

---

**CHAPTER 2**  
**DIP TECHNIQUE**

---

## 2.1. Introduction :

Possibility of deposition by simple immersion and withdrawal is a highly attractive one. Many approaches were made to deposit films using this technique. Deposition of Ag, Au and Cu layers onto a solid surface by precipitating them from solutions were known from the last century. But the work on dielectric layers from solutions was initiated only about 30 years earlier. Following the work of Langmuir [1] and Blodgett [2], a method was developed to deposit films from solutions. The process of deposition by slowly draining the solution or by raising the substrate was not popular at that time, due to its limitation and widespread use of vacuum evaporation and other techniques.

It was only recently that there has been a renewed interest in this type of method for the deposition of a number of thin films from solutions. In 1969 dip-coating

technique was applied by Schroeder [3] to modify the optical properties of glasses and plastics. It was also found [4] that the dip-coating method using metal alkoxides is very useful for modifying the properties of large surfaces and provide substrates with new active properties.

Dip coating is useful for protecting particular electrical characteristics of the substrate and providing the substrate with particular electrical and magnetic properties in addition to modification of optical properties and increase in chemical durability.

In recent years, the dip-coating technique is gaining attraction as the demand for new electronic materials has increased. It is hoped that, in the future, dip-coating will be widely applied.

As briefly mentioned in Chapter 1, in this technique, the substrate is withdrawn from a solution containing suitable metal compounds in an organic solvent, at a controlled speed, when a liquid layer adheres to the substrate. It is then subjected to a high temperature treatment, when the liquid film is converted into a solid one.

The solutions used must possess the following characteristics

- (i) Sufficient solubility of the starting material.
- (ii) Small contact angles between the solution and the substrate for good wetting of the substrate. Sometimes a wetting agent may be necessary to improve the wetting property of the solution.
- (iii) Finally, transformability of the liquid film adhering to the substrate in a solid homogeneous layer by heat treatment.

During the formation of the liquid film on the substrate the lifting movement of the carrier holding the substrate should be kept completely smooth and shockless. If irregularities in the liquid level and uncontrolled air currents are avoided then the liquid film develops in a horizontal dipping line along the substrate. And the uniformity in the film can be checked by observing the interference fringes, which are formed due to the evaporation of the solvent from the substrate surface.

The quality of the films and thickness depend on the concentration of the starting solution and the speed of withdrawal. Factors like viscosity, surface tension and vapour pressure, which are characteristics of each solution, can be summarized in a constant of proportionality ( $K$ ).  $K$  also depends on ambient temperature and humidity.

For a solution in a constant temperature and humidity condition the thickness is determined by

- (i) Speed ( $V$ ) of withdrawal,
- (ii) Concentration ( $C$ ) of the solution, and
- (iii) Angle of inclination ( $\phi$ ) of the substrate relative to the horizontal line. The usual value of  $\phi$  is  $90^\circ$ , i.e. vertical withdrawal.

## 2.2. Dip Deposition Setup

In Fig.2.1, is shown, the setup used by us for the deposition of films by the dip technique. Here, the precleaned substrate in its holder, moving freely at the end of a thread. The thread passes through a pulley and is driven by a geared motor arrangement. The substrate is immersed into the solution in such a way that the holder remains just outside the liquid level. For smoothly drawing the substrate outside the liquid level, irregularities in the liquid level and uncontrolled air currents are avoided. A long cylinder is used as a container of the liquid, because sometimes it is required to keep the substrate with its adhering liquid film after withdrawal from the liquid within the environment of the solution vapour for a few minutes before abruptly exposing to the outside atmosphere.

Thus with the help of this setup, one obtains a uniform liquid film on the substrate. It is then subjected to high

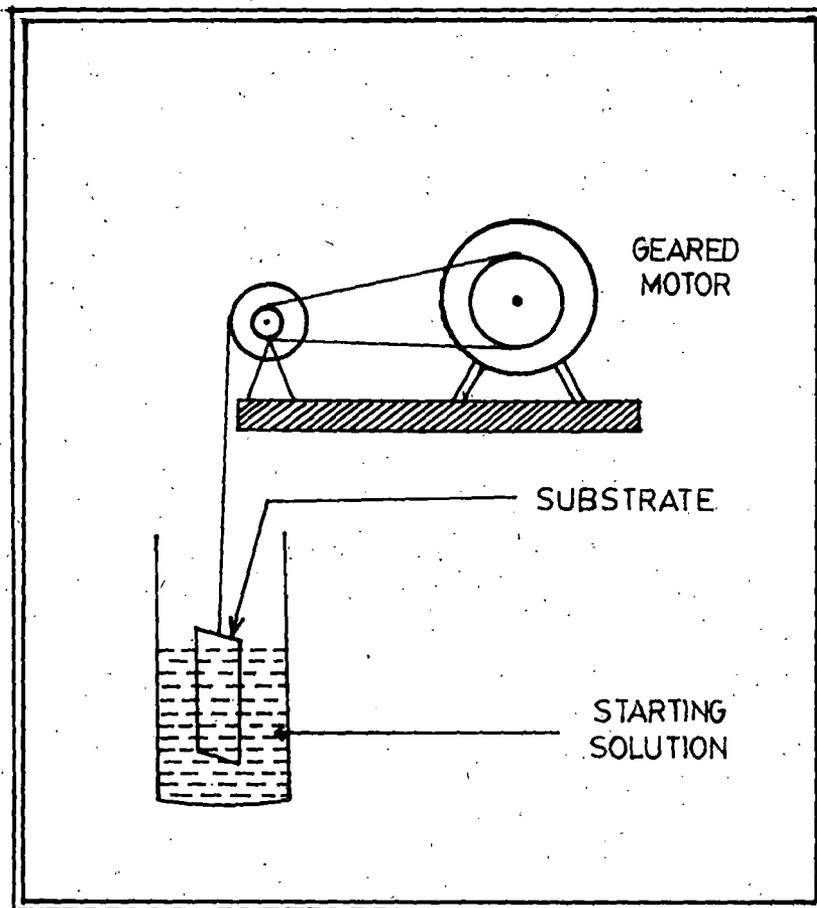


Fig. 2.1. Experimental arrangement for thin film deposition by the dip technique.

temperature treatment to convert into a solid one.

Thus film formation by the dip technique requires heating as an essential step. This is advantageous because heating forms chemical bonds between the film and the substrate. Relatively low ( $\sim 300^{\circ}\text{C}$ ) baking temperatures are sufficient in most of the cases, hence highly heat-resistant substrates are not essential. Another advantage of the dip technique is that, it is possible to coat surfaces with much larger areas as compared to other standard methods such as sputtering, vacuum evaporation, spray pyrolysis.

A characteristic of the dip technique is the thickness of the film. Thin films of thicknesses between  $50\text{\AA}$  ———  $5000\text{\AA}$  can be obtained in one dip-bake cycle. The small thickness is usually an advantage for films for electronic applications; while it is usually a disadvantage for protecting layers. Thicker films can also be obtained by this technique by repeating the whole process of dipping-withdrawal-baking a number of times. Since multiple deposition is somewhat laborious, this technique is not very suitable for films of several micrometers and thicker films. It is not usually possible to deposit a layer having a thickness much more than  $5000\text{\AA}$  in one dip-bake cycle. Attempts to increase the thickness of the deposited film in one dip-withdrawal-bake cycle by

increasing the concentration of the solute or the speed of withdrawal was invariably found to produce powdery and poorly adherent deposits.

Various films deposited by dip technique have been reported by Dislich [5]. A recent review by Sakka [6] on the dip deposited films by the alkoxide route, pointed out some future possibilities of this technique.

Dip technique is a simple and low-cost method, which requires no sophisticated specialized setup. In the following chapters, we will describe deposition of oxide and sulphide films by the dip technique.

### 2.3. Insulating Oxide Films

#### 2.3.1. Introduction :

Insulating oxide films are important because of their possibility of application in miniaturized solid-state devices, such as diodes, hot electron triodes, variable capacitors, photo cells and electroluminescent cells [7]. Oxide coating are also useful in various optical device applications such as antireflection coatings, absorbing coatings, partially reflecting coatings, selectively reflecting layer systems, various filter fabrication and for protective layers [3].

A number of methods including vacuum evaporation, anodizing, chemical vapour deposition, spray pyrolysis, solution growth and screen printing have been used to deposit these films.

Dip technique as described earlier in this chapter, is a simple method by which various oxide films could be obtained easily. As the liquid films are baked in air, they normally pass over to the highest oxidation stage compatible with the given temperature. Coatings on both sides of a substrate can be obtained with the help of dip technique, which is advantageous in some special cases. It is also possible to coat otherwise inaccessible surfaces.

This is a simple and low-cost method, which requires no sophisticated specialized set up.

In the following articles, deposition of alumina ( $\text{Al}_2\text{O}_3$ ) and the tin dioxide ( $\text{SnO}_2$ ) films by the dip technique have been described.

### 2.3.2. Alumina ( $\text{Al}_2\text{O}_3$ ) Films

Alumina is a promising coating material for its wide application as a insulating layer, also for wear and corrosion resistance. It has good secondary emission characteristics [8]. For selective coatings, alumina is

used as a host matrix [9]. It is generally deposited by evaporation, anodization, chemical vapour deposition, spray pyrolysis and solution growth.

Deposition and characterisation of alumina films prepared by the dip technique is described in the following.

The starting solution was prepared by dissolving requisite amount of hydrated aluminium nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in t-butanol. A small amount of distilled water was added to this solution, to decrease the rate of evaporation of the solvent and to increase the wetting property. Addition of water was found necessary to obtain crack-free, smooth films. Films obtained without water added to the starting solution tended to be grainy and opaque. Typically, a solution with 200 gms/litre of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  required about 9% of water by volume.

To ensure perfect wetting of the micro-slide substrates the cleaning procedure was to wash them in detergent, chromic acid, detergent and distilled water. Vapour degreasing was carried out by exposing the substrates to acetone, methanol and trichloroethylene successively. The slides were finally dried by an air blower.

The cleaned slide was then dipped into the above solution and withdrawn vertically (Fig.2.1) at slow speeds

( $\approx 1$  mm/sec), and left for  $\approx 30$  sec within the container above the solution level, i.e. inside an atmosphere of t-butanol vapour. This latter step was found necessary to avoid formation of cracks in the final film. At higher speeds the film formed was observed to be non-uniform. Due care was taken to protect the experimental set-up from mechanical vibrations and air currents. A liquid film was thus obtained that adhered well to the slide.

The liquid film thus obtained was pre-baked at a temperature of  $65^{\circ}\text{C}$  <sup>for</sup> 2 minutes, exposed to air for few seconds, then again baked at  $120^{\circ}\text{C}$  for 5 minutes and eventually at  $550^{\circ}\text{C}$  for 1 hour. This series of steps were found necessary to obtain good quality films. Otherwise, particularly if the liquid film was directly baked at a temperature of  $550^{\circ}\text{C}$ , opaque and grainy films were produced. This may be due to abrupt release of gaseous reaction products and thermal shock.

### \*2.3.3. Tin dioxide ( $\text{SnO}_2$ ) Films

Tin dioxide is highly useful semiconducting oxide for its use as a transparent conductor in a variety of display devices and imaging tubes. It is also used as a

---

\*Presented at the "National Symposium on Thin Film Science and Technology"; Proceedings, Indian Institute of Science (I.I.Sc), Bangalore, 9-11 January, 1985.

transparent electrode for electrochemical studies, infrared reflectors, antistatic coatings, thin film resistors [10].

Various methods have been used to deposit transparent conducting tin dioxide films which includes hydrolysis of chlorides, pyrolysis, evaporation and sputtering of tin, reactive evaporation and sputtering, sputtering of oxide targets, screen printing, doctor-blade and glowdischarge decomposition of organotin compounds or tin halides.

In the following, we describe the method of preparation of  $\text{SnO}_2$  films by the dip technique.

Here the starting solution was prepared by dissolving a requisite amount of stannous chloride into ethanol. The film deposition procedure is the same as in the case of alumina film (described in the last section). The only exception is that the substrate with the liquid film adhering to it was first dried in a desiccator containing sulphuric acid and then directly heated at a temperature of  $400^\circ\text{C}$ . The liquid film was dried to remove water from it as much as possible, before heating, to prevent the unwanted hydrolysis which results in an insulating layer.

#### 2.4. Results

Both  $\text{Al}_2\text{O}_3$  and  $\text{SnO}_2$  films were hard, smooth, transparent and strongly adherent. They also showed interference

colours at thicknesses  $\geq 4000\text{\AA}$ . They were uniform in thickness, except for the trouble zones at the bottom ( $\approx 5$  mm) and edges ( $\approx 1$  mm). The trouble zone were produced due to the adhesion of an extra amount of liquid at the bottom due to the surface tension and excess thickness at the sides of the substrates was due to edge non-uniformities. Measurements were done on the uniform central part of the film.

It is possible to deposit both  $\text{Al}_2\text{O}_3$  and  $\text{SnO}_2$  films of any thickness from  $50\text{\AA}$  to  $2000\text{\AA}$  in one dip-bake cycle. The thickness of the films was measured with the help of standard interferometric method.

As mentioned before, by repeating the dip-bake cycle a number of times, films of higher thicknesses could be obtained easily.

#### 2.4.1. Thickness Measurement

##### (a) $\text{Al}_2\text{O}_3$ Films

If the starting solution is kept at a constant temperature and humidity condition and the substrate is withdrawn at a fixed angle ( $90^\circ$  in this case), then the thickness of the resulting film depends only on the speed of lifting ( $v$ ) and concentration ( $c$ ) of the solution.

(i) Speed of lifting (v) vs thickness (t) :

This study was carried out using a solution of fixed concentration (c). By varying the speed of lifting (v), films of different thicknesses were obtained (Fig.2.2). This shows that film thickness increases nearly parabolically with the increase in the speed of lifting (v) for each concentration.

(ii) Concentration of the starting solution (c) vs thickness (t) :

By varying the concentration of the starting solution (c) for a fixed speed of lifting (v), films of different thicknesses were obtained. Fig.2.3 shows the relation between the concentration and thickness for a fixed speed of withdrawal.

2.4.2. Microstructural Details

Microstructural studies were carried out with the help of x-ray diffractometer and scanning electron microscope.

(a) (i) X-ray Diffraction of  $Al_2O_3$

X-ray diffraction studies were carried out on the thick films ( $>1000\text{\AA}$ ) to determine whether the deposited

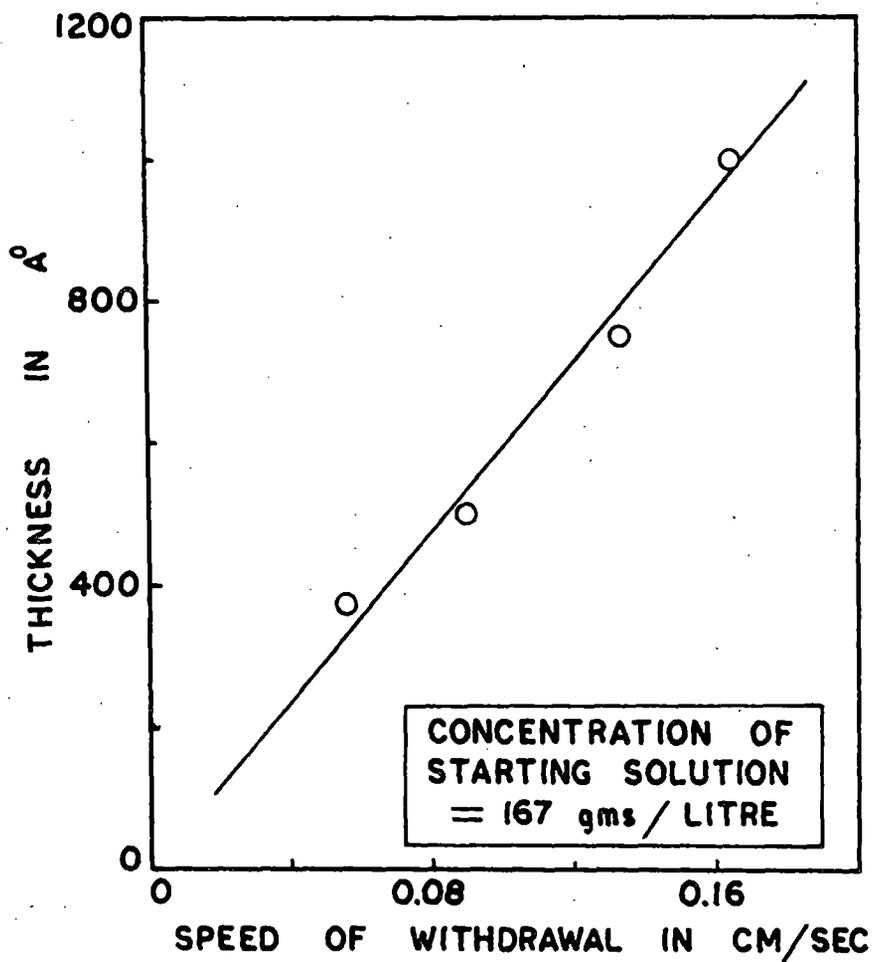


Fig. 2.2. Variation of thickness of typical  $Al_2O_3$  films with the speed of withdrawal of the substrate.

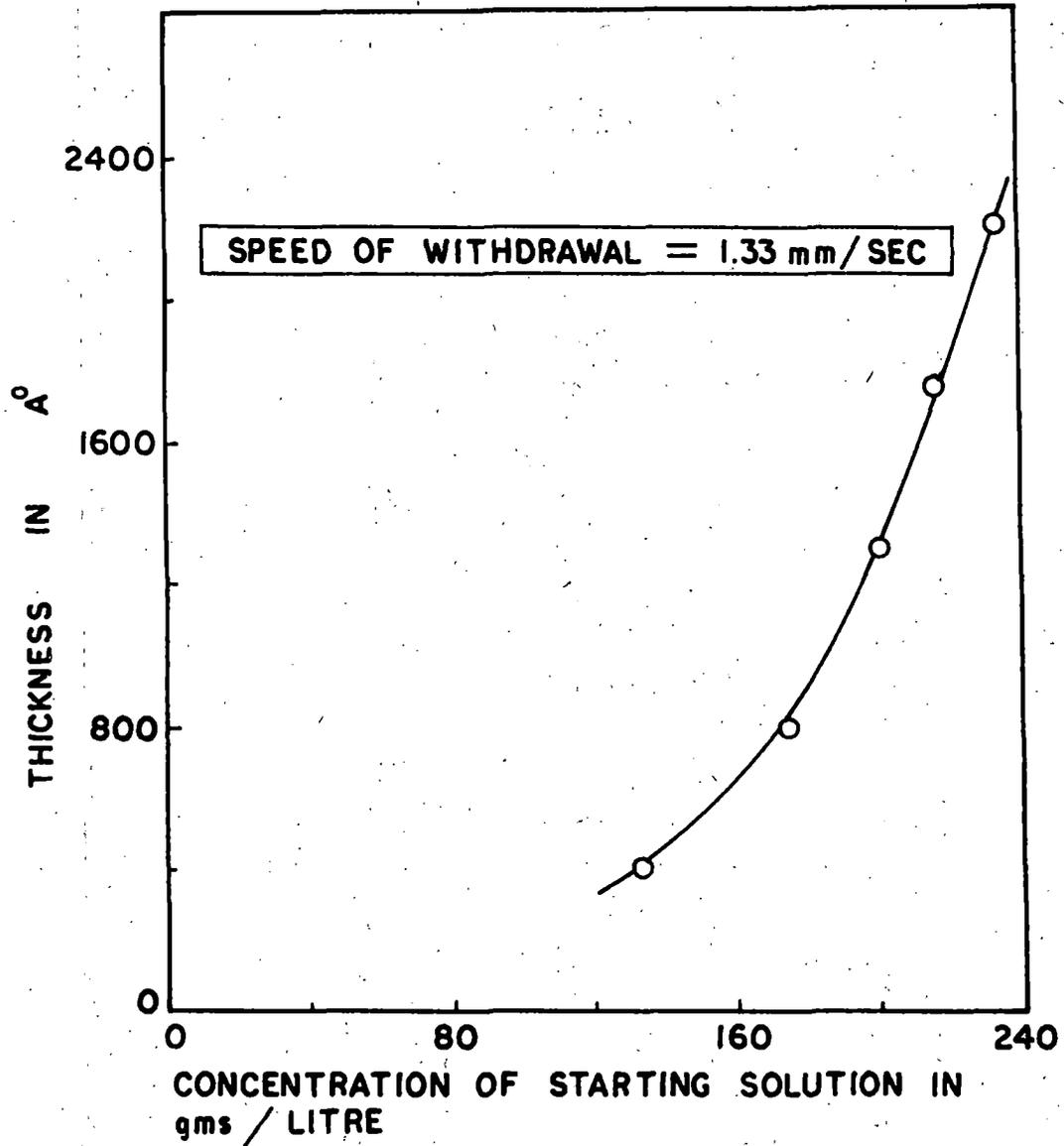


Fig.2.3. Variation of thickness of typical  $Al_2O_3$  films with the concentration of the starting solution.

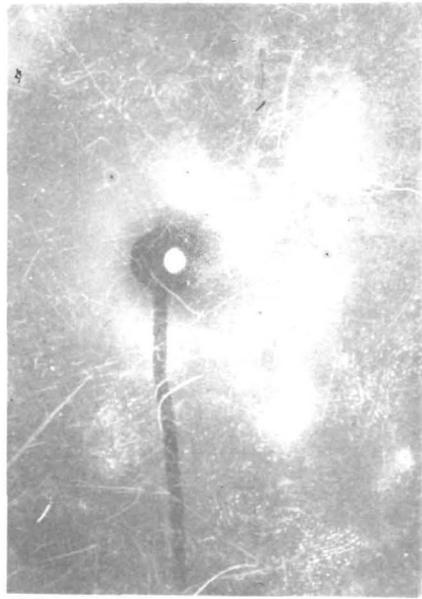
films are polycrystalline or amorphous. The resulting transmission laue diffraction photographs in Fig.2.4(a) and Fig.2.4(b) of alumina film on glass and mica substrates indicate that the films are amorphous in nature. In Fig.2.4(a) the halos are due to the glass and the deposited film, where as in Fig.2.4(b) the diffraction spots are due to the crystalline mica substrate. The amorphous nature of the alumina film is again confirmed by the X-ray diffractogram (Fig.2.5).

#### (ii) X-ray Diffraction of SnO<sub>2</sub> Films

Fig.2.6 shows, the x-ray diffractogram of SnO<sub>2</sub> films deposited by the dip technique. The x-ray diffractogram shows the presence of two very small peaks at about 26.5° and 33°. These occur at the same position as the peaks obtained in the XRD for SnO<sub>2</sub> films with a well-defined crystal structure (art 3.3.2(i), Fig.3.2). It is clear that a very small amount of crystalline SnO<sub>2</sub> is formed in this case, which is responsible for its low conductivity.

#### (b) Scanning Electron Microscopy

Scanning electron micrographs were made for alumina films (1000A°) on mica and glass substrates. Fig.2.7 is the scanning electron micrograph of transparent Al<sub>2</sub>O<sub>3</sub> film on glass substrate (obtained on addition of water). Which



(a)



(b)

Fig. 2.4. Diffraction pattern of  $\text{Al}_2\text{O}_3$  film  
(a) on glass substrate  
(b) on mica substrate.

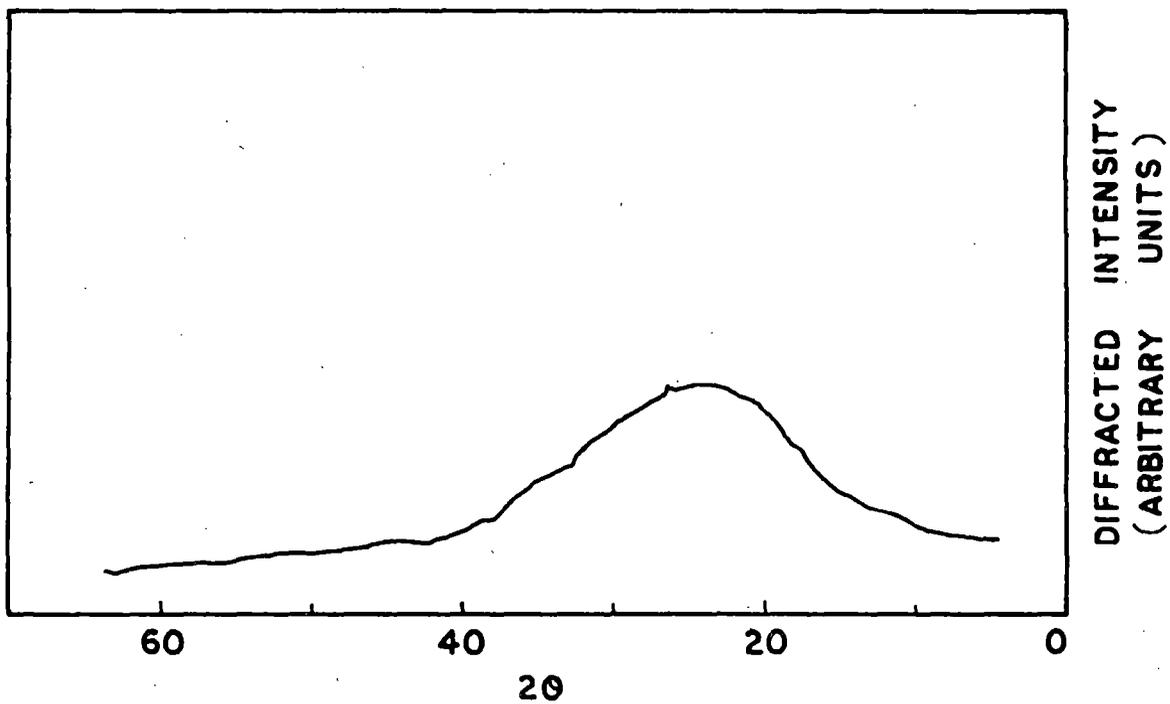


Fig. 2.5. An X-ray diffractogram of a typical  $\text{Al}_2\text{O}_3$  film deposited by the dip technique.

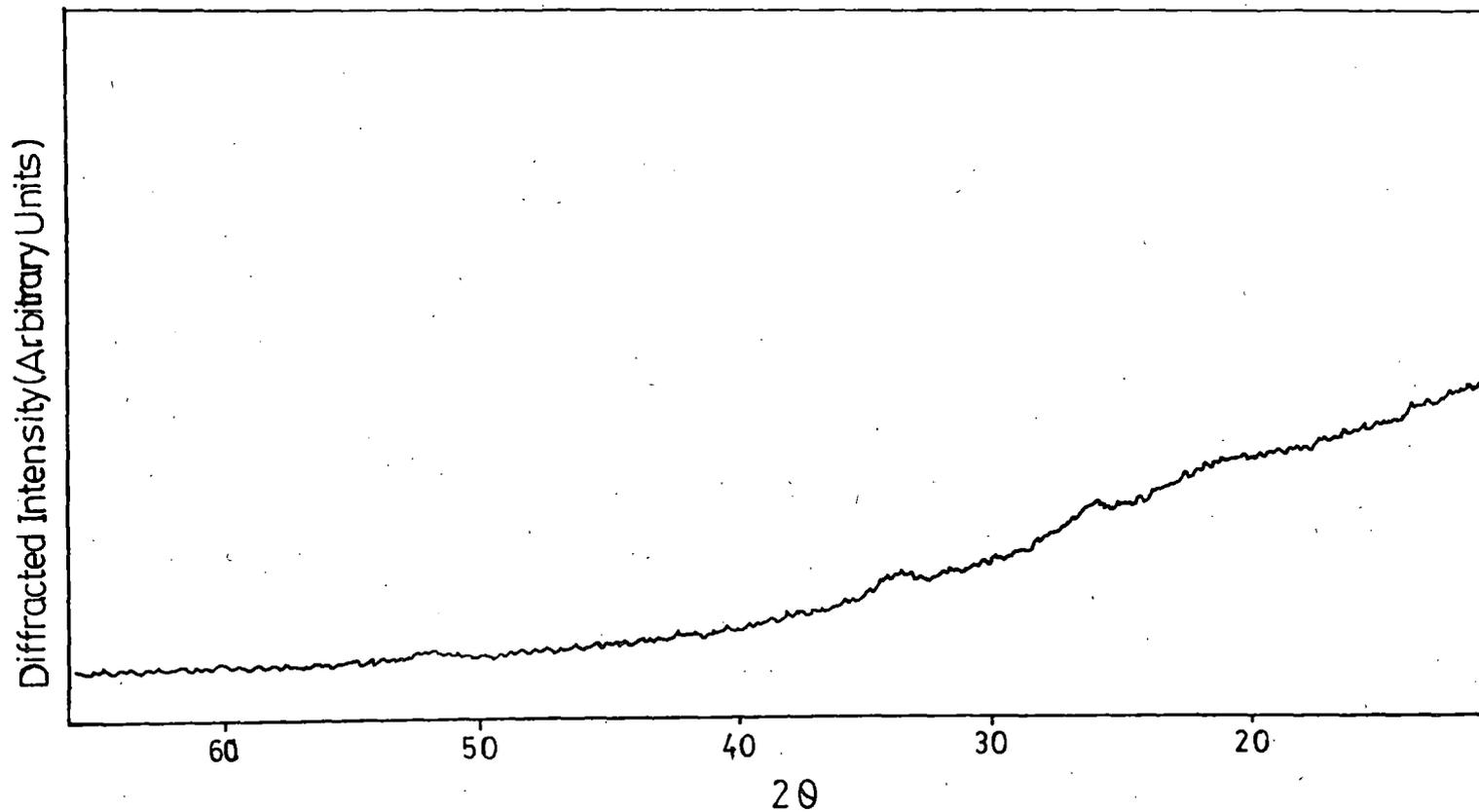


Fig. 2.6. An X-ray diffractogram of a typical SnO<sub>2</sub> film deposited by the dip technique.

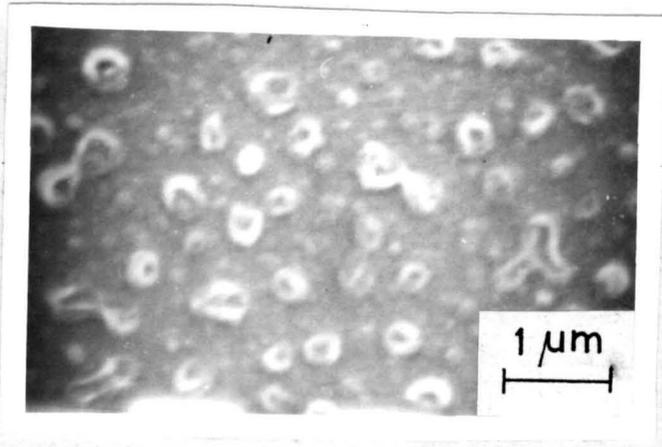


Fig. 2.7. A Scanning Electron Micrograph of a typical Al<sub>2</sub>O<sub>3</sub> film deposited by the dip technique.

shows the presence of extremely small grains  $\approx .1 \mu\text{m}$  linear dimensions. Larger ( $\approx .5 \mu\text{m}$ ) ring like structures were also observed. These are apparently caused by the escape of the gaseous reaction products while the liquid film was being converted to solid form by baking.

Scanning electron micrograph of dip deposited  $\text{SnO}_2$  films were featureless.

#### 2.4.3. Resistance

Alumina films produced by the dip technique were insulating with a sheet resistance  $\sim 1 \times 10^{10} \Omega/\square$  for a thickness of  $1000 \text{ \AA}$ . The sheet resistance of  $\text{SnO}_2$  films deposited by the dip technique was also high  $\sim 10^4 \Omega/\square$  for a thickness of  $1000 \text{ \AA}$ . This high value of sheet resistance of  $\text{SnO}_2$  films may be due to the formation of hydrates of  $\text{SnO}$  and  $\text{SnO}_2$ , which are insulating in nature [10].

#### 2.4.4. Optical Property

$\text{SnO}_2$  films produced by the dip technique were highly transparent with an average optical transmission  $\sim 90\%$ .

## 2.5. Discussions

With the help of this simple and low-cost technique, it is possible to deposit large surfaces and the surfaces which are inaccessible by other conventional techniques.

Oxide films prepared by the dip technique are highly adherent, due to the fact that, the OH group or H<sub>2</sub>O always present on ceramic surfaces lead to solid chemical bonds between the coating materials and the substrate.

### 2.5.1. Al<sub>2</sub>O<sub>3</sub> films

Extreme care is necessary in processing for the preparation of good quality alumina films. It is presumed that both addition of water to the starting solution and leaving the substrate after withdrawal in the atmosphere of the solvent vapour for some time slow down the rate of evaporation of the solvent from the liquid film adhering to the substrate and protects it from formation of cracks. Again, pre-baking in two steps before the final baking allows the gaseous reaction products like H<sub>2</sub>O and NO<sub>2</sub> to escape slowly and leave the final film intact.

### 2.5.2. SnO<sub>2</sub> films

Dip deposited SnO<sub>2</sub> films prepared from SnCl<sub>2</sub> and ethanol solution, though highly transparent have a high resistivity value  $\sim 4.5 \times 10^{-1} \Omega\text{-cm}$ . The resistivity is essentially unchanged even if other solvents, such as methanol, amyle alcohol, butanol are used. Hence it is difficult to reduce the resistivity of the dip deposited SnO<sub>2</sub> films in this way. The residual water present in the starting solution gives rise to a hydrolysis reaction on heating, leading to production of hydrated tin oxides and tin oxychlorides, both of which have a high resistivity. High temperature annealing for a long time may eventually complete the conversion to the dioxide and improve the conductivity.

References

- [1] J.Langmuir, 1917, J.Am.Chem.Soc. 39, 1848.
- [2] K.B.Blodgett, 1935, J.Am.Chem.Soc. 57, 1007.
- [3] H.Schroeder, "Physics of Thin Films" Ed. Hass and Thun. Vol.5, Academic Press, New York and London, 1969.
- [4] H.Dislich and E.Hussmann, Thin Solid Films 77 (1981) 129.
- [5] H.Dislich, J.Non-crystalline Solids 57(1983) 371.
- [6] S.Sakka, J.Non-crystalline Solids 73 (1985) 651-660.
- [7] K.L.Chopra and I.Kaur, Thin Film Device Applications, Plenum Press, New York, 1983.
- [8] L.P.Anderson, E.Grusec and S.Berg, J.Phys.E.Sci. Instrum, Vol.12, pp.1015-1022, 1979.
- [9] C.G.Granqvist, "Thin Film Technology and Applications", Ed. K.L.Chopra and L.K.Malhotra, Tata McGraw-Hill Publishing Company Ltd., New Delhi, 1985.
- [10] J.L.Vossen, "Transparent Conducting Films" in Physics of Thin Films, Ed. G.Hass, M.H.Francombe and R.W.Hoffman, Vol.9, pp.1-70, Academic Press, New York, 1979.