

THE DEPOSITION OF THIN FILMS OF ZnO BY SOL GEL METHOD AND THEIR CHARACTERIZATION



A Thesis

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By

Syed Ansar Md. Tofail

Roll No. 9411002 F

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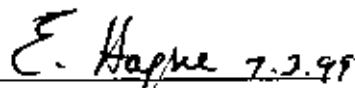
Department of Materials and Metallurgical Engineering
Bangladesh University of Engineering and Technology
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1. Dr. Ehsanul Haque

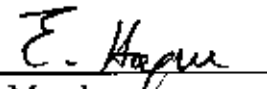
Professor

Dept. of Mats. and Met. Engg.
BUET, Dhaka.


Chairman & Supervisor

2. Head

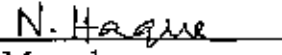
Dept. of Mats. and Met. Engg.
BUET, Dhaka.


Member

3. Dr. Md. Nasrul Haque

Professor

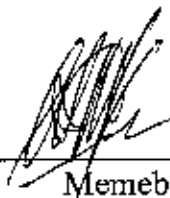
Dept. of Mats. and Met. Engg.
BUET, Dhaka.


Member

4. Dr. A.S.M.A. Haseeb

Associate Professor

Dept. of Mats. and Met. Engg.
BUET, Dhaka.

 07/03/99
Member

5. Dr. S.M. Feroz Hasan

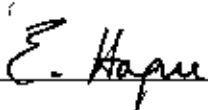
Physics and Materials Science Div.
Atomic Energy Centre, Dhaka

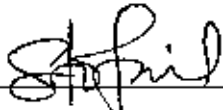

Member (Ext.)

DECLARATION

This is to certify that this thesis which is presented for an MSc in Engineering degree by the candidate includes the results of investigations carried out by him under the direct supervision and guidance of Dr. Ehsanul Haque, Professor, Department of Materials and Metallurgical Engineering, BUET, Dhaka. The work of this thesis has not been presented for any other degree or diploma in any other university and no other person's work has been used without due acknowledgement.

Countersigned


(Supervisor)


Signature of the author

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ABSTRACT

Thin films of zinc oxide have been deposited on Pyrex glass substrate by using sol gel process and characterized by means of different characterization techniques including optical microscopy, X-ray diffractometry (XRD), thermogravimetry and spectrophotometry. The sol has been prepared by reacting zinc acetate and ethylene glycol and dissolving the resultant solution in n-propanol. Glycerol was added to the sol to increase its stability. A proton acceptor like diethyl amine was added to assist hydrolysis of zinc acetate. Thin films of zinc oxide were cast on the substrate by dip coating method and gelled in humid air. The as deposited film was annealed at various temperatures ranging from 150 C to 450 C for 15 minutes at each set temperature. It has been found that the cleanliness of the glass substrate, the humidity during the gelation of the film as well as the time and temperature of the heat treatment affect the appearance and the morphology of the film. Cleaning of the glass substrate for the successful deposition of the film was achieved by the use of deionized water, acetic acid and absolute ethanol. Relative humidity less than 50% during the deposition of the film on to the glass substrate was found to be favorable for yielding good transparent film. It has been found that annealing of the film pyrolyzes gelled film to zinc oxide, drives out moistures and other volatiles and at higher temperatures decomposes the metalorganic complexes. The amorphous as-deposited film transforms to polycrystalline as a result of annealing above 275 C and the XRD peaks become sharper and more intense with the increase in annealing temperature. The films annealed at higher temperature, especially those annealed above 400 C, are denser and less porous and annealing leads to the increase in the size of the ZnO crystallites in them. The thin films of ZnO formed are randomly oriented without showing any preferred orientation. The ZnO crystallites have the hexagonal wurtzite structure, with $c = 5.271 \text{ \AA}$ and $a = 3.285 \text{ \AA}$. The average thickness of the films from thermogravimetric analyses has been found to be about $1 \text{ }\mu\text{m}$ after annealing at 450 C for 15 minutes and the film and the film exhibited about 80% transmission.

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CHAPTER ONE

INTRODUCTION



1.1. THIN FILM AND ITS DEVELOPMENT

A thin film is regarded as a plane parallel layer of essentially infinite extent whose thickness is comparable with the wavelength of light. A multilayer thin film is a finite combination of such layers¹. Thin films of metals, semiconductors and dielectrics have become of increasing importance for the fundamental studies in many fields of science and technologies and are also used in numerous practical applications. Since certain measurements can more conveniently be made by using thin films, such films are often used to obtain information about the properties of solids in general. However, fundamental properties of solids in thin film form frequently differ considerably from those of the bulk materials¹. So, extensive studies of the optical, electrical, magnetic, and superconducting properties, and investigations of structural order, dislocations, migrations phenomena etc. are being made on thin films. The results obtained by such fundamental studies are of great commercial and practical importance in the use of such films.

Physical phenomena peculiar to thin films are generally the consequence of their planar geometry, size and unique structure. The technical interests which stimulated these studies have also been rewarded in the form of useful invention such as a variety of active and passive microminiaturized components, solar cells, radiation sources and detectors, magnetic memory devices, bloomers, interference filters, and reflection and anti-reflection coatings².

The study of thin film phenomena dates well over a century. However, it is over the last few decades that they have been used to a significant extent in practical

situations. Since the properties of thin films are rather different from the bulk material theoretical explanations regarding the properties of thin films were required. Thompson in 1901 was the first to propose a size-effect theory³ in order to explain the observed high electrical resistivity of thin specimen as compared with that of the bulk metal albeit thin solid films were probably first obtained² by electrolysis in 1838. The "size - effect theory" for a free-electron model was, however, worked out by Fuchs⁴ in 1938 for a spherical fermi surface and extended by Sondheimer⁵ in 1950 as to include galvanomagnetic effects. The size-effect theory for temperature coefficient of resistance was computed by Campbell⁶ in 1966.

Thin film technology had a rapid growth between the two world wars when vacuum evaporated metal and dielectric films were used in optics for mirrors and anti-reflection coatings respectively. The development of diffusion pump made possible the construction of large vacuum systems and vacuum evaporation apparatus began to be widely used in the optical industry. Since then a new branch of optical technology has emerged based on the optical film interference system.

Rapid increase of interest in technical applications of thin film that has taken place in last few decades has given rise to a correspondingly rapid development of thin film optics — the branch of physical optics dealing with reflection, transmission and absorption of light by single and multilayer films. The optoelectronic thin films find their extensive use in many applications including photovoltaic applications.

The most modern development in the field of thin film physics is that of the optoelectronic devices. Photovoltaic, photocunductive and solid state laser devices are now under considerations. Now a days, extensive studies on different properties of thin films proceeded along different lines throughout the world. Recently an even greater application known as thin film microelectronics has emerged in the field of

electronics and consequently a rapid development occurred in the microelectronics industry.

Many experiments on magnetic ultra thin films, sandwiched between non magnetic materials have shown that the magnetic interface anisotropies can be several orders of magnitude larger than the magneto crystalline anisotropies found in bulk crystals². In general these studies were focused on films or multilayers with only one type of magnetic layer coated with a non magnetic metal.

1.2. CHARACTERISTICS OF THIN FILM:

The properties of thin films are something different from that of the bulk material due to various reasons. Actually, the properties of a thin film changes appreciably when it is cooled to a very low temperature or heated to a high temperature². A study of the changes in the properties of thin films, when the films are heated to higher temperatures provides a good deal of information about the properties of films.

The physical properties of thin films are determined by a number of factors², e.g.

(i) *The nature of substrate*: Substrate may be non-crystalline solids e.g. glass or vitreous silica or crystalline material e.g. cleavage plates of rock salt or mica.

(ii) *The temperature of the substrate during deposition of the films* : At low temperature micro-polycrystalline films with high densities of structural imperfections are formed on both vitreous and crystalline substrates, but at high deposition temperatures oriented films are formed on crystalline substrate particularly in vacuum processes. Similar effects of temperature of the substrate have been observed in spray pyrolysis process also.

(iii) *The relative values of the minimum annealing temperature*: heating the film to a higher temperature after deposition and cooling it back to room temperature affect the ultimate film properties especially by affecting its grain size and morphology.

(iv) *Annealing cycle*: plays an important role in the surface mobility of the atoms at the temperature of the substrate during deposition.

(v) *Deposition conditions*: various properties of thin films have been found to depend on relevant pressure, current, time etc. during the deposition.

1.3 APPLICATIONS OF THIN FILMS

Thin films are widely used in today's technology, and their applications are expected to be even more widespread in future. It is not possible to give an exhaustive survey over thin film applications, but a listing may, nevertheless, be of some interest. The applications areas for thin films are:

A. Optically Functional: Mirrors, architectural glazing, automotive windows, spacecraft temperature control, solar absorbing coatings, anti-reflection layers on optical components, coatings for laser optics, display devices etc.

B. Electrically Functional: Conductors, semiconductors, insulators (resistors, capacitors), super-conductors, contacts, micro electronic devices, solar cells etc.

C. Magnetically functional: Computer memories, computer logic elements, radio-frequency and microwave materials etc.

D. Mechanically functional: Hard coatings for cutting tools, lubrication coating, wear and erosion resistant coating etc.

E. Chemically functional: Corrosion resistant layers like catalytic coatings, diffusion barriers,

batteries etc.

F. Decorative functional: Watch bezels and bands, eye-glass frames, costume jewellery etc.

These days thin films have a great role in photovoltaic applications also. Thin film photovoltaic solar cells are defined as those cells in which the active energy converting layer is either a polycrystalline or amorphous film⁷, with the total thickness for the active region of no more than 5 μ m. Such thin films are commonly characterized as having less perfect layers than are associated with the single crystal materials leading to reductions in the cell performance and efficiency. However, when we consider the cost- performance ratio we will see that thin film solar cells generally offer a low cost per unit area. So thin films have a great potentiality if the performance of these cells can be improved.

Various thin films in collecting solar energy find their uses in i) metallization films, ii) protective films, iii) antireflection coatings, iv) chemically persisting films, v) abrasion resistant coatings, vi) transparent conducting coatings, vii) semiconductors for absorbing the light energy⁸ etc. These all account more or less to the overall performance and so each require close investigation and characterization so that the ultimate assembly gives a well performing cell at a reasonable cost.

1.4 OBJECTIVE OF THE PRESENT WORK :

During the last few years transparent conducting oxides (TCO) have been studied extensively ⁹⁻¹⁰ especially when deposited by means of spray - pyrolysis techniques¹⁰. The exploration of the sol-gel route for such TCO thin films is much more recent ¹¹⁻¹⁴.

Zinc oxide is a promising material for many different applications such as solar cells, gas sensors, ultrasonic oscillators, varistors and transducers¹⁵. It has been

found that ZnO, when doped, shows good electrical conductivity and hence is likely to be a good candidate as a TCO to substitute indium tin oxide (ITO) and tin oxide (SnO_2) in conductive electrodes of amorphous Si-solar cells¹⁶. As a low cost alternative to the ITO, ZnO could be used as TCO for the use as a window layer for solar cells.

Several film growth techniques like sputtering¹⁷⁻¹⁸, metalorganic chemical vapor deposition (MOCVD)¹⁹, spray pyrolysis^{15-16,20-21} and pyrosol²² techniques have been employed to deposit good quality ZnO thin film. The sol-gel^{12-13,23} route is comparatively a novel one in this expedition. In the present study the sol-gel route for the preparation of ZnO thin film has been used. The main reason behind selecting this route is the ease of fabrication and the elimination of costly equipment.

It appears that a systematic approach on the morphology of the ZnO film, nor any deeper view inside the thermal treatments has been projected. Hence there is a need to study how the various deposition conditions as well as the thermal treatment affect the film morphology. The present study, therefore, is primarily designed for the preparation of good quality transparent zinc oxide film and optimization of the process variables.

The objectives of this study can therefore be stated as:

- i) To suggest an optimum sol-gel route for the production of smooth and transparent zinc oxide thin film which in turn will have good electrical and optical properties.
- ii) To find out the various changes in the film morphology as a consequence of changes in the conditions during the deposition of ZnO thin film by using sol-gel route.
- iii) To find out the morphological changes of the film during the process of heat treatment by some characterization techniques.

CHAPTER TWO

LITERATURE REVIEW: PART ONE

DEPOSITION AND GROWTH OF THIN FILM

2.1 DEPOSITION OF THIN FILMS

2.1.1 General

There are many deposition techniques available for various thin films. These techniques includes sputtering²⁴⁻²⁸, spray-pyrolysis, ²⁹⁻³² metalorganic chemical vapor deposition (MOCVD)¹⁹ etc. The deposition techniques available for the deposition of thin films can be divided into two categories viz.: high temperature methods and lower temperature methods ³³. Sputtering, vacuum evaporation, metalorganic chemical vapor deposition(MOCVD) etc. constitute the high temperature methods. These requires high temperature along with vacuum and are much costly and capital iuteusive. The high temperature methods can further be divided into physical vapor deposition and chemical vapor deposition techniques. Lower temperature methods does not require vacuum for deposition and requires much lower temperatures. These made them less capital intensive requiring no-high cost equipment.

The selection of a particular process for the deposition of any particular film, however, depends on several factors like a) material to be deposited, b) rate of deposition, c) limitations imposed by the substrate e.g. maximum deposition temperature, d) adhesion of deposit to substrate, e) purity of target material, f) apparatus required and its availability, g) cost, h) ecological considerations, i) abundance of deposition material in the world³⁴ etc.

2.1.2. High Temperature Deposition Method

2.1.2.1 **Physical Vapor Deposition:**

The basic physical vapor deposition processes are known as evaporation, sputtering and ion plating. Vasanelli¹⁷ *et. al.* had produced ZnO thin film on CdTe by sputtering while Tominaga¹⁸ *et. al.* prepared transparent ZnO: Al films by co-sputtering of ZnO: Al with either a Zn or an Al target . In general the physical vapor deposition techniques consists of three steps viz.:

Step-1: Creation of vapor phase specie. The material can be transferred into vapor phase in three ways: evaporation, sputtering, or chemical vapors and gases

Step-2: Transport from Source to substrate in molecular flow condition or as a plasma

Step-3: Film Growth on the Substrate.³⁴

2.1.2.2 **Chemical Vapor Deposition:**

Chemical vapor deposition and other modifications have also found uses in depositing ZnO thin films. Among these the metal organic chemical vapor deposition (MOCVD) method using a variety of oxygen sources in conjunction with either dimethyl zinc or diethyl zinc has been proved to be one of the best techniques for obtaining high quality ZnO films. kim¹⁹ *et. al.* has produced ZnO thin films by MOCVD using Zn-acetate as the source material.

2.1.3 Low Temperature Deposition Method

2.1.3.1 **Spray Pyrolysis:**

Spray pyrolysis^{15,16,20,21} is a lower-temperature low cost deposition technique and gaining much importance in last few years. In this method, a mixture of the salt solution and a solution of the organic compound sprayed directly on to the heated substrate³⁵. Since the reaction products are volatiles of the chosen compound only, a pure film of the desired composition forms on the substrate. The spray method can be used for the preparation of films with good cathodo - luminescence, photoconductivity and photovoltaic properties.

Krunk et. al.¹⁵ produced doped and undoped ZnO thin films by spray pyrolysis method using Zn-acetate dihydrate as the precursor. Same method was adopted by Kobayashi et. al.¹⁶ to produce zinc oxide/n-Si Junction solar cells. Studenikin²¹ et. al. also produced ZnO films by spray pyrolysis method but they used zinc nitrate solutions as the precursor. Lee²² et. al. used pyrosol method, a modification of spray method, to produce ZnO thin film.

2.1.3.2 **Sol Gel Method:**

2.1.3.2. a) Terms and Definitions:

Of many physical or chemical deposition techniques for the synthesis of thin films, sol-gel synthesis method particularly yield films which are quite pure without requiring high temperatures or pressures. It is likely that the sol-gel route will find applications in very specialized bulk uses e.g. windows in the films for structural and electronic uses³⁶. However, before going for the detail of the process we need to glimpse over certain terms and definitions regarding the process.

Sol is a general term usually applied to the dispersions of solid in liquid, solid or gaseous media³⁷. More commonly, it has been considered as the colloidal dispersions of solids in a fluid³⁸.

A *colloidal dispersion* is a mixture in which the particles of one (or more) substances are smaller than those in suspensions, but larger than those in solutions. They will have at least one dimension in the range³⁹ of 1~10 nm. Colloidal dispersions are characterized by *Tyndall Effect* and *Brownian Movement*. They can not be separated by filtration and their stability to gravity is lower than that of solutions.

The stability of a colloidal dispersion, that it does not settle under gravity nor its elements are separated, depends on particle size, Brownian movement and electrical charge character of the dispersion. As a rule, the smaller the size of the colloidal particles are, the more stable is the dispersion and the less effective is gravity in causing a separation³⁸.

If the dispersion medium of a sol is water, it is a *hydrosol*; if an organic one, an *organosol* or more specifically, an *alcosol*, *benzosol* etc. Dispersions of solid in solid are termed as *solid sols* (certain gems, black diamond etc.). Dispersions of either solid or liquid in gas are called *aerosols*³⁷.

As a matter of fact, there are no sharp differences between mechanical suspensions, colloidal dispersions and true solutions. There is a gradual and continuous transition from the first through the second to the third³⁹. Only solutions are homogeneous in the sense that only in solutions the intermixed particles are in atomic, ionic, or molecular levels or size. Thus, the relative sizes of the mixed particles is the chief

criterion for distinguishing these three types of mixtures. Even then, it is much difficult to identify any sol from solution only by naked eye.

Sols that adopt a semi-solid, semirigid form are called *gels*³⁸. These owe their rigidity to a kind of network structure³⁷. The two forms of gels are *gelatinous precipitate* and *jellies*. A gelatinous precipitate comes down under such conditions that it leaves a supernatant liquid, whereas jelly encloses all the liquid phase. *Hydrogel*, *alcogel* and *benzogel* signify that the gel liquid is water, alcohol, and benzene respectively.

Another classification of certain colloid systems is based on the attraction or affinity of the dispersed phase and the dispersion medium for each other. If the mutual affinity is small, the system is called *lyophobic*; whereas if the affinity is great, the system is *lyophilic*. If water is the medium, the system is termed *hydrophobic* or *hydrophilic*. A given dispersed phase may be lyophobic in one medium or lyophilic in another. For example, starch gives lyophobic systems in alcohol and lyophilic in water³⁷.

2.1.3.2. b) Preparation of Sols:

To prepare stable sols, it is necessary to prevent the agglomeration of the individual or primary particles into aggregates. These aggregates are sufficiently large to settle out under the influence of gravity. Two methods are employed to prevent this agglomeration³⁷:-

- a) the keeping down of the concentration of the coagulating electrolyte either by a suitable choice of reaction or by dilution, and

- b) the addition to the solution of strongly adsorbed protecting agents such as protecting colloids, which forms a water-soluble film around the primary particles and prevent their coalescence.

The precipitation of oxides and salts is frequently prevented from going beyond the colloidal range and hence the dispersed phase is kept in the sol state by the addition of substances which are strongly adsorbed such as protecting colloids, and sugar or glycerol. Glycerol is effective in stabilizing ferric oxide sol and calcium phosphate sol³⁷. In the same manner it increases the solubility of alkoxides in alcohols to form a sol of ZnO. That is why some authors preferred to use glycerol in order to stabilize the ZnO sol¹³.

2.1.3.2. c) Sol-Gel Transformation:

When a stable sol is prepared and followed by a gelation step, the overall process may be called a *sol-gel process*³⁶. As has been discussed in earlier sections, in a sol the solid matter is composed either of small particles and of macromolecules. A gel differs from the sol in that it is characterized by a chemical and structural three dimensional network. This network is formed and the connectedness established at a point called the *gel point*.

A general outline of sol-gel processes includes: i) the chemistry of precursors, ii) the resulting dispersed sol, iii) gelation or precipitation to a shape which may range from powders to monoliths and includes coatings, films and fibers, iv) drying, v) densification, and in some cases crystallization, to a final ceramic product³⁶ (Fig. 2.1.1). The sol-gel process thus begins with a reactive precursor material that is converted into a final product by chemical and thermal means. The precursor is prepared in a colloidal suspension or sol that undergoes a gelling stage (gel) and a final fusion. So the thermal treatment is critical and it differs greatly depending on

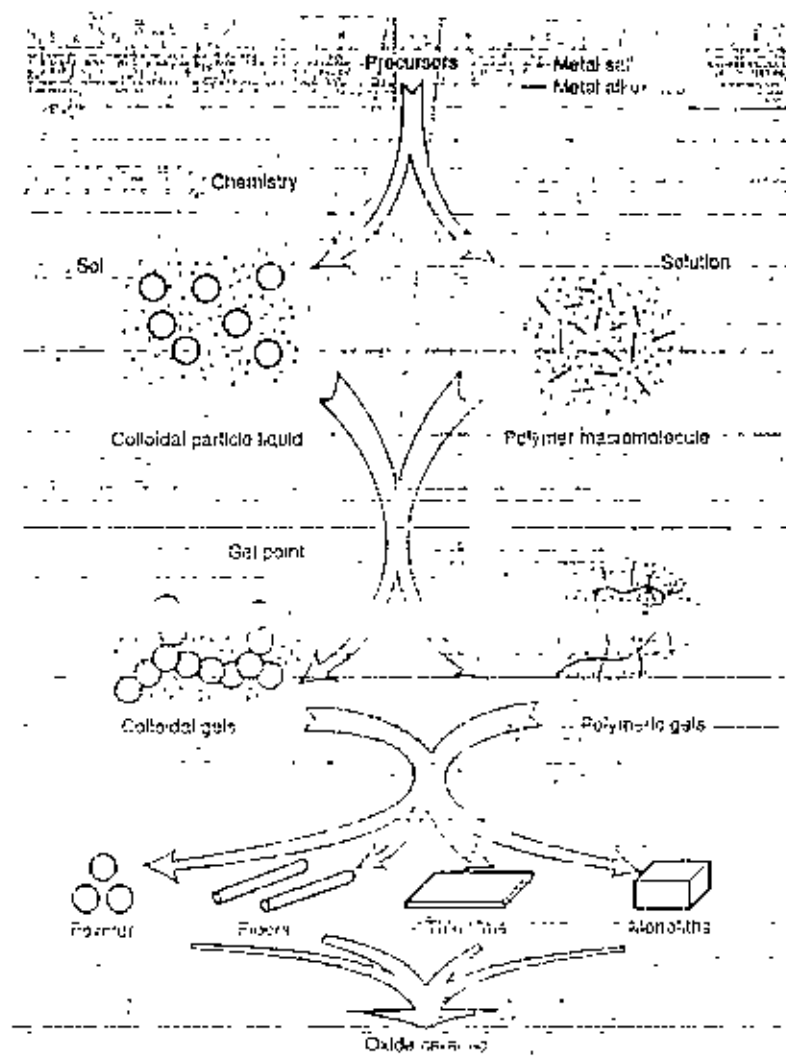


Fig. 2.1.1 Map of sol gel process route.³⁶

the gel properties before the treatment and the desired properties. The precursors which are used most often are the *metal salts* and *metal alkoxides*. The metal salts are generally cheaper and metal alkoxides are more expensive than metal salts, but they allow one to obtain high purity materials at the end.

The mostly studied sol-gel process in recent years are *internal gelation methods* in which metal alkoxides are hydrolyzed i.e. chemically decomposed by splitting chemical bonds and adding the elements of water. In these processes, the organic metal salts are dissolved in an organic solvent e.g. in an alcohol. This is the basis behind the sol gel syntheses usually employed for thin films^{12,13,23} and behind the present study as well.

2.1.5.5 Advantages and Disadvantages of Sol-Gel process :

The world wide goal of all sol-gel work is to achieve ultra-homogeneity and small particle size. Sol-gel process is used to convert metal salt / alkoxide solutions into ceramic solids and the gel structure and the gel properties are of controlling importance to the preparation and properties of the solid ceramic products.

Sol-gel processes take the advantage of the high degree of homogeneity, that can be achieved by mixing on the colloidal scale, and the excellent bonding and sintering properties of colloids resulting from their very high specific surface energy.

Specifically, oxides can be synthesized via plasma, aerosol, flame hydrolysis, hydrothermal or sol-gel processes. The particles made via plasma may be too fine and the particle size control may be difficult. The aerosol process can give narrow distributions, produce spherical powder and has the capability of producing mixed oxides. Flame hydrolysis produces oxide powders of very high purity. Sol-gel process can yield powders which are quite pure without requiring very high

temperatures or pressures as have been mentioned earlier. Moreover, process control is obtained through control of the surface chemistry of polymerization reactions. Most sol-gel activities in the past, therefore, concentrated on producing fibers, coatings, films or monoliths.³⁶

However, since the amount of ceramic materials in the starting precursor (c.g. Zn-acetate in the case of ZnO-deposition) is quite low, dramatic shrinkage occurs during the final firing. This leads to significant difficulties in producing stress-free, net-shaped and near-net shaped (NNS) parts. For this reason, large-cross-section parts at full density are difficult to achieve.³⁶

Organics, which are the essential part to the sol-gel process, result in pores after they burn out upon firing. The resulting porosity may be minimized in bulk ceramics by consolidating to near theoretical density e.g. as by hot isostatic pressing. However, since this is not much a feasible way to reduce porosity in the films or coatings deposited by sol-gel method due to the risk of sticking to the plunger, porosity may accompany the final film.

2.2 CRYSTALLIZATION AND GROWTH IN THIN FILMS

2.2.1 General

Many crystallization phenomena lead to crystal aggregates in which a crystallographic axis of the individual crystals is more or less aligned along a preferred direction. The resulting preferred orientation of the crystals, called *fiber texture*, can strongly influence the physical properties of the crystal aggregates. This can be due to a dependence of the physical properties of the individual crystals upon crystallographic direction (*crystal anisotropy*), upon the shape of the crystals (*shape anisotropy*), or, in the case of asymmetrically shaped crystals, upon their

arrangement (*order anisotropy*).⁴⁰ To control the properties of the whole aggregate we have to study the conditions leading to fiber texture and try to understand the mechanism responsible for its formation. Although the ideas presented here are derived for evaporated films, they may, with minor alterations, also be applied to fiber textures formed in other deposition processes, e.g., sputtering, vapor decomposition and reduction, chemical displacement, electroplating or sol-gel processes.

2.2.2 Structure Formation and the Evolution of the Structural Features

Structure evolution usually comprises nucleation, grain growth, thickness growth etc. by complete coalescence of impinging grains (leading to single crystals), or incomplete coalescence (leading to polycrystalline islands). The growth stages of polycrystalline films are shown schematically⁴⁰ in Fig. 2.2.1 and has been given a detail treatment in the following section.. The final structure of the film is a result of the creation and growth of the structural units (like grains) and their periodic reorganization during the formation of the film.

The fundamental structure forming phenomena are the phenomena which

- a) start the condensation on the substrate → nucleation
- b) incorporate the impinging (deposited)
adatoms into the growing individual grain → film growth
in the film structure
- c) reorganize the unit structure of the film → grain growth by
coalescence and
GB migration

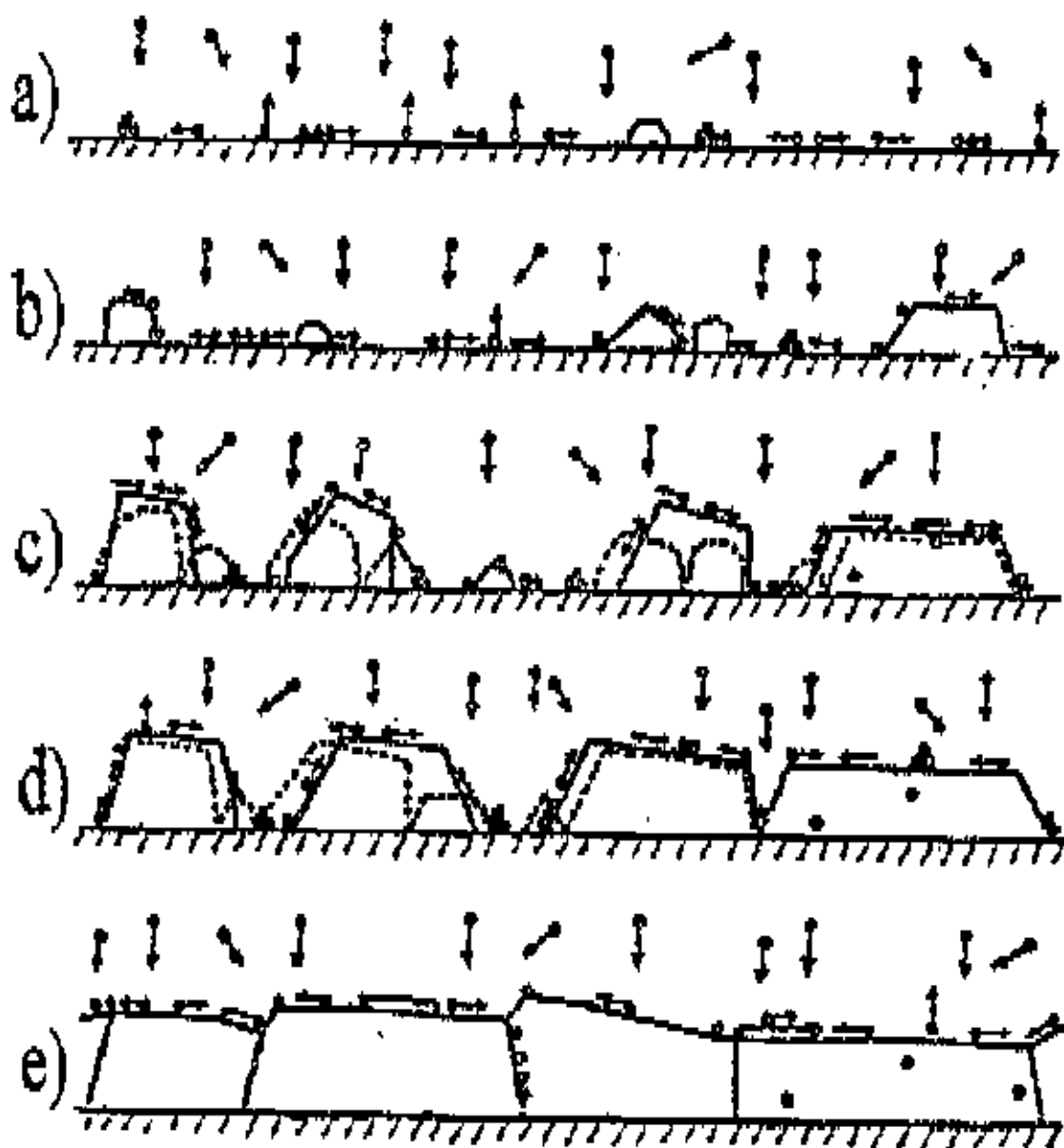


Fig. 2.2.1 Growth stages of polycrystalline film formation;

- a) nucleation
- b) crystal growth
- c) coalescence
- d) growth by filling of the channel
- e) thickness growth of the continuous film .

Crystals before coalescence are marked by broken line.

OCCURRENCE NATURE	PHENOMENA	PLACE
time to time at activation	<i>NUCLEATION</i> clustering	on the substrate
continuous	<i>CRYSTAL GROWTH</i> monolayer crystal growth	on crystal faces
time to time at activation time to time at activation	<i>GRAIN GROWTH</i> coalescence GB migration	on the substrate in continuous films
continuous time to time at activation	<i>PROCESS INDUCED SEGREGATION OF IMPURITY SPECIES</i> due to monolayer crystal growth due to GB movement	on crystal faces in the bulk of film

Table 2.2 1 The fundamental structure forming phenomena.⁴⁰

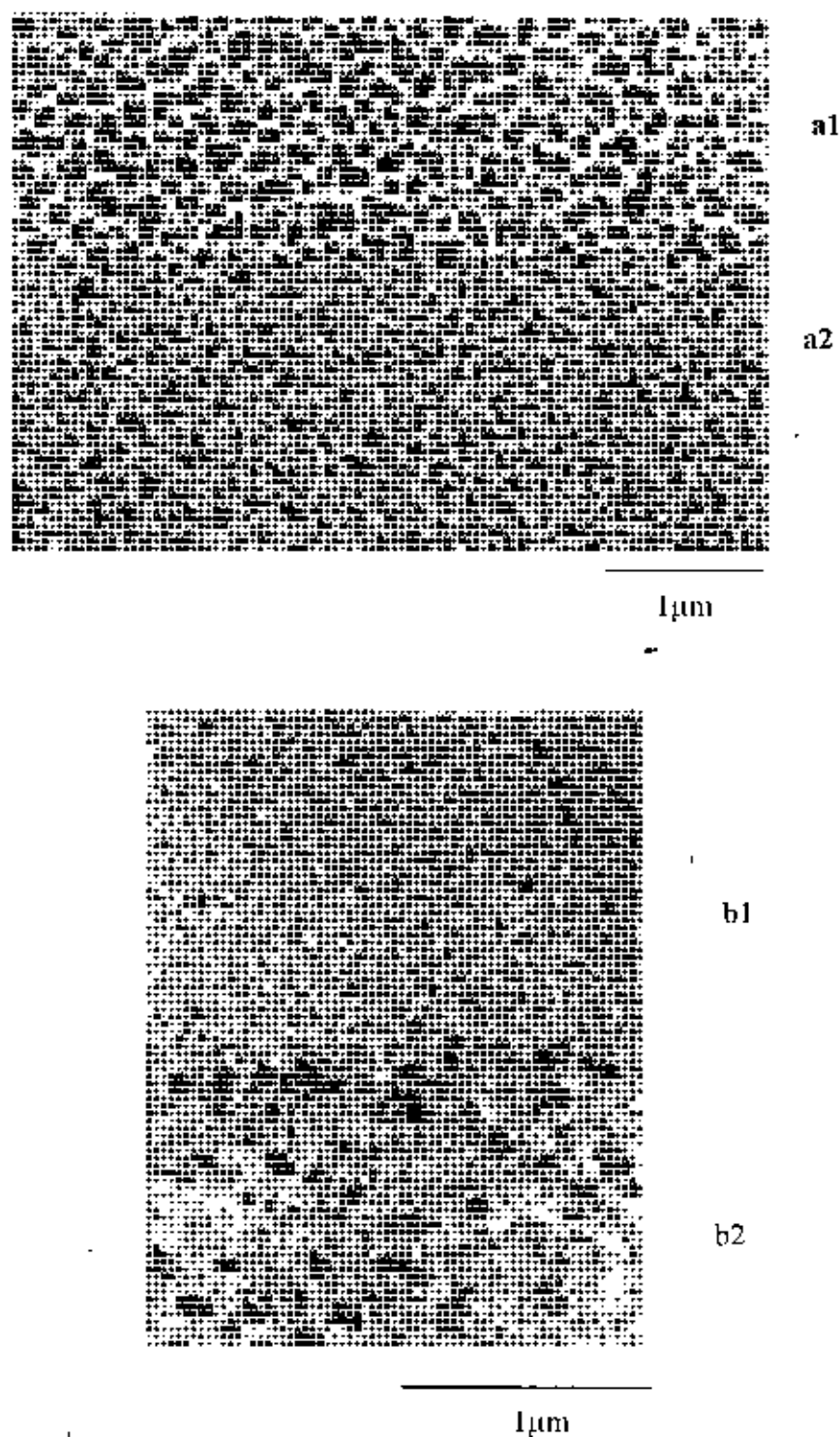


Fig. 2.2.2 TEM images of films deposited on amorphous substrates at different impurity levels of oxygen contamination.

- a) Indium thin film with (1) low and (2) high level of contamination
- b) Aluminium thin film with (1) medium and (2) low level of contamination.⁴⁰

d) develop the phases of impurities or additives	→ process induced segregation
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This is summarized in Table 2.2.1.⁴⁰

Two main cases of crystal growth should be considered in polycrystalline thin films:

- a) the growth of discrete crystals dispersed on the substrate surface and,
- b) the growth of crystals which are parts of a polycrystalline structure.

The discrete crystals dispersed on the substrate surface are growing independently of each other disregarding the fact that their adatom collection areas may overlap (Fig. 2.2.1a and b). The defect structure of the crystals as well as their orientation on the substrate together with their coverage with possible phases of segregated impurities will control the crystal growth processes.

The growth of crystals as parts of a polycrystalline structure generally starts when the coalescence stage is completed, i.e. the film is continuous. In that stage the film is composed of crystals developed during the coalescence stage with sizes and orientations determined both by the temperature and impurity content⁴⁰ (Fig. 2.2.2). Fig. 2.2.2 shows the TEM images of In and Al thin films deposited on amorphous substrates. Fig. 2.2.2.a.1 shows the low level of oxygen contamination while 2.2.2.a.2 shows the high level of contamination. Clearly, oxygen chemisorption has rendered the grains to a finer size.⁴⁰ Fig. 2.2.2.b.1 and 2 shows similar results on Al thin films.

At high purity conditions and noticeable self surface diffusivity of adatoms, smooth crystal faces can develop. The parts of these crystals protruding over the surface are faceted which reflect the orientation of the crystals. In case of textured film the whole surface is smooth and built up of crystal faces according to the orientation of the texture. In case of contamination or lower purity, smoothness as well as preferred orientation may be hindered.⁴⁰

Coalescence of polycrystalline films occurs during the coalescence stage and during the thickness growth (in polycrystalline island and continuous film). It takes place when the growing adjacent discrete crystals approach and touch each other. During this process the previously isolated grains interact by interfusing their structure. At the coalescence an intergranular area develops and the coalesced crystals mutually influence the reorganization and growth of their structure.

According to the theory of sintering, the main processes of coalescence are: (i) neck formation, (ii) filling of necks by surface self diffusion, (iii) formation of grain boundaries (GB) upon joining the lattices of the crystals, (iv) moving out of the GB by diffusion controlled GB migration (recrystallization)⁴⁰.

The coalescence is considered complete when all the above mentioned processes take place and a single crystal develops, or incomplete when the recrystallization is not accomplished and a polycrystalline island containing intergranular area (defects, large or small angle GB-s) is formed.

The contamination of the contacting surfaces can hinder not only the realization of the complete coalescence but also the filling up of the necks. Pores can develop in the areas of these necks and the GB-s will be covered and stabilized by the impurity phase.

The structure evolution of polycrystalline films can be followed from Table 2.2.2. The fundamental structure forming phenomena which were discussed before and the elementary atomic processes of these phenomena together with the structural preconditions determining the processes and the developing structures are summarized here for the subsequent stages of film formation⁴⁰. One has to remember that the structure forming phenomena and the involved atomic processes are different and characteristic to each stage of the structure evolution. This is because the structural conditions of each growth stage are unique and the elementary processes in each stage are determined by the structural conditions.

2.2.3. Two Dimensional Growth

There are three primary modes of film growth of material A on substrate B⁴¹ as illustrated in Fig. 2.2.3³⁰. During three dimensional island (3-D), or Volmer-Weber (VW) growth, small clusters are nucleated directly on the substrate surface. The structures then grow into islands which in turn coalesce to form a continuous film. This type of growth occurs when the film atoms are more strongly bound to each other than to the substrate e.g. metal films on insulators or contaminated substrates⁴². Two dimension (2-D) layer by layer, or Frank -van Merwe (FM) growth occurs when the binding energy between film atoms is equal to or less than that between the film atoms and the substrate. The third growth mode, Stranski-Krastanov (SK) is a combination of the first two. After first forming of one or more monolayers further layer growth becomes unfavorable and 3-D islands starts to form.

Ozawa⁴³ *et al* has shown by *Monte - Carlo* simulations of film growth that the growth mode of this film is mainly determined by the energy parameters rather than the deposition conditions. The growth mode is FM type for $E_{ff} < E_{fs}$ where E_{ff} is the energy for the film atom pair, E_{fs} for the substrate atom pair. VW type growth

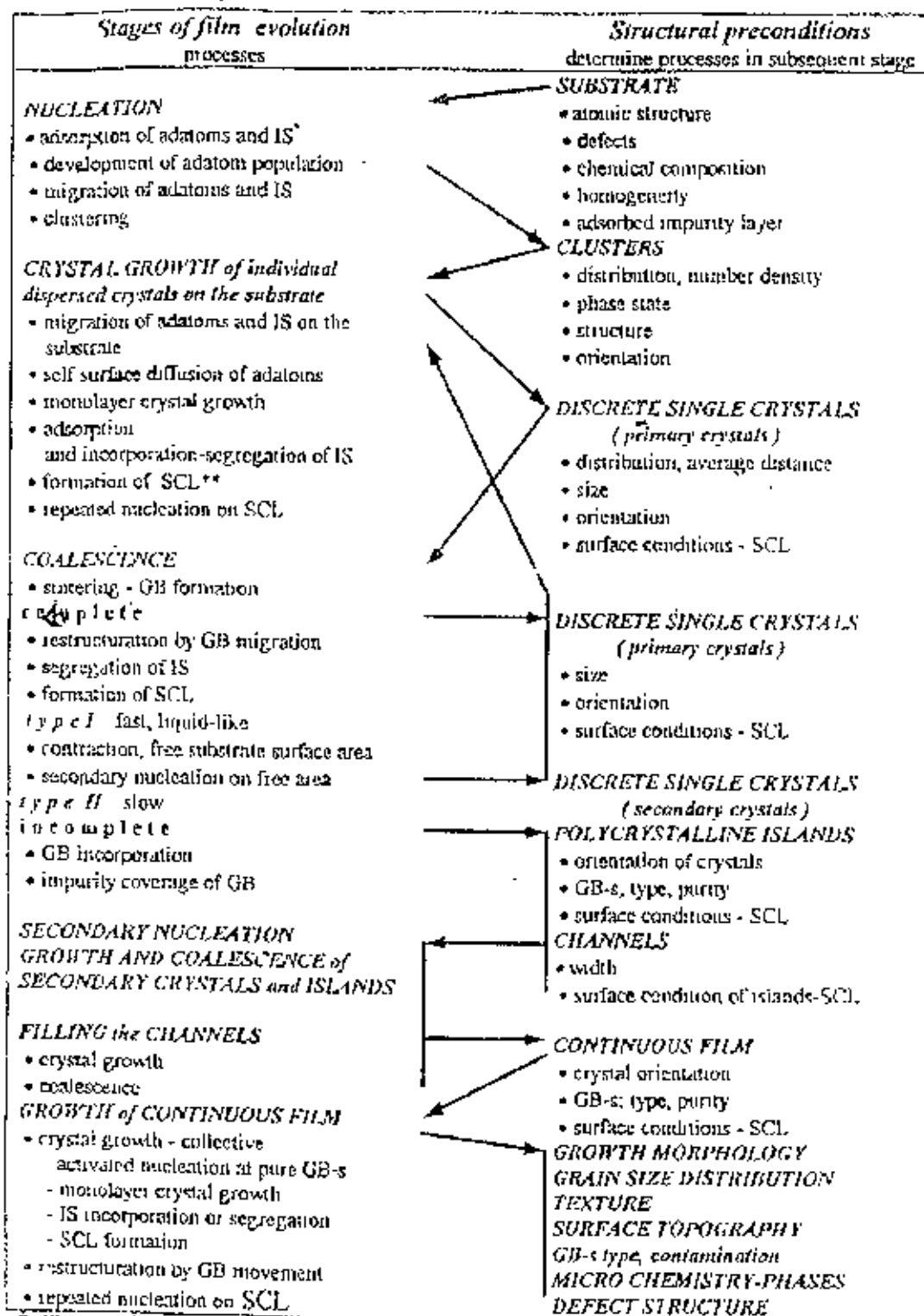


Table 2.2.2 Structure evolution in polycrystalline thin films.

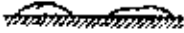
Coverage Mechanism	$\theta < 1 \text{ ML}$	$1 < \theta < 2$	$\theta > 2 \text{ ML}$
3-D Island Growth			
2-D Layer-by-Layer Growth			
Stranski-Krastanov Growth			

Fig. 2.2.3 Schematic representation of three film growth modes θ is the overlayer coverage in mono layers (ML) ⁴⁷

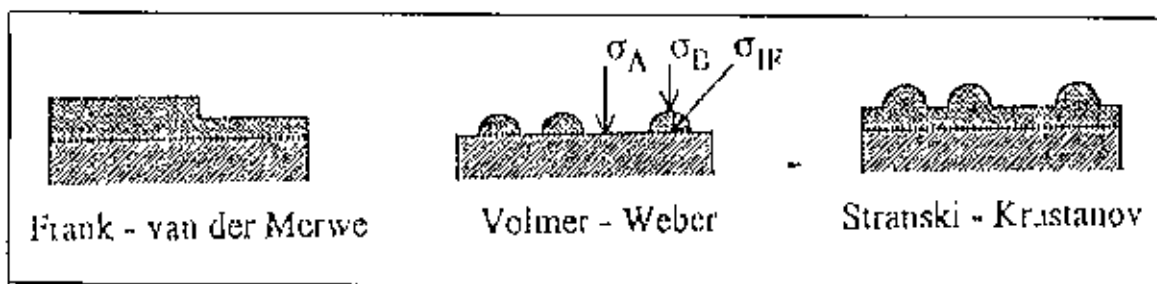


Fig. 2.2.4 Epitaxial growth modes. ⁴¹

occurs when $E_{\text{if}} > E_{\text{fs}}$. In the case where $E_{\text{if}} = E_{\text{fs}}$, the nucleus become very flat and the difference between the two modes is not much noticeable.

Qualitatively these three modes can be understood by considering the various surface free energies σ_A , σ_B and σ_{IF} ⁴³ (Fig. 2.2.4) where

- σ_A = solid/vapor interface energy for material A
- σ_B = solid/vapor interface energy for material B, and
- σ_{IF} = interfacial energy between the two materials

VW growth is expected when, $\sigma_B > \sigma_A + \sigma_{\text{IF}}$ ⁴³ i.e. film/substrate interaction is weaker than the film/film interaction. When $\sigma_B < \sigma_A + \sigma_{\text{IF}}$, layer-by-layer growth becomes possible. Let, a and b be the lattice parameter of the substrate and the over layer, respectively. Then geometric misfit, $f = (b-a)/a$; when $f = 0$, lattice is matched to the substrate.

The presence of misfit is essential for SK growth. If the film/substrate interaction is very strong compared with the film/film interaction, first monolayer deposited will cover the substrate completely. The atoms of the next monolayer will experience a potential with the same periodicity but with a smaller amplitude. Because of the weaker interaction with the substrate for the next monolayer, atoms will feel even less the presence of the substrate and nucleation of islands of the latter monolayer over the first monolayer will occur.

2.2.4 Texture Evolution

In many cases all or a part of the grains of polycrystalline films are oriented in a preferred direction with respect to the substrate. This property of thin films is called *texture* (macrotexture). As a consequence of the development of macrotextures

other crystallographic properties of thin films can be identified. If one considers the texture on a small scale i.e. a few hundred grains, one can find that the distribution of the preferentially oriented grains might be inhomogeneous i.e. the film might have a *microtexture*. This inhomogeneity of the texture might be related to substrate inhomogeneities and to their effects on the fundamental structure forming phenomena. In textured films the grain boundaries have also a preferential geometry which is called *misorientation texture* (mesotexture).⁴⁰

However, Bauer⁴⁴ classified the textures according to the kind of orientation of the crystals as follows:

One degree orientation (I-0) (fiber texture) means that only one crystallographic axis of most crystals points preferentially in a given direction, which is the orientation direction, or fiber axis. The random orientation of all crystals is the limiting case of the I-0 texture for increasing deviations from the preferred direction.

Two degree orientation (II-0) means that two axes of most crystals point in preferred orientations. The single crystal orientation is the limiting case of II-0 texture for increasing deviation of all crystals, which can be realized completely only on single crystal substrates in case of epitaxy.⁴⁰

The universal validity of this classification has been supported by the large number of experiments. . The fiber texture is the general case in polycrystalline films and the existence of two fiber textures in a film (e.g. $\langle 111 \rangle$, $\langle 100 \rangle$ in Al films^{45,46}) is also common and mainly related to the preparation conditions. The developments of II-0 texture is mainly related to oblique deposition in the presence of impurities⁴⁶.

The classification of textures according to their origin can promote the understanding of their evolution and the interpretation of the textures of films prepared by different techniques at various parameters. The following types of textures according to their origin can be identified.

1. activated nucleation texture
2. evolutionary growth texture
 - restructuration growth texture
 - competitive growth texture.

This classification involves the mechanisms of their evolution. Experiments have shown that on amorphous substrates the nuclei are randomly oriented ⁴⁷. From these results one can conclude that initial or nucleation textures are to the orienting influence of the single crystalline or polycrystalline substrates (e.g. underlayer), therefore the nucleation texture can be only an activated one. This is observed in experiments applying textured underlayers ⁴⁸.

In the evolutionary growth texture, the preferred orientation of the crystals develops during the evolution of the film structure. In that case one has to understand which of the fundamental phenomena are active in the development of the crystals with preferred orientation and how the deposited material or a part of it is accumulated into those crystals.

The general condition for the restructuration growth texture is that texture develops mainly during the growth of grains by coalescence. The further grain growth in thicker films, i.e. the completion of the abnormal grain growth, increases the strength of the texture. In that case the restructuration occurs in the whole thickness of the films dissolving also the initially formed randomly oriented small grains.⁴⁰

With the increase in impurity content in continuous films, both coalescence and grain growth are more and more limited because of the increasing contamination level of the crystal surfaces and the surface of coalescing crystals and of the grain boundaries⁴⁰. The complete coalescence is more and more limited and the film will be composed of small grains with increasing part of random orientation when it becomes continuous. This is shown in Fig. 2.2.2.a.2. and b.2. From this structure containing contamination stabilized GB-s, either a columnar, or a globular structure of randomly oriented grains results. Sometimes, a texture may also develop due to the competitive growth of random grains⁴⁰.

Competitive growth of randomly oriented crystals can take place at the end of the coalescence stage when the GB movement is limited either because of the low temperature or the presence of impurities. At higher impurity concentration the GB migration is limited by the adsorbed impurities and the developing impurity phase can grow over the free surfaces of crystals hindering their growth. The small grained structure of randomly oriented crystals formed during the first stage of the film formation on the substrate which is present till the end of the first stage and a competitive growth of these crystals starts during the growth of the continuous film. A valuable competition of the growing crystals develops when an anisotropy exists in the surface chemical interaction of the impurities on the various crystal faces. Only those crystals can grow continuously which are growing with faces not segregating the impurity species. The growth of crystals of other orientations will be blocked by the developing surface covering layer of impurities at different growth stages resulting in a random orientation.⁴⁰

CHAPTER-3

LITERATURE REVIEW: PART TWO

PROPERTIES OF ZnO AND ITS SOL GEL DEPOSITION

3.1 BULK PROPERTIES OF ZINC OXIDE (ZnO) THIN FILM

Ceramics based on zinc oxide (ZnO) are materials in everyday use which have the current - voltage (I-V) characteristics as shown in Fig. 3.1.1. The microstructure of such a ceramic for the use as a voltage-dependent resistor(VDR) is shown in Fig. 3.1.2. The microstructure shows intergranular layers of varying thickness between grains. It has been established that the resistance is controlled by the region in which the ceramic grains contact each other. However, the role of the intergranular layers between the grains are yet to be determined.⁴⁹

The presence of excess zinc ion in the interstices of ZnO makes it an n- type semiconductor.^{49,50} Fig. 3.1.3 shows the non-stoichiometric deviation in zinc oxide⁵⁰. The excess cations in the crystals remaining as interstitials must be balanced by two mobile electrons to keep the crystal electrically neutral. These electrons are free to move in the crystal under the influence of an electric field and thereby accounting for some electronic conductivity in ZnO making it an n-type semiconductor.

ZnO has an wurtzite structure^{49,51} in which the oxygen atoms are arranged in a hexagonal close - packed type of lattice (Fig. 3.1.4) with zinc atoms occupying half the tetrahedral sites⁵¹. The two types of atoms, Zn and O are tetrahedrally coordinated to each other and are, therefore, equivalent in position. The ZnO structure is thus relatively open with all the octahedral and half the tetrahedral sites empty. It is, therefore, relatively easy to incorporate external dopants into the ZnO lattice⁵². The open structure has also a bearing on the nature of defects and the

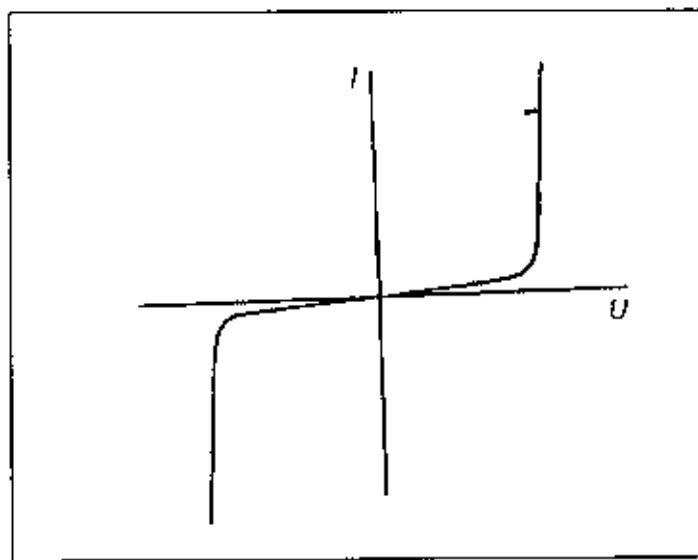


Fig. 3.1.1 Typical current voltage relation for a voltage dependent resistor made of ZnO.⁴⁹

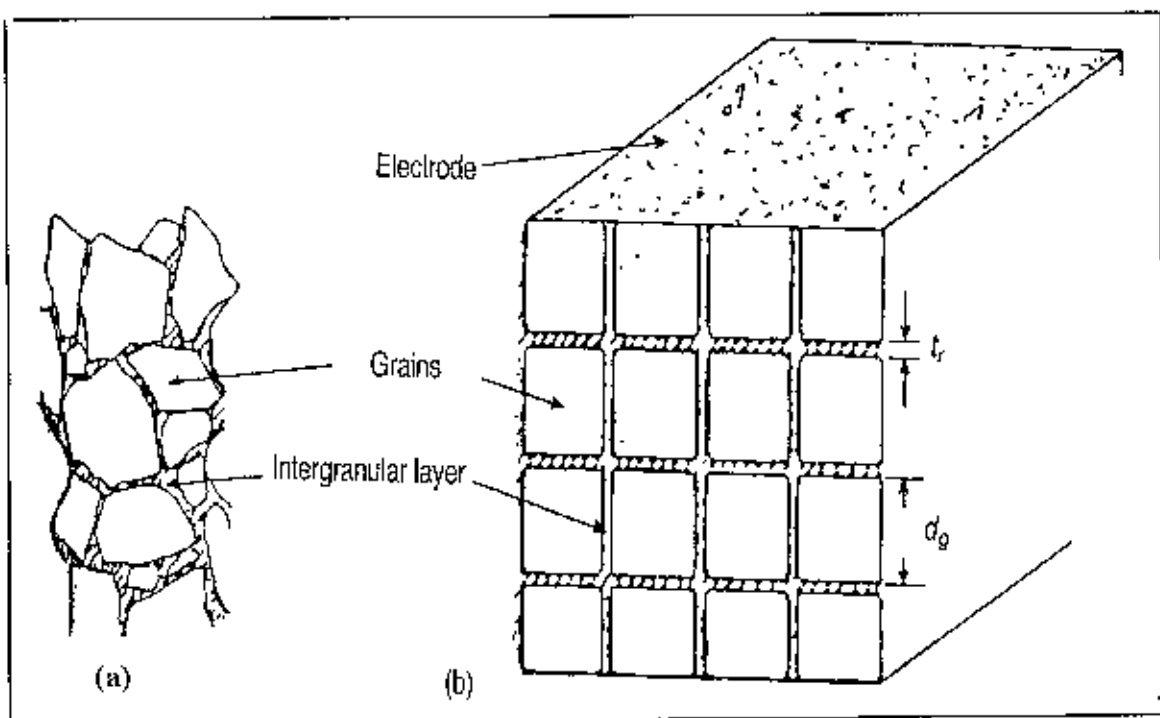
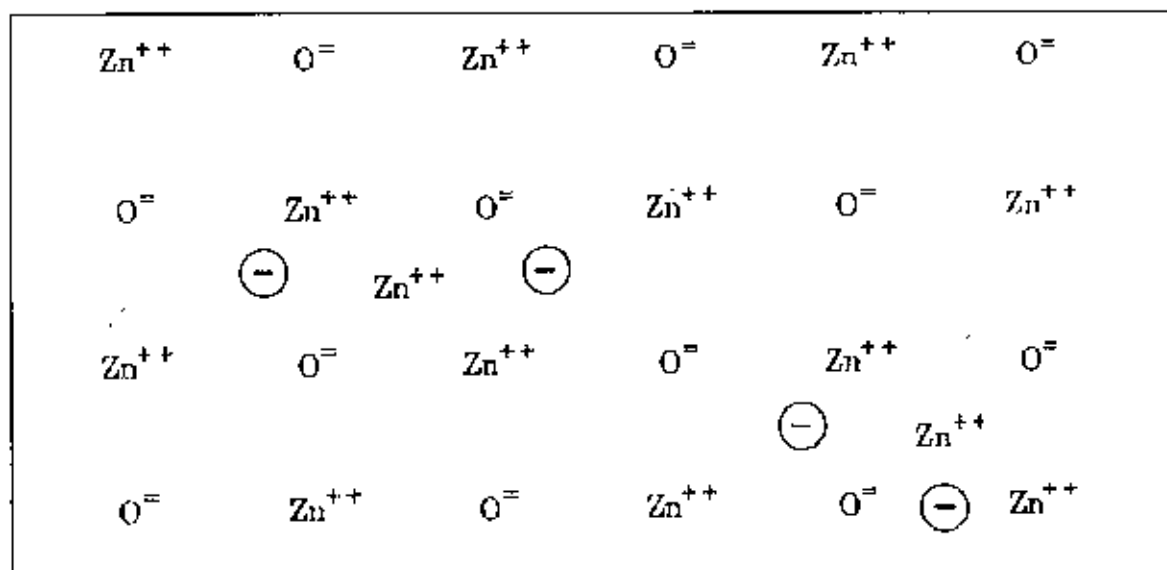


Fig 3.1.2 Illustration of (a) actual and (b) idealized microstructure of a ZnO - varistor.⁴⁹



$\ominus$ MOBILE ELECTRON

Fig.3.1.3 Non- stoichiometric deviation in ZnO making it an n-type semiconductor.⁵⁰

mechanism of diffusion. The most common defect in ZnO is the metal in the open interstitial sites leading to a non-stoichiometric metal excess n-type semiconductor.

Fig. 3.1.5 shows the band structure of ZnO. The band gap of ZnO has been determined to be 3.2 - 3.3 eV^{50,51}. Thermodynamically formed natural defects occupy the donor and acceptor levels within the band gap. The interstitial Zn-ion has the fastest diffusion rate among the natural defects and ZnO therefore commonly exist as a metal excess crystal⁵¹. Under the influence of high potential fields ZnO crystal exhibits low resistivity. The behavior is similar to a zener diodes in some respects.⁴⁹ But unlike a diode, ZnO varistors can limit overvoltage equally in both polarities and hence gives rise to a I-V characteristics analogous to two back to back diodes.⁵¹ The wide band gap of ZnO is large enough to be transparent to most of the useful solar spectrum and ZnO powders find its interesting use in commercial sun-cream.

3.2 PROPERTIES OF ZnO AS A THIN FILM

The optical and electrical properties of semiconductor thin films are determined by an interplay

between the epitaxy, the microstructure and the state of strain achieved in them. ZnO thin films recently have gained much attention for many of their optoelectronic applications because of their chemical stability in a reducing atmosphere and non toxicity^{53,54}. However for transparent conducting oxide applications in addition to obtaining low resistivity, stability at high temperature is required⁵⁵. ZnO then becomes a good selection as it does not undergo any phase change at high temperature.

As a thin film, ZnO also exhibits piezoelectric properties which are used in various pressure transducers and acousto-optic devices, surface and bulk acoustic wave

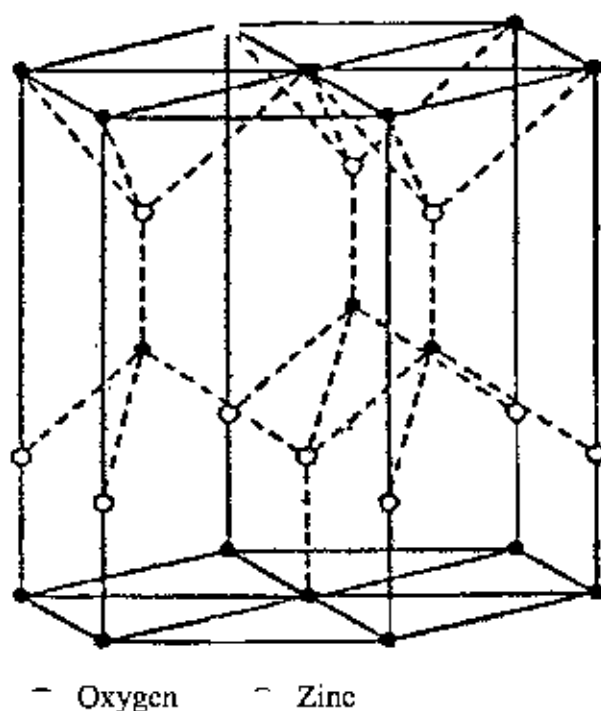


Fig. 3.1.4 Hexagonal Würtzite structure of zinc oxide. Oxygen atoms are arranged in a hcp lattice with zinc atoms occupying half the tetrahedral sites. Zn and O are tetrahedrally coordinated to each other.

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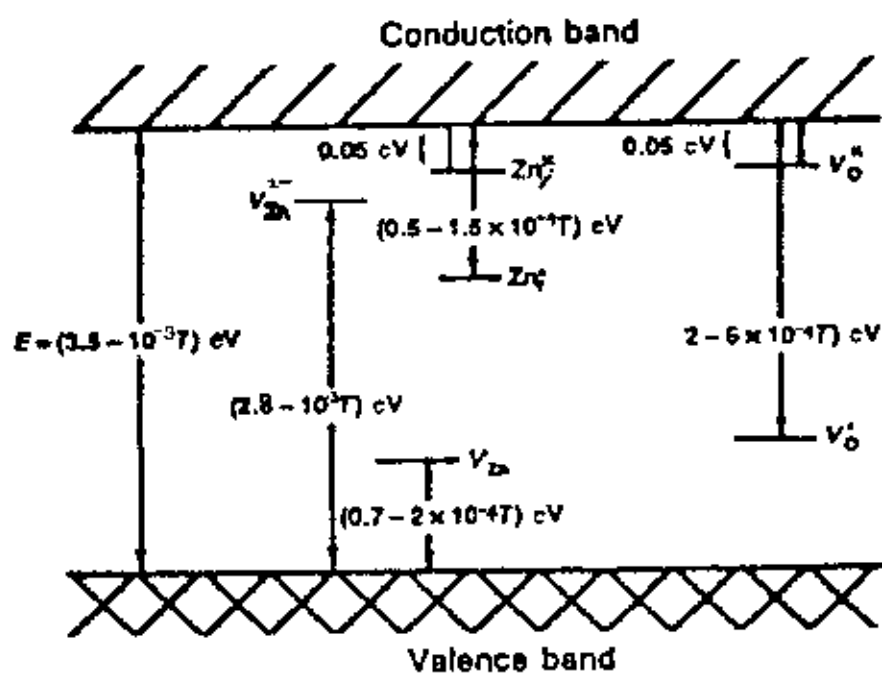


Fig. 3.1.5 Electronic energy levels of native imperfection in ZnO. ⁵¹

devices^{52,56,57}. Doped ZnO, along with indium tin oxide (ITO) is also the material of choice for many transparent conducting electrodes applications e.g. low cost thin film solar cells and flat panels^{56,58}

ZnO thin film is an attractive material for the window layer in CdTe based solar cells⁴⁹⁻⁶¹. As a matter of fact, ZnO holds a unique position among materials because it is transparent in the visible spectra, and yet can be made conducting by controlling stoichiometry or by the use of appropriate dopants^{50,56}.

For undoped ZnO, Nanto⁶² *et al.* found that low resistivity films (the lowest value $4.5 \times 10^{-4} \Omega\text{-cm}$) can be obtained by depositing on "vertical" glass substrates by rf-sputtering²⁰. Resistivity of the order of $10^2 \Omega\text{-cm}$ was found¹² for the undoped ZnO film which was deposited by sol-gel process and annealed at 450°C. Using aluminium as dopant Minami and co-workers found that low resistivity ZnO films ($1.9 \times 10^{-4} \Omega\text{-cm}$) can also be deposited on glass substrates suspended perpendicular to the target in rf-sputtering⁶³. On the other hand, Tang¹² *et al.* found it to be of the order of $10^{-3} \Omega\text{-cm}$ for sol-gel derived films.

For the low resistivity ZnO films without doping, the electrical properties have been reported to be unstable at high temperatures whereas rf-sputtered Al-doped ZnO films⁶³ showed no degradation after a heat treatment in vacuum at 400°C. Qiu⁵⁸ *et al.* found for In-doped rf-sputtered ZnO films that electrical resistance of the films deposited on horizontal substrates was stable when annealed in air at temperatures below 250°C.

The effect of temperature in expelling the impurities as well as in increasing the grain size can be further elucidated from the observations made by Lee²² *et al.* They found from the surface topographs of ZnO films deposited by pyrosol method that in undoped ZnO film deposited at 375 °C more number of fine pores were present

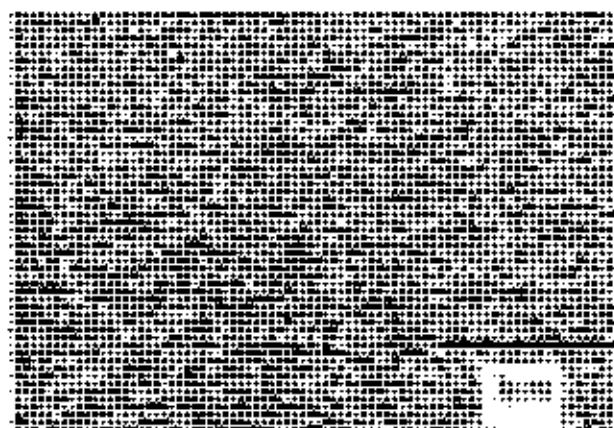
between the fine crystallites (Fig. 3.2.1a) while undoped film deposited at 475 C had large but less holes between the large crystallites (Fig. 3.2.1b). Actually higher temperature ensures better decomposition of metalorganic complexes and denser structure. That is why ZnO thin film annealed at 450 C appeared much more smooth and dense than the film annealed at 400 C. Clearly the grains of the ZnO film deposited at higher temperature (Fig. 3.2.1b) are much more grown than those of the film annealed at lower temperature. Expulsion of organic complexes are much more complete at higher temperature which can be evidenced from the holes between the crystallites. The holes are larger but lesser in amount in the film annealed at higher temperature. Although these observations were made by Lee *et. al.* with the help of scanning electron microscopy, the significance of these observations can not be ignored even at much lower magnifications.

The preceding discussions lead to the fact that both stoichiometry and dopants affect the electrical and optical characteristics to the point that ZnO can be a near insulator or a semimetal¹². A potential low cost alternative to tin doped indium oxide (ITO), ZnO films could be used as less expensive transparent conducting oxide (TCO) for electrode application as a window layer in solar cells and as a transparent conducting layer for electroluminescent devices. It has also been found that, for practical applications, undoped ZnO films are inferior to ITO albeit doped films can be made to have very stable properties.

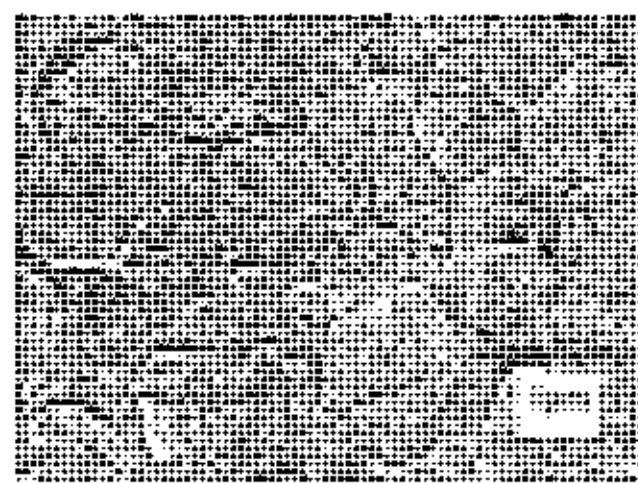
3.3 DEPOSITION OF ZnO THIN FILM BY SOL-GEL METHOD

3.3.1 Lactic Acid and Alcohol Method

W. Tang and D. C. Cameron produced ZnO thin film from a solution of ZnO precursor made by dissolving zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in either anhydrous ethanol or methanol¹². Solutions were prepared in increasing



(a)



(b)

Fig. 3.2.1 Effect of annealing on the surface topograph of the pyrosol deposited ZnO thin film²²:

a) substrate temperature 375 C

b) substrate temperature 475 C.

concentrations to establish maximum solubility. Without any acid additions the maximum concentration reached was 6 wt.% in ethanol and 12 wt.% in methanol. To achieve aluminium doping, anhydrous aluminium chloride (AlCl_3) or aluminium nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was added to the solution. As various parameters involved in the process are mutually dependent on each other, only the doping concentration was changed in their method. The doping concentration, i.e. aluminium/zinc atomic ratio as a percentage (Al/Zn atomic weight %), was varied from 0 to 4.5 atomic % in the solution.

The solutions were hydrolyzed with 2 mol H_2O per mol metal acetate by adding water dissolved in ethanol at 10 wt.% concentration dropwise together with roughly 5wt.% lactic acid. Turbidity and precipitation occurred which was readily eliminated by introducing additional concentrated lactic acid until the turbidity permanently disappeared. Using this procedure the stable solutions were prepared as required to carry out the experiments described.

The drain coating¹² method was used in which case the substrate remained stationary, and the solution was drained from a vessel. The thickness of the coating layer depended upon the speed at which the solution level had fallen, the concentration of the solution, the viscosity of the solution, the surface tension of the solution and the vapour pressure, temperature and relative humidity above the coating bath. The average baked thickness was determined to be 30-50 nm per coating cycle. Thicker films need multiple coatings. After coating, the substrates were loaded carefully into an electrically heated furnace, where they were heated in circulating air to the desired temperature at a rate greater than 10 C/min. Repeating the above process of coating and heating, the thickness of ZnO films was increased on the substrates. Fig. 3.3.1 presents the flow diagram for ZnO films from preparation of the solution to production of the coated substrates.

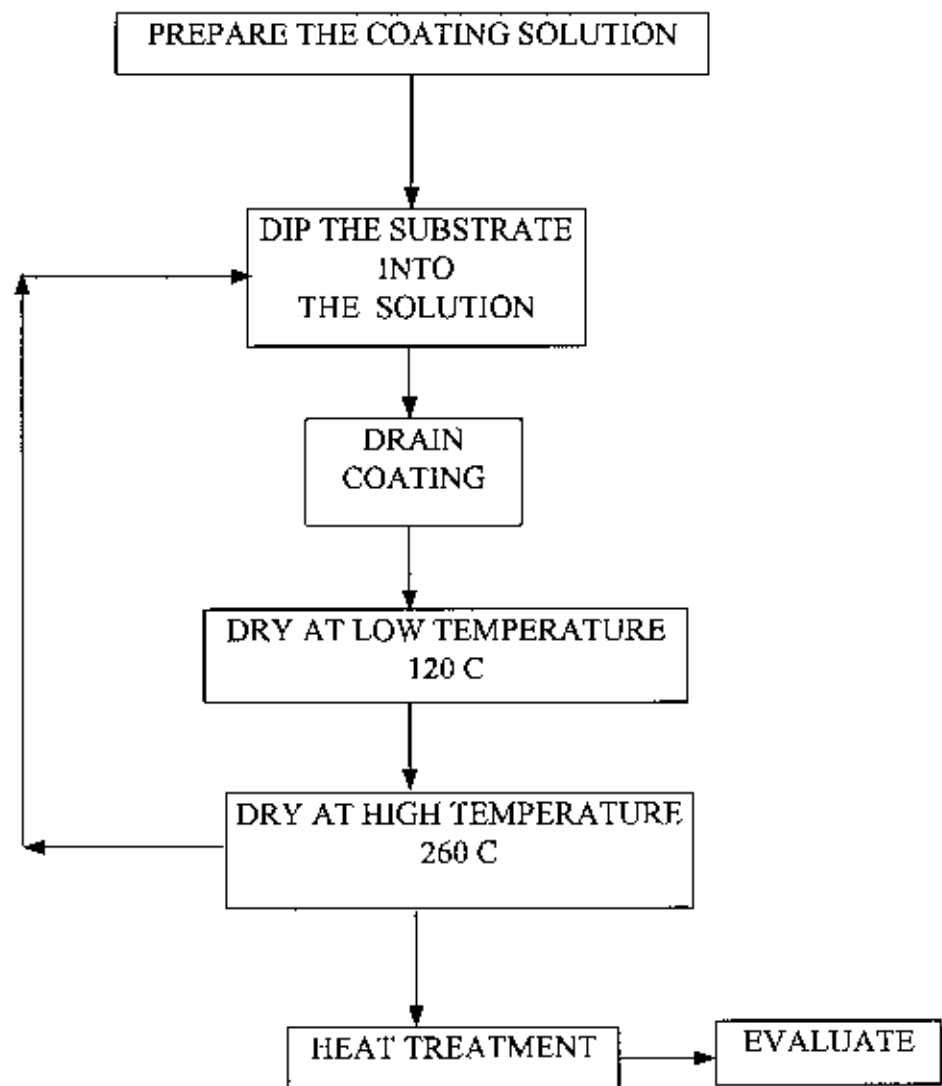


Fig. 3.3.1 Sol gel drain coating method for the deposition of ZnO thin film.¹²

3.3.2 Glycol Method

M. N. Kamalasanan and Subhas Chandra¹³ reported that sols prepared from zinc acetate dihydrate in alcohol did not gel properly on addition of water which was essential for sol gel processing⁴⁰. So they introduced the use of ethylene glycol in order to facilitate the dissolution of the acetate into the alcohol. The sol was prepared using zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), n-propyl alcohol ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$), and glycerol ($\text{C}_3\text{H}_8\text{O}_3$). 2.5 ml of ethylene glycol was added to 10 gm of zinc acetate dihydrate in a round bottomed flask fitted with a condenser and kept at 150 C for 15 minutes over a hot plate to obtain a uniform transparent solution. During the heating, water vapor evolved from the mixture equivalent to the water of hydration of zinc acetate dihydrate. On cooling to room temperature the content of the flask solidified to a transparent brittle solid which could be dissolved in alcohol such as methanol, ethanol, n-propanol etc. The solubility as well as film formation property of the sol could be enhanced by adding 0.5 ml of glycerol. The solution thus obtained was highly water sensitive and it readily gels on addition of a few drops of water. Triethylamine (1 mol equivalent) was also added to assist hydrolysis of zinc acetate. Excessive addition of glycerol however produced black films which could be made colorless by heating at elevated temperatures only. In their studies, zinc acetate-ethylene glycol precursor solid was dissolved in 20 ml n-propanol and 0.5 ml glycerol. The resulting solution was colorless and transparent. Dust and other particulate matter was removed from the solution by filtration using Whatman's GF/C glass fiber filters.

Thin films of zinc oxide were prepared by the spin coating technique. The precursor sol was placed on the required substrate using a dropper and spun at 3000 rpm for 20 s. The thickness of the precursor film thus obtained was about 1 μm . The substrates used were soda glass, silicon wafers, and KBr single crystals. After spin

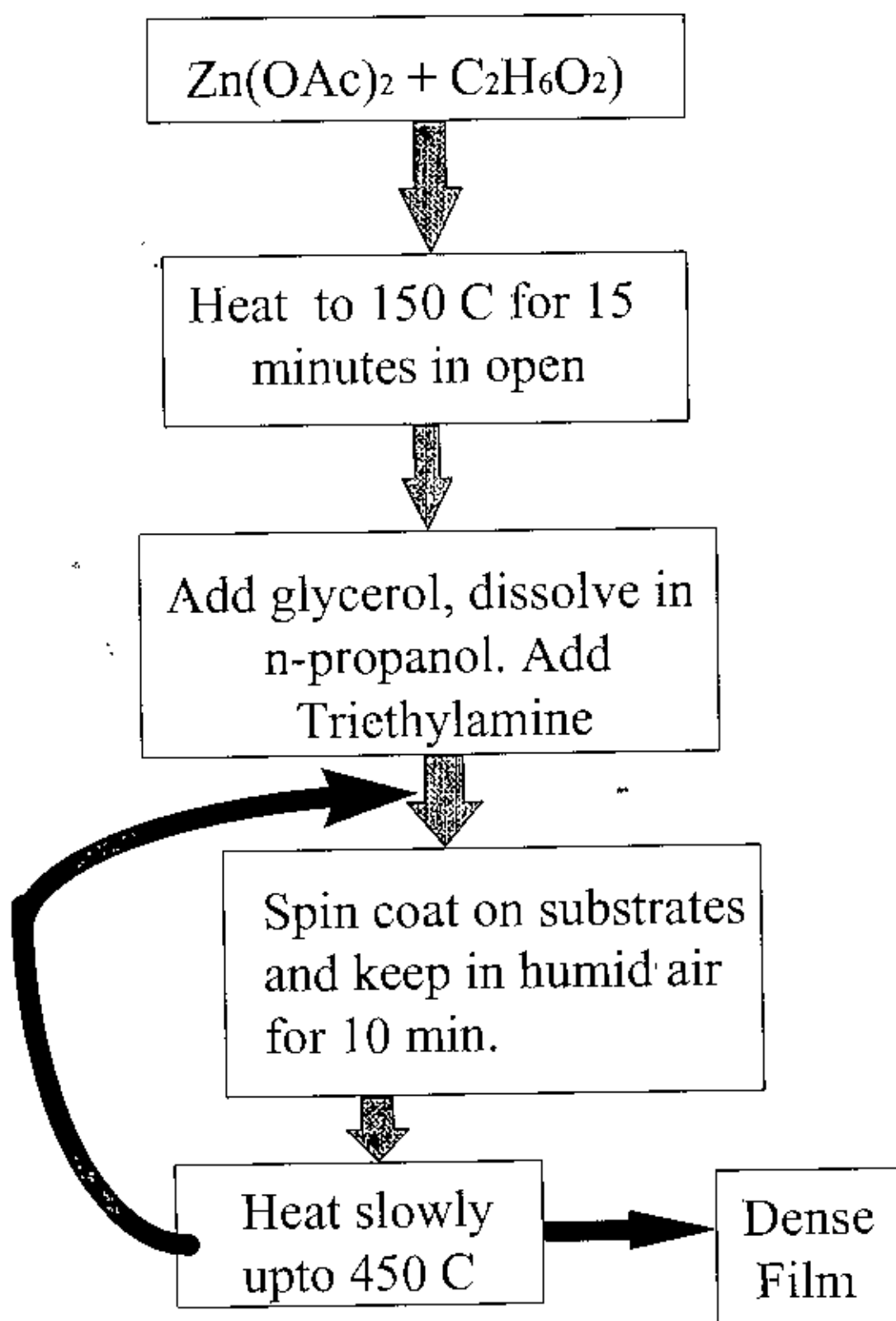


Fig. 3.3.2 Sol gel spin coating process for the deposition of ZnO thin film by glycol method. ¹³

coating, the precursor films were kept in humid air (RH 40%) for 10 minutes to facilitate hydrolysis. The films were then slowly heated to about 450°C to make them polycrystalline. The thickness of the ZnO film obtained from a single coating and firing process was about 0.2 µm. Thicker films were prepared by repeating the above process. Fig. 3.3.2 shows a flow chart of the film preparation steps.

3.3.3 Methoxy Ethanol Method

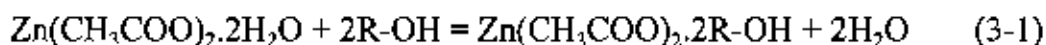
M. Ohyama²³ *et. al.* prepared ZnO films on silica glass substrates by the sol-gel method from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ - 2-methoxyethanol solutions containing monoethanolamine (MEA) or diethanolamine (DEA). Smooth and transparent ZnO films were obtained by heating at temperatures from 200 to 500 °C for 10 min after each coating and finally at the same temperatures for 1h. The films prepared from coating solutions containing MEA were strongly oriented along the (002) plane. The effects of heating temperature and ethanolamines on the film morphology, grain size distribution and crystallographic orientation are discussed based on X-ray diffraction and scanning electron microscopy.

3.3.4 Sol gel Transformation to ZnO

Tang¹² *et. al.* reported successful dissolution of zinc acetate dihydrate in anhydrous ethanol or methanol. However, Kamalasanan¹³ *et. al.* observed that sol prepared from zinc acetate dihydrate in alcohols do not gel properly on addition of water. However, in depositing the film Tang¹² *et. al.* used a drain coating method and Kamalasanan¹³ *et. al.* used spin coating techniques.

There were no major reaction taking place during the treatment with ethylene glycol in the method adopted by Kamalasanan *et. al.* except the exchange of water of

hydration with glycol without causing any disturbance to the zinc acetate bond^{13,33}. The reaction was represented as:



It is known that polar solute in presence of water forms a complex hydration envelope around it, named the *coulombic hydration*⁶⁴. The innermost strongly electrostricted water molecule of hydration(i.e. primary hydration) remains attached to the ion when they are crystallized (water of hydration). The zinc cation in zinc acetate is surrounded by a coulombic hydration sheath which remains with it even in a solvent like alcohol and prevents it from dissolving in the alcohol. That was why alkoxides are so difficult to transform in to a stable sol with the help of alcohol only¹³.

The treatment with ethylene glycol disturbs this hydration sheath and allows the solute to dissolve in an alcohol. Boiling with ethylene glycol thus forms a uniform transparent solution which turned to a transparent brittle solid on cooling to room temperature¹³.

The addition of water for hydrolysis to the sol restores the water of hydration to the zinc cation in order to form $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ which is having a lower solubility in alcohol. This forces zinc acetate to precipitate in alcohol giving an appearance of gelation. The resulting 'gel' was a white powdery material which slowly crystallized to zinc acetate upon drying¹³. The addition of a proton acceptor like di- or tri- ethyl amine deprotonated the water added for hydrolysis and thereby gave a transparent gel of zinc hydroxide which could undergo a condensation reaction to form ZnO on drying. Diethyl amine also had the effect of increasing the pH of the solution³⁷.

CHAPTER FOUR

LITERATURE REVIEW: PART THREE

PREPARATION AND CHARACTERIZATION OF THIN FILMS

4.1 INTRODUCTION

Although earlier “classical” methods for characterization of materials have been in existence for many years, modern techniques to analyze microstructural properties of materials have only been in practice since the late sixties. Presently there are well over 300 techniques that have been used in some form or manner to characterize materials.

In recent years, several new surface probe techniques for determining the elemental and chemical composition of solid surfaces and thin films have been developed. All of these techniques exhibit fundamental strengths and weaknesses, but some offer greater practical utility than others. Since for total characterization, the needed information cannot be provided by any one technique alone, data from two or more techniques is required to solve many real-world material problems.⁶⁵

The Microstructure and properties obtained by a new or existing process are studied and the relationship between the two is established. The deposition process can then be refined according to the requirements of the application. Thus there exists a closed loop of integrated research in thin film. Keeping this loop in view, the pros and cons of the experimental techniques relevant to the experiments in the present study will be discussed through a review of the literatures.

4.2 SURFACE PREPARATION

4.2.1 Surface Preparation

The term surface preparation has many interpretations depending on the application. Substrate preparation for our purposes may be defined as the conditioning of the substrate surface prior to film deposition in order to obtain desirable processing and film properties. Substrate preparation may involve the reduction of the type and amounts of 'contaminants' to an acceptable level (cleaning), modification of the physical or mechanical properties of the surface, activation of a surface species to enhance reactions, or the addition of desirable species to the substrate surface to aid in nucleation and reaction (sensitization) and in the extreme case, surface preparation may mean forming a "new" surface by adding a primer or glue layer. However, here the discussion is confined mainly to the cleaning of the substrate surface.

Substrate preparation determines the surface properties and these are directly or indirectly related to the film formation stages of adatom nucleation, interface formation, and film growth. These, in turn, affect film properties such as adhesion, pinhole density, porosity, film microstructure, morphology and mechanical properties. Often local surface properties determine film properties such as pinholes which determine the product yield.

Surface preparation is an integral part of any film /coating deposition process. The objective of surface preparation processes is to allow the fabrication of an acceptable product in the most reproducible and economical way. As the technological demands on films and coatings increase, the need for better and more reproducible surface preparation techniques also increase. Typically, surface

preparation processes are developed empirically and controlled by good processing specifications.

An important factor in surface preparation is the condition of the initial surface. A process developed for one surface condition may not be satisfactory for another surface condition. The initial substrate material, condition and history (contamination) should be known, and its condition and properties should be specified where possible. Monitoring of the surface preparation is often difficult since any testing of the surface usually contaminates the surface.

In addition to the surface preparation process, the handling and storage of prepared surfaces is an important part of the fabrication process. The prepared surfaces may be used immediately or the final step of the cleaning process may be done as a part of the deposition process. In these cases, storage or handling poses minimal of difficulty.

4.2.2 CONTAMINATION

A *contaminant* is any material on a surface that interferes with the processing or performance of the surface. Contaminants may be the reacted layers e.g. oxides, adsorbed layers e.g. hydrocarbons, segregated surface layers, or particulates. The contaminants may originate from: (i) natural reaction with the ambient (oxides, sulfides), (ii) adsorption from the ambient (hydrocarbons, water), (iii) processing steps (oils, fingerprints), (iv) handling and storage (polymers, oils), (v) settling from the ambient (particulates), (vi) electrostatic attraction in the ambient (particulates), (vii) Outgassing or out-diffusion from the bulk (plasticizers, water, solvent-plastics), (viii) contact with contaminated surfaces (silicone oils have a high creep rate). Of these, some recontamination are unavoidable but some are avoidable with proper fabrication, handling and storage techniques.

The presence of contaminants can be detected without necessarily identifying the composition of the contaminant. For instance, if a glass surface is contaminated with a hydrocarbon (hydrophobic), the wetting angle of a fluid drop will be high (doesn't wet)⁶⁶. However, this type of test must be used with caution since soap residue (hydrophilic) on the surface will make it wettable like a clean surface.

Surface adsorption can be very dependent on the surface and the adsorbing species. For instance, most oxide surfaces do not adsorb oxygen while conducting and semiconducting oxide surfaces do so easily⁶⁷. The reason behind this may be that the chemisorption of oxygen over these surfaces may change the stoichiometry of the deposited material.

Recontamination of surfaces that have been cleaned is a major concern in cleaning operation. Recontamination can occur by adsorption of vapors from the environment and can come also from a number of other sources such as poor environment control, poor handling and storage, contamination by subsequent processing, etc.. The contaminants are assumed to be condensed hydrocarbon vapors and its rate and amount are the functions of time, temperature and environment.. Recontamination may begin immediately after cleaning.

Recontamination can also occur in the cleaning process itself. Complete rinsing is necessary; otherwise residues from the processing chemicals will recontaminate the surface. For example, in the final rinse, if the part is submerged in the rinse tank then drawn up through the liquid surface on which particles have accumulated, the particles will be painted on the surface and must be removed before they are allowed to dry.

During storage and handling, the type and degree of recontamination is dependent on : (i) time, (ii) temperature, (iii) environment and (iv) surface condition. Many contaminants “harden” with time and become more difficult to remove, so after exposing the surface to a contaminating process or environment it is best to clean the surface as soon as possible⁶⁷. Examples of processing recontamination include : (a) plasma desorption and activation of contaminants in plasma processing, (b) outgassing of thermal vaporization source material, (c) particulate generation in the deposition system, (d) particulate deposition due to turbulence in a vacuum pumping system, etc.

4.2.3 CONTROL OF ENVIRONMENT

A key aspect of surface preparation is the control of the processing environment to avoid contamination during processing and subsequent handling, storage and processing. Environmental factors include: (i) particulates, (ii) ambient gases, (iii) processing gases, (iv) condensable vapors, (v) fluids and (vi) contacting solids.

Particulates come in all sizes. Metal smokes, aerosols, viruses and tobacco smoke provide some of the smallest particle sizes. This type of contamination can be minimized by:

- (a) minimizing dust and particulate generating activities and materials
(e.g., clothing/ skin/ cosmetics, soldering, aerosols)
- (b) low velocity air currents and little turbulence.
- (c) elimination of electrostatic charging insulator surfaces.
- (d) air filtration – “clean” rooms and stations.⁶⁷

The humidity in a clean room is normally controlled by dehumidifying using cold surfaces (air conditioning, or air compression).

Contaminant pick-up from environment is controlled by the control of surface materials, good housekeeping, smooth surfaces, use of covering (finger cots, lint-free cloth), high molecular weight organics (nylon and teflon) or metal for holders and tools, and the use of vacuum tools for handling wherever possible. Vacuum tooling for holding is preferable to other types of handling tools since it minimizes abrasive transfer of materials.

If impure fluids are allowed to dry on a surface, they leave residues. These residues are then very difficult to remove. Residues can be minimized by rinsing in copious amounts of ultrapure water or other appropriate solvent. Wet surfaces should not be allowed to dry without rinsing with a low residue solution.

Chemicals can be contaminated by “carry-over” from a previous process. Carry-over can be minimized by good rinsing between cleaning / processing steps. The most common rinsing technique is to use successive rinses (cascading rinses) in ultrapure water until the rinse water has a high resistivity ($>15 \text{ M}\Omega$)⁶⁷. This is called “rinse to resistivity”. Ultrapure water is a widely used chemical for cleaning and rinsing since it leaves a minimum of residues.

4.2.4 CLEANING PROCESSES

“*Cleaning*” is the reduction of surface contamination to an acceptable level⁶⁷. As a practical matter, a “clean” surface is one that contains no significant amounts of undesirable material; thus what constitutes a clean surface (degree of cleaning) depends on the requirements. Cleaning processes should be as simple and effective as possible in order to meet the requirements of the processing . Elaborate cleaning processes are often expensive and self-defeating.

Effective cleaning generally consists of two or three stages. The first is removal of gross contamination by fluxes, etchants, or abrasion. In the second stage, the cleaning steps are designed to remove specific types of contaminants such as particulates and organics, by solvents, saponifiers, emulsifiers, oxidation techniques, etc. Cleaning solutions may have several actions to attack specific contamination, such as detergents, solvents, wetting agents and mild etchants. Next the surface is rinsed, dried and outgassed, (if necessary). Lastly, a final or in situ cleaning step may be used in a very controlled environment such as in a vacuum or plasma deposition chamber or electrochemical solution.

Particulate contamination may be removed by detergent washing, liquid spray (high pressure), blow-off, brush-off (in liquid or air), flow-off (liquid or condensing vapor), or spin-off (copious fluids) techniques. The most effective technique seem to be detergents (with wetting agents) and mechanical rubbing in a fluid. When using any mechanical rubbing technique, care should be taken to prevent contamination by abrasive transfer from the rubbing media. Use of gentle pressures is recommended.

Hydrocarbon contaminants may be removed from surfaces by solvents which dissolve the contaminants. Polar solvents such as water are used to dissolve polar contaminants (ionic material) while non polar solvents such as the chlorinated hydrocarbon solvents, are used to remove non-polar contaminants (grease, resin, solder flux, etc.). Often a mixture of solvents is used to solvate both polar and non-polar contaminants⁶⁷.

Elevated temperatures are often used to increase detergent solvation, and etching activities. This is often done using immersion heaters (materials must be compatible) or externally heated tanks. Application methods of solvent and fluid

type cleaning includes: soaking, mechanical scrubbing, mechanical agitation, spraying, vapor degreasing, ultrasonic agitation(20-60 kHz).

In mechanical scrubbing, lint-free, de-sized cloths make good towelling (sizing can't be removed by multiple washing). For brushes, there is a variety of materials including : camel hair, mohair, polypropylene, teflon and nylon.

Whether the surface has been cleaned is to be monitored carefully. The best monitoring techniques monitor those elements which are critical to providing a surface that can be further processed. A common check of the cleaning of glass substrate uses the contact angle of a water drop on the surface of the cleaned glass. If the surface has no hydrophobic contamination (oil, grease, hydrocarbons, silicones etc.), the water will wet and spread over the surface. This technique must be used with care since, if a hydrophillic contaminant e.g. a soap residue is present, water will still wet the surface even in the presence of surface contaminants. So, if a glass surface is clean, water will sheet over the surface without breaking up to avoid areas of contamination (water break test). Observation of this sheeting during the rinsing operation is a check that an experienced operator can use in the cleaning process. If the water film breaks up, then surface is not clean. If we breathe on clean glass surface, the moisture will condense uniformly over the surface giving the "black breath figure"⁶⁸. We can see this effect in our bathroom where condensing moisture shows up the dirt swipes on the mirror.

Handling and storage during processing and after cleaning is a major source of recontamination. Storage invariably should be in a non-recontaminating environment. Desiccators provide a passive non-contaminating environment².

4.3 ANNEALING OF THE THIN FILM

Annealing means heating to and holding at a suitable temperature and then cooling at a suitable rate, for such purposes as producing a desired microstructure, relieving stress or obtaining desired mechanical, physical or other properties. Annealing phenomena represent the irreversible change from a state of low structural order to a structure of higher perfection. If a film is annealed at a temperature higher than the deposition temperature, the resulting grain sizes are considerably smaller than those found in films which have been deposited initially at the anneal temperature.⁶⁹

The crystallite size may undergo large changes upon annealing⁷⁰. Palatnik⁷¹ *et. al.* indicates that the random diffraction ring tends to disappear on annealing, leaving only isolated spots in the diffractographs as a proof of the microcrystallization which occurs. Upon further annealing, the number of spots decreases, indicating that large crystallites grew at the expense of smaller and more randomly distributed grains.

Another important effect of annealing is the stress relieving. Residual stresses in films are of two types. The first kind arises from the growth (growth stress). An increase in the deposition temperature produces a marked decrease in the magnitude of the stress⁷⁰. The other source of residual stress is the mismatch in the thermal expansion coefficient between the film and the substrate. Its values and magnitude depends on the expansion coefficient as well as the thickness and the size of the substrate and deposits.

High residual stresses can cause plastic deformation (buckling or bending), cracking etc. in the film or the substrate, or cracking at the substrate- film interface. Annealing is therefore a prerequisite in obtaining good quality film.

4.4 X-RAY DIFFRACTOMETRY :

The chemical composition of the deposited films are identified by x ray diffractometry. Here the film is scanned with x ray. Various crystallographic planes of the film which satisfy the Bragg's condition diffract the incident beams. The values of twice the Bragg angles (2θ) are determined for various peaks in the XRD pattern then the patterns are indexed by the standard indexing method⁷² by using the 'JCPDS - International Centre for Diffraction Data' cards⁷³.

For the determination of lattice parameters the procedure given by Cullity⁷² can be followed. Here, lattice parameters for hexagonal crystals are calculated by putting the 2θ values of two major peaks into the equation: $\sin^2 \theta = \lambda^2/4[4/3 \times (h^2 + hk + k^2)/a^2 + (l^2/c^2)]$ and solving simultaneously, where:

2θ	=	Angle of rotation of the film
θ	=	Bragg angle
λ	=	Wavelength of X-ray
(hkl)	=	Miller indices of the reflecting plane
a, c	=	Lattice parameters

The film which is turned to polycrystalline from as grown amorphous film as a result of thermal treatment is always associated with non uniform strain. The presence of such strain can easily be identified from the broadening of x-ray diffraction peaks⁷².

4.5 THERMOGRAVIMETRIC ANALYSIS

In the thermogravimetric method^{21,74,75} weight measurements of the samples are made by weighing the samples before and after deposition and also before and after

the heat treatment at the chosen temperature in order to determine the mass loss. The thickness of a film may be determined by knowing the amount of material deposited. Given the density and x-sectional area of the final film one can easily determine the thickness of the film from its thermogravimetric data. This method has the advantage of simplicity albeit it does not give enough accuracy. However, where precision thickness measurement is not a *prima facie* rather a tool to be used as a rule of thumb, this method can safely be employed.

There are of course many methods of thickness measurements of thin films. Thickness may be obtained from the measurements of optical properties by using a spectrophotometer from the interference maxima in transmission spectra¹⁵. Microscopic determination of thin film has been proven to be an erroneous way since these films are too thin to be resolved by ordinary optical microscope. In stead Scanning Electron Microscopy (SEM) can be used for measurement of thickness¹³.⁷⁶. In comparison to them thermogravimetric analysis gives inaccurate results. However, its another implication is that it can closely follow the transformation in the film that occurs during the heat treatment.

4.6 OPTICAL MEASUREMENTS

The region of importance for optical methods of analyses ranges within a narrow region in the centre of the electromagnetic spectrum (200nm-25 μ m). This region encompasses the near ultraviolet (near-UV: 200- 400nm), visible (VIS), near-infrared (near-IR) and middle infra-red (middle IR) regions. The adjectives near and far, when used to modify UV and IR, relate to the visible region as the reference region. the UV and VIS region on the electromagnetic spectrum corresponds to wavelength between 150-800nm.⁷⁷

From Beer's law of radiation absorption⁷⁷ it follows that absorption coefficient (α) is directly proportional to the concentration (C) of a solute. To apply this law,

optimum wavelength must be selected, and for this purpose a spectral curve is determined. In practice, either percent transmission (%T) or absorbance (% α) is plotted as a function of wavelength holding concentration of the specimen constant. The resulting curves are called the transmission spectra and absorption spectra, respectively. Most instruments give linear readouts in % transmission rather than absorbance because detectors respond to the amount of light transmitted rather than to the light absorbed or missing.

Spectral curves are characteristics of the absorbing substances and thus curves can be used for thickness measurements. For qualitative analysis a wavelength is selected where the desired solute absorbs strongly and interfering substances absorb minimally. A spectrophotometer is used for measuring the absorbance (or transmission) of UV or VIS radiation. This instrument can successfully be used in the determination of thickness in thin film by measuring the interference⁷⁸. Interference of rays reflected from two different planes can give rise to pronounced maxima and minima. These in turn can be correlated to the separation of the two planes.

Fig. 4.6.1a shows the simplest case where there is an isolated film surrounded by air. When the path length through the film corresponds to an integral number of the wavelength (λ), constructive interference will occur and for paths of an odd number of half wavelengths, minima of intensity will occur. Thus the relation between the thickness(t) and the wavelength λ_0 , where a particular maxima or minima occurs is given by :

$$t = m\lambda_0 / (2n \cos\phi') \quad (\text{maxima})$$

$$\text{or, } t = (m + \frac{1}{2})\lambda_0 / (2n \cos\phi') \quad (\text{minima})$$

where m is an integer which becomes progressively smaller as λ increases and ϕ' is the angle of incidence of the beam as it hits the lower reflecting surface. In principle, these effects can be observed for very thick samples. The configuration of

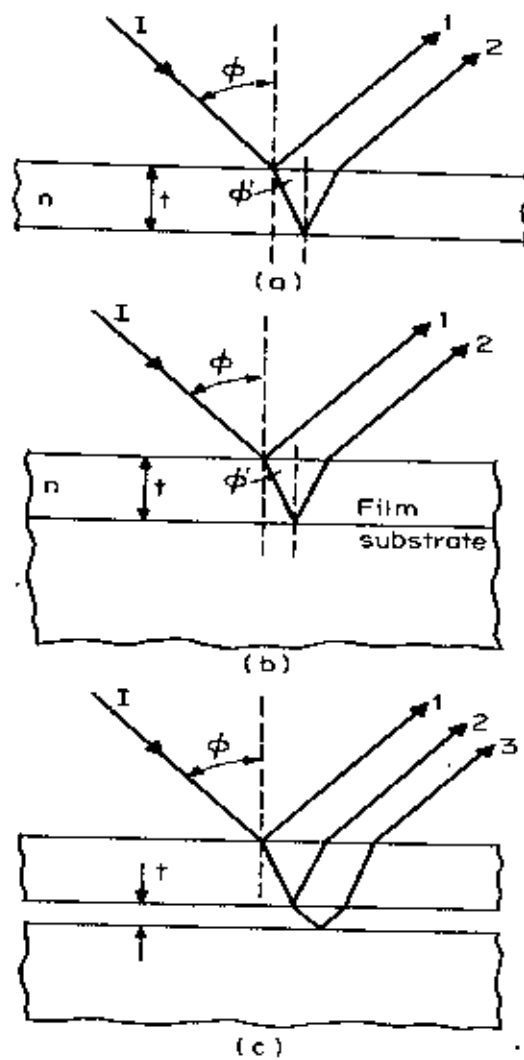


Fig. 4.6.1 Reflections from various combinations of interfaces. ⁷⁸

Fig. 4.6.1b is a common one, and could be, for example, for a thin film on a glass substrate. The equations for interference maxima and minima are the same as the previous one. However, phase shift differences between the two interfaces and change of reflection coefficient with wavelength may need to be considered. In a spectrophotometer with a specular reflection attachment, the wavelength can be varied. At the same time, the reflected intensity will vary cyclically, for a fixed separation (or thickness) t . The aforementioned equation can be applied to one of the peaks and valleys of the transmission scan. If the first minimum is recorded:

$$t = \lambda / (4n \cos \phi')$$

For transparent films like oxides, which are usually 2000 to 10,000 Å thick⁷⁹, the conditions of this equation are relatively easy to fulfil and can be used for measurement.

From the theory of optical transitions in semiconductors it is known that in the vicinity⁸⁰ of a band edge there is a peak in the reflectance. To determine the energy gap from absorption scan, the following model has been used for direct inter band transitions:

$$\alpha n \cdot hv = \text{const.} (hv - E_g)^{1/2}$$

in which hv is the photon energy, n is the index of refraction and α is the absorption coefficient. In this approximation $(\alpha nhv)^2$ should be a linear function of hv and from the intercept, band gap E_g should be found.

In contrast, according to Studenikin²¹ *et. al.* this model may not be suited to wide band gap materials like ZnO because the absorption band edge is strongly disturbed by a coulombic electron-hole interaction. Because of the sharpness of the absorption edge, Studenikin *et. al.* suggested that, photon energy at the half height of the maximum absorption could give a band gap value very close to the extrapolated one.

From Beer's law transmission (T) is given by, $T = I / I_0$ and absorbance, $\alpha = \ln(I_0/I)$. Here I is the intensity of the transmitted beam and I_0 is that of the incident beam. Hence,

$$\alpha = -\ln T \text{ or, } T = e^{-\alpha}$$

i. e. transmission is a function of absorbance. This argument can be used in rough calculation of the band edge of ZnO thin film from the transmission scan. The tangent to the high transmission region and tangent to the region where absorption starts and suddenly reaches maximum (i.e. transmission abruptly falls) intersects each other. The corresponding value of the wavelength to this point gives the wavelength of the absorption edge. This is shown in Fig. 4.6.2. If this wavelength is denoted by λ_{edge} , we will get the energy gap :

$$E_g = h\nu_{\text{edge}} = hc / \lambda_{\text{edge}}$$

Putting $h = 4.136 \times 10^{-15} \text{ eV}$, $c = 2.998 \times 10^8 \text{ m/s}$, λ_{edge} in nanometer will directly give the energy gap as:

$$E_g = 1239.8547 / \lambda_{\text{edge}} (\text{nm})$$

However, this type of rough calculation has its limitations in precise calculations.

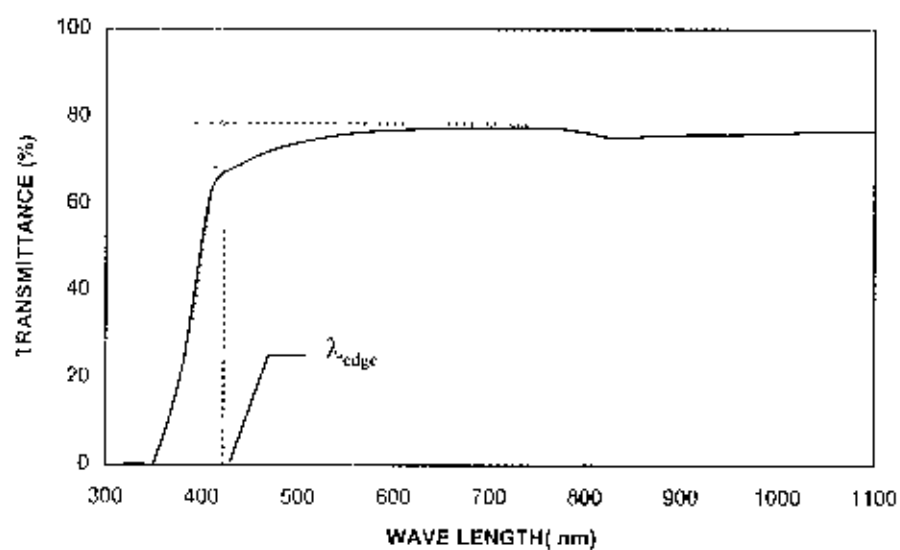


Fig.4.6.2 Determination of optical absorption edge from transmission scan

CHAPTER FIVE

EXPERIMENTAL TECHNIQUES

5.1 CLEANING OF THE SUBSTRATE

In the deposition of ZnO thin film by sol-gel process, microscope slides made of Pyrex glass were chosen as the substrate primarily for their standard quality and availability. The slides were typically 2.5" x 1" x 1/16" in dimensions. These slides were first thoroughly rinsed with deionized water and then brushed with nylon brushes which were soaked in acetic acid. The process was repeated once more and finally brushed with nylon bristles using absolute ethanol as the cleaning solvent in order to dissolve grease and other dirt on the slide. The cleaning operation was completed through the rinsing of the slides with deionized water. These slides were then dried in an oven at around 120 C for 15 minutes so as to expel the moisture and other carbonaceous residues from the surface.

In a systematic way, the proper cleaning sequence for the successful film deposition on the glass substrate may be represented in the following manner;

1. Thorough rinsing with deionized water and brushing with soft nylon brushes,
2. Gentle brushing with nylon bristles using acetic acid as the cleaning agent,
3. Rinsing with deionized water to remove last traces of the acid,
4. Brushing with nylon bristles soaked in absolute ethanol,
5. Final rinsing with deionized water to remove the traces of alcohol, and
6. Drying in a drier at around 120 C for 15 minutes.

Worthy to mention that step 1-5 is to be done at room temperature.

The clean and dry slides were then used for dipping into the ZnO sol. In case where they were to be used at a later period, they were transferred to a desiccator for storage and were used within 24 hours of cleaning.

5.2 DEPOSITION OF ZnO THIN FILM :

5.2.1 Preparation of the sol :

The technique adopted in the present study for the deposition of ZnO thin film was a sol gel dip coating technique. The technique was a modification of the methods described by Tang¹² *et. al.* and Kamalasanan¹³ *et. al.* for the sol gel deposition of ZnO thin film and Chatelon¹¹ *et. al.* for sol gel dip coating deposition of SnO₂ thin film. Fig. 5.2.1 provides the flow diagram of the route adopted for the sol gel synthesis of ZnO thin film.

A solution of ZnO precursor was made by dissolving 10 grams. of dihydrated zinc acetate with 4 ml ethylene glycol in a 40 ml. glass beaker and then heating them for 15 minute to boiling over a hot plate. When the last traces of zinc acetate went into the solution and a transparent solution resulted the beaker was removed from the hot plate and cooled to room temperature with the result that the content of the beaker turned to a transparent solid. This was redissolved into 20 ml of n-propyl alcohol by boiling again. Alternately, n-propyl alcohol was added to the transparent solution being on the cooling stage exactly when the last trace of white zinc acetate went to the solution. In order to stabilize the sol 0.5 ml glycerol was added to the sol. Few drops of diethyl amine were also added .

Appendix A gives the literature values of the important physical properties of the various reagents required in the sol gel synthesis of ZnO thin film⁸¹.

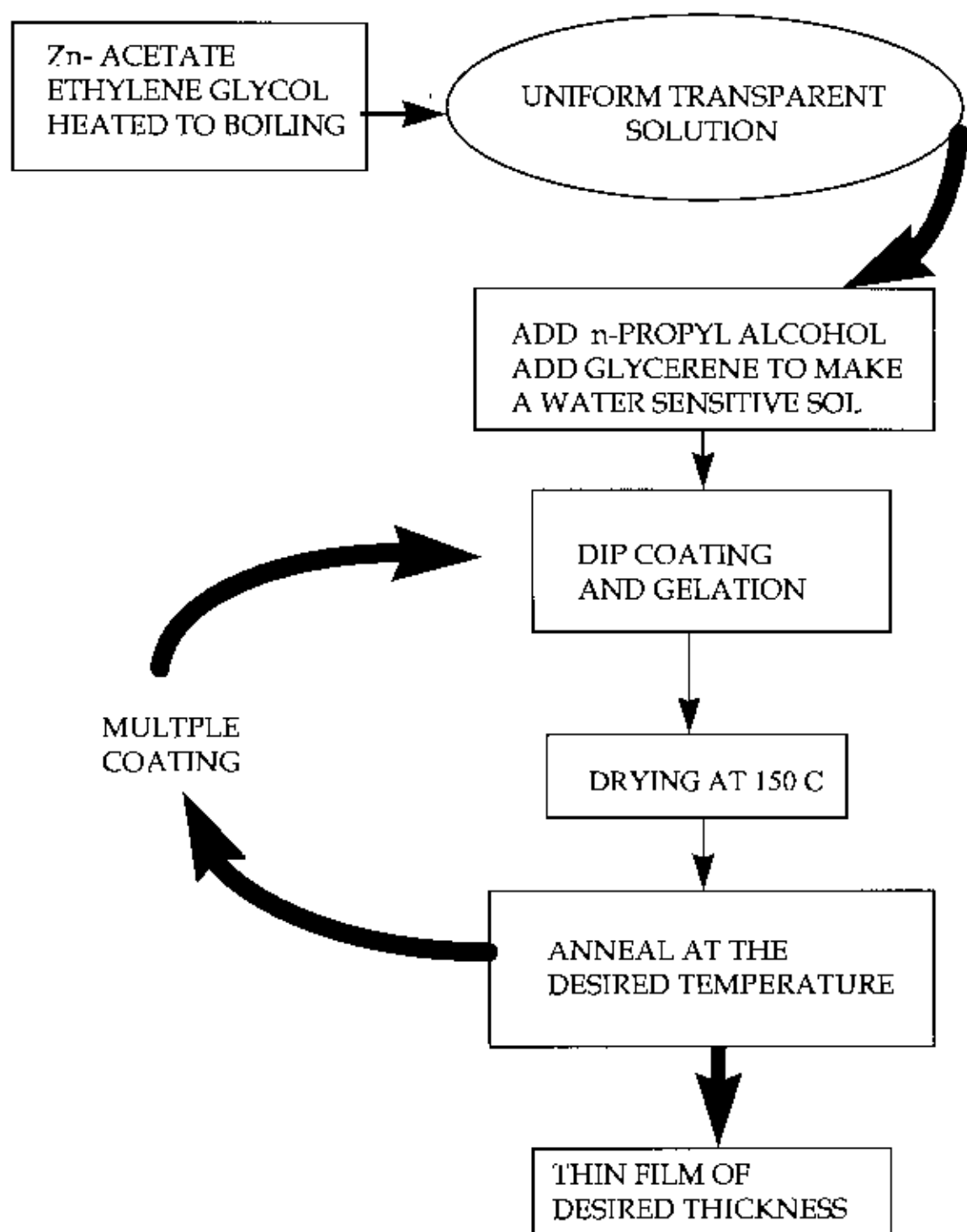


Fig. 5.2.1 The flow diagram of the sol gel route used for the preparation of ZnO thin film by dip coating method.

5.2.2 Dip Coating

A slight modification of the dip coating apparatus suggested by Chatelon *et. al.* had been adopted for the present study. Fig. 5.2.2 shows the schematic diagram of such a modified apparatus. The apparatus has a crocodile clip in order to captivate the glass substrate. The crocodile clip was firmly attached to a mild steel rod having a diameter of 2.5 mm and length 18 inch. The rod at its top was hanged from a pulley with the help of a non expanding dial cord. The pulley was driven by an electrical motor. The built-in gear arrangement reduced the speed of the primary rotation of the electrically driven motor. The high rotational speed of the motor was further reduced by controlling the size of the pulley arrangement. In order to move the substrate up and down, the dial cord was moved by rotating the pulley in the required direction. The change in the direction of rotation of the pulley was achieved by simply changing the polarity of the current flowing to the electric motor. A SPDT(single pole double throw) electric switch was used for this purpose.

The essential components of the dip coating apparatus and their functions are described below:

- | | |
|------------------|--|
| Crocodile clip | : To hold the substrate firmly and to remove it when necessary. |
| Vertical rod | : To increase the self load so that the fall in the height of the dial cord is spontaneous and its withdrawal from the ZnO sol is smooth. |
| Dial cord | : To transform the rotational motion from the pulley into the reciprocating motion of the vertical rod. |
| Pulley and Gears | : To reduce the high rotational speed from the electric motor and for winding and loosening of the dial cord so that its length decreases or increases respectively. |

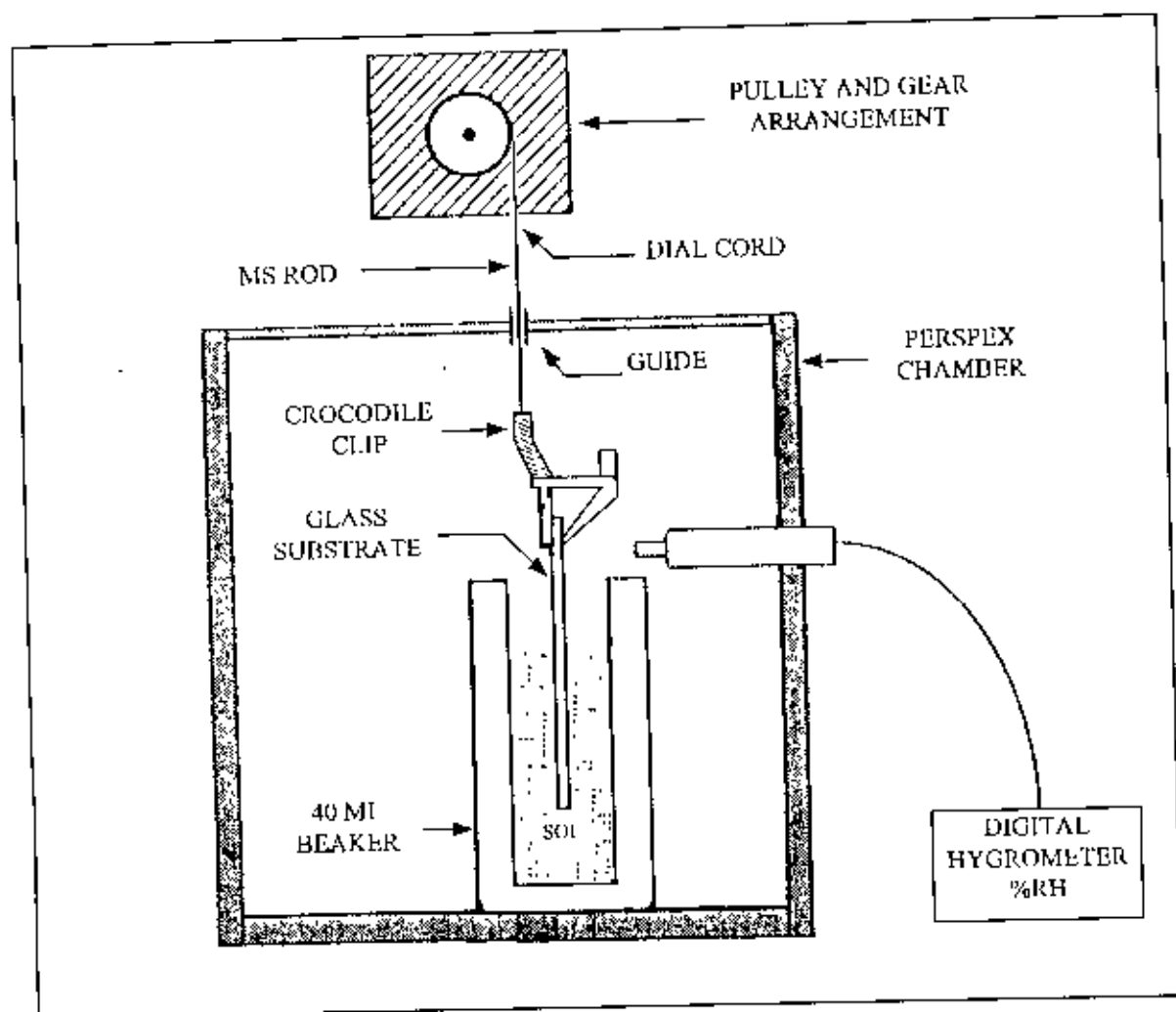


Fig. 5.2.2 The Dip-Coating Apparatus for the deposition of ZnO thin film by sol gel method.

- Electric motor : To provide rotation
- Guide : To restrict the swinging of the rod, clip, as well as the glass substrate
- Lubricants in guides: To reduce the friction between the guide and the vertical rod
- Digital Hygrometer : To indicate the relative humidity (%RH)
- Perspex Chamber : To protect from dust and air convection
- SPDT : To change the polarity of the motor so as to change the direction of the motion of the motor and hence that of the substrate.

With the help of such an arrangement the substrates could be slowly dipped vertically into the sol, held there for 1-2 seconds and then withdrawn smoothly from the bath at a constant rate(200 mm/min). The relative humidity inside the perspex chamber was measured by a JB 913 R Electronic Thermo-Hygrometer but no attempt to control the humidity was taken. The coated substrates were then kept in ambient air for 15 minutes for gelation. If one side of the glass slides is required to be made free from any coating, acetone- soaked cotton was used to wipe the film off from this side. The film was kept for gelation both in horizontal and vertical positions. Horizontal samples were kept over watch glasses or porcelain leads, whereas vertical samples were hanged from a custom-made mild-steel slide rack, with the help of paper clips. The vertical slides were hanged keeping such a distance between them that any contact or collision is avoided . Otherwise one slide might destroy the film on the adjacent slide.

5.3. ANNEALING OF THE ZnO THIN FILM

The gelled films were dried in both horizontal and vertical positions at 150 ± 10 C for 15 minutes in an oven. The difference between the set temperature and

the actual temperature of the oven was properly calibrated with a chromel- alumel thermocouple so that the actual temperature in the neighborhood of the film can accurately be determined. For drying and annealing up to temperatures 250 C, an oven was used. For experiments above 250 C, a muffle furnace with a heating rate over 20 C/min. had been used. The films were held at the annealing temperature ± 10 C for 15 minutes. The samples were then furnace cooled to room temperature from the anneal temperature by keeping them inside the furnace. The annealing cycle is shown in Fig. 5.3.1. After the treatment, the cooled samples were transferred into a desiccator for storage. Fused calcium chloride was used as the desiccant.

5.4 XRAY DIFFRACTOMETRY

The as-grown film as well as the films annealed at different temperatures were placed inside the sample holder of a JEOL JDX-8P X-ray Diffractometer. The samples were scanned over the 2θ range of $30-70^\circ$ with $\text{CuK}\alpha$ radiation. X-ray patterns made by $\text{CuK}\alpha$ radiation were taken into consideration for analyses e.g. in identification of the presence of ZnO and indexing of the reflecting planes, in the determination of lattice parameters, etc. Various parameters in X-ray Diffractometry e.g. current and voltage, scanning speed, chart speed and time constants, cps (counts per second) values etc. were kept constant. The typical values of them were:

Target:	Cu
Filter:	Ni
Voltage:	30 kV
Current:	20 mA
Scanning speed:	2 deg./min
Chart speed:	10 mm/min

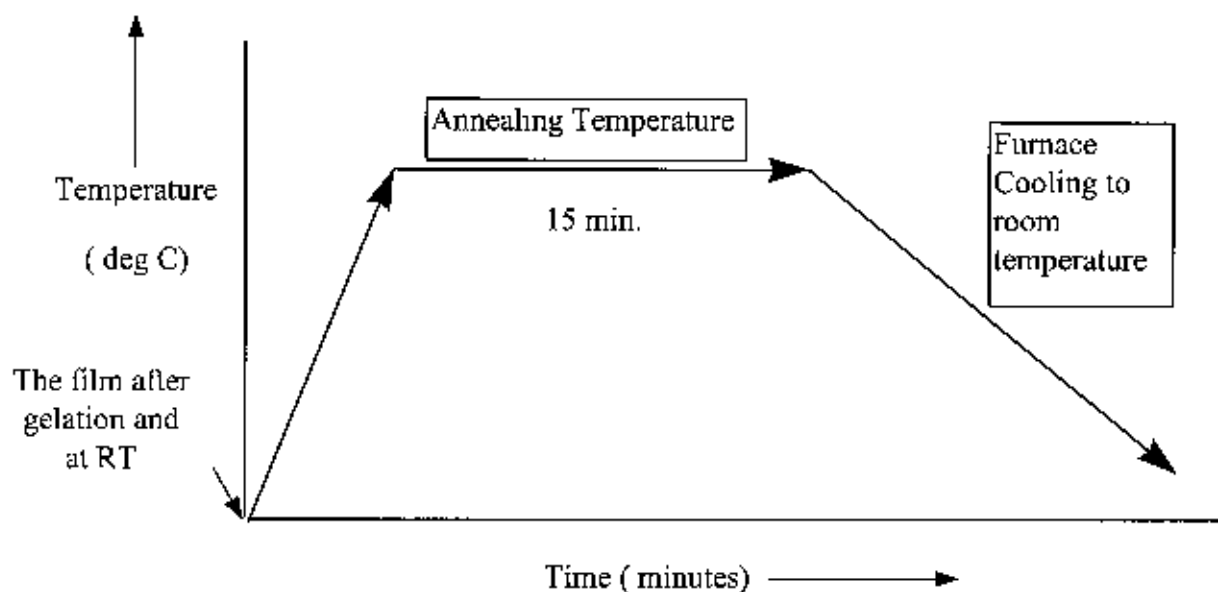


Fig. 5.3.1 Annealing cycle for the thin film of ZnO deposited by sol gel method

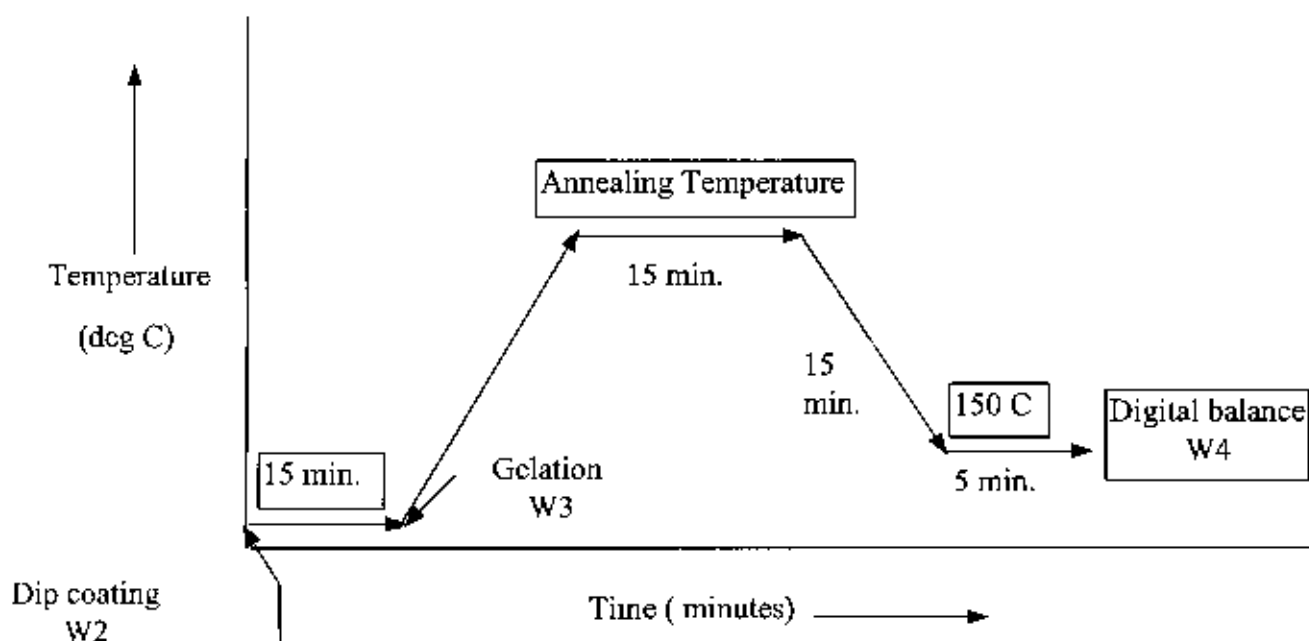


Fig. 5.5.1 Heating cycle for the thermogravimetric analysis of the thin films of ZnO deposited by sol gel method

Full scale: 4×10^4 cps
intensity

Time constant: 4

Range of 2θ : 30 -70 deg.

5.5 WEIGHT LOSS MEASUREMENT

Thermogravimetric method was used for the measurement of weight loss and there from the measurement of thickness was made. Here the slides were first weighed before deposition in a Libror AEG 220 G digital balance with an accuracy of up to four digits after the decimal. This gave the slide weight (W_1). The film was then deposited on to the slide with the help of the dip-coating apparatus and both sides of the slide were coated. The bottom part of the slide, which was to be placed on a watch glass for the purpose of loading into the furnace or drier, was wiped off the coating with the help of cotton buds. These buds were soaked with acetone. This step avoided any accidental dust catching or contamination from the watch glass. Care was taken so that acetone does not cross over to the top part as it would either dissolve the as-deposited film or affect its purity. At this condition the sample was weighed to get the weight W_2 . The length and width of the film after the final heat treatment were carefully measured with a callipers and their product gave the value of the surface area (A) of the final film. The slide was then placed in ambient air for gelation at room temperature for 15 minutes. After gelation, the slide was again weighed at room temperature to get the weight W_3 and then sent for annealing.

Annealing cycle for the samples was similar to that suggested by Fig. 5.3.1 except that after holding for 15 minutes at the annealing temperature the films were cooled in 15 minutes to the drying temperature 150 C, kept inside a drier at 150 C for

another 5 minutes and then quickly transferred to the digital balance for weight measurements. This will give the weight W_4 . The heating cycle for thermogravimetric analysis has been shown schematically in Fig. 5.5.1.

Hence,

$$\text{the weight of as-deposited film, } W_x = W_2 - W_1$$

and,

$$\text{the weight of the film after gelation, } W_g = W_3 - W_1.$$

$$\text{Weight loss after gelation} = W_x - W_g$$

$$\% \text{ weight loss after gelation} = [(W_x - W_g)/W_x] \times 100\%$$

Similarly for films after annealed at any desired temperatures,

$$\text{Weight of the film } W_i = W_4 - W_1$$

$$\text{Weight loss after annealing at a particular temperature } i,$$

$$= [(W_x - W_i)/W_x] \times 100\%$$

Then the final weight of the film after annealing, $W_f = W_i - W_1$, where W_a is the weight of the slide along with the film after annealing at the final temperature.

Hence, the thickness of the film is given by

$$t = W_f / (d \cdot A) \quad (5-1)$$

where, d = density of the ZnO film, gm/cm^3

A = surface area of the film, cm^2

5.6 OPTICAL MEASUREMENTS

Optical measurements of three best samples deposited at three different conditions were performed. The measurements were carried out in a Shimadzu UV-VIS 3100 Spectrophotometer where the wave length of the incident light was varied from the around 1100 nm to around 300nm.

5.7 OPTICAL MICROSCOPY :

Optical surface topographs of the films were taken with a metallurgical microscope at 100X magnification and using a camera. Since the film was transparent, transmitted light was used for the micrography in stead of reflected light. Few macrophotographs of the deposited and annealed films were also taken for comparison.

CHAPTER SIX

RESULTS AND DISCUSSIONS

6.1 EFFECTS OF SURFACE PREPARATION ON THE ZnO THIN FILM FORMATION

Several attempts with distilled water wash followed by ultrasonic (US) cleaning of the glass substrate in distilled water had failed to yield a uniform film (Fig. 6.1.1) after annealing at 450 C, since this type of substrate cleaning was not adequate for the present purpose. Hence, cleaning of the substrate for the deposition of ZnO thin film was found to be critical in the formation of thin films of zinc oxide(ZnO). Contaminants on the glass substrate prevented the formation of uniform film as because they force the sol-coating to cluster into spots³³ in stead of spreading on or wetting to the substrate surface completely. Lack of wetting of the substrate by the sol means lack of adherence between the substrate and the film and so even if the as-deposited film looked uniform, it might break to smaller spots and islands on drying or during heat treatment (Fig. 6.1.1). As evidenced from Fig. 6.1.2 , the broken bubble on the film in Fig. 6.1.1 actually depicts the occurrence of partial wetting⁸² . It has been discussed in section 4.2.2 that presence of contaminants on the substrate surface increases the wetting angle to non-wetting and partial wetting⁶⁶. This type of lack of wetting leads to lack of adherence of the film to the substrate which ultimately affects the nniformity and smoothness of the final film. So, we can safely say that the presence of surface contaminants prevented smooth film formation for the sample shown in Fig. 6.1.1.

Fig. 6.1.3, on the other hand, shows the ZnO film deposited on a glass snbstrate which has been cleaned properly and carefully through the steps mentioned in section 5.1. This confirms the necessity of careful cleaning of the substrate. Use of

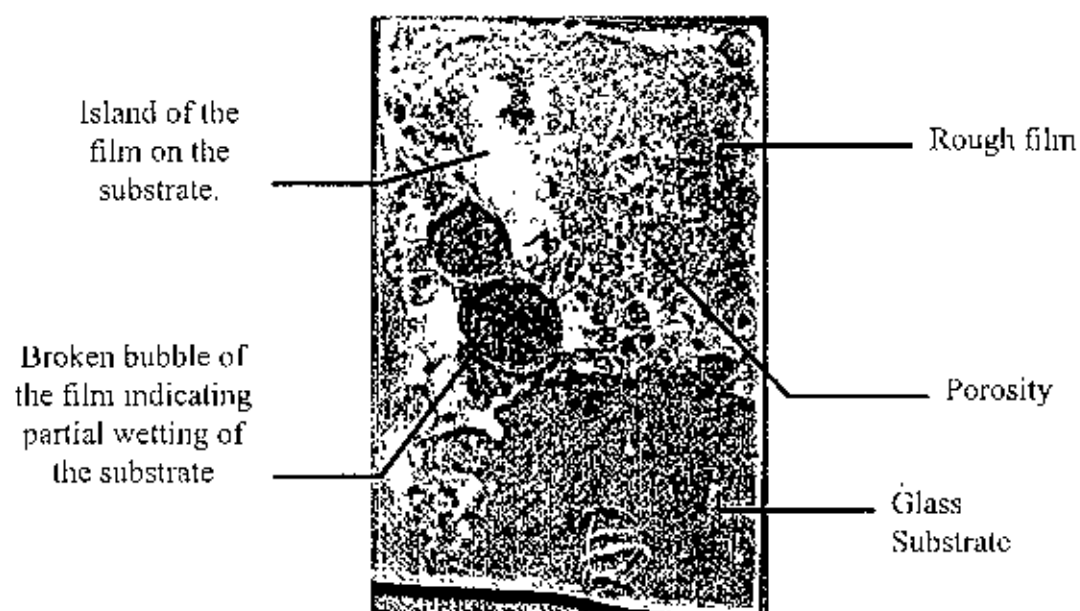


Fig. 6.1.1 Macrograph of ZnO thin film deposited by sol gel dip coating method on a glass substrate which was cleaned by washing with distilled water and then by ultrasonic cleaning.

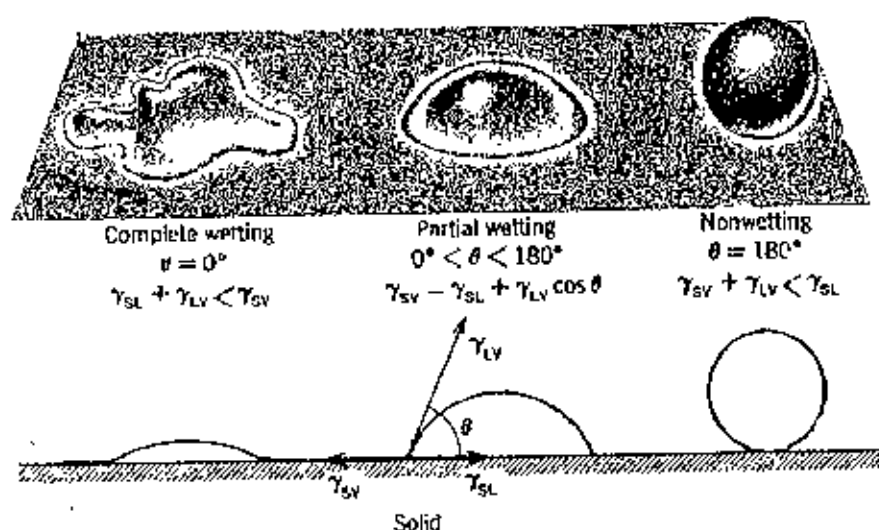


Fig. 6.1.2 States of wetting of a substrate by a liquid drop. Higher wetting angle means lower extent of wetting.^{s1}

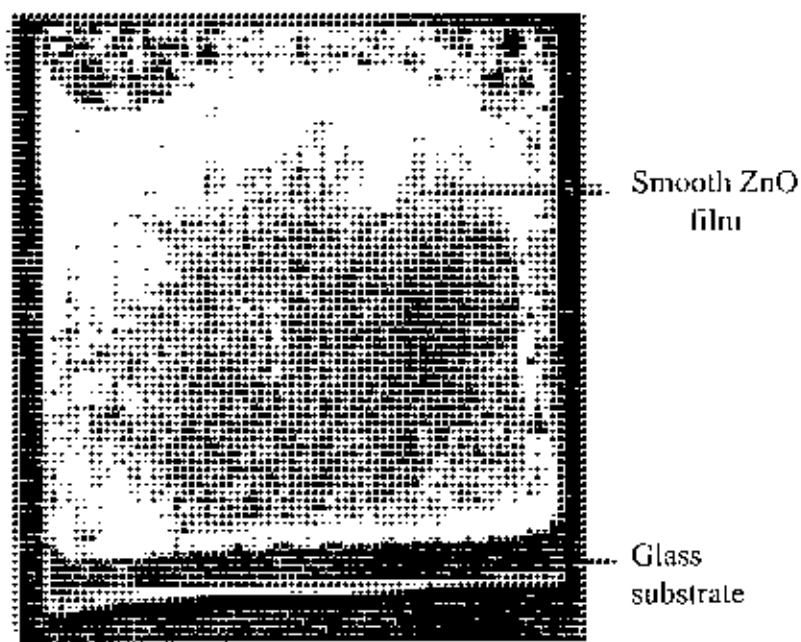


Fig. 6.1.3 Macrophotograph of ZnO thin film deposited by sol gel dip coating method on a glass substrate which was cleaned by following the recommended procedure in section 5.1. The film is much more dense, smooth and uniform than that shown in Fig. 6.1.1.

Use of HCl or HNO₃ was avoided so as to ensure immunity from chloride or nitrate ion contamination since zinc might form zinc chloride or nitrate. The use of any soap, soda or detergents was also avoided, mainly because they might present a wettable substance even in the presence of contaminants ⁶⁷(sec. 4.2) and might cause metal ion contamination in the final film.

Since polar solutes are usually dissolved in polar solvents and non-polar in non-polars, acetic acid which is polar and ethanol which is non-polar have been used in order to remove both types of surface particulates. Thorough rinsing with deionized water after each successive stages of treatment with acid or alcohol prevented the recontamination by painting (sticking of the floating particles on to the surface) of the particulates, which had been loosened by the previous cleaning step, over the glass substrate. The glass slides were then dried in an oven in order to expel the volatiles and any moisture over the glass surface.

Most of the dried substrates for deposition were used just after the drying of the substrate since the storage of the substrate (i.e. glass slides) might pose a problem as recontamination might occur during the interval between the cleaning and storage⁶⁷. In case where the substrates were to be used at a later period, we stored them in a desiccator and used them within 24 hours of storage thereby reducing the risk of recontamination.

6.2 SOL GEL TRANSFORMATION TO ZnO THIN FILM

In the present study, a modification of the method described by Kamalasanan¹³ *et. al.* was used. In the present method dip coating method was used to coat rather than spin coating which was adopted by Kamalasanan *et. al.* Another important deviation was that the deposited films were allowed to be hydrolyzed after their withdrawal from the sol. The perspex chamber (Fig.5.2.2) helped to maintain a still

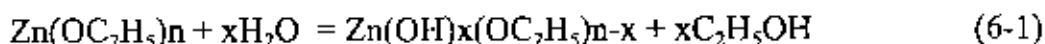
air and a more or less constant ($\pm 2\%$) humidity inside it and thereby helped the formation of film. Since any attempt to control the humidity was virtually absent, only the value of the relative humidity was taken with the help of the hygrometer. The perspex chamber created an effective obstacle to the fluctuations of humidity inside it. Thus it kept a steady humidity at the meniscus of the film (Fig. 5.2.2).

It was anticipated that the most difficult step in deposition of ZnO film from Zn-acetate would be the preparation of a stable sol³³ because of the insoluble nature of zinc alkoxide in most of the alcohol⁴⁰. Coulombic hydration⁸² was set liable for this difficulty by Kamalasanan¹³. The zinc acetate salt was therefore heated to boiling along with the ethylene glycol. Treatment with ethylene glycol eliminates the difficulty of the dissolution of zinc alkoxide into alcohols¹³. Boiling, on the other hand, reduces the size of the zinc acetate to a level that permitted 'sol' – formation because the smaller the size of the colloidal miscellies are, the more stable the dispersion will be and less effective will be the gravity in causing a separation or destabilizing the sol³⁸ (sec.2.5.2.1). It is, therefore, possible to form a stable sol without any addition of glycerol or any amine if the acetate dispersion is of proper size. Addition of glycerol, however, increased the solubility as well as enhanced the film formation properties¹³. Glycerol acted as a stabilizer in ferric oxide sols³⁷ and in the same manner it was expected to stabilize the ZnO sol also.

The hydrolysis of the sol to form a gel before the dipping step has been discarded. In stead, gelation was allowed to occur after the withdrawal of the substrate from the sol. Since the sol has been kept in a beaker inside the perspex chamber, the chamber helps to prevent any undesirable air convection effect around the film during the pulling stage and maintained a steady humidity. During the gelation stage the as grown coating of the ZnO-sol attracts water from the ambient air and form $\text{Zn}(\text{OH})_2$ thereon. Actually the addition of water to the sol restores the water of hydration to the zinc cation in order to form zinc acetate dihydrate again¹³. This

dihydrate has a lower solubility in alcohol and it is forced to precipitate in alcohol. Diethyl amine, as a proton acceptor, deprotonates this water of hydration and thereby gives a transparent gel of $Zn(OH)_2$. However, the preparation of the zinc hydroxide gel with the help of water addition had been found very difficult and often the sol transformed into a suspension giving a milky appearance. That is why, gelation of the film was preferred to be done after the deposition of the film on to the substrate.

In discussing the mechanism of the sol-gel transformation by the dip coating method it is therefore suggested that the hydrolysis of the as grown film should start during the pulling stage and should continue during the gelation stage. The reaction is likely to occur in the following way:



analogously from the observations made by Chatelon¹¹ *et. al.* for the deposition of SnO_2 from Sn-alkoxide starting from Sn-acetate and ending to SnO_2 through the formation of $Sn(OH)_2$:

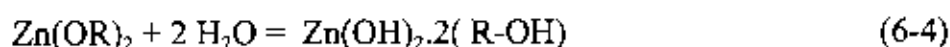


So equation (4 -1) suggested by Kamalasanan¹³ *et. al.* should be changed in the following way:

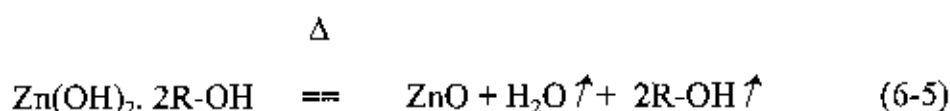


The expulsion of acetic acid during the boiling of Zn-acetate was well identified from the characteristic smell of acetic acid and confirmed that reaction occurred in a likewise manner to equation (6-3).

The hydrolysis then occurs as :



and the condensation reaction as:



This reaction suggests that on heating to higher temperature water of hydration of ZnO as well as the organic volatiles will be expelled. The bulk Zn(OH)₂ starts decomposing at around 125 C (Appendix A). So, it is expected that the drying temperature is enough to cause the sol gel transformation to ZnO. However this ZnO is still in amorphous form which has been confirmed by the XRD scan to be discussed later.

6.3 EFFECTS OF HUMIDITY

Neither in preparing the sol nor during the dipping of the substrate into the sol had humidity was controlled except noting the value of relative humidity from a digital hygrometer. However the relative humidity varied between RH 40% to RH 75% from one experiments to another during the course of the study. Fig. 6.3.1.(a) shows the macrophotograph of a film deposited at relative humidity (RH) 75% which is very high, and Fig. 6.3.1.(b) illustrates the film deposited at RH 60%. Both the films were annealed at 400 C for 15 minutes and then cooled in a furnace. Many spotty areas were present in both the films and the films were not smooth at all. On the contrary, films deposited at RH 50% (Fig. 6.3.2.a), and RH 40%(Fig. 6.3.2.b), both annealed at 400 C, were less porous and denser. Clearly the film deposited at lower

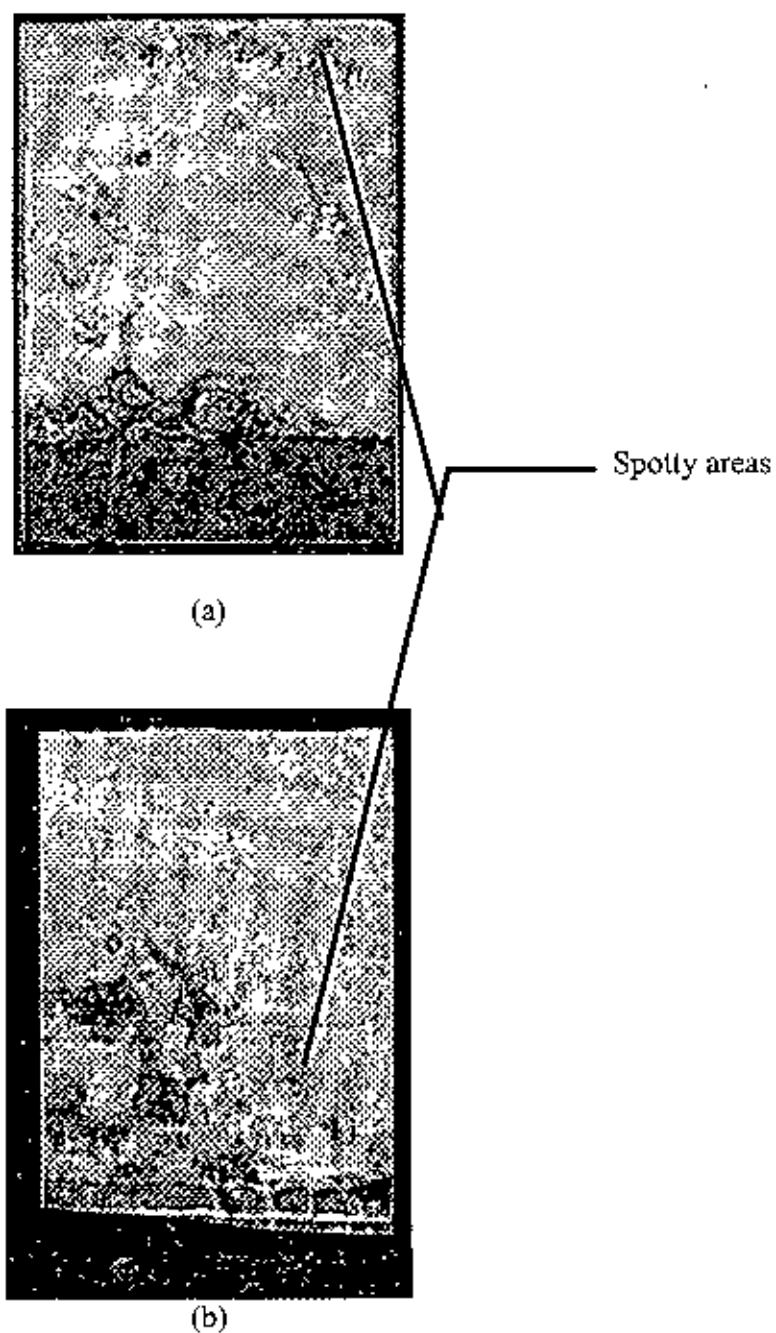


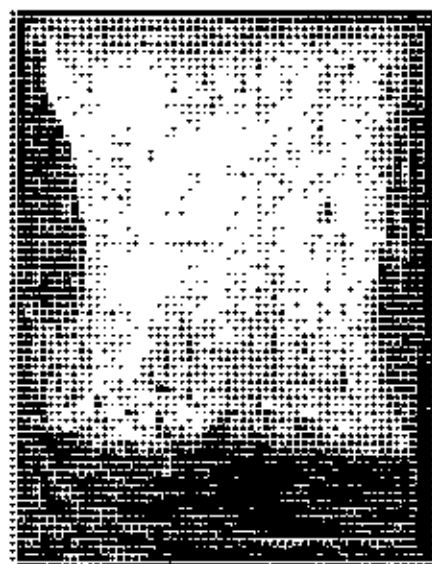
Fig. 6.3.1 Macro photographs of thin films of ZnO deposited by sol gel dip coating method at different humidity and annealed at 400 C for 15 minutes:

(a) RH 75%

(b) RH 60%



(a)



(b)

Fig. 6.3.2 Macro photographs of thin films of ZnO deposited by sol gel dip coating method at different humidity and annealed at 400 C for 15 minutes:

(a) RH 50%

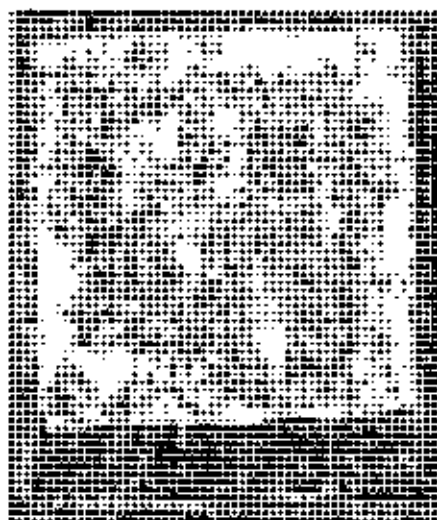
(b) RH 40%

humidity (Fig. 6.3.2.b) was much more smooth, transparent and, of course, more desirable. So, the relative humidity should be controlled so as to keep it at a lower value.

In fact the relative humidity plays a vital role in the film appearance and quality. Higher humidity means higher amount of hydroxide to be attached with Zn - cation which, in turn, means that more water had to be evaporated leading to the necessity of heating at higher temperatures or for longer time in order to expel the water completely. Higher humidity also means that the films suffer from inhomogeneous packaging¹¹ of the crystallites. Since as unvaporized water drops tends to migrate to the surface at high temperature water may destroy the bonding of grains and crystals²² and vigorous cracking in the film may occur (Fig. 6.3.1a). Similar observations were made by Chatelon¹¹ *et. al.* that all the sol gel deposited thin films of SnO₂ prepared from Sn-alkoxide presented good transparency and uniformity over the whole surface, except for the films prepared at higher values of relative humidity (>50%). So, humidity control is very much important in the formation of smooth and transparent ZnO thin film.

6.4 EFFECT OF ANNEALING

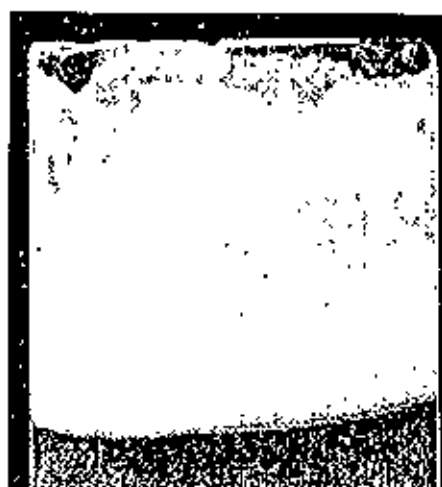
Annealing has been found to play a much pronounced effect on the structure of the ZnO thin film. In the present study sol gel deposited ZnO thin films are annealed in the temperature range from 150 C to 450 C. The films annealed at temperatures up to 275 C are highly transparent. At around 275 C the films turn black as a result of annealing. This blackening can be eliminated only by heating or annealing at higher temperatures. This can be evidenced from Fig. 6.4.1. The film which was turned black due to annealing at lower temperatures showed traces of white areas (Fig. 6.4.1.a) after annealing at 375 C while the amount of white areas increased to a great extent at 400 C (Fig. 6.4.1.b). The black portions at the bottom edge of the



(a)



(b)



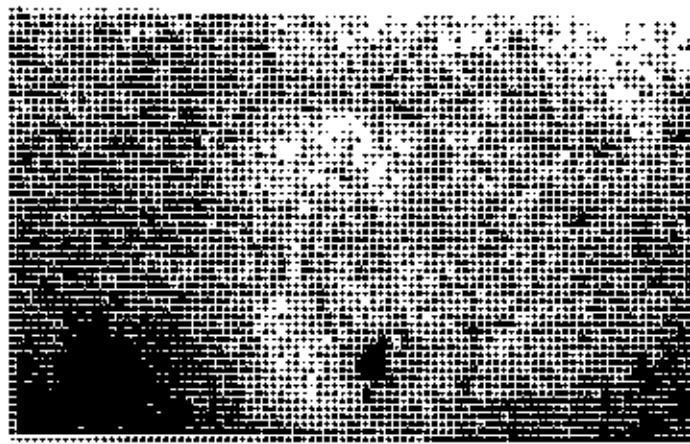
(c)

Fig. 6.4.1 Effect of annealing on the appearance of thin ZnO film deposited by solgel dip coating method at 75% humidity and annealed for 15 minutes at: (a) 375 C. (b) 400 C. (c) 450C

latter film indicates that the transition is not wholly over and expulsion of organics is waiting to be completed. A still higher temperature is, therefore, needed in order to get a film which is completely free from black spot. Fig. 6.4.1.c shows the result of annealing such film at 450 C. Annealing at higher temperature also resulted in smooth macroscopic appearance in the film. Comparison between film annealed at 400 C (Fig. 6.4.1.b) and that at 450 C (Fig. 6.4.1.c) reveals this fact.

Fig. 6.4.2 shows the photomicrographs at the magnification of 100X of films annealed at 400, 425 and 450 C temperatures for 15 minutes and then cooled inside the furnace. The micrographs were taken at the middle of the films. Although these all exhibited dendritic growth, the film annealed at 450 C shows larger grain growth (Fig. 6.4.2c). This may be explained from the simple effect of temperature. Higher temperature provides higher energy and hence promotes large crystal growths. Besides finer grain size means greater extent of impurities^{40,85}. So, it may be assumed that presence of impurities coming from the organics present in the ZnO thin film rendered the structural features to be finer at lower temperatures like 400 C or 425 C. Higher temperatures like 450 C achieves better decomposition of the metalorganic complexes and leads to better and larger size structures.

Fig. 6.4.3.(1-9) show the photomicrographs taken at different locations on the ZnO thin film deposited at RH 40% and annealed at 450 C. These locations are shown in Fig. 6.4.4. The wide variation in the microstructure, particularly the variations in grain size, reveals that although we have assumed that the film achieves the set temperature uniformly during the annealing this is not the case in actual. Irrespective of the method of loading the film (horizontal or vertical) similar trends in the variation of microstructure in other films were found. It seems that there are variations in temperatures on different locations in the film which resulted in different extent of decomposition of the metalorganic complexes and ultimately affected the purity and hence the size of the crystallites.



(a)



(b)



Fig. 6.4.2 Microphotographs of thin films of ZnO deposited by solgel dip coating method and furnace-cooled after annealing for 15 minutes at :

- (a) 400 C,
- (b) 425 C and
- (c) 450 C

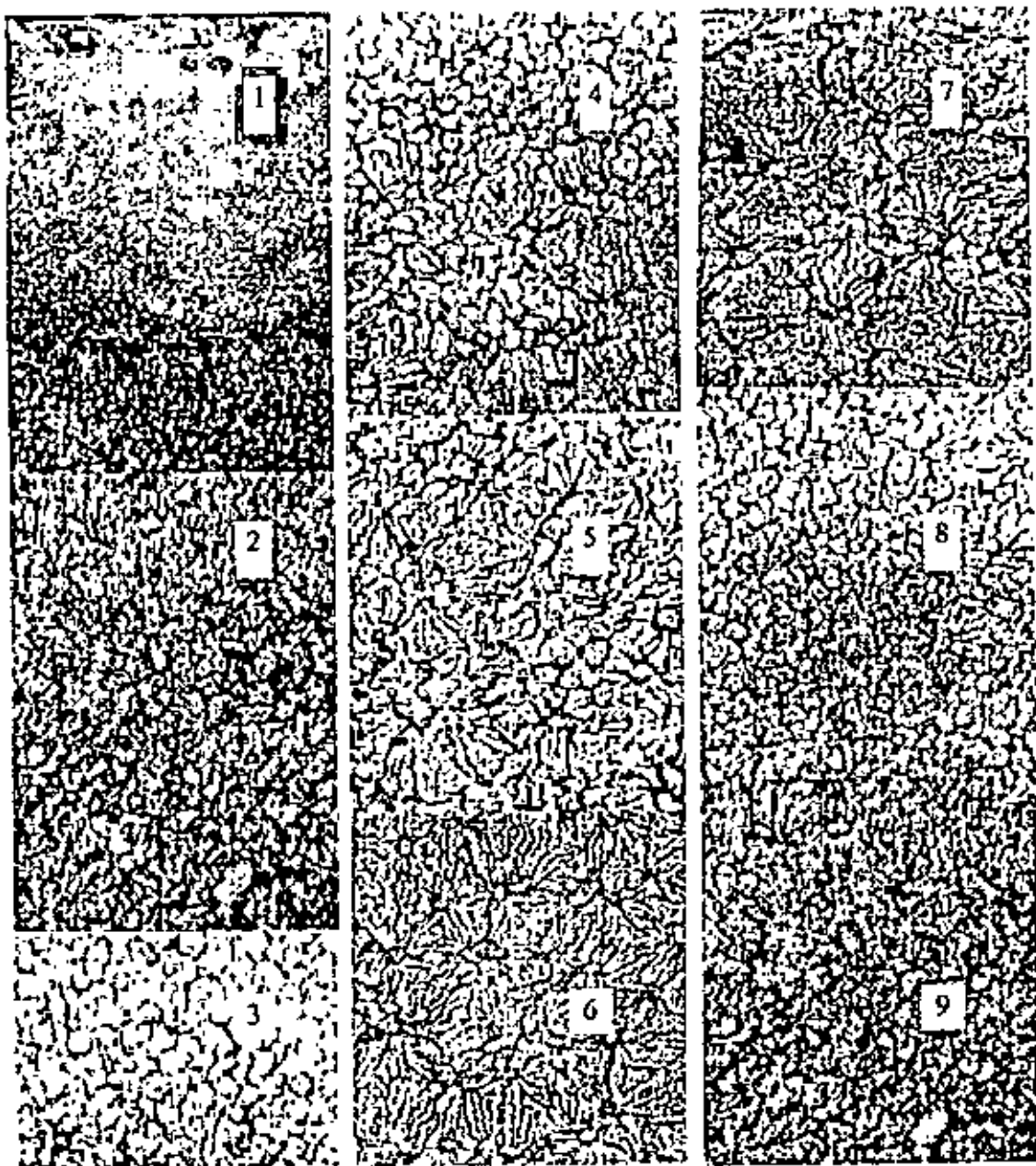
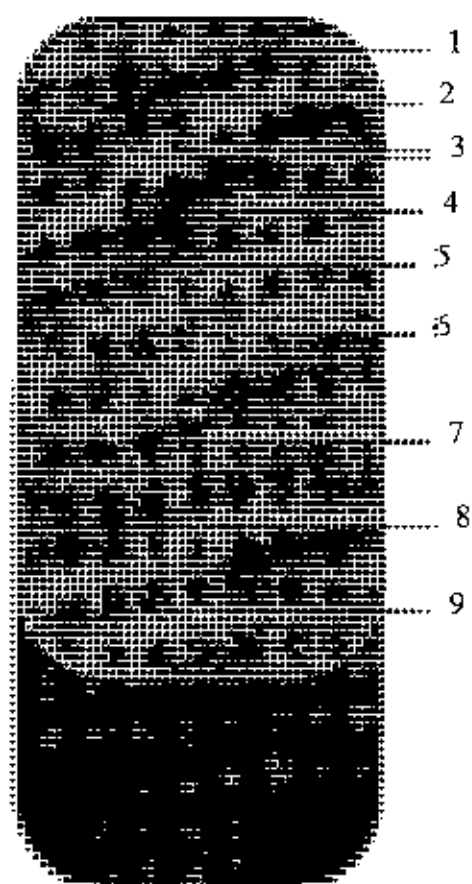


Fig. 6.4.3 (a) Photomicrographs of the various positions on the thin film of ZnO deposited by sol gel dip coating method at RH 40% and Annealed at 450 C for 15 minutes and then furnace cooled (100X).



Plan View

Fig. 6.4.4 Various positions on the film at which photomicrographs in Fig. 6.4.3 were taken

The evidence of 'mud cracking' can easily be observed from Fig. 6.4.5. This is one of the films used for thermogravimetric analysis. The film was annealed by following the annealing cycle given in Fig. 5.5.1. After measuring the weight at the end of each annealing cycle the same sample was again loaded into the furnace and heated to a still higher temperature. The above mentioned cycle was repeated until the final annealing at 450 C. Such a sort of heating and cooling cycle developed high residual stress⁸⁵ and thermal expansion mismatch between the film and the substrate with the result mud cracking occurred. The samples which followed the annealing cycle mentioned in Fig. 5.3.1, however, did not show any evidence of mud cracking. Observations made by Srikant⁵⁶ *et. al.* on ZnO thin film grown by laser ablation method revealed that 'mud cracking' of the film was a manifestation of the residual biaxial tension in the film. According to them, the mud cracking was due to the tension in the film arising from the 'thermal expansion mismatch' between the film and substrate. The 'growth stresses' in these films lead to compressive strains in the plane of the substrate⁵⁶. Since cooling in the furnace eliminates the effects of thermal shock and helps relieving the residual stress after annealing at higher temperature for longer period the samples which were furnace cooled could avoid mud cracking.

Fig. 6.4.6 and Fig. 6.4.7 show the x-ray diffraction (XRD) patterns obtained from sol gel deposited ZnO thin film annealed for 15 minutes at 400 C and 450 C respectively for single coating. The patterns were indexed by the analytical method described by Cullity⁷² in order to identify the various reflecting planes (Appendix B). The various d-values obtained from the observed 2 θ -values matches closely with the ZnO powder patterns as in JCPDS – International Centre for Diffraction Data⁷³. The patterns indicate that the ZnO thin films so obtained have a hexagonal wurtzite structure.



Cracks

Fig. 6.4.5 Evidence of mud- cracking in sol gel deposited ZnO thin film which has undergone under severe thermal shock.(100X)

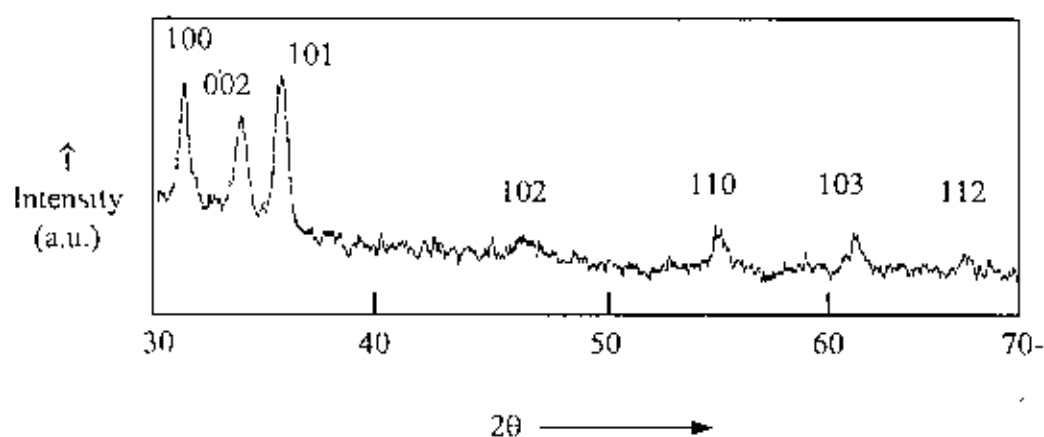


Fig.6.4.6 XRD spectra of single coated sol gel deposited ZnO film which was annealed at 400 C for 15 minutes and then cooled in the furnace.

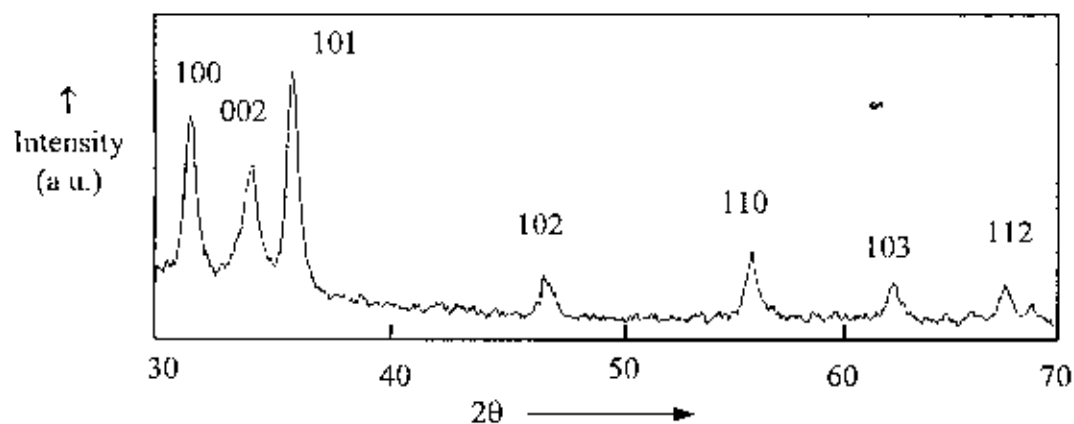


Fig.6.4.7 XRD spectra of single coated sol gel deposited ZnO film annealed at 450 C for 15 minutes and then cooled in the furnace. Mark the sharpening and strengthening of the peaks particularly of those at higher angles.

Fig. 6.4.8-10 show the effect of annealing on the height of the four major peaks for single, double and triple coatings. Appendix C shows the value of these peaks obtained from the XRD scan of different films deposited by sol-gel deposition method and annealed at different temperatures mentioned. For all the three cases XRD peaks were obtained at around 275 C and below 275 C no appreciable peaks were identified for any of the samples. This means that the films are amorphous below 275 C and polycrystallinity develops as a result of thermal treatment. This fact can also be evidenced from the XRD patterns of as-grown films and those of the films annealed at different temperature (Fig.6.4.11).

It is therefore derived from Fig. 6.4.8-10 that the polycrystallinity in ZnO thin films deposited by sol gel method developed during the annealing around 275 C and the polycrystallinity persisted and gained strength with increasing temperature because of the increased purity of the ZnO crystallites⁶⁹ and the gradual elimination of internal stresses as a consequence of annealing⁸⁰. Initially the intensity of the XRD peaks was low because of heavy contamination from the organics. As the temperature increased, organics were decomposed in increasing extent and were gradually expelled out. There is a characteristic drop in the peak height at around 375 C for all the films annealed at that temperature. This is an anomalous behavior the reason behind which is yet to be explained. However, annealing at higher temperatures than 400 C leads to better ordering of the structure of the ZnO film and the crystallites gain strength again⁶⁹. Since higher temperature also reduce the effect of residual strains in the film⁸⁵ the line broadening in the XRD peaks due to residual strain decreases and the peaks appear sharper and more intense(Fig. 6,4.11). This tendency also indicates better crystallinity and increased grain size^{69,83} in the annealed film and is continued even at 450 C.

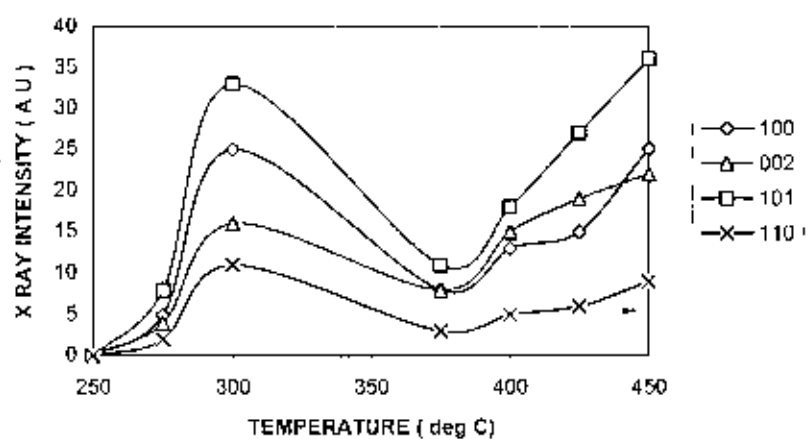


Fig. 6.4.8 Effect of annealing on the four major peaks obtained for single coated ZnO thin film deposited by sol gel method.

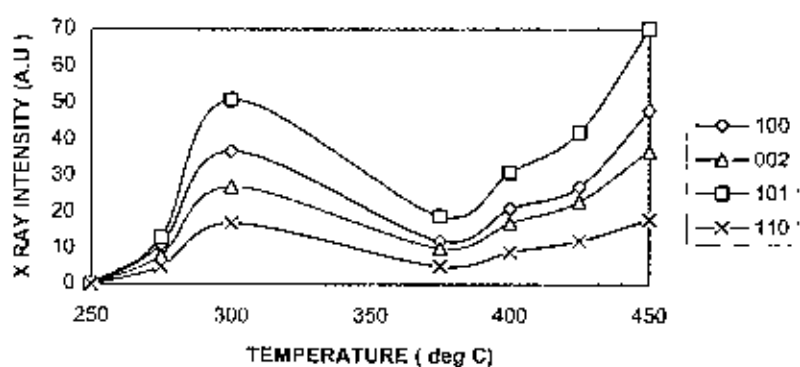


Fig. 6.4.9 Effect of annealing on the four major peaks obtained for double coated ZnO thin film deposited by sol gel method.

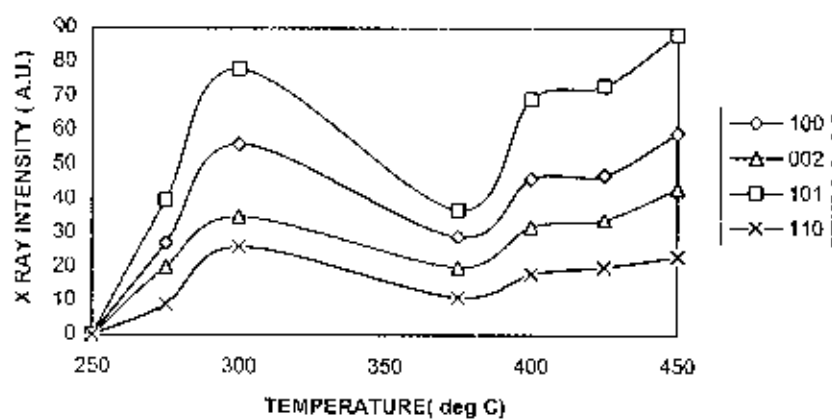


Fig. 6.4.10 Effect of annealing on the four major peaks obtained for triple coated ZnO thin film deposited by sol gel method.

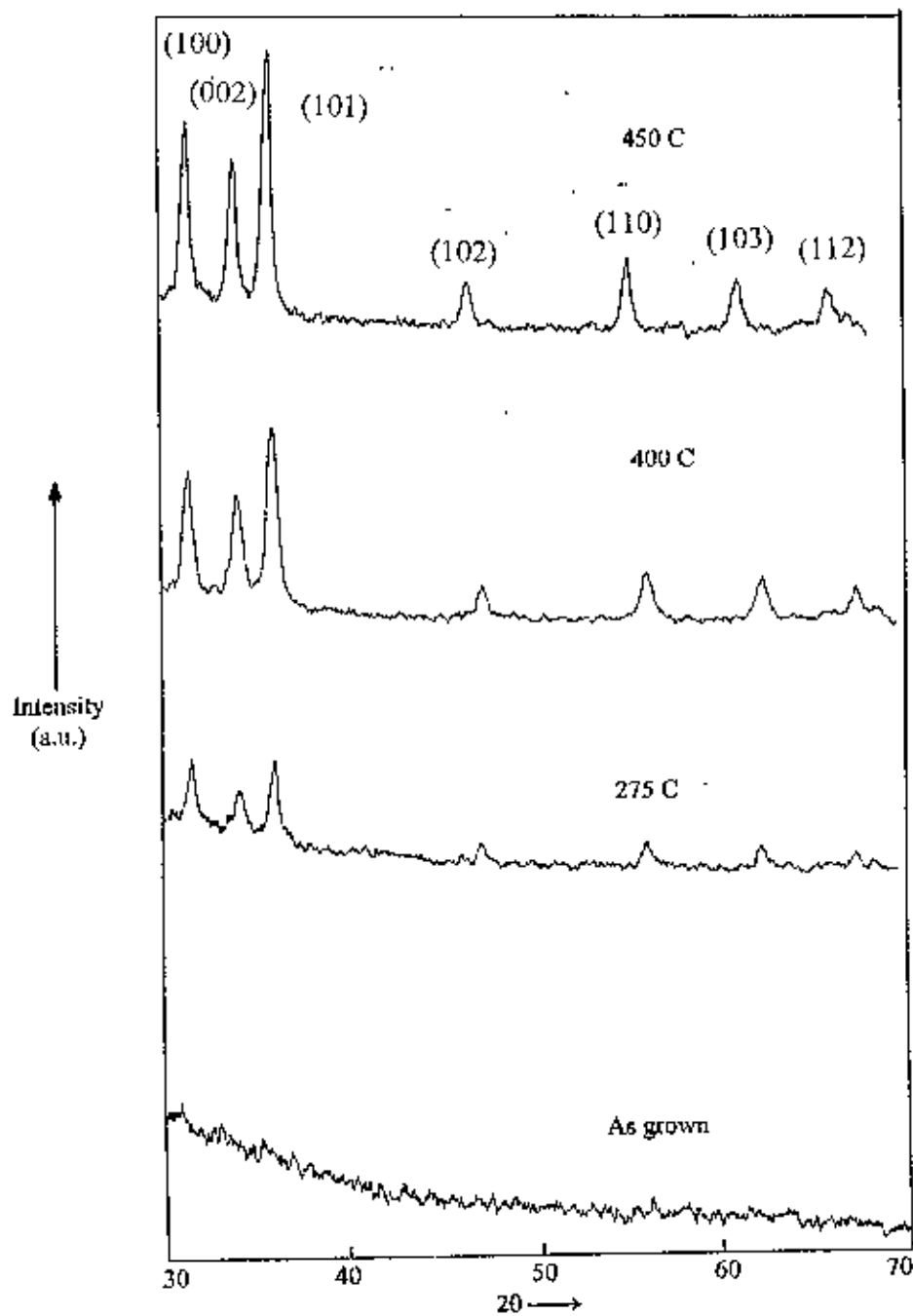


Fig.6.4.11 Comparison of xrd patterns of thin films of ZnO deposited by sol gel dip coating method and annealed at different temperature.

6.5 EVOLUATION OF CRYSTALLINITY

Comparison of the relative intensities of the reflections from various reflecting planes in Fig 6.4.6, 7 and 11 with the relative intensities for ZnO powder as mentioned in JCPDS–International Centre for Diffraction Data⁷³ cards reveals that the crystallographic orientation in the ZnO thin films is random. Neither of the XRD scan exhibited any preferred orientation. In fact, throughout the study, we have found no film with any preferred orientation. It may be mentioned that preferred orientation is very likely in ZnO thin films deposited by other similar methods^{15,21,22,58}. However, Tang¹² *et. al* and Kamalasanan¹³ *et. al* also found random orientation in the thin films of ZnO deposited by them in sol gel method.

Randomly oriented polycrystalline film with weak (101) orientation was found by Lee²² *et. al* in pyrosol deposited zinc oxide thin films, when undoped. On the other hand In-doped ZnO films exhibited a strong c-axis (002) orientation, perpendicular to the substrate. Krunk *et. al.*¹⁵ had also found for ZnO films deposited by spray pyrolysis process from zinc acetate precursor that the films produced at temperatures lower than 180 C had a random orientation while those with higher growth temperature had a progressively dominant preference towards (002) orientation. The preferred orientation was explained by them to be related with the higher chemical purity of higher temperature films. It was also shown by them that the chemical purity of the film was controlled by the level of thermal decomposition of metalorganic complex compounds formed in the starting solution.

The above explanation is also convincing in searching any preferred orientation in sol-gel deposited ZnO thin films since Ohyama *et. al.*²³ produced ZnO films with strong preferential orientation along the (002) plane by heating the films initially at the set temperature for 10 minutes after each coating and then annealing at the same set temperature for 1 hour. Earlier workers like Tang¹² *et al.*, starting with a (100)

Si-substrate, could not achieve any but weak (002) preferred orientation in the ZnO film with or without Al-doping, and also with or without any vacuum annealing. In contrast, Kamalasanan¹³ *et. al.*, found randomly oriented crystallites with undoped films. Noteworthy to mention that the orientation of the ZnO thin film in our case is also random. Achievement of the preferred orientation in the ZnO film prepared by Ohyama²³ *et. al.* may be attributed to the longer annealing time (10 minutes at first and then 1 hour) at higher temperatures which permitted better decomposition and hence better purity in the film. Absence of such a longer time and temperature may have led to the failure in achieving the preferred orientation in the ZnO thin films deposited by sol gel dip coating method in the present study (Fig. 6.4.6-7 and Fig. 6.4.11).

Such a randomly oriented structure with disordered surface and gaps between grains can also be attributed to sensitive oxygen chemisorption in undoped ZnO films²⁴. It can be inferred that oxygen can diffuse into grain boundaries easily through the gap between the grains. Lee²² *et. al.* provided the evidence of oxygen chemisorption by undoped ZnO thin film under air annealing. The chance of chemisorption can not be ignored since annealing was not performed in vacuum in the present study.

So, undoped ZnO thin film deposited by sol-gel method in the present study showed no preferred orientation due to the combined effect of incomplete decomposition and chemisorption of oxygen simultaneously. This is also depicted in Fig. 6.4.8-10 where no film showed any tendency to reach the saturation in XRD intensity rather the trends were still increasing even at 450 °C indicating the incompleteness of the decomposition. The chemisorption of oxygen is also very likely for the films since, although the annealing operation was performed in a closed muffle furnace, the sealing could not guarantee a 100% airtight furnace.

6.6 LATTICE STRUCTURE AND LATTICE CONSTANTS

The XRD patterns of the ZnO thin films annealed at various temperature confirm that the ZnO thin films deposited in the present study had a hexagonal wurtzite structure (theoretically $a = 3.243 \text{ \AA}$, $c = 5.207 \text{ \AA}$)⁷³. Appendix D shows the data used in calculation of the c- and a- axes values for the films whose XRD peak values were given in Appendix C. The lattice constants calculated from these data are $a = 3.285 \text{ \AA}$, and $c = 5.271 \text{ \AA}$. Although the c/a ratio (1.601) complies with the theoretical c/a ratio(1.604), the calculated c or a values showed some distortion in the lattice which was caused due to the residual stress and impurities. Fig. 6.6.1 shows the plot of c, and a, against the temperature. It exhibits almost constant values of the lattice parameters over the temperature range mentioned.

6.7 WEIGHT LOSS AND THICKNESS MEASUREMENTS

Fig. 6.7.1 shows the result of thermogravimetric analyses of the ZnO films and Appendix E gives the corresponding data. All the samples, after gelation at around 25 C, lost weight in a similar manner on drying at 150 C and then maintained a more or less steady rate of weight loss. Theoretical data for Zn(OH)_2 and Zn - acetate (Appendix A) show that water of hydration should be removed around this temperature. Around 275- 280 C, there was a rise in the weight loss in Fig. 6.7.1. Analyses of XRD data and microphotographs suggest that polycrystallinity in the amorphous ZnO films starts to develop from this temperature. Around 275 C the film turns brown or blackish which can be turned to transparent again only by heating at higher temperature. On heating to still higher temperatures the rate of weight loss became more gradual and the tendency to lose weight does not reach any saturation even at 450 C. This indicates incomplete decomposition of metalorganic complexes even at such temperatures.

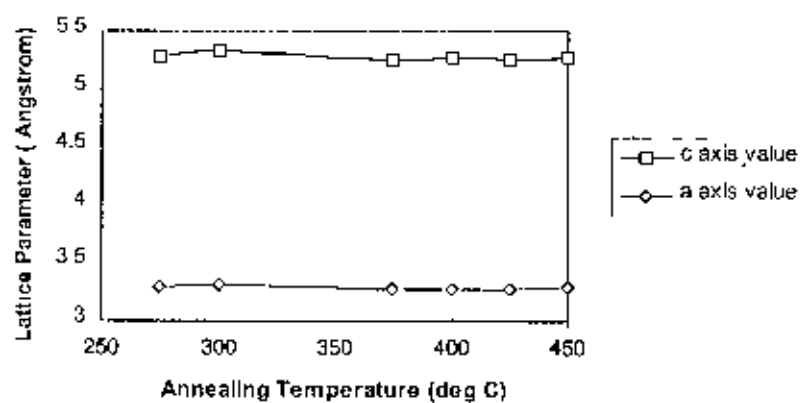


Fig 6.6.1 Variation of the lattice parameters of ZnO crystals with temperature in single coated thin film of ZnO deposited by sol gel method at RH 50%.

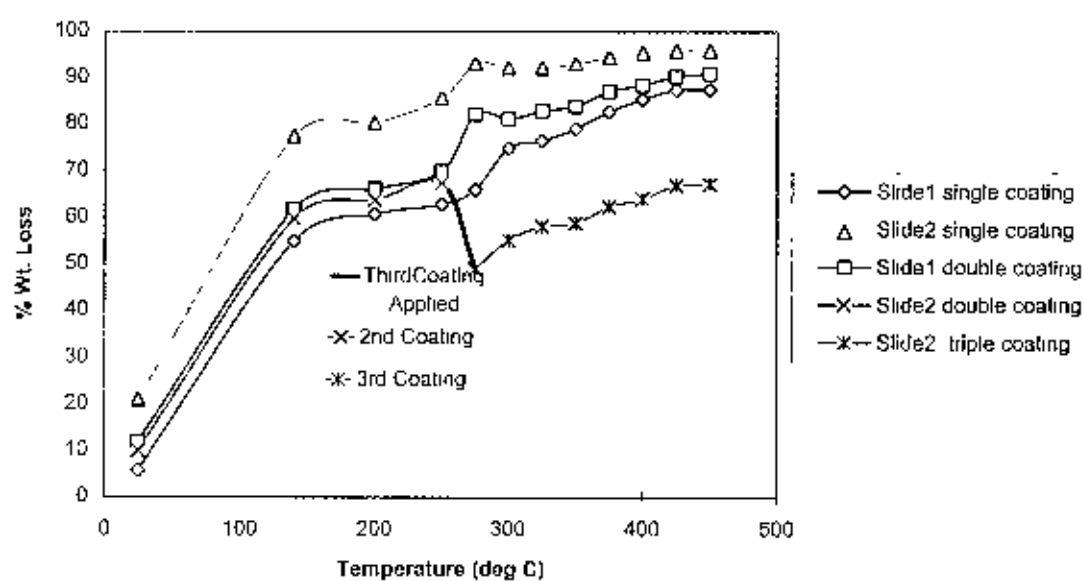


Fig 6.7.1 Effect of temperature on the percentage weight loss of thin film of ZnO deposited by sol gel dip coating method at relative humidity 50% (slide 1) and, 60% (slide 2)

Fig. 6.7.1 actually presents the weight loss analysis for two samples prepared from the same sol but at different humidity. While film coating was deposited on slide 1 at RH 50%, that was deposited on slide 2 at RH 60%. The higher extent of weight loss by the film deposited on slide 2 is due to its higher moisture content derived from its higher humidity. From the final weight of the film after each annealing cycle at 450 C, assuming all the moistures and organic volatiles have been expelled at this temperature, the thickness of the film has been roughly calculated. Appendix F gives the result of such calculations to be about 1 μm on an average. The standard deviation of such data indicates that the variation in thickness is quite high (S.D. = 0.2 μm). The variation in thickness occurred because we did not control the fluid mechanics - variables like the sol temperature, viscosity of the sol etc.

6.8 OPTICAL PROPERTIES

Fig. 6.8.1 gives the result of the spectrophotometric measurement of the transmission in the near UV -VIS region of the ZnO films which was deposited at RH 50%, annealed for 15 minutes at 450 C and then furnace cooled . The transmission at the band edge was found to be about 80% which is fairly comparable to the transmission of the ZnO film deposited by similar or different methods^{12-13,15,22}. The transmission spectra for the film annealed at 400 C (Fig. 6.8.2) and at 375 C (Fig. 6.8.3) shows that transmittance of the films annealed at lower temperatures are of lower values and transmittance increases with increasing temperature. The transmittance of the film annealed at 375 C is quite low. This is expected since the macrophotograph of the film (Fig.6.4.1) annealed at this temperature has already showed presence of black areas in the film.

One of the curious features of the literature on ZnO is that there remains substantial disagreement as to the value of its optical band gap ranging from 3.1 to 3.3 eV ⁸⁶. The wavelength of the optical band edge from such figures was roughly calculated

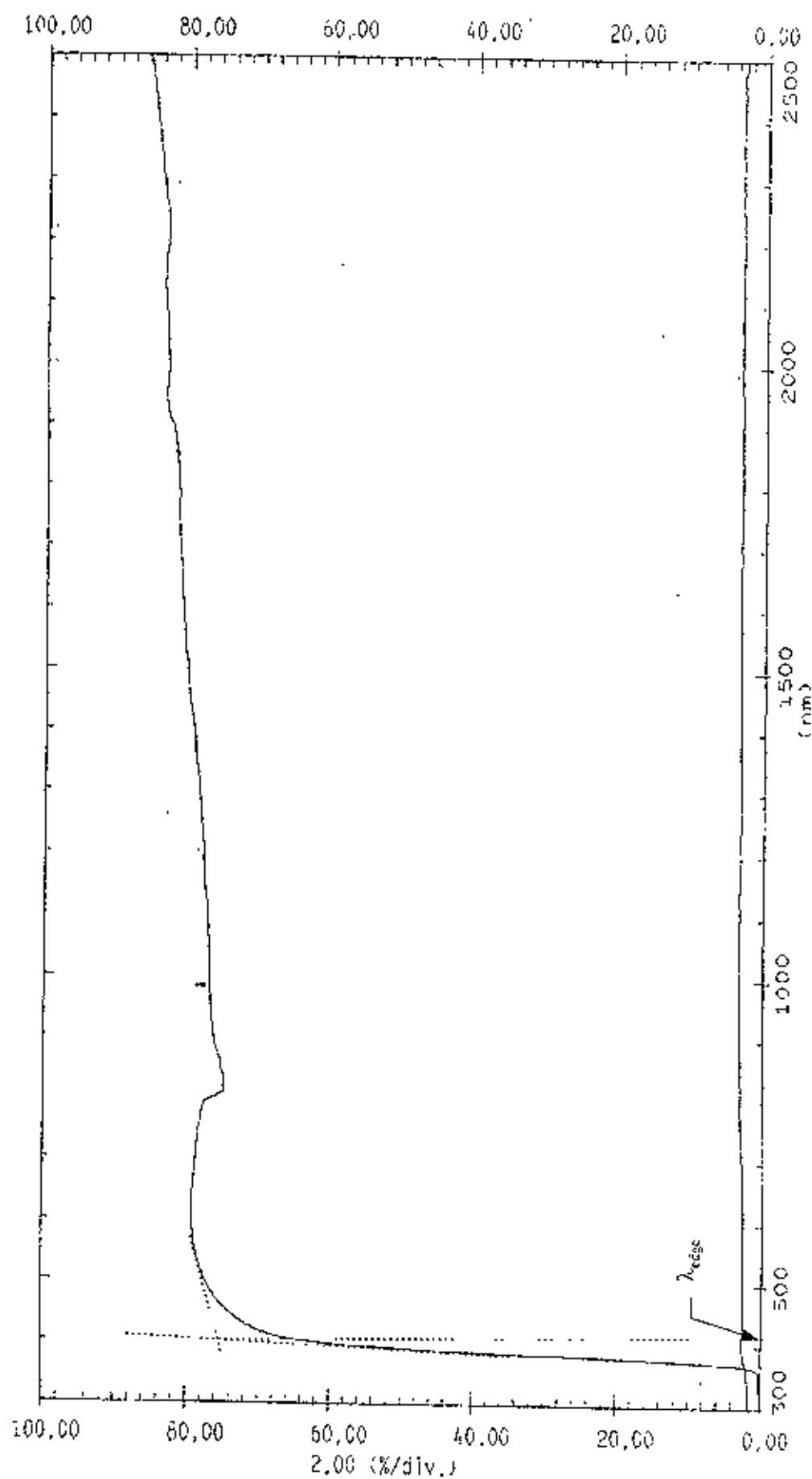


Fig.6.8.1 The optical transmission spectra of sol gel deposited ZnO thin film on glass substrate. The film was deposited at 50 % relative humidity , annealed for 15 minutes at 450 C and then cooled in a furnace.

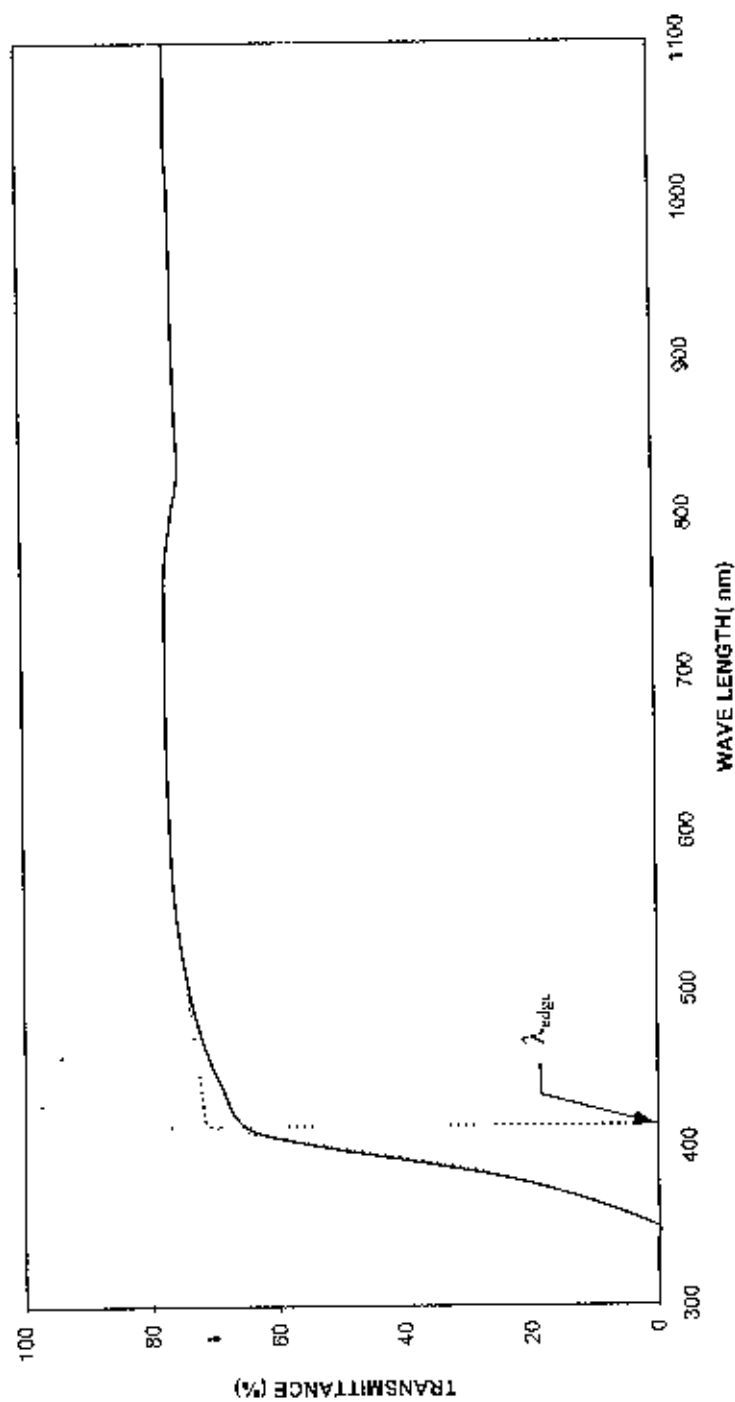


Fig. 6.8.2 The optical transmission spectra of sol gel deposited ZnO thin film on glass substrate. The film was deposited at 50% relative humidity, annealed for 15 minutes at 400 C and then furnace-cooled.

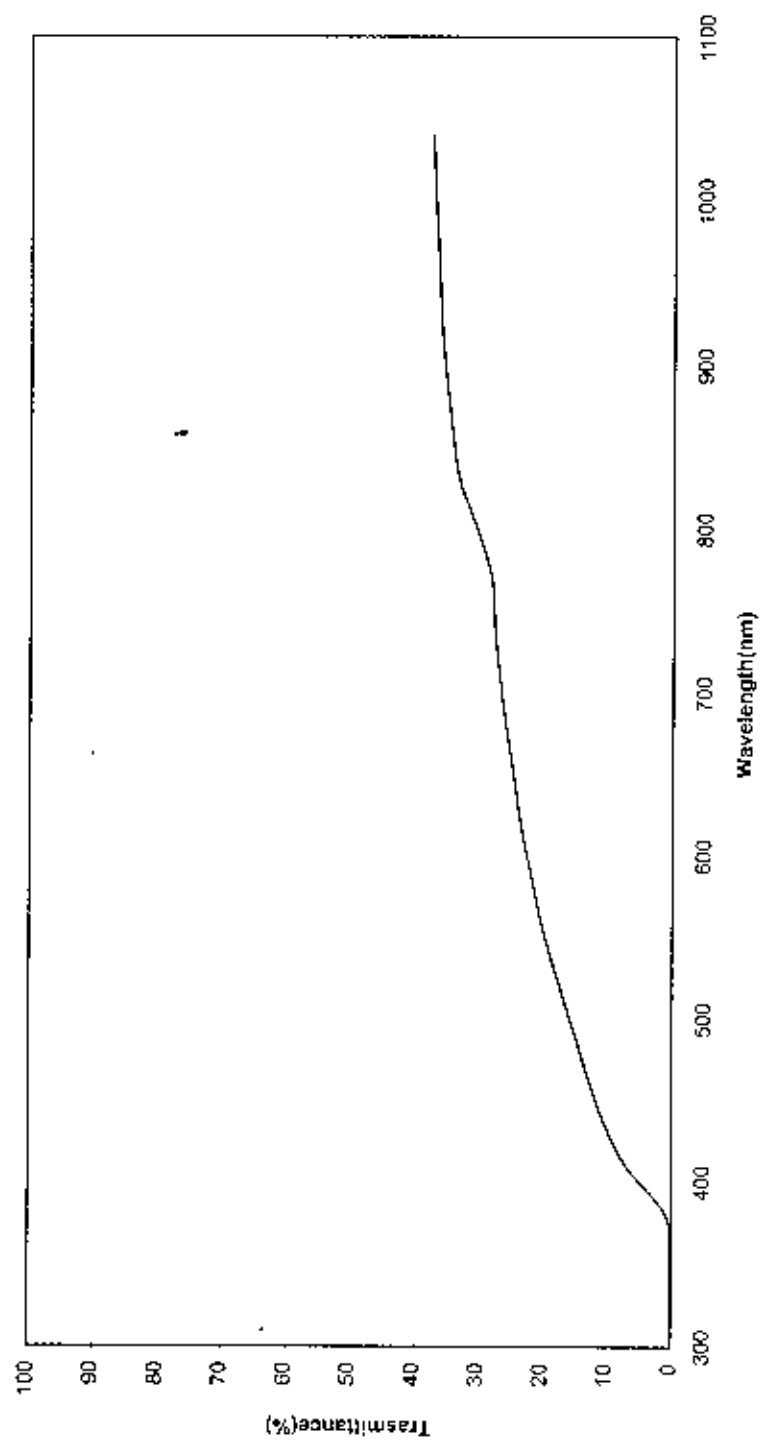


Fig. 6.8.3 The optical transmission spectra of sol gel deposited ZnO thin film on glass substrate. The film was deposited at 50% relative humidity, annealed for 15 minutes at 375 C and then furnace-cooled.

to be 410 nm. This value gives the value of band gap energy to be about 3 eV from equation (4-1) which is fairly low. Since the band gap has been roughly calculated from the transmission scan which is not the usual or standard practice, any conclusion on the part of optical band gap from such calculations may be misleading.

CHAPTER SEVEN

CONCLUSIONS

7.1 CONCLUSION

The main aim of this study was to deposit thin films of zinc oxide by sol gel method and its characterization by using optical microscopy, x-ray diffraction, optical spectrophotometry, etc. Although thin films of ZnO deposited by other processes received intense attention in terms of characterization, sol gel -deposited ZnO films did not get much. So the study and the conclusions made from this study will definitely help to clear the turbidity in this particular field of knowledge.

The important conclusions derived from this study are given below:

1. Successful preparation of the thin films of ZnO has been achieved by sol gel dip coating method on glass substrates. The sol has been made from zinc acetate dihydrate by dissolving it into n-propanol with the help of ethylene glycol. Such a sol was made stable and water sensitive with the addition of glycerol and diethyl amine respectively.
2. During the preparation of the ZnO sol zinc acetate dihydrate gives out acetic acid and water of hydration and forms zinc alkoxide by reacting with n-propanol. This alkoxide dissolves into the propanol. On gelation the ZnO in the coating forms zinc hydroxide which undergo condensation reaction on heat treatment and yields thin films of ZnO.
3. Cleaning of the glass substrate with deionized water, acetic acid and absolute ethanol is capable of producing smooth and uniform film.

Higher humidity surrounding the film during the withdrawal of the substrate from the sol increases the moisture content in the as-deposited film. High moisture results in a less uniform, porous, or even cracked films. The relative humidity at the meniscus of the sol to the substrate should therefore be less than 50 % for the achievement of film which will not be destroyed during the heat treatment.

4. Annealing of the ZnO thin film decomposes zinc hydroxide to zinc oxide. At the same time annealing at high temperature decomposes the metalorganic complexes and drives out moistures and other volatiles.

Annealing above 275 °C transforms the amorphous as-deposited film to polycrystalline. This polycrystallinity gains strength with the increase in annealing temperature and the residual stress inside the film reduces as a result of annealing.

Annealing at higher temperature (especially above 400 °C) leads to the increase in the size of the ZnO crystallites and the films are denser and less porous.

5. The films formed are randomly oriented and no preferred orientation is found. This is attributed to the incomplete decomposition of the metalorganic complexes as well as to the chemisorption of oxygen by the film.
6. The sol gel deposited ZnO crystallites have the hexagonal wurtzite structure, the values for c- and a-axes being 5.271 Å and 3.285 Å respectively. The discrepancy with the theoretical value could be due to the presence of contamination from the part of metalorganic complexes.
7. The average thickness of the films after annealing at 450 °C for 15 minutes has been found to be about 1 µm and the films have good transparency.

7.2 Suggestions for Future Works:

The future research in this particular field may follow the guidelines given below:

- Improvement of the 'Dipping apparatus' so as to achieve a slower withdrawal rate.
- Designing of a chamber in order to allow humidity control.
- Vacuum annealing of the deposited film
- Setting the correlation between the annealing temperature and electrical as well as optical properties of the ZnO thin film.
- Setting the structure- property relationship for the ZnO film.

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APPENDICES

APPENDIX A

Material	Properties
ZnO	Mol. wt. 81.38 whitish/yellowish amorphous, polycrystalline when annealed Sp. gr. 5.47-5.61 Refractive index 2, Energy gap = 3.4 eV m.p. 1975 C Hexagonal
Zinc Hydroxide($\text{Zn}(\text{OH})_2$)	Mol. wt. 99.40 Sp. gr. 3.053 Decomposes at 125 C
Zincite (ZnO)	Red Ore of Zinc Sp-gr. 5.43-5.70 hcp. structure.
Zn-acetate	m.w. 219.46 Sp. - gr. 1.735 m.p. 237 Loss of water of hydration 100°C
Acetic acid	Sp.- gr. 1.047 m.p. 16.6°C b.p. 118.1°C
Ethylene Glycol $\text{CH}_2\text{OH CH}_2\text{OH}$	mol. wt. 62.05 Sp. gr. 1.1176 m.p. - 17.4°C b.p. 197.2°C
Glycerol $\text{CH}_2\text{OH CHOH CH}_2\text{OH}$	mol. wt. 92.06 m.p. - 17.9°C b.p. 220°C
n- Propanol (1 propanol) $\text{CH}_3 \text{CH}_2\text{CH}_2\text{OH}$	mol. wt. 60.06 Sp. gr. 0.804 m.p. = - 127°C b.p = 97.19°C

Rf. H. Bennett, *Concise Chemical and Technical Dictionary*, Chemical Publishing Co. Inc., New York, 1974

APPENDIX B

INDEXING OF THE REFLECTING PLANES OBTAINED FOR ZnO THIN FILM DEPOSITED BY SOL GEL METHOD

Sample	2X	X	Xrad	SinXSq	SinXSq/3	SinXSq/4	SinXSq/7	SinXSq - A	Sin2XSq- 3A	hkl
	31.6	15.8	0.2758	0.0741	0.02471	0.0185	0.01059	0		100
	34.2	17.1	0.2985	0.0865	0.02882	0.0216	0.01235	0.0123597		002
	36	18	0.3142	0.0955	0.03183	0.0239	0.01364	0.0213915		101
ZnO film	47	23.5	0.4102	0.159	0.053	0.0398	0.02271	0.0849008		102
anneal 450 C	56.3	28.15	0.4913	0.2226	0.07419	0.0556	0.0318	0.1484778		110
	62.4	31.2	0.5445	0.2684	0.08945	0.0671	0.03834	0.194252	0.044222	103
	67.2	33.6	0.5864	0.3062	0.10208	0.0766	0.04375	0.2321422	0.0821122	113
	31.4	15.7	0.274	0.0732	0.02441	0.0183	0.01046	0		100
	34	17	0.2967	0.0855	0.02849	0.0214	0.01221	0.0122812		002
ZnO film	35.9	17.95	0.3133	0.095	0.03166	0.0237	0.01357	0.0217792		101
anneal 400 C	47	23.5	0.4102	0.159	0.053	0.0398	0.02271	0.0858008		102
	56.1	28.05	0.4896	0.2211	0.07371	0.0553	0.03159	0.1479274		110
	62.4	31.2	0.5445	0.2684	0.08945	0.0671	0.03834	0.195152	0.048752	103
	66.6	33.3	0.5812	0.3014	0.10048	0.0754	0.04306	0.2282261	0.0818261	113

APPENDIX C •

INTENSITIES OF FOUR MAJOR PEAKS

Annealing Temp. (deg C)	No. of Coating	100	002	101	110
	1	0	0	0	0
250	2	0	0	0	0
	3	0	0	0	0
	1	5	4	8	2
275	2	11	8	13	5
	3	27	20	40	9
	1	25	16	33	11
300	2	37	27	51	17
	3	56	35	78	26
	1	8	8	11	3
375	2	12	10	19	5
	3	29	20	37	11
	1	13	15	18	5
400	2	21	17	31	9
	3	46	32	69	18
	1	15	19	27	6
425	2	27	23	42	12
	3	47	34	73	20
	1	25	22	36	9
450	2	48	37	70	18
	3	59	43	88	23

APPEND D

Anneal Temp -No. of coating	Peak	2X	X	Xrad	SinXsq	c	Avg c	a	Avg. a	c/a	Avgc/a
	100	31.3	15.65	0.27314	0.0728						
275-1	002	34	17	0.29671	0.0855	5.2741	5.2708				
	101	35.8	17.9	0.31241	0.0945			3.293	3.285	1.602	1.604
	100	31	15.5	0.27053	0.0714						
275-2	002	34	17	0.29671	0.0855	5.2741					
	101	35.8	17.9	0.31241	0.0945			3.293		1.602	
	100	31.4	15.7	0.27402	0.0732						
275-3	002	34	17	0.29671	0.0855	5.2741					
	101	35.8	17.9	0.31241	0.0945			3.293		1.602	
	100	31.4	15.7	0.27402	0.0732						
300-1	002	34	17	0.29671	0.0855	5.2741					
	101	35.9	17.95	0.31329	0.095			3.282		1.607	
	100	31	15.5	0.27053	0.0714						
300-2	002	33.7	16.85	0.29409	0.084	5.3197					
	101	35.6	17.8	0.31067	0.0934			3.308		1.608	
	100	31.4	15.7	0.27402	0.0732						
300-3	002	34	17	0.29671	0.0855	5.2741					
	101	35.8	17.9	0.31241	0.0945			3.293		1.602	
	100	31.6	15.8	0.27576	0.0741						
375-1	002	34.2	17.1	0.29845	0.0866	5.2442					
	101	36	18	0.31416	0.0955			3.276		1.601	
	100	31.6	15.8	0.27576	0.0741						
375-2	002	34.1	17.05	0.29758	0.086	5.2591					
	101	35.9	17.95	0.31329	0.095			3.284		1.601	
	100	31.4	15.7	0.27402	0.0732						
375-3	002	34	17	0.29671	0.0855	5.2741					
	101	35.8	17.9	0.31241	0.0955			3.27		1.613	
	100	31.5	15.75	0.27489	0.0737						
400-1	002	34.1	17.05	0.29758	0.086	5.2591					
	101	36	18	0.31416	0.0955			3.273		1.607	
	100	31.4	15.7	0.27402	0.0732						
400-2	002	34	17	0.29671	0.0855	5.2741					
	101	35.9	17.95	0.31329	0.095			3.282		1.607	
	100	31.6	15.8	0.27576	0.0741						
400-3	002	34.1	17.05	0.29758	0.086	5.2591					
	101	36	18	0.31416	0.0955			3.273		1.607	
	100	31.4	15.7	0.27402	0.0732						
425-1	002	34.1	17.05	0.29758	0.086	5.2591					
	101	35.9	17.95	0.31329	0.095			3.284		1.601	
	100	31.4	15.7	0.27402	0.0732						
425-2	002	34.1	17.05	0.29758	0.086	5.2591					
	101	36	18	0.31416	0.0955			3.273		1.607	
	100	31.4	15.7	0.27402	0.0732						
425-3	002	34	17	0.29671	0.0855	5.2741					
	101	35.9	17.95	0.31329	0.095			3.282		1.607	
	100	31.2	15.6	0.27227	0.0723						
450-1	002	33.9	16.95	0.29583	0.085	5.2892					
	101	35.8	17.8	0.31067	0.0934			3.313		1.598	
	100	31.3	15.65	0.27314	0.0728						
450-2	002	34	17	0.29671	0.0855	5.2741					
	101	35.8	17.9	0.31241	0.0945			3.293		1.602	
	100	31.4	15.7	0.27402	0.0732						
450-3	002	34.1	17.05	0.29758	0.086	5.2591					
	101	36	18	0.31416	0.0955			3.273		1.607	

APPENDIX E

DATA OF WEIGHT LOSS MEASUREMENTS ON THIN FILMS OF ZnO BY SOL GEL METHOD

	Slide 1 Single coating	Slide 2 single coating	Slide 1 Double coating	Slide 2 Double coating	Slide 2 Triple coating	
Slide wt	2.4482	2.5847	2.4482	2.5847	2.5847	
Deposition	2.4673	2.6065	2.4768	2.6098	2.6155	
Area(Sq.cm)	6.578	6.674	6.578	6.674	6.674	
Final Film Wt	0.0024	0.0033	0.0028	0.0082	0.0102	
Thickness(mm)	0.000667006	0.000903942	0.000778174	0.00224616	0.002794002	
Film Wt	0.0191	0.0218	0.0286	0.0251	0.0308	
Temp.	Slide 1 Single Coat %Wt. loss	Slide 2 Single Coat %Wt. loss	Slide 1 Double Coat %Wt. loss	Slide 2 Double Coat %Wt. loss	Slide 2 Triple Coat %Wt. loss	
25	0.0011	0.0046	2.4734	2.6073	2.6137	5.8441
140	0.0105	0.0169	2.4591	2.5948		
200	0.0116	0.0175	2.4579	2.5938		
250	0.012	0.0187	2.4568	2.5929		
275	0.0126	0.0203	2.4533			
300	0.0143	0.0201	2.4536			
325	0.0146	0.0201	2.4531			
350	0.0151	0.0203	2.4528			
375	0.0158	0.0206	2.4519			
400	0.0163	0.0208	2.4515			
425	0.0167	0.0209	2.451			
450	0.0167	0.0209	2.4508			

APPENDIX F

THICKNESS MEASUREMENT FROM WEIGHT LOSS DATA

Number of coating in the film	Thickness (mm)					Standard Deviation
	Slide 1	Slide 2	Avg. For Slide 1	Avg. For Slide 2	Avg. thickness	
1	0.000667	0.000904	0.00066701	0.000903942		0.000282
2	0.000778	0.002246	0.00038909	0.001123079	0.000986118	
3		0.002794		0.000931334		

