced as described in the preceding paragraph is hydrolysed on contact with the heated substrate to yield the desired tin dioxide film. These films were found to be highly transparent (70-90% average transmission for visible light) with sheet resistance of the order of  $100-5000 \Omega/\square$  for a thickness of  $1000 \text{ \AA}$ . Sb-doped  $\text{SnO}_2$  films have also been deposited by this technique.

The dip technique has also been adapted for the deposition of sulphide films. By adding a sulphur containing compound (thiourea) to a solution in methanol of cadmium nitrate, zinc nitrate or a mixture of the two, cadmium sulphide ( $\text{CdS}$ ), zinc sulphide ( $\text{ZnS}$ ) and mixed cadmium-zinc sulphide films could be produced.  $\text{CdS}$  films were studied in detail by varying Cd:S ratio, baking temperature, depositing on different substrates and increasing the number of dippings. The best films were obtained at a temperature of  $400^\circ\text{C}$  with Cd:S ratio 1:1. The  $\text{CdS}$  films were predominantly of the zinc blende structure, whose grain size was found to increase with the number of dipping upto 5 or 6 dippings (dip-withdrawal-bake cycle). X-ray

diffraction study suggests that ZnS films are amorphous in nature, whereas  $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$  films are of a mixed phase with partially crystalline CdS and amorphous ZnS. For single dipping, grain size of the CdS film was dependent on the substrate. For example, grains for transparent conducting  $\text{SnO}_2$  substrate was nearly double that for soda-glass ones. Similarly, grain size for multiple dippings was also larger than for single-dipping, as here the fresh CdS layer is really deposited on the underlying (earlier-deposited) CdS "substrate". It was also found that thickness of the CdS films on first dipping (on amorphous substrate) is less than that obtained for subsequent dippings (on underlying crystalline CdS layer).

Two types of solid state devices, namely Parallel-plate electron multiplier (PEM) and Photo Conductive (PC) cell were fabricated using films deposited by the above techniques. In the fabrication of PEM, dip deposited  $\text{SnO}_2$  and  $\text{Al}_2\text{O}_3$  films were used as semiconducting and secondary emitting layer respectively. The laboratory built PEM was tested in a vacuum  $< 10^{-5}$  torr. The typical secondary emitting pulse consists of a number of peaks, which are caused by ionic feedback. The gain is estimated to be of the order of  $10^7$ - $10^8$ .

For the fabrication of PC cell, the dip deposited CdS films were sensitised with Cu, Cl by dipping them in a

solution of  $\text{CdCl}_2$  and  $\text{CuCl}_2$  and baking under atmospheric condition. PC cells were then fabricated by evaporating aluminium electrode in a comb-like configuration. Higher concentration of  $\text{CdCl}_2$  in the sensitising solution increases the dark current while photocurrent remains the same. For a fixed  $\text{CdCl}_2$  concentration, the maximum photocurrent is obtained for a baking time of about 3 minutes and then decreases slowly, which may be due to the partial decomposition of  $\text{CdS}$  films. Tendency of coalescence of the  $\text{CdS}$  grains was observed with the increase in  $\text{CdCl}_2$  concentration in the sensitising solution. The PC cell was studied by plotting voltage-current (V-I) curves for different illumination levels and equivalent luminance-resistance ( $\Phi$ -R) curves for different baking times. The spectral response of photoconductivity showed a maximum at 520 nm (2.4 eV) for unsensitised  $\text{CdS}$  films. For sensitised sample a sharp peak at 505 nm (intrinsic) and broad peak at 590 nm (impurity) were observed. The maximum photosensitivity of the PC cell is estimated to be 10 mA/lumen.