CHAPTER-2

*OXIDE FILMS PREPARED BY THE DIP TECHNIQUE

2.1. INTRODUCTION

The dip technique provides a very simple and cost-effective method for the deposition of thin films. It does not require any complex sophisticated specialized setup. In this chapter we describe the dip technique in detail and its use for the deposition of oxide films and their characterisation.

2.2. DIP TECHNIQUE

The earliest investigations concerning oxide coatings deposited from solution were those of Geffcken and Berger [1] and of Geffcken [2] about 60 years ago. Further work on this technique was carried out by Schroeder [3-6] and later by Dislich [7-8]. It was Geffcken [1-2] who laid the cornerstone by showing how to convert relatively simple hydrolysable metal compounds into well-defined layers of metal oxide. Schroeder [3-6] made a thorough analysis of the film forming process and discussed its application to the deposition of a large number oxide films.

In 1980, H. Dislich and Eckart Hussmann [8] showed that it is possible to synthesize by dip coating thin films of glasses, crystals and glass ceramics which are not easy to fabricate in bulk form. Dislich et al. [8] has deposited amorphous and crystalline oxide films from organometallic solution using dip-coating technique. They used large panes (nearly 3m X 4m) for deposition of oxide films, which are carefully cleaned, inserted into an organometallic solution, and then withdrawal and baked in an atmosphere. In this process, atmospheric hydrolysis and condensation process take place until transparent metal oxide layers are obtained. The liquid film partly flows down the plate and partly adheres to it and solidifies after evaporation of the solvent. Finally the

film is hardened in a high temperature (300° C - 400° C) cycle until a transparent metal oxide film has been formed. In this process, film- forming oxides are mainly those of the elements of groups 3-8 of the periodic table (provided that these lead to stable oxide) and especially oxides of the following elements: Al, Si, Zr, Sn, Pb, Ta, Cr, Fe, Ni, Co, and some other earth elements. The technique has also been used to deposit mixed oxides such as SiO_2-TiO_2 [9] whose refractive index could be varied over the range from 1.45 (SiO_2) to 2.20 (TiO_2) depending on the composition. These oxides may be amorphous or crystalline depending on the treatment at higher temperatures, or the influence of the surface of the substrate. It should be possible to deposit transparent conducting oxides such as cadmium-tin-oxide (CTO) and zinc stannate by this technique. Dislich et al. also found that dip-coating method using metal alkoxides is very useful for modifying the properties of large surfaces and provide substrates with new active properties. The first saleable products for optical applications were made in 1953. Since 1969 large panes of window glass have been coated by this method for sun-shielding windows. These are sold under the trade name Calorex [10]. Schott have been producing vehicle rear-view mirrors by the dip-coating procedure since 1959 and anti-reflection layers on glass panes since 1964 [11].

As briefly mentioned in chapter 1, in this technique, the substrate is withdrawn vertically from a solution containing suitable metal compounds (e.g. nitrate or chloride or alkoxides) 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 a chemical reaction takes place, leading to the formation of the corresponding metal oxide film onto the substrate surface.

The solution (starting solution) which is to be used for deposition by dip technique should have the following characteristics.

(i) Adequate solubility of the starting material and at the same time very little tendency of the dissolved substances towards crystallization during evaporation of the solvent.

(ii) Sufficiently small contact angles between the solution and the substrate to be coated in order to obtain good wetting of the latter. Wettability of a substrate can be improved in some cases by the addition of wetting agents to the solution.

(iii) Adequate durability of the solution and constancy of processing conditions.

During the formation of liquid film on the substrate in this technique, the lifting movement of the carrier holding the substrate should be kept completely smooth and shockless. If the irregularities in the liquid level and uncontrolled air currents are avoided then the liquid film develops in a horizontal dipping line alone the substrate. 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.

In an excellent review of this topic, Scriven [12] states that when the substrate is withdrawn from the solution or solution is dragged out from the substrate then the thickness of the deposited films is dependent upon many factors. These factors are viscous drag on the liquid by the moving substrate, force of gravity, resultant force of surface tension in the concavely shaped meniscus, inertial force of the boundary layer liquid arriving at the deposition region, surface tension gradient and the disjoining or conjoining pressure.

According to Scriven when the liquid viscosity, η and substrate speed (v) are high enough to lower the curvature of the gravitational meniscus, the deposited film thickness of the liquid layer, h, is that which balances the viscous drag (η v/h) and gravity force (ρgh) [12]:

$$h = c_1(\eta\, v/\rho g)^{1/2} \text{----(2.1)}$$

where the constant c_1 is about 0.8 for Newtonian liquids. When the substrate speed and viscosity are low (often the case for sol-gel dip coating film deposition), this balance is modulated by the ratio of viscous drag to liquid-vapour surface tension, η, according to the relationship derived by Landau and Levich [13]:

$$h = 0.94(\eta\, v)^{2/3} /\eta_{1v}{}^{1/6} (\rho g)^{1/2} \text{----(2.2)}$$

However, 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 value. This constant also depends on ambient temperature and humidity.

The thickness of the film also depends upon the angle of inclination (θ) of the substrate relative to the horizontal line. The usual value of θ is 90°, i.e. vertical withdrawal.

2.3. DIP DEPOSITION SETUP

The setup used by us for the deposition of thin films by the dip technique is shown in figure 2.1.

Here, the precleaned substrate in its holder, moves freely at the end of a thread. The thread passes through a pulley which 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 out of the liquid, air currents are avoided. The liquid is usually kept inside a long cylinder. Often it is found that abrupt exposure to air after withdrawal of the substrate leads to patchy films with cracks. To avoid this shock, the substrate with its liquid film is kept for a few minutes in an atmosphere of the solution vapour within the long cylinder before its transfer to the furnace for baking.

2.3.1.SUBSTRATE CLEANING

The cleanliness of the substrate surface exerts a decisive influence on film growth and adhesion. The choice of cleaning technique depends on the nature of the substrate, the type of contaminants present in it and the degree of cleanliness required. Residues from manufacturing and packaging, lint, fingerprints, oil and airbone particulate matter are examples of frequently encountered contaminants. Ordinary soda-glass, mica, conducting glass (SnO_2-coated) and aluminium substrate have been used for deposition of films. When the glass substrate is polished during manufacture, the surface develops an electrostatic charge, which firmly holds minute particles on the cleaned surface. In addition, a small amount of grease may also be present. To remove these contaminants, acid cleaners such as chromic acid is used to convert them to more soluble compounds. The effectiveness of solvents is probably more dependent on the ability to wet the substrate than their solvent action. The solvent to be used must be of a high purity.
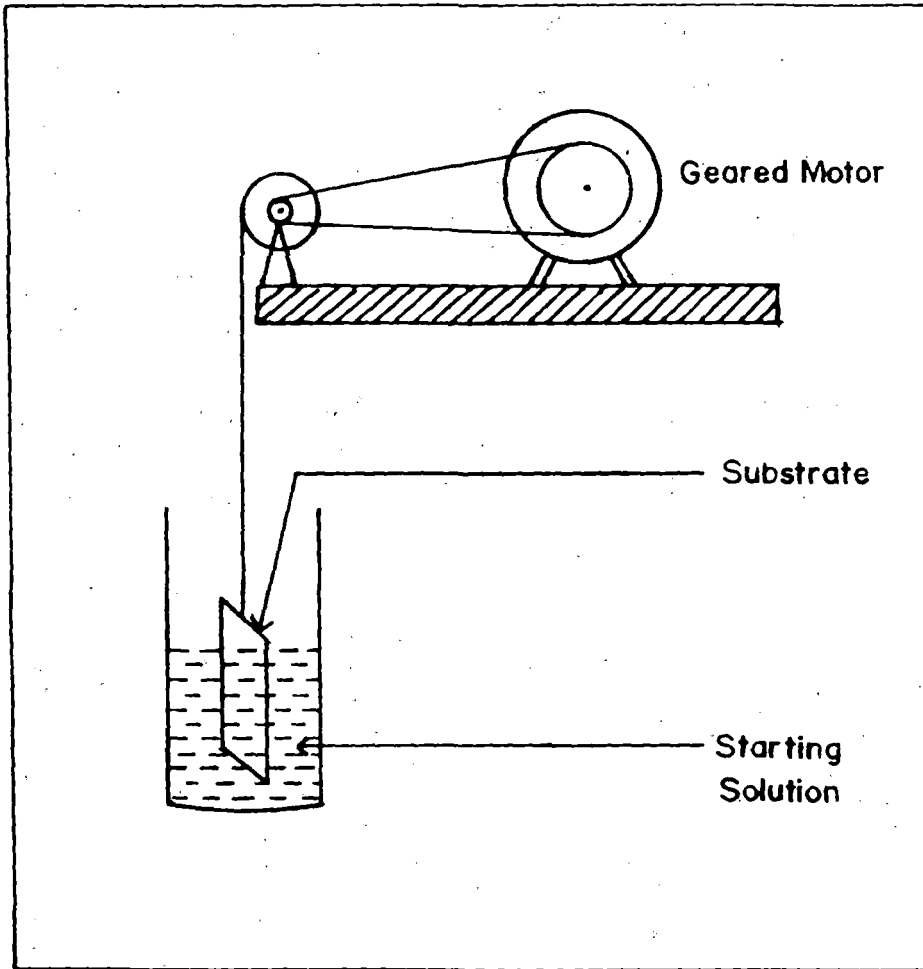
Figure 2.1. Experimental setup of dip technique for deposition of thin films.

Common solvents used in cleaning are methanol, acetone, trichloro-ethylene and distilled water. In this method substrates were initially cleaned in detergent solutions, dipped into chromic acid, then again in detergent solution and finally washed in running water.

The preferred method for degreasing a substrate is to expose it to solvent (methanol) vapours by keeping it above the boiling liquid in a vapour degreasing chamber. The solvent vapours condense on the substrate and fall back into the liquid. In this way, the substrate is cleaned by the action of the pure solvent.

By cleaning test, it can be confirmed whether the substrates have been properly cleaned or not. A common such test is to slowly withdraw the clean substrate from a container filled with pure water, when a continuous film of water will be observed to remain on the substrate surface if the cleaning has been properly done. This method is known as water-break test.

Substrates cleaned by the above method shows a remarkably high coefficient of friction for the liquid layer which adheres strongly to the surface. For all types of substrates used, dipping in chromic acid, washing in soap solution and then distilled water followed by vapour degreasing was found to produce surfaces which were sufficiently clean for the deposition of films by the dip technique.

Thus with the help of the above setup, one can obtain a uniform liquid film on the substrate. It is then subjected to a high temperature treatment to convert it into a solid one.

2.3.2. DEPOSITION PROCESS

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 leading to strong adhesion. Relatively low (~ 300° C) baking temperatures are sufficient in most of the cases, hence highly heat - resistant substrates are not essential. As previously mentioned, the precleaned substrate is withdrawn vertically from a starting

solution and baked at a high temperature in a furnace for a few minutes in atmospheric condition, when the adhered liquid chemicals in the form of a uniform liquid layer reacted on the substrate surface and formed the desired solid film. The liquid layer adhering to the substrate is mostly uniform, except for a region of ~1-2 mm wide near the bottom and the side of the substrate. This non-uniform portion of the substrate usually known as the trouble zone is dependent on the lifting speed as well as concentration of the starting solution. If the lifting speed is very small (~ 1 mm) or the solution is very dilute, then the length of the trouble zone is quite negligible (< 1 mm).

However, the film thickness was found to be uniform over a central region of few cm length. Studies were carried out on this uniform central part of the films.

2.3.3. THICKNESS OF THE FILM

Film thickness depends primarily on the lifting speed of the substrate and the concentration of the metal compounds present in the starting solution. Although as previously mentioned, a number of factors, such as viscosity and surface tension of the starting solution, atmospheric humidity and the angle of inclination (θ) determine the thickness of the liquid layer sticking to the substrate as it is pulled out, and thus the thickness of the final film. But for practical purposes characteristics of the solution and ambient condition is essentially constant and films are deposited by vertical withdrawal ($\theta=90^o$). So, thickness of the films is varied by key parameters such as lifting speed of the substrate, concentration of the solution and multiple dipping (dip-withdrawal-bake cycle) for thicker films.

A characteristic of the dip technique is the thickness of the film. With the help of this technique the thicknesses ranging from 50 A^o - 5000 A^o can be obtained in one dip-bake cycle. The small thickness is 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 thickness and thicker films.

In the following articles, deposition of tindioxide-based (SnO_2) transparent semi-conducting oxide and copper oxide (CuO) thin films by the dip technique have been described.

*2.4. TIN DIOXIDE-BASED (SnO_2) TRANSPARENT SEMICONDUCTING THIN FILMS

Transparent and conducting tin dioxide films have assumed importance in research as well as in technology owing to their applications in the field of electronics, ferroelectric memories, selective coatings etc. The presence of various impurities and the deposition parameters drastically alter the properties of the tin dioxide films, thereby influencing the efficiency of various devices such as photoconductive and solar cells, thin film transistors and electroluminescent cells etc. Several deposition techniques for preparation of tin dioxide films have been widely used [14-34].

For transparent conducting oxide applications, in electronics for instance, a very high quality of the films is required, and this method is able to lead to very high-quality SnO_2 layers, as far as the structure and morphology are concerned. However, there are not many reports in the literature on SnO_2 films prepared by this technique, which tend to have resistivity at least an order of magnitude higher than those prepared by other techniques such as CVD [35]. This high value of resistivity, while not suitable for photovoltaic cells, would however not be a problem for low current applications, such as liquid crystal displays.

To prepare the transparent semi-conducting tin dioxide based films in this technique, the starting solution was prepared by dissolving a requisite amount of stannous chloride ($SnCl_2$ $2H_2O$) into methanol such as 0.33 kg. $SnCl_2$ $2H_2O$ in one litre methanol. A clean substrate was then dipped into the starting solution and withdrawn vertically at a controlled speed (1.33 mm/sec), under atmospheric conditions using the setup described previously (section 2.2). After withdrawal, the substrate with its liquid film adhering to it is baked at 400º C - 500º C for five minutes. In this method, as also in the related sol-gel method [29,30] a metal oxide (SnO_2) film is produced by hydrolysis of the corresponding metal alkoxide, nitrate or chloride on a substrate and subsequently heat treated at a high temperature.

For F-doped film preparation, requisite amount of ammonium fluoride is added to the starting solution. In this method undoped and doped films were prepared for different baking temperatures. Variation of their thickness with lifting speed and concentration was studied. Thicker films could be obtained by repeating the whole cycle (dip-withdrawal-bake) a number of times. Films were deposited on soda-glass microscope slides and mica sheet. The characterization was mostly done on those deposited on glass substrate.

2.4.1. EXPERIMENTAL RESULTS

In this section, electrical and optical properties as well as surface morphology and crystal structure of undoped and F-doped tin dioxide-based transparent semiconducting thin films deposited by the dip technique have been discussed.

The films were deposited at different baking temperatures and at various lifting speeds. It was found that at 1.33 mm/sec lifting speed and the baking temperature of 400º C - 500º C was necessary to obtain films of useful quality in terms of low sheet resistance and high optical transmission. Within this temperature range there is no noticeable variation in the film properties. Results reported in this section refer to films prepared at a baking temperature of 400º C. The films were highly homogeneous and mechanically and chemically stable.

2.4.1.1. THICKNESS

The thickness of resulting films depends only on the lifting speed and concentration of the solution if the starting solution is kept at a constant temperature and humidity condition and the substrate is withdrawan at a fixed angle (90° in this case). Film thickness can be also increased by repeating the whole cycle (dip-withdrawal-bake) a number of times. Figure 2.2 - 2.4 shows the variation of film thickness with speed of withdrawal, concentration and number of dippings, respectively. It is observed that the thickness of the deposition layer increases linearly upto 7-8 dippings, beyond which the rate of increase is slower. Thickness of deposited films was measured by stylus method. In this method a step is made in a deposited film by removing part of the film from the substrate, and then the "shoe" or "skid" of the stylus instrument is placed on the substrate. The stylus instrument, travels across the sample surface with the movement of "shoe" or "skid". The vertical displacement is converted to electrical signals by means of a transducer. The signal is then amplified and recorded on a strip chart. Then the film thickness was measured from the corresponding vertical distance between the lower and upper portions of the trace.

2.4.1.2. X-RAY DIFFRACTOMETRIC STUDY

X-ray diffractometric studies were carried out by PHILIPS diffractometer (model PW 1390) with CuK_α radiations (Ni-filter) at 1.54 A°. Figure 2.5 shows the X-ray diffractograms of undoped films on glass substrate for five different numbers of dippings. It is evident from the diffractograms that crystallinity of the films improve with number of dippings upto a value of 20, beyond which a slight reduction in peak height is observed. Single dip films are almost totally amorphous, whose resistivity is rather high, of the order of 2.7 Ωcm. The sheet resistance drops sharply as the thickness increases to about 1 μm.
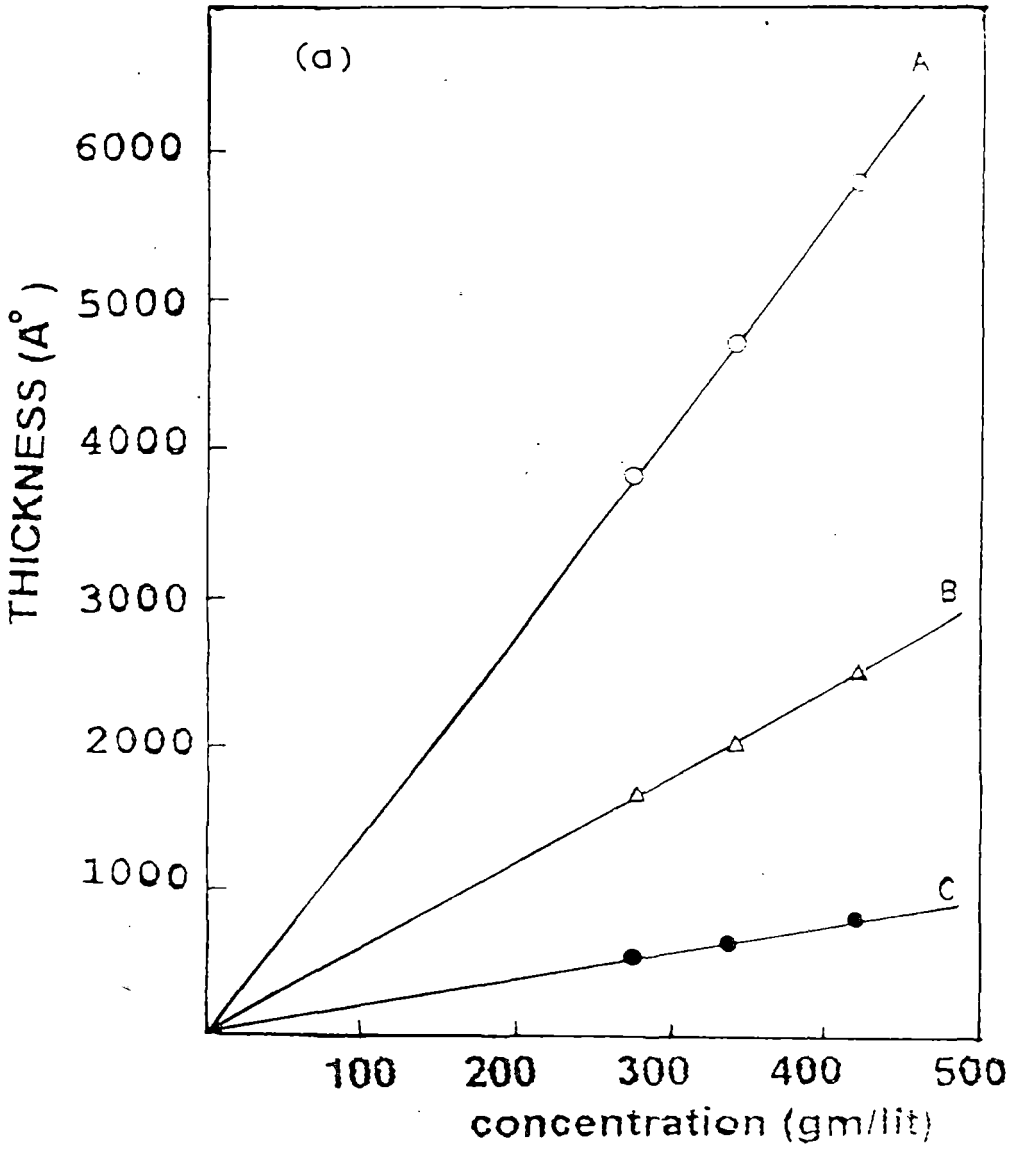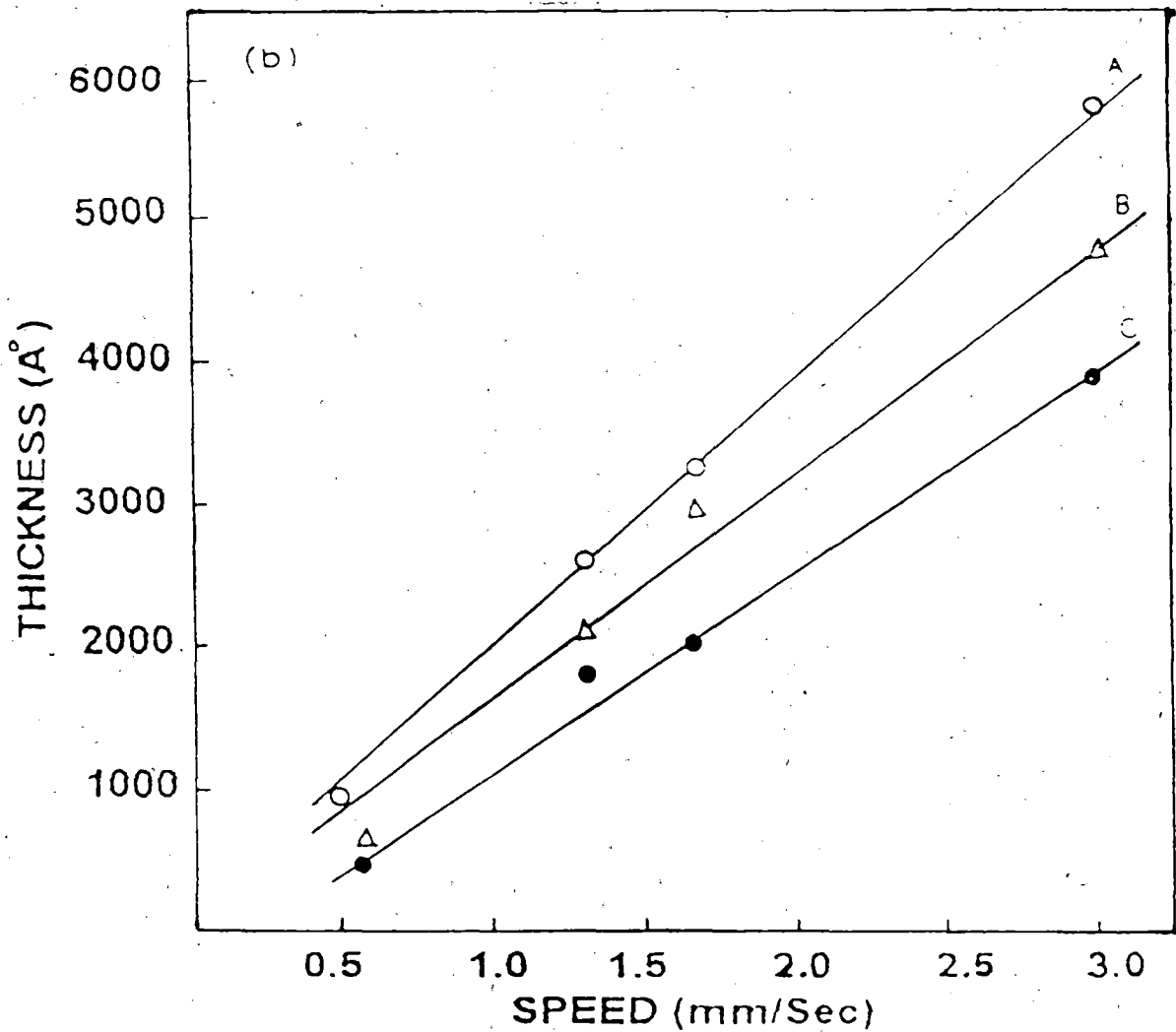
Figure 2.2. Variation of thickness of films deposited on glass substrates with concentration of the starting solution [speed of withdrawal: A = 3 mm/sec, B = 1.3 mm/sec, C = 0.56 mm/sec].

Figure 2.3. Variation of thickness of films deposited on glass substrates with speed of withdrawal [concentration of the liquid starting solution: A = 410 gms/litre, B = 330 gms/litre, C = 250 gms/litre].
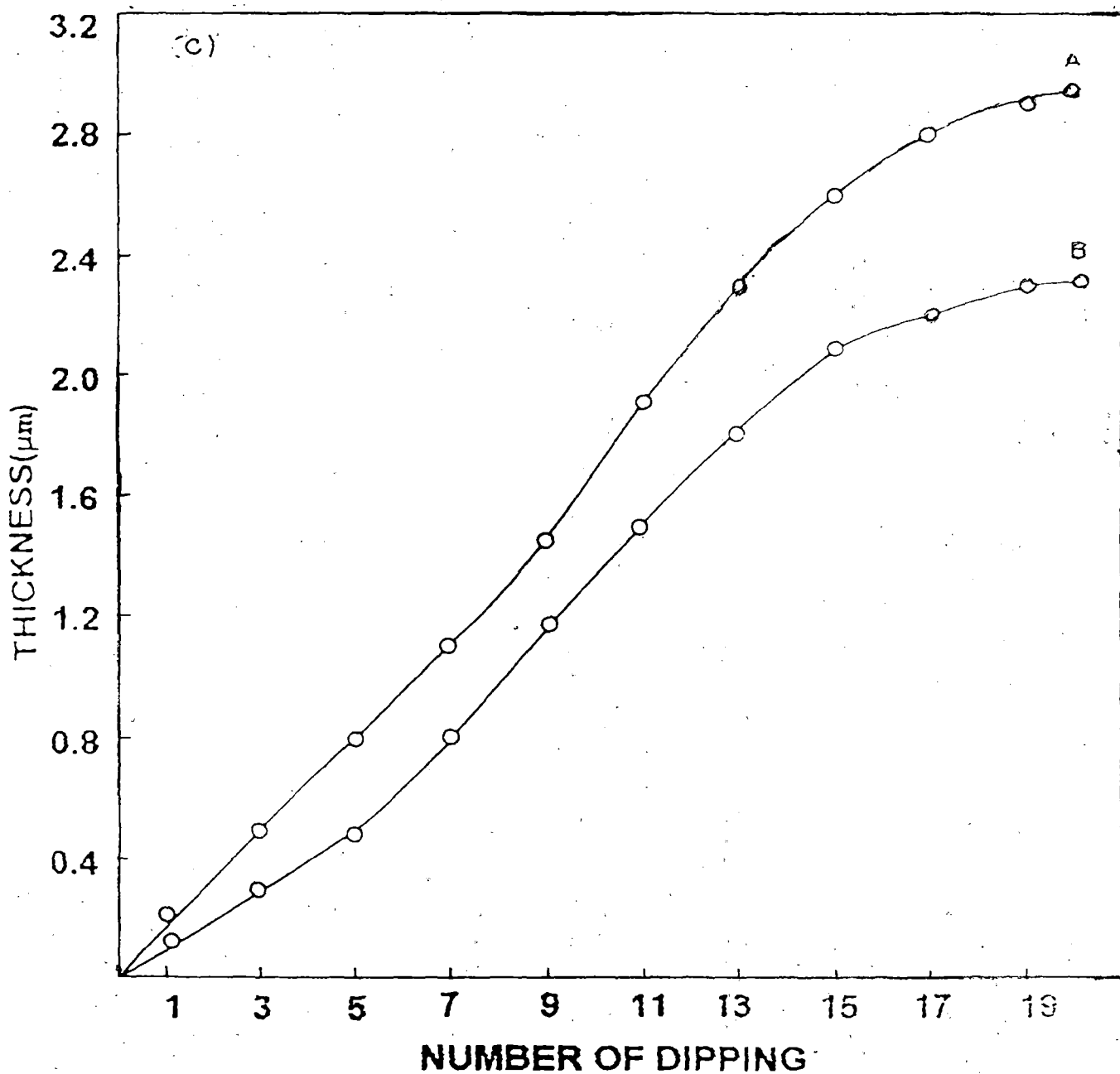
Figure 2.4. Variation of thickness of films deposited on glass substrates with number of dippings at a speed of withdrawal 1.3 mm/sec [concentration of the starting solution: A = 330 gm/litre, B = 250 gm/litre].

This type of behavior has also been observed previously by Procia et. al. [35]. It is possible that at low thickness only isolated small crystallites are formed, which become larger and more densely packed at larger thicknesses [36]. Figure 2.6 shows the X-ray diffractogram of a typical 10-dip film on mica substrate. The peaks are observed to be much sharper compared to those for films deposited on soda-glass substrates. Prominent peaks and their corresponding d- values for typical films deposited on soda-glass (20 dip) and on mica (10 dip) substrate are listed and compared with d-values from ASTM data file in table - 2.1 & table - 2.2 respectively.

Table - 2.1.   *Prominent peak position (2θ values) of x-ray diffraction peaks, corresponding d-values and their identification for SnO$_2$ - based transparent semi-conducting films deposited on glass substrate.*

(2θ)	Observed d- values (A⁰)	Comparable d-values (A⁰) from ASTM data file no 21-1250	h k l
26.6	3.348	3.351	110
33.75	2.653	2.644	101
37.8	2.378	2.369	200
38.9	2.313	2.309	111
51.63	1.769	1.765	211
55.0	1.668	1.675	220
58.12	1.586	1.593	002

Table - 2.2. *Prominent peaks position (2θ values) of x - ray diffraction peaks, corresponding d-values and their identification for SnO_2 based transparent semiconducting films deposited on mica substrate.*

(2θ values)	Observed d - values (A°)	Comparable d - values (A°) ASTM data file no. 21-1250	from h kl
26.75	3.330	3.351	110
34.3	2.612	2.644	101
38.1	2.360	2.369	200
45.6	1.988	2.120	210
52.0	1.757	1.765	211
55.4	1.657	1.675	220
58.1	1.586	1.593	002

The position of the peaks are in conformity with the standard tetragonal crystal structure of SnO_2. Comparison with (I/Io) data from ASTM data file indicates that there is no significant preferential growth in any direction.
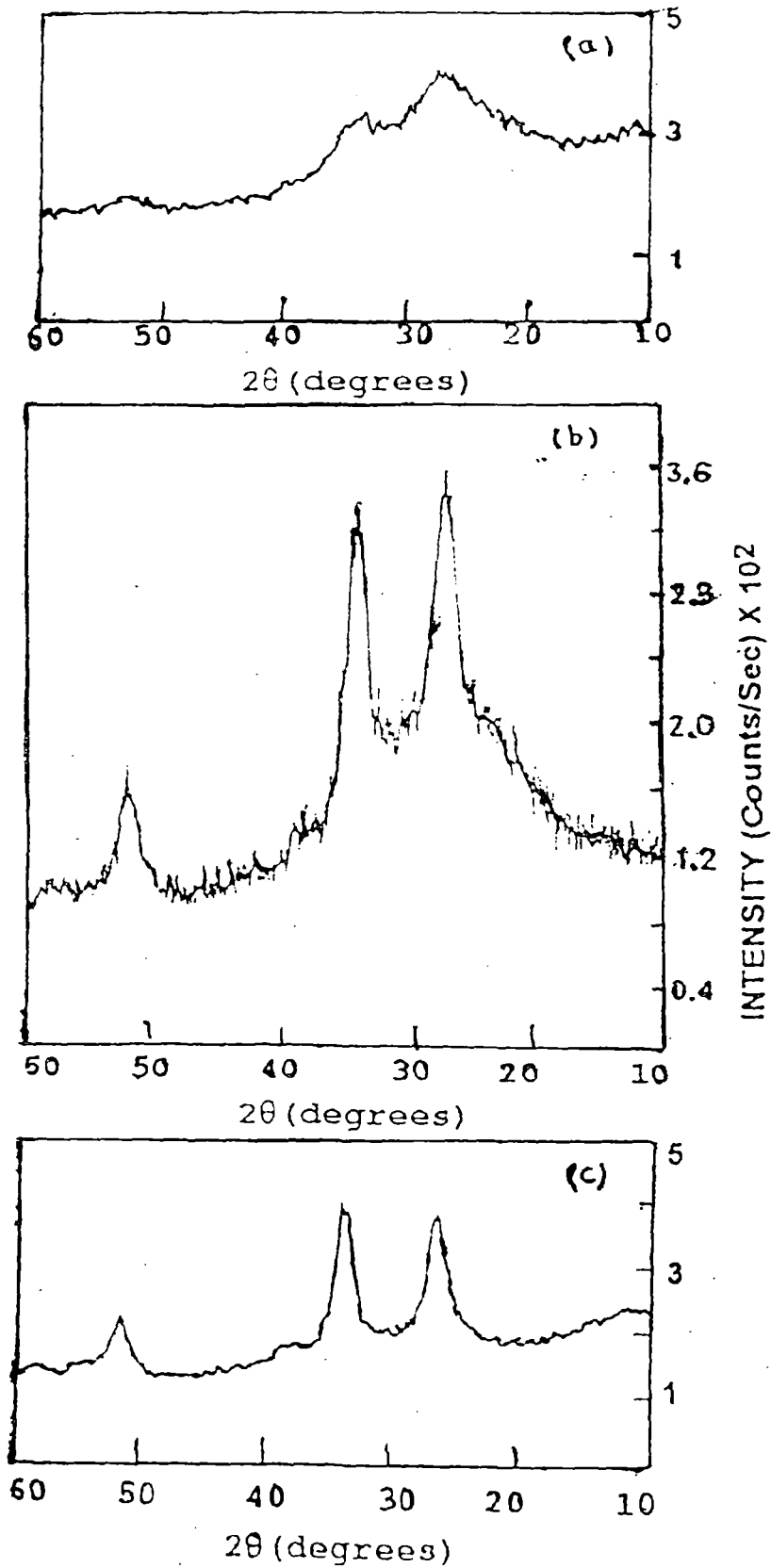
Figure 2.5. X-ray diffractograms of dip coated undoped film on glass

substrate (a) 1st dip (b) 5 dip (c) 10 dip
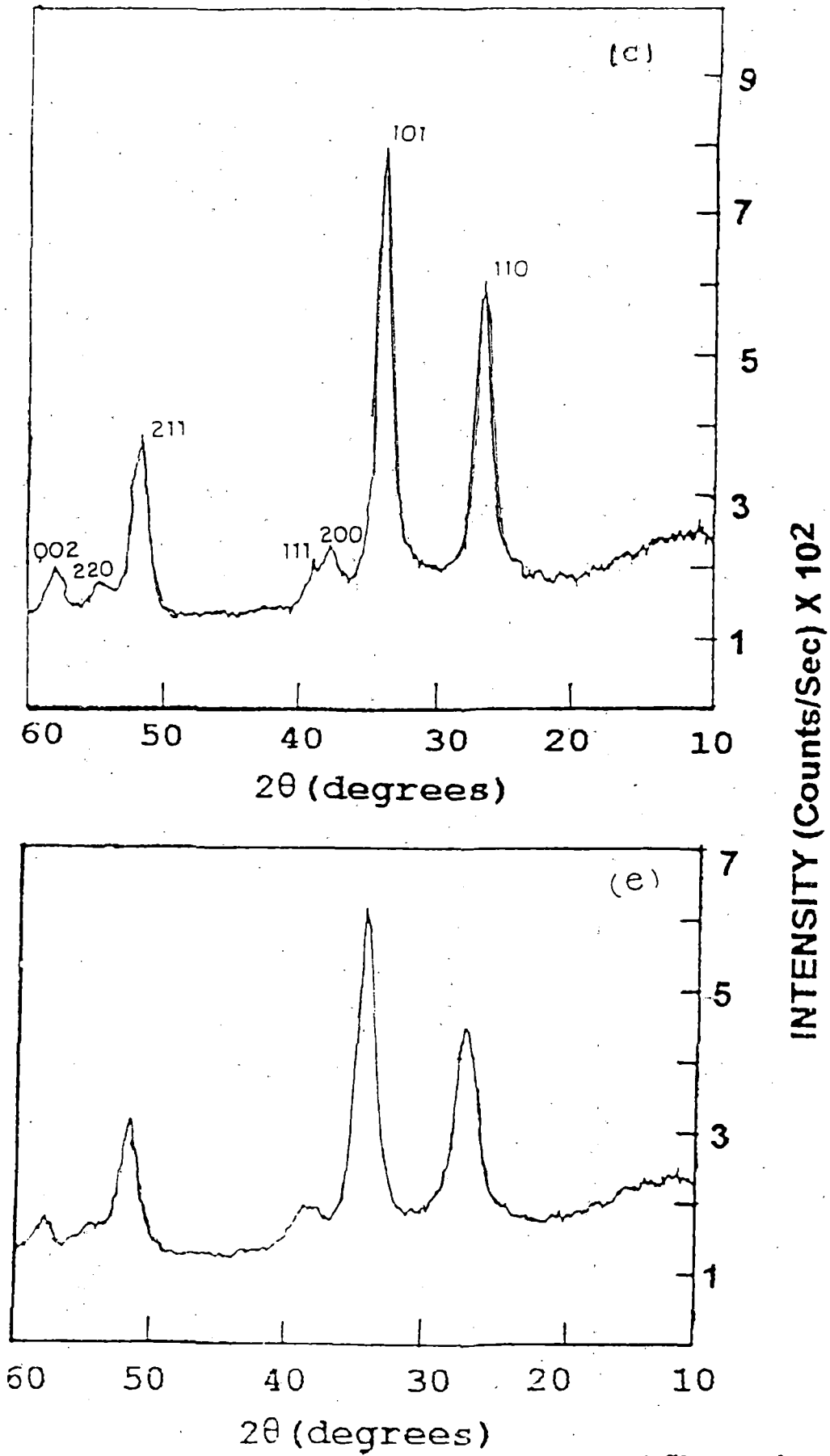
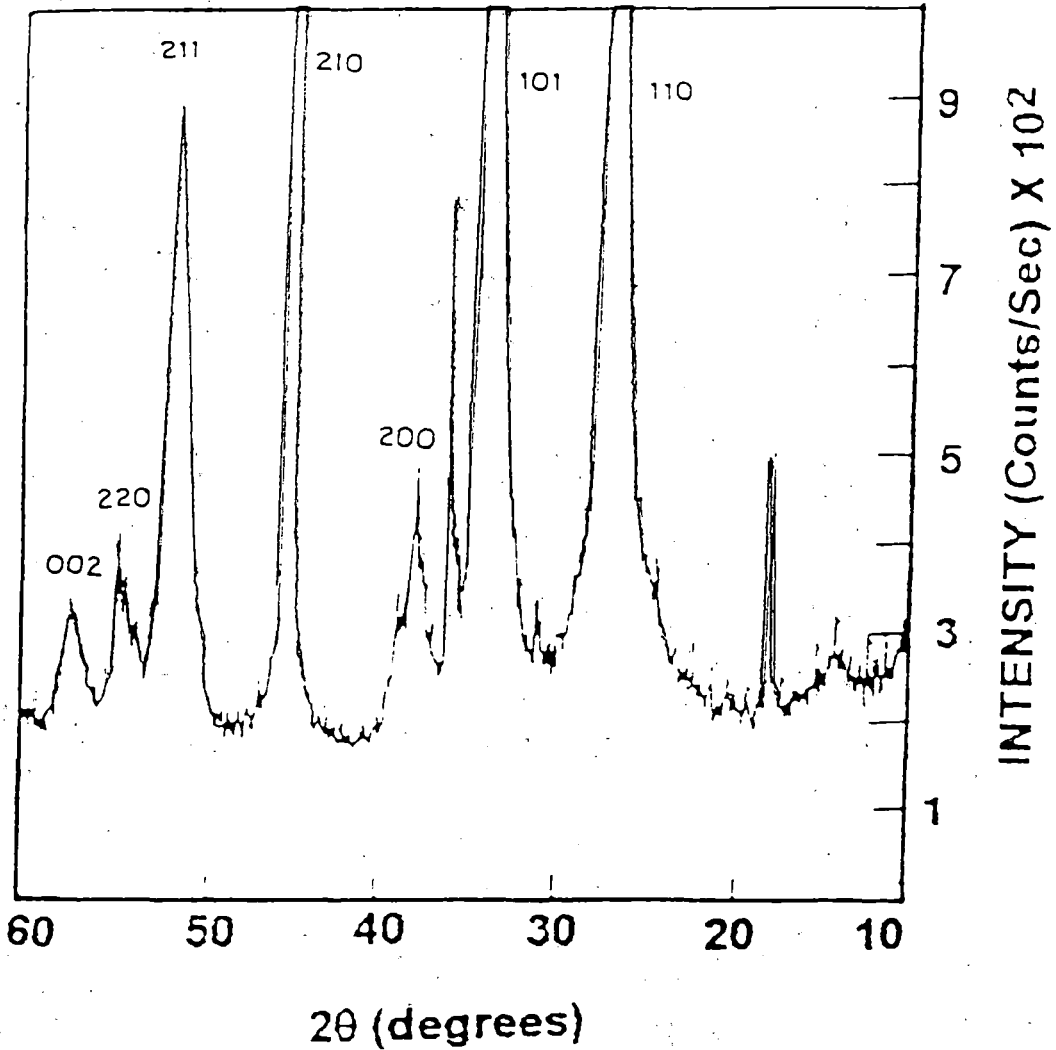Figure 2.5. X-ray diffractograms of dip coated undoped film on glass substrate (d) 20 dip (e) 25 dip

2θ (degrees)

Figure 2.6. X-ray diffractograms of a typical film on mica substrate (10 dip). peaks which are unmarked do not correspond to SnO_2 and probably arises from the substrate itself.

2.4.1.3. ELECTRICAL PROPERTIES

Films of various sheet resistance from 80 - 10^6 $\Omega/\square$ could be obtained by varying the concentration of the starting solution, speed of withdrawal and number of dippings. Figure 2.7 shows the variation of sheet resistance of undoped and F-doped films (4.5 at%) with thickness. The sheet resistance was measured by standard four probe arrangement. It is observed from the curves that sheet resistance decreases with the increase in thickness. The lowest value of sheet resistance of undoped and 4.5 at% F-doped films are 300 $\Omega/\square$ and 80 $\Omega/\square$ respectively for a thickness of 2.96 μm which corresponds to resistivity values of 8.9 x 10^{-2} Ω cm and 2.4 x 10^{-2} Ω cm respectively. It was found that film prepared by single dipping in a high concentration solution has a much higher value of sheet resistance compared to one having the same thickness but prepared by multiple dippings using a lower concentration dip solution. For example, at a thickness of 0.58 μm the sheet resistance of a single dip film was 4 x 10^4 $\Omega/\square$, while that prepared by 5 dippings was 8 x 10^3 $\Omega/\square$. The possible reason may be that for single dipping, a number of loosely packed crystallites are formed, while for multi-dipping these crystallites formed at every deposition step tend to merge together and produce a continuous conduction path. Support for this argument is obtained from figure 2.7, where the sheet resistance of undoped films is seen to drop sharply at a thickness of about 1 μm. For F-doped films the drop occurs at a thickness of about 0.5 μm.
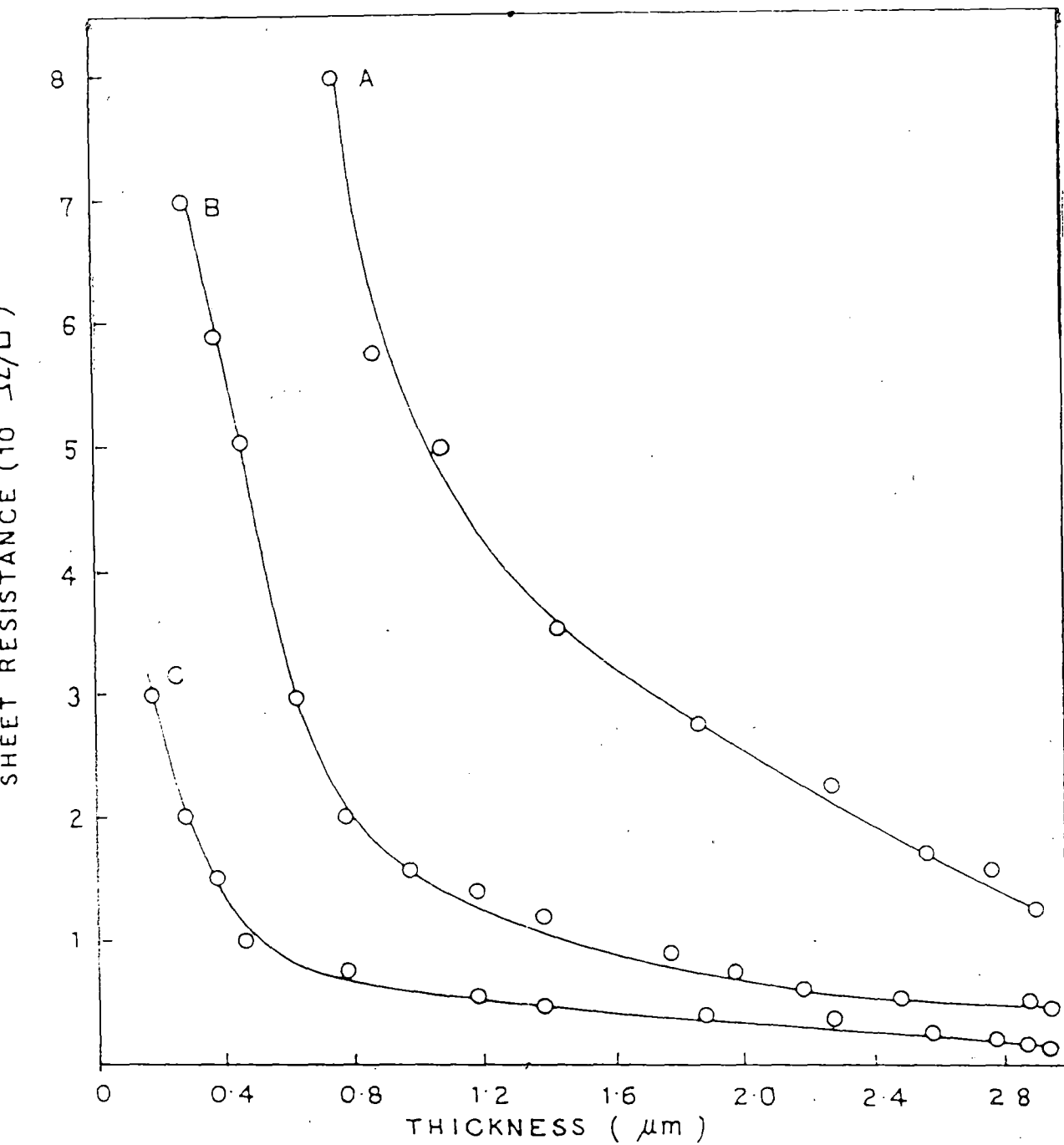
Figure 2.7. Variation of sheet resistance of film deposited on glass substrates with thickness. Undoped: A = 250 gms/litre, B=330 gms/litre and 4.5 at% F-doped: C= 250 gms/litre.

2.4.1.4. SURFACE MORPHOLOGY STUDY BY SEM

Figure 2.8 shows the scanning electron micrograph of undoped and 4.5 at% F-doped film which was studied by HITACHI S-530 scanning electron microscope. It is clear from the micrographs that for the undoped film, grain size increases upto 20 dippings. The initial layer (1st dip) films over an amorphous glass substrate is nearly amorphous, which is evidenced from the XRD pattern also.

Figure 2.9 shows the surface morphology of the films on mica. The grain size is observed to be significantly larger in case of mica substrate than that on glass substrate (Fig. - 2.8.C). The much sharper XRD peaks observed in this case are also consistent with the larger grain size. It is possible that formation of bigger crystallites is facilitated by the single - crystal substrate, which is in contact with the growing film.

2.4.1.5. OPTICAL PROPERTIES

Dip deposited films are highly transparent. Figure 2.10 shows the optical transmission versus wavelength curves for undoped and 4.5 at% F - doped films with different sheet resistance values. These optical transmission data were obtained by SHIMADZU UV-240 double beam spectrophotometer (air reference). It is seen that the optical transmission is reduced as a result of doping. A similar phenomenon has also been observed by chopra et. al. [37] and De et. al. [36] and attributed by them to a high surface roughness of SnO_2 films having low sheet resistance compared to undoped ones. Average optical transmission of 85 % - 90 % for undoped and 75 % - 80 % for doped films are obtained for a thickness of 2.96 μm over a range 400 nm to 800 nm.
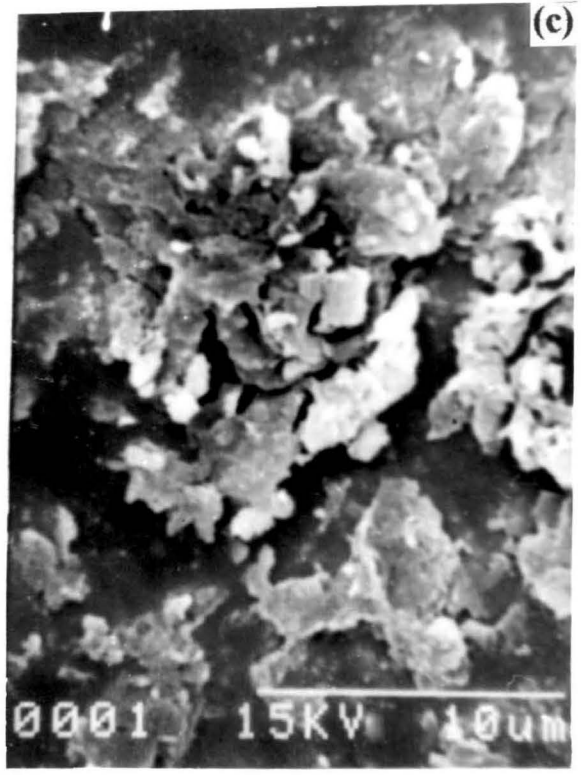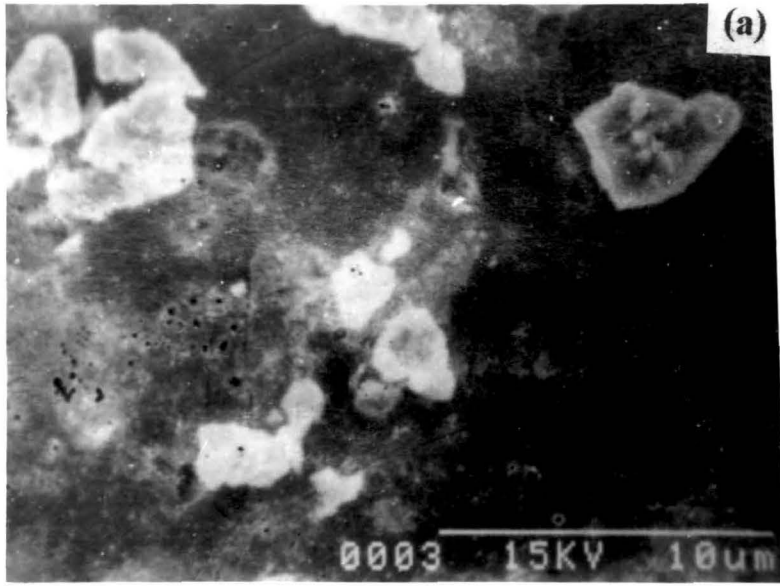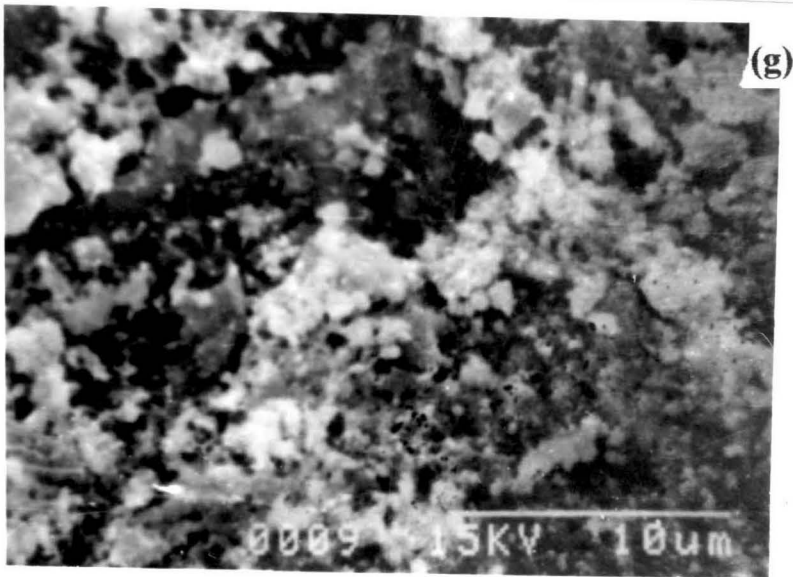
Figure 2.8. Electron micrographs of undoped films on glass substrate undoped: (a) 1st dip, (b) 5 dip, (c) 10 dip.
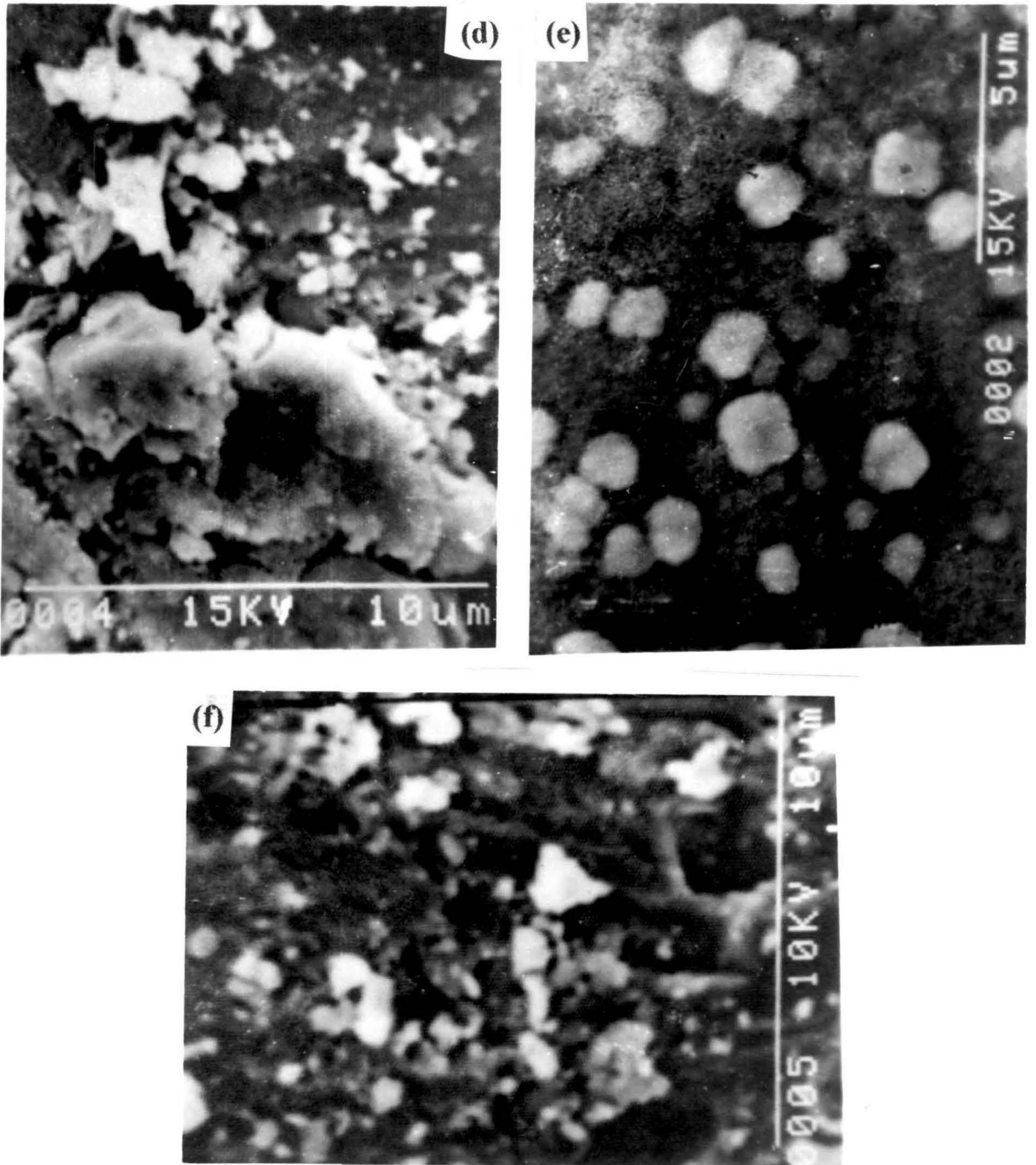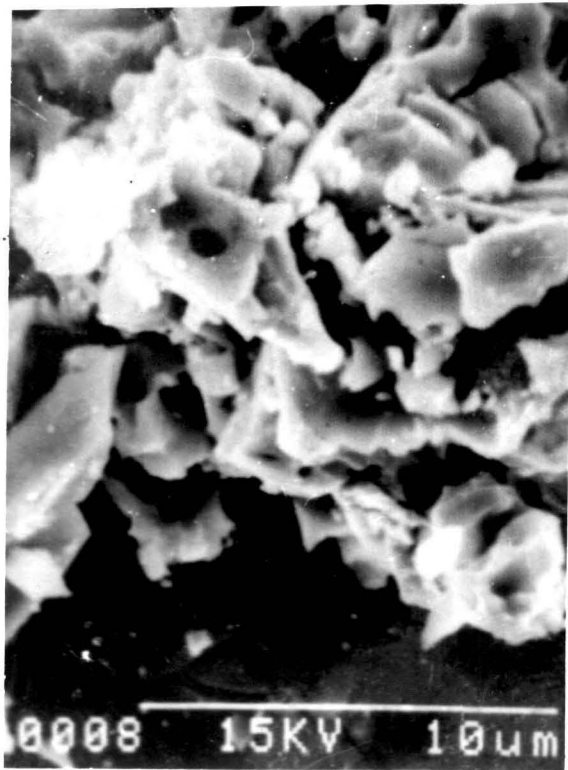
Figure 2.8. Electron micrographs of undoped films on glass substrate undoped: (d) 15 dip, (e) 20 dip, (f) 25 dip.

Figure 2.8. Electron micrographs of doped films on glass substrate 4.5 at% F-doped: (g) 20 dip.

Figure 2.8. Electron micrographs of undoped films on mica substrate (10 dip).
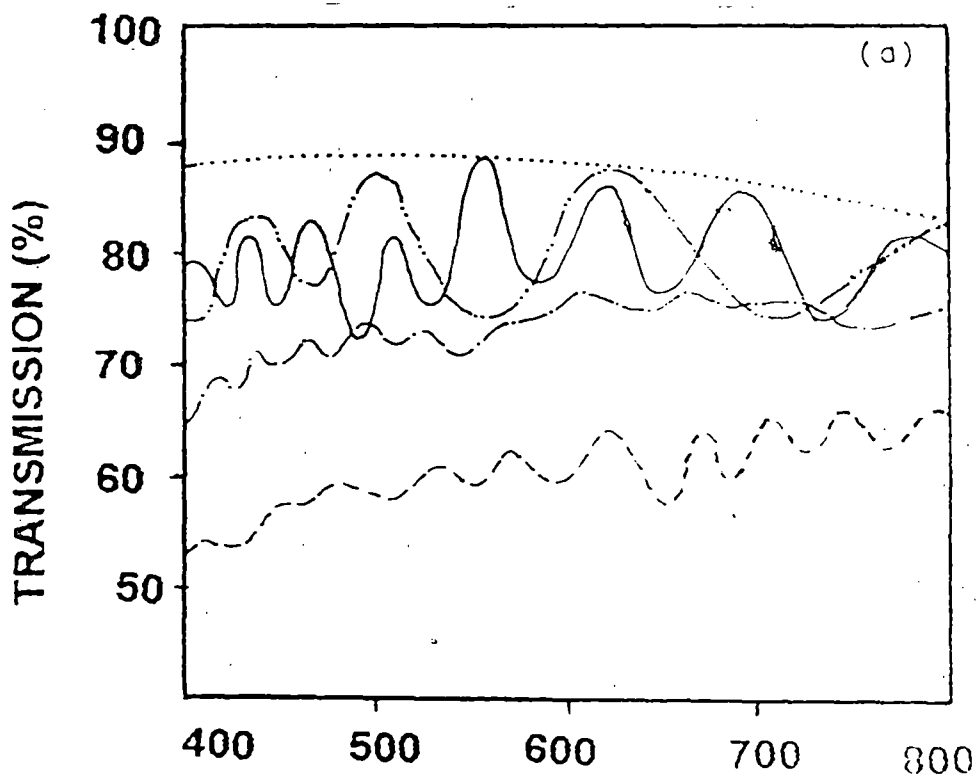
Figure 2.10. Optical transmission versus wavelength for typical films of various sheet resistances (a) Undoped: (......), bare ubstrate; (_____) 4000 $\Omega/\square$; (-..-..-..-) 1250 $\Omega/\square$; (-.--.-.-) 600 $\Omega/\square$; (——) 250 $\Omega/\square$.
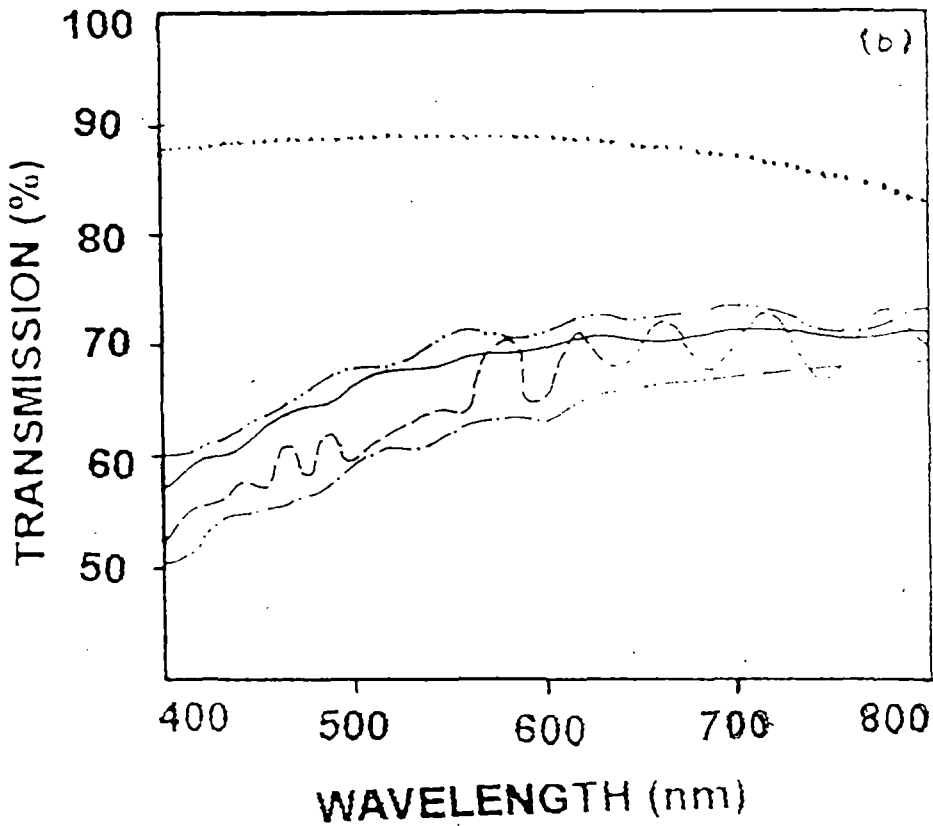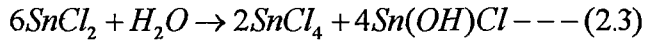
Figure 2.10. Optical transmission versus wavelength for typical films of various sheet resistances (b) 4.5 at% F-doped films:(........) bare substrate; (_____) 800 Ω/; (-------) 500 Ω/; (-...-...-..-) 200 Ω/; (-..-..-..-) 90 Ω/.

2.4.1.6. DISCUSSION

It is known [38,39] that $SnCl_2$ undergoes hydrolysis in presence of atmospheric oxygen according to the equation

$$6SnCl_2 + H_2O \rightarrow 2SnCl_4 + 4Sn(OH)Cl - - - (2.3)$$

This reaction is relatively slow at room temperature, but is accelerated on heating, $SnCl_4$ in turn, readily hydrolyses to SnO_2 at a high temperature as given below

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl - - - (2.4)$$
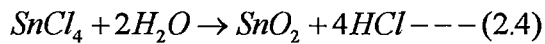
This forms the basis of preparation of conduction tin dioxide films by the paste-heat or OACVD method [39 & 40, details are given in chapter 4]. In these methods, $SnCl_4$ produced from reaction 2.4 taking place in a separate area is allowed to hydrolyse on the substrate and yield SnO_2 films, which is discuss earlier. In contrast, in the present method the Sn(OH)Cl also remains on the substrate and forms the amorphous matrix, while most of the $SnCl_4$ produced escapes. A small fraction of this $SnCl_4$ however, is hydrolysed on the substrate and produce small SnO_2 crystallites. Repeated dipping increases the number of these crystallites which form a continuous film after about 15-20 dippings. This can be seen from the XRD spectra, the variation of sheet resistance with thickness and the SEM photographs. We see that the sharp drop in sheet resistance, appearance of sharp XRD peaks and merging of SnO_2 grains., all take place at a thickness of about 1 μm. However, even at this stage there is a large amorphous background present., as shown in by the high value of resistivity. viz, 2.4 x 10^{-2} Ω cm compared to 2.4 x 10^{-4} Ω cm for CVD SnO_2 films.It may be interesting to note that in the work of Gordillo et al. [41] also on spray-deposited SnO_2 films, a strong amorphous

background is seen to be present in the XRD pattern when $SnCl_2$ was used as a starting material.

Thus although an amorphous background, most probably $Sn(OH)Cl$, is present in the films, it is highly transparent and leads to no significant drop in optical transmission. This amorphous background is also responsible for making the resistivity about two orders of magnitude higher than that obtained for CVD films. However, their high optical transmittance makes these films suitable for those display applications where the currents requirement is low, e.g. liquid crystal or electrochromic displays. In addition, the simplicity of the deposition method could make it attractive for enhancing the IR reflectivity at a low cost, e.g. in solar cookers.

The effectiveness of a transparent conducting film depends on its optical transmission as well as its sheet resistance. As already discussed, the high sheet resistance of the dip-deposited films is to a great extent compensated by their large optical transmittance. Haacke [42] has introduced a figure of merit for transparent conducting films defined by the relation $\Phi_{TC} = T^{10}/Rs$, where T is the optical transmittance and Rs is the sheet resistance. This parameter can be used to evaluate the performance of a candidate material from its fundamental parameters. A typical Φ_{TC} value for our 4.5 at% F-doped, dip-deposited film is $2.5 \times 10^{-3} \ \Omega^{-1}$, which compares quite favorably with the value of $2.6 \times 10^{-3} \ \Omega^{-1}$ for CVD SnO_2 films [14, 43].

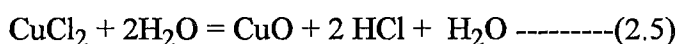# 2.5. COPPER OXIDE (CuO) THIN FILMS BY THE DIP TECHNIQUE

Copper oxide, which is a promising semiconductor material for fabrication of photovoltaic devices like solar cells [44], has been the subject of a number of studies in the past. The investigations carried out concern mainly its growth and optical properties [45-51]. Recently, with the discovery of high temperature superconductivity study of decomposition of CuO/CuO_x employing both metallic and oxide sources has assumed special importance in the preparation of the thin film high temperature superconductors (HTSCS). Thin films of copper oxide have been prepared using various thin film deposition techniques such as chemical vapour deposition, electro-deposition, thermal oxidation and sputtering process [52-54]. Electron - beam evaporation technique also has been reported in the literature for the growth of Cu_2O thin films [45-50].

However, in comparison with other thin films of oxide semiconductors such as In_2O_3, ZnO and SnO_2, few data are available in the literature on the characterization of copper oxide films.

In the following section, preparation of CuO thin films and their structural and optical properties have been discussed.

2.5.1. PREPARATION OF CuO THIN FILM

Methanolic solution of cupric chloride ($CuCl_2.2H_2O$) is taken as a starting solution for the deposition of CuO thin films by the dip technique. The solution was prepared using 0.25 kg cupric chloride in one litre methanol. Cupric chloride ($CuCl_2.2H_2O$) hydrolysed and reacted on the heated substrate inside the furnace at high temperature in open air and formed thin solid films according the following reaction.

$$CuCl_2 + 2H_2O = CuO + 2\,HCl + H_2O \text{ ---------(2.5)}$$

The copper oxide thin films were deposited by the dip technique on glass substrate in atmospheric condition at three baking temperature of 360° C, 400° C and 500° C. The film deposition procedure is same as in the case of SnO_2 film (described in 2.2 section). Films were uniform and black in colour. Films which were characterized had a thickness of the order of one micrometer.

2.5.2. RESULTS AND DISCUSSION

The X-ray diffraction spectra of the CuO films prepared at three baking temperatures are shown in figure 2.11. The relevant diffraction planes are indicated in the spectra. Analysis of diffraction spectra indicates that the peak positions correspond to CuO phase. The films prepared at 360° C show ($\bar{1}$11) and (200) planes whereas films prepared at 400° C and 500° C film show (002) and (111) planes of CuO. Results of peak position observed for the films prepared at three different temperatures and their, comparison with the ASTM data values (file No. 5-661) are given below in the table 2.3.

Table 2.3. *Comparison of observed value and ASTM data value of CuO thin films deposited by dip technique.*

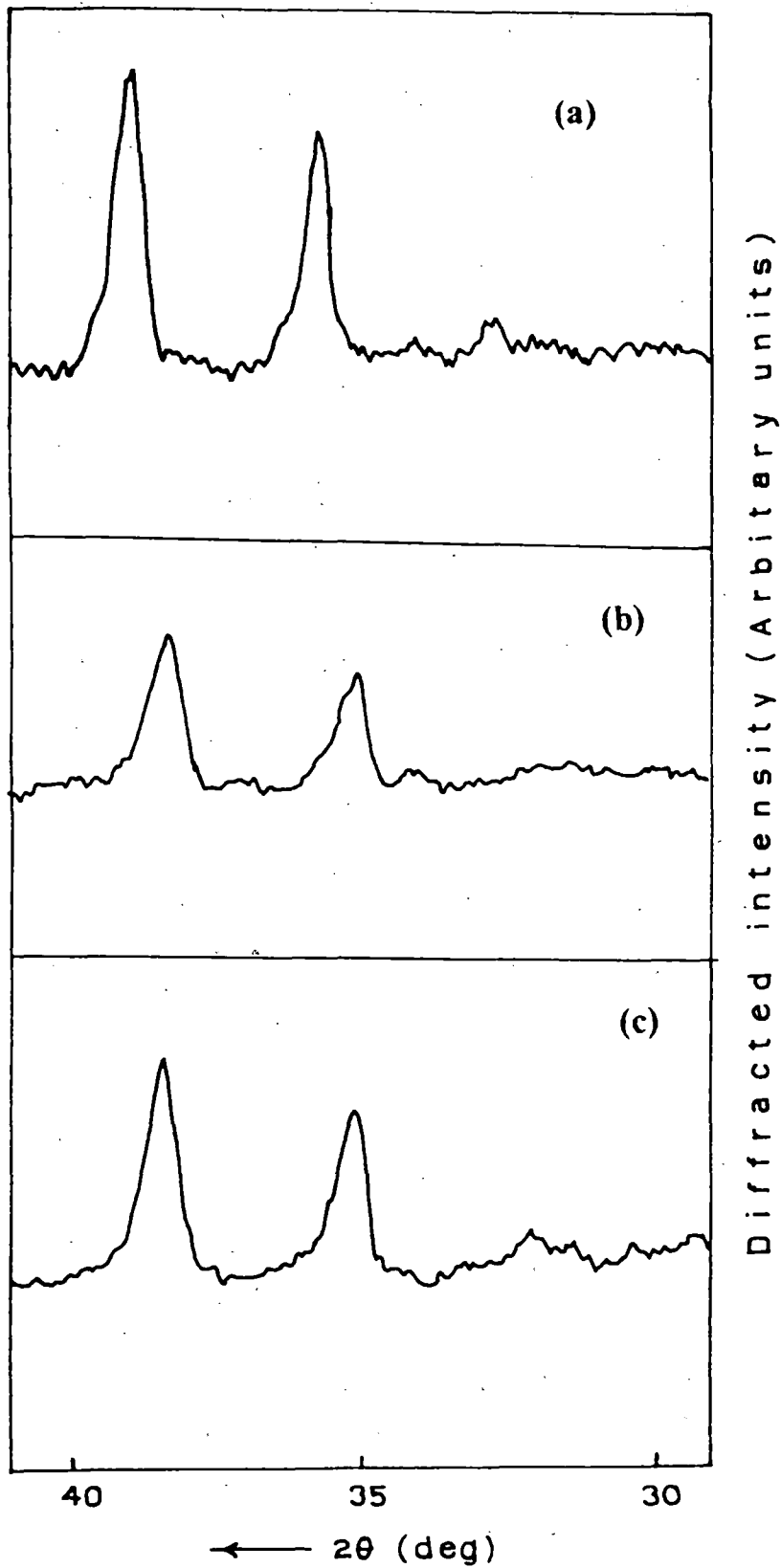| OBSERVED VALUE			ASTM DATA VALUE			h k l
2θ	d (A°)	(I/Io)	2θ	d (A°)	(I/Io)	
T_B = 360° C						
35.7	2.51	78	35.6	2.52	100	$\bar{1}$11
38.9	2.31	100	38.9	2.31	30	200
T_B = 400° C and T_B = 500° C						
35.3	2.56	78	35.4	2.53	49	002
38.3	2.35	100	38.7	2.32	96	111

Figure 2.11. X-ray diffractogram of CuO thin films deposited on glass substrate at three different baking temperature [(a), 360⁰ C; (b), 400⁰ C; 500⁰ C].

The optical absorption of the copper oxide thin films was measured using SHIMADZU UV - 240 double beam spectrophotometer in the range 350 - 800 nm. A typical recording for the optical absorption of copper oxide film is shown in figure 2.12. To analyse these results, $(\alpha h\nu)^2$ is plotted against hν [Fig. 2.13] and from the intercept of the straight line on the hν axis the band gap is estimated. The band gap value thus obtained is about 1.85 eV, which is in good agreement with the value 1.80 eV obtained by Miller et.al. [51].

2.6. CONCLUSION

It has been demonstrated that the dip-coating technique can be used to deposit CuO and SnO_2-based transparent conducting oxide films in a simple manner using metallic chlorides ($SnCl_2.2H_2O$ for SnO_2 and $CuCl_2.2H_2O$ for CuO) as a starting material.

Tin dioxide based transparent conducting films contain crystalline SnO_2 in addition to an amorphous background, probably of Sn(OH)Cl. The resistivity of these films is somewhat higher compared to SnO_2 films prepared by CVD or spray pyrolysis. This is probably due to the presence of the amorphous constituent. However, the films are highly transparent and have a figure of merit value comparable to that for conventionally-prepared SnO_2 films. The films would be potentially useful for low-current application such as display devices.

Copper oxide films are prepared using methanolic solution of cupric chloride ($CuCl_2.2H_2O$) at three 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 value.

Dip technique is a very simple and low-cost method, which requires no sophisticated specialized setup. Coating of the substrate of a large surface area can be
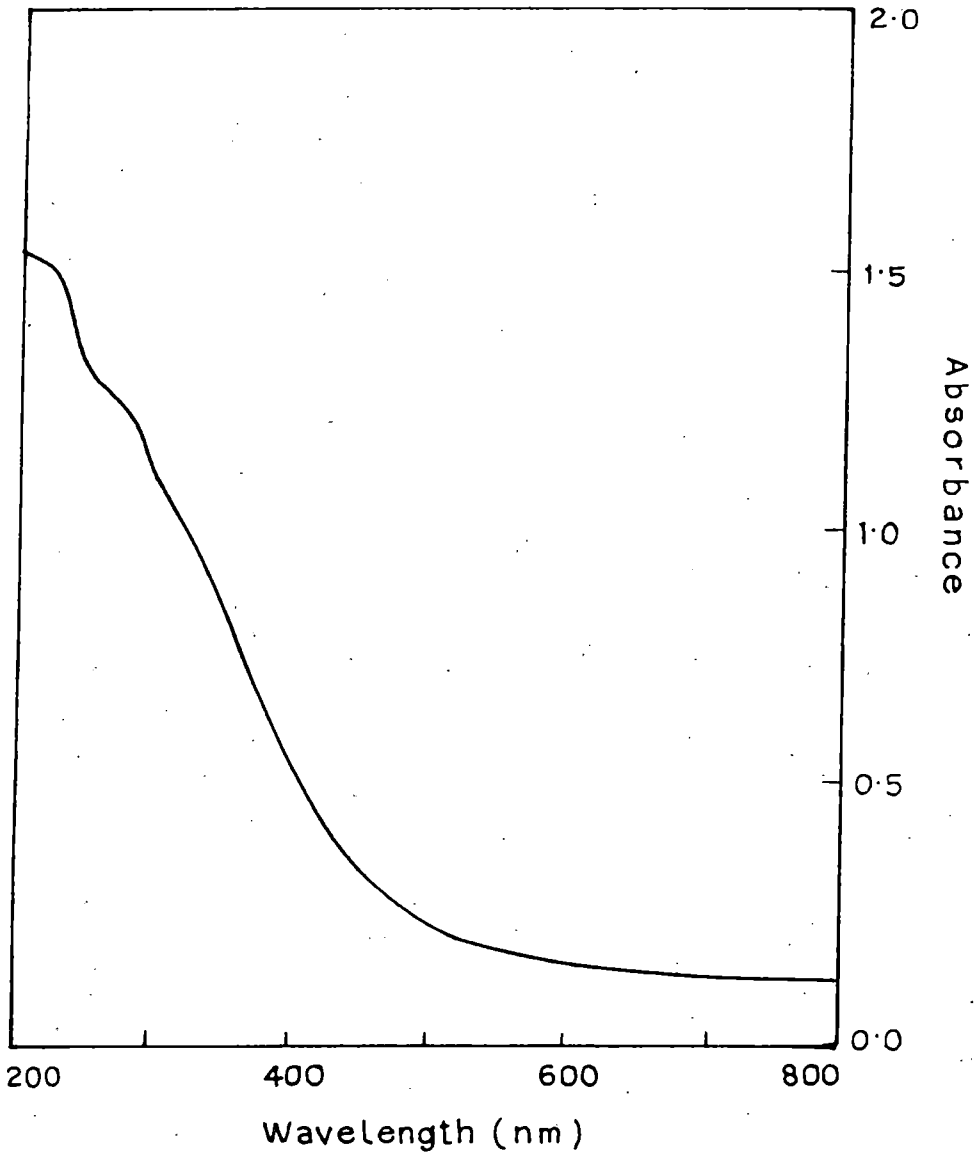
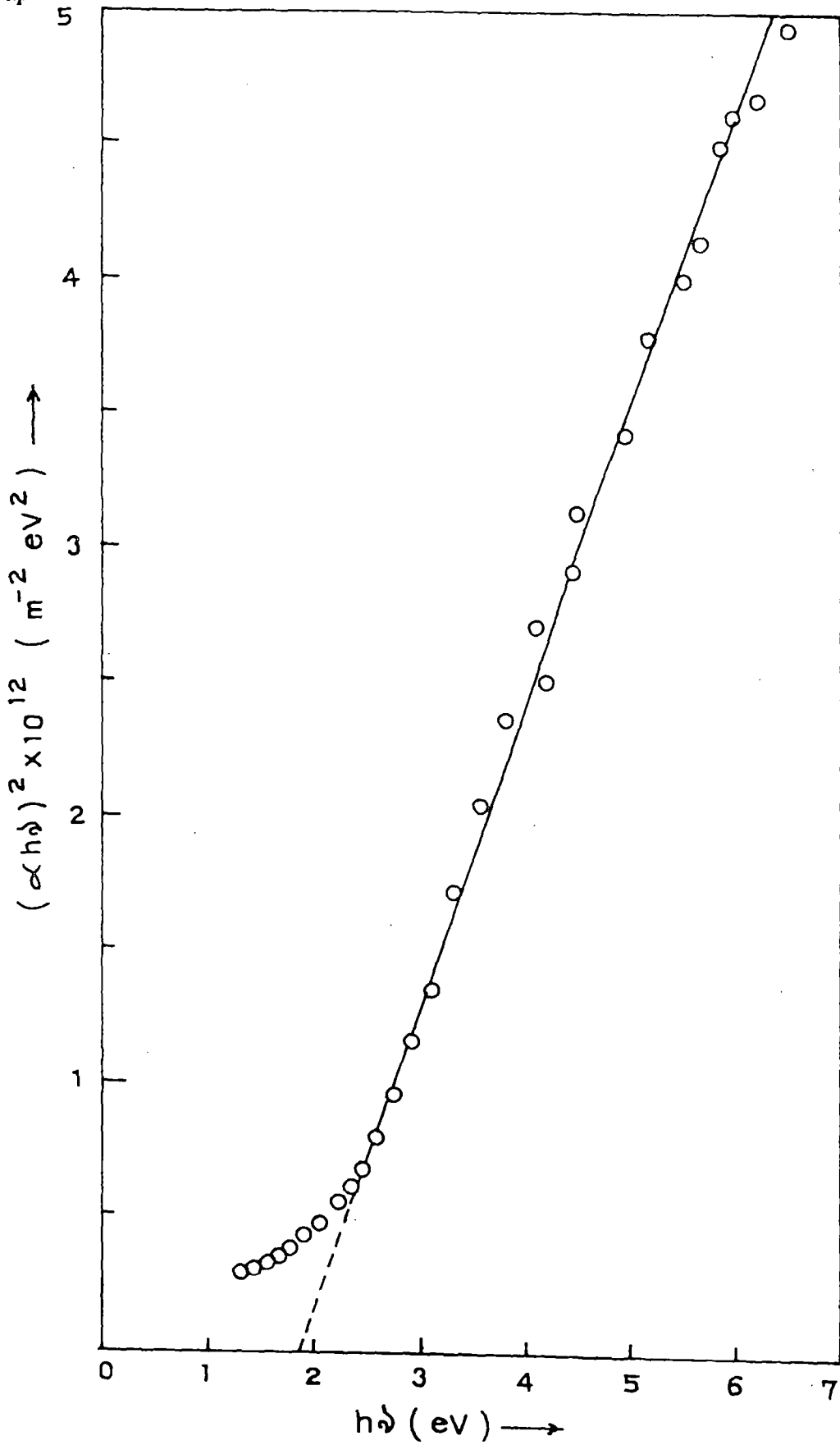Figure 2.12. Optical absorption spectra of CuO thin films deposited on glass substrate at 400º C.

Figure 2.13. Plots of (αhv)² against hv curves for CuO films deposited on glass substrate at 400° C.

easily obtained by this technique compared to that in sputtering, vacuum vapour deposition and spray pyrolysis. Another advantage of the dip technique is that it is very easy to coat both sides of the substrate instead of only one and to deposit otherwise inaccessible surfaces. This method is well suited for applying coating on the inner and outer surfaces of tubes of various diameters and shapes. The main advantage of the dip coating method lies in fact that it is possible to deposit a variety of layers having good homogeneity and mechanical and chemical stability with a very simple setup. Multilayer thin films of different metal oxide layers one after another can be deposited easily by this technique. It should be stressed that both the oxide films produced by the dip technique have been found to be stable after several months observation in laboratory conditions.

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