

A STUDY OF
ELECTRICAL AND OPTICAL PROPERTIES
OF TRANSPARENT CONDUCTING SnO_2 AND
 In_2O_3 THIN FILMS PREPARED BY
PYROSOL PROCESS



by

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Dedicated to

my

Parents

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A B S T R A C T

The design and construction of a simple and low-cost device for the deposition of thin films by the pyrosol process has been described. Doped and undoped films of SnO_2 and In_2O_3 have been prepared on glass substrates. These films were highly conducting and at the same time highly transparent. They were non-stoichiometric but homogeneous and polycrystalline in structure. It is found that an activation energy of about 0.2 eV is associated with the growth process of these films. The sheet resistance of these films shows a size effect below a thickness of about $0.3\text{ }\mu\text{m}$. Doping has been performed by adding antimony(Sb) and fluorine(F) in SnO_2 film and higher figure of merit in comparison to other earlier reports has been obtained. In In_2O_3 film Sn has been used as doping element to obtain films of higher conductivity and Hall mobility.

The electrical transport properties and the optical transmission coefficients in the UV-VIS range of these films in the carrier concentration range $\sim 6 \times 10^{18}$ to $\sim 1.3 \times 10^{21} \text{ cm}^{-3}$ for SnO_2 and from $\sim 3 \times 10^{18}$ to $\sim 7 \times 10^{20} \text{ cm}^{-3}$ for In_2O_3 films with thickness about $0.2\text{ }\mu\text{m}$ have been studied in detail to establish a tentative energy band picture of these degenerate samples. The thermoelectric power of the films were measured in the temperature range 27° to 160°C for SnO_2 and upto 175°C for In_2O_3 films. Using the thermopower and optical transmission

data the effective masses of electrons and of holes have respectively been determined as a function of the carrier concentration. The optical band gap and the position of the Fermi levels were determined. It has been observed that the Fermi levels are pinned near the conduction band edge at decreasing carrier concentrations, and the optical band gap shows an appreciable Moss-Burstein shift in the investigated range of carrier concentration.

The effect of post-deposition heat treatment on some of the SnO_2 and In_2O_3 films has been studied. It has been observed that heat treatment in different ambients have remarkable effects on the film resistivity. No appreciable change of carrier concentration was noticed in SnO_2 film but it was noticed in the In_2O_3 films. Hall mobilities in these films are found thermally activated at temperatures ranging from room temperature upto about 250°C . Oxygen diffusion mechanism at the grain boundaries of these films has been discussed critically to explain the observed mobility data. It is inferred from the heat treatment experiments that the role of oxygen diffusion process in the film is only to modulate the inter-grain boundary potential barrier heights.

For SnO_2 thin films two distinct scattering processes viz the grain boundary scattering and the ionized impurity scattering are found to play a predominant role in limiting the Hall

mobility in the two different ranges of carrier concentrations at room temperature. For the In_2O_3 films however the lattice scattering is found to be the dominant process limiting the carrier mobility.

Finally, an attempt has been made to determine the electron affinity and work function of these samples on an empirical basis using the electronegativity concept. The crystal bindings of these samples were also determined and were found to be of fairly ionic in nature.

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CHAPTER - 1

INTRODUCTION

CHAPTER - 1

INTRODUCTION

Successful applications of thin films in various scientific, industrial and engineering purposes and the increasing demand of microelectronic components in different branches of technology have greatly expanded the sphere of thin film research. Enough research has been carried out on different kinds of thin films covering metallic, semiconducting, insulating and cermet (granular metal) materials during the last two decades in which a substantial period has been utilized in search of newer coating materials having special electro-optical properties. These include spectrally selective coating, transparent conducting coating, photoconductive and photochromatic coating, solar absorbing coating etc. These coating may either be a single or multilayer on a suitable neutral substrate or may be layers forming a composite structure with the substrate. Of all the above varieties the transparent conducting oxide coatings have initially drawn much attention because of their application in solar cells but ultimately the sphere of application has been greatly extended to different branches of science and technology. These oxide films have become the object of study since 1910 and are still being investigated in various ways with enough research interests and prospects.

1.1 A BRIEF REVIEW OF TRANSPARENT CONDUCTING MATERIAL

1.1.1 The SnO₂ Material :-

Tin oxide material has been prepared and studied in three

different forms: (a) Single crystal of SnO_2 (cassiterite), (b) Sintered SnO_2 material and (c) Polycrystalline and amorphous SnO_2 material.

(a) Single crystal of SnO_2 :

SnO_2 crystallizes with tetragonal rutile structure with space group $D_{4h}^{14} [P4_2/mnm]$ ⁽¹⁾. The unit cell contains six atoms two tin and four oxygen as illustrated in figure 1.1. Each tin atom is at the centre of six oxygen atoms and every oxygen atom is surrounded by three tin atoms. Thus it is a structure of 6:3 coordination. The lattice parameters determined by Baur ⁽²⁾ are $a = b = 4.737 \text{ \AA}$ and $c = 3.185 \text{ \AA}$. The ionic radius of O^{2-} is $1.4 \text{ \AA}$ and that of Sn^{4+} is $0.71 \text{ \AA}$ ⁽³⁾.

(b) Sintered SnO_2 material :

Van Daal ⁽⁴⁾ has described a method of preparing pure sintered tin oxide with a high density of about 95 % of the bulk density by applying a gas transport reaction method ⁽⁵⁾. Loch ⁽⁶⁾ has obtained Sb-doped sintered SnO_2 . The behaviour of electrical conductivity, quasi-free electron concentrations and Hall mobility of these samples were found to be similar to those of impure single crystal. Recent studies on sintered SnO_2 are hardly available.

(c) Polycrystalline and amorphous SnO_2 material :

These materials are available mainly in the form of thin films. Vincent et al ⁽⁷⁾ have described in detail a method of producing polycrystalline doped and undoped tin oxide by precipitation from a solution and are probably not thin films. Reports on amorphous SnO_2 are not so common. Very recently Jousse et al ⁽⁸⁾ have prepared

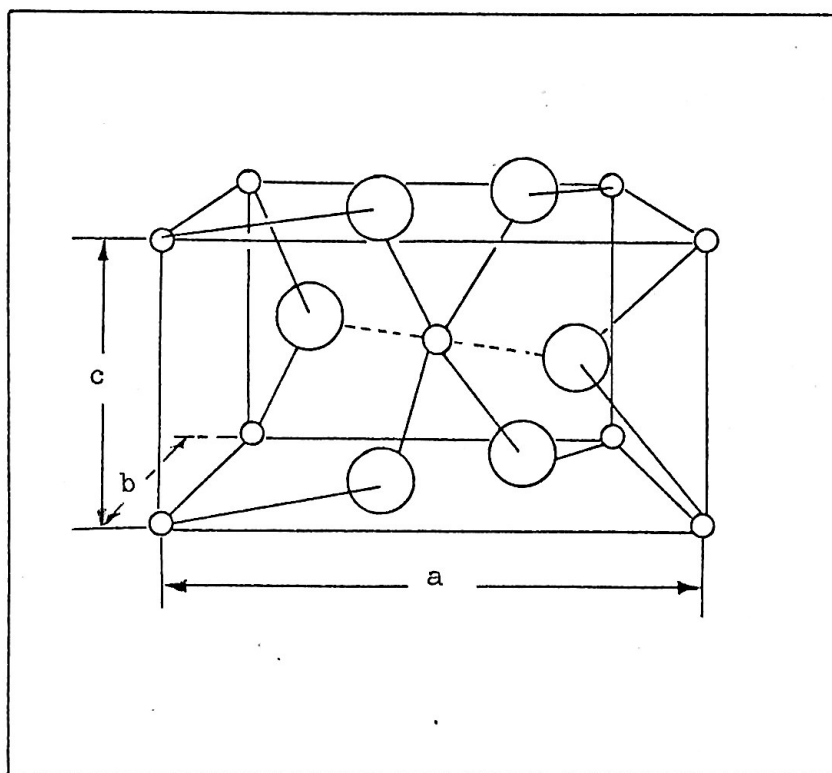


Figure 1.1 : Unit cell of the crystal structure of SnO_2 .
Larger circles indicate oxygen atoms and
the small circles indicate tin atoms.

and studied amorphous SnO_2 films and this is perhaps the only report available to date. All other reports are on polycrystalline SnO_2 thin films and are described in the next section.

1.1.2 Thin Films of SnO_2 as Transparent Conductor :

Transparent conducting coatings of some metallic oxide like tin oxide have been known for about half a century⁽⁹⁾ since 1942 when Mc Masters⁽¹⁰⁾ synthesized transparent conducting tin oxide thin films for the first time. There are many metallic thin films which for thickness less than 10 nm become transparent but very fragile converse to SnO_2 which is found very hard and stable against chemical attack and decay. Moreover SnO_2 thin film is highly adherent to many substrates and can withstand high temperature. All these unique combination of properties have rendered this material technologically very important⁽¹¹⁾.

1.1.2.1 Preparation of SnO_2 thin film :

A number of deposition techniques can be applied to prepare SnO_2 thin films in doped and undoped forms. These include -

(i) Evaporation : -

Transparent conducting thin films of SnO_2 can be prepared by direct evaporation of SnO_2 powder either by electron beam⁽¹²⁾ or flash evaporation method⁽¹³⁾. Due to the high melting point of SnO_2 (1127°C) thermal evaporation yields opaque SnO_2 films of inferior quality.

Reactive evaporation of SnO_2 films can be achieved by

the vacuum evaporation of metallic Sn in an oxygen atmosphere⁽¹⁴⁾ onto substrates heated to about 400°C. Post-oxidation of vacuum evaporated metallic tin film may also yield SnO₂ film⁽¹⁵⁾ but of inferior quality. On the other hand activated reactive evaporation method⁽¹⁶⁾ gives excellent quality transparent conducting SnO₂ films.

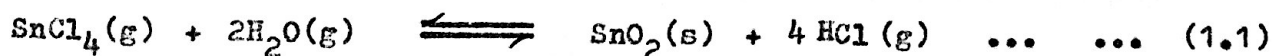
(ii) Sputtering : -

All types of sputtering methods have been employed to deposit SnO₂ thin films. Reactive sputtering⁽¹⁷⁾, ion beam sputtering⁽¹⁸⁾ and other similar methods⁽¹⁹⁾ are found to yield very good results. As-sputtered films are usually amorphous in nature but elevated substrate temperature or a post-deposition heat treatment gives polycrystalline films.

(iii) Chemical Vapour Deposition (CVD) : -

CVD is a widely used method for the deposition of SnO₂ thin film of good quality. Films have been prepared by the pyrolysis of tetramethyltin⁽²⁰⁾, dibutyl tin diacetate⁽²¹⁾ and by pyrolysis and hydrolysis of both the stannous and stannic chlorides⁽²²⁾.

Heterogeneous reaction and mechanism of formation of SnO₂ film from SnCl₄ has been given in detail by Ghoshagore⁽²⁰⁾. The hydrolysis reaction is given by



ofcourse within some uncertainties, as mentioned by the authors^(20,22). In pyrolysis the undesirable homogeneous volume phase reactions at

high temperature affect the quality of the film by producing haziness on the surface.

(iv) Reactive Chemical Spray (RCS) :-

This technique^(23,24) involves spraying of an ionic solution, usually aqueous, containing soluble salts of the constituent atoms of the desired compound onto heated substrates. Hydrolysis and pyrolysis are the main chemical reactions involved in the process. This technique is only very slightly different from CVD in the sense that here the chemicals vaporize and react on the substrate surface after reaching on it⁽²⁵⁾. But in CVD vaporization takes place before reaching the substrate surface. This demarcation is obviously not very sharp and in practice a combination of both the processes may take place in either case of CVD or RCS techniques. In principle RCS technique is very simple and is suitable for industrial applications.

Transparent conducting films of SnO_2 have been deposited by spraying alcoholic solution of SnCl_4 ⁽²⁴⁾ and SnCl_2 ⁽²⁶⁾ using H_2O or H_2O_2 ⁽²²⁾ by different workers. Antimony doping was performed by adding SbCl_3 and fluorine doping was performed by using NH_4F or HF ⁽²⁷⁾ with the spray solution. The optimum substrate temperature for better film was reported to be about $400 - 500^\circ\text{C}$. Typically, a gas flow rate of about $5 - 10 \text{ l/min}$ at a pressure of about 0.5 kg/cm^2 with a solution flow rate of about $5 - 20 \text{ cm}^3/\text{min}$ were commonly used. The size of the spray particle and their distribution affect the uniformity of the film surface and their optical transmission decreases⁽²⁸⁾.

(v) Dip technique : -

The dip technique⁽²⁹⁾ consists essentially of inserting the substrate into a solution containing hydrolysable metal compounds and pulling it out at a constant speed into an atmosphere containing water vapour. In this atmosphere hydrolysis and condensation process take place. Finally the films are hardened by a temperature cycle to form transparent metal oxides. This technique has been used commercially to deposit large area coatings (about $10 - 12 \text{ m}^2$) of SnO_2 .

(vi) Other techniques : -

Other techniques like chemical solution growth, glow discharge decomposition of SnCl_2 , $\text{Sn}(\text{CH}_3)_4$ or SnCl_4 in oxygen have also been used to prepare SnO_2 films^(30,31).

Dopants used :

Except antimony and fluorine several other dopants have been studied in SnO_2 films^(32,33). They are phosphorus, zinc, arsenic, thallium, tellurium, tungsten, chlorine, bromine, iodine and indium. They did not give good results with respect to transparency and conductivity.

1.1.2.2 Properties of SnO_2 thin film and Single crystal :

(i) Structural : -

All types of structural investigations including X-ray and electron microscopy were performed on SnO_2 films by many

workers. The deposited films were found to present granular polycrystalline structure with a tetragonal rutile lattice⁽³⁴⁾. Both the SnO_2 and SnO phases were detected in the film. The grain size as reported may vary from $50 \text{ \AA}$ to $\sim 10^4 \text{ \AA}$. The measured atomic ratios of the dopants impurity in the deposited films vary from that of the solution used. Sodium and chlorine contamination are very usual in the case of using soda lime glass substrates and SnCl_4 solution⁽³⁴⁾ in spray deposition process.

(ii) Electrical :-

The electrical properties of SnO_2 thin films are very much sensitive to their method of preparation. Since the method of preparations are diverse, a large scatter in the electrical properties were reported. Comprehensive studies of SnO_2 films have been carried out by Aitchison⁽³⁵⁾. He found that stoichiometric SnO_2 film is highly resistive ($\sim 10^8 \Omega \text{ cm}$) at room temperature. Resistivity decreases drastically if pentavalent dopant (Sb) is added. Trivalent dopant (In) on the other hand could not lower the resistivity. Minimum resistivity lies within 10^{-3} - $10^{-4} \Omega \text{ cm}$ for doped SnO_2 films of moderate thickness ($\sim 0.3 \mu\text{m}$ to $0.5 \mu\text{m}$). Conducting transparent films have a quasi-free electron concentration of $\sim 10^{18}$ - 10^{20} cm^{-3} and Hall mobility⁽³⁶⁾ $\lesssim 30 \text{ cm}^2/\text{V}.\text{sec}$. This value of Hall mobility is certainly very small in comparison to those of single crystal samples, where it was found that⁽³⁷⁾ Hall mobility may be as high as $300 \text{ cm}^2/\text{V}.\text{sec}$ for carrier concentration of the order of $\sim 10^{15} \text{ cm}^{-3}$. This lowering of Hall mobility in thin film has been attributed to

the increased scattering effects in the sample. There is variations of opinion regarding the exact nature of the scattering process in the film. Grain boundary scattering⁽³⁸⁾, ionized impurity scattering^(37,39) and lattice scattering⁽⁴⁰⁾ all of these processes were considered independently by different workers to be the dominant scattering mechanism in these films at room temperature.

Nagasawa et al⁽⁴¹⁾ and Fonstad et al⁽⁴²⁾ have conducted studies with pure single crystal of SnO_2 . They found that at room temperature these crystals are good conductors. The carrier concentration was $\sim 10^{17} \text{ cm}^{-3}$. Impure single crystals and intentionally doped single crystals were also investigated⁽⁴³⁻⁴⁵⁾. Density of states effective mass (m^*) were found to lie within $0.1m_0$ to $0.8m_0$ in the carrier concentration range $\sim 10^{15}$ to 10^{20} cm^{-3} for the doped samples. The cyclotron resonance experiment gives⁽⁴⁶⁾ value of m^* for the pure single crystal of SnO_2 as $0.275m_0$ where the carrier concentration was $\sim 7 \times 10^{15} \text{ cm}^{-3}$ and room temperature Hall mobility was about $250 \text{ cm}^2/\text{V}\cdot\text{sec}$.

(iii) Optical :-

Several authors^(14,35,36,47,48) have studied the optical properties of SnO_2 thin film. Spence⁽¹⁴⁾ found that the absorption edge occurs at about 3.7 eV with direct transitions indicated at about 4.3 eV and indirect transition at about 2.7 eV. Ishiguro et al⁽³⁶⁾ measured the transmission and reflection coefficients of highly conductive SnO_2 film obtained by hydrolysis of SnCl_4 on fused quartz or rock salt substrates. These specimens were highly

transparent in the visible region and the fundamental absorption started at about $0.3\mu\text{m}$ extending to a shorter wavelength. High infra-red reflection was also observed. The carrier concentrations of the samples were $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$. The refractive index, as reported for the samples were found to vary with the wavelength from 1.92 at $\lambda = 0.5\mu\text{m}$ to a minimum value of 0.87 at about $3.5\mu\text{m}$ and 5.53 at $30\mu\text{m}$. Absorption coefficients were found to increase with the addition of dopants (Sb)^(47,48). T.Arai⁽⁴⁸⁾ found that in the visible region the optical properties of conductive and nonconductive SnO_2 thin films are similar.

The first optical studies on single crystal of SnO_2 were carried out by Kohnke⁽³⁷⁾ on natural cassiterite. He found the fundamental optical band gap $E_g \geq 3.54 \text{ eV}$. Summitt and his coworkers have found⁽⁴⁹⁻⁵²⁾ that in SnO_2 single crystal UV absorption coefficient takes the value of the order of $\sim 10^3 \text{ cm}^{-1}$. High IR reflection and visible transmissions were also noticed^(4,41). The static dielectric constant have been found to be 9.58 and 13.5 for direction parallel and perpendicular to the c-axis respectively.

(iv) Hardness of the coating:-

The hardness of SnO_2 on the Mohs' scale is around 7-8, as for crystalline aluminium silicate and fluoride. The coating being oxide is inert to most of the acids and alkalies and resistant to corrosion.

In short, it has however been accepted in general that SnO_2 in its undoped form is an n-type wide band gap semiconduc-

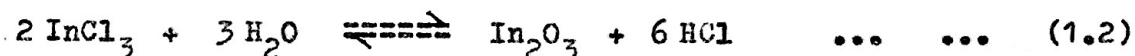
tor which is optically transparent in the visible region of the spectrum and is very stable in normal atmosphere.

1.1.3 Thin Films of In_2O_3 as Transparent Conductor :-

Intensive research work on In_2O_3 thin film started just in the last decade. These films are in many respect similar to SnO_2 films when they are considered in doped condition. In most of the cases In_2O_3 thin films are prepared using tin (Sn) as a doping material and the resulting films are known as tin-doped indium oxide film ($\text{In}_2\text{O}_3:\text{Sn}$) or indium-tin-oxide (ITO) films. Other dopants which have been studied in In_2O_3 films include titanium⁽⁵³⁾, antimony⁽⁵⁴⁾, lead⁽⁵⁴⁾ and fluorine⁽⁵⁵⁾.

1.1.3.1 Preparation of In_2O_3 thin film :-

Almost all the deposition methods suitable for SnO_2 film including the reactive ion plating method⁽⁵⁶⁾ have been applied to prepare In_2O_3 thin films. When to deposit this film by spray pyrolysis from its chloride the following well known reversible endothermic reaction takes place at the substrate surface⁽³⁴⁾



and the sample of In_2O_3 is obtained normally in an unintentionally doped condition. Sn-doping for ITO films can be achieved here by mixing SnCl_4 in the working solution. Except InCl_3 other compounds of indium which are easily hydrolysable could also be used for the

preparation of In_2O_3 film by hydrolysis.

1.1.3.2 Properties of In_2O_3 thin film and single crystal :-

Structural, electrical and optical properties of undoped and doped In_2O_3 thin films were studied by several authors⁽³⁴⁾. In_2O_3 like SnO_2 is an n-type broad band semiconductor. The main difference of In_2O_3 thin film from SnO_2 is that the former crystallizes in the cubic b.c.c structure with $a = 10.118 \text{ \AA}$ whereas the latter is rutile. Hall mobilities of undoped In_2O_3 film may be of the order of 10 to 74 $\text{cm}^2/\text{V}\cdot\text{sec}$ ⁽⁵⁷⁾ and is greater than that of SnO_2 film. Other properties are comparable to those of SnO_2 thin film.

In_2O_3 coating is not so hard as SnO_2 is but is comparable to other hard oxides in stability and inertness.

Initial studies on single crystal of In_2O_3 has been reported by Weiher⁽⁵⁸⁾ and his coworkers⁽⁵⁹⁾. Very recently Kanai⁽⁶⁰⁾ has prepared and studied doped single crystal of In_2O_3 . He found that doping by Ti, Nb, Ta, W and Ge have no significant effect on the electrical and optical properties of In_2O_3 single crystal but Zr and Hf have strong effect as donor impurities. It has been observed that ITO single crystal has the Hall mobility about $\sim 100 \text{ cm}^2/\text{V}\cdot\text{sec}$ and is comparable to Zr and Hf doped In_2O_3 crystals having carrier concentration $\sim 10^{20} \text{ cm}^{-3}$ and resistivity $\sim 2 \times 10^{-4} \Omega \text{ cm}$. Hall mobilities of other doped In_2O_3 single crystals vary within 25 to 70 $\text{cm}^2/\text{V}\cdot\text{sec}$.

Past reports on amorphous In_2O_3 thin film are uncommon.

Direct optical band gap of In_2O_3 lies between 3.55 and 3.75 eV^(58,61) and the refractive index in the visible ranges are found to vary from ~ 1.9 to 2.08⁽⁶²⁾. Doping and substrate temperature have remarkable effects on these parameters. Other optical properties are almost similar to those of SnO_2 thin films.

1.1.4 Other Transparent Conductors : -

Several other oxides e.g ZnO , CdO , Bi_2O_3 , MoO_3 , TiO_2 etc have been found to show various degrees of transparent conductive properties. Of all these oxides ZnO and CdO have been studied extensively^(63,64).

Except all these oxides, cadmium stannate (Cd_2SnO_4) thin film can exhibit good transparent conductive properties as have been reported by different authors⁽⁶⁵⁾. Zinc-stannate is another possible member of this variety. Transparency of ZnO films are superior to SnO_2 and In_2O_3 films but are not so conductive in the undoped (and some times in the as-deposited) condition; on the other hand cadmium stannate is highly expensive. All of these transparent conductive materials show n-type conductivity in the undoped and doped conditions.

1.1.5 Figure of Merit of Transparent Conducting Coating : -

The relative usefulness of a transparent conductive film can be quantized considering its two fundamental requirements : high optical transmission and high electrical conductivity. Haacke⁽⁶⁵⁾ has proposed a figure of merit ϕ_{TC} which permits a comparison

between different transparent conductors. This can be expressed as

$$\text{Figure of merit } \phi_{TC} = T^{10} / R_{\square} \dots \dots (1.3)$$

where $R_{\square}$ is the electrical sheet resistance and T is the optical transmission.

Collecting some recent reported data about the figure of merit of SnO_2 thin films, it is observed that the highest figure of merit may be $131.0 \times 10^{-3} \Omega^{-1}$ for $\text{SnO}_2:\text{Sb}$ film⁽⁶⁶⁾ deposited by activated reactive evaporation method. For films deposited by spray^(67,68) or CVD methods the maximum ϕ_{TC} may lie within 52.6×10^{-3} and $56.4 \times 10^{-3} \Omega^{-1}$. Highest figure of merit of ITO film so far obtained is $184.0 \times 10^{-3} \Omega^{-1}$ for heat treated films deposited by CVD method⁽⁶⁹⁾. Maximum ϕ_{TC} for spray deposited ITO is lower to that of SnO_2 film. For cadmium stannate the highest ϕ_{TC} as reported by Haacke et al⁽⁷⁰⁾ is $258.0 \times 10^{-3} \Omega^{-1}$ for film deposited by sputtering method and perhaps it is the highest figure of merit of all the transparent conductors so far reported.

1.1.6 Applications of Transparent Conducting Coatings :-

Transparent conducting coatings have attracted enough interest only because of their wide applications, some of which are given below :

(i) Transparent heat reflecting coatings :-

Because of the high reflecting power of IR radiation and high visible transmission SnO_2 and In_2O_3 thin films are spectrally selective and have application in solar thermal energy conversion,

solar photovoltaic conversion, solar heating, window and incandescent lamp insulation etc. In conventional incandescent lamp the tungsten filament emits only 10% visible and about 90% heat radiation. Here a heat reflecting coating on the glass envelope could help reflecting this thermal part back to heat the filament and can save enough power.

For space craft instruments thermal balance is an important and delicate parameter. This requires heat retention under cold and heat radiation under hot conditions. This is essential for the performance of its very sensitive and sophisticated electronic equipments. This heat regulation becomes possible by switchable composite coatings of spectrally selective materials.

(ii) Application to solar cells :-

Both single crystal and polycrystalline silicon and several other binary and ternary compounds have been found to form junctions with SnO_2 and ITO yielding high efficiency solar cells⁽⁷¹⁾. For these cells transparent conducting coatings are useful in many ways. The coating permits the transmission of solar radiation directly to the active region with little or no attenuation and can serve simultaneously as a low resistance contact to the junction and as an antireflection coating for the active region. The ease of fabrication and greater stability of these films help manufacturing the cells at relatively lower costs.

(iii) Antistatic coatings :-

Antistatic coatings on polyester flexible substrates

are used to fabricate packaging for delicate integrated circuits during their transport and storage. Another use of these coatings for antistatic purposes is in space crafts. Field intensity fluctuations in the earth's magnetosphere and continuous irradiation of UV and other charged particles may differentially bias space craft areas to a dangerously high potential⁽⁷²⁾. In_2O_3 and ITO coatings could show excellent stability when exposed to combined UV and charge particles irradiation⁽⁷³⁾ and these coatings therefore could bring uniformity of potential on the exterior of the craft.

(iv) Gas sensors :-

Most of the gas sensors used so far are based on doped or undoped tin oxide⁽⁷⁴⁾. SnO_2 doped with ThO_2 are used as carbon monoxide gas sensors. SnO_2 doped with Pd, Rh, or MgO are used to detect hydrogen gas, SnO_2 doped with Nb, Va, Ti and Mo are used for propane gas detectors. Other transparent conducting oxides are also important for gas sensing applications.

(v) Other applications :-

Other important applications are- the production of resistive heating layers protecting vehicle wind glasses and window glasses of residential houses, laser damage resistant coatings in high power laser technology⁽⁷⁵⁾, photocathode in photo-chemical cells and surface layers in electroluminescent applications. These oxide layers could reduce the coefficient of friction and thereby can protect glass containers in high speed filling lines.

1.2 FUNDAMENTAL AND TECHNICAL PROBLEMS OF OBTAINING TRANSPARENT CONDUCTING FILMS

There is a fundamental conflict between transparency and electrical conductivity. Incident photon when creates electron-hole pairs in a material it limits the transparency at short wavelengths. Again the steep increase of reflectivity due to free carrier absorption limits the transparency at long wavelengths. Since the conductivity of a material is directly proportional to its free carrier content higher electrical conductivity therefore automatically brings opacity in the films. This is why electrical conductors are generally opaque in nature. Some basic considerations indicate that materials with long mean free path should produce layers with larger figure of merit. Long mean free path in highly conducting metal films are obtained with relatively thick films and consequently opaque one. Again in the case of semiconductors if the band gap is sufficiently high (≈ 3 eV) thicker films with high transmission are possible, but conductivity would be hindered due to high band gap. The only way to obtain good transparent conductor is to create electron degeneracy in a wide band gap semiconductor by introducing non-stoichiometry in a controlled way. Oxide semiconductors are of wide band gap material and are therefore suitable candidate for transparent conductors.

Substrate material sometimes creates problem in obtaining transparent conducting films. In cheap soda lime glass substrates this problem is noticeable. Alkali ions of the substrate diffuse into the film and compensate the effect of free electrons by producing p-type

doping agents in n-type material. This imparts high resistivity to the sample.

Another important factor, especially associated with the spray deposition system is the quality of the spray particles obtained at the time of film deposition. Uniform size of the spray particle could only produce films of relatively better quality. Therefore the design of the spray apparatus is very important. Opaque suspended foreign dust particles in the deposition environment may bring haziness in the film. The working liquid and the atmosphere should therefore be clear enough to obtain transparent films.

1.3 THE AIM OF THE WORK

Considering the immense application of transparent conducting films, particularly in heterojunction solar cells, it becomes meaningful to prepare transparent conducting thin films in our laboratory. In view of the past information and the problems (mentioned in the previous section) it seems wise at present to select an easy film deposition method, the chemical spray method as we think, and to modify the deposition system in a way such that relatively better transparent conducting films could be obtained in an easy and efficient way. Therefore the job would be to try to design an apparatus for the deposition of thin film by a spraying method and to prepare SnO_2 and In_2O_3 thin films. To utilize these films more fruitfully it is essential to characterize the sample and a study of their electrical and optical properties is necessary. Some of these studies have been performed and reported in this work.

1.4 THE STRUCTURE OF THE THESIS

Some experimental work on the deposition and characterization of SnO_2 and In_2O_3 thin films have been presented in this thesis. It contains six major chapters in which only the second chapter consists of two parts.

The present chapter contains an introduction to SnO_2 and In_2O_3 thin films and their applications. Detail description of the design of a spray apparatus and that of the film deposition process and the experimental prerequisites for the preparation of different samples have been given in chapter - 3. A description of the adopted experimental techniques and related appliances for the study of the different properties of the prepared films have also been given in this chapter.

The theoretical background of the apparatus design consideration and various analytical techniques for the analysis of different results have been given respectively in part-1 and part-2 of chapter-2.

Chapter-4 deals with the effects of different deposition variables on the SnO_2 film characteristics. With a view to obtaining a tentative energy band picture of the material a systematic analysis of different structural, electrical and optical properties of the samples have been presented in this chapter. Similar studies on In_2O_3 thin films have been presented in chapter-5.

In each of the chapters - 3, 4 and 5 the experimental observations, their interpretations and possible implications of the obtained results have been discussed.

The conclusions of the present work and a few suggestions for future work have been given in chapter-6.

Relivant references or bibliography for the respective chapters have been given at the end of each chapter. At the end of the thesis a list of research publications made from the text of the thesis has been given.

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CHAPTER - 1

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C H A P T E R - 2

THEORETICAL CONSIDERATIONS

CHAPTER - 2

THEORETICAL CONSIDERATIONS

Non-vacuum methods could not produce films of the same nature as that obtained by vacuum methods although the basic principles of condensation and nucleation of thin films from its vapour phases are not very different in these methods. It is known that the chemical spray deposition method is a non-vacuum method and can operate in open atmosphere. With the increasing stringent quality requirements imposed on chemically deposited films a thorough understanding of the underlying principles of the method becomes necessary. In this chapter the 1st part includes a short description of the nucleation and growth aspects of thin film from its vapour phase in addition to some aspects of the process itself, and the 2nd part describes the methods of analysis of various properties of semiconducting thin film.

PART - I : THEORETICAL ASPECT AND FILM GROWTH PROCESS IN A CHEMICAL METHOD

2.1 THEORETICAL BACKGROUND OF THE CHEMICAL SPRAY METHOD

To form a qualitative as well as quantitative background of the method one is to know the chemistry, the thermodynamics and possible chemical kinetics of the method. Relative usefulness of these studies are briefly described below.

2.1.1 Chemistry of the Method :-

It has already been mentioned that chemical (spray) deposition method is a material synthesis method in which the constituents of the vapour phase react to form a solid film at some surface. Thus the occurrence of chemical reaction is an essential characteristic of the method. The nature and extent of chemical reaction can be deduced if one knows the composition of the solid and vapour phases in the system. The composition of the solid product can be analysed after the deposition, but that of the vapour phase must be determined in situ at the particular reaction condition because many high temperature species disappear or change upon cooling to room temperature. At present there are several experimental methods for doing the job, e.g., mass spectrometry, Raman spectroscopy, absorption spectroscopy, gas chromatography etc.

2.1.1.1 Chemical reaction :-

There are several types of chemical reactions which may take part in the film formation process in a chemical method, e.g.

- (a) Pyrolysis (b) Hydrolysis (c) Oxidation (d) Reduction
- (e) Synthesis reaction (f) Disproportionation (g) Carbide and Nitride formation (h) Combined reaction etc.

For a spray deposition method the first four varieties (a), (b), (c) and (d) are important and are very frequently encountered.

Pyrolysis is the process of chemical decomposition

of a substance by the action of heat and hydrolysis is the chemical decomposition caused by the action of water. In hydrolysis reaction water itself also decomposes. We are presently interested with these two types of reactions for the preparation of SnO_2 and In_2O_3 films. The formation reactions are given by equations (1.1) and (1.2) respectively.

2.1.1.2 The reactor system :-

The reactor is a basic part of any pyrolytic deposition system. The design of the reactor should be such that it could provide equipments to accomplish the following functions -

- (a) Transport, meter and time the diluent and reactant gases entering the reactor,
- (b) Provide heat to the site of reaction, namely the substrate material being coated, and control of this temperature,
- (c) Remove the by-product exhaust gases from the deposition zone and safely dispose of them.

The quality of the deposited film depends on the degree of fulfillment of these functions and to meet these requirements one should also look into the simplicity of construction of the reactor.

The geometry and construction materials of the reactor are determined by the physical and chemical characteristics of the whole system and by the process parameters. The reactor system in the chemical spray deposition process can be broadly classified as -

- (i) Low temperature reactor for using at temperatures $< 500^\circ\text{C}$

at normal pressure.

(ii) High temperature reactors for using at temperatures $> 500^{\circ}\text{C}$ at normal pressure.

(iii) Low pressure reactors.

Low pressure reactors are generally hot-wall type but the low temperature or high temperature reactors may either be of hot-wall or cold-wall type.

In hot-wall reactors it is assumed that due to low gas velocities employed a fully developed thermal field exists in the reactor. These reactors are generally tubular in design. In cold-wall reactors the situation is more complex. The existence of rather sharp temperature gradients perpendicular to, as well as along the surface of the substrate (in the horizontal configuration)⁽¹⁾ affect the gas flow and the transport phenomena considerably as shown diagrammatically in figure 2.1.

Hot-wall reactors are used in the case of systems where the deposition reaction is exothermic in nature since the high wall temperature minimizes or even prevents undesirable deposition on the reactor walls. In the case endothermic reaction cold-wall reactors are more useful.

2.1.1.3 Transport phenomena in the reactor :-

Transport phenomena in fluids are related to the nature of the fluid flow. The following parameters affect the nature of gas flow in reactors :

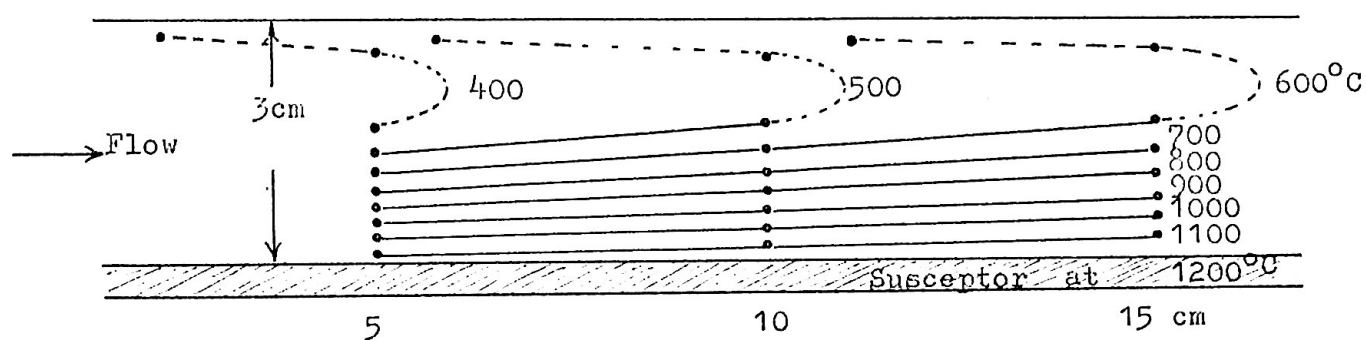


Figure 2.1 : Isotherms in horizontal reactor when heated from the bottom [V.S.Ban, J.Electrochem.Soc. 125,317 (1978)] .

- (i) velocity of flow,
- (ii) temperature and temperature distribution in the system,
- (iii) pressure in the system,
- (iv) geometry of the system and
- (v) gas or vapour characteristics.

The transport phenomena is therefore important due to two basic reasons -

- (a) the requirement of thickness and semiconducting doping uniformity which can be fulfilled only when equal amounts of reactant gases and dopants are delivered to all the substrates in the system,
- (b) the requirement of high chemical efficiency to achieve satisfactory growth rates and utilization of input chemicals; this means that sufficient amounts of reactants must be delivered to the film growth surfaces.

All of the above points should be considered at the time of designing the reactor.

2.1.2 Thermodynamics of the Method :-

The main function of thermodynamics in relation to chemical spray method is to predict the feasibility of the process under some specified conditions and to provide quantitative information about the process. In order to perform necessary thermodynamic calculations for this purpose one requires a set of relative thermodynamic data of the system. The most useful of them are the

free energy of formation of all the associated vapour and condensed constituents. The thermodynamics, however can be used as only a guide line because in most of the cases actual situation deviates enough from the thermodynamical prediction; moreover it can not provide any information about the rate of the deposition process.

2.1.3 Kinetics of the Method :-

Some of the factors that cause deviations of thermodynamical prediction from reality are generally studied in the kinetics. It is known that the deposition reaction in chemical spray deposition process is almost always a heterogeneous reaction. The sequence of events in the usual heterogeneous process can be described as follows :

- (i) Diffusion of reactants to the surface,
- (ii) Adsorption of reactants at the surface,
- (iii) Surface events, such as chemical reaction, surface motion, lattice incorporation etc,
- (iv) Desorption of products from the surface and
- (v) Diffusion of products away from the surface.

The application of kinetics in film deposition process has been exemplified by Eversteijn⁽²⁾ and that can be of use in the present case of SnO_2 film deposition. Dependence of SnO_2 film deposition rate on the substrate temperature has been described in chapter-4, but it would be meaningful here to mention that the most likely rate controlling step at lower temperatures is the weak adsorption

of reactants on the substrate surface. In the upper temperature range however the most probable rate controlling step is the diffusion of reactants and product to and from the substrate surface respectively. The rate of deposition r is exponentially dependent on temperature T as given by Arrhenius equation -

$$r = a \exp (-\Delta E/k_B T) \quad \dots \quad \dots \quad (2.1)$$

where ΔE is the activation energy for the process and a is the frequency factor.

Another important side of the film deposition process where kinetics has its role to play is to determine the variations of the deposition rate on the substrate orientation. This is however useful for epitaxial films with which we are not presently dealing in this work.

2.2 FILM GROWTH ASPECTS

Properties of thin film are very much related to their structure. Thus understanding of the factors governing the structure of the film is important. A brief discussion about the nucleation and formation of polycrystalline and amorphous thin films has been given in this section.

2.2.1 Nucleation and the Stages of Film Growth :-

The modern theory of nucleation is based upon the

atomostic nucleation concept⁽³⁾ which states that not all surface sites have equal bonding characteristics. Those with strong bonds are particularly favourable nucleation sites. Again, after nuclei reach a certain size it becomes energetically more favourable for them to grow than to reevaporate. The growing nuclei come into contact and finally coalesce to form a continuous film.

The sequence of the nucleation and growth steps to form a continuous film as revealed by an electron microscopic observation^(4,5) are -

(a) The island stage : where the first evidence of condensation is observed via sudden burst of nuclei of fairly uniform size.

(b) The coalescence stage : which occurs between the islands in less than 0.1 sec. The character of coalescence is liquid like and enlargement of the islands occurs covering larger areas of the substrate.

(c) The channel stage : when larger islands grow together they leave channels of interconnected holes of exposed substrate in the form of a network structure on the substrate. As deposition continues, secondary nucleation occurs in these channels and forms the last stage of the nucleation viz -

(d) The continuous film : which then grows in thickness as the time passes.

2.2.2 Polycrystalline and Amorphous Thin Film :-

These two structural forms are actually more common

in spray deposited films. In general, lower temperature and higher gas phase concentration favour formation of polycrystalline deposit. Under these conditions the arrival rate at the surface is high, but the surface mobility of adsorbed atoms is low. Many nuclei of different orientation are formed, which upon coalescence result in a film consisting of many differently oriented grains. Further decrease in temperature and increase in supersaturation result in even more nuclei and consequently in finer grained films, eventually leading to the formation of amorphous film when crystallization is completely prevented.

2.2.3 Formation of Defects During Growth :-

When the islands during the initial stages of film growth are still quite small, they are observed to be perfect single crystals⁽⁵⁾. However as soon as the islands become large enough so that they touch, grain boundaries or lattice defects will be incorporated into the film, unless the islands coalesce to form a single grain. Again during the process of recrystallization of the grains which also occurs at the early stage of film formation, a large number of defects are incorporated in the film. The types of defects those are often encountered in spray deposited films are lattice vacancies, stoichiometric excess and grain boundary. Another type of defect namely the surface roughness which stems from the quality of the sprayer is especially important in the case of spray deposited films. Rough surface can affect the overall properties of the film if the thickness is small. Dislocations are

mainly found in evaporated films and are therefore not very important here.

2.2.3.1 The grain boundaries : -

Effects of grain boundaries in polycrystalline thin film are very much significant. The grain size and hence the boundary regions in thin films depend on the deposition variables such as (a) film thickness, (b) substrate temperature, (c) annealing temperature and (d) the deposition rate. Thus the number of such boundaries are controllable parameters.

A schematic representation⁽⁶⁾ of the dependence of grain size on different parameters as mentioned above, has been given in figure 2.2. In this figure the dependence of grain size on the deposition rate is less obvious, but can be understood on the basis that film atoms just impinged on the surface, although they may possess a large surface mobility, become buried under subsequent layers, at high deposition rates, before much diffusion can take place⁽⁶⁾. In order to operate this effect, however a certain minimum rate must be exceeded. Below this threshold rate, grain size is limited by temperature alone.

Dependence of grain size of SnO_2 thin film (CVD) on the substrate temperature has been studied by T.Muranoi et al⁽⁷⁾, where it was observed that grain size increases with the substrate temperature. It is naturally expected because of an increase in surface mobility due to an increasing substrate temperature allows the film to decrease its total energy by growing larger grains.

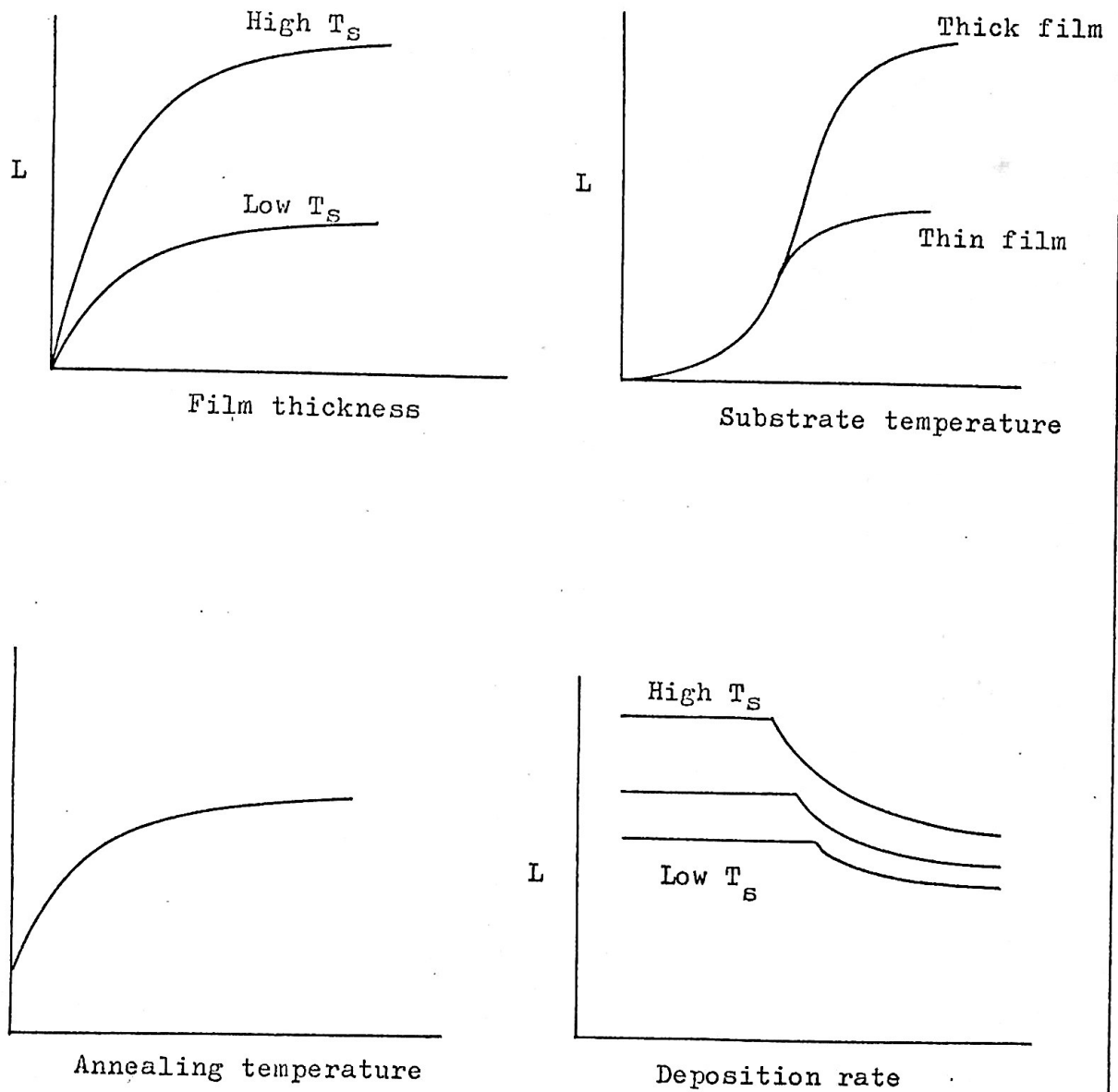
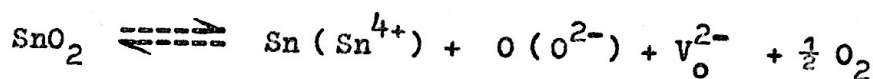


Figure 2.2 : Dependence of grain size L on film thickness, substrate temperature T_s , annealing temperature and deposition rate.

2.2.4 Defect Structure in SnO_2 and In_2O_3 Thin Film :-

It is well known that the physical properties of oxides depend strongly on the deviation from the stoichiometric composition and on the nature and concentrations of foreign atoms incorporated into the host lattice. The exact nature of the defect structure in SnO_2 and In_2O_3 thin films are still mostly uncertain.

Since SnO_2 is n-type, either oxygen vacancies V_o or interstitial tin atom Sn_i are expected to be donors in pure SnO_2 . Thus either of the defect reactions -



may take place⁽⁸⁾. In the case of Sb-doped and F-doped SnO_2 cations and anions of SnO_2 may be replaced respectively by Sb^{5+} and F^- ions. When deposited SnO_2 from SnCl_4 by spray pyrolysis, Cl^- ions may also replace O^{2-} ions in the lattice at low substrate temperatures⁽⁹⁾.

In undoped In_2O_3 thin film oxygen vacancies and in Sn-doped In_2O_3 film both the substitutional tin and oxygen vacancies may be present⁽¹⁰⁾. Cl^- ion concentration is also important when In_2O_3 is spray deposited from InCl_3 . Formation of all these defects are strongly dependent on the preparational conditions. Contamination from substrate material is also important for these films.

PART - II : ANALYTICAL METHODS FOR THE
STUDY OF FILM PROPERTIES

Electrical and optical properties of semiconducting materials are generally analysed by statistical methods. Such methods are divided into two main branches - the classical statistics and the quantum statistics. The more commonly used method for semiconductor physics is the classical statistics, but there are cases where the application of quantum statistics becomes essential to have adequate analysis of the results.

In the spray deposition process SnO_2 and In_2O_3 thin films are obtained almost always in a degenerately doped condition and thus the degenerate electron gas models would be best applicable to these samples. In this part of the chapter different theoretical principles underlying the various analytical methods for the properties of semiconducting materials with special emphasis on degenerate semiconductors have been briefly discussed.

2.3 DEGENERATE AND NON-DEGENERATE SEMICONDUCTOR

Fermi level in most of the semiconductor is located at least a few $k_B T$ below the bottom of the conduction band. In that case the electrons in the conduction band follow closely Boltzmann statistics, and the electron gas is said to be non-degenerate.

Under certain circumstances, however, the Fermi level may enter into the conduction band and the electron gas in the conduction band may become degenerate. The conditions favourable for such a situation are-

- (i) Relatively high donor density ($\sim 10^{19} \text{ cm}^{-3}$)
- (ii) Small donor ionization energy and
- (iii) Low density of states near the bottom of the conduction band i.e., small effective mass of the electrons.

Under these conditions all the statistical calculations should be performed by taking the Fermi-Dirac statistics into account.

As temperature increases from absolute zero, the donors begin to ionize and as a result of the low density of states the lower energy states in the conduction band become completely filled. The position of the Fermi level relative to the bottom of the conduction band is then given by⁽¹¹⁾

$$E_F = \left(\frac{h^2}{8 m_e^*} \right) \left(\frac{3n}{\pi} \right)^{\frac{2}{3}} \quad \dots \quad \dots \quad (2.2)$$

where n is the density of electrons in the conduction band. As long as $E_F \gg k_B T$, the electron gas is degenerate. Clearly as the electron effective mass m_e^* is reduced, degeneracy may occur at lower electron density ($\sim 10^{18} \text{ cm}^{-3}$). As temperature is increased further the degeneracy is removed and Fermi level leaves the conduction band again. The approximate condition for degeneracy is that the Fermi level be no lower than $k_B T$ below the conduction

band edge and the temperature T_{deg} at which this condition is satisfied can be obtained from equation 2.2 as

$$T_{\text{deg}} = \left(\frac{h^2}{8k_B m_e^*} \right) \left(\frac{3n_{\text{deg}}}{\pi} \right)^{\frac{2}{3}} \quad \dots \quad \dots \quad (2.3)$$

Here T_{deg} is the temperature upto which degeneracy exists and is known as degeneracy temperature and n_{deg} is the carrier concentration at that temperature known as the degeneracy concentration (concentration for the onset of degeneracy).

2.3.1 The Mott-Critical Density of Electrons :-

The Mott-critical density n_c for the metal-insulator transition in a doped semiconductor is estimated from the Mott-criterion

$$n_c^{\frac{1}{3}} a_H \approx 0.25 \quad , \quad a_H = \epsilon_0 \hbar^2 / m_e^* e^2$$

The effective Bohr radius is a_H and ϵ_0 is the static dielectric constant of the host lattice. This critical density is not a constant quantity for a material but it depends on the method of sample preparation and impurity content.

2.4 THE HALL CONSTANT, ELECTRICAL CONDUCTIVITY AND MOBILITY

Hall effect is observed when a magnetic field is applied at right angles to a conductor carrying a current I as

shown in figure 2.3. In presence of a magnetic field, a magnetic force vB acts on the electrons having an average velocity v due to the current I . This force is at right angles to both the direction of B and v and therefore each electron (for n-type material) is deflected towards one side of the conductor. When the electrons reach the surface of the conductor they produce an additional electric field $\mathcal{E}_H$. Under equilibrium conditions, the side ways force on the moving carriers due to this field just balances that arising from the magnetic field.

The magnitude of the transverse Hall field $\mathcal{E}_H$, is found by equating the side wise forces -

$$e \mathcal{E}_H = e v B \quad \dots \quad \dots \quad \dots \quad (2.4)$$

The average velocity can be expressed in terms of the current density J and the conduction electron density n from the relation $J = nev$, and the result is

$$\mathcal{E}_H = (1/ne) JB = R_H JB \quad \dots \quad \dots \quad (2.5)$$

where the Hall constant

$$R_H = 1/ne \quad \dots \quad \dots \quad \dots \quad (2.6)$$

gives the carrier concentration directly. The experimentally observed quantity is the Hall voltage V_H , which is obtained from

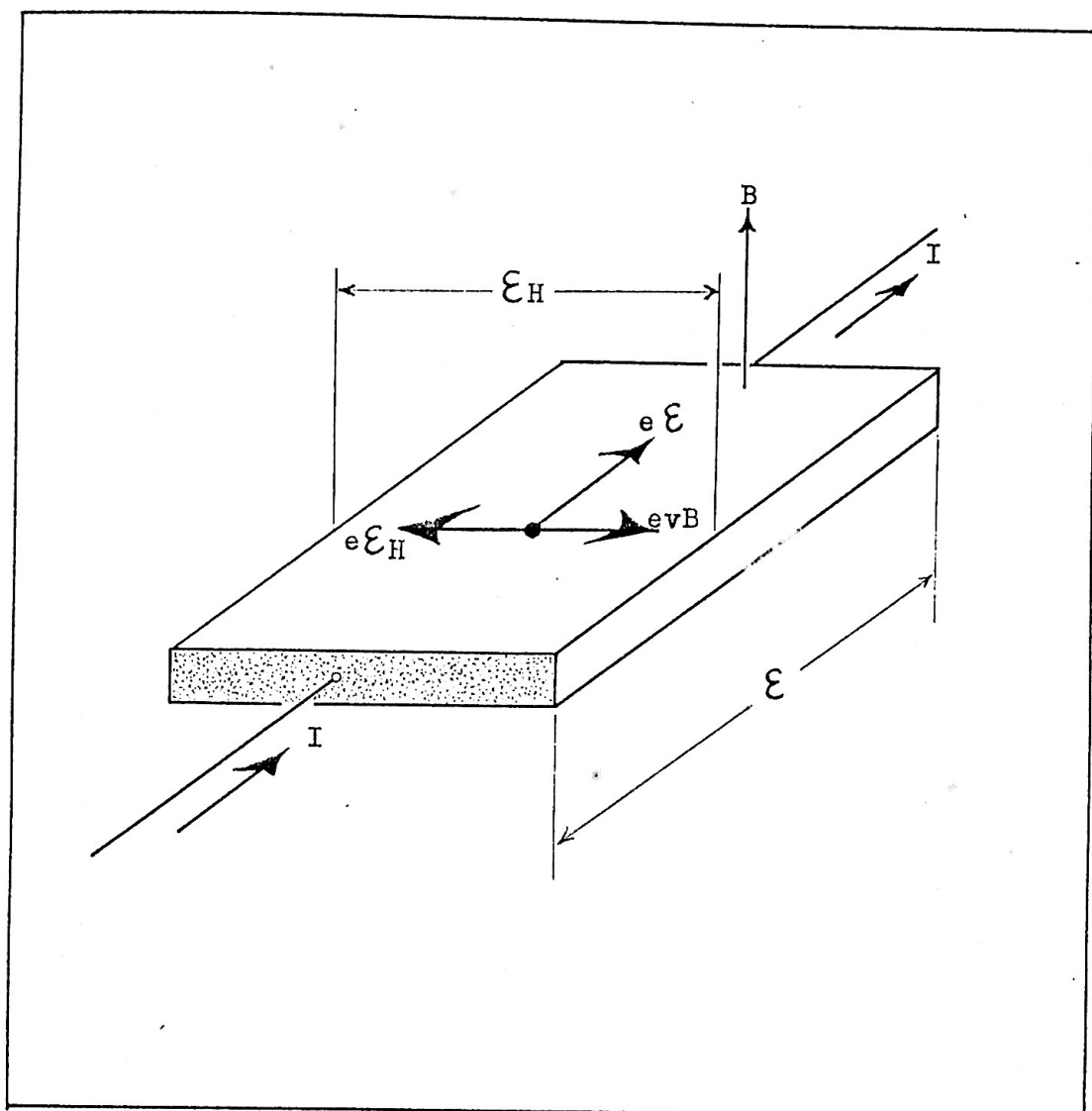


Figure 2.3 : The forces acting on a current carrier in a conductor placed in a magnetic field leading to the observable Hall field $\mathcal{E}_H$.

equation 2.5 since

$$\mathcal{E}_H = V_H/w, \text{ and } J = I/wt,$$

where w is the sample width and t its thickness. Therefore eqn. 2.5 becomes

$$R_H = 1/ne = V_H t / IB \quad \dots \quad \dots \quad (2.7)$$

In equation 2.7, e is the magnitude of electronic charge and the algebraic sign of the Hall voltage tells whether the carriers are holes or electrons.

This is a very simple treatment of the Hall effect which considers a spherical constant energy surface for the specimen. A more rigorous treatment for multivalley semiconductors with ellipsoidal constant energy surfaces leads to the following expression for the Hall constant⁽¹²⁾

$$R_H = (r/ne) \frac{3K(K+2)}{(2K+1)^2} \quad \dots \quad \dots \quad (2.8)$$

where r is a constant equal to 1 for degenerate semiconductors and K is the ratio of the longitudinal to transverse effective masses of the carriers. For our SnO_2 and In_2O_3 thin films the quantity $3rK(K+2)/(2K+1)^2$ is not very different from unity.

Hall mobility μ and Electrical Conductivity σ :

Hall mobility of the charge carrier in an electr-

ic field $\mathcal{E}$ is the average velocity of the electrons per unit electric field, i.e.,

$$\mu = v/\mathcal{E} \quad \dots \quad \dots \quad \dots \quad (2.9)$$

Combining this with the ohm's law $\sigma = J/\mathcal{E}$ we get the conductivity-

$$\sigma = ne\mu$$

or, $\mu = R_H \sigma \quad \dots \quad \dots \quad \dots \quad (2.10)$

Due to thermal energies the electrons and holes in a semiconductor are in rapid random motion colliding among themselves. If τ is the average time between such collisions then the rate of change of velocity is $-v/\tau$. Under steady state condition this rate of change must be equal to the acceleration due to the field $-e\mathcal{E}/m^*$. Therefore

$$e\mathcal{E}/m^* = v/\tau = \mu\mathcal{E}/\tau$$

$$\text{or, } \mu = e\tau/m^* \quad \text{and} \quad \sigma = ne^2\tau/m^* \quad \dots \quad \dots \quad (2.11)$$

In the above derivation the relaxation time τ has been assumed to be independent of the electrons' velocity v for simplicity.

For semiconductor with spherical constant energy surfaces it has been observed that over a considerable range of energies⁽¹²⁾

$$\tau = a E^{-r} \quad \dots \quad \dots \quad \dots \quad (2.12)$$

where r is a constant and a may vary with temperature. The value of r is generally derived from the observed variation of mobility with temperature and is dependent on the scattering processes. To determine the exact nature of dependence of τ on energy of the electrons is a fundamental problem of semiconductor physics.

2.5 VARIATION OF CARRIER CONCENTRATION WITH TEMPERATURE (FOR EXTRINSIC SEMICONDUCTOR)

The temperature variation of electron concentration n (or hole concentration p) may be seen in the following way. We consider only the region of partial ionization of the donors so that $n < N_D$ (or, $p < N_A$) where N_D is the donor density. Taking the case of n -type material ($N_D > N_A$), the rate of loss of electrons from donor centres to the conduction band is proportional to the number of filled donors $[N_D - (N_A + n)]$ and the number of empty conduction band states N_C . Thus it is given by-

$$k_1 N_C (N_D - N_A - n)$$

The rate of return of electrons to the donors states is proportional to the number of electrons in the conduction band n and to the number of empty donor states $(N_A + n)$ each of which must be counted twice (due to spin degeneracy). This rate is then

$$k_2 n [2 (N_A + n)]$$

At equilibrium these rates are equal, so that

$$n \left[2 (n + N_A) \right] / N_c \left[N_D - (N_A + n) \right] = k_1/k_2 = K \quad \dots \quad (2.13)$$

where K is the equilibrium constant a function only of temperature.

In classical approximation it is given by-

$$K = \exp \left[-(E_C - E_D)/k_B T \right]$$

where $(E_C - E_D)$ is the donor ionization energy, E_C is the conduction band edge and

$$N_c = 2(2\pi m_e^* k_B T/h^2)^{3/2}$$

is the effective density of states. For degenerate case N_c would be given by-

$$N_c = 4\pi/h^3 (2m_e^* k_B T)^{3/2}$$

If $n \ll N_A$, equation(2.13) reduces to

$$n = \left[(N_D - N_A)/N_A \cdot N_c/2 \right] \exp \left[-(E_C - E_D)/k_B T \right] \quad \dots \quad (2.14)$$

On the other hand if $N_D > n \gg N_A$, then equation (2.13) reduces to

$$2n^2/N_c N_D = \exp \left[-(E_C - E_D)/k_B T \right]$$

$$\text{or, } n = (N_c/2 \cdot N_D)^{\frac{1}{2}} \exp \left[-(E_c - E_D) / 2 k_B T \right] \dots (2.15)$$

where the pre-exponential term has a slight temperature dependence but is usually neglected. Equation (2.14) and (2.15) operate so long as the sample is extrinsic and remain outside the exhaustion range. In the exhaustion region where all the donors are ionized the electron concentration is approximately constant. The electron concentration where the (n vs. T) plot is horizontal equals the donor concentration N_D .

2.5.1 The Activation Energy :-

The simple activation energy related to the electronic conduction process of a material is often expressed by a conventional Arrhenius type relation-

$$\sigma = \sigma_{\infty} \exp (-E_a / k_B T) \dots \dots \dots (2.15a)$$

where E_a is the activation energy and σ is the electrical conductivity. For semiconductors the following two distinct cases may arise.

Case - I

Intrinsic semiconductor:- For n-type conduction, the carrier concentration in this type of material is expressed as-

$$n = (N_v N_c)^{\frac{1}{2}} \exp (-E_g / 2 k_B T) \dots \dots (2.15b)$$

where N_V and N_C are the carrier concentrations in the valence and conduction bands respectively, and E_g is the band gap. Since σ ($= ne\mu$) is directly proportional to the carrier concentration, n , at constant mobilities, the activation energy can be obtained by comparing eqn(2.15a) and (2.15b), and is given by-

$$E_a = E_g / 2 = \text{half the band gap} \quad \dots \quad \dots \quad (2.15c)$$

Case - II

Extrinsic semiconductor :- For extrinsic semiconductor additional trap levels are present in the regular band gap. Therefore the activation energies can be obtained by comparing equation (2.14) or eqn (2.15) with equation (2.15a). Two cases may again arise-

(i) Uncompensated semiconductor :-

In this situation $N_D > n \gg N_A$ and the activation energy is obtained from eqn (2.15),

$$E_a = (E_C - E_D) / 2 = \text{half the trap depth} \quad \dots \quad \dots \quad (2.15d)$$

(ii) Partly compensated semiconductor :-

In this regime $n \ll N_A < N_D$ and the activation energy is

$$E_a = (E_C - E_D) = \text{the trap depth} \quad \dots \quad \dots \quad (2.15e)$$

Compensated semiconductors behave like intrinsic material and the activation energy is comparable to half the band gap.

A sample may change from one category to other depending on its temperature. At high temperature, in extrinsic sample, intrinsic conduction may set in. From the above discussion it is however understood that the activation energy studies in semiconductors should be performed with great care.

2.6 THOMSON COEFFICIENT AND THERMOELECTRIC POWER

It has been observed that when a temperature gradient is imposed on a conductor an e.m.f is set up between its two ends under condition even when no electric current is drawn. This effect is a rudimentary conception of thermoelectric effect in conductors. Phenomenologically one may define at this point the Thomson coefficient, T_h , as the coefficient of proportionality relating the electric field and temperature gradient as follows -

$$E_x = -T_h (\partial T / \partial x) \quad \dots \quad \dots \quad \dots \quad (2.16)$$

Physically, the effect can be seen as the result of increased energy of electrons at the hot end of the material causing a diffusion of electrons towards the cold end; the charge imbalance caused by this diffusion sets up an electric field sufficient to oppose further flow of charge in this direction. A quantity commonly used to describe the effect is the thermoelectric power Q_{ab} . This refers to two materials denoted by a and b. If we have a circuit containing two junctions at A and B as shown in figure 2.4

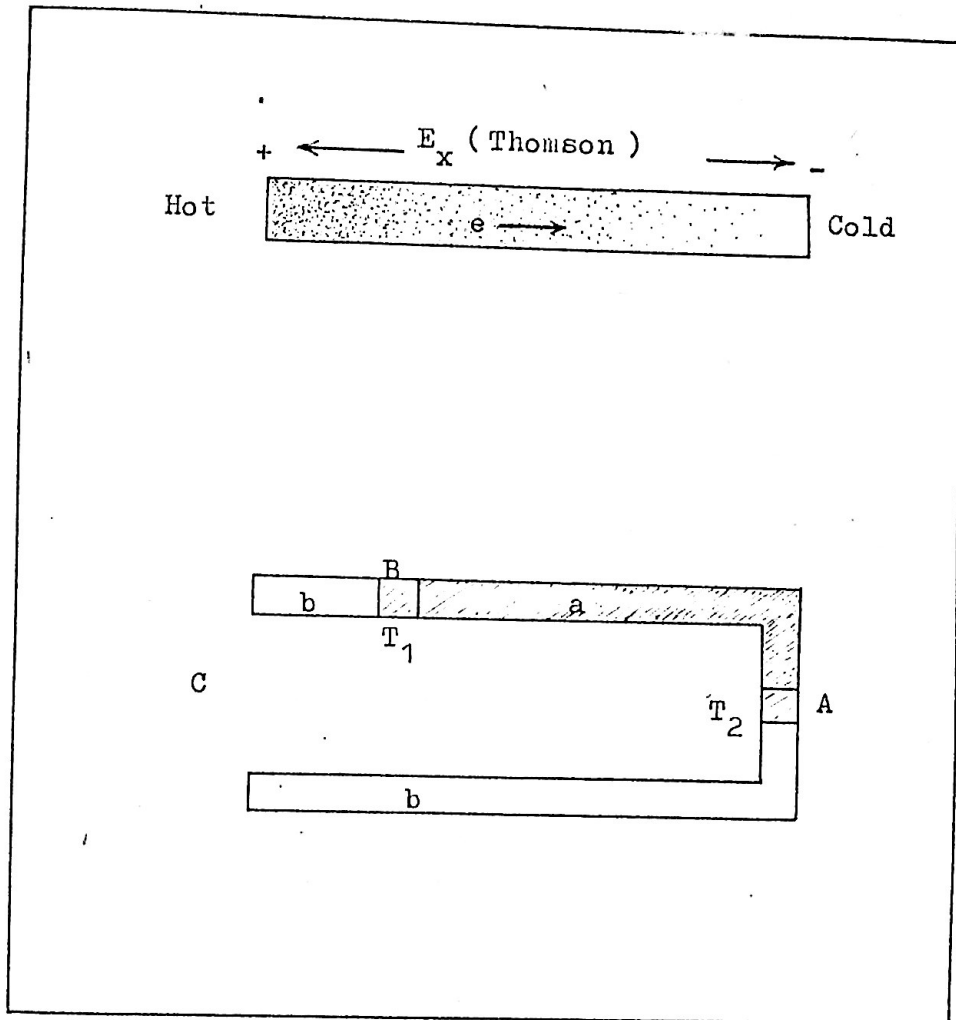


Figure 2.4 : Origin of thermopower in semiconductor.
A and B are two junctions in two types
of materials a and b .

at temperatures T_2 and T_1 , the material is being open at point C, (C may have other temperature T_0) the open circuit voltage V_0 at C is given by

$$V_0 = \int_{T_1}^{T_2} Q_{ab}(T) dT$$

If $T_2 = T_1 + \Delta T$, when ΔT is small, we have

$$V_0 = Q_{ab} \Delta T \quad \dots \quad \dots \quad \dots \quad (2.17)$$

This equation defines Q_{ab} the thermoelectric power of the material a with respect to material b, and is practically the specific thermoelectric power.

2.6.1 Absolute Thermoelectric power :-

If $T_h^{(a)}$ and $T_h^{(b)}$ are the Thomson coefficients for the two materials then from thermodynamical argument⁽¹³⁾

$$T_h^{(a)} - T_h^{(b)} = T (dQ_{ab}/dT) \quad \dots \quad \dots \quad (2.18)$$

If we choose for the material b one for which $T_h^{(b)} = 0$ (usually lead, Pb), and for the thermoelectric power relative to this material write $Q_{ab} = Q_a$, then Q_a is sometimes called the absolute thermoelectric power.

For non-degenerate semiconductor with scalar effective

mass m_e^* and relaxation time τ of the form $\tau \propto E^{-r}$, we have the expression for thermoelectric power⁽¹²⁾

$$Q(n,p) = \mp \left[(5/2 - r) - E_F/k_B T \right] k_B/e \dots \quad (2.19)$$

Q is negative for n-type semiconductor and positive for p-type, r is the scattering index and E_F is the Fermi energy with reference to the conduction band edge.

2.6.2 Degenerate Case :-

When the semiconductor is extrinsic and degenerate then the situation is more complex and the formula for Q may be given by⁽¹⁴⁾

$$Q(n,p) = \pm (k_B/e) \left\{ \left[(r+2)/(r+1) \right] \left[F_{r+1}(\eta^*)/F_r(\eta^*) \right] - \eta^* \right\} \dots \quad (2.20)$$

where, $\eta^* = E_F/k_B T$ is the reduced Fermi energy, and

$$F_r(\eta^*) = \int_0^\infty x^r \left\{ 1/[1 + \exp(x - \eta^*)] \right\} dx \dots \quad (2.21)$$

is the Fermi integral^(15,16). Here $r=0$ for lattice phonon scattering and $r=2$ for ionized impurity scattering.

2.6.3 The Position of Fermi Level :-

In the case of electronic semiconductor where the crystal binding is mostly ionic in nature, an expression for the thermoelectric power Q similar to equation (2.20) has been derived and exemplified for oxide semiconductor by R.W.Wright⁽¹⁵⁾. This is given by

$$Q = k_B/e \left\{ \left[(3/2) F_2(\eta^*) / F_1(\eta^*) \right] - \eta^* \right\} \quad \dots \quad \dots \quad (2.22)$$

where $F_1(\eta^*)$ and $F_2(\eta^*)$ are Fermi integrals given by equation (2.21) and the other symbols have their usual meanings. For SnO_2 and In_2O_3 thin films this equation (2.22) may be suitable for the determination of Fermi levels.

2.6.4 Effective Mass of Electrons :-

For semiconductors obeying Fermi-Dirac statistics the expression for carrier concentration is given by⁽¹²⁾

$$n = 4\pi/h^3 (2 m_e^* k_B T)^{3/2} F_{\frac{1}{2}}(\eta^*) \quad \dots \quad \dots \quad (2.23)$$

where $F_{\frac{1}{2}}(\eta^*)$ is again the Fermi integral and m_e^* is the effective mass of electrons in the conduction band. Let us put $m_e^* = Gm$, where m is the free electron rest mass and G is a constant. Then equation (2.23) can be rewritten as

$$F_{\frac{1}{2}}(\eta^*) = (h^3/4\pi)(2mk_B T)^{-3/2} n/G^{3/2} \dots \dots (2.24)$$

so that from a knowledge of either η^* or $n/G^{3/2}$ (effective electron density), the other can be determined at any temperature. η^* can be determined from equation (2.22) and measuring n by Hall experiment the value of G and hence m_e^* can be found.

If the semiconductor is non-degenerate then the effective mass of electrons can be easily determined from the expression⁽¹¹⁾ for thermoelectric power

$$Q = -86.2 \ln [4.7 \times 10^{15} R_H + (3/2) \ln(m_e^*/m) + (3/2) \ln T + 2] \mu V/^{\circ}K \dots (2.25)$$

where R_H is Hall constant and T is absolute temperature. This expression however gives good result only near room temperature.

2.7 SCATTERING PROCESSES

During the course of free electron's motion in a real crystal they suffer numerous collisions among themselves as well as with the lattice phonons and other crystal imperfections resulting in a phenomenon of scattering. The effect of any scattering interaction i may be evaluated by calculating the relaxation time τ_i associated with the process. The over all relaxation time τ may then be expressed by

$$1/\tau = \sum_i 1/\tau_i \quad \dots \quad \dots \quad \dots \quad (2.26)$$

It is clear that the scattering process which leads to the shortest relaxation time τ_i is the dominant one. Once the relaxation time τ is known, the mobility may be easily calculated.

The processes those can scatter carriers and therefore affect the mobility have been briefly described below.

2.7.1 Lattice Scattering :-

Carriers may be scattered in the lattice either by the (i) electric potential due to optical polarization of the lattice or by the acoustic lattice vibrations creating a lattice deformation potential via (ii) lattice dialation or via (iii) piezoelectric polarization field.

Optical mode scattering has been treated by many

theoretical physicists. For non-degenerate semiconductor Howarth and Sondheimer⁽¹⁷⁾ have given a very useful expression for the mobility-

$$\mu_o = \left[\hbar^2 / e (2k_B)^{3/2} \right] \theta_D^{-1/2} m_e^{*-3/2} \left[\epsilon_\infty / (\epsilon - \epsilon_\infty) \right] \left[\exp(\theta_D/T) - 1 \right] \\ \text{at } T \ll \theta_D \quad \dots \quad \dots \quad (2.27)$$

where θ_D is the Debye temperature, ϵ is the dielectric constant and ϵ_∞ is the high frequency(optical) dielectric constant. Similar formula for degenerate semiconductor may also be obtained⁽¹⁸⁾.

For SnO_2 (rutile) estimated value of θ_D is $\sim 500^\circ\text{K}$. Calculation by Bardeen and Shockley⁽¹⁹⁾ shows that the mobility, for scattering due to lattice dialation caused by the acoustic lattice vibration, is

$$\mu_a = (8\pi)^{1/2} \hbar^4 C_{ii} / [3 E_{1n}^2 m_e^{5/2} (k_B T)^{3/2}] \quad \dots \quad (2.28)$$

where, C_{ii} is the average longitudinal elastic constants and E_{1n} is the shift of the conduction band edge per unit dialation in ev.

Piezoelectric scattering may not be so important in SnO_2 thin films.

2.7.2 Impurity Scattering :-

Impurities in extrinsic semiconductors may remain as ionized or as neutral. Both of them may scatter carriers under

specific conditions.

2.7.2.1 Ionized impurity scattering :-

When the concentration of ionized donors or acceptors are high, the electrons suffer Rutherford scattering due to the presence of ions. For theoretical treatments Blatt⁽²⁰⁾ used partial wave method and discussed ionized impurity scattering in non-degenerate semiconductors. Using Kohn's variational principle in partial wave method Csavinszky⁽²²⁾ has analytically showed that this scattering process in the case of degenerate semiconductor can be adequately described by considering only the zeroth-order phase shift of the partial waves. Appropriate scattering potential for this purpose would be the screened Coulomb potential as used by Blatt having the screening length⁽²³⁾

$$R = (\pi/3)^{1/6} \hbar \epsilon^{1/2} (4\pi e m_e^{*1/2} n^{1/6}) \dots \dots (2.29)$$

beyond which the scattering potential is assumed to be negligible. ϵ is the dielectric constant of the medium and n is the carrier concentration. The expression for the total scattering cross-section Q_0 is then given by

$$Q_0 \approx (4\pi/k^2) \sin^2 \eta_0 \dots \dots (2.30)$$

where k is the wave number of the scattered particle and η_0 is the zeroth-order phase shift.

To determine an expression for the mobility, limited by ionized impurity scattering alone, one has to compute the average relaxation time $\langle \tau \rangle$ at first. τ in terms of the total scattering cross-section Q_0 , the number of scatterers N^+ , and the velocity of electrons v , is given by⁽²⁴⁾

$$\tau = (N^+ v Q_0)^{-1} \quad \dots \quad \dots \quad \dots \quad (2.31)$$

For degenerate semiconductor the above expression for average τ can be written as

$$\langle \tau \rangle = (N^+ v^F Q_0^F)^{-1} \quad \dots \quad \dots \quad \dots \quad (2.32)$$

where the superscript F indicates that the corresponding quantities are to be taken at the Fermi energy. Thus the expression for mobility is given by-

$$\mu_I = \langle \tau \rangle e / m_e^* = 0.323 e / (\hbar Q_0^F N^+ n^{\frac{1}{2}}) \quad \dots \quad (2.33)$$

2.7.2.2 Neutral impurity scattering :-

Neutral impurity scattering is relatively less important at about room temperature but may be important at low temperature limit. Erginsoy⁽²⁴⁾ has calculated the mobility associated with this type of scattering alone and obtained

$$\mu_n = m_e^* e^3 / (20 \epsilon N_0 h^3) \quad \dots \quad \dots \quad (2.34)$$

where N_0 is the concentration of neutral impurity centres.

2.7.3 Scattering at Dislocations :-

This form of scattering has been discussed theoretically by Dexter and Seitz⁽²⁵⁾. They showed that this type of scattering would not be significant unless the dislocation density exceeds 10^8 cm^{-2} . At a density of 10^{11} cm^{-2} scattering should be comparable to lattice scattering at room temperature. Dislocation appear as a charged cylinder in the path of an electron and causes scattering. The relaxation time for the process is given by

$$\tau_d = 3 / (8 R N v) \quad \dots \quad \dots \quad \dots \quad (2.35)$$

where N is dislocation density and R is the radius of the dislocation line and v is the velocity of the electron. This type of scattering is also unimportant at room temperatures but may be important at low temperature limit. For spray deposited samples dislocations are less important as have been mentioned earlier.

2.7.4 Scattering by Grain Boundaries :-

Grain boundary scatterings are very important for polycrystalline samples obtained either in bulk or in the form

of thin films.

From the grain boundary potential barrier theories it is found⁽²⁶⁻²⁹⁾ that the boundary regions are characterized by a potential barrier of height E_μ and a density of traps Q_t . They are related by

$$E_\mu = e^2 Q_t^2 / (8 \epsilon_0 n) \quad \dots \quad \dots \quad (2.36)$$

where n is the carrier concentration. The barrier height is also dependent on the grain size. However, depending upon the nature of this barrier height the scattering process and thereby the carrier transport process in the sample may be influenced either by the (i) thermionic emission of carriers over the barrier or by the (ii) quantum mechanical tunnelling or by the (iii) barrier reflection mechanism. A combination of all these different mechanisms may also be present. Due to all these possibilities the situation becomes very complex in degenerate semiconductors.

R.E.Jones et al⁽³⁰⁾ have pointed out that when $E_\mu \ll E_F$ for a strongly degenerate sample with the Fermi level E_F at least $2k_B T$ above the conduction band edge, quantum mechanical barrier reflection model would be appropriate and the relaxation time τ for the material with grain size L can be given by -

$$\tau_B = 2L \hbar^2 E / (m_e^* a^2 E_\mu^2 v) \quad \dots \quad \dots \quad (2.37)$$

Since $E = 1/2 (m_e^* v^2)$ is the energy of the electron having velocity

v , and $a = Q_c/n$ is the width of the square barrier of height E_μ , expression (2.37) thus takes the form $\tau \propto E^{-r}$ and gives the value of $r = -1/2$ for barrier scattering. It can be noted here that for pure lattice scattering $r = 1/2$. For strongly degenerate case the temperature broadening of the Fermi surface will only slightly change the velocity distribution of the electrons and thus barrier reflection leads to almost temperature independent scattering mechanism. On the other hand Petritz⁽³¹⁾ has pointed out that when thermionic emission of the carriers predominate then the associated mobility is strongly temperature dependent; whereas in the case of tunnelling, carrier transport is temperature independent⁽³²⁾.

The nature of grain boundary scattering in polycrystalline semiconductor is presently an interesting subject of study to many workers.

2.7.5 Carrier-Carrier Scattering :-

In highly degenerate electron gas model this type of scattering is important, but since the contribution is very small, they are generally neglected. In some cases, however, (discussed latter in this chapter) this type of scattering can play an important role in determining the band shape of the specimen. The effect of inter-electron collision on mobility has been discussed by Frohlich et al⁽³³⁾. When the effective mass of holes are larger than those of electrons then the electron-hole collision

may reduce the electron mobility.

2.7.6 Inter-valley Scattering :-

Inter-valley scattering⁽³⁴⁾ is important for semiconductors where a multivalley conduction band is present. Such scattering usually involves the participation of energetic phonons and hence is inelastic and strongly temperature dependent. This is however noticeable at high temperature only because at low temperature energetic phonons are not available.

2.7.7 Effect of Inhomogeneity on Mobility :-

It is usual that thin film samples may possess some inhomogeneity in their structure. This inhomogeneity has large effect on the carrier mobility. Such inhomogeneity may result from (i) anisotropic impurity segregation, (ii) impurity complex formation, (iii) formation of cluster in solid-solution samples or from (iv) composition fluctuations during growth.

The neighbourhood of an inhomogeneity is usually characterized by a space-charge region to which carriers suffer hard-sphere like collision. The mobility is therefore given by⁽³⁵⁾

$$\mu = (e/NS) (2m_e^*k_B T)^{-1/2} \dots \dots (2.38)$$

where N is the density of space charge region with effective scattering cross-section of S. This type of scattering is

prominent in high resistive materials.

2.8 OPTICAL PROCESSES

To investigate the optical behaviours of a semiconductor it is necessary to study its ultraviolet (UV), visible and infrared (IR) characteristics. SnO_2 and In_2O_3 thin films are transparent to visible radiation and therefore their UV and IR characteristics are important. Optical studies therefore should include absorption and reflection phenomena in these regions and transmission phenomenon in the visible region.

2.8.1 Inter Band Optical Transition and the Band Gap :-

When an electron in the valence band absorbs energy in some form it may make a transition to the conduction band under certain circumstances. When this transition between the bands occurs at the same value of the wave vector k then the transition is considered as vertical and is allowed. Non vertical transitions are nominally forbidden. For the simple case shown in figure 2.5(a) the absorption of radiation would be intense for all $h\nu > E_g$ and cease more or less abruptly at $h\nu = E_g$, where E_g is called the absorption edge or the optical band gap. These types of transitions do not involve any phonon for the conservation of energy. Therefore the transition is called direct. Bardeen, Blatt and Hall⁽³⁶⁾ have given an expression for the absorption process as

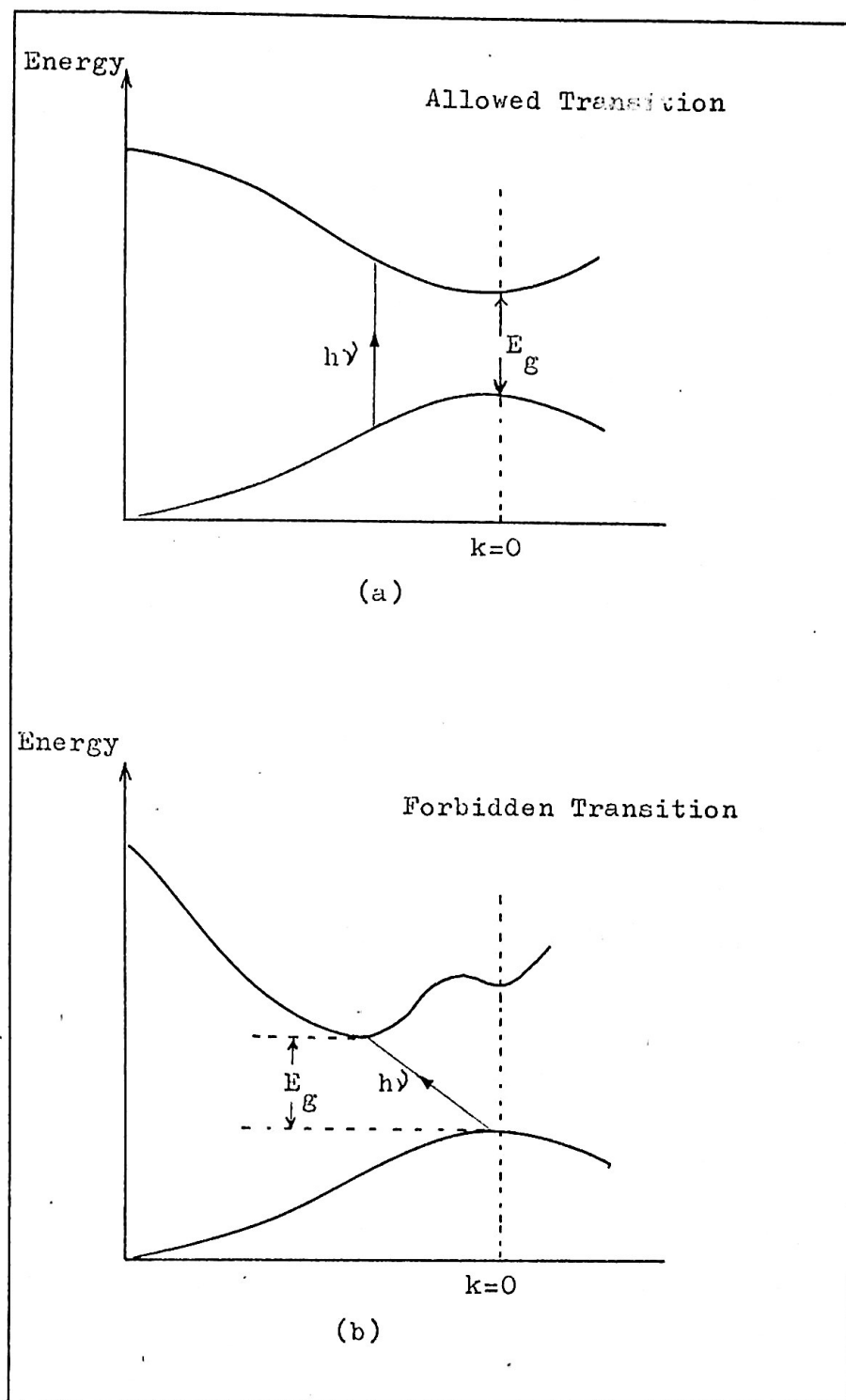


Figure 2.5 : Optical transition in semiconductor, .
 (a) Allowed transition, (b) Forbidden transition.

$$\alpha_d = B (h\nu - E_g)^s / h\nu \quad \dots \quad \dots \quad (2.39)$$

where $s = \frac{1}{2}$ for allowed transition and $3/2$ for the forbidden transition, B is constant and α_d is the absorption coefficient.

The process of indirect transition has also been treated by the same authors⁽³⁶⁾. This type of transition always includes phonons. The absorption coefficient is given by -

$$\alpha_i = A (h\nu - E_g \pm E_p)^s / h\nu \quad \dots \quad \dots \quad (2.40)$$

where $s = 2$ for allowed transition and 3 for forbidden one.

Allowed transitions are less probable in indirect process. Here E_p is the energy of the phonon absorbed (+) and/or emitted (-).

From all of these expressions it is clear that a plot of $(\alpha h\nu)^s$ vs $h\nu$ curve would give the value of E_g when carefully drawn for a particular transition process.

2.8.2 Dependence of Optical Absorption Edge on the Carrier Concentration : -

For degenerate semiconductor a dependence of the optical absorption edge on the carrier concentration is often observed. The effect has been explained independently by Moss⁽³⁷⁾ and Burstein⁽³⁸⁾ when they observed in InSb sample a shift of the absorption edge towards higher energy as a function of its carrier concentration.

In fact the magnitude of the shift is determined by two competing mechanisms. There is a band gap narrowing which is a consequence⁽³⁹⁾ of many body effects on the conduction and valence bands. This shrinkage is counteracted by the Moss-Burstein effect⁽³⁸⁾ which gives a band gap widening as a result of the blocking of the lowest states in the conduction band. At high carrier density, well above the Mott-critical density, (also depending on the level of doping) either of the two mechanisms may predominate. This effect has been observed very distinctly in both the SnO_2 and In_2O_3 thin film samples.

The Theory of the Shift (Moss-Burstein):

If E_{go} is the intrinsic band gap, then the energy E of the electron making a transition from some place of the valence band to the conduction band can be written as

$$E = \hbar^2 k^2 / (2 m_e^*) + E_{go} + \hbar^2 k^2 / (2 m_h^*) \quad \dots \quad \dots \quad (2.41)$$

at the same wave vector k . As the density of states in k -space is simply

$$dN/dk = 2 (4\pi k^2) \quad \dots \quad \dots \quad (2.42)$$

we obtain directly

$$dN(E)/dE = 8\pi \hbar^{-3} \left[2 m_r^*{}^3 (E - E_{go}) \right]^{1/2} \quad \dots \quad \dots \quad (2.43)$$

Here $N(E)$ is the density of states function and m_r^* is the reduced effective mass given by

$$1/m_r^* = 1/m_e^* + 1/m_h^* \quad \dots \quad \dots \quad (2.44)$$

Now integrating (2.43) over the range 0 to ΔE_g (figure 2.6) we get

$$N = \int_0^{\Delta E_g} dN(E) = [8\pi/(3h^3)] (2m_r^* \Delta E_g)^{3/2}$$

Thus the Moss-Burstein shift is given by

$$\Delta E_g^{MB} = (\hbar^2/2m_r^*) (3\pi^2 N)^{2/3} \quad \dots \quad \dots \quad (2.45)$$

This expression is exactly similar to equation (2.2) which gives the position of Fermi level in a degenerate semiconductor.

This is however a very simplified method of obtaining ΔE_g where the self energies due to electron-electron (e-e) and electron-impurity (e-i) scatterings have not been considered. If they are taken into account the expression for the shifted band gap can be represented by⁽⁴⁰⁾ -

$$\Delta E_g = \Delta E_g^{MB} + \hbar \sum_c (k_F, \omega) - \hbar \sum_v (k_F, \omega) \quad \dots \quad (2.46)$$

where $\hbar \sum_c$ and $\hbar \sum_v$ represent the self energies due to (e-e) and (e-i) scattering and can be derived by quantum mechanical

methods. In the above derivation it has been assumed that the conduction band is parabolic. But if the band is non-parabolic with a linear dependence of E on k for example; then we obtain⁽⁴¹⁾

$$\Delta E_g \propto N^{\frac{1}{3}} \text{ in place of } N^{\frac{2}{3}} \text{ in equation (2.45).}$$

2.8.3 Refractive Index of Transparent Films :-

Figure 2.7(a) represents a thin film with a complex refractive index $\eta = n_f - ik$ bounded by two transparent media with refractive indices n_0 and n_1 . Considering a unit amplitude for the incident light, and for normal incidence the amplitude of the transmitted wave is given by⁽⁴²⁾

$$A = t_1 t_2 \exp(-2\pi i \eta t / \lambda) / [1 + r_1 r_2 \exp(-4\pi i \eta t / \lambda)] \dots \quad (2.47)$$

in which t_1 , t_2 , r_1 and r_2 are the transmission and reflection coefficients at the front and rear faces. The transmission of the layer is given by -

$$T = (n_1 / n_0) |A|^2 \dots \dots \dots (2.48)$$

For transparent film (weak absorption) with $k^2 \ll (n_f - n_0)^2$ and $k^2 \ll (n_f - n_1)^2$, k being the extinction coefficient, T is given by

$$T = (16n_0 n_1 n_f^2 K) / [C_1^2 + C_2^2 K^2 + 2C_1 C_2 K \cos(4\pi n_f t / \lambda)] \dots \quad (2.49)$$

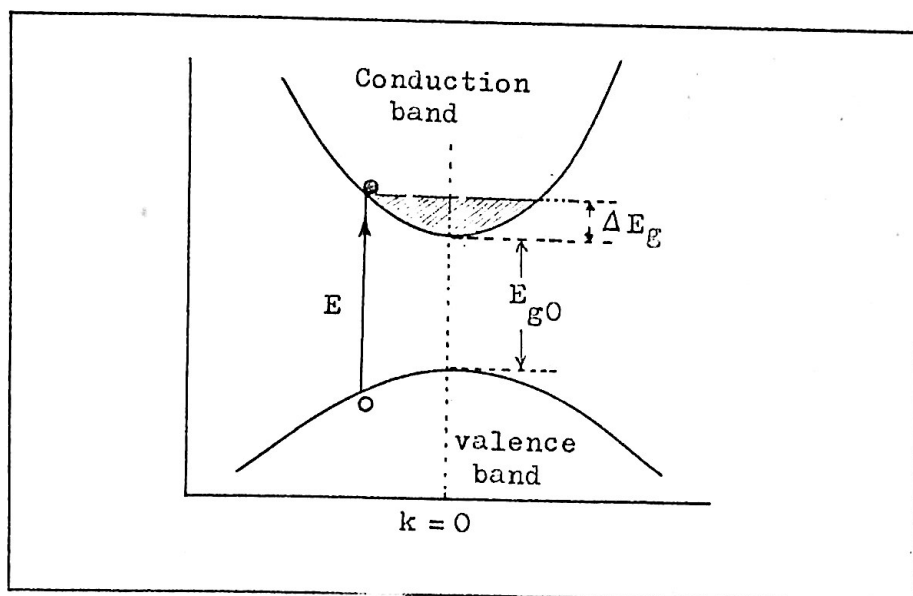


Figure 2.6

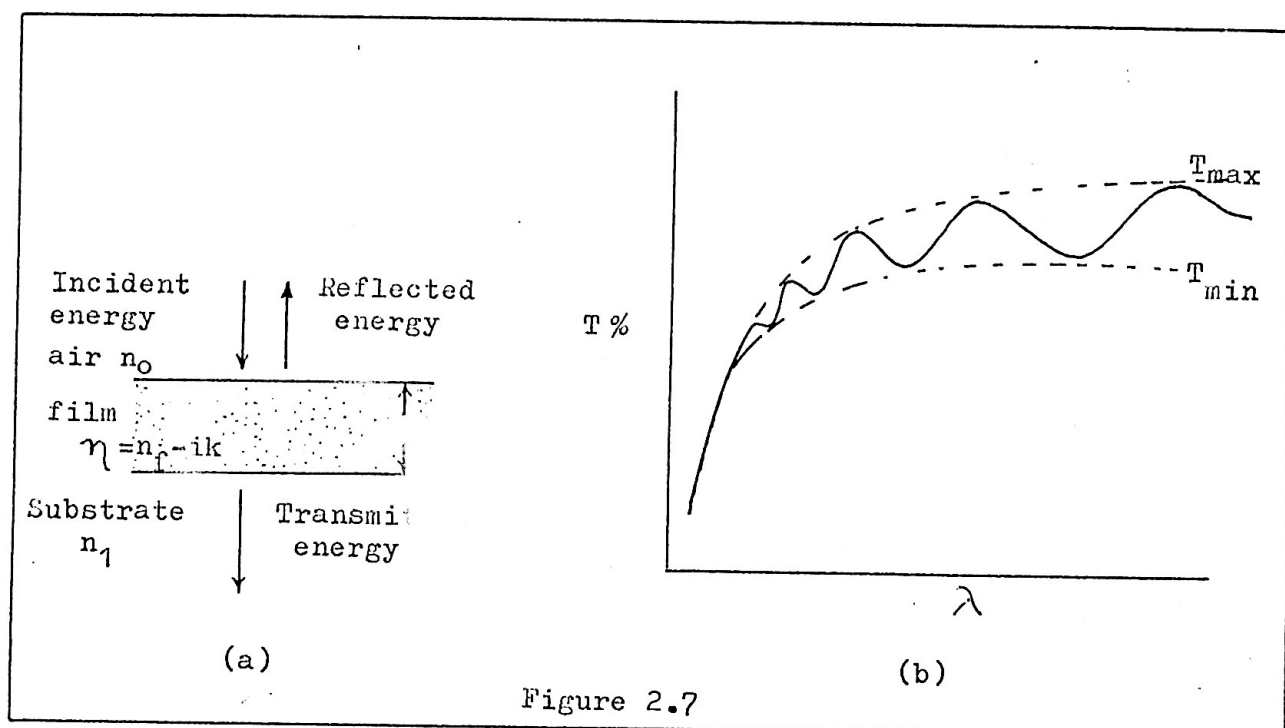


Figure 2.7

Figure (2.6) : Origin of Moss-Burstein shift .

Figure 2.7 : Typical transmission spectrum for a thin film of uniform thickness t .

where $C_1 = (n_f + n_o)(n_1 + n_f)$, $C_2 = (n_f - n_o)(n_1 - n_f)$ and

$$K = \exp(-4\pi k t / \lambda) = \exp(-\alpha t) \quad \dots \quad \dots \quad (2.50)$$

α is the absorption coefficient of the thin film.

Generally outside the region of fundamental absorption ($h\nu > E_g$) or of the free carrier absorption (at higher wavelengths), the dispersion of n_f and k is not very large. The maxima and minima of T in equation (2.49) occur for

$$4\pi n_f t / \lambda = m\pi \quad \dots \quad \dots \quad (2.51)$$

where m is the order number. Using equation (2.51) in (2.49) for transparent film on a nonabsorbing substrate we obtain⁽⁴²⁾

$$n_f = \left[N + (N^2 - n_o^2 n_1^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad \dots \quad \dots \quad (2.52)$$

where $N = (n_o^2 + n_1^2)/2 + 2n_o n_1 (T_{\max} - T_{\min}) / T_{\max} T_{\min}$

$T_{\max}$ and $T_{\min}$ are shown in figure 2.7(b).

2.8.4 IR Characteristics :-

In the transmission region the major IR losses are due to free carrier absorption within the film. The expression for the absorption coefficient α in this region can be derived from the classical dispersion relation for the complex dielectric function $\epsilon = \epsilon' - i\epsilon''$ for a free electron gas, where

$$\epsilon' = n_f^2 - k^2 = \epsilon_L \left[1 - \omega_p^2 / (\omega^2 + \gamma^2) \right] \quad \dots \quad (2.53)$$

$$\text{and } \epsilon'' = 2 n_f k = (\gamma / \omega) \omega_p^2 \epsilon_L / (\omega^2 + \gamma^2) \quad \dots \quad (2.54)$$

ϵ_L is the dielectric constant of the material if there are no free electrons, $\gamma = e / (m_e^* \mu) = 1/\tau$, τ is the relaxation time. The screened plasma frequency ω_p is given by

$$\omega_p = \left[4\pi n e^2 / \epsilon_0 \epsilon_L m_e^* \right]^{1/2} \quad \dots \quad (2.55)$$

or, the plasma edge,

$$\lambda_p = c_0 \left[(\epsilon_0 \epsilon_L m_e^* \pi) / n e^2 \right]^{1/2} \text{ in C.G.S. } \dots \quad (2.56)$$

Since the absorption coefficient

$$\alpha = 4\pi k / \lambda \quad \dots \quad (2.57)$$

therefore combining equations (2.53) to (2.57) we obtain

$$\alpha = (\lambda^2 e^3 n) / (4\pi^2 \epsilon_0 c_0^3 n_f m_e^* \mu) \quad \dots \quad \dots \quad (2.58)$$

where, c_0 is the velocity of light in free space, and other symbols have their usual meanings.

IR Reflectivity:

One of the important optical characteristics of SnO_2 and In_2O_3 thin films is their IR reflectivity. The reflectivity in the free carrier absorption region can be obtained by using $\rho = 1/ne\mu$ in the classical dispersion relation⁽⁴³⁾ as-

$$1 - R = 4 (\pi \epsilon_0 c_0 \rho / \lambda)^2 \quad \dots \quad \dots \quad (2.59)$$

The IR reflection for very thin films can be calculated very briefly using the impedance change description. In this case the impedance at the film surface is the sheet resistance of the film $R_{\square}$ shunted by the background impedance. If for simplicity the latter is assumed to be the same as in the foreground, i.e., the free space impedance $1/\epsilon_0 c_0 = 376 \Omega$, we obtain

$$R = (1 + 2 \epsilon_0 c_0 R_{\square})^{-2} \quad \dots \quad \dots \quad \dots \quad (2.60)$$

With some substitution we obtain for the IR reflection loss at high reflection level an approximate relation -

$$1 - R = (4 \epsilon_0 c_0 / e) / (1 / n t \mu) \quad \dots \quad \dots \quad (2.61)$$

A comparison of equation (2.58) with (2.61) reveals that both the losses cannot be minimized simultaneously.

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CHAPTER - 3

EXPERIMENTAL DETAILS

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EXPERIMENTAL DETAILS

This chapter deals with mainly the design and construction of different experimental apparatuses, and preparation of experimental samples (SnO_2 and In_2O_3 thin films) on glass substrates. Various experimental methods which were adopted throughout the course of the work for the analysis of the structural, electrical and optical properties of the deposited films have also been described here.

3.1 INTRODUCTION

It is already known that the process of spray deposition is one of the simplest and least expensive one of all the film deposition methods available to date. Because of this extreme simplicity one has to face a number of difficulties in controlling the process variables. Moreover the qualities of the deposited films are relatively inferior to those of films obtained in other complex methods. Experimental arrangements have been put forward by many workers⁽¹⁻⁸⁾ to promote ease of operation and to overcome difficulties which were often encountered at the time of film deposition. But still more work is needed to improve the process of deposition and to

reduce the cost of production, since for solar cell and other device technology the low cost production of semiconducting thin films has become a necessary precondition.

Pyrosol process^(8,9) is a chemical spray deposition process where an aerosol is prepared from the working solution in one section of the apparatus and simultaneously carried to the other section where pyrolysis of the aerosol takes place. We have described in the following sections a new apparatus for this process. It could be mentioned here that like the SnO_2 and In_2O_3 thin films, several other semiconducting thin films of binary and ternary compounds such as ZnO , CdS , CdTe , CuInSe_2 etc. can also be easily prepared by this apparatus only by adjusting some of the parameters of the process.

It was observed that in all spray deposition process common defects like the surface roughness and thickness inhomogeneities of the deposited films are often encountered. Therefore the role of the deposition apparatus is very important in preparing good quality films free from these defects.

3.2 DIFFICULTY WITH THE CONVENTIONAL PNEUMATIC SPRAY SYSTEM

It is an inherent property of a pneumatic spray gun that it produces spray particles of various sizes at the exit nozzle whatever fine the nozzle is. Sometimes the size of the droplets depends on the cone angle covered by the spray

particles^(10,11). This creates difficulty in the film deposition process. The chemical reaction which is a fundamental mechanism of the process, takes place in the vapour phase. Droplets of different sizes reaching at the same site of the substrate at a constant temperature would take different fraction of time for their vaporization and reaction. Therefore an unwanted interaction between the reacted and unreacted species may take place at the substrate surface which results in films that are not uniform in structure and are also inhomogeneous in composition.

To obtain good results therefore, the uniformity and fineness both of these physical qualities of the spray particles are to be assured first. To prepare a good sprayer it is thus necessary not only to make the spray nozzle with care, but also it is equally important to try to filter the produced spray particles so that a very fine and uniform droplet size could be obtained at the output. With this end in view we proceed to design a new apparatus for the spray system.

3.3 DESIGN OF A NEW SPRAY DEPOSITION APPARATUS

The spray deposition apparatus obviously should perform a number of functions e.g., the production of aerosol, their filtration for uniformity, transport of them to the reactor section and formation of films. The different stages of

the apparatus required for these purposes are described below.

3.3.1 The Spray Nozzle and its Modification :-

The spray nozzle consists of two capillary glass tubes fitted at right angle to each other as shown in figure 3.1(a). When compressed air is passed rapidly through the upper tube P in a direction tangential to the mouth of the lower tube A, a partial vacuum is created at the upper part of the tube A whose lower end is kept immersed in the spray liquid. Due to this partial vacuum the liquid rises up through the tube A and the compressed air drives it away in the form of fine spray particles (aerosol). The thinner the spray nozzle the finer would be the spray particles.

This type of spray guns have been directly used by many of the earlier workers for the deposition of thin films of various materials⁽¹⁻⁷⁾. The problem of nonuniformity of droplet size remains with this type of spray guns.

Modification :⁽⁹⁾

During the course of the present work this conventional spray gun system has been modified in a way as shown in figure 3.1(b). Here the spray gun has been kept in a large capacity (> 1500 ml) round bottom flask F having a little protuberance at the bottom and an outlet at the top where a bent pipe C

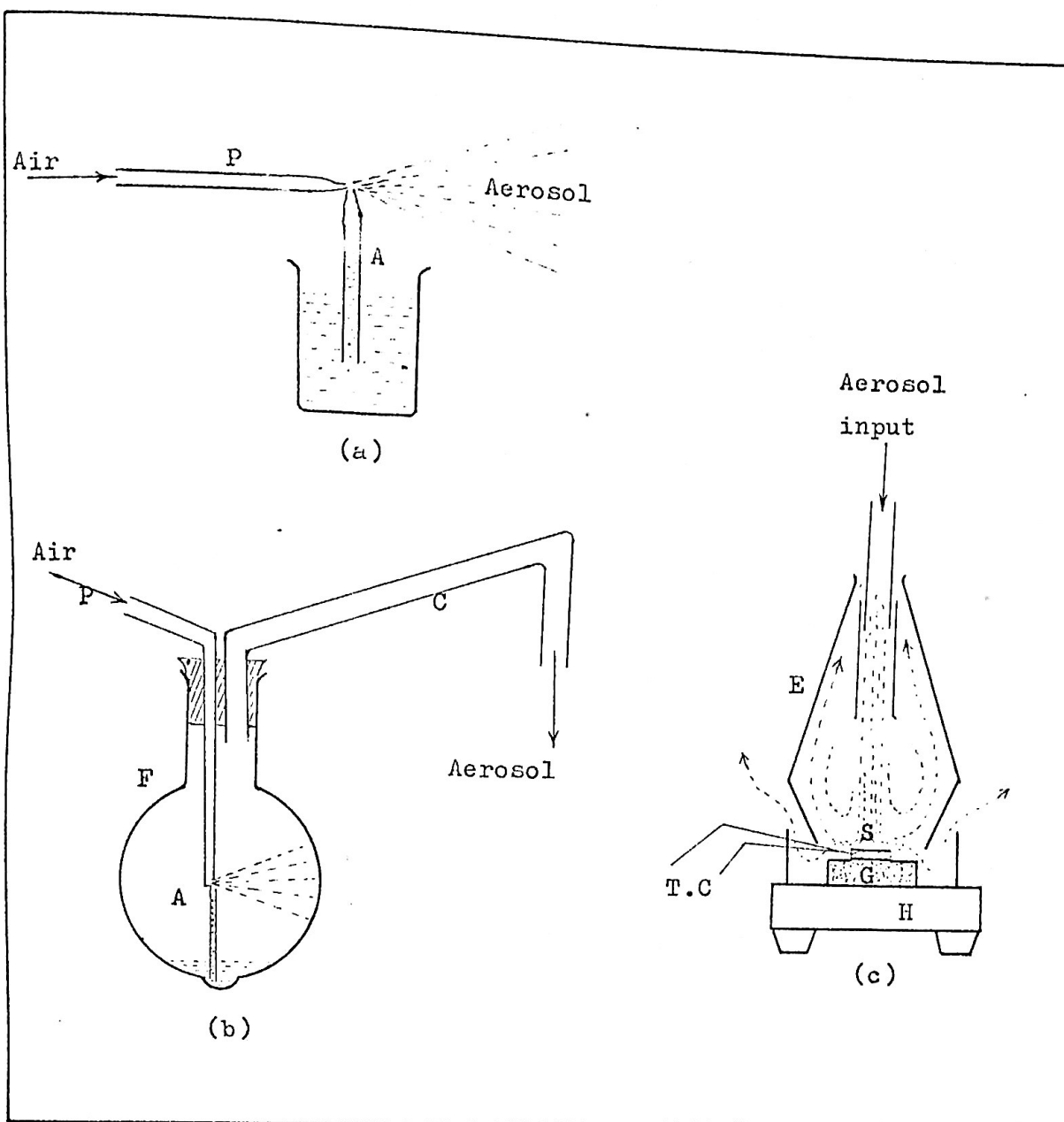


Figure 3.1 (a): Conventional pneumatic spray gun ;
 (b) and (c) are respectively the spray system and the
 pyrolysis reactor designed in our laboratory.

is fitted. The protuberance is blown there because a very small amount of fresh liquid (~ 5 ml) can then be used at each run without wastage.

Aerosol is produced in the flask and during their way out of it through the pipe C they are automatically separated into heavier and lighter droplets due to the action of vertical air current and gravitational effects. It is then more likely that the larger droplets would be coalesced in the flask and/or in the conduit pipe C and finally drop down again in the flask to be fed back. The lighter and relatively smaller droplets on the other hand, will be carried by the same incoming carrier gas to the reactor zone. This is how a virtual filtration process works in the spray system producing almost uniform and very small droplet size at the outlet of the sprayer.

Other facilities which are associated with this arrangement are -

(a) the rate of flow of the working solution can be controlled to a better accuracy by suitably designing the nozzle A and adjusting the air flow rate. For example, in preparing SnO_2 film the solution flow rate was kept constant to 0.25 ml/min, which is 10-100 times less than used by the earlier designers⁽¹⁻⁷⁾.

(b) Due to this small flow rate, the time of deposition is increased which provides a better thickness control and larger grain size⁽⁵⁾ of the film.

(c) Extra loss of working solution which was apparent in conventional setups⁽¹⁻⁷⁾ can be greatly minimized by fixing the flow rate to its required lower limit.

(d) Very fine droplets obtained at the reactor section are easily vaporizable and require no extra pre-heating furnace⁽⁵⁾. This saves excess power consumption.

The system is therefore economic in all respects.

3.3.2 The Design of the Reactor :-

The design of the reactor is shown in figure 3.1(c). It is a vertical batch type reactor composed of a stainless steel enclosure E having a pyrex glass jacket inside, a heater H, and a heat susceptor thick graphite block G. Substrate is placed on the susceptor, and the temperature of the substrate is monitored by a chromel-alumel thermocouple T.C. For different temperature requirements the heater power is controlled accordingly. For the rapid expulsion of the byproduct gases there are openings at the side and at the top of the reactor. The double cone shape of the reactor wall E has two fold action. It helps focussing the incoming aerosol towards the substrate S and also provides a chimney action to the exhaust gas upwards.

This reactor system is an intermediate case of a hot-wall and a cold-wall reactor (described in the previous chapter). The chemical reactions (eqn. 1.1 and eqn. 1.2) which occurs

in the reactor are both endothermic and therefore a cold wall reactor should be adequate as mentioned in chapter- 2. But since the incoming aerosol for the reactor is cold, this will give a tremendous thermal shock to the heated substrate and the glass substrate may be cracked at once. Moreover the reaction process would be disturbed due to a rapid fall of substrate temperature. To overcome these difficulties the temperature of the reactor wall should be maintained at a level much higher to the room temperature but lower to that of the optimum substrate temperature or the reaction temperature. This temperature is maintained automatically here by the metallic enclosure E placed over the heater H, and thus it can provide a pre-heating action easily to the input aerosol. Hot-wall reactors are seldom used for these purposes^(4,5).

3.3.2.1 The heater :-

The heater H is an ordinary hot plate 2 kwatt nichrome wire heater. The top of the plate is covered by a piece of asbestos sheet with a small opening at the centre where a mica sheet is attached. A thick stainless steel or graphite plate G (fig.3.1(c)) is placed on this mica sheet. Substrate is placed on this susceptor plate G to have a uniform temperature throughout the substrate surface. Another mica sheet is placed on this susceptor block to protect it from chemical corrosion. The heater

power is controlled by an electronic power controller.

3.3.2.2 The fume chamber :-

It is a large box type chamber with a slanting top and is provided with a chimney. There is an exhaust fan with regulated power supply fitted at the mouth of the chimney. The slanting top and the side walls are made of glass. There are air tight doors in the front side. The chamber has purging facilities. The whole spray system and the reactor are kept inside this fume chamber at the time of film deposition because of

(i) safety grounds and

(ii) to check air current disturbances at the deposition site.

These two points just stated, are very important for the pyrosol process when deposition is carried out in open air atmosphere.

3.3.3 The Carrier Gas :-

The carrier gas is chosen for its suitability in relation to the chemical reaction taking place. For instance, for the deposition of an oxide layer air may be used, so as to supply the oxygen needed for the reaction. In other cases a neutral gas such as nitrogen, argon or helium may be used. In the present experiments compressed dry air from an air compre-

essor has been used as carrier gas. The pressure of the gas is to be maintained constant and appropriate to the requirement of the spray rate. We have found 20 psi pressure as standard for the spray system.

3.3.3.1 The air compressor :-

It is a reservoir type electrical air compressor. A rotary pump in its suction mode draws atmospheric air and keeps it reserve in a large capacity air tank. At the outlet of the tank a pressure gauge is attached which records the pressure of the air at the time of supplying it from the tank. There is a by-pass control valve which can keep the output pressure constant. The air was passed through a silica gel column to make it dry before passing it into the sprayer.

3.4 SELECTION OF THE SPRAY SOLUTION

(a) Source compound :

The choice of the source compound must satisfy a number of essential conditions ; it should be a stable compound at room temperature, it should not oxidize in air or in the presence of water at room temperature, it should have a decomposition temperature below 500°C and preferably higher than its boiling or sublimation temperature.

For SnO_2 and In_2O_3 thin films (anhydrous or hydrated) SnCl_2 or SnCl_4 and InCl_3 may respectively be used as the source compounds. SnCl_2 or SnCl_4 is available in the form of liquid but InCl_3 is a crystalline solid at room temperature.

(b) Solvent :

The type of solvent is chosen in relation to the source compounds. The concentration and viscosity of the solvent must permit a high aerosol flow rate. Since the spray system used in the present experiment operates via a partial vacuum path at the mouth of the spray nozzle, the concentration of the solution prepared by the solvent should be such that it could at least be drawn by the nozzle. The higher the solution concentration the lower would be the spray rate. It is preferable to select a solvent that is not easily inflammable to avoid sudden combustion in the reactor. The most commonly used solvents are water and methanol. We have used water to facilitate hydrolysis and ethyle alcohol ($\text{C}_2\text{H}_5\text{OH}$) as diluent. Since the surface tension of alcohol is small it can also produce finely dispersed aerosol more easily.

3.4.1 Composition of the Ionic Solution for SnO₂ film.

A mixture of fuming SnCl₄, deionized water and pure alcohol in the ratio 1:2:6 by volume was taken as the ionic solution. This composition was selected arbitrarily so as to keep the specific gravity of the solution nearly equal to unity. This is a 0.94 molar (M) solution of SnCl₄ in a mixture of water and alcohol. It is always preferable to keep the solution concentration constant to assure a constant flow rate. Other composition of the ionic solution may also be taken.

For doped SnO₂ films antimony (Sb) in the form of SbCl₃ and fluorine (F) in the form of NH₄F and HF were used separately in different runs with the working solution. For the present study 0.3 to 6.0 mole per cent (m%) of Sb-doping and 4 to 70 mole percent of F-doping have been taken in SnCl₄. It is to be noted here that Sb is a cationic dopant whereas F is anionic. Since HF can attack glass wares, in measuring HF therefore a plastic pipette should be invariably used.

3.4.2 Composition of the Ionic Solution for In₂O₃ films :-

Since InCl₃ is a solid, it is easier to express the concentration of the ionic solution in terms of molarity (M). We have used a mixture of equal volume of water and alcohol as an adequate solvent for InCl₃ solution. After trying with

solutions of different concentrations from 0.1 M to 1.0 M, we find 0.44 M solution as a better one for In_2O_3 films. The specific gravity remains slightly greater than unity at this concentration and is kept constant for the present studies.

For Sn-doped In_2O_3 films Sn-doping has been achieved by using SnCl_4 as dopant. We have studied 1-16 mole % of Sn-doping in In_2O_3 films.

For all the doped films dopants were always used with the working solution. Purity of the chemicals used in the present work were of reagent grade and supplied by E.Merk, Germany. All the working solutions were acidic in nature.

3.5 SUBSTRATE CLEANING

The cleanliness of the substrate surface exerts a decisive influence on film growth and adhesion. A thoroughly cleaned substrate is a pre-requisite for the preparation of films with reproducible properties. The choice of cleaning techniques depends on the nature of the substrate, the type of contaminants and the degree of cleanliness required. We have used glass substrates (supplied by the Corning Glass Works U.S.A) which were ordinary microscope slides and cover slides and therefore residue from manufacturing and packaging, lints, fingerprints, oils and air borne particulate matters were supposed to be the contaminants.

The following procedure was found adequate for substrate cleaning in our laboratory. The gross contaminations of each of the substrates are first removed by luke warm aqueous solution of sodium carbonate in an ultrasonic cleaner. After washing in a stream of cold water they are dipped at first into nitric acid for some time and then into chromic acid mixture (potassium dichromate in sulphuric acid) for several days. Taking them out of the chromic acid bath one by one they are washed and thoroughly rinsed with deionized water several times and finally made dry by blowing hot air. They are then preserved in desiccator. The water-break cleanliness test⁽¹²⁾ was performed for the substrates before the deposition of films onto them. During the whole process the substrates were always held by slide-holding forceps.

3.6 SHAPE OF THE SAMPLE AND PREPARATION OF MASKS

For the purpose of various experimental studies, films of specific size and shape are required. Masks are used for this purpose. These are suitably shaped apertures through which deposition is made to get a desired pattern of the film. In the case of chemical spray deposition process it is needless to say that the mask materials should be inert to the chemicals used for the process. We found mica and stainless steel as suitable masking materials, because they are chemically inert and

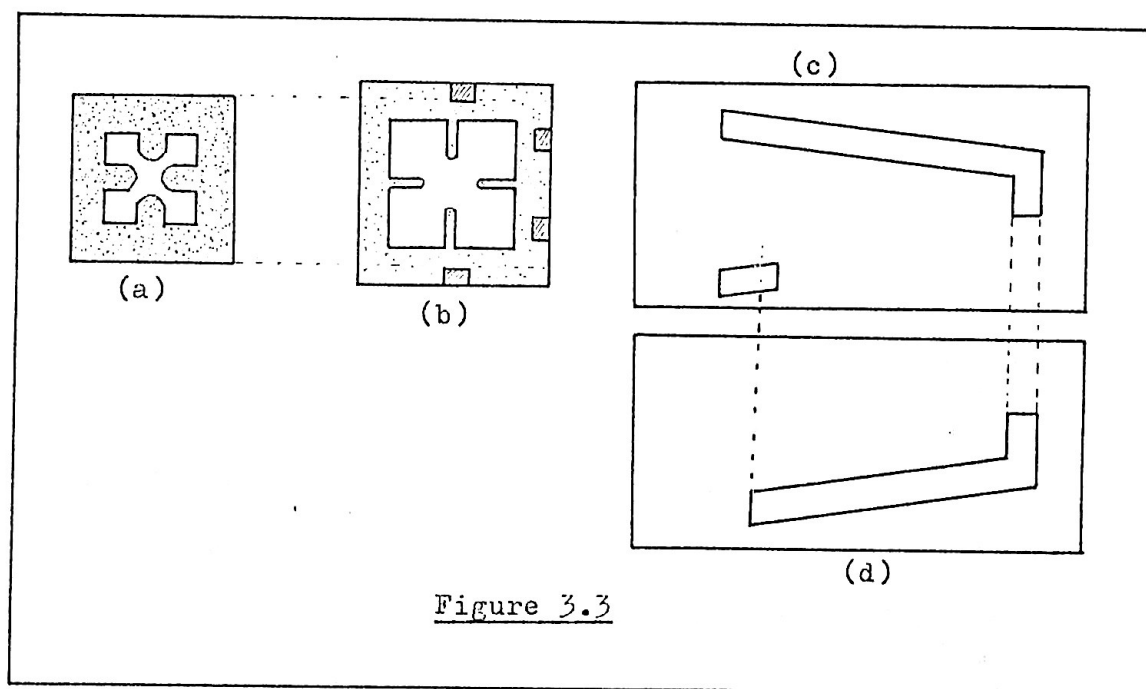
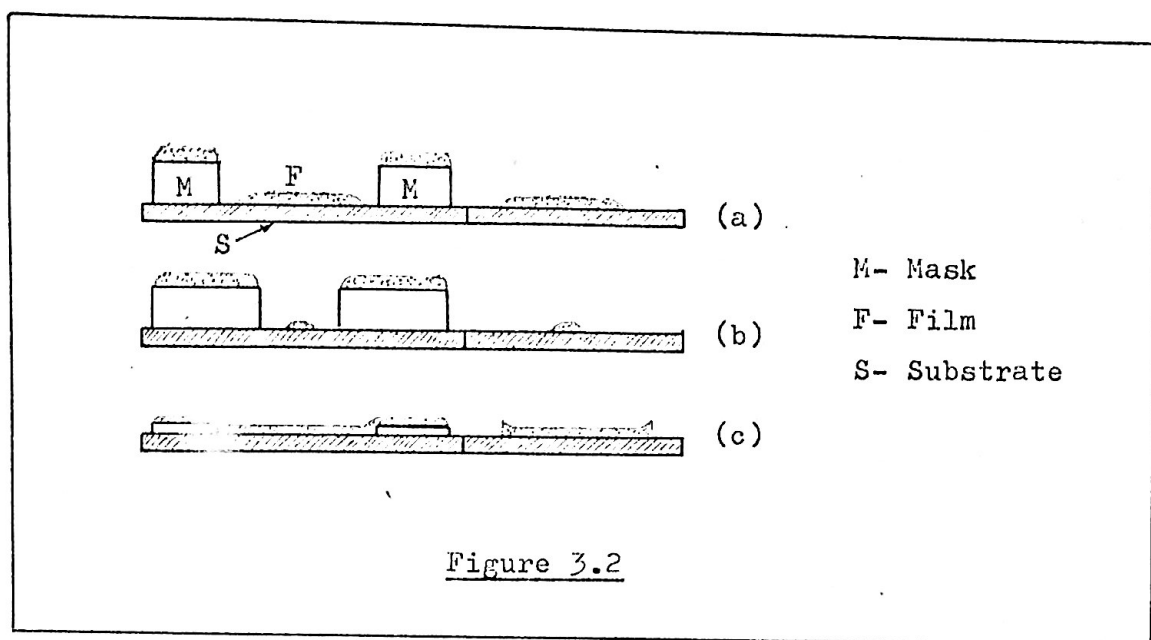


Figure 3.2 : The effect of size of mask on the deposited film in pyrosol process.

Figure 3.3 : (a) Mica mask with the design cut on it,
(b) A stainless steel frame to hold the mask and the substrate intimately in contact,
(c) Mask to deposit Pb-film for thermopower reference contact,
(d) Mask to deposit experimental sample for the thermopower measurement.

can withstand high temperature. Since the film thicknesses are of the order of $0.2 - 0.4 \mu\text{m}$ the mask should be as thin as possible so as to obtain uniformity of thickness throughout the film pattern. The smaller is the dimension of the pattern the thinner should be the mask. The effect of the mask thickness on the film size and uniformity has been clearly illustrated in figure 3.2(a), (b) and (c). Since it is assumed that in pyrosol process vapour phase reaction takes place at the substrate surface or at its close vicinity this effect is therefore very important and should be taken into account. An almost single layer mica sheet may then be adequate for preparing masks.

Van der Pauw's method⁽¹³⁾ was adopted for the measurement of resistivity and Hall mobility of our samples. A suitable mask as shown in figure 3.3(a) was therefore used so that the deposited film assumes the shape of Van der Pauw specimen. Figure 3.3(b) shows a stainless steel frame that can hold the mask on the substrate intimately in contact with each other. Figure 3.3(c) and (d) are masks to prepare samples for thermopower measurement. Mask (c) is made of mica sheet and is used for SnO_2 and In_2O_3 films but (d) is made of stainless steel or aluminium foil and is used to deposit metal (Pb) film as contact to SnO_2 or In_2O_3 films. Metal contact was prepared by vacuum evaporation method. The patterns shown in figure 3.3 are cut in the mask materials. Due to the very delicate and brittle nature of a thin mica sheet a great care is needed to prepare these masks. A freshly cleaved

mica was always used to avoid cleaning procedures.

Apart from using masks post-deposition etching procedures were also required. For SnO_2 film zinc-dust in HCl is the best and rapidly etching material. Covering the film surface by paraffin wax the required shape was marked on the wax layer. The unwanted portion of the film was then etched out by Zn-dust in HCl. After completion of etching the wax was removed from the film surface by using organic solvent. The required pattern of the film was thus obtained.

3.7 FILM DEPOSITION PARAMETERS

Because of the reversibility of the chemical reactions (1.1) and (1.2) the structure, composition and other characteristics of the deposited films depend on a number of deposition parameters (process variables), such as the temperature of the substrate, the flow rate of the aerosol and carrier gas, deposition time, quality of the substrate material, size of the atomized spray particles, concentration of the ionic solution, distance between the substrate and the source (mouth of the pipe supplying the aerosol) and the doping levels for intentionally doped films. Obviously the substrate temperature is the most important factor and must be controlled with care.

In preparing films for the present work all of the above parameters except (i) the deposition time t_d , (ii) the sub-

trate temperature T_s , (iii) the concentration of the solution and (iv) doping levels were kept unchanged. To study the effect of any one of these four parameters on the film properties the remaining other should be kept reasonably constant.

To achieve uniformity of thickness and the homogeneity of the film, air current disturbances become another parameter. It has also been noticed that in depositing photosensitive films such as ZnO, CdS etc. control of light at the deposition site becomes necessary. The whole fume chamber should then be covered externally by a black screen.

3.8 FILM DEPOSITION

Prior to the deposition of film the whole setup should be properly cleaned. A little amount of spray solution (≈ 5 ml) is taken in the flask F fitted up with the spray nozzle A (Fig. 3.1b). A clean substrate with a suitable mask is put on the susceptor of the heater H. Before supplying the compressed air the heater is kept on for some time so that the substrate and the reactor wall E attain the requisite temperature. The substrate temperature T_s is to be kept at a level slightly higher than the required substrate temperature because at the onset of deposition a slight fall of temperature is likely.

When compressed air is passed through P at a cons-

tant pressure (~ 20 psi), a fine aerosol cloud is produced in the flask and is automatically carried to the reactor zone where film is deposited on the substrate. 4 to 5 minutes of spray produces SnO_2 film of thickness about $0.2 \mu\text{m}$ at a substrate temperature of $T_s = 400^\circ\text{C}$. To deposit In_2O_3 films of similar thickness the time required is 8-10 minutes at similar range of substrate temperature.

3.8.1 Film Thickness Control : -

Deposition time t_d is the main thickness controlling factor in the present spray deposition process, provided the other parameters remain constant. Since the deposition is carried out in normal atmosphere a direct and insitu control of thickness t is not so easy. To control the film thickness therefore calibration charts may be used. These charts are generally t_d vs. t plots, and should be prepared at different constant substrate temperatures prior to the preparation of a particular experimental sample using the same solution and deposition variables. Since the rate of deposition in the present setup is rather small, the thickness control is therefore easy.

3.8.2 Evaporation of Metal Film for Contact :-

For the measurement of thermoelectric power, lead (Pb) has been used as a reference contact material. Pure metallic lead has been thermally evaporated on a requisite substrate at a pressure of $\sim 10^{-4}$ torr in Edward's high vacuum coating unit (Model 6E). Evaporation was carried out from a molybdenum boat.

3.9 OPTIMIZATION OF THE DEPOSITION PROCESS

To optimize the deposition process one should have to select at first the requirement with respect to which the process is to be optimized. Since there are several process variables, the optimization process would therefore be lengthy. We have selected the high transparency as well as the high electrical conductivity (or in other word the high figure of merit) of the films as our basic requirement. We have proceeded to optimize the process under certain limitations and it cannot be taken as the ultimate optimization.

First a set of films was deposited at various substrate temperatures T_g keeping all other deposition variables constant at an arbitrary level. From this set of films the substrate temperature T_g was selected corresponding to the best conducting and transparent film. Then at this temperature T_g

films were again deposited by varying only the distance between the substrate S and the exit of the conduit pipe C (may be called source). From this set of films the best one was taken to fix the distance d between the substrate and the source. Keeping this distance d and temperature T_s as fixed the pressure P of the carrier gas was then varied and a third set of films was deposited. From this set the adequate pressure P of the carrier gas corresponding to the best film was selected. Since the process variables are to some extent mutually interdependent, the resulting optimization was undoubtedly a tentative one. We found $d = 20$ cm for SnO_2 film and 8-10 cm for In_2O_3 film to produce the best result at a pressure of 20 psi of the carrier gas. All the experimental samples for our present work have been prepared by taking this value of d and pressure P .

3.10 LEAD ATTACHMENT TO THE FILM

Usually, two methods are used for attaching lead to thin films; (i) solid phase bonding and (ii) alloy bonding. The solid phase bonds are formed by thermocompression and ultrasonic means whereas, the alloy bonds are formed by soldering.

In the present work, metallic indium (without flux) was used as soldering material to make electrical contacts. Since the experimental samples were very hard, good contacts were obtained by indium. Indium dots were first soldered to the clean film surface. One end of a clean fine copper whisker was then wetted by indium and then placed in contact with the indium dot on the film and the whisker was heated with the help of a 25 watt fine tip soldering iron. The applied heat just melted the upper part of the indium dot and made a good ohmic contact with the film. Slight pressure was sometimes applied to the contact points to make it very tight.

For the measurements at high temperatures (above 100°C) the contact points were thickly covered with an insulating hard adhesive resin that can withstand high temperature upto $\sim 300^{\circ}\text{C}$. Indium contacts were then found to remain operative at temperatures upto $\sim 260^{\circ}\text{C}$ without any disturbance.

3.11 MEASUREMENT OF FILM THICKNESS

In thin film experiments thickness measurement is an essential job. All most all the electrical parameters except the Hall mobility and sheet resistance need for their evaluation the value of film thickness. Therefore thickness should be measured with precision as far as possible. There are several methods of measuring the film thickness, some of which are briefly described below.

(a) Method adopted for the present work :

Since the experimental samples are transparent to the visible light the measurement of thickness by interferometric method would be adequate. The interferometric method for the determination of film thickness using Fizeau fringes has been developed to a remarkable degree by Tolansky⁽¹⁴⁾ and is now accepted as a standard method. To make the Fizeau fringes of equal thickness visible in a multiple beam interferometer formed by a thin absorbing film on a glass substrate, generally an auxilliary reflecting coating on the film surface is required. But if the experimental sample is transparent with a very smooth surface no such auxilliary coating is necessary⁽¹⁵⁾.

The film to be measured is required to form a step on a glass substrate over which another plane glass plate (Fizeau plate) is placed. This forms the interferometer as shown in figure 3.4(a). When the interferometer is illuminated with a parallel monochromatic beam of light a fringe system as shown in figure 3.4(b) is produced. The displacement h of the fringe system across the film-substrate step is then measured to calculate the film thickness t , using the relation

$$t = (h / \text{fringe spacing}) \times \lambda / 2 = h\lambda / 2l$$

The accuracy of the method depends on how accurately the fraction h of the fringe space l has been measured. Thickness measurement from $30 \text{ \AA}^{\circ}$ to $20,000 \text{ \AA}^{\circ}$ can be made with an accuracy of $\pm 10 \text{ \AA}^{\circ}$.

(b) Other methods :

At present there are several other methods of determining thicknesses of transparent films. A few very simple methods are mentioned below.

(i) Gravimetric method :

This is one of the oldest techniques for the

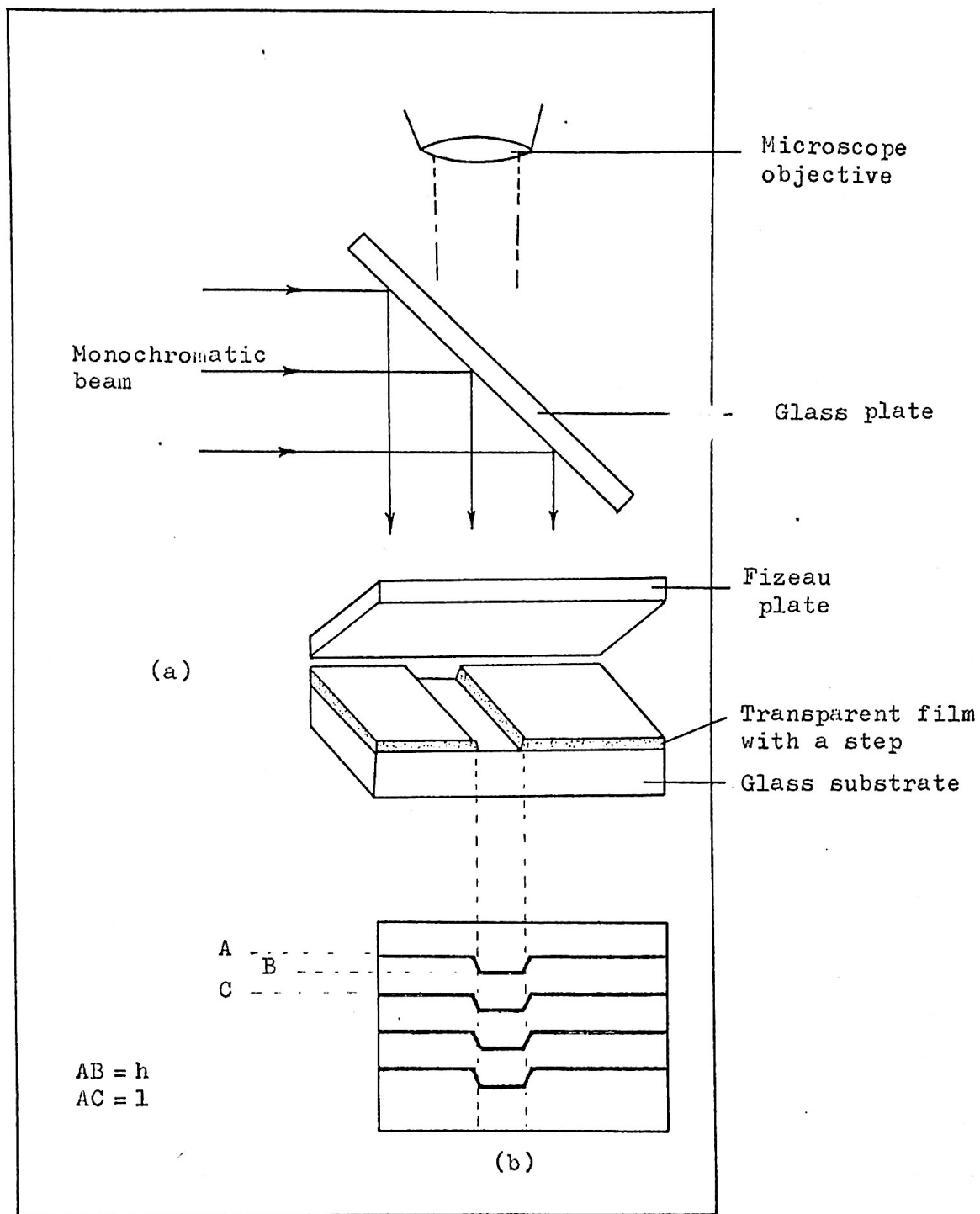


Figure 3.4 (a): Enlarged view of the interferometric arrangement for the measurement of film thickness,
 (b): The fringe pattern with step height h and fringe spacing l .

determination of film thickness. The mass m of a film of area A is determined by a microbalance by weighing the substrate before and after deposition. The thickness is then calculated by assuming bulk density ρ of the film material. Thickness t of the film is given by

$$t = m/A\rho$$

There are several difficulties and sources of errors in this method, especially the value of ρ cannot be known with precision. This method is therefore avoided.

(ii) Stylus instrument :

Stylus instruments are largely used for the measurement of surface roughness and surface finishes. Here also a film step is required. In principle the instrument compares the vertical movements of the stylus travelling across the sample surface with the movement of a "shoe" or "skid" on a smooth and flat reference surface, the substrate. The mechanical signals produced by the stylus movement is converted to electrical signals which are then amplified and recorded on a strip chart. From the pattern of the chart thickness of the film is evaluated. For hard films like SnO_2 and In_2O_3 this method is very much suitable. The main advantage of this

method is that it does not depend on the optical nature of the sample. If the sample can just support the load of the stylus then the method can be applied. Here the accuracy depends on the sensitivity of the stylus.

(iii) Colour comparison :

This is a crude but very simple and rapid method of estimation of thickness of transparent film on a reflecting substrate. Transparent films display colours when viewed through ordinary reflected day light. The colour depends on the thickness of the film. First precise colour thickness gauge was made by Blodgett⁽¹⁶⁾ who had deposited layers of barium stearate on a lead-glass plate producing a very colourful and useful thickness gauge.

In making colour comparison, one must be careful not to confuse different film thicknesses which give rise to similar colours but in different orders. This can be done by comparing the colours of the films while varying the angle of observation. The value of the refractive index however limits this method in some cases.

3.12 REFLECTION ELECTRON DIFFRACTION (RED) METHOD

In all cases where the surface properties of reasonably flat crystalline materials are of importance RED is usually capable of providing valuable structural information. Furthermore the technique has the particular advantage of being nondestructive and of requiring minimal specimen preparation. The precision of the method is however inferior to that of transmission electron diffraction method.

3.12.1 The Camera Equation and the Camera Length : -

In RED technique a mono-energetic beam of electron with energy in the range 10-100 kev is used to obtain diffraction from the atomic planes at the surface of a crystalline specimen. The wavelength λ corresponding to an accelerating voltage V (measured in volts) is given by the expression⁽¹⁷⁾

$$\lambda = [150 / V (1 + 10^{-6} V)]^{\frac{1}{2}} \text{ \AA} \quad \dots \quad \dots \quad (3.1)$$

Thus for the energy range given above, the associated wavelength of the electrons varies from 0.12 to 0.04 Å.

The requirement for Bragg diffraction is that

$$\lambda = 2 d_{hkl} \sin \theta \quad \dots \quad \dots \quad \dots \quad (3.2)$$

where, d_{hkl} is the inter-planar spacing and θ is the Bragg angle. For most metals, d_{hkl} is typically of the order of $2 \text{ \AA}$, so for the above range of wavelengths the Bragg angle varies from about 1.5 to 0.5° . Consequently in the RED technique, only those crystal planes that are inclined at less than a few degrees to the surface of a specimen will diffract an electron beam that strikes it at grazing incidence.

The condition necessary to produce an electron diffraction pattern are illustrated in figure 3.5. When the incident beam strikes the crystal plane (hkl) at the Bragg angle θ , then it is diffracted to form a diffraction spot at P on the photographic plate (or fluorescent screen) placed at a distance L from the sample.

L is known as the camera length, and it depends on whether the sample is placed outside or within the influence of the magnetic lens system of the diffraction instrument. From consideration of elementary geometry when inspecting figure 3.5 the distance R_{hkl} from the diffraction spot P to the spot O made by the direct beam is given by

$$R_{hkl} = L \tan 2\theta \quad \dots \quad \dots \quad \dots \quad (3.3)$$

For high energy electron diffraction, the value of θ is typically of the order of 1° as stated above, so that following small angle approximation may be made -

$$R_{hkl} \simeq 2L\theta \text{ and } \sin\theta \simeq \theta$$

Thus the Bragg relation of equation (3.2) may be written as

$$\lambda = R_{hkl} d_{hkl} / L \text{ or } \lambda L = R_{hkl} d_{hkl} \dots \quad (3.4)$$

This is known as the camera equation. The value of L is best determined with reference to a standard specimen of known crystal structure and lattice parameters.

3.12.2 Interpretation of the Diffraction Patterns :-

The diffraction patterns usually obtained in the deposited films may be classified in the following three categories.

(a) Diffuse patterns :

Amongst the materials with the least amount of crystalline order, there are two similar types that give rise to diffuse patterns in electron diffraction. Firstly, there are the structures with no crystalline order that are usually described as being amorphous. These exhibit a low degree of long range order and consequently produce just a few very diffuse diffraction rings. Secondly, materials that are crystalline,

but have an extremely small grain size of about 3 to 100 unit cells in diameter, also have poor long range order by virtue of their grain size. These similarly yield diffraction patterns containing diffuse rings. The wider is the diffuse ring pattern the smaller is the grain size.

(b) The ring patterns :

If the grain size of a material is larger than that which can give rise to broadening of diffuse diffraction rings as mentioned above but is smaller than about 0.5 mm, for example, then the resulting diffraction pattern will consist of a number of continuous rings which become less continuous and more "spotty" as the grain size increases. These rings arise from diffraction by a large number of randomly oriented crystallites. Measurement of the radii of the diffraction rings enables the interplanar spacing corresponding to each to be calculated using equation (3.4) and the known camera length L . The calculated values can then be compared with the ASTM index values⁽¹⁸⁾ and in doing this it is usually helpful to make an estimate of the relative intensities of the rings. However, when comparing the estimated relative intensities with the ASTM index values, it may be necessary to take into account the fact that the scattering factor for X-rays and for electrons are different. Furthermore, due to the increased probability

of dynamical effects in electron diffraction, anomalous intensities may occur⁽¹⁹⁾. Despite these factors, general agreement between estimated and ASTM index values of intensities is found to exist.

(c) Arc patterns :

The next level of crystalline order beyond the polycrystalline state occurs when grains have a preferred common orientation or fibre axis. There is a wide range of materials exhibiting this characteristics including deposited layers. Diffraction from such structures can give rise to two quite different types of patterns depending on the orientation of the fibre axis in relation to the direction of the electron beam. When the preferred orientation is approximately parallel to the beam, the resulting pattern still consists of rings but the relative intensities of these are abnormal and in certain cases, allowed reflections may even be absent. In other special condition when the fibre axis is approximately perpendicular to the direction of the electron beam, the diffraction patterns are characterized by arcs of intensity instead of rings, where the length of the arcs is a measure of the misorientation of the grains. For deposited layer it is usual for grains to exhibit a preferred orientation that is nearly perpendicular to the surface of the sample and such specimens give rise to RED

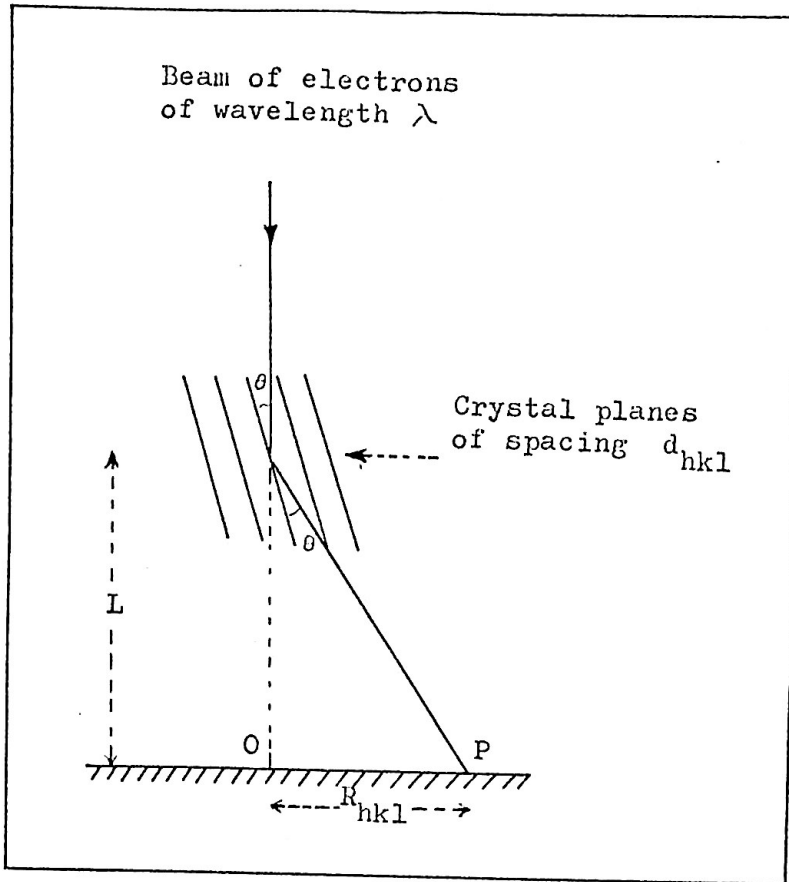


Figure 3.5 : Schematic diagram
of diffraction for the
derivation of the camera
equation

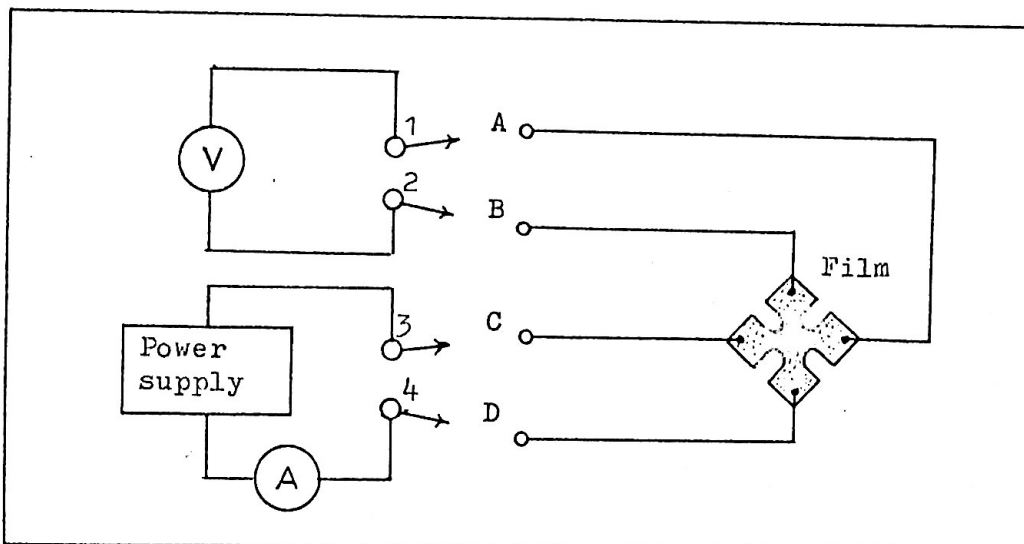


Figure 3.6 : Schematic diagram for the measurement of film
resistivity. 1,2,3&4 are meter terminals and
A,B,C&D are the film terminals. Arrows
indicate commutating switches.

patterns containing intensity arcs.

3.13 RESISTIVITY, HALL MOBILITY AND CARRIER CONCENTRATION MEASUREMENT

For thin film samples Van der Pauw's method⁽¹³⁾ is used most extensively for the measurement of resistivity and Hall constants, and we have followed this method throughout the work.

Using this method, both resistivity and Hall constant can be obtained from measurement on any uniform sheet of material of arbitrary shape with four small contacts applied to the periphery. Figure 3.6 shows the Vander Pauw's specimen with four small contacts A, B, C and D in order. 1, 2, 3 and 4 are terminals of the electrometers that measure voltages and currents. Digital multimeters were used for this purpose. The arrows indicate commutating switches which can make connections between the film and meter terminals. If a dc current I_{AB} entering the specimen through the contact A and leaving it through the contact B produces a potential difference V_{CD} between the contacts D and C then $R_{AB,CD}$ is defined as V_{CD}/I_{AB} . Similarly, $R_{BC,DA}$ is defined as V_{DA}/I_{BC} and $R_{BD,AC}$ as V_{AC}/I_{BD} . $\Delta R_{BD,AC}$ measures the change in $R_{BD,AC}$ due to the application of magnetic field B. For a plate of arbitrary shape and of constant thickness t , the resistivity and Hall constant are given by

the expression

$$\rho = [(\pi t / \ln 2) (R_{AB,CD} + R_{BC,DA}) / 2] f(R_{AB,CD} / R_{BC,DA}) \dots (3.5)$$

and the Hall constant

$$R_H = \Delta R_{BD,AC} (10^8 t / B) = \Delta R_{AC,BD} (10^8 t / B) \text{ cm}^3 / C \dots (3.6)$$

where the magnetic field B is in Gauss and film thickness t is in cm. The function f can be evaluated from

$$(R_{AB,CD} - R_{BC,DA}) / (R_{AB,CD} + R_{BC,DA}) =$$

$$(f / \ln 2) \operatorname{arc} \cosh [\exp (\ln 2 / f) / 2] \dots (3.7)$$

The function f of this equation depends only on the ratio $R_{AB,CD} / R_{BC,DA}$. Figure 3.7 shows in graphical form, the dependence of f on the ratio $R_{AB,CD} / R_{BC,DA}$.

The shape of the sample is taken in the form of a "quatrifoil leaf" so as to eliminate the influence of contacts and to keep the ratio $R_{AB,CD} / R_{BC,AD}$ approximately equal to unity. Under this condition the resistivity ρ is given by

$$\rho = 2.266 t (R_{AB,CD} / R_{BC,AD}) \text{ ohm cm} \dots (3.8)$$

The magnetic field B is always perpendicular to the plane of the sample.

The Hall mobility μ and the carrier concentration n can then be calculated from the relation $\mu = R_H / \rho \text{ cm}^2/\text{V}.\text{sec}$ and $n = 1 / R_H e \text{ cm}^{-3}$. In calculating ρ , appropriate correction factor evaluated from figure 3.7 was used where it was at all necessary.

3.14 THE MAGNETIC FIELD B

The magnetic field used for the study of Hall effects was provided by an electromagnet (Type A designed and supplied by Newport Instruments Ltd. England). The magnet was adjusted for the best homogeneity such that with a face gap of 2.5 cm at a field of 3.5 k Gauss, a resolution of 7.5 parts in 10^6 was obtained with a cylindrical sample of 6 mm diameter and 19 mm length when the plane pole-faces are fitted. Magnetic fields of the order of 3.5 to 7.35 k Gauss were used for the present experimental studies on SnO_2 and In_2O_3 thin films. For this purpose the electromagnet was previously calibrated with respect to supplied current through its coils.

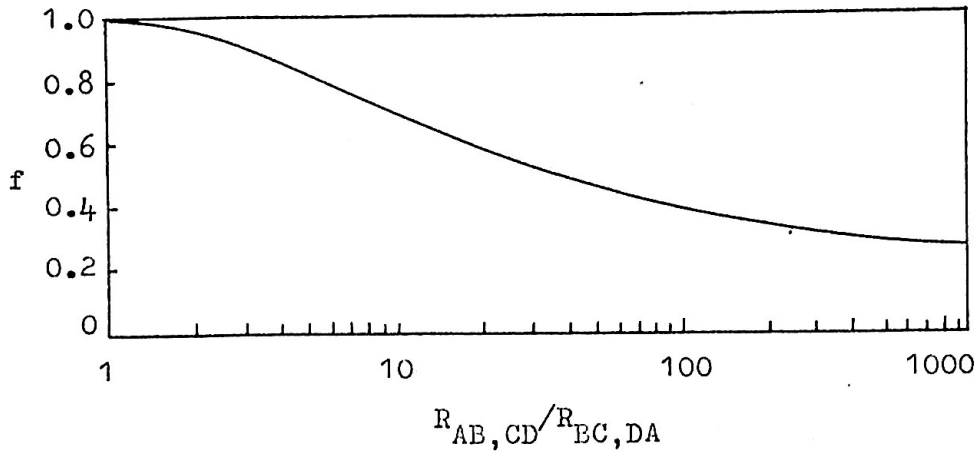


Figure 3.7 : The dependence of function f on the resistance ratio $R_{AB,CD}/R_{BC,DA}$ •

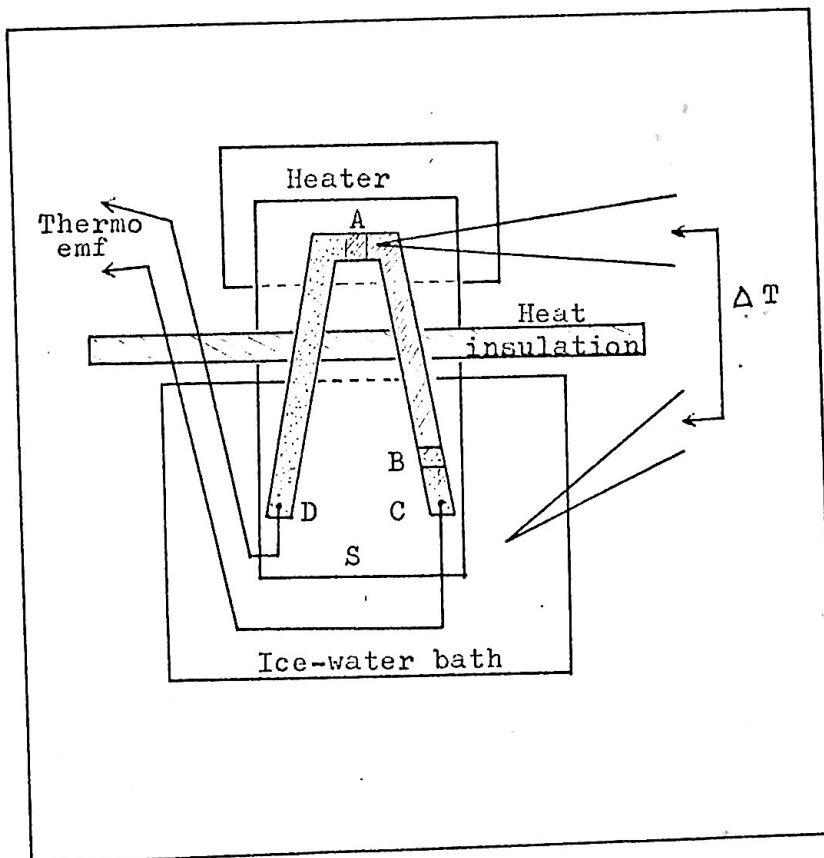


Figure 3.8 : Schematic diagram of the thermoelectric power measuring setup.
AB- Experimental sample,
DA & BC- Lead film.

3.15 MEASUREMENTS AT ELEVATED TEMPERATURE

The work presented in this thesis includes some measurements performed at temperatures ranging from room temperature upto about 250°C . For all such measurements a nichrome wire flat heater $2.5 \times 5 \text{ cm}^2$ in size and properly insulated by mica sheet in conjunction with thick aluminium heat sink (4 mm) has been used. The temperature of the surface of the heat sink could be kept constant for a considerable time. Applying voltages from 5 to 50 volts a.c. across the heater coil, temperature could be varied from room temperature to about 280°C . The temperature of the specimen was measured by a copper-constantan thermocouple.

3.15.1 Measurement of Thermoelectric Power (TEP) :-

Figure 3.8 shows the experimental arrangements for the measurement of thermoelectric power of SnO_2 and In_2O_3 films. The shape DABC of the sample with two junctions at A and B required for the measurement was prepared by using masks of figure 3.3(c) and (d) during the time of film deposition. Lead (Pb) has been taken as the reference metal for TEP measurement. After the deposition of SnO_2 (or In_2O_3) film AB the substrate with the film was placed inside a vacuum evaporation

chamber where thick lead film AD and BC were deposited by thermal evaporation of pure metallic lead. A spring-pressure clipping arrangement provided intimate contact between the substrate and the heater. The technique used for the measurement of Seebeck coefficient is the integral method namely keeping one end of the film at a constant temperature and varying the temperature of the other end. The cold junction of the sample was immersed into an ice-water bath at 0°C and the temperature of the hot junction was made to vary over the temperature range 27° to 160°C for SnO_2 film (and upto 175°C for In_2O_3 film). An appropriate heat insulating barrier E was inserted between the hot and cold ends to minimize heat radiation from the hot to the cold end. The immersed portion of the sample was electrically insulated to eliminate the possibility of leakage of emf between D and C due to contact with ice/water. All air currents were minimized by a suitable enclosure around the setup.

The temperature of the hot junction was raised slowly by definite intervals and when the temperature of each of these points become steady the thermo-emf was noted from the electrometer attached to the terminals. After the TEP measurements the samples were etched with Zn-dust and HCl to shape them into Van der Pauw's specimen⁽¹³⁾ and the carrier concentration and Hall mobilities of the samples were measured. In TEP experiments the thicknesses of the samples were kept

almost constant ($\approx 0.2 \mu\text{m}$) for the present work.

3.15.2 Post-deposition Heat Treatment Experiments :-

For thin film devices the temperature stability and reproducibility of the film properties are very important for the device operation and reliability. For the fabrication and optimization of electronic devices it has been observed that a common process of heat treatment often comes in the way. Polycrystalline oxide films deposited in the open air atmosphere are very sensitive to post-deposition heat treatments especially in the case of films deposited by pyrosol process. Therefore studies on post-deposition heat treatment of these samples (SnO_2 and In_2O_3) are necessary for improved understanding of the behaviour of the deposited films under thermal cycling.

For the heat treatment experiments the sample immediately after its deposition was cooled down to room temperature, at an average rate of $\sim 100^\circ\text{C}/\text{min}$ and was kept in desiccator. All the films were deposited at a constant substrate temperature of $\sim 400^\circ\text{C}$. Heat treatment operations were performed in air

(i) at normal pressure, and

(ii) in vacuum of the order of $\sim 10^{-1}$ to $\sim 10^{-5}$ torr.

By heat treatment we mean a heating cycle from room temperature

to 250°C followed by a cooling cycle back to room temperature in the same ambient. Heating temperature was raised at an average rate of $\sim 10^{\circ}\text{C}/\text{min}$ upto a maximum temperature of 250°C at which the sample was kept for an hour before the commencement of the return operation of cooling. Cooling rate was maintained almost the same as that of heating. Resistivity and Hall constants were the main objects of study in this experiment. Optical transmission of the films were also studied before and after the heat treatment operation.

An as-deposited SnO_2 film was first heat treated in air and after completion of this operation the sample was put into a vacuum chamber where it was again heat treated in a similar way. To see the effect a reverse step was also followed, i.e., an as-deposited sample was first heated in vacuum and then in normal pressure. In vacuum no electrical measurements were taken and therefore the reported values of the different parameters correspond to samples in air. Repeated heat treatments of the same film in the same ambient were also performed.

3.16 MEASUREMENT OF OPTICAL TRANSMISSION

Optical transmission experiments presented in this thesis were carried out in the wavelength range 0.27 to 0.95 μm . For this purpose the samples of SnO_2 and In_2O_3 were prepared

on a special type of glass substrates which were almost transparent in this range of wavelength.

A double beam spectrophotometer (Shimadzu UV-180) was used for the measurement of transmission coefficients. A sample (with the substrate) and an uncoated substrate were placed respectively in the incident and reference beam of the instrument. Optical transmission (in percentage) for normal incidence was then directly obtained for the film at different wavelengths. A curve was then plotted taking the percentage transmission T as the ordinate and the different wavelengths as the abscissa. The transmission spectra of the sample was thus obtained.

Optical absorptions were then calculated for the sample at different wavelengths from this curve. Due to the extreme transparency of the sample in the visible wavelength range the reflection coefficients for normal incidence were considered to be negligible. The value of the refractive index of the film was calculated from the transmission data.

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CHAPTER - 3

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C H A P T E R - 4

RESULTS AND DISCUSSION

STUDIES ON SnO_2 FILM

CHAPTER - 4

STUDIES ON SnO₂ FILM

In this chapter the results of the various experimental investigations on SnO₂ thin films have been presented. Possible explanations and discussion of the results are also given here. The details of the experimental techniques for these studies have already been given in the previous chapter.

4.1 STRUCTURAL STUDIES

The physical nature of the doped and undoped SnO₂ films deposited at substrate temperatures 300° and 400°C were investigated by the reflection electron diffraction (RED) method. Figure 4.1 shows typical RED patterns of some undoped and Sb-doped SnO₂ films. All the films were found to show polycrystalline structure. In figure 4.1(a) the diffraction rings are present but they are diffuse rings indicating that the film of 300°C possesses grains that are very small in diameter. Films of 400°C on the other hand possess larger grains in comparison to film of 300°C. These are indicated by the clear rings of figure 4.1(b) and (c). The tendency of the

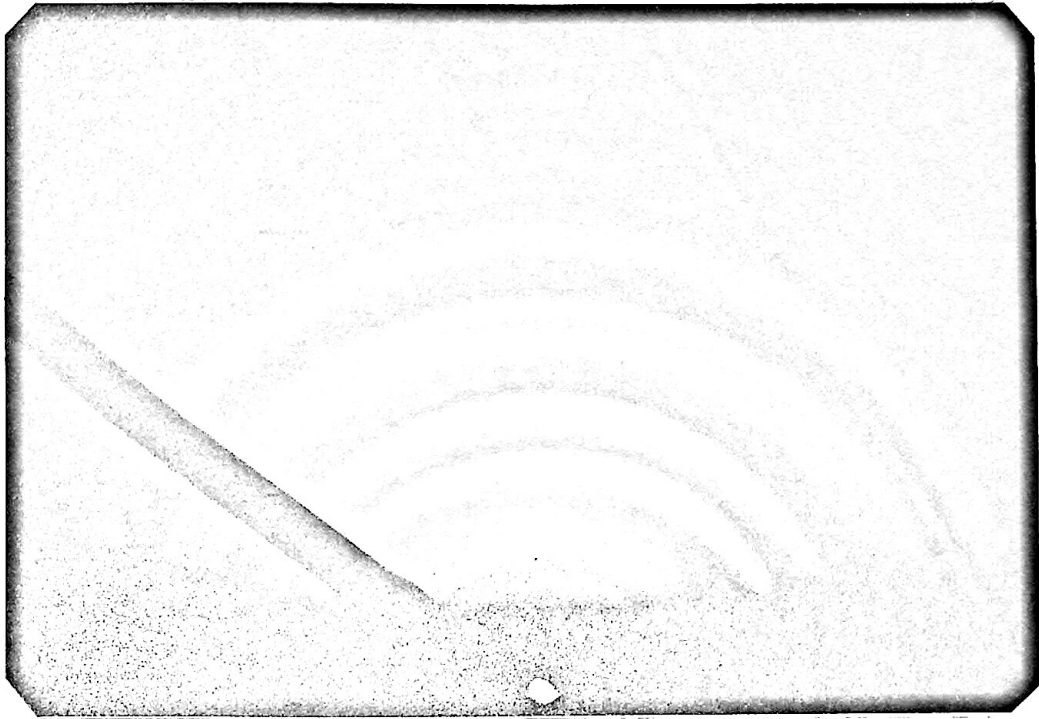


Figure 4.1(a) : RED pattern of undoped SnO_2 film deposited at $T_s \approx 300^\circ\text{C}$ on glass substrate.

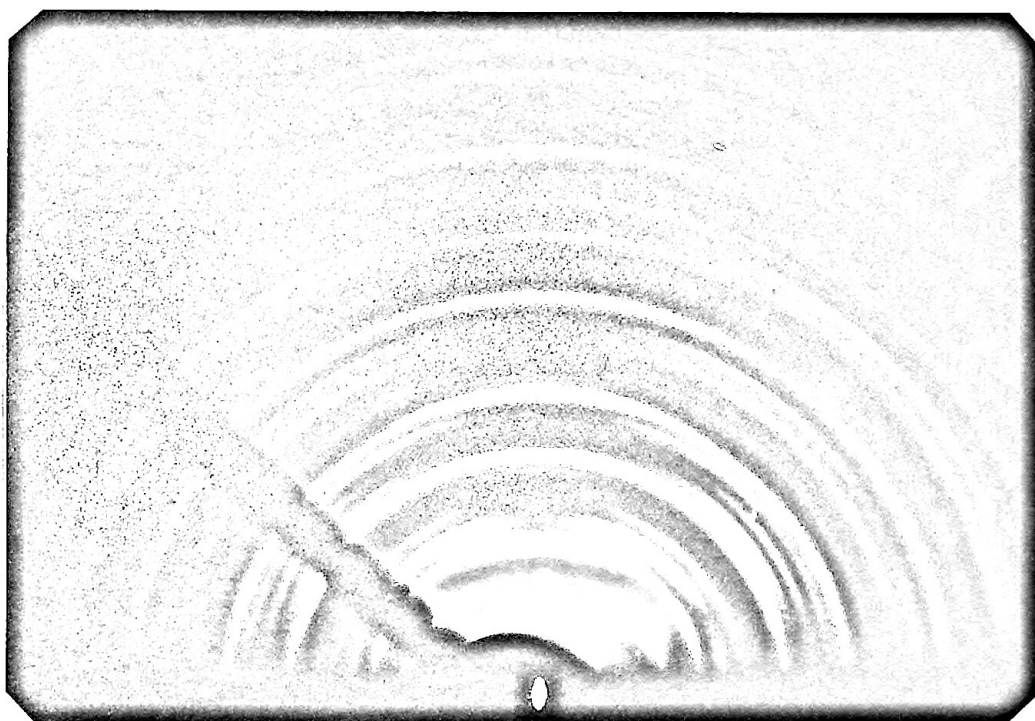


Figure 4.1(b) : RED pattern of SnO_2 film deposited
at $T_s \approx 400^\circ\text{C}$ on glass substrate.

Figure 4.1(c) : RED pattern of 0.3 mole % Sb-doped SnO_2 film deposited at $T_s \approx 400^\circ\text{C}$ on glass substrate.



continuous ring patterns towards a less continuous (arcy) patterns are also noticed. This is an indication that there may have a preferred orientation of the grains in the sample, possibly perpendicular to the surface of the film.

From the study of the relative intensities of these rings using ASTM index values for the SnO_2 crystal, the SnO_2 phase of the film was definitely identified. The detail discussion of the pattern analysis process has been given in chapter-3.

4.2 UNIFORMITY OF DEPOSITION

A test of the uniformity of thickness and of resistivity of the film was performed on a $4 \times 4 \text{ cm}^2$ film deposited in the shape shown in figure 4.2. With a current passing through the film the voltage drop V for successive 2 mm segments was measured along the line of the film by a fine two point probe. Thicknesses were also measured for each part of the film (AB, BC ... etc). It was observed that the maximum variation in V between the segments was within 8 to 10% for the peripheral regions, but when a $2 \times 2 \text{ cm}^2$ area PQRS of the film was considered in the central part of the film this variation then reduced to less than 0.5%. Thickness measurements also gave similar results. This indicates that the central part of the film is more homogeneous and can be used more effectively than the peripheral parts.

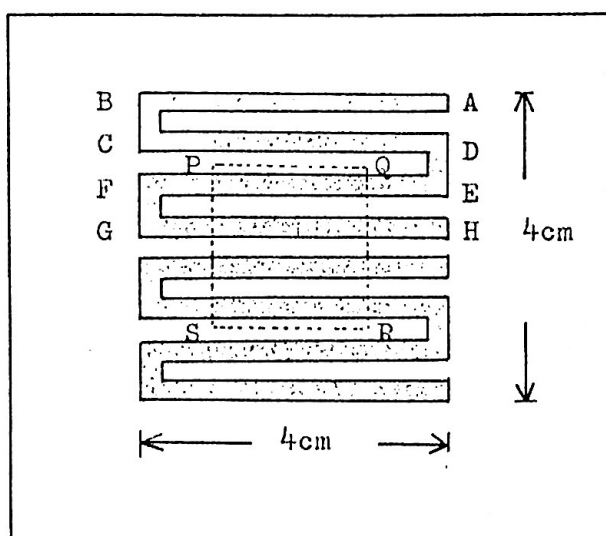


Fig.4.2

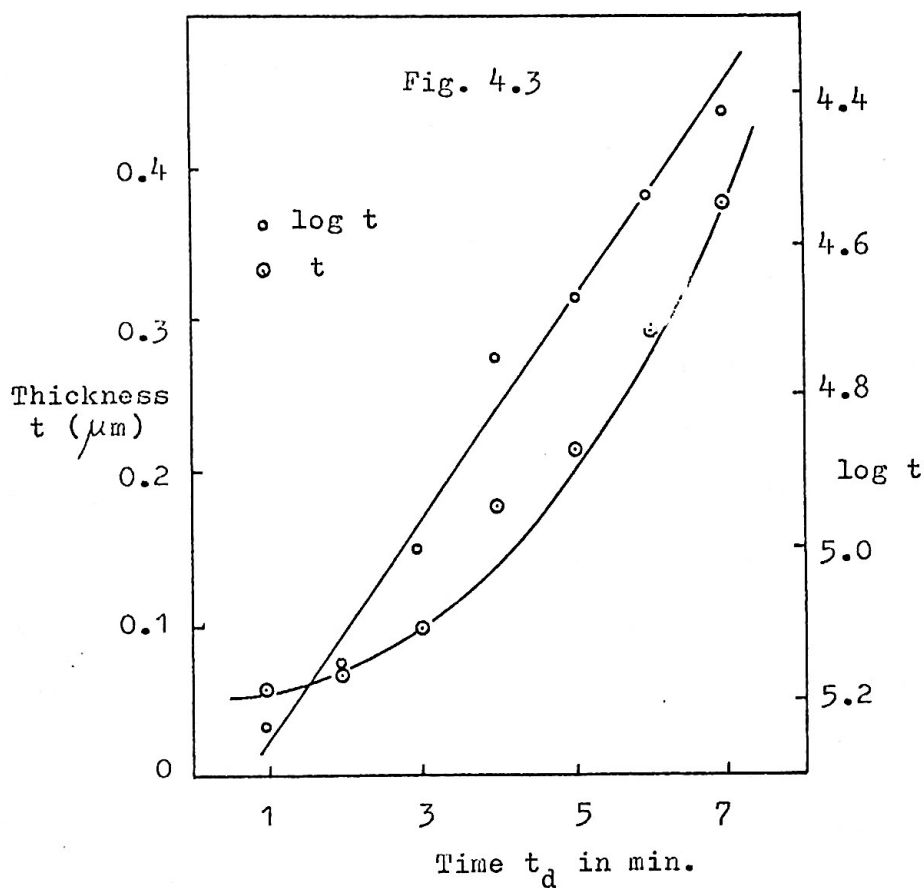


Figure 4.2 : Shape and size of SnO_2 film deposited for testing the uniformity of the film. PQRS is the most uniform portion.

Figure 4.3 : Variation of film thickness t with the deposition time t_d .

4.3 EFFECT OF THE DEPOSITION TIME

Figure 4.3 shows the dependence of film thickness t on the deposition time t_d . It is observed that the variation of t with t_d is not linear, but $\log t$ varies approximately linearly with t_d . This is natural because at the beginning of the spraying a portion of the aerosol is distributed in the reactor chamber and does not reach at the substrate (for a period known as the incubation time). This results in a lower deposition rate⁽¹⁾. After some time the process becomes steady and the thickness of the film increases.

4.4 THE EFFECT OF SUBSTRATE TEMPERATURE

Substrate temperature T_s has a remarkable effect on the film growth rate. Figure 4.4 shows the variation of the average growth rate (t/t_d) with substrate temperature. It is observed from curve (a) that the average rate of growth increases sharply with T_s between 300° and 400°C , showing an activation energy of growth ≈ 0.2 eV. The latter is calculated from the plot of $\ln(t/t_d)$ against T_s^{-1} , curve (b) of the same figure. At higher substrate temperature (t/t_d) becomes almost temperature independent. This phenomenon indicates that in the lower temperature region the surface reaction (equation 1.1) is dominated mainly by two factors: the temperature T_s , and the rate of reactant supply;

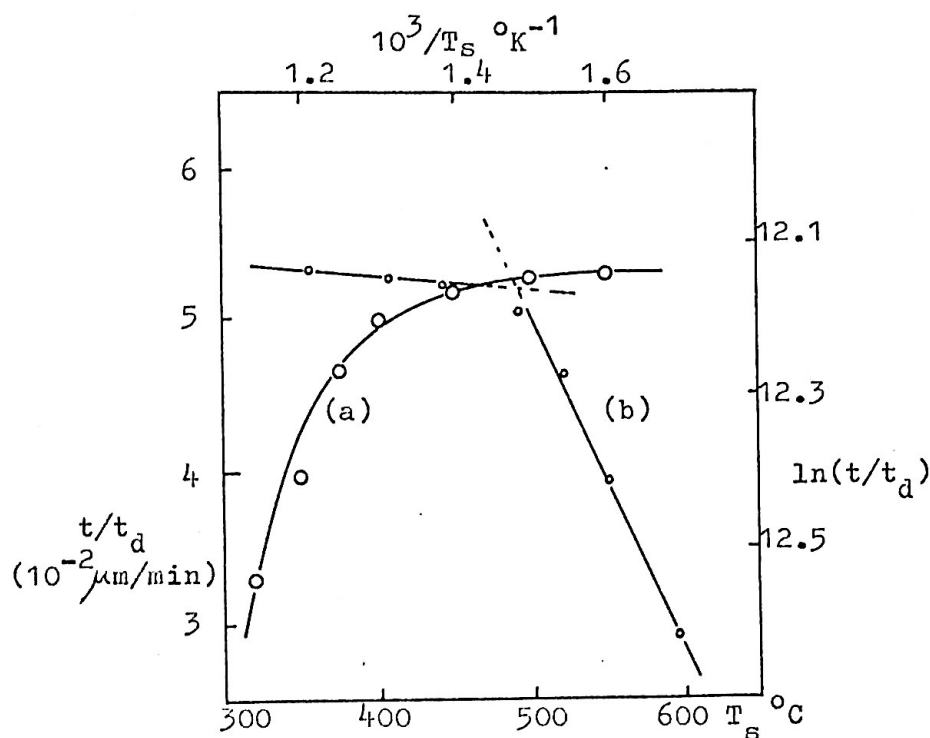


Fig. 4.4

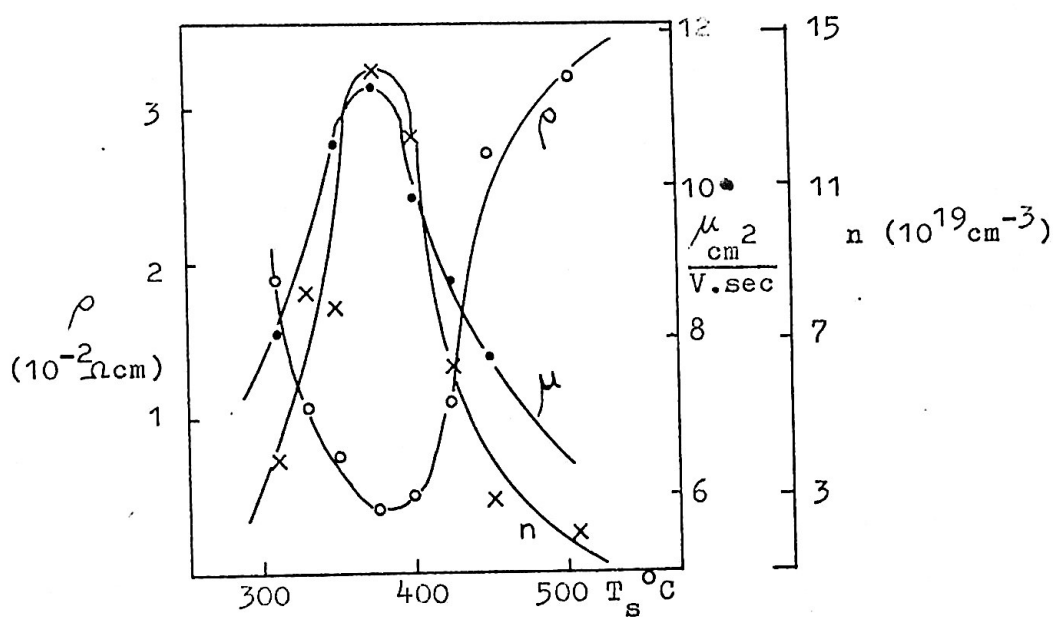


Fig. 4.5

Figure 4.4 : Variation of film growth rate t/t_d with substrate temperature T_s . (a) t/t_d vs. T_s , (b) $\ln(t/t_d)$ vs. $10^3/T_s$.

Figure 4.5 : Variation of ρ , μ , and n of undoped SnO_2 film with substrate temperature T_s .

but at higher temperature the reaction rate is so fast that the film growth rate becomes mostly dependent on the rate of reactant supply⁽¹⁾, which was kept constant in the present investigation.

Resistivity ρ , Hall mobility μ and the carrier concentration n have been measured at room temperature for undoped films deposited at different substrate temperature T_s , and the values are plotted in figure 4.5. All the films are found to show n-type conductivity. It is observed that ρ shows a minimum value at $T_s \approx 380^\circ\text{C}$, where μ and n show their peak values.

It is well known that conducting SnO_2 thin films are defect semiconductors⁽²⁾ and their high conductivity is due to the presence of oxygen vacancies, interstitial Sn atoms, Cl^- ion impurities (from the starting material) and other foreign impurities. At higher temperatures ($T_s \gtrsim 425^\circ\text{C}$) alkali ions may diffuse from the glass substrate and create acceptor centres in the film which can decrease the carrier concentration and increase the resistivity. At the same time the film starts to become relatively more opaque at these temperature limits. On the other hand at lower temperatures ($T_s \lesssim 350^\circ\text{C}$), probably because of the incomplete hydrolysis of SnCl_4 and slow reaction rate, the film tends to become amorphous to a greater degree and the conduction process is hindered. It has been observed that below

280°C of substrate temperature no substantial deposition is possible, even at this temperature the adhesion of the film to the substrate is rather low. At $T_s \approx 380^\circ\text{C}$ the film stoichiometry becomes adjusted in such a way that high quality transparent conducting films are obtained with a very high sticking coefficient.

4.5 THE SHEET RESISTANCE

Figure 4.6 shows that, as the film thickness t increases the sheet resistance $R_\square$ decreases first very rapidly and then it gradually tends to become independent of thickness. From this behaviour it is inferred that the sheet resistance size effect in SnO_2 films is pronounced only below a thickness of about $\sim 0.3 \mu\text{m}$ and above this thickness bulk properties may set in⁽¹⁾.

4.6 EFFECT OF DOPING

Doped SnO_2 films were prepared at a constant substrate temperature $T_s \approx 380^\circ\text{C}$ using the different working solutions as mentioned in chapter-3. Two types of doped films were prepared as described below.

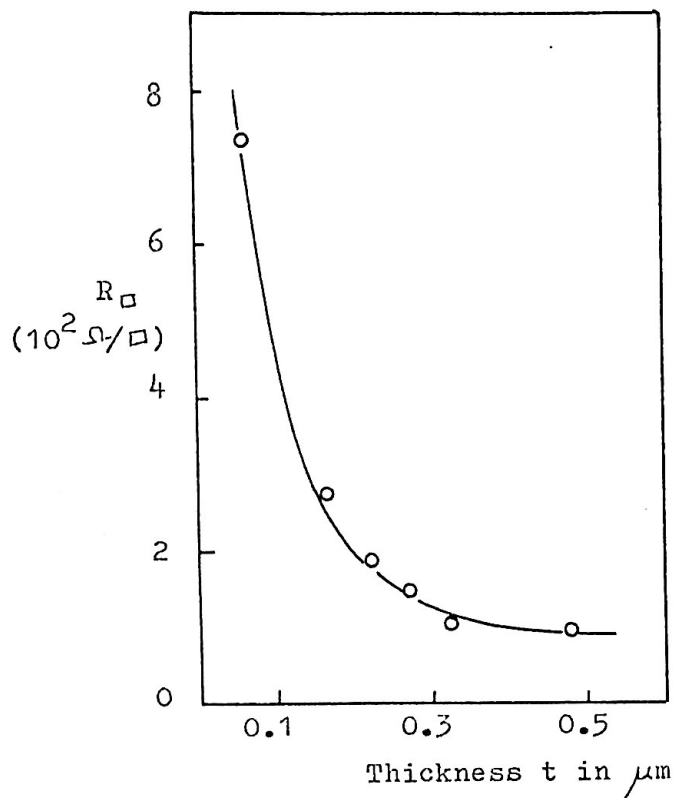


Figure 4.6 : Variation of sheet resistance $R_{\square}$ with the thickness t of SnO_2 films .

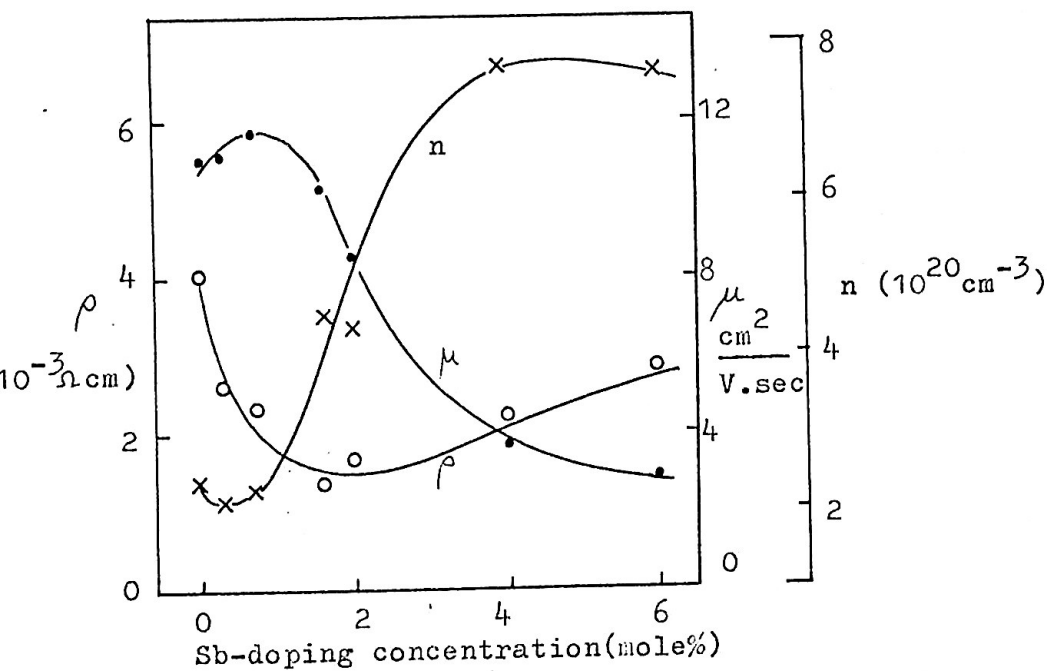


Figure 4.7 : Variation of ρ , μ and n of SnO_2 films with the Sb-doping concentration.

4.6.1 Sb-doped Films :-

Figure 4.7 shows the variation of ρ , μ and n of SnO_2 film with the Sb-doping concentrations in the working solution. Higher Sb-doping does not give good result with respect to both conductivity and transparency. Films tend to become darkish at higher Sb-concentrations ≥ 6 mole %. The lowest resistivity was obtained with 1.6 mole % of Sb in SnO_2 films deposited in our laboratory.

4.6.2 F-doped Films :-

Fluorine doping was achieved in two ways as have been mentioned in chapter - 3. By using NH_4F and by using HF in SnCl_4 solution. It was observed that F-doping by using HF could decrease the film resistivity substantially. Doping by NH_4F can also decrease the film resistivity but not so efficiently as HF can. To achieve minimum sheet resistance therefore HF is preferred. But there is a problem here in using HF as dopant. HF like Sb creates a bit darkish colour of the film when the doping level is high > 40 mole %. On the other hand NH_4F does not produce such colouration even at very high doping levels.

Figure 4.8 shows the variation of ρ , μ and n of SnO_2 films with the F-doping concentration when doping was performed by using NH_4F . Minimum resistivity and mobility was

obtained at about 20-25 mole % of fluorine. Similar curves were obtained when the doping was performed by using HF but at that time minimum resistivity was obtained at about 60-65 mole % of F.

The gross electrical conductivity of doped films is greater than that of the undoped films because of the additional donor levels in the doped material. Due to the similar ionic radii of F^- ($\approx 1.36 \text{ \AA}$) and O^{2-} ($\approx 1.40 \text{ \AA}$), the fluorine (F^-) may substitute for the anion (O^{2-}) in SnO_2 lattice and act as a donor⁽³⁾. On the other hand Sb^{5+} from $SbCl_3$ may replace the cation (Sn^{4+}) in the lattice, but since the ionic radius of Sb^{5+} ($\approx 0.62 \text{ \AA}$) is not so clearly matched with that of Sn^{4+} ($\approx 0.71 \text{ \AA}$), doping efficiency of Sb is thus slightly less than that of F. But still higher conductivity is achieved by these doping effects. The difference between using NH_4F and HF as F-doping agents is not so clear. Probably it may be due to the incorporation of some NH_4^+ ion in the lattice, while using NH_4F , which produces additional defect centres in the film and act as electron capture centres.

Doping also increases the grain size of the film and therefore a limited increase of Hall mobility was also observed in the doped films.

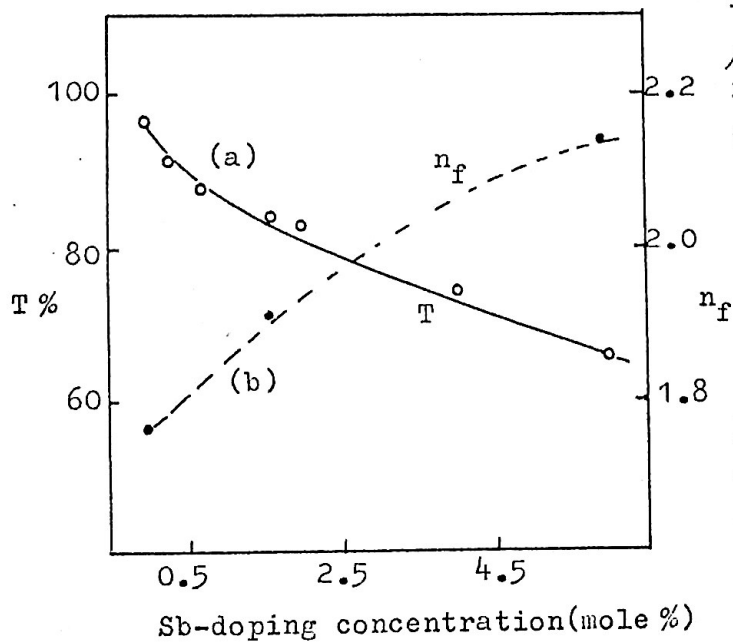
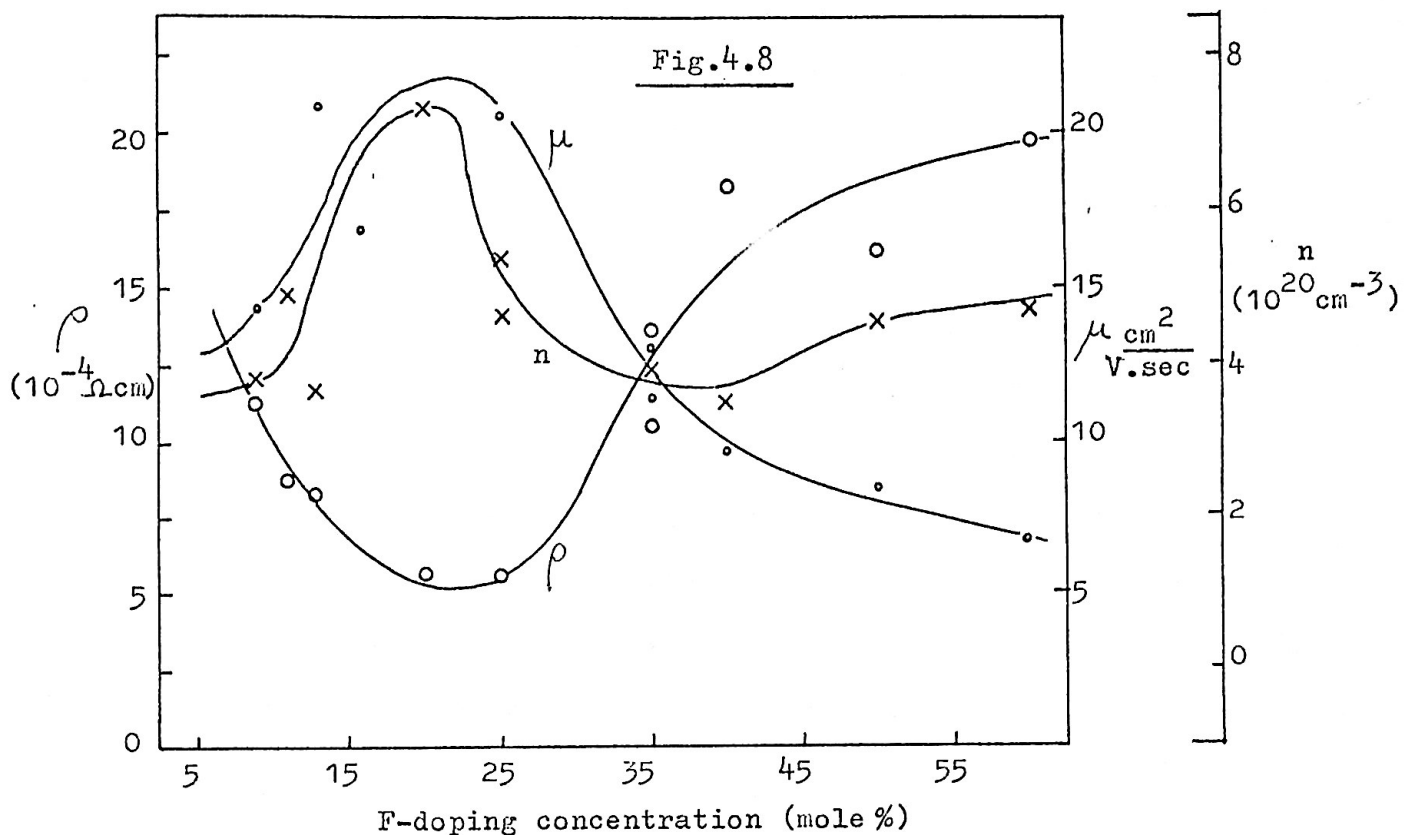


Figure 4.8: Variation of ρ , μ , and n of SnO_2 films with respect to F-doping concentration.

Figure 4.9: Variation of optical transmission T and refractive index n_f of SnO_2 film as a function of Sb-doping concentration. Both are at $\lambda = 0.55 \mu\text{m}$.

4.7 OPTICAL TRANSMISSION AND REFRACTIVE INDEX

The variation of optical transmission coefficient T as a function of Sb-doping concentration is shown in figure 4.9 (curve-a). The optical transmission gradually decreases with the Sb-doping concentration. F-doping does not decrease the optical transmission at lower doping levels. The refractive index (n_f) of the film increases with Sb-doping concentration as represented by curve (b) of figure 4.9. The value of the refractive index was found to be 1.75 for undoped and 2.18 for 6 mole % Sb-doped SnO_2 films respectively. Both T and n_f were evaluated at $\lambda \approx 0.55 \mu\text{m}$.

Figure 4.10 shows the optical transmission vs. sheet resistance plot of $\text{SnO}_2:\text{F}$ films when doping was performed by using HF. From these curves it is clear that sheet resistance below $6 \Omega/\square$ is accompanied by a drastic fall of optical transmission in the visible range. Different curves of the figure represent values of the transmission coefficients T at different fixed wavelengths.

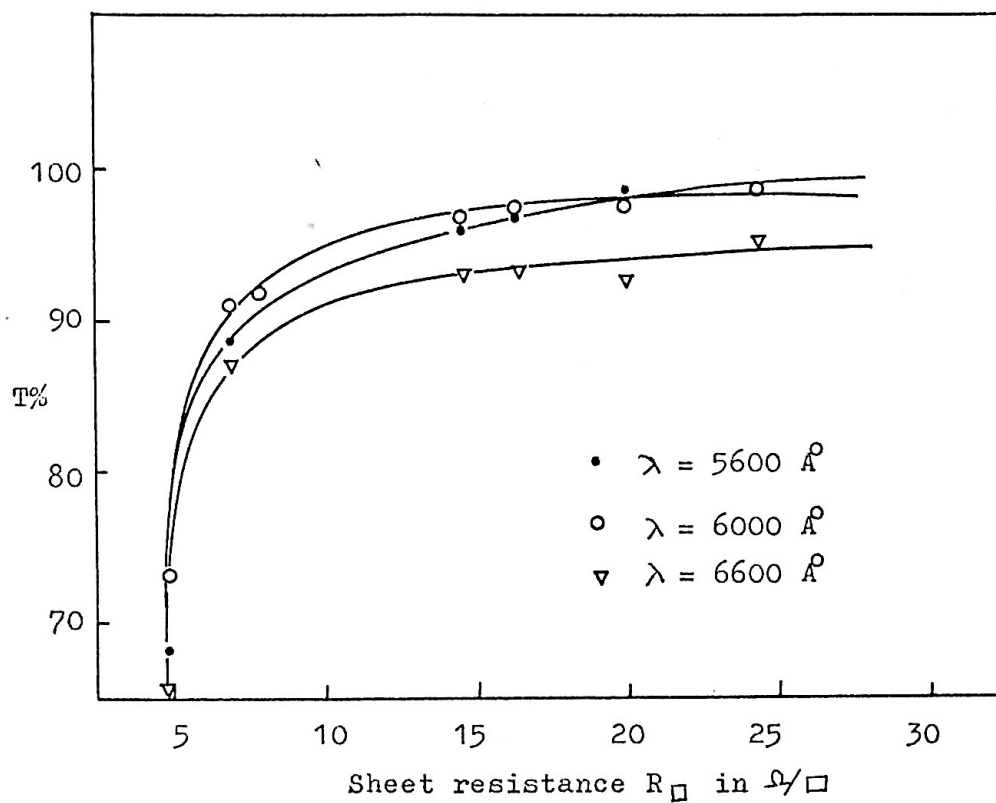


Figure 4.10 : Optical transmission versus sheet resistance curves of F-doped SnO_2 films.

4.8 THE FIGURE OF MERIT OF THE COATING

It is known from the above discussion that higher doping increases the electrical conductivity of the film but at the cost of optical transmission. For a highly conductive film with high transparency therefore some compromise is required and this has been expressed in terms of a quantity known as the figure of merit of a transparent conducting film, ϕ_{TC} . Haacke's figure of merit⁽⁸⁾ for a thin transparent film is given by (equation 1.3)

$$\phi_{TC} = T^{10} / R_{\square}$$

which allows for transparency, conductivity and thickness at the same time. The best figure of merit of the films as obtained in our present work are listed in table 4.1. The table shows that the present technique of film deposition can produce a better ϕ_{TC} compared to earlier samples obtained elsewhere. For F-doped SnO_2 film optimum figure of merit could be obtained from the curves of figure 4.10. We obtained the highest ϕ_{TC} of spray deposited $\text{SnO}_2:\text{F}$ film to be about $56.5 \times 10^{-3} \Omega^{-1}$ at $\lambda = 6000 \text{ \AA}$, and about $57.0 \times 10^{-3} \Omega^{-1}$ at $\lambda = 5900 \text{ \AA}$. These values are supposed to be the highest value of ϕ_{TC} for the spray deposited SnO_2 film so far as we know from the recent literatures.

TABLE 4.1

Spray deposited films	Figure of merit ϕ_{TC} ($10^{-3} \Omega^{-1}$)	Wavelength μm	Reference
SnO_2	1.26	0.55	4
$SnO_2:F$	18.5	0.55	4
$In_2O_3:Sn$	22.0	0.55	4
$SnO_2:F$	48.5	0.75	5
$SnO_2:F$	4.98	-	6
$SnO_2:F$	52.6	0.65	7
In_2O_3 (Commercial BALTRACON)	1.2	-	8
SnO_2	7.12	0.55	Present Work
$SnO_2:Sb$	5.14	0.55	..
$SnO_2:F$	57.0	0.59	..
In_2O_3 (Unoptimized)	0.57	0.55	..
$In_2O_3:Sn$..	22.4	0.55	..

4.9 POST-DEPOSITION HEAT TREATMENT OF SnO_2 FILM

The temperature dependence of resistivity ρ , Hall mobility μ and carrier concentration n of some as-deposited films of SnO_2 with thickness of the order of $\sim 0.2 \mu\text{m}$ have been studied between 27° and 250°C . It was observed that post-deposition heat treatment lowers the value of ρ without any appreciable change of carrier concentration n . Group of samples with similar initial characteristics show similar behaviour in heat treatment but the relative magnitudes of ρ and μ differ from sample to sample, and this variation is probably due to the previous history of the film preparation. The variation of ρ with temperature T of two typical samples of SnO_2 film having slightly different initial characteristics have been shown in figure 4.11(a) and (b). It is observed that ρ vs. T curves follow irreversible paths in the heating and cooling cycles. ρ decreases with increasing temperature in the case of as-deposited films, but if the films are initially heat treated in vacuum then ρ shows an increase with the increasing temperature. This indicates a positive temperature coefficient of resistivity (TCR) for the vacuum heat treated films and negative for the as-deposited films. This alteration of the sign of TCR is repeatable for a sample. Two consecutive heat treatments in the same ambient do not alter the sign of TCR. The calculated values of TCR for the experimental samples are shown in table 4.2.

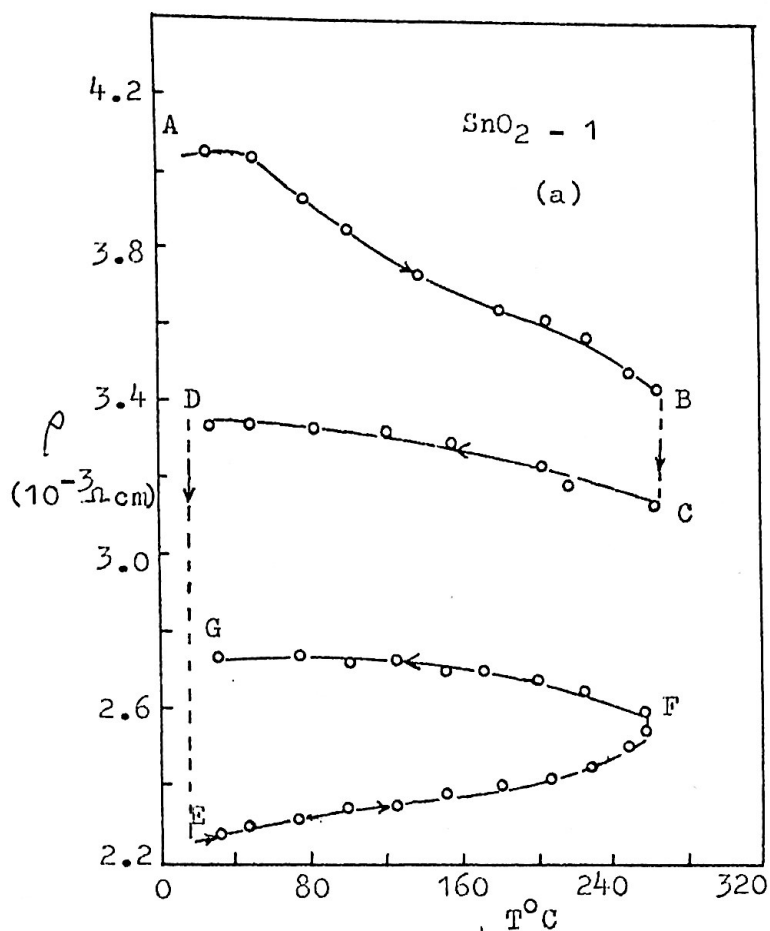


Figure 4.11 (a) and (b) :

Variation of resistivity ρ of SnO_2 film with temperature.

AB & CD represent heating and cooling cycles in air, BC

represents change of ρ at a constant temperature of 250°C

in one hour. Resistivity drops from point D to E due to a

heat treatment in vacuum ($\sim 10^{-5}$ torr). EFG cycle represents

a 3rd time heat treatment in air.

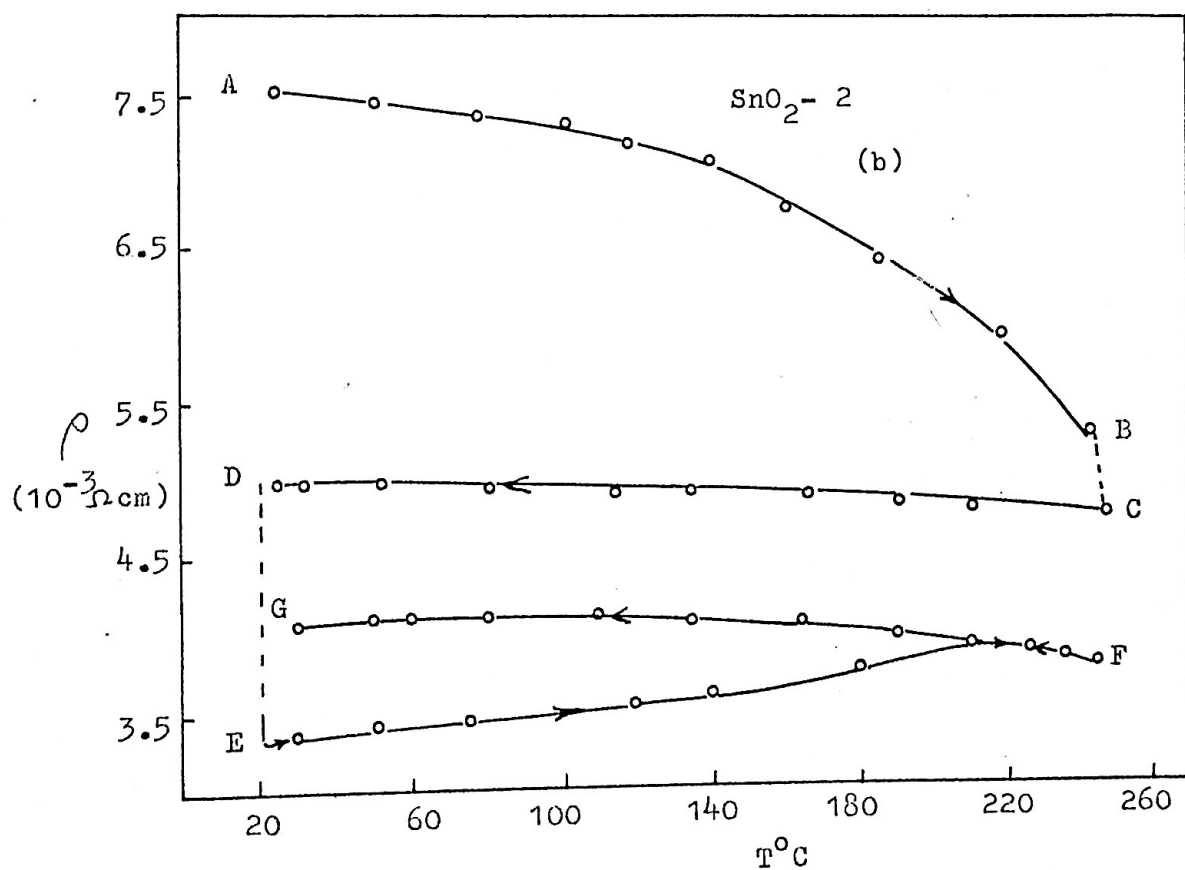


Figure 4.12 shows the change of resistivity due to heat treatment in different ambient pressures, starting from normal pressure down to $\sim 10^{-5}$ torr. Each time heating was continued for an hour at a constant temperature of 250°C , then the samples were cooled and measured. Here a time of one hour was considered sufficient because equilibrium was found to be attained within 30 minutes at a constant temperature and pressure. It is clear from figure 4.12 that lower ambient pressure helps to decrease the resistivity to its lower limit. It was also observed that the values of ρ once attained after a heat treatment did not subsequently change, so long as the sample was kept under normal temperature and pressure conditions.

Discussion

Several mechanisms may take part in bringing about the observed changes in the film by heat treatment, e.g.,

- (i) Recrystallization of the amorphous part of the film.
- (ii) The highly resistive SnO phase which is present in addition to the SnO_2 phase in the film⁽⁴⁾ may change to the relatively low resistive SnO_2 phase.
- (iii) Reorientation of the existing crystallites.
- (iv) Change of frozen-in stresses or generation

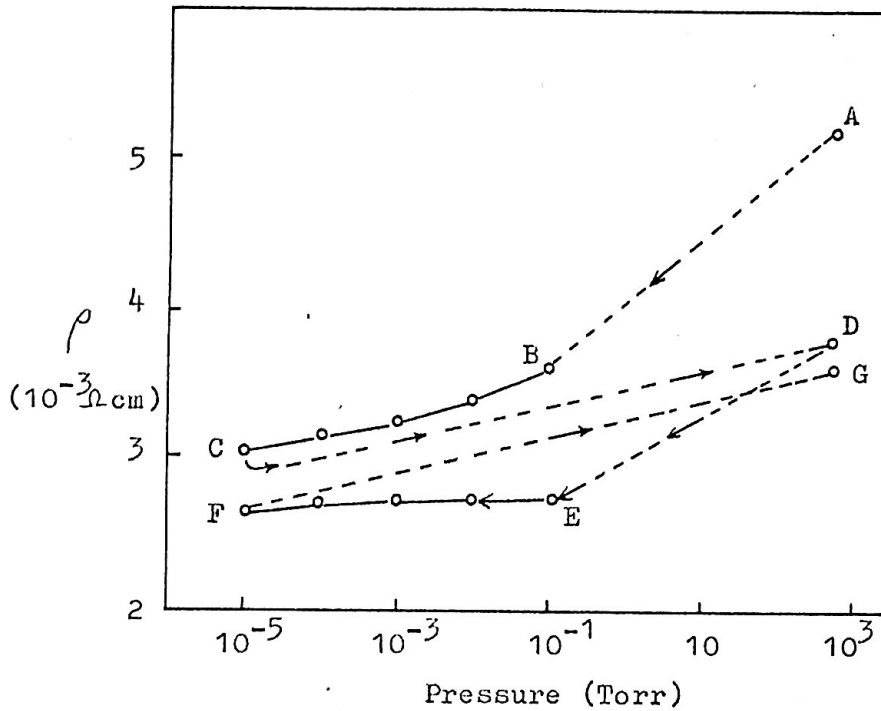


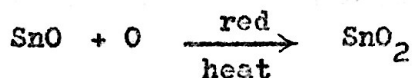
Figure 4.12 : Change of resistivity of an SnO_2 film due to heat treatment in different ambient pressures. Point A represents value of ρ after a first heat treatment in air at normal pressure. Points B to C represent 1st, 2nd, 5th time heat treatment in different orders of vacuum from 10^{-1} to 10^{-5} torr. Resistivity rises from point C to D due to a 2nd time heat treatment again in air. The operation cycle from A to D is repeated for a 2nd time and the cycle DEFG is obtained.

of internal stresses in the film due to heat treatment, and

(v) oxygen chemisorption/desorption mechanism at the grain boundaries of the film.

All of the above mechanisms may not be equally important for the present case.

The deposition temperature of the samples were $\sim 400^{\circ}\text{C}$ which is much greater than the post-deposition heat treatment temperature, 250°C , and therefore it is quite likely that mechanism (i) may not take place. The SnO phase of the film is less stable than the SnO_2 phase, and so there is some possibility that this type of phase transition may take place due to heat treatment in air, but in vacuum such transition is not possible. Due to low heating temperature this phase transition mechanism, (ii), is however not at all possible because the reaction



would not take place. Moreover since a vacuum heat treatment followed by a second heat treatment in air could return the qualitative features of the as-deposited film, it is apparent that no major structural change in the film occurs. The change of resistivity then can only be attributed to the change of

mobility of the carriers for the same concentration.

The mechanisms (iii) and (iv) are somewhat inter-related. M. Just et al⁽⁹⁾ have pointed out that when the elastic stresses on a film decreases during a heat treatment the resistivity decreases simultaneously. These frozen-in stresses and the random orientation of the crystallites were produced in the film during their initial period of nucleation and this probably depends on the cooling rate of the samples after the completion of deposition. It may be mentioned here that the linear coefficient of thermal expansion of semiconducting SnO_2 material is $\sim 4 \times 10^{-6}$ per $^\circ\text{C}$, whereas that of the glass substrate is about $\sim 9 \times 10^{-6}$ per $^\circ\text{C}$. Therefore during the initial period of cooling of the film there is some possibility of stresses to be locked-in. In the subsequent heat treatment these stresses may be minimized.

The value of TCR of thin film is greatly affected by thermal expansion mismatch between the film and the substrate. P.M. Hall⁽¹⁰⁾ has derived the relationship

$$\alpha_f = \alpha_b - 4.2 (a_f - a_s) \quad \dots \quad (4.1)$$

where α_f and α_b are the TCR values of the film and the corresponding bulk materials respectively, $(a_f - a_s)$ is the difference between the coefficients of thermal expansion of the film and substrate. For SnO_2 film since $(a_f - a_s)$ is very small, the

correction factor would not be very significant.

Mechanism (v) is thought to be the most important here because of the polycrystalline nature of the oxide films. This can be successfully analysed invoking the existing grain boundary trapping models⁽¹¹⁻¹⁴⁾. The model considers the film to be composed of rectangular array of square grains separated by grain boundary regions; (a detail discussion about the model has been given in chapter-5). In the case of highly degenerate SnO_2 samples if it is expected that the dominating current is due to the thermionic emission over the grain boundary barriers, then the expression for thermally activated mobility can be given by^(14,15)

$$\mu = A \mu'_0 T^{-\frac{1}{2}} \exp(-\phi_b/k_B T) \quad \dots \quad (4.2)$$

where $\mu'_0 T^{-\frac{1}{2}} = \mu_0$ has the dimension of mobility and corresponds to the value of the carrier mobility of the sample in absence of such grain boundaries and ϕ_b is the potential energy barrier height between the grain and boundary regions.

A is an empirical factor which can account for the various reflection, transmission and scattering coefficients at the grain boundaries and their slow temperature dependence⁽¹⁶⁾.

μ'_0 is a parameter related to the grain size of the sample. Also ϕ_b is given by⁽¹³⁾

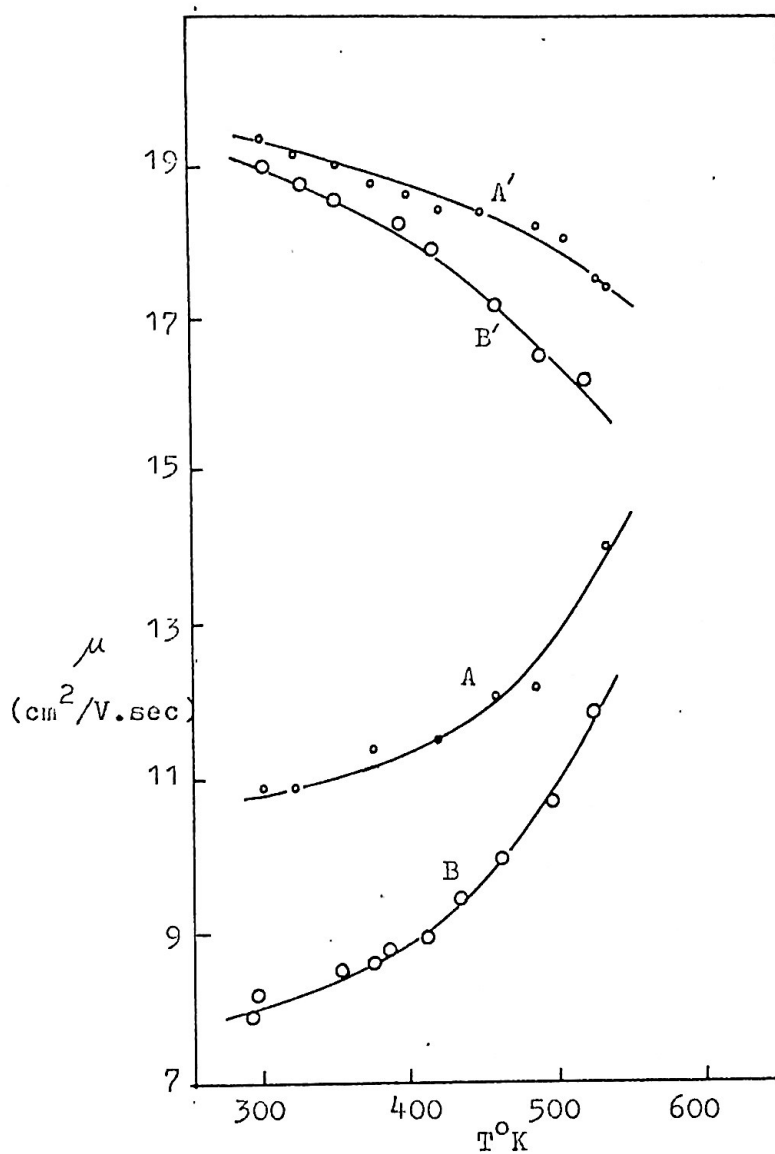
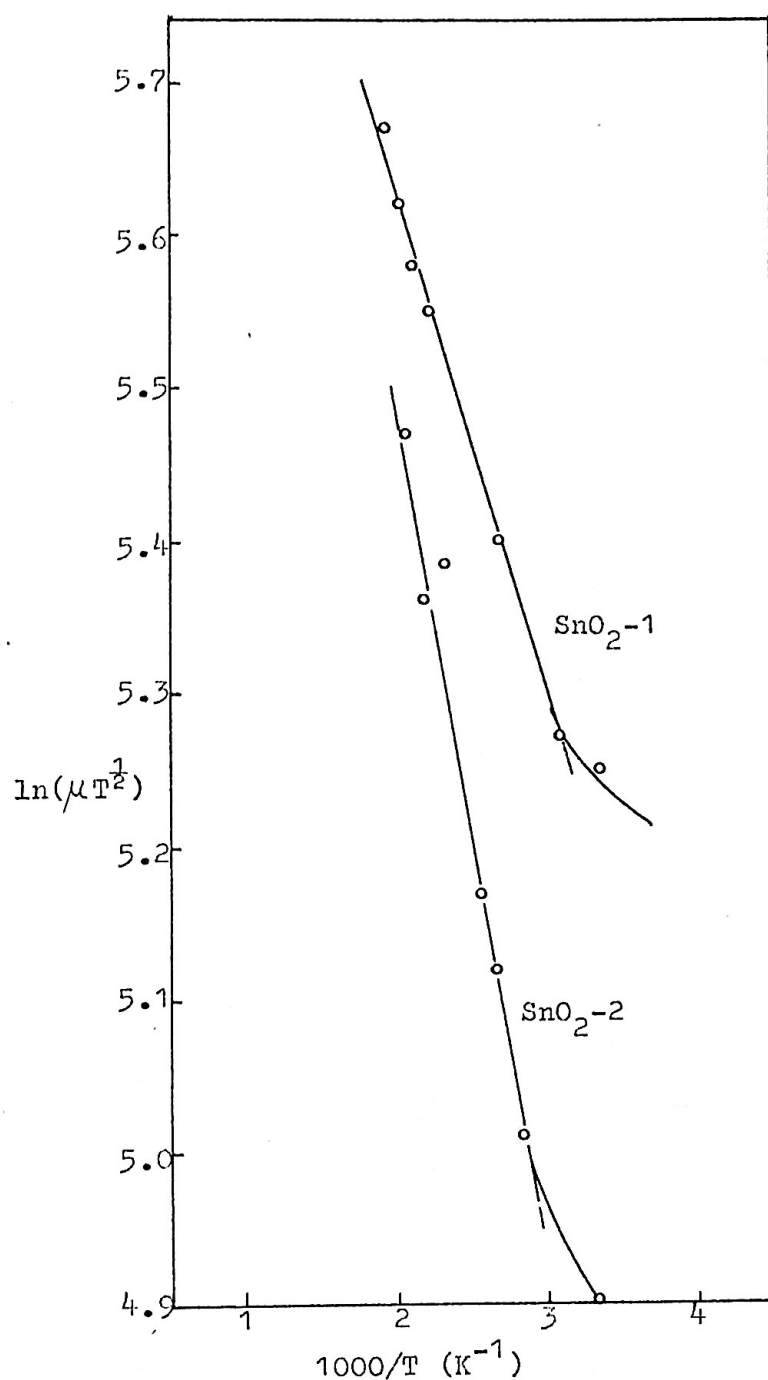


Figure 4.13 : Variation of Hall mobility μ with temperature $T^\circ\text{K}$. Curves A and B are for as-deposited films of SnO_2 -1 and SnO_2 -2 respectively. Curves A' and B' are obtained for the same films but after a vacuum heat treatment.

$$\phi_b = k_B T \ln(n_1/n_2) \quad \dots \quad \dots \quad (4.3)$$

where n_1 and n_2 are the carrier concentrations in grains and in boundary regions respectively. Identifying n_1 as the carrier concentration corresponding to the measured Hall coefficient R_H , the values of n_2 can be calculated. These values are now given in table 4.2.

Figure 4.13 shows the variation of Hall mobility μ of as-deposited and vacuum heat treated films with the temperature. Plotting $\ln(\mu T^{\frac{1}{2}})$ against T^{-1} for the samples in the temperature range 27° to 250°C , as shown in figure 4.14, it is observed that the data points are approximately fitted by equation 4.2 and thus mobility is thermally activated throughout the investigated temperature range. Values of ϕ_b obtained from the slopes of the curves are 0.036 eV and 0.053 eV for the as-deposited samples. After a vacuum heat treatment these values are changed to 0.011 eV and 0.009 eV respectively for the same two films having carrier concentrations 1.3×10^{20} and $9.7 \times 10^{19} \text{ cm}^{-3}$. It can be seen from table 4.2 that the values of ϕ_b for as-deposited films are higher to those of vacuum heat treated films and also that ϕ_b for the as-deposited films increases with the decrease of carrier concentration. Approximately a 25 % change in n_1 ($9.7 \times 10^{19} \leq n_1 \leq 1.3 \times 10^{20} \text{ cm}^{-3}$) is accompanied by a relatively larger change in n_2 (60 %) for

Fig. 4.14 (a)

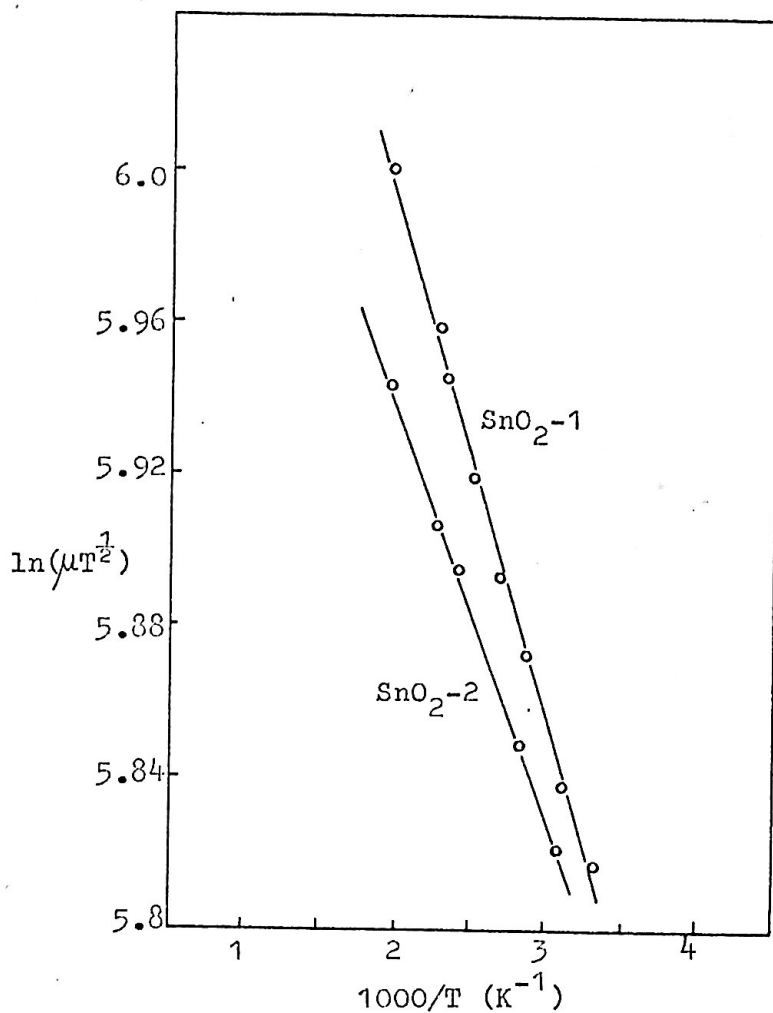


Fig.4.14(b)

Figure 4.14 : $\ln(\mu T^{1/2})$ vs. $10^3/T$ plots for the two samples of SnO_2 . (a) for as-deposited films and (b) for the vacuum heat treated films.

as-deposited films and almost equal change ($\sim 21\%$) for vacuum heat treated films.

Since oxygen vacancies are the major sources of donors in SnO_2 films⁽²⁾, the incorporation of oxygen states in the grain boundaries are important. It appears that the population of oxygen states in the grain boundaries relative to the ambient oxygen pressure over the film could determine the condition of the inward or outward diffusion of the associated charges and that at any temperature either of the processes, chemisorption or desorption may take place to reach an equilibrium. As-deposited films having excess of chemisorbed oxygen are, when heated either in air or in vacuum, subject to desorption of oxygen from the grain boundaries and this lowers the resistivity by lowering the inter-grain boundary barrier height. For these conditions TCR is negative. On the other hand the same film after a vacuum heat treatment and then heating again in air shows a positive TCR indicating oxygen chemisorption has taken place. This is because the population of oxygen at the grain boundaries was decreased by the prior heat treatment operation. In air ambient at normal pressure, if a heating cycle produced desorption, the following cooling cycle would produce chemisorption and vice versa; but in vacuum, desorption predominates due to low pressure and oxygen deficiency in the ambient.

Optical transmission of the films was measured before and after the heat treatment but no significant change of transparency was noticed.

TABLE - 4.2

Samples of SnO_2	Resistivity ρ at room temp. ($10^{-3} \Omega \text{cm}$)	Hall mobility μ at room temp. ($\text{cm}^2/\text{V}.\text{sec}$)	Carrier conc. $n = n_1$ (10^{19}cm^{-3})	TCR (10^{-4}K^{-1})	ϕ_b (meV)	n_2 (10^{19}cm^{-3})
SnO_2 # 1 (as-deposited)	7.5	8.0	9.7	- 10.0	53.0	1.24
SnO_2 # 1 (vac. heat treated)	3.8	18.91	~ 9.7	7.65	9.2	6.7
SnO_2 # 2 (as-deposited)	4.0	11.02	13.0	- 5.78	36.6	3.14
SnO_2 # 2 (vac. heat treated)	2.27	19.42	~ 13.0	3.82	11.0	8.48

4.9.1 Activation Energy of SnO₂ samples :-

Conductivity activation energy E_a of our samples has been determined from the temperature dependence of electrical conductivity σ . For this purpose a set of $\ln \sigma$ vs. T^{-1} curves were plotted in the temperature range 27° to 250°C for the samples of different carrier concentrations. Figure 4.15 shows these plots for three typical samples. The figure shows two distinct regions for each curve and these two regions have different slopes. The calculated values of E_a with their effective range of temperature are shown in table 4.3. In the room temperature side the activation energy E_a^I is very low and lies in the range of 3.88 meV to 5.22 meV, whereas in the high temperature side E_a^{II} is of the order of 40 to 63 meV. The existence of two activation energies indicate that there may have two donor impurity levels in our SnO₂ samples. With the increase of net carrier concentration (donor density), the shallower level may merge with the extended conduction band and results in temperature independent conductivity in the room temperature side. This phenomenon may lead to a shrinkage of the optical band gap E_g of the material at high carrier concentration levels. For our SnO₂ sample we have noticed a similar shrinkage of E_g at about $\geq 10^{21} \text{ cm}^{-3}$ of carrier concentration (described later in section 4.11.1).

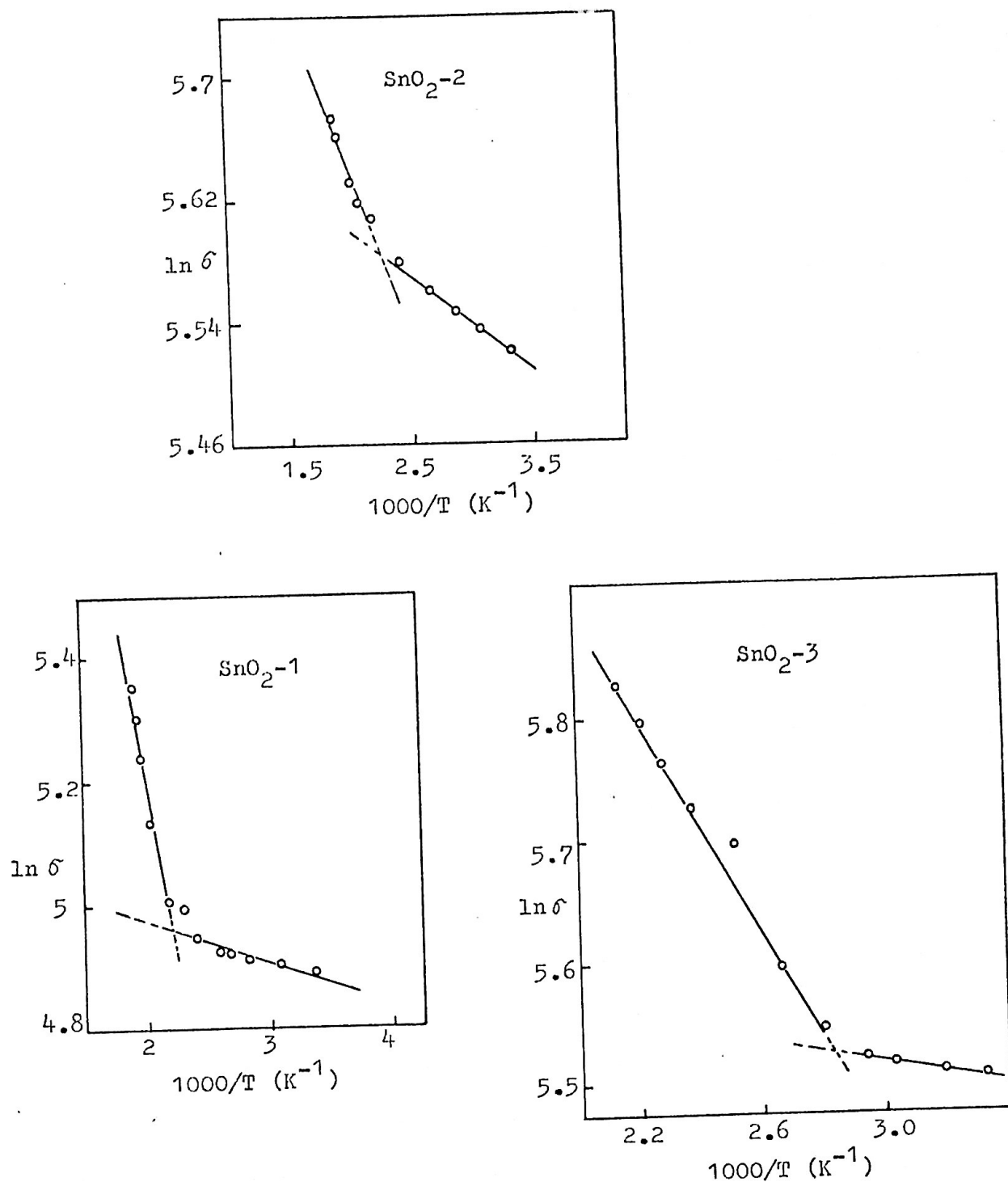


Figure 4.15 : Plot of $\ln \sigma$ vs. $10^3/T$ for three typical samples of SnO_2 .

TABLE - 4.3

Sample	Carrier conc. n (10^{19} cm^{-3})	E_a^I (meV)	Temp. range I ($^{\circ}\text{K}$)	E_a^{II} (meV)	Temp. range II ($^{\circ}\text{K}$)
$\text{SnO}_2 \# 1$	9.7	4.3	300 - 400	63.0	450 - 523
$\text{SnO}_2 \# 2$	13.0	5.2	300 - 500	43.0	500 - 523
$\text{SnO}_2 \# 3$	14.0	3.88	300 - 365	40.5	370 - 523

The decrease of activation energy (E_a^{II}) with increasing donor concentration (N_D) is commonly observed in both elemental and compound semiconductors. Pearson and Bardeen⁽¹⁷⁾ have proposed a model to explain this effect. Their hypothesis is that- there is appreciable electrostatic attraction between the electrons and ionized impurity centres which increases with the increase of donor concentrations. They have obtained the following equation from a study on boron-doped silicon samples.

$$E_D = E_0 - a N_D^{\frac{1}{3}} \quad \dots \quad \dots \quad \dots \quad (4.4)$$

where E_0 is the donor ionization energy at infinite dilution, and E_D is the donor ionization energy. Fitting our data in the above equation (noting that $E_D = 2 E_a$ for highly degenerate samples and $n \approx N_D$) we obtain for our as-deposited SnO_2 films

$$E_D = 0.482 - 8.24 \times 10^{-8} n^{\frac{1}{3}} \text{ eV} \quad \dots \quad \dots \quad (4.5)$$

On the other hand for SnO_2 crystals⁽¹⁸⁾ heat treated in oxygen the above equation (4.4) reduces to

$$E_D = 0.15 - 8.7 \times 10^{-8} N_D^{\frac{1}{3}} \text{ eV} \quad \dots \quad \dots \quad (4.6)$$

4.10 THERMOELECTRIC POWER OF SnO_2 FILM

The thermoelectric power (TEP) of some samples of SnO_2 having different carrier concentrations were measured in the temperature range 27° to 160°C . Measured values of TEP are plotted as a function of temperature in figure 4.16. All the samples showed an almost reversible character when subjected to thermal cycling from 27° to 160°C . The sign of the thermo-emf was negative corresponding to the n-type character of the sample as was obtained earlier in Hall effect experiments.

Since our measurements were limited to high temperature range only, the contribution from phonon drag to the TEP may be assumed negligible. From figure 4.16 it can be seen that the TEP can be expressed as⁽¹⁹⁾

$$Q = bT + c \quad \dots \quad \dots \quad \dots \quad (4.7)$$

where Q is the TEP value at absolute temperature T , b and c are independent of temperature but may depend on the film thickness and heat treatment. The first term bT is the electron diffusion term and c represents the temperature independent contribution to the TEP.

The charge carrier concentrations obtained from the Hall coefficients of these samples are of the order of

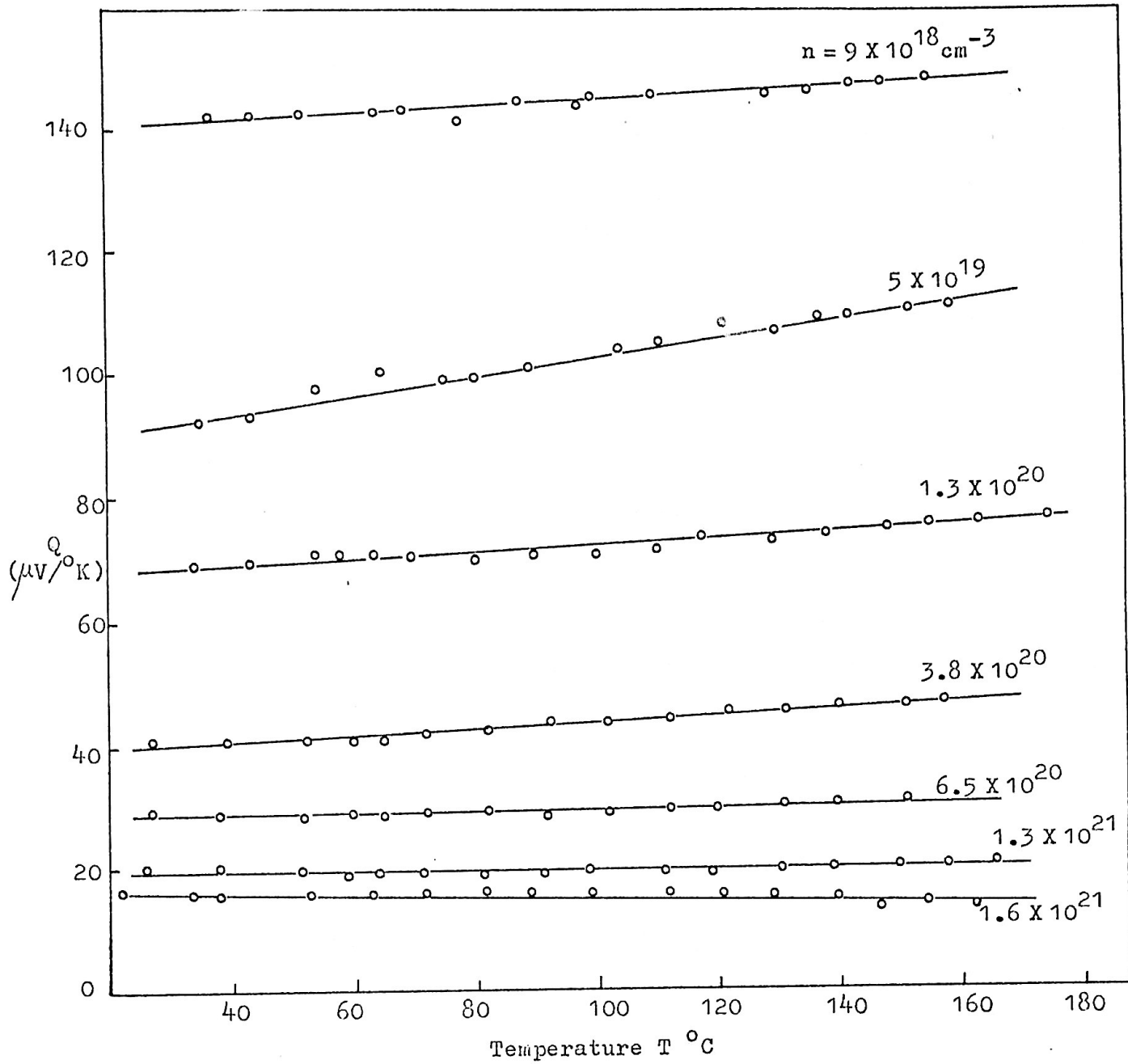


Figure 4.16 : Variation of thermoelectric power of SnO_2 film with temperature. Different curves are for samples of different carrier concentrations.

$\sim 10^{19}$ to $\sim 10^{21} \text{ cm}^{-3}$, and so all the samples are considered to be degenerate at room temperature. The degeneracy temperature calculated from the expression

$$T_d = (h^2 / 8k_B m_e^*) (3n / \pi)^{2/3}$$

is found to be $\sim 10^3 \text{ }^\circ\text{K}$.

Figure 4.17 shows the variation of TEP with the carrier concentration n at three different temperatures. It is observed that with the increase of carrier concentration the TEP values tend to become temperature independent (figure 4.16). This corresponds to a saturation effect that implies a pinning mode of the Fermi levels possibly at lower carrier concentrations.

4.10.1 The Position of Fermi level and Its Variation with Carrier Concentration and Temperature : -

The position of Fermi level of our SnO_2 samples can be obtained from the thermo-power data. The expression for the thermoelectric power of a degenerate semiconductor can be given by⁽²⁰⁾

$$Q = (k_B/e) [(3/2) F_2(\eta)/F_1(\eta) - \eta] \dots \dots (4.8)$$

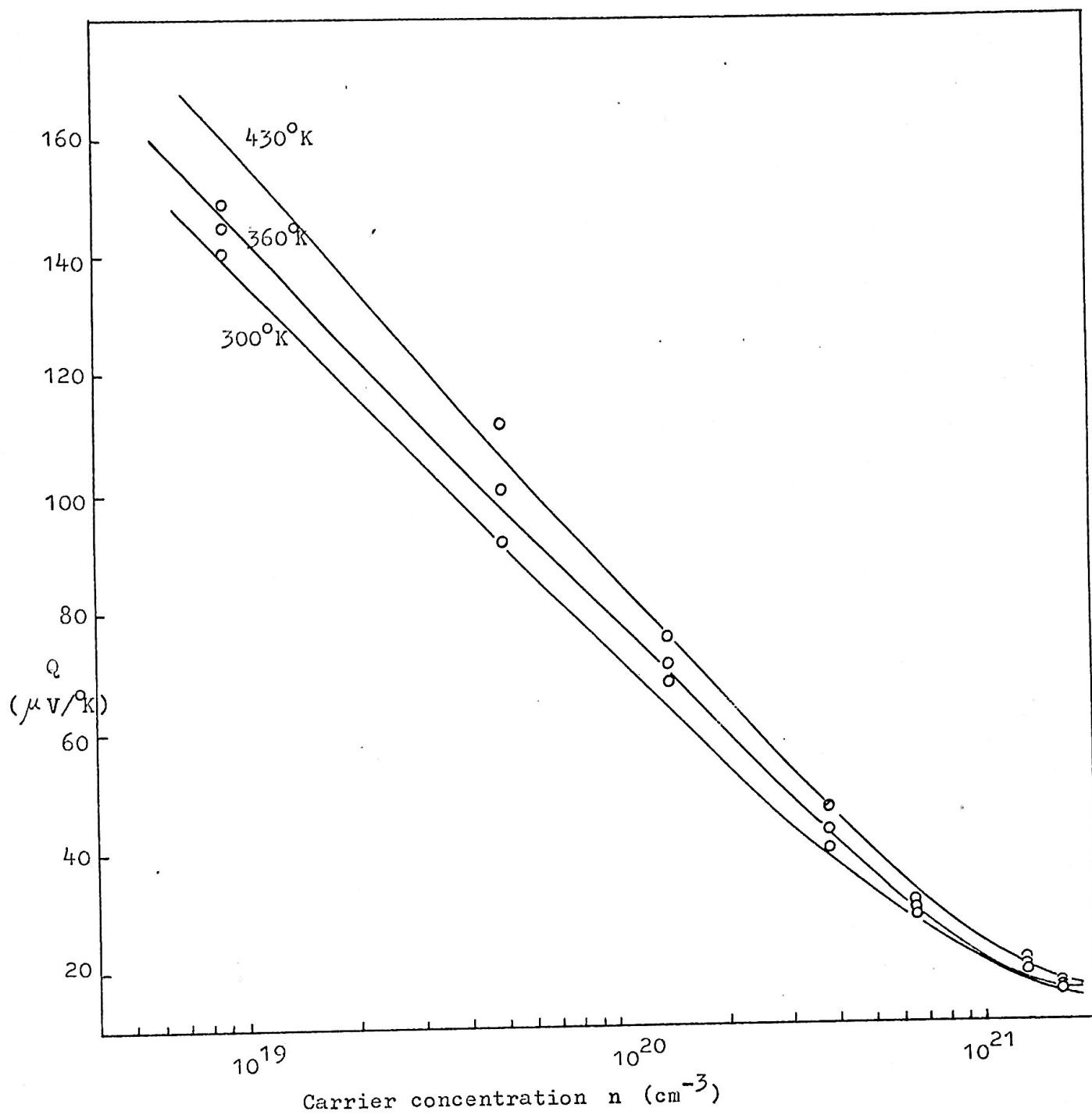


Figure 4.17 : Plot of the thermoelectric power Q as a function of carrier concentration n of SnO_2 film at three different temperatures.

where,

$$\eta = E_F / k_B T \quad \dots \quad \dots \quad (4.9)$$

is the reduced Fermi energy. Here the position of Fermi level is with respect to the conduction band edge. $F_r(\eta)$ are the Fermi integrals of order r defined by equation 2.21, and their values are obtained in standard tables^(20,21). Now from the measured values of thermoelectric power Q and solving equation (4.8) numerically with the help of Fermi integral values, the value of η and hence the position of the Fermi levels E_F have been determined. It was found that the Fermi levels lie in the conduction band for all the samples. This shows a complete degenerate nature of our spray deposited SnO_2 films. The variation in the position of the Fermi levels at two different temperatures (300° and 400°K) with respect to the carrier concentration of the samples are shown in figure 4.18. It is now clear from this figure, curve(a) and (b), that the Fermi levels at different temperatures are being gradually pinned near the band edge with decrease of carrier concentration^(22,27). This confirms our prediction made in the previous section 4.10.

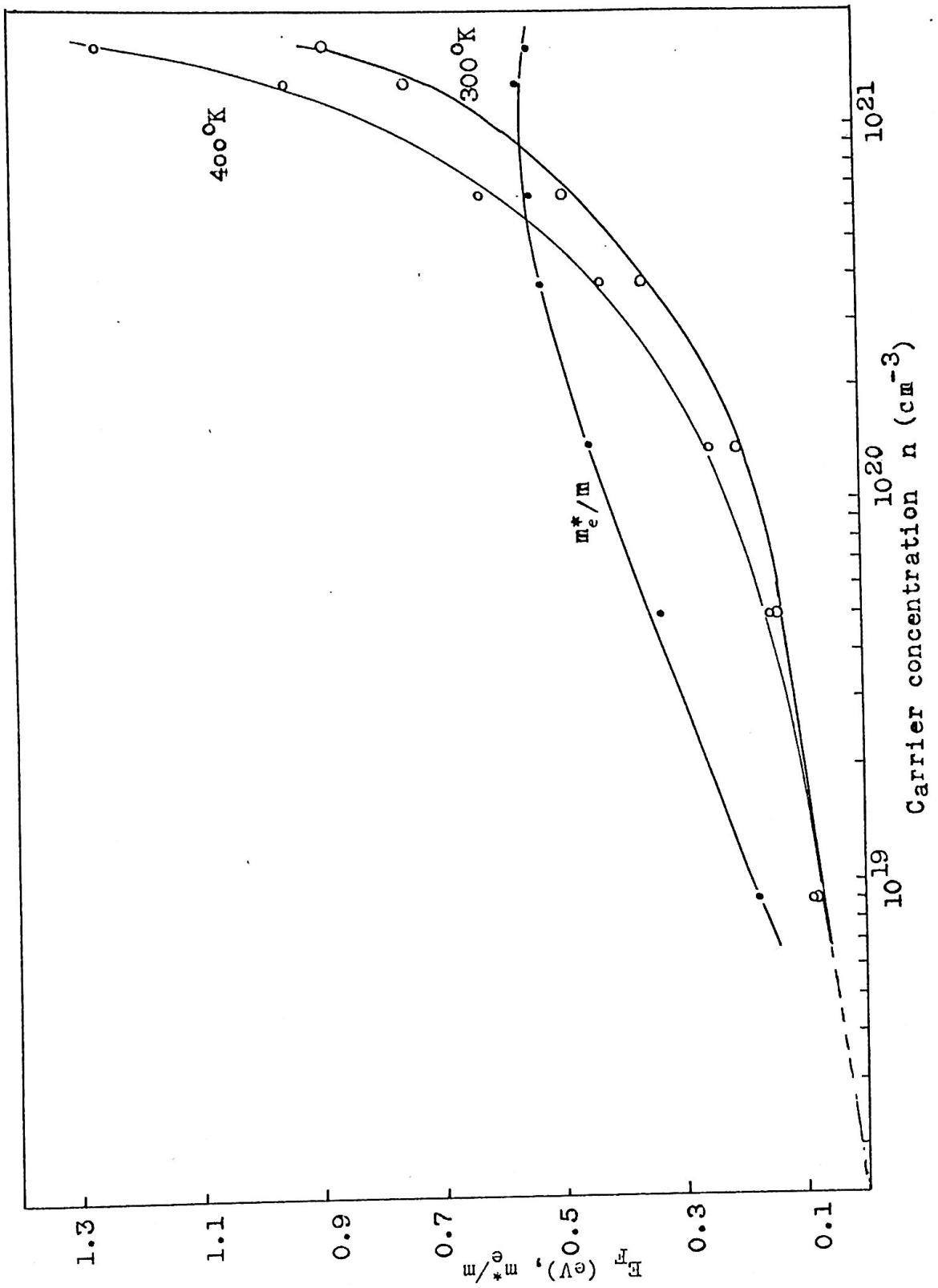


Figure 4.18 : Variation of Fermi energy E_F and effective mass of electron m_e^* with carrier concentration n of SnO_2 film.

4.10.2 Effective Mass of Electrons :-

Knowing η from the above calculations it is now easier to obtain the electron effective mass m_e^* in the conduction band. It is known that, for a degenerate semiconductor, m_e^* can be related to the free carrier concentration n by the following relation,

$$n = (1/h^3) 4\pi (2m_e^* k_B T)^{3/2} F_{\frac{1}{2}}(\eta) \dots \dots (4.10)$$

where $F_{\frac{1}{2}}(\eta)$ is again the Fermi integral. Measuring n from the Hall effect, the value of m_e^* for all the samples of SnO_2 have been determined at room temperature. These values are plotted as a function of the carrier concentration in figure 4.18, curve (c). It is observed from this curve that the variation of m_e^* with carrier concentration is limited mostly in the concentration range $\sim 10^{18}$ to $2 \times 10^{20} \text{ cm}^{-3}$, and above this range m_e^* becomes almost constant. We found m_e^* to increase from 0.14 m to 0.56 m in the carrier concentration range 6×10^{18} to $1.3 \times 10^{21} \text{ cm}^{-3}$ for our SnO_2 samples.

4.10.3 Carrier Concentration for Nondegenerate SnO_2 Film :-

The extrapolated end of the E_F vs. n curve, curve(a) of figure 4.18, to $E_F = 0$ corresponds to a carrier concentration

$1.5 \times 10^{18} \text{ cm}^{-3}$, and this may be taken as the upper limit of the carrier concentration, n_0 , for nondegenerate SnO_2 film. Because at a concentration $n < n_0$ the Fermi level ϕ the sample should leave the conduction band and lie in the band gap.

4.11 THE OPTICAL ABSORPTION

Optical absorption coefficients of SnO_2 film have been determined from the transmission spectra. It is already mentioned that over the entire visible range of frequencies SnO_2 films are found highly transparent. Figure 4.19 shows the transmission spectra of undoped and Sb-doped SnO_2 films with reference to an uncoated substrate in the wavelength range $0.28 \mu\text{m}$ to $0.9 \mu\text{m}$. Sb-doped films show lower transmission than that of undoped films in the visible range. Similar curves were also obtained for F-doped films.

In the fundamental absorption region, which lies in the ultra-violet range, the transmission coefficient T is given by⁽²³⁾

$$T = A \exp(-\alpha t) \quad \dots \quad \dots \quad \dots \quad (4.11)$$

where $\alpha = 4\pi k/\lambda$, and k is the extinction coefficient at

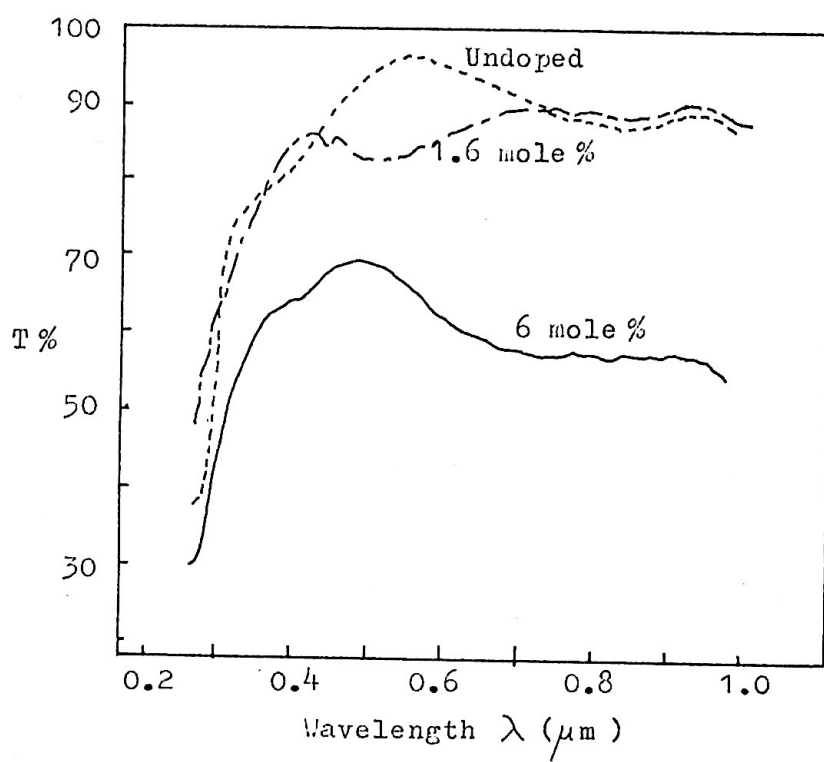


Figure 4.19 : Transmission spectra of undoped and Sb-doped SnO_2 thin films.

wavelength λ and t is the film thickness. For $k^2 \ll n_f^2$, which is found valid for our SnO_2 films (n_f is the refractive index of the film), the value of A that accounts for the reflection effects can approximately be taken as unity⁽⁴⁾. Therefore the absorption coefficient α can be determined from the value of t and T . The calculated values of α as a function of wavelengths is shown in figure 4.20(a).

4.11.1 Evaluation of The Optical Band Gap :-

Assuming that the transition probability becomes constant near the absorption edge, the absorption coefficient α for direct allowed transition for a simple parabolic band scheme can be described as a function of incident photon energy $h\nu$ as

$$\alpha \propto (h\nu - E_g)^{1/2} / h\nu$$

where E_g is the optical band gap. Now from a plot of $(\alpha h\nu)^2$ against $h\nu$, the value of E_g can be determined by extrapolating the straight portion of the curve to $\alpha = 0$. Figure 4.20(b) shows such plots for some of the SnO_2 samples having different carrier concentrations. It is observed from this figure that the fundamental absorption edge shifts gradually to the shorter

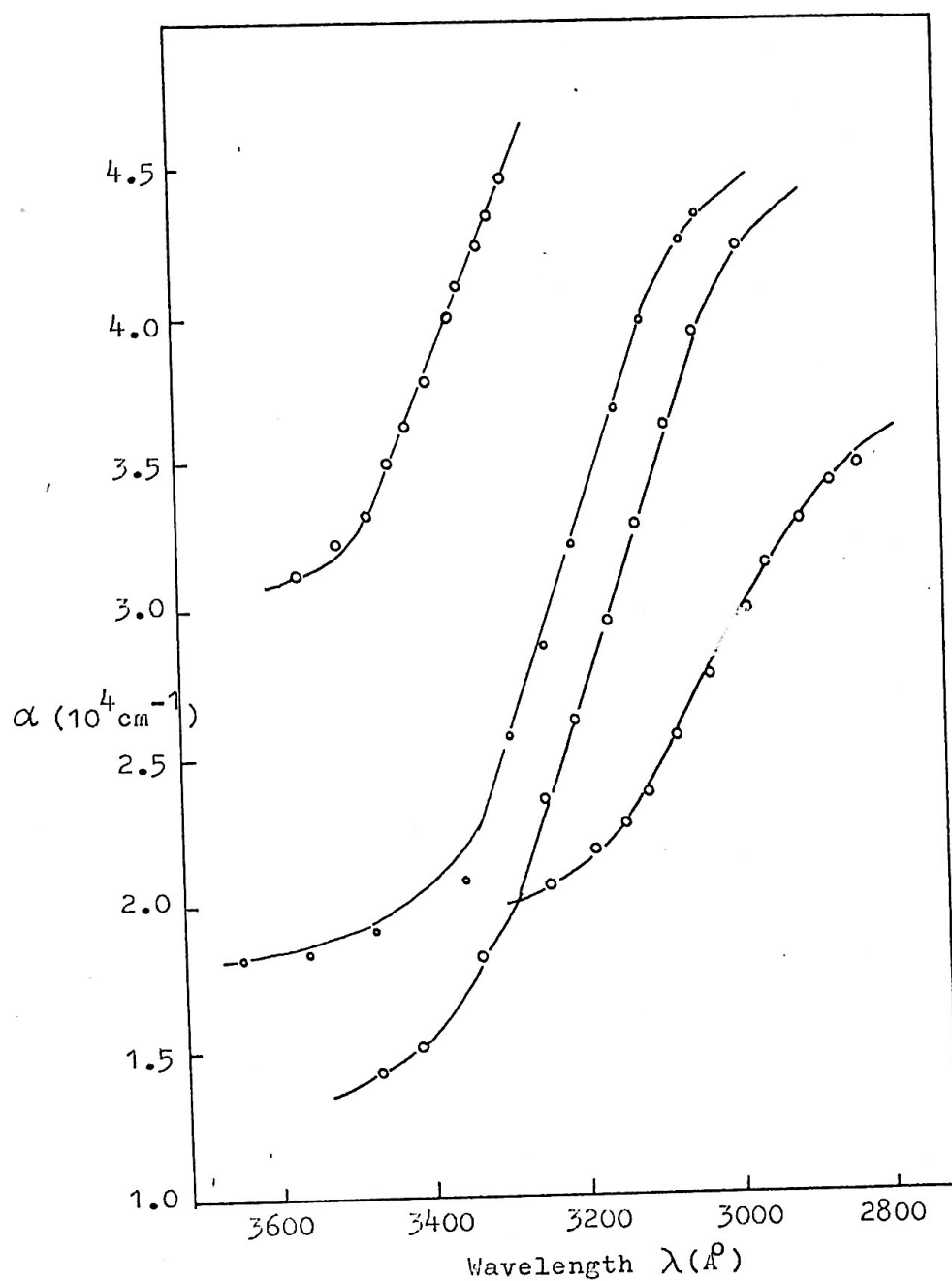


Figure 4.20 (a): Variation of absorption coefficient α of SnO_2 film at different wavelengths in the fundamental absorption region. Different curves are for samples of different carrier concentration as shown in figure 4.20 (b).

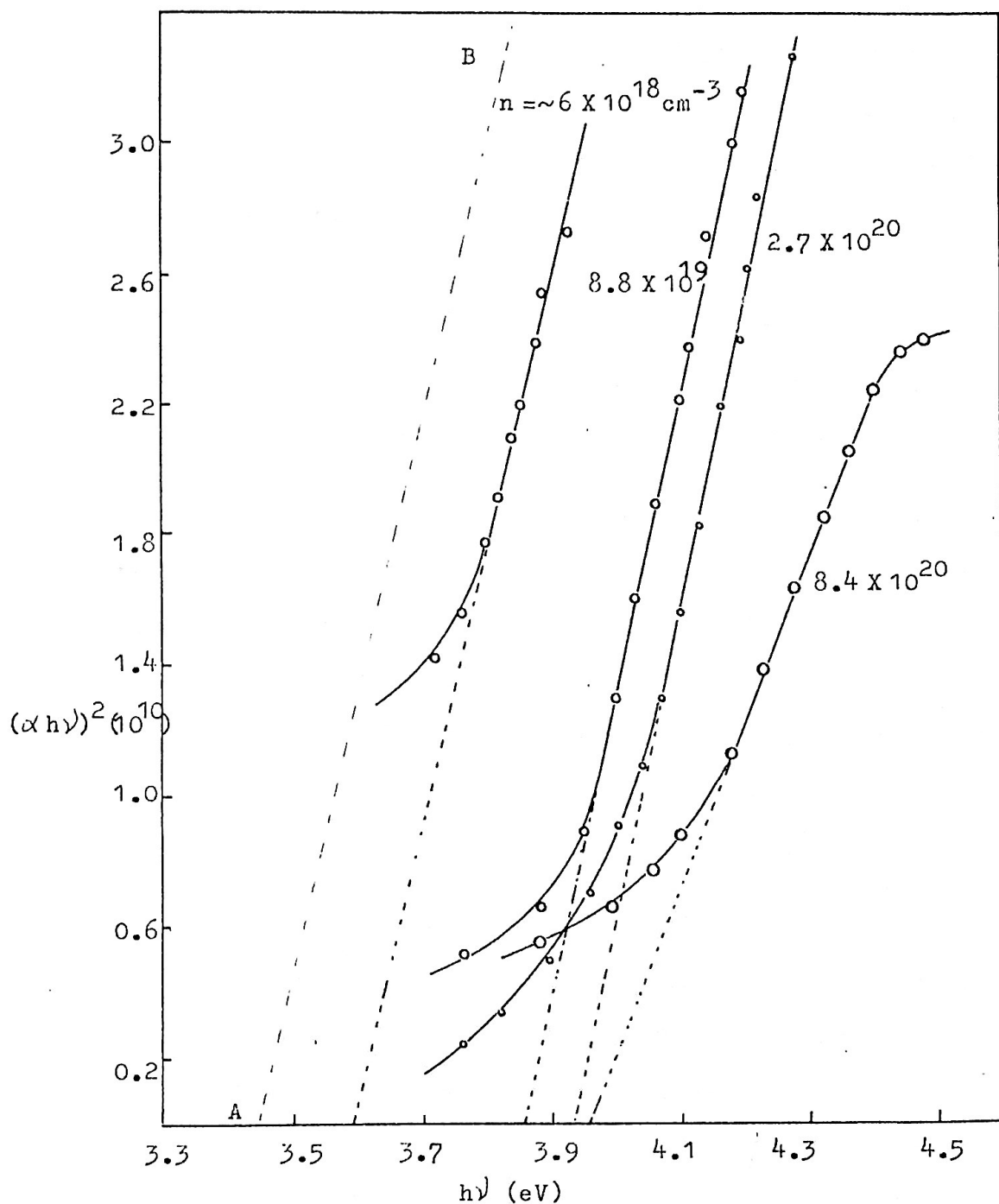


Figure 4.20(b): Plot of $(\alpha h\nu)^2$ vs. $h\nu$ showing the shift of absorption edge with respect to the carrier concentration n (cm^{-3}) of SnO_2 film.

wavelength (higher energy) with the increase of carrier concentration. This effect of widening of the band gap is known as the Moss-Burstein shift in semiconductors⁽²⁴⁾ as has already been mentioned in chapter-2. Figure 4.21 shows the variation of E_g with the carrier concentration n of the samples. It is noticed from this figure that the value of E_g starts from 3.59 eV for a sample with carrier concentration $6 \times 10^{18} \text{ cm}^{-3}$ and increases upto 3.96 eV for a sample with carrier concentration $6 \times 10^{20} \text{ cm}^{-3}$.

Above $\sim 10^{21} \text{ cm}^{-3}$ of carrier concentration the value of E_g is slightly decreased locally from its maximum value of 3.96 eV. This shrinkage may be due to (i) the merging of the shallower donor levels with the extended conduction band⁽²⁵⁾ or, it may be due to a (ii) many body effect in heavily doped semiconductors, which produces an increased shielding effect of the impurity centres by the free electrons.

However, while such a shift is present with the optical absorption edge, it is very difficult to detect the actual conduction band edge, E_c , of the material from the optical absorption studies. But still an approximate estimation of the same can be made in the following way.

The carrier concentration at which the Fermi level coincides with the conduction band edge is $n_0 = 1.5 \times 10^{18} \text{ cm}^{-3}$ as obtained in section 4.10.3, and the energy gap corresponding

to this value of $n (= n_0)$ obtained from the extrapolated part of the n vs. E_g curve (figure 4.21) is 3.45 eV. The value of E_g just obtained should correspond to the lower limit of the absorption edge and may be taken as the actual band gap of our SnO_2 sample⁽²⁷⁾. This value is in excellent agreement with the value of 3.4 eV obtained by Arai⁽²⁵⁾ and 3.44 eV obtained by Kohnke and Hurt⁽²⁸⁾ from the maximum of the conductivity spectral response curve. In the above analysis it has been assumed that the nondegenerate SnO_2 sample would not suffer any appreciable Moss-Burstein shift. The shift of E_g from 3.45 eV to 3.96 eV for our SnO_2 film in the carrier concentration range $\sim 10^{18}$ to $\sim 10^{21} \text{ cm}^{-3}$ is very large and shows that SnO_2 is a broad band semiconductor⁽²⁾.

The probability of indirect transition has also been considered but the values of E_g then obtained were very low and seemed to be unimportant.

4.12 HOLE EFFECTIVE MASS

In section 4.10.2 it has been observed that m_e^* varies from 0.14 m to 0.56 m in the carrier concentration range 6×10^{18} to $1.3 \times 10^{21} \text{ cm}^{-3}$. Such a wide variation of m_e^* is an indication that the curvature of the conduction band is large⁽²⁹⁾ and is probably influenced by the valence band curvature. In such a situation the shift of the absorption edge with the carrier concentration can be described in the same way as the

Fermi energy of a free electron gas because E_F must comply with the shift. Therefore we may write⁽²⁷⁾

$$\text{Shift of } E_g \propto E_F \approx \hbar^2 / 2 m_r^* (3\pi^2 n)^{2/3} \quad \dots \quad (4.12)$$

where m_r^* has been used in place of m_e^* to account for the effect of the valence band curvature to the conduction band. m_r^* can be given by

$$1/m_r^* = 1/m_e^* + 1/m_h^* \quad \dots \quad (4.13)$$

Here m_h^* is the hole effective mass in the valence band. In principle m_r^* may have a slight dependence on n in equation 4.12 but may be treated as constant for approximation. Therefore plotting E_F against $n^{2/3}$ the value of m_r^* can be determined. Figure 4.22 shows such a plot where it is observed that $n^{2/3}$ law is excellently obeyed. The value of m_r^* obtained from the slope of the straight line is 0.64 m. Now using the values of m_e^* in equation 4.13 the values of m_h^* can be determined. For a sample with $n = 8.8 \times 10^{19} \text{ cm}^{-3}$, $m_e^* = 0.4 \text{ m}$ and $E_F = 0.17 \text{ eV}$, m_h^* comes out to be -1.06 m. The negative sign of the hole effective mass implies that the valence band is curved in the same direction as the conduction band and is an indication that the conduction band and the valence band extrema do not lie at the same wave vector $k_e = 0$ ⁽²⁹⁾. The values of m_h^* for other samples can be determined in a similar way.

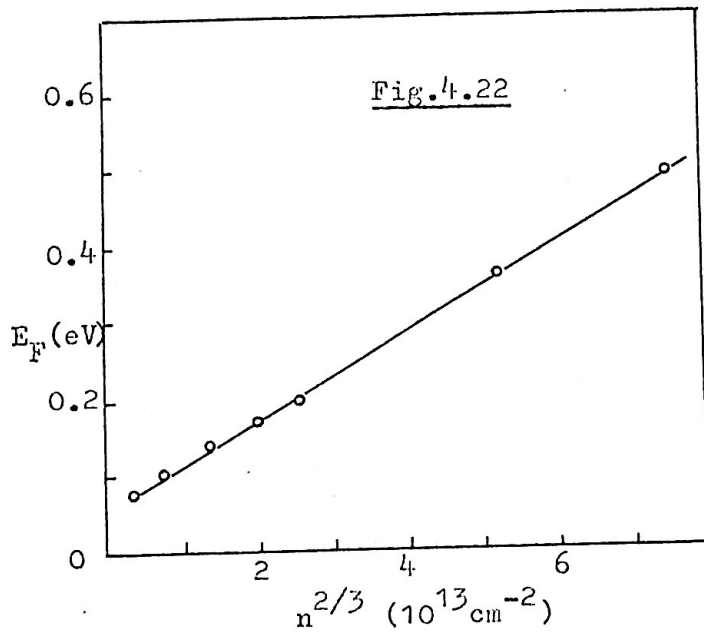
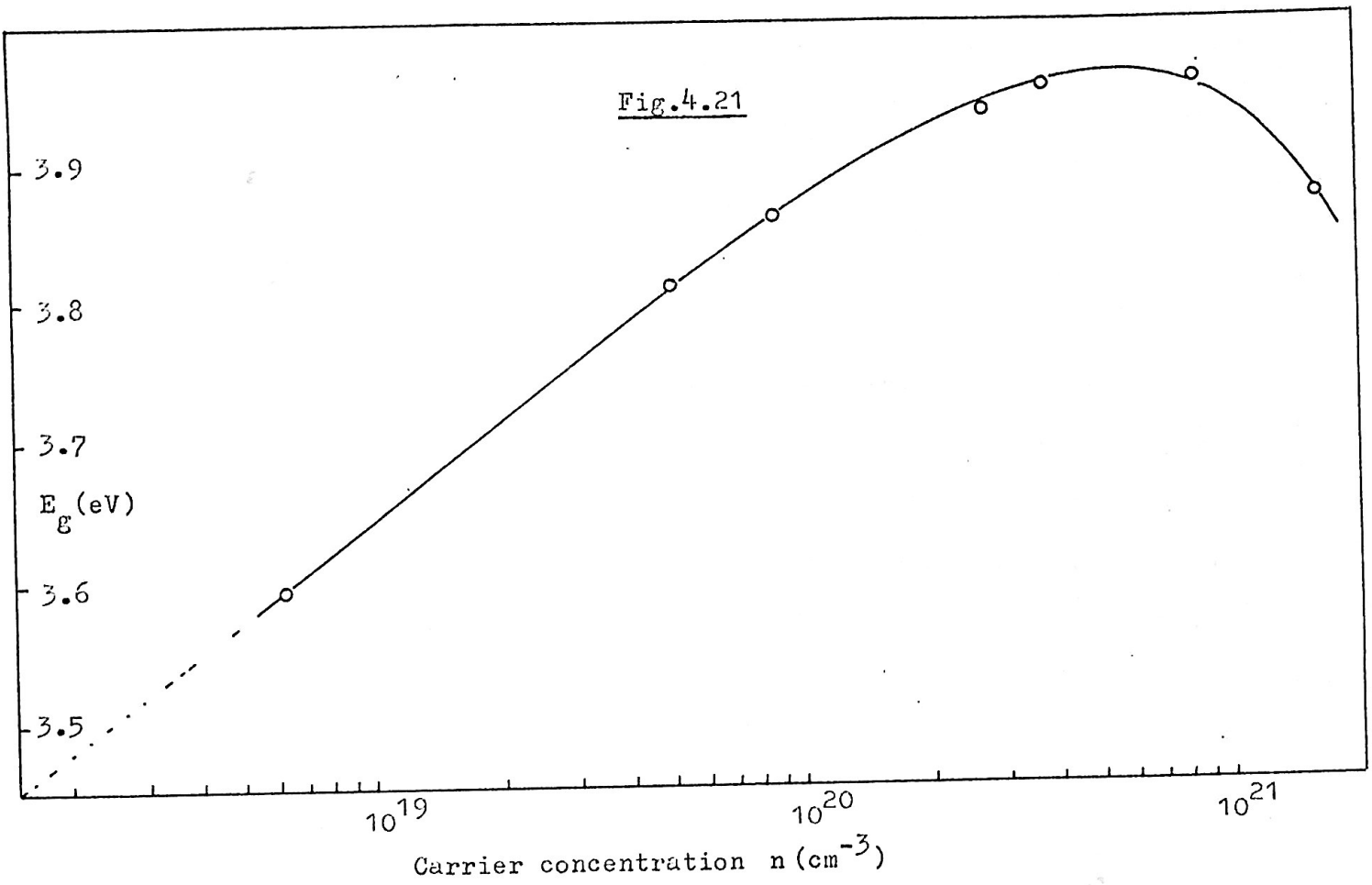


Figure 4.21 : Variation of the optical energy gap E_g as a function of carrier concentration of SnO_2 film.

Figure 4.22 : Plot of the Fermi energy E_F at room temperature as a function of $n^{2/3}$ of SnO_2 film

4.12.1 Consistency of the Values of E_F and m_h^* :-

In order to confirm whether the values of the Fermi energy obtained from the thermopower data and the values of m_h^* obtained above are consistent with the Burstein shift obtained from the optical absorption studies can be tested by calculating the values of $h\nu(\alpha)$ from the following expression given by Kaiser and Fan⁽³⁰⁾.

$$h\nu(\alpha) = E_g + (1 + m_e^*/m_h^*) [E_F - k_B T \ln \{(\alpha_0 - \alpha)/\alpha\}] \dots (4.14)$$

where the second term on the R.H.S accounts for the shift. Here $h\nu(\alpha)$ is the photon energy corresponding to an absorption coefficient α , α_0 is the absorption coefficient if the excited state corresponding to the same $h\nu(\alpha)$ is unoccupied (here nondegenerate SnO_2) and E_g is the energy gap of the sample. The value of α_0 may approximately be taken here from the straight line AB of figure 4.20 (b) drawn at $h\nu = E_g = 3.45$ eV and parallel to that due to $n = 6 \times 10^{18} \text{ cm}^{-3}$. For a sample with $n = 8.8 \times 10^{19} \text{ cm}^{-3}$ and $E_g = 3.86$ eV the calculated value of $h\nu(\alpha)$ comes out to be 3.98 eV corresponding to the experimental value of 4 eV. Thus the agreement is very good. For another sample with $n = 2.7 \times 10^{20} \text{ cm}^{-3}$, $E_g = 3.93$ eV, $E_F = 0.29$ eV, $m_e^* = 0.5 m$ and $m_h^* = -2.2 m$ the calculated value of $h\nu(\alpha)$ comes out to be 4.14 eV corresponding to the experimental

value of 4.09 eV, therefore the agreement is again very good. Thus the position of the Fermi levels are consistent with the observed Moss-Burstein shift for our SnO_2 samples.

4.13 CARRIER SCATTERING MECHANISM IN SnO_2 FILM

It is observed that SnO_2 thin films possess considerably lower Hall mobility at room temperature of $\sim 9.1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ in comparison to the corresponding single crystal⁽³¹⁾ mobility of $\sim 87 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ for the same carrier concentration of $\sim 8.8 \times 10^{19} \text{ cm}^{-3}$. Different scattering processes and the grain boundary barrier effects are probably responsible for this. The measured Hall mobility of the samples are plotted as a function of their carrier concentration in figure 4.23 curve(a).

Since the samples are polycrystalline in structure the contribution of grain boundary scattering may be important. Roy et al⁽³²⁾ have mentioned that the grain boundary limited mobility, μ_g , in a polycrystalline sample is related to the effective mobility, μ_e , by the relation

$$1/\mu_e = 1/\mu_s + 1/\mu_g \quad \dots \quad \dots \quad (4.15)$$

where, μ_s is the corresponding mobility in a single crystal

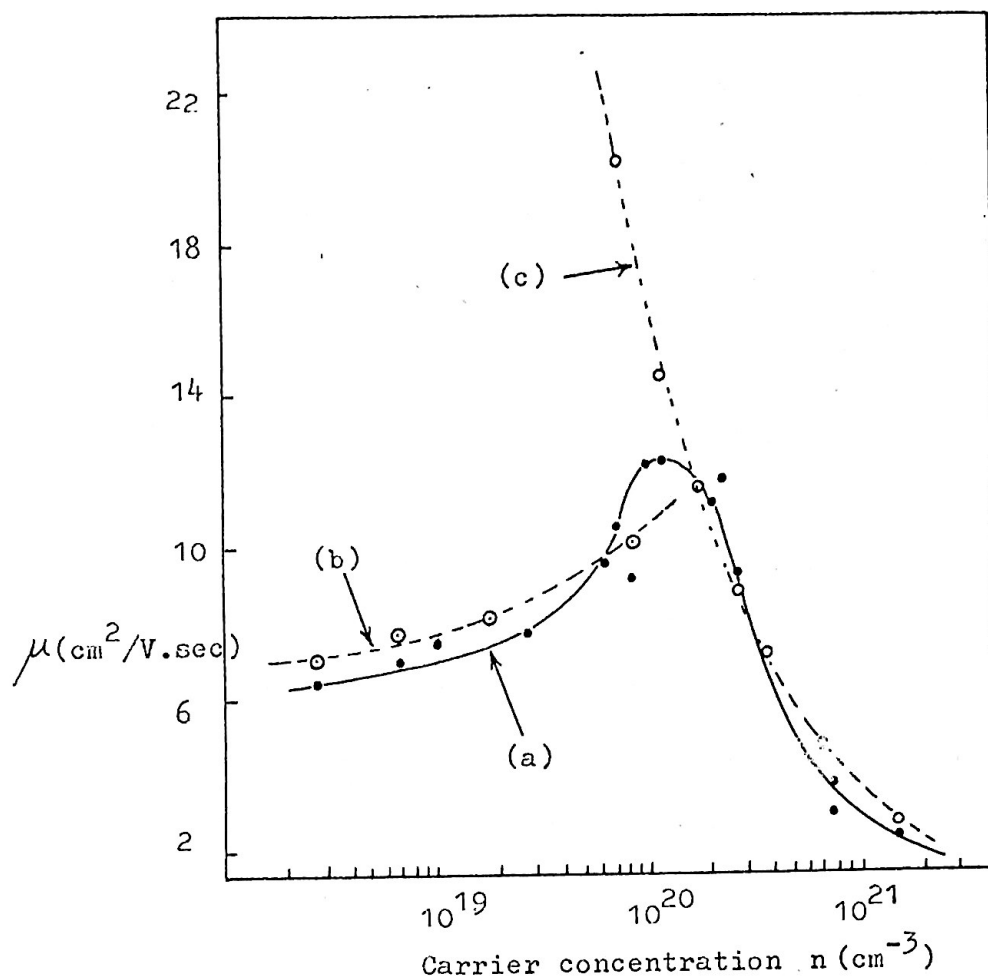


Figure 4.23 : Variation of electron mobility μ as a function of carrier concentration n . (a)-Experimental curve; (b)-Grain boundary scattering limited mobility and (c)-Ionized impurity scattering limited mobility. (b) and (c) are calculated curves. Mobility values are for the as-deposited films of SnO_2 at room temperature.

where no grain boundary is present at the same carrier concentration. By taking the values of μ_g from the literature^(31,33,34) and taking μ_e as the experimental mobilities, the values of μ_g were determined from equation 4.15 and are plotted as a function of the carrier concentration in figure 4.23, curve(b).

The contribution of ionized impurity scattering to the carrier mobility at different carrier concentrations in degenerate SnO_2 films have been calculated by the process worked out by Csavinszky⁽³⁵⁾. The calculated values of the mobility are also plotted as a function of the same carrier concentration in figure 4.23, curve(c). Now from the nature of the three curves (a), (b) and (c) of figure 4.23 it is clearly understood that these two processes, the grain boundary scattering and the ionized impurity scattering are distinctly predominant in the two different ranges of carrier concentrations⁽²²⁾. The close agreement between the theoretical and experimental curves shows that at room temperature, the contribution due to scattering processes other than these two would probably be very small at least in the range of carrier concentration investigated⁽²⁾. Thus we conclude that for spray deposited SnO_2 thin film samples two distinct scattering processes viz the grain boundary scattering and the ionized impurity scattering are predominant in the two different ranges of carrier concentrations from $\sim 10^{18}$ to $\sim 10^{20} \text{ cm}^{-3}$ and from $\sim 10^{20}$ to $\sim 10^{21} \text{ cm}^{-3}$.

respectively, at room temperature⁽²⁷⁾. It may be mentioned here that our observation on samples of carrier concentration $\geq 10^{20} \text{ cm}^{-3}$ agrees well with those of Imai⁽³⁶⁾, who on the basis of thermopower measurement concluded that ionized impurity scattering is the predominant scattering mechanism in SnO_2 sample at room temperature.

4.14 NATURE OF THE SnO_2 CRYSTAL BINDING

Semiconductors are generally covalent in nature, but it is an established fact that no chemical bond is purely covalent or purely ionic in character but is a mixture of the both. From the electronegativity concept of Pauling the percentage of ionic character, y , of the bond between Sn and O (oxygen) can be determined by using the Pauling's electronegativity values⁽³⁷⁾ in an empirical relation⁽³⁸⁾ given by him-

$$\log (100 - y) = 2.0 - 0.11 [\Delta \text{EN} (\text{Sn-O})]^2 \quad \dots \quad (4.16)$$

$$\text{or, } y = 56 \%$$

Here $\Delta \text{EN} (\text{Sn-O})$ is the electronegativity difference between Sn and O. In polycrystalline extrinsic SnO_2 samples if the bonds between Sn and O are taken as the principal bond for the crystalline phase then it can be inferred that SnO_2 is more

an ionic crystal than covalent.

4.15 THE ELECTRONEGATIVITY OF BULK SnO_2 MATERIAL

According to Mulliken's assumption⁽³⁷⁾, the electronegativity of a neutral atom is the arithmetic mean of the atomic electron affinity (A_f) and the first ionization energy (E_I) of the atom; and we know, the electronegativity equalization concept of Sanderson⁽³⁷⁾, the bulk electronegativity of a compound is the geometric mean of the electronegativities of the constituent atoms. Therefore, the electronegativity of SnO_2 can be written as

$$\text{EN}(\text{SnO}_2) = \left[\frac{1}{2} \{A_f(\text{Sn}) + E_I(\text{Sn})\} \times \frac{1}{4} \{A_f(\text{O}) + E_I(\text{O})\}^2 \right]^{\frac{1}{3}} \dots (4.17)$$

Using the respective values of electron affinity and ionization energies in this equation we get

$$\text{EN}(\text{SnO}_2) = 6.25 \text{ eV} \dots \dots \dots (4.17a)$$

4.16 THE ELECTRON AFFINITY AND WORK FUNCTION OF SPRAY DEPOSITED SnO_2 THIN FILM

The electron affinity and work function are the two important parameters of a semiconducting specimen. For the fabrication of junction device like solar cell these two parameters are especially needed for the constituent components to have a better selection of the materials.

Electron affinity and work function are defined, respectively as the energy required to remove an electron from the bottom of the conduction band E_c and from the Fermi level E_F to a position just outside the surface of the material (vacuum level).

Determination of the electron affinity of a bulk semiconductor is not so straight forward as that of the Fermi surface. Therefore, an indirect and empirical method⁽³⁹⁾ based on the electronegativities of the atoms may be used. In the case of semiconductors the bulk electronegativity, EN , corresponds to the intrinsic Fermi level, E_F^i , such that relative to vacuum⁽⁴⁰⁾

$$E_F^i \approx EN = \chi + E_g/2 \quad \dots \quad \dots \quad (4.18)$$

where, χ is the electron affinity and E_g is the optical band

gap between the conduction and valence bands. Since the position of E_F^i in a bulk semiconductor is determined by the regular crystallographic structure of the intrinsic material, the electronegativity could therefore be assumed here as an approximately constant parameter, and the effect of change of the possible impurity contents in the material can be accounted for by a net change in the electron affinity of the sample⁽⁴⁰⁾.

In polycrystalline semiconductor at least in simple cases, the charge carriers responsible for electrical conduction are the free charges and they correspond to the defect centres inherent in the individual crystallites as well as in the bulk, but in no way they should affect the structural formula of the host compound. The concentration of such charge carriers in the bulk material is determined from the measurement of Hall constants at low magnetic field. Therefore, equation 4.17 and 4.18 can be taken into account to estimate the electronegativity and hence the electron affinity of SnO_2 samples of various carrier concentrations.

Depending on the substrate temperature ranging from 350° to 550°C , it has been observed that the carrier concentration of undoped SnO_2 thin film varies from $\sim 10^{18}$ to $\sim 10^{20}\text{ cm}^{-3}$. The optical band gap E_g of each sample for the above range of carrier concentrations can be obtained from figure 4.21. Then the electron affinity χ of each sample can be obtained from

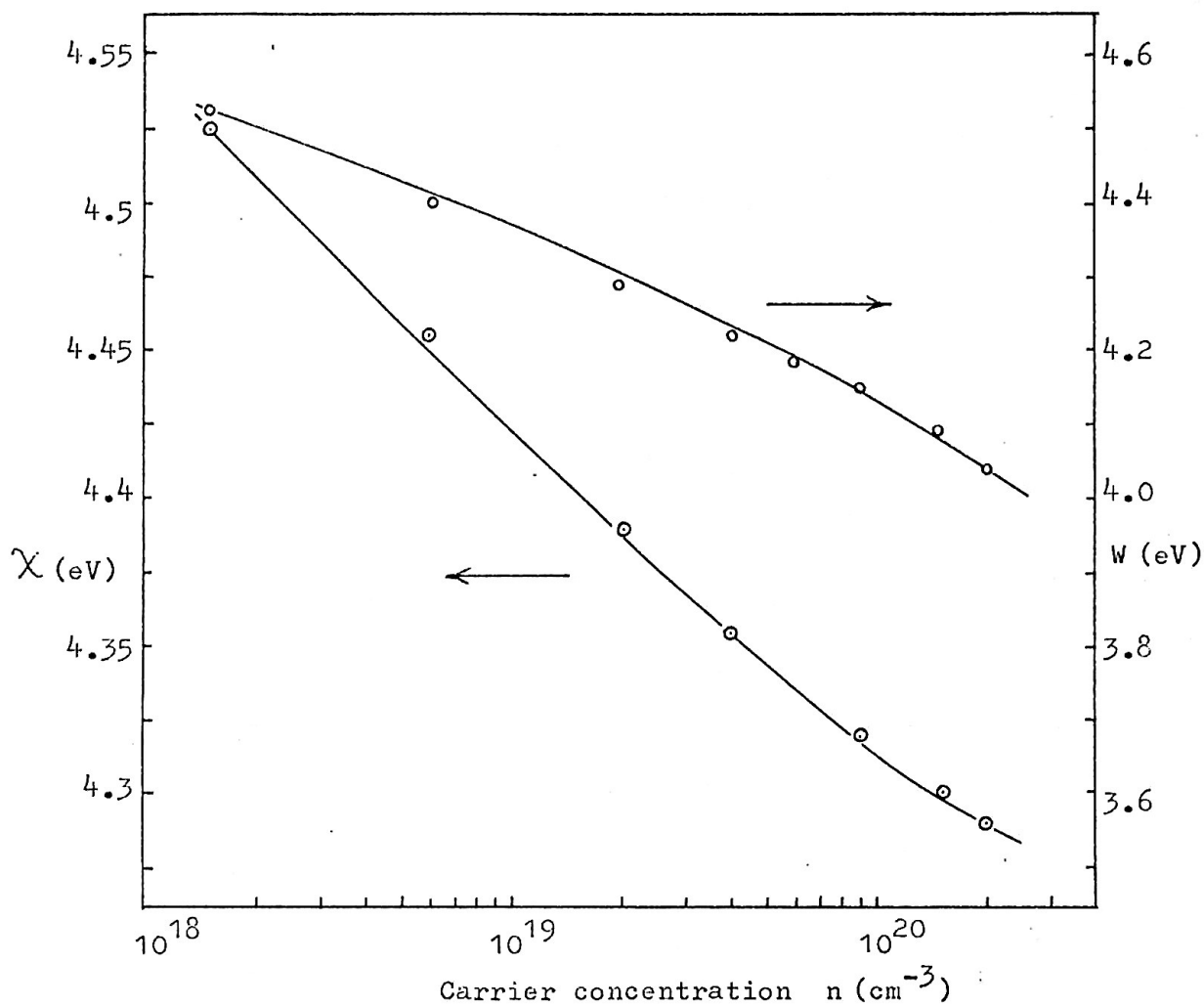


Figure 4.24 : Variation of electron affinity χ and work function W of undoped SnO_2 film as a function of free carrier concentration of the sample.

equation 4.18 using $E_N = 6.25$ eV.

The position of the Fermi level as a function of carrier concentration has been given in figure 4.18. Now using these values of E_F and the values of χ determined above, the work function W for the samples can be easily determined from the relation

$$W = \chi - E_F \quad \dots \quad \dots \quad \dots \quad (4.19)$$

The values of electron affinity χ obtained for our sample are found to vary from 4.29 eV to 4.53 eV in the carrier concentration range $\sim 10^{20}$ to $\sim 10^{18}$ cm^{-3} , and is slightly less than the experimental value of 4.8 eV (for SnO_2 sample with $E_g = 3.5$ eV). The work function W of our sample is found to vary from 4.04 eV to 4.53 eV in the same carrier concentration range. The experimental value of the work function in the case of pure SnO_2 sample as reported by Feucht⁽⁴¹⁾ is 4.75 eV and is slightly higher than our estimated values. The variation with n of χ and W are graphically shown in figure 4.24.

The following two significant reasons may be mentioned here for the present discrepancy existing between the values estimated here and experimentally obtained else where for the above two parameters.

Firstly :

The work function W obtained from the measurement of photoelectric threshold in vacuum, corresponds to the amount of energy required to extract one electron from the binding forces in the bulk and is given by

$$W = -\mu_c + q\phi \quad \dots \quad \dots \quad \dots \quad (4.20)$$

where μ_c is the chemical potential measured with respect to vacuum and $q\phi$ accounts for the surface dipole effects⁽⁴²⁾. The position of Fermi level relative to the vacuum therefore depends on the surface structure. On the other hand the position of Fermi level determined from the thermoelectric power data corresponds to the chemical potential relative to the conduction band edge and it does not account for the surface dipole effects. Therefore, for degenerate materials the present method of estimation of work function would always lead to an under-estimated value.

Secondly :

Since the surfaces of solids with different crystallographic orientation and stoichiometry have different surface dipole layers, the value of work function for the same material may vary from sample to sample. Particularly, for the spray deposited oxide semiconductors this effect is more significant

because of the probable oxygen adsorption mechanism at the surface which helps to increase the experimental work function values. However, since the surface structure of spray deposited SnO_2 samples depends very much on the preparational technique, some limited discrepancy between the values of work function or electron affinity or the band gap of the sample studied here and elsewhere may exist⁽⁴³⁾.

From the above study it appears that the work function and electron affinity of degenerate SnO_2 thin film samples increase with the decrease of carrier concentrations. Starting from different values in the conduction band they attain the same value of 4.53 eV at the band edge (figure 4.24). The rate of increase of the work function is relatively slower than that of the electron affinity and is due to the gradual pinning mode of the Fermi levels⁽²⁷⁾ that exists near the conduction band edge with the decrease of carrier concentration of the sample.

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CHAPTER - 4

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CHAPTER - 5

RESULTS AND DISCUSSION

STUDIES ON In_2O_3 FILM

CHAPTER - 5

STUDIES ON In_2O_3 FILMS

Indium oxide (In_2O_3) thin films have enough similarities with the SnO_2 thin films particularly with respect to the properties like transparency and conductivity. Therefore, the experimental studies on In_2O_3 films have been carried out in a like manner as was done for our SnO_2 films.

5.1 INTRODUCTORY STUDIES

Structural investigations on In_2O_3 films revealed a granular polycrystalline structure with grain size slightly larger than that of the SnO_2 films. The variation of the film thickness t with the deposition time t_d for In_2O_3 films was found to show a relatively flat nature than that was obtained for the SnO_2 films. The sheet resistance size effect was almost similar to that of the SnO_2 films described in section 4.5. Substrate temperature dependence of the electrical conductivity and Hall mobility showed that $400^\circ - 425^\circ\text{C}$ of substrate temperature is adequate for a low resistive film and therefore all the experimental samples of In_2O_3 (doped and undoped) were

prepared at this temperature limit.

The hydrolysis reaction of InCl_3 proceeds at a slower rate in comparison to the reaction rate of SnCl_4 at a constant temperature and also that the former is less sensitive to a small change of substrate temperature. Therefore, the average growth rate (t/t_d) of In_2O_3 film was smaller and the film growth activation energy was found slightly less than that of the SnO_2 film at about 400°C of substrate temperature. From this point of view the growth process of In_2O_3 film is said to be a favourable one for larger grain size formation.

The rate of growth and the electrical properties of undoped and Sn-doped In_2O_3 films were found to depend substantially on the working solution concentration as well as on the use of alcohol in the solution. A brief study regarding this behaviour has been given in the following section.

5.2 THE EFFECT OF SOLUTION CONCENTRATION

Purely aqueous solution of InCl_3 of different concentrations from 0.2 M to 0.5 M were taken as working solution and keeping all other associated deposition variables constant a set of undoped In_2O_3 films were prepared. Resistivity ρ , Hall mobility μ and the carrier concentration n of these samples

were measured. The values are graphically shown in figure 5.1. It is observed from these curves that ρ increases from 4.9×10^{-2} to $8.5 \times 10^{-2} \Omega \text{ cm}$ with the increase of solution concentration from 0.2 M to 0.5 M. The mobility values correspondingly decrease from $26.5 \text{ cm}^2/\text{V}\cdot\text{sec}$ to $\sim 16 \text{ cm}^2/\text{V}\cdot\text{sec}$ in this interval where the carrier concentration shows a minimum value of $4.5 \times 10^{18} \text{ cm}^{-3}$ at 0.35 M of solution concentration.

When an alcoholic solution was used for depositing the films, the above picture changed and better result was obtained at a concentration of $\sim 0.44 \text{ M}$. A brief table is given here to show this effect (table 5.1). It was also observed that films prepared from purely aqueous solution are more transparent than the films prepared from alcoholic solution, but due to the lower growth rate of the former films, solution containing alcohol was preferred. Moreover alcoholic solution gives better results in preparing a more useful variety of films, namely the Sn-doped In_2O_3 films or ITO films. From the above description and from table 5.1 it is found that when the films are prepared from alcoholic solution, the increase of working solution concentration produces higher conductivity and Hall mobility; but if the films are prepared from purely aqueous solution conductivity and Hall mobility both decrease with the increase of solution concentration.

In comparison to purely aqueous solution, alcoholic

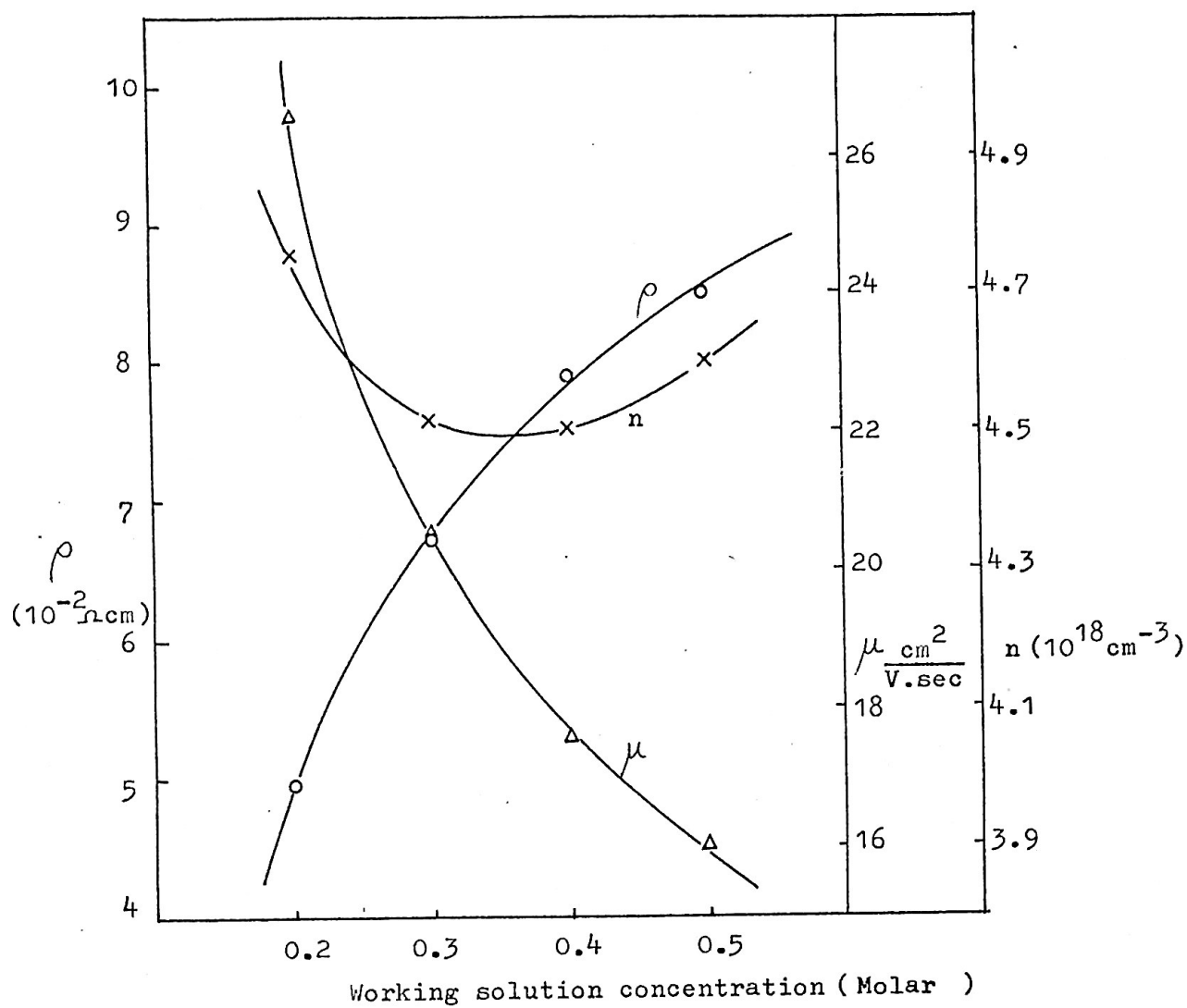
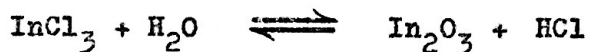


Figure 5.1 : Variation of resistivity ρ , Hall mobility μ and carrier concentration n of undoped In_2O_3 film with the concentration of the working solution (aqueous).

solution produces finely dispersed aerosol which is easier for the vaporisation and reaction. But if then the reaction takes place above the substrate surface, the resulting film on the substrate may be slightly hazy⁽¹⁾. In this situation the distance between the mouth of the aerosol supplying tube and the substrate should be lowered.

The lower deposition rate of the film obtained in using purely aqueous solution may be due to the reversibility of the reaction (1.2) viz



When alcohol is used ($\text{C}_2\text{H}_5\text{OH}$) in the starting solution, then it becomes easier for the above reaction to proceed more efficiently in the forward direction than in the backward direction, because alcohol then reacts with the evolved HCl to form ethylchloride and is readily evaporated out from the deposition site. Thus alcoholic solution should give higher deposition rate of the films.

TABLE - 5.1

Solution concentr- ation(M)	Nature of the solu- tion.	Films of In_2O_3	Resisti- vity ρ ($10^{-2} \Omega \text{cm}$)	Hall mobility $\mu \text{cm}^2/\text{V} \cdot \text{sec}$	Carrier conc. (10^{18}cm^{-3})	Optical transm- ission, T % at $\lambda = 0.55 \mu\text{m}$
0.2	Alcohol + Water	Undoped	5.15	25.0	5.0	95.4
0.2	Purely Aqueous	Undoped	4.95	26.5	4.76	96.8
0.44	Alcohol + Water	Undoped	5.03	28.4	5.0	94.3
0.44	Purely Aqueous	Undoped	8.15	17.55	4.53	96.5

5.3 THE EFFECT OF Sn-DOPING

Sn-doped In_2O_3 films were prepared by using different mole % of SnCl_4 in InCl_3 solution. The effect of this doping on the electrical properties of $\text{In}_2\text{O}_3:\text{Sn}$ film has been represented by two sets of typical curves in figures 5.2(a) and 5.2(b) for two different solution concentrations 0.2 M and 0.44 M respectively. The solution was alcoholic.

It is observed from these figures that the nature of variations of ρ , μ and n of the films with the Sn-doping levels are almost similar in these two cases of solution concentrations. About 2-3 mole % of Sn can produce the highest Hall mobility. The resistivity decreases with the increase of doping level almost upto 9 mole % in these two cases. The carrier concentration also gradually increases with the addition of dopant. A minima in the mobility variation curve is found near about 5 mole % of Sn in the case of 0.44 M solution and at about 10 mole % of Sn in the case of 0.2 M solution. It is however clear that films with higher conductivity, Hall mobility and carrier concentration can be obtained from 0.44 M solution rather than 0.2 M solution at similar doping levels. The working solution concentration is thus a valuable parameter for $\text{In}_2\text{O}_3:\text{Sn}$ films, particularly in controlling the Hall mobility values and needs precise optimization if higher mobility is required.

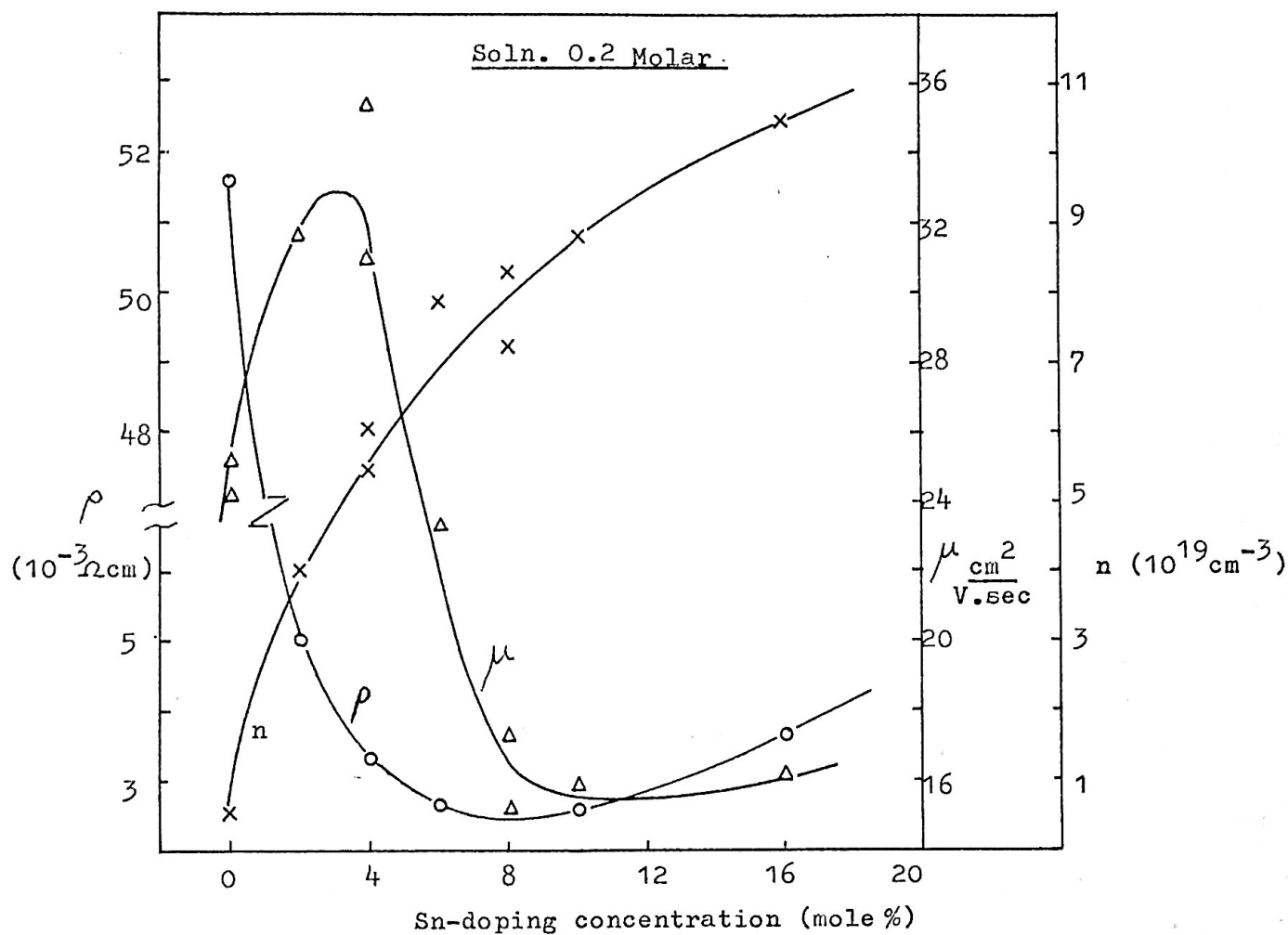


Figure 5.2(a) : Variation of resistivity ρ , Hall mobility μ and carrier concentration n of In_2O_3 film with the Sn-doping concentration when the working solution concentration is 0.2 Molar in equal volume of water and alcohol.

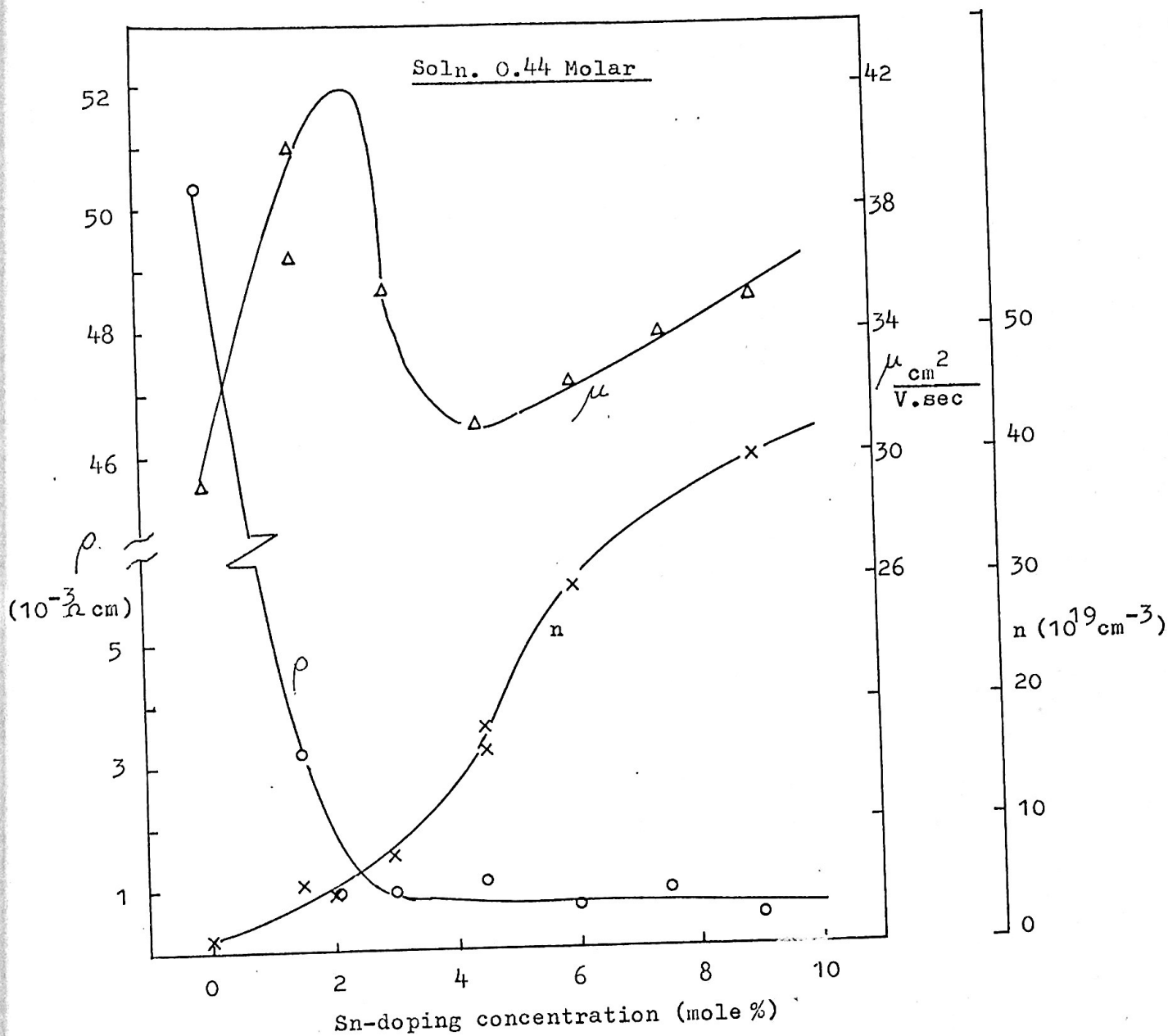


Figure 5.2(b): The variation of resistivity ρ , Hall mobility μ and carrier concentration n of In_2O_3 film with Sn-doping concentration when the working solution concentration is 0.44 Molar in equal volume of water and alcohol.

5.4 POST-DEPOSITION HEAT TREATMENT OF In_2O_3 AND $\text{In}_2\text{O}_3:\text{Sn}$ FILMS

Post-deposition heat treatment of a set of In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films have been performed in air at normal pressure and in vacuum of the order of $\sim 10^{-5}$ torr. The heating temperature was varied from 30° to 250°C . The details of the experimental procedure have been described in chapter-3. Obtaining similarities in the nature of the variations of different electrical parameters in heat treatments of several specimens of this category we have reported here only results of four typical samples. Two of them are undoped and the other two are Sn-doped In_2O_3 films.

5.4.1 Heat Treatment at Normal Atmosphere :-

During this heat treatment operation a simultaneous measurement of resistivity and Hall coefficient were performed. The results are discussed below.

5.4.1.1 Temperature dependence of resistivity :-

The variation of resistivity ρ with temperature T of the samples are shown by two sets of curves in figure 5.3(a) and 5.3(b) for undoped and Sn-doped films respectively. It can be seen from these curves that initially the resistivity slightly increases between room temperature and $\sim 70^\circ\text{C}$ (region I), then

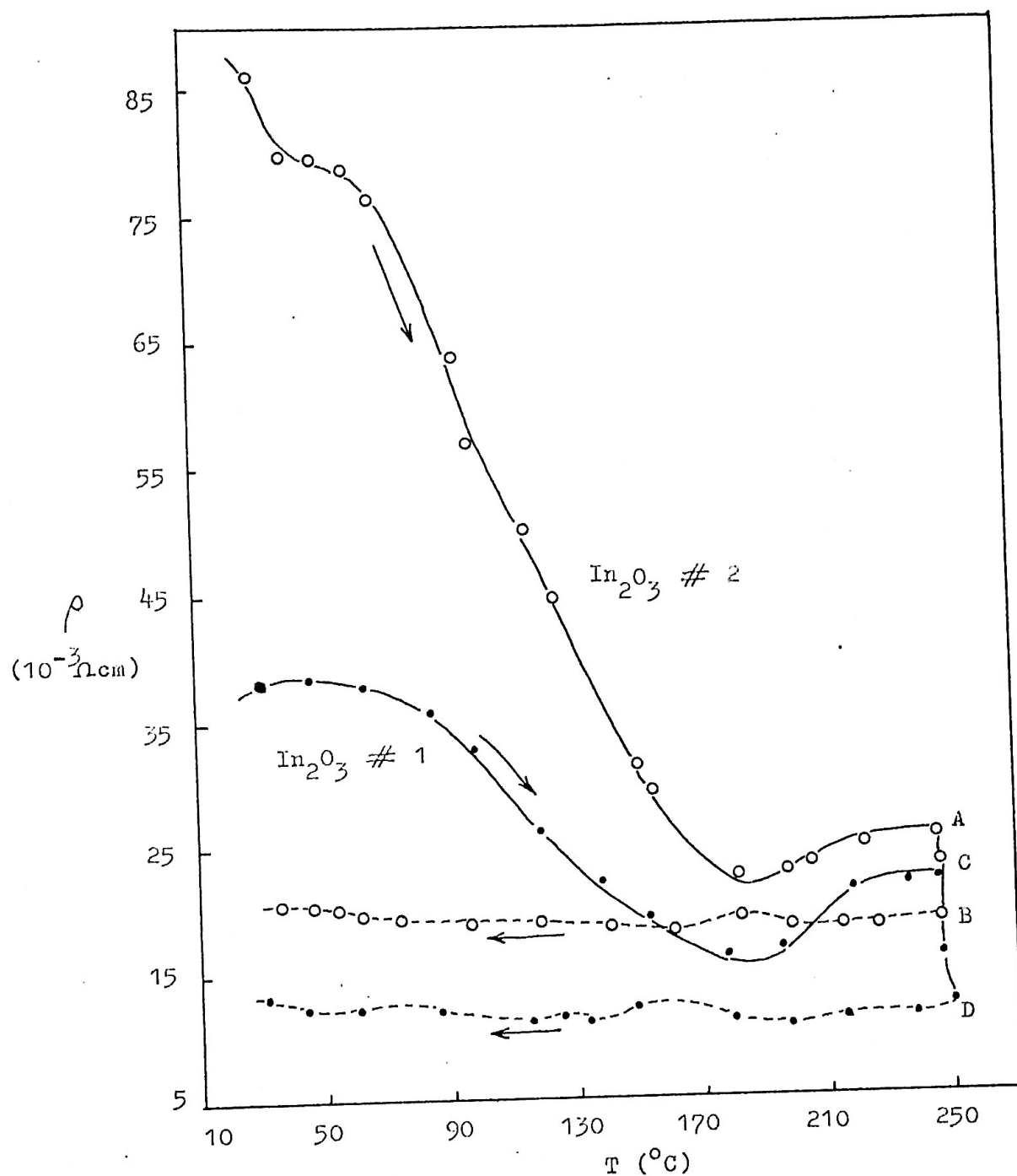


Figure 5.3(a) : Variation of resistivity ρ of undoped In_2O_3 films with temperature T . Solid line represents heating cycle and dotted line represents cooling cycle. AB and CD represent change of ρ due to heating at a constant temperature of 250°C .

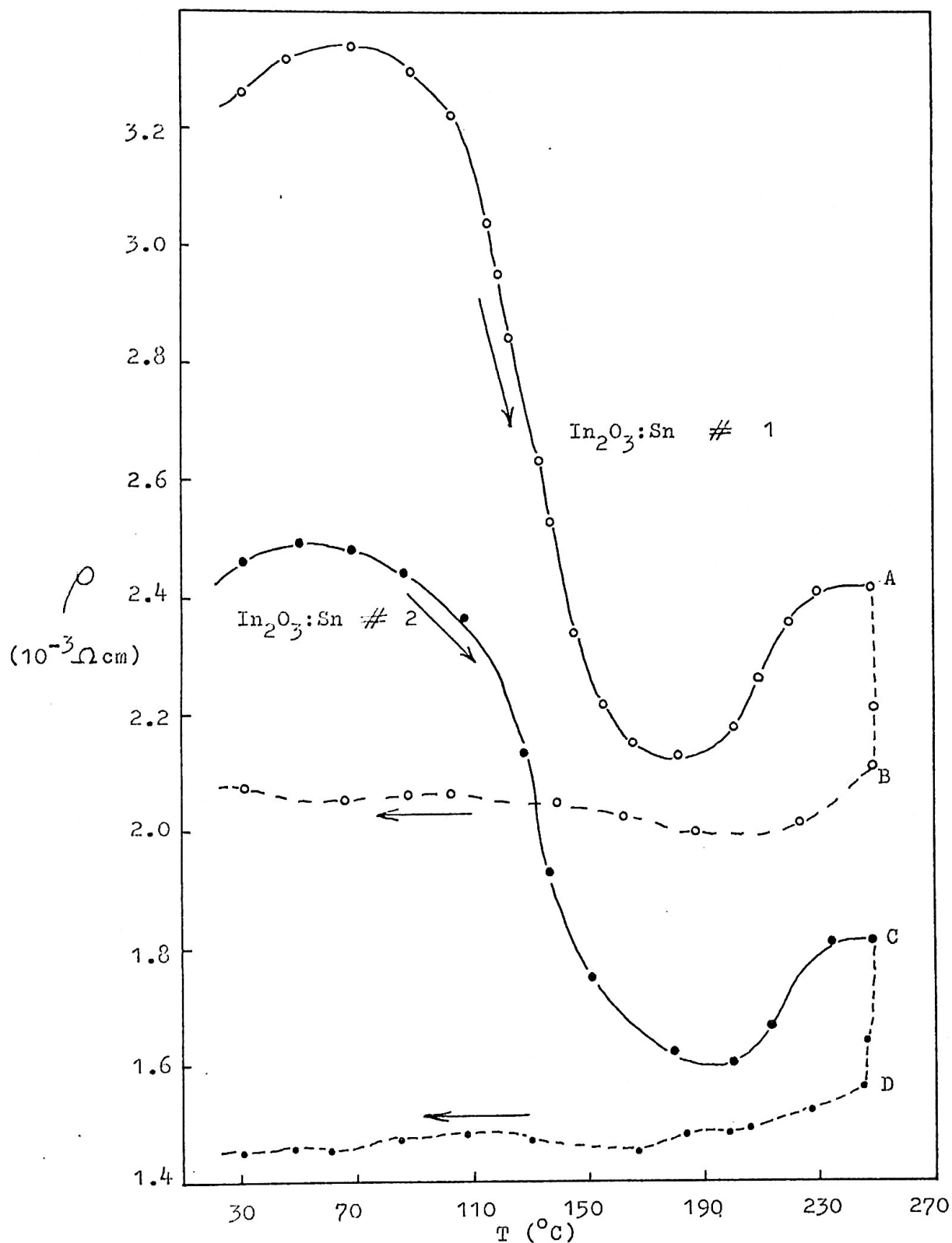


Figure 5.3(b): Variation of resistivity ρ of Sn-doped In_2O_3 film with temperature T . The arrows indicate direction of the cycle. AB and CD show the effect at a constant temperature of 250°C .

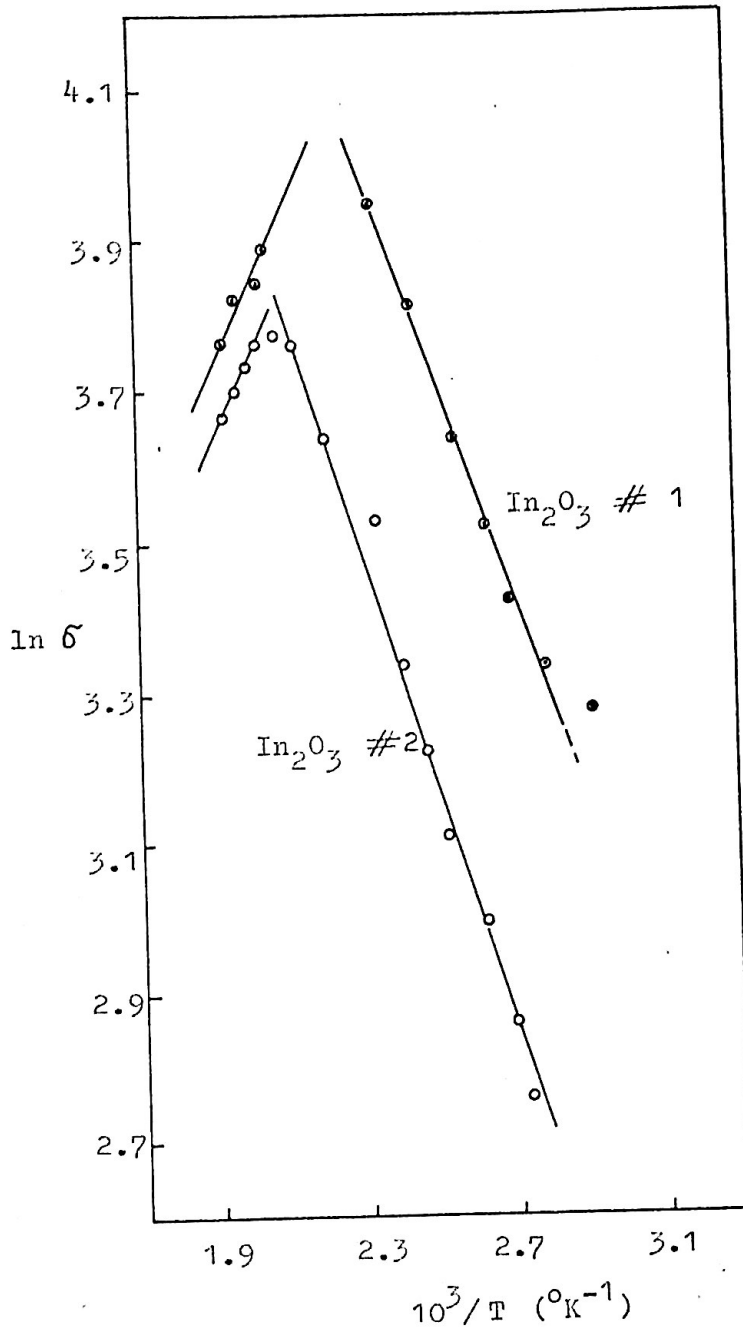


Figure 5.4(a): $\ln \sigma$ vs. $10^3/T$ plots for undoped In_2O_3 films.

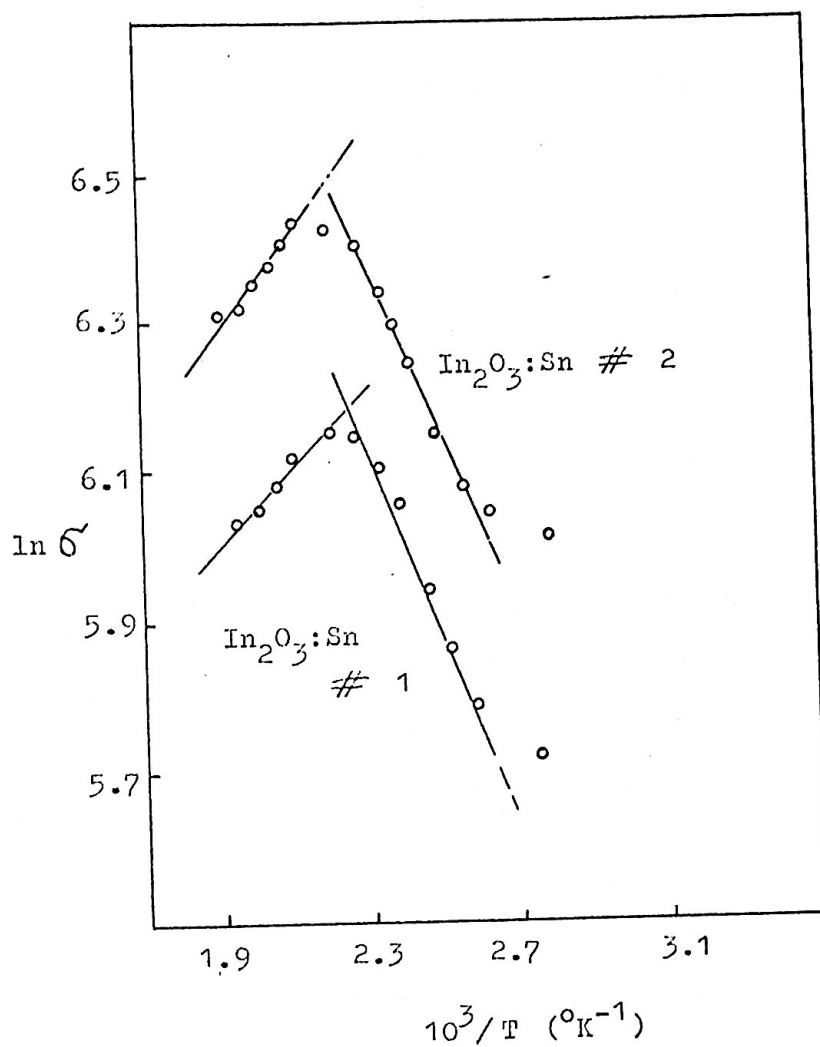


Figure 5.4(b): $\ln \sigma$ vs. $10^3/T$ plots for Sn-doped In_2O_3 films.

it gradually decreases with the rise of temperature upto $\sim 190^{\circ}\text{C}$ (region II), and again increases very slightly with the rise of temperature upto $\sim 250^{\circ}\text{C}$ (region III). Finally, ρ drops down at the same (constant) temperature of 250°C during a period of 1 hour and attains a steady state value. The return operation of cooling does not alter appreciably the value of ρ once attained at the maximum temperature.

The value of TCR :

In the temperature range 70° to 180°C where the resistivity of all the films decreases maximum, the temperature coefficient of resistivity (TCR) have been calculated for the as-deposited samples and are shown in table 5.2. TCR is found negative for all the films in this region, whereas it is positive for region III.

5.4.1.2 The donors and the donor ionization energy :-

During the variation of ρ , the carrier concentration n and the Hall mobility μ of the samples were also found to vary slowly with temperature. From the temperature variation of n in region II, the donor ionization energy ($E_c - E_d$) may be determined by plotting $(\ln n)$ against T^{-1} and using equation 2.15 considering the samples to be in the uncompensated regime. The obtained values

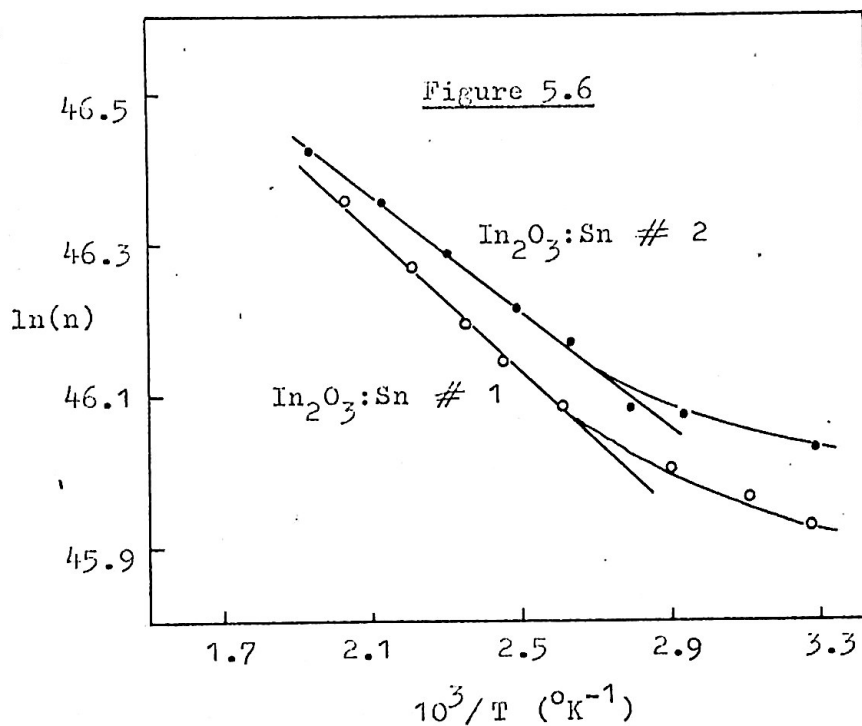
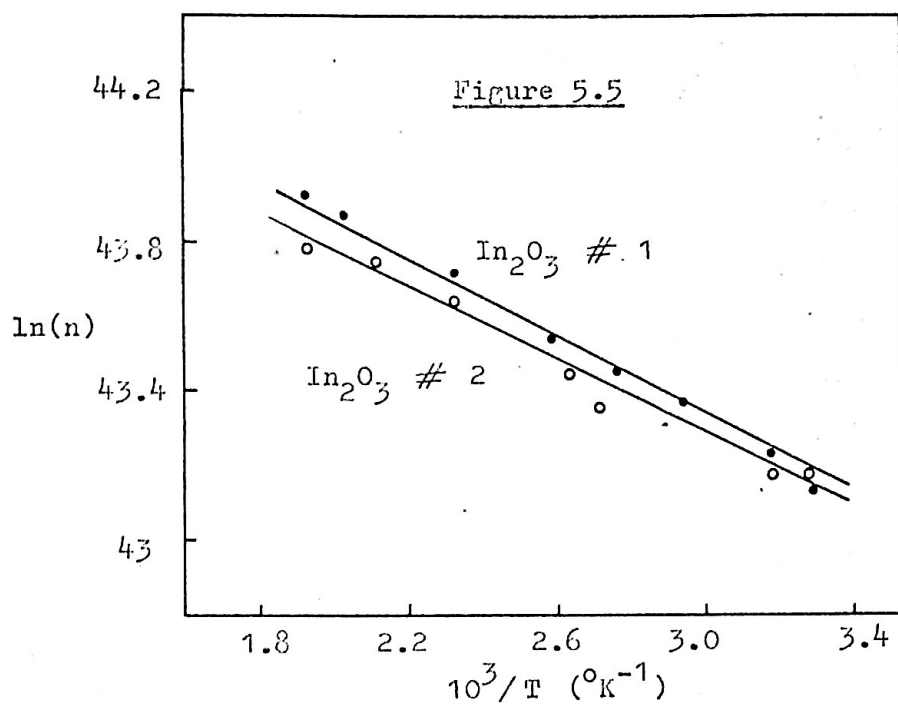
of $(E_c - E_d)$ with reference to the conduction band edge E_c are given in table 5.2. The values are of the order of ~ 0.069 to 0.1 eV as obtained from figures 5.5 and 5.6; and are all very small indicating that the possible donor levels are very shallow.

Whether this sort of donor levels are reasonable in In_2O_3 films can be justified by calculating the dielectric constant ϵ_L for the samples. For this purpose a hydrogenic model for the medium could be assumed where the donor ionization energy E_d is given by⁽²⁾

$$E_d = (e^4 m_e^*) / (2 \epsilon_L^2 h^2), \text{ in C.G.S.} \quad \dots \quad (5.1)$$

Here m_e^* is the effective mass of the conduction electrons, and may be obtained from the thermopower data. For undoped In_2O_3 films the value of ϵ_L comes out to be $3.9 - 4$ and are in excellent agreement with the reported value of 4 by Kostlin et al⁽³⁾ and by Clanget⁽⁴⁾. For the Sn-doped samples the donor levels are more close to the conduction band and the calculated value of ϵ_L is about ~ 5.36 and is slightly higher than the reported one, ~ 4.45 by Fan and Bachner⁽⁵⁾ for rf diode sputtered ITO films of different carrier concentration. Thus the obtained donor levels appear to be consistent with the energy bands, and the samples in this region (region II) could be safely considered as uncompensated.

It is already known that In_2O_3 thin films like the



Figures 5.5 and 5.6 : Plot of $\ln(n)$ vs. $10^3/T$ of undoped and Sn-doped In_2O_3 films.

SnO_2 films are impurity semiconductors with n-type conductivity. The energy levels of the impurity states lie at the energy gap near the bottom of the conduction band. In undoped films oxygen vacancies and interstitial chlorine ion (as impurity coming from InCl_3) can act as the major sources of donors. Interstitial In^{3+} cations are also important in this case⁽⁶⁾.

For the Sn-doped films we have a solid solution where Sn^{4+} ion may substitute for In^{3+} ions in the In_2O_3 lattice. This is logical since among the two valence states of Sn viz Sn^{2+} and Sn^{4+} , the ionic radius of Sn^{4+} ($\approx 0.71 \text{ \AA}$) is less than the ionic radius of In^{3+} ($\approx 0.81 \text{ \AA}$), whereas the ionic radius of Sn^{2+} ($\approx 0.93 \text{ \AA}$) is greater than this⁽⁷⁾. In this situation if covalent bonds are formed between Sn^{4+} and surrounding In^{3+} ions the surplus 1 electron of Sn^{4+} would be contributed to the conduction process and Sn^{4+} ion would be a positive trap centre leading to an electronic energy level just below the conduction band. Manificier et al⁽⁸⁾ have pointed out that a combination of both the controlled valence semiconductor $\text{In}_{2-x}^{3+} \text{Sn}_x^{4+} \text{O}_3^{2-}$ and nonstoichiometric semiconductor $\text{In}_2^{3+} \text{O}_{3-x}^{2-} \text{e}_{2x}$ may be formed to create possible donor levels in these films. Fraser and Cook⁽⁹⁾ have pointed out that the resistivity of $\text{In}_2\text{O}_3:\text{Sn}$ film is more sensitive to the oxygen vacancies than it is to the Sn content.

Apart from these donor levels, there are some excess oxygen occupying the interstitial sites of the In_2O_3 lattice

which create acceptor levels just above the valence band⁽¹⁰⁾. With the increase of temperature these acceptor states may be excited to negate the donor action (compensation effect).

5.4.1.3 The experimental curves : (Figure 5.3)

The gross decrease of resistivity due to a heat treatment in air can be explained as mainly due to the desorption of oxygen from the grain boundaries of the films. This type of explanation in detail has already been given in connection with the heat treatment experiments of SnO_2 films in chapter-4. The only exception here is that an increase of carrier concentration in addition to an increase of mobility are noticed with the observed decrease of resistivity, whereas for SnO_2 films there was no appreciable change of carrier concentration due to heat treatment.

It has been mentioned in section 4.9 that chemisorption and desorption both may occur at all temperature. The process that dominates is determined by their respective rates which are functions of the ambient temperature and relative concentrations of the chemisorption species available in the ambient and in the chemisorption site. The small increase of resistivity between 30° and 70°C at the beginning of the heating cycle may be due to the predominance of such chemisorption effect⁽¹¹⁾ which may also give rise to oxidation of the grain boundaries⁽¹²⁾. Maissel has

mentioned that the oxidation of the grain boundaries could occur either as a result of oxygen diffusing in from the surface or from trapped oxygen diffusing internally and then precipitating at the grain boundaries as an insulating phase. But as the temperature increases further (in region II), an overwhelming majority of desorption is observed and the resistivity decreases. It is very difficult to explain at present the minor increase of resistivity in region III when the sample temperature crosses 190°C .

Three possible mechanisms may be present here :

- (i) a generation of internal stresses in the film⁽¹³⁾,
- (ii) a predominance of partial carrier compensation effect due to the excitation of possible acceptor levels in the film⁽¹⁴⁾, and
- (iii) a dissociative chemisorption effect.

Let us first discuss the latter effect in some detail for our samples.

In studying the gas-solid interaction of various gases with tin oxide and zinc oxide, it was found that in a high oxygen ambient the electrical conductivity σ of the semiconductors showed anomalous behaviour in some temperature regions⁽¹⁵⁻¹⁷⁾. The slopes of $\ln \sigma$ vs. T^{-1} plots changed from negative value (normal semiconductor characteristics) to positive value when the sample temperature was below or above a certain temperature T_c . This critical temperature for tin oxide film as obtained by the authors⁽¹⁵⁻¹⁷⁾ was around 160°C and for zinc oxide it was

about 220°C. In our SnO₂ sample we did not observe such critical temperature upto 250°C, but in our In₂O₃ and In₂O₃:Sn films a similar T_c is being observed around 195°C, figure 5.4(a) and (b). This type of anomalous behaviour was broadly referred to as a result of strong electronic interaction between chemisorbed oxygen and the semiconductor bulk(at the surface region)^(16,17). A more detail explanation for our samples may then be as follows.

At room temperature the principal species of chemisorbed oxygen was O₂¹⁻. When the sample temperature rises, the chemisorbed O₂¹⁻ desorbed from the sample donating an electron to the indium oxide (O₂¹⁻ → O₂ + e), hence causing the resistivity to decrease(in region II, figure 5.3 and 5.4.). On further raising the temperature and as the sample temperature crosses T_c dissociative chemisorption occurs (in region III), yielding O¹⁻ or O²⁻ by accepting electrons from indium oxide (O₂+2e → 2 O¹⁻, or $\frac{1}{2}$ O₂ + 2e → O²⁻). As a result resistivity may increase at temp. beyond T_c. If the above explanation is valid here then it can be said that the mechanism (iii) is mostly effective in a narrow temperature region of 200° - 230°C for In₂O₃ and In₂O₃:Sn films.

On the other hand if mechanism (ii) holds, then it seems that the acceptor level is exhausted at temperature 230° - 240°C while the donor ionization or the usual desorption process again predominates and the resistivity decreases for the last time at a constant temperature of 250°C. Here the reason of invoking this partial carrier compensation effect is that the activa-

tion energy determined for region III using partially compensated semiconductor model agrees well with the previously determined donor ionization energy using uncompensated semiconductor model. Table 5.2 shows these values. Since for region III, a similar behaviour was noticed for all the doped and undoped films, it is definitely a characteristic of the host lattice (In_2O_3) rather than of the Sn-donors. Therefore it appears that mechanism like partial carrier compensation may dominate in this temperature region due to which resistivity increases locally over a general declining background.

Regarding mechanism (i) it can be said that semiconducting In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films have the linear coefficient of thermal expansion $\sim 10.2 \times 10^{-6} / ^\circ\text{C}$ which is very close to that of the glass substrate $\sim 9 \times 10^{-6} / ^\circ\text{C}$, and also that the films are highly adherent to the glass substrate. Therefore, the generation of internal stresses in the film due to which its resistivity may increase, should not be attributed here to the expansion coefficient mismatch between the film and glass substrate but to the film-substrate combination.

5.4.1.4 The activation energies for In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films :-

It has been pointed out in section 2.5.1 that the thermal activation energy for electronic conduction in semiconductors and in insulators is traditionally interpreted in three possible ways, i.e., half the band gap when the material is intrinsic; some trap depth when the material is extrinsic or half the trap depth when the material is highly doped. Even in these simple cases the analysis of thermal activation energy becomes difficult when the material is polycrystalline and degenerate in nature. In these situations the grain boundary trapping model is very convenient and is frequently used. The dc conductivity characteristics of various polycrystalline materials can be successfully explained with the help of this model as have been done by many authors in the past⁽¹⁸⁻²²⁾. Before going detail into the analysis of our present experimental results it is necessary to summarize the important features of the model.

It is assumed that the polycrystalline material is composed of a linear chain of identical crystallites having a grain size L separated by a narrow boundary region that contains a concentration N_t (per unit area) of traps located at an energy level in the forbidden gap. The traps are assumed to be initially neutral and become charged by trapping a carrier which leads to a potential barrier at the boundary. According to the theory of

trap levels the properties of the film change markedly depending on the combination of two conditions; one is the degree of depletion of the grains and the other is the degree of trap occupancy. Two cases may then arise :

Case I :

If the density of trap states is high and is comparable with the carrier concentration in the grains, a severe depletion of the grains exist throughout the bulk of the crystallites. This situation may also be created if the grain size is less than or comparable to the Debye screening length L_D . Under this circumstances the carrier concentration may practically be temperature independent while the mobility is thermally activated⁽²²⁾.

Case II :

At the other extreme when the carrier concentration is quite high compared to the trap density, the depletion region exists only adjacent to the grain boundaries, the carrier distribution is inhomogeneous and carrier transport occurs by thermionic emission over the grain boundaries. This situation may also exist when the grain size is greater than the Debye screening length. However in this case the free carrier concentration and the Hall mobility both are thermally activated^(23,24).

For degenerate semiconductor where the case II applies, the effective mobility μ_{eff} is given by⁽²⁵⁾ (equation 4.2),

$$\mu_{\text{eff}} = A \mu'_0 T^{-\frac{1}{2}} \exp(-E_\mu / k_B T) \quad \dots \quad \dots \quad (5.2)$$

where μ'_0 is a function of grain size L and effective mass m_e^* , given by

$$\mu'_0 = eL / (8\pi m_e^* k_B)^{\frac{1}{2}} \quad \dots \quad \dots \quad \dots \quad (5.3)$$

Equation 5.2 is strictly valid when the effective mobility is limited mainly by the grain boundary scattering. Otherwise the case would be an approximate one. E_μ is the effective barrier height known as the mobility activation energy. E_μ is usually temperature independent for purely thermionic emission case but it may show a slight temperature dependence if thermionic field emission exists. At low temperatures tunnelling may be the predominant mechanism and at high temperature thermionic emission dominates. The carrier concentration n for such a material can be expressed by

$$n = n_0 \exp(-E_n / k_B T) \quad \dots \quad \dots \quad \dots \quad (5.4)$$

where $E_n = (E_c - E_d)/2$ is the activation energy for the carrier concentration. E_n depends on the relative carrier concentration of the grains n_1 and of the barrier regions n_2 . Petritz⁽²⁶⁾ has given the relation between E_μ , n_1 and n_2 as

$$E_\mu = k_B T \ln(n_1 / n_2) \quad \dots \quad \dots \quad \dots \quad (5.5)$$

The thermally activated conductivity can be expressed similarly by

$$\sigma = \sigma_{\infty} \exp(-E_{\sigma}/k_B T) \quad \dots \quad \dots \quad \dots \quad (5.6)$$

where $E_{\sigma}/2 = E_a$ is the conductivity activation energy and σ_{∞} is the value of σ at $1/T = 0$. The relation between E_n , E_{μ} and E_a can be easily established⁽²²⁾ as

$$E_n \approx |E_a - E_{\mu}| \quad \dots \quad \dots \quad \dots \quad (5.7)$$

In the absence of grain boundaries or in the absence of any thermal activation of mobility, $E_{\mu} \rightarrow 0$ and at that time $E_n \approx E_a$. On the other hand if the material is in the exhaustion range then $E_n \rightarrow 0$ and $E_a \approx E_{\mu}$ for a polycrystalline material.

When partial depletion of the grains exists in the material then there must have a critical concentration of donors N_D^* below which this partially depleted region may extend to a fully depleted region. The quantity N_D^* is related to the interfacial trap density N_t by an approximate relation $N_D^* \approx N_t/L$.

TABLE - 5.2

Sample	Resistivity, ρ ($10^{-3} \Omega \text{cm}$)	Hall mobility, μ ($\text{cm}^2/\text{V}\cdot\text{sec}$)	Barrier Height, E_{μ} (meV) (for region II)	$E_c - E_d$ (meV) (for region II)	$E_c - E_d$ (meV) (for region III)	E_a (meV) (for region II)	TCR ($10^{-3}/\text{deg}$) (for region II)
In_2O_3 # 1	38.0	31.08	69.0	97.0	100	119	-5.45
In_2O_3 # 2	86.0	12.0	76.0	85.0	83	118	-6.35
$\text{In}_2\text{O}_3:\text{Sn}$ # 1	3.27	21.78	79.0	81.0	83	120	-3.31
$\text{In}_2\text{O}_3:\text{Sn}$ # 2	2.46	25.37	71.0	69.0	67	104	-3.67

* Determined by using uncompensated model.

** Determined by using partially compensated model.

For In_2O_3 film $m_e^* = 0.1m$ and for $\text{In}_2\text{O}_3:\text{Sn}$ film $m_e^* = 0.17m$.

Regions II and III are temperature regions mentioned in the text.

It was also assumed that no appreciable change of static dielectric constant and optical band gap of the material occurred in these temperature ranges.

5.4.1.5 The grain boundary parameters :-

In the light of the description given in the previous section (5.4.1.4), the values of some of the grain boundary parameters of our polycrystalline In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films are calculated and tabulated in table 5.2 and 5.3. Our samples are supposed to correspond to the case II of the trapping model (page 167), and we have considered for simplicity $n \approx N_D$ at room temperature.

A plot of $\ln(\mu T^2)$ vs. $1000/T$ for the set of samples are shown in figure 5.7(a) and (b). It is clear that mobility is thermally activated in the investigated range of temperature. The validity of equation 5.7 may be checked. The estimated values of N_t appear to be slightly over-estimated but still the validity of the case II can be justified. On the other hand the estimated values of the grain size L appear to be slightly under-estimated because the values of μ_{eff} at room temperature are not strictly limited by the grain boundary scattering alone. However the values are of expected order and the condition $L_D \ll L$ holds good.

Assuming n_1 to be the carrier concentration corresponding to the measured Hall coefficient, the values of n_2 (carrier concentration in the boundary region) were calculated. It is observed that when n_1 of undoped film increases about 13% it is accompanied by $\sim 14\%$ decrease of the n_2 values; whereas for Sn-doped films about 11% increase in n_1 is accompanied by almost 50% increase in the n_2 values. This may lead to a qualitative inference

that when dopants are added to increase n_1 then the barrier regions become increasingly populated by new charge carriers.

TABLE - 5.3

Sample	Carrier conc. n_1 (10^{18} cm^{-3})	Carrier conc. n_2 (10^{18} cm^{-3})	Trap Density N_t (10^{12} cm^{-2})	N_D^* (10^{18} cm^{-3})	Debye screening length L_D (Å)	Estima- ted gra- in size, L (Å)	Mean free path l (Å)
In_2O_3 # 1	5.18	0.357	2.48	0.908	10.38	273	10
In_2O_3 # 2	5.85	0.307	2.8	0.843	10.12	332	4
$\text{In}_2\text{O}_3:\text{Sn}$ # 1	88.0	4.15	12.8	3.64	2.95	351	19.7
$\text{In}_2\text{O}_3:\text{Sn}$ # 2	98.1	6.26	13.3	4.18	2.9	318	27

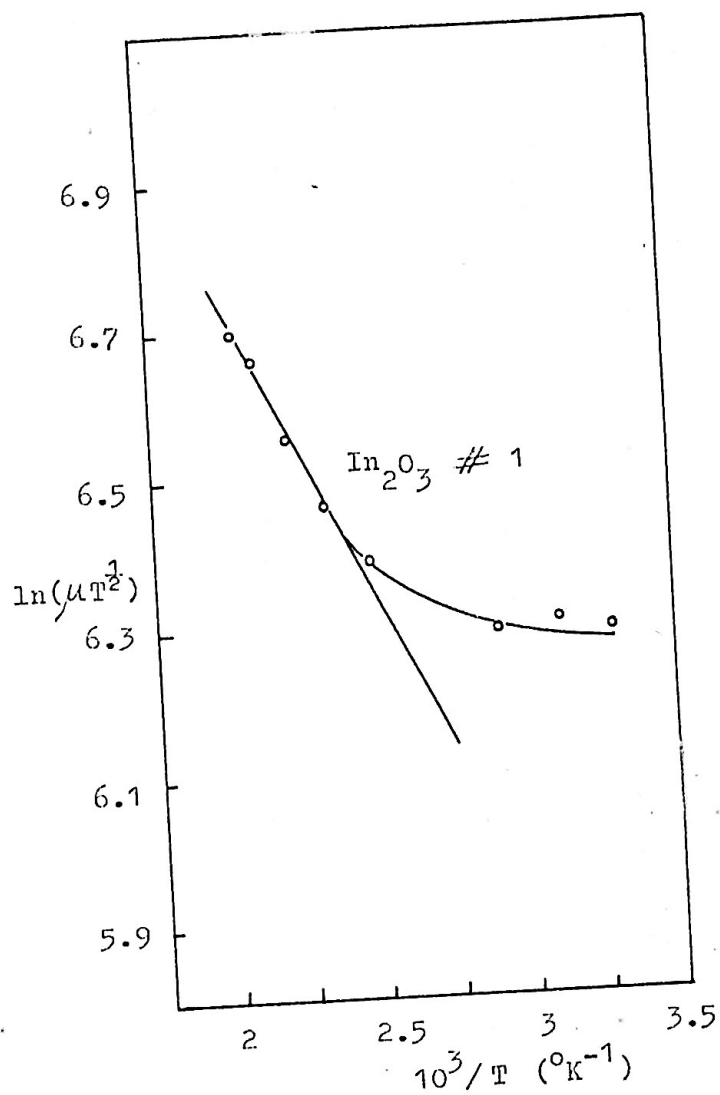
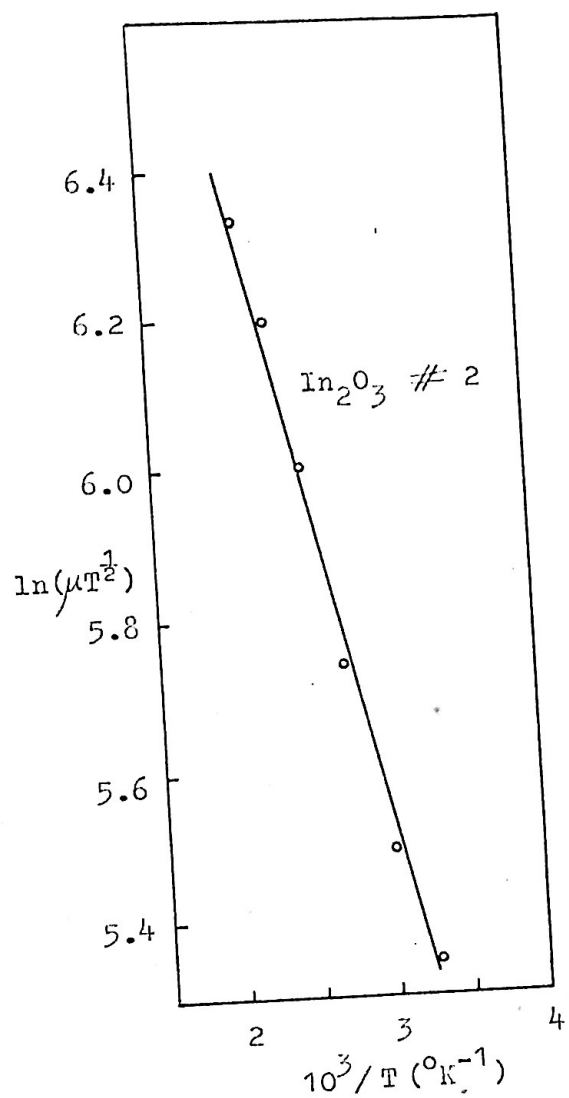


Figure 5.7(a): $\ln(\mu T^{1/2})$ vs. $10^3/T$ curves for undoped In_2O_3 films.

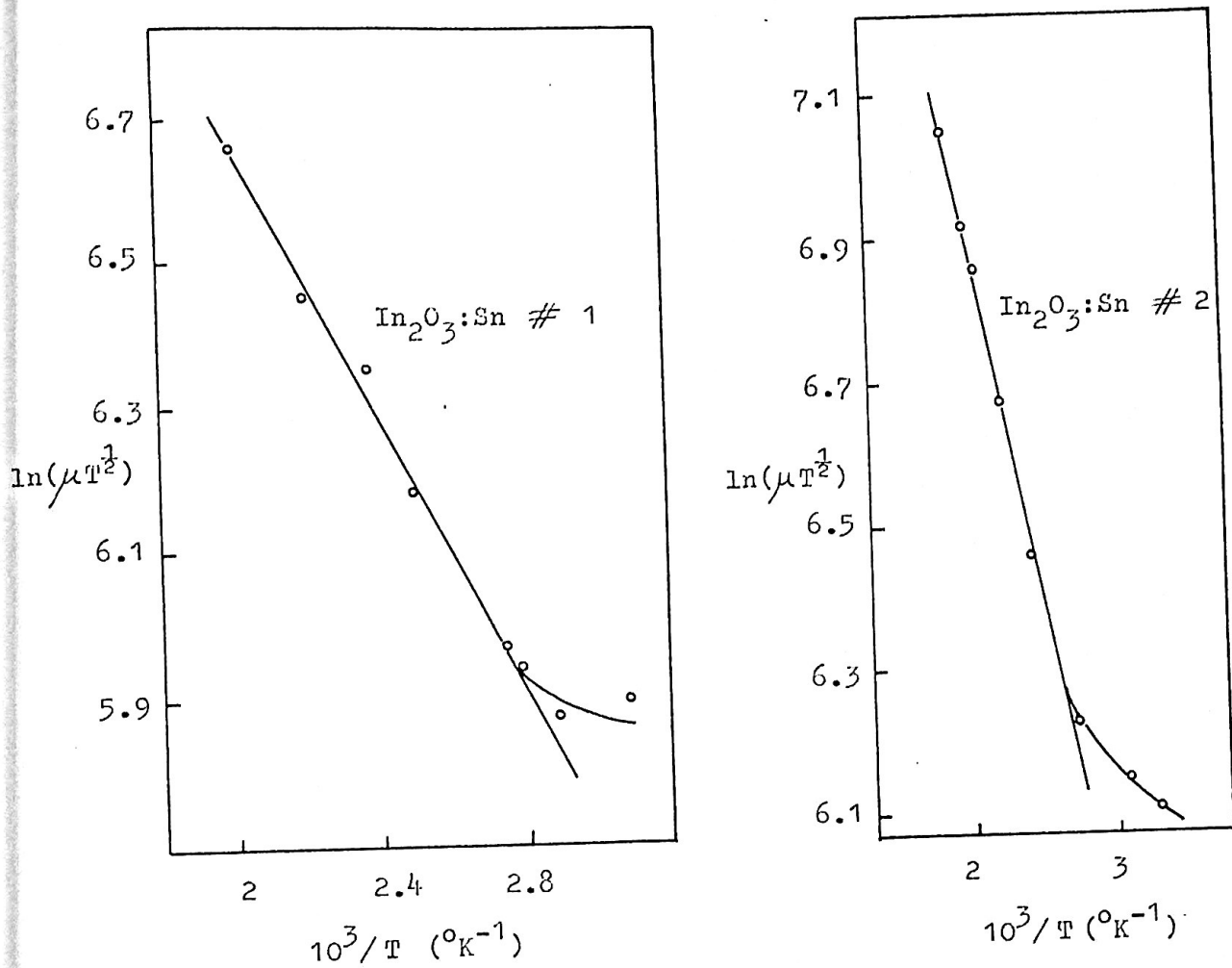


Figure 5.7(b): $\ln(\mu T^{1/2})$ vs. $10^3/T$ curves for Sn-doped In_2O_3 films.

5.4.2 Heat Treatment in Vacuum :-

Some of the In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films were heat treated at a constant temperature of 250°C in vacuum of the order of $\sim 10^{-5}$ torr for 1 hour. The effect of the heat treatment is shown in table 5.4. It is observed that vacuum heat treatment substantially increases the Hall mobility values. The rate of the increment is found to depend inversely on the doping level. Mobility increases $\sim 72\%$ for undoped films, $\sim 61\%$ for 2 mole % Sn-doped films and 38% for 9 mole % Sn-doped films respectively. This implies that a vacuum heat treatment is more efficient to increase the Hall mobility values at lower doping levels. This is obvious because the carrier concentration of the as-deposited films increases with the increase of doping concentration and produce a greater fraction of carrier-carrier scattering in the films. Heat treatment could not eliminate this effect due to excess free carriers in the material⁽²⁷⁾. On the other hand undoped films have relatively lower concentrations of free carriers, and in this case $\sim 72\%$ increase of mobility in a vacuum heat treatment is mainly due to the reduction of grain boundary barrier heights. It has already been mentioned that grain boundary barrier heights are greatly reduced due to a heat treatment in vacuum for the films with lower carrier concentrations. At the time of lowering the barrier heights, some carriers are made free from the traps lying therein in addition to the usual ionization of donors of other centres causing a simultaneous increase of carrier concentrations.

The drastic fall of resistivity of the as-deposited films due to the heat treatment is thus attributed to the cumulative effect of the increase of mobility as well as carrier concentration.

Like the SnO_2 films here also the values of ρ , μ , and n attained after a vacuum heat treatment do not change subsequently so long as the sample is kept at normal temperature and pressure.

TABLE - 5.4

Doping Level	Sample	Resistivity ρ ($10^{-3} \Omega \text{cm}$)	Carrier concentration, n (cm^{-3})	Hall mobility μ ($\text{cm}^2/\text{V}.\text{sec}$)	Percentage increase of μ
Undoped	As-deposited	291	1.3×10^{18}	16.49	72 %
	Vac. Heat treated	20.59	1.06×10^{19}	28.4	
2 mole % Sn-doped	As-deposited	0.862	2.1×10^{20}	34.43	61 %
	Vac. Heat treated	0.49	2.29×10^{20}	55.56	
9 mole % Sn-doped	As-deposited	0.446	3.98×10^{20}	35.14	38 %
	Vac. Heat treated	0.271	2.11×10^{21}	48.67	

5.5 THERMOELECTRIC POWER

The thermoelectric power (TEP) of several doped and undoped samples of indium oxide having different carrier concentrations were measured with reference to pure metallic lead (Pb). During measurement the cold junction of the experimental sample was kept at 0°C and the temperature of the hot junction was varied upto 175°C . The detail experimental technique has been described in chapter- 3. The experiment was carried out with a view to determining the position of Fermi level and the approximate values of the carrier effective mass in the conduction band.

The measured values of TEP as a function of temperature is shown in figure 5.8 for 4 typical samples of different carrier concentrations. The general pattern of variation of TEP with temperature is almost similar for all the samples. From 30° upto $\sim 100^{\circ}\text{C}$ the TEP increases nonlinearly, but above 100°C it rises very slowly but linearly with temperature.

The sign of the thermo-emf was found negative which indicates electrons to be the majority carriers. The n-type character of these samples was also indicated by the -ve sign of the Hall coefficients. From figure 5.8 it is clearly observed that with the increase of free carrier concentration of the samples the TEP values decrease very rapidly. We have studied

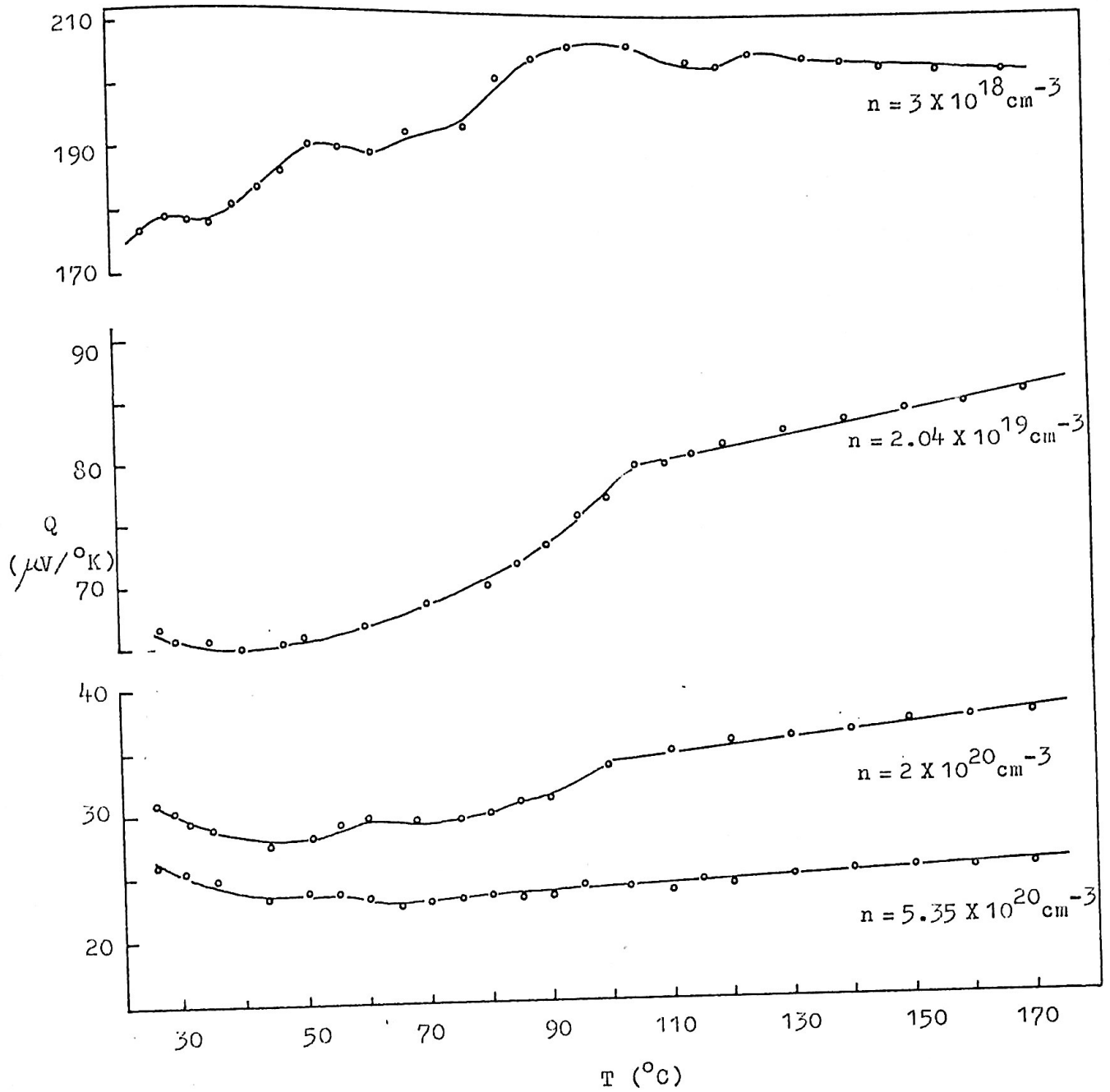


Figure 5.8 : Variation of tl. thermoelectric power Q with temperature T .
 Different curves are for samples of different carrier concentrations n indicated under each curve.

samples of carrier concentration ranging from 10^{18} to 10^{21} cm^{-3} and observed that the TEP values run from 200 to $16 \mu\text{V}/^\circ\text{K}$, in this carrier concentration range at room temperature.

5.5.1 The Position of Fermi Level :-

From the measured values of the thermoelectric power the position of Fermi levels were determined for the samples following the same procedure as have used for the SnO_2 films. Fermi levels in spray deposited In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ are found to lie in the conduction band and the samples are thus degenerate in nature. The variation of the positions of the Fermi level E_F as a function of carrier concentration n is shown in figure 5.9(a). The three curves represent variations of E_F at three different temperatures. It is noticed that the value of E_F gradually increases with the increase of carrier concentration upto about $5 \times 10^{20} \text{ cm}^{-3}$ and then it decreases a little. At decreasing carrier concentrations the Fermi levels tend to become almost temperature independent which indicates a gradual pinning mode of the Fermi levels at lower carrier concentrations⁽²⁸⁾. The carrier concentration n_0 corresponding to $E_F = 0$ can be obtained from the extrapolated part of the curve at room temperature. $n_0 = 1 \times 10^{18} \text{ cm}^{-3}$ is thus obtained. This may be taken as the carrier concentration at which the Fermi level coincides with the conduction band edge E_c and may approximately be taken

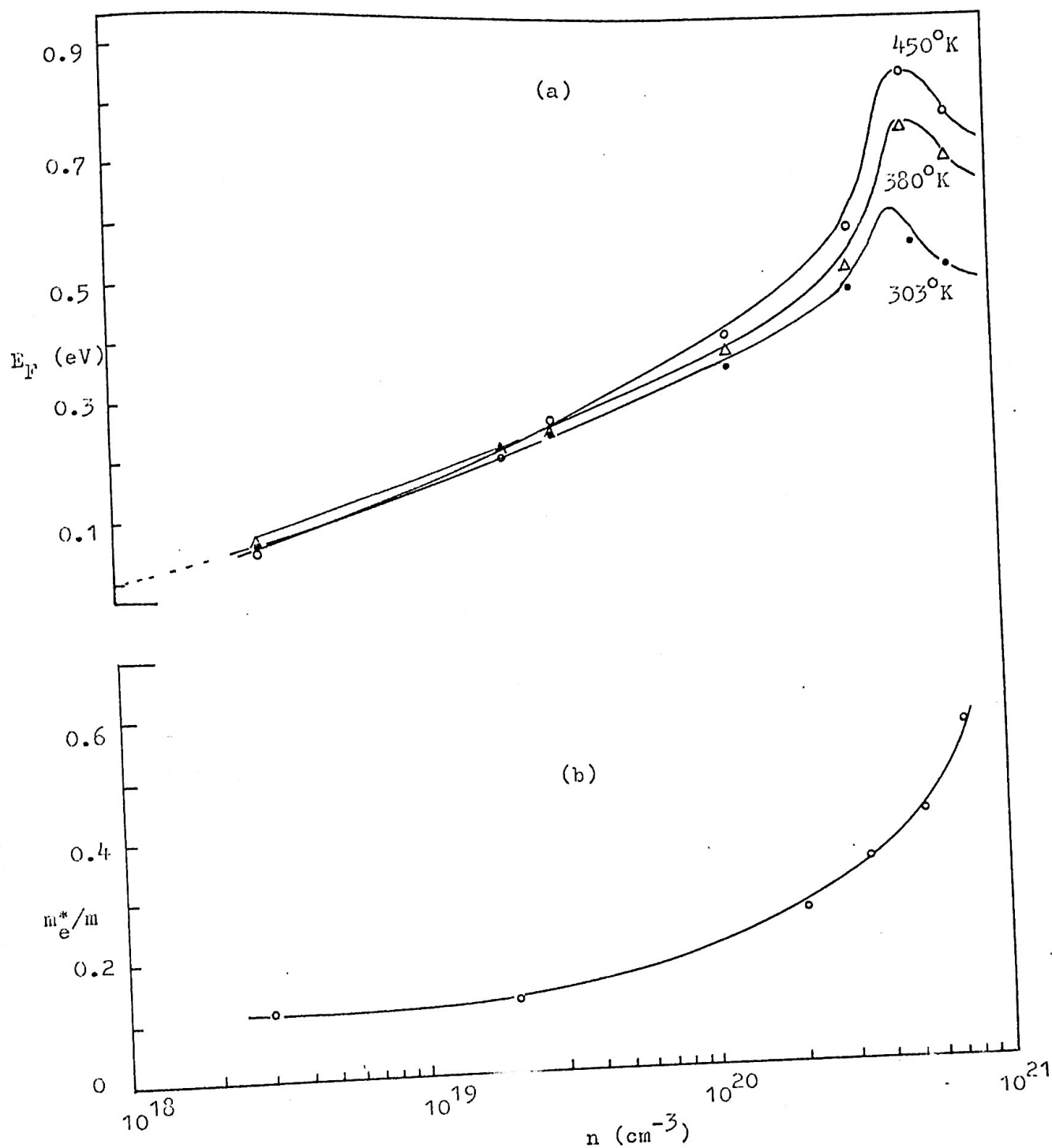


Figure 5.9: As a function of carrier concentration, n , of the indium oxide sample the variation of (a) the Fermi energy E_F at three different temperatures and (b) the effective mass of electrons m_e^* at room temperature.

as the upper limit of n for nondegenerate indium oxide film.

5.5.2 The Effective Mass of Electrons :-

The effective mass of electrons are also found to vary with the carrier concentration. Figure 5.9(b) shows the variation of electron effective mass m_e^* with carrier concentration of the sample at room temperature. The values of m_e^* vary from $0.1 m$ to $0.56 m$ in the carrier concentration range $\sim 10^{18}$ to $7 \times 10^{20} \text{ cm}^{-3}$. In the higher concentration side the change of m_e^* is more pronounced and may be due to a rapid change of the curvature of the bands. Similar values of m_e^* were obtained by Clanget⁽⁴⁾ and also by Vainshtein and Fistul⁽²⁹⁾ for indium oxide films deposited by different methods.

5.6 THE OPTICAL BAND GAP E_g AND ITS VARIATION WITH THE CARRIER CONCENTRATION

Optical band gap E_g of the samples were determined from the absorption coefficient data at short wavelength limit. For this purpose samples of different carrier concentrations were selected and their optical transmission coefficients were determined at different wavelengths. Figure 5.10 shows some of these λ vs T curves. We have studied both the possibilities of

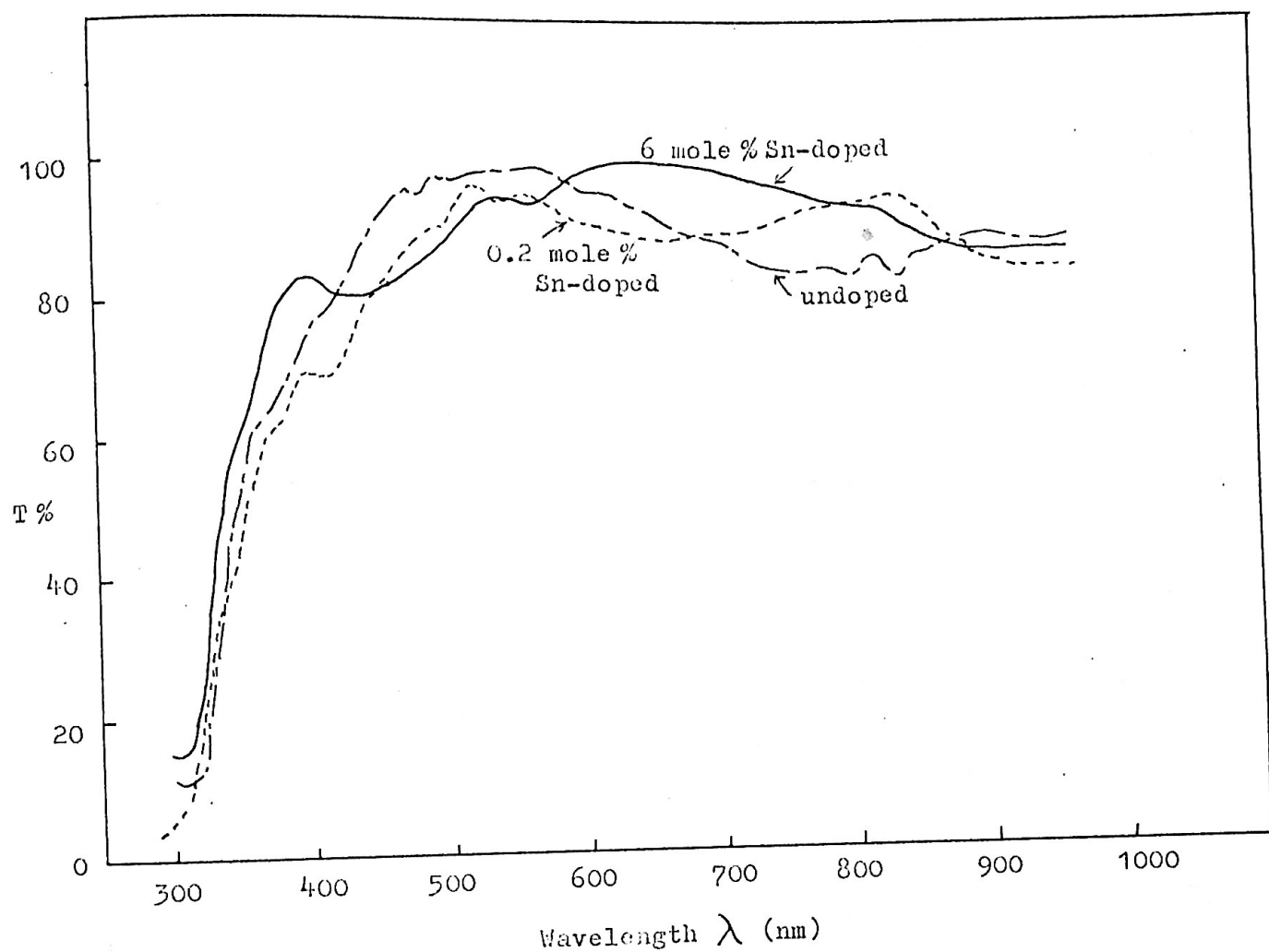


Figure 5.10: Transmission spectra of undoped and Sn-doped In_2O_3 films. Doping levels are indicated for each curve.

direct and indirect transitions.

For the direct allowed transition $(\alpha h\nu)^2$ vs. $h\nu$ curves are plotted for a set of typical samples of indium oxide with different carrier concentrations, as shown in figure 5.11. Similarly a set of $(\alpha h\nu)^{\frac{1}{2}}$ vs. $h\nu$ curves are plotted for the same set of films for indirect allowed transition in figure 5.12. The nature of the curves of these two figures are such that it is very difficult to determine whether a direct or indirect transition is predominant in these films. But it seems that direct transition may be more probable. In the carrier concentration range $\sim 10^{18}$ to $7 \times 10^{20} \text{ cm}^{-3}$ the value of E_g for direct transition varies from 3.53 to 3.73 eV, whereas for indirect transition E_g lies between 3.27 and 3.56 eV. Indirect transition always leads to lower value of E_g . Figure 5.13 shows an approximate linear variation of E_g with the carrier concentration for direct allowed transition. The observed values of E_g and its gradual increase with the increasing carrier concentration are in good agreement with the observation of Ohhata et al⁽³⁰⁾ and Swati et al⁽³¹⁾ for sputtered ITO films. For the indirect transition however, they obtained slightly lower values of E_g compared to those of the present work.

Like our SnO_2 films here also the shift of E_g with the carrier concentration can be attributed to the Moss-Burstein effect, as has been explained in chapter-2 and 4. The value of E_g corresponding to $n_0 = 1 \times 10^{18} \text{ cm}^{-3}$ for direct transition is found to be 3.53 eV (from figure 5.13), and this may be considered

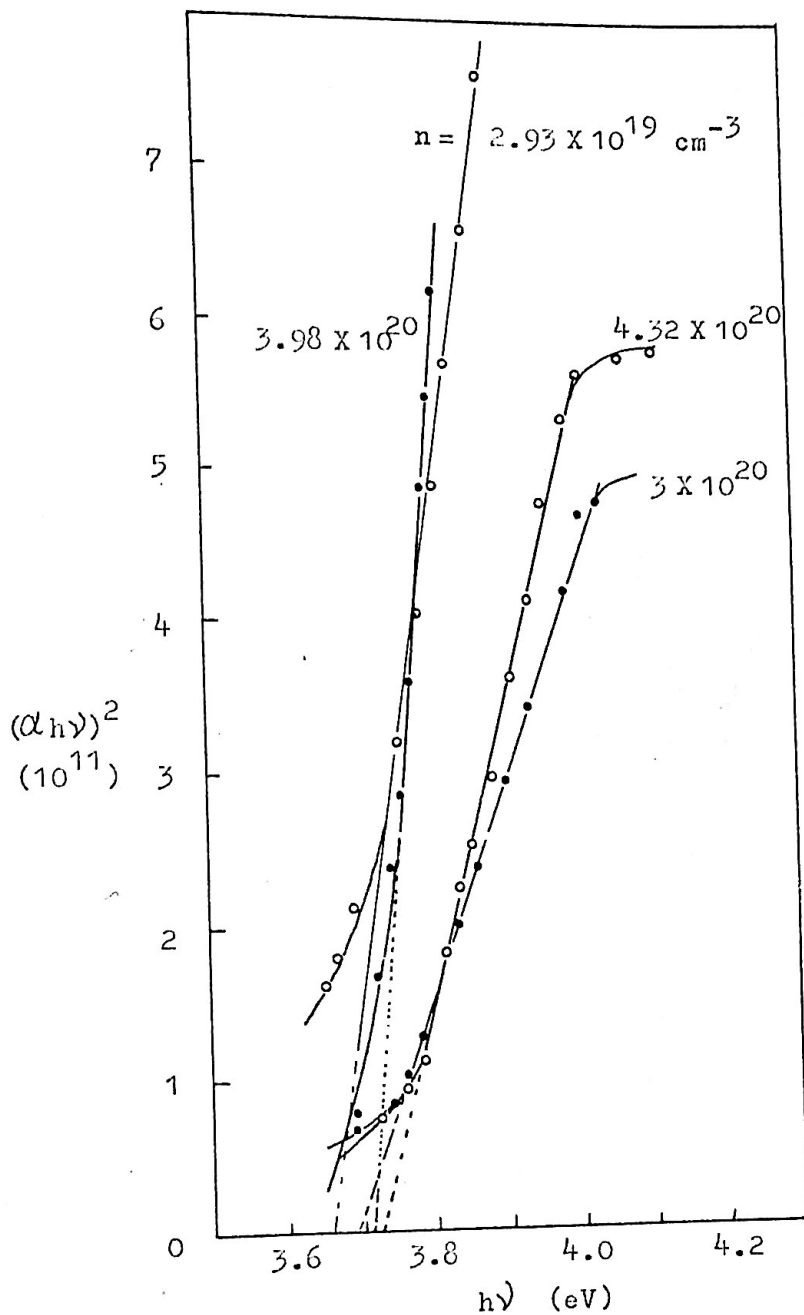


Figure 5.11 : $(\alpha h\nu)^2$ vs. $h\nu$ plots for several Sn-doped In_2O_3 films. The carrier concentrations of the samples are indicated at each curve.

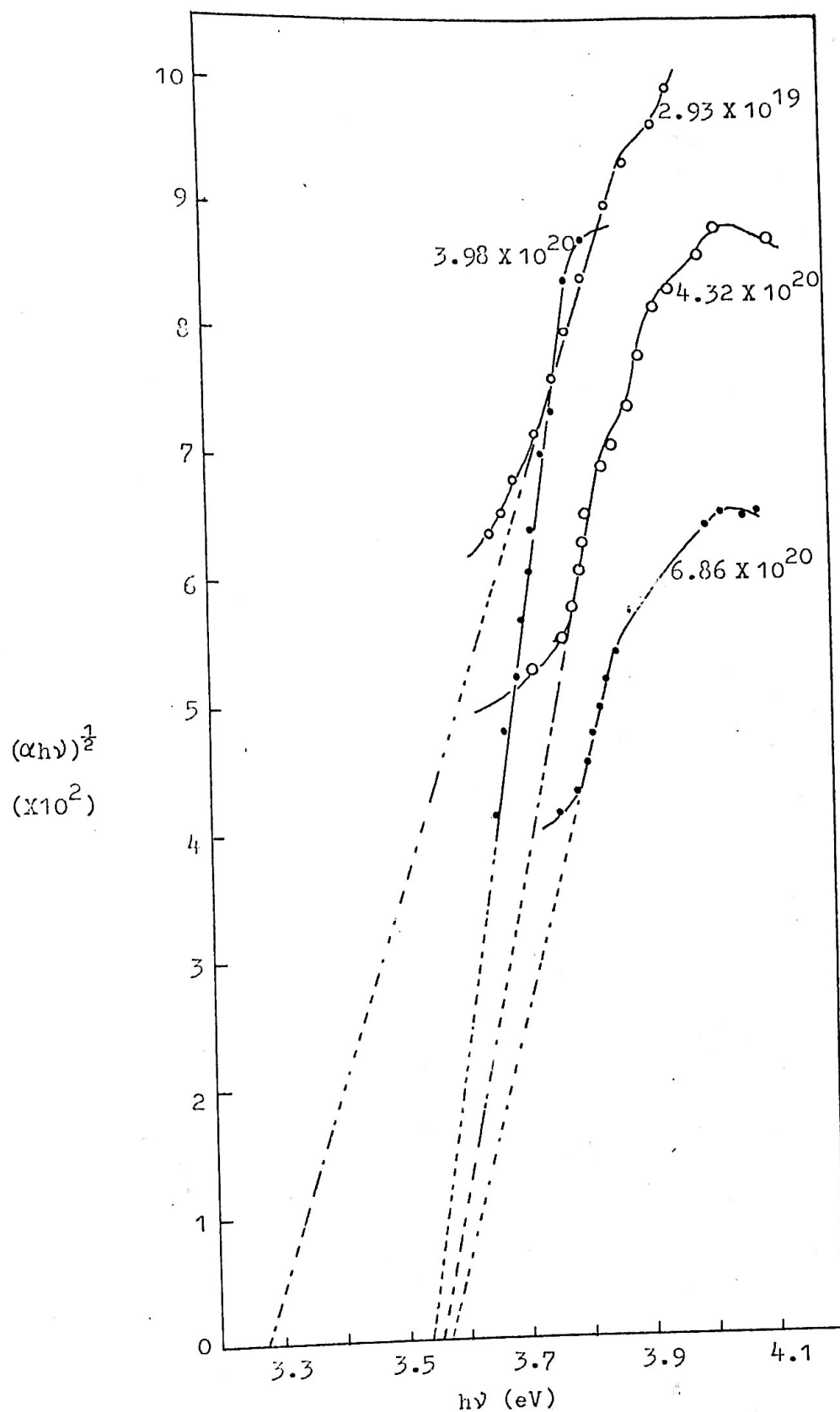


Figure 5.12 : $(\alpha h\nu)^{\frac{1}{2}}$ vs. $h\nu$ plots for several Sn-doped In_2O_3 films. The carrier concentration of the samples are indicated at each curve.

as the position of the conduction band edge E_c if zero of the energy lies on the top of the valence band. In the above analysis it has been assumed that E_g corresponding to n_0 has not suffered any appreciable shift. The values of E_g were determined at room temperature for all the samples.

5.6.1 The Plasma Edge :-

The very onset of infra-red (IR) reflection in In_2O_3 and $\text{In}_2\text{O}_3:\text{Sn}$ films can be obtained from the direct measurement of IR reflection coefficients. Theoretically it can be calculated from the screened plasma frequency given by

$$\omega_p = (4\pi n e^2 / \epsilon_0 \epsilon_L m_e^*)^{1/2}$$

The plasma edge λ_p is therefore obtained by using the calculated values of ϵ_L and m_e^* in the above equation, noting that

$$\lambda_p = 2\pi c / \omega_p,$$

c being the free space velocity of light. The plasma edge λ_p of our sample corresponding to the different carrier concentrations are shown in table 5.5. From this table it is clear that the plasma edge shifts towards the shorter wavelength with the incr-

ease of carrier concentration. This observation and the values of λ_p given in table 5.5 are of expected order and follow our experimentally observed values. Thus it appears that the optically transparent region is almost constant for the samples and the whole transmission spectrum shifts to the shorter or longer wavelength according as the free carrier concentration of the sample increases or decreases.

TABLE - 5.5

Sample	In_2O_3	In_2O_3	$\text{In}_2\text{O}_3:\text{Sn}$	$\text{In}_2\text{O}_3:\text{Sn}$
Carrier conc. $n \text{ (cm}^{-3}\text{)}$	5.18×10^{18}	5.85×10^{18}	8.8×10^{19}	9.81×10^{19}
Plasma edge (μm)	9.23	8.73	3.4	3.35

5.6.2 The Refractive Index :-

The refractive index of these samples, n_f , were calculated using the method pointed out in chapter - 2. The values of n_f were found to vary from ~ 1.69 to 1.8 for the $\text{In}_2\text{O}_3:\text{Sn}$ films in the visible wavelength range. The thickness of the samples were about $0.1 \mu\text{m}$.

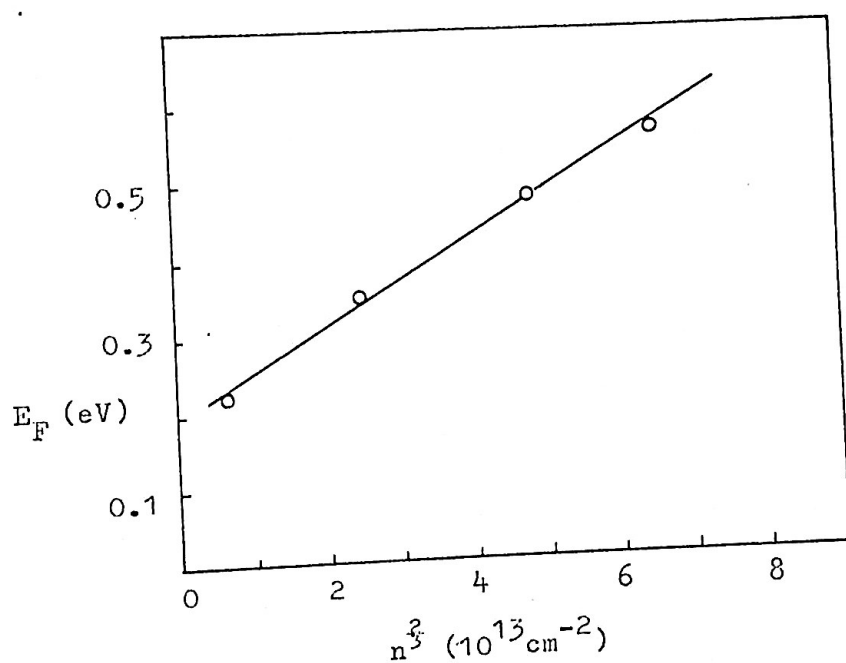
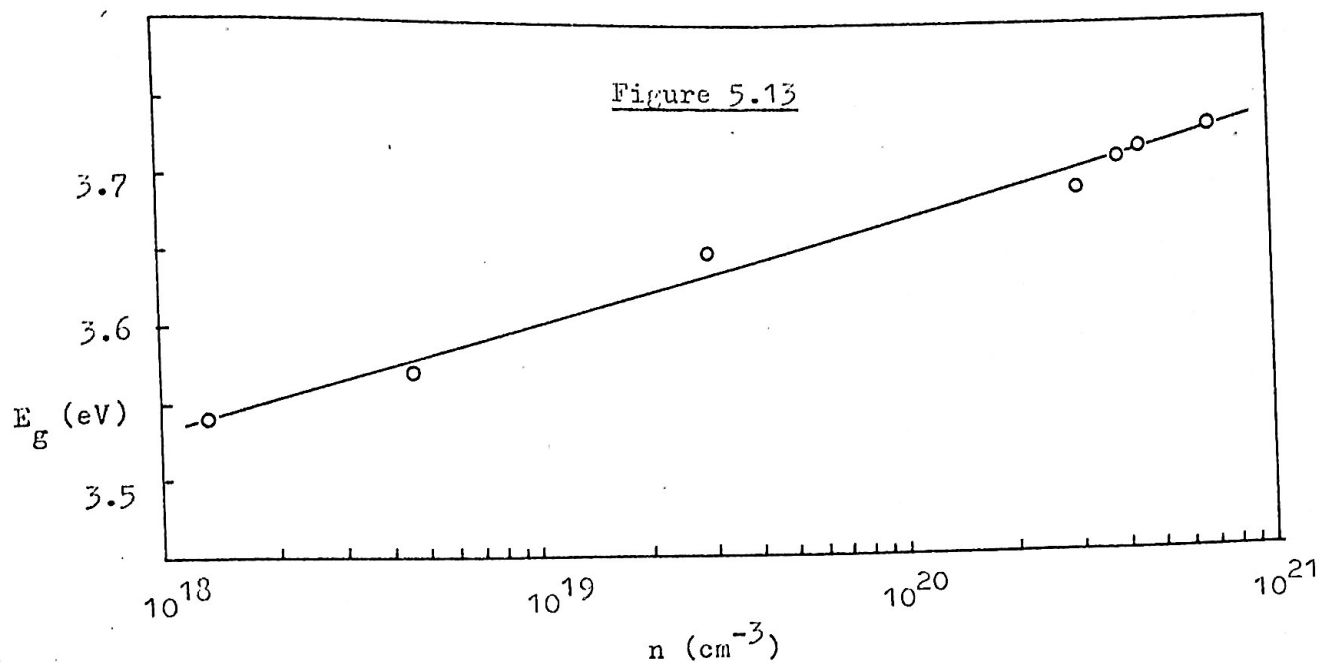
Figure 5.14

Figure 5.13 : Variation of optical band gap E_g with the carrier concentration n of indium oxide thin films.

Figure 5.14 : Fermi level E_F plotted as a function of $n^{2/3}$ of Sn-doped In_2O_3 films.

5.7 THE EFFECTIVE MASS OF HOLES

Figure 5.14 shows a plot of E_F as a function of n^3 of $\text{In}_2\text{O}_3:\text{Sn}$ films. The curve is almost a straight line in the range of carrier concentrations from 1×10^{19} to $5.25 \times 10^{20} \text{ cm}^{-3}$. From the slope of the straight line the value of the reduced effective mass m_F^* has been obtained as 0.618 m and is in excellent agreement with the reported value^(30,31). Now using the known values of m_e^* , the value of m_h^* can be calculated. The calculated values of these parameters are shown in table 5.6. The negative sign of m_h^* (which was also obtained for the SnO_2 samples) implies that the valence band is curved in the same direction as the conduction band and probably the conduction and valence band extrema donot lie at the same wave vector $k_e = 0$ ⁽³²⁾. The holes in $\text{In}_2\text{O}_3:\text{Sn}$ film appear to be heavier than the electrons.

TABLE - 5.6

Sample	Carrier conc. (cm^{-3})	m_e^*	m_h^*
$\text{In}_2\text{O}_3:\text{Sn}$	2×10^{19}	0.12 m	- 0.15 m
$\text{In}_2\text{O}_3:\text{Sn}$	3.35×10^{20}	0.35 m	- 0.79 m
$\text{In}_2\text{O}_3:\text{Sn}$	5.25×10^{20}	0.42 m	- 1.27 m

5.8 THE CARRIER SCATTERING MECHANISM

The dominant scattering mechanism in indium oxide thin film can be determined from the thermo-power data. We may analyse our thermo-power results in terms of a well known thermoelectric power theory for degenerate n-type crystalline semiconductor, which gives⁽³³⁾

$$Q = - (\pi^2 k_B^2 / e) (k_B T / E_F) (1/2 - r/3) \dots \dots (5.8)$$

Here r is the charge carrier scattering index and the Fermi level E_F is with respect to the conduction band edge. Then selecting a reference thermo-emf V_1 at a reference temperature T_1 (in some temperature region where r is almost constant), integration of the above equation gives

$$V - V_1 = - (\pi^2 k_B^2 / 2 e E_F) (1/2 - r/3) (T^2 - T_1^2) \dots \dots (5.9)$$

Rearrangement of this equation yields

$$- (V - V_1) / (T + T_1) = A (T - T_1) \dots \dots (5.10)$$

where, A is a thermo-power parameter given by

$$A = (\pi^2 k_B^2 / 2 e E_F) (1/2 - r/3) \dots \dots (5.11)$$

Our data above room temperature is replotted in terms of $-(V - V_1)/(T + T_1)$ vs. $(T - T_1)$ with $T_1 = 303^\circ\text{K}$ in figure 5.15. We see that the polycrystalline experimental results are in excellent agreement with the crystalline theory. Therefore using the values of E_F and Q at room temperature in equation 5.8 the value of r can be determined. In table 5.7 some of the calculated values of r are given corresponding to their carrier concentration. Since the value of $r = -\frac{1}{2}$ corresponds to optical

TABLE - 5.7

Carrier conc. (cm^{-3})	1.3×10^{18}	3×10^{18}	2.04×10^{19}	2×10^{20}	5.35×10^{20}	7.48×10^{20}
Scattering index, r	+ 0.48	+ 0.26	- 0.41	- 0.46	- 0.45	- 0.47

mode scattering⁽³⁴⁾, we may infer that in spray deposited $\text{In}_2\text{O}_3:\text{Sn}$ films having carrier concentration $n \gtrsim 10^{19} \text{ cm}^{-3}$ optical mode scattering is predominant; on the other hand for undoped In_2O_3 films having carrier concentration $n \lesssim 10^{18} \text{ cm}^{-3}$ acoustic mode scattering ($r = \frac{1}{2}$) may be predominant at room temperature. It may be noted here that the value of $r = -\frac{1}{2}$ also corresponds to barrier scattering, but then the process should be a temperature

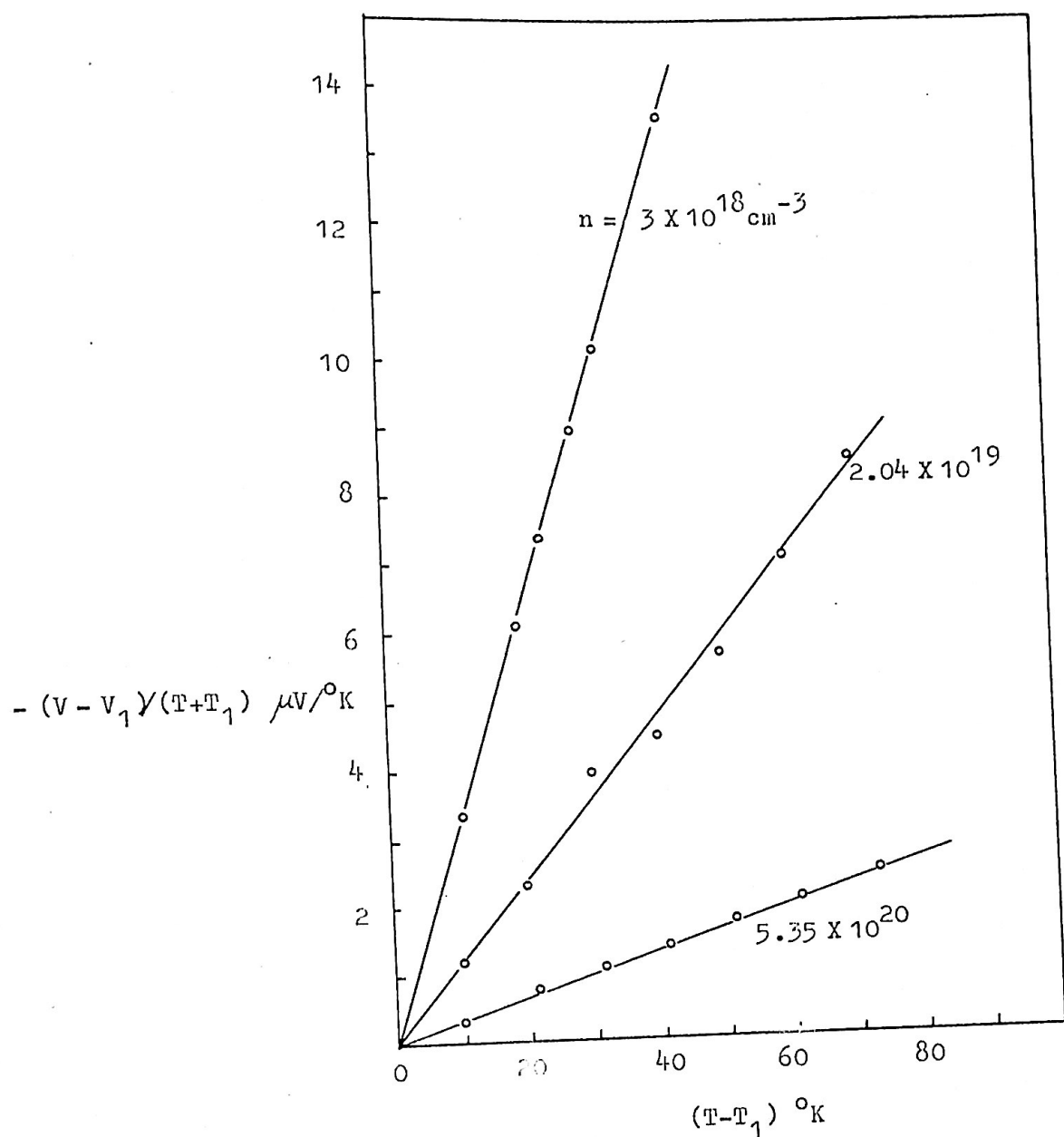


Figure 5.15 : Thermopower plotted in terms of $-(V - V_1)/(T - T_1)$ vs. $(T - T_1)$ for indium oxide films. The carrier concentrations n of the samples are indicated in the diagram.

independent one, and is contrary to our present observation; moreover from table 5.3 we see that the mean free paths of the carriers are very small in comparison to the estimated grain size, so that the contribution of barrier scattering may not be dominant here.

5.9 THE NATURE OF CRYSTAL BINDING

According to Pauling's empirical relation the percentage of ionic character of the bonds between In and O (oxygen) is calculated out to be 63.64%. Therefore, In_2O_3 crystal binding is largely ionic in nature.

5.10 THE ELECTRONEGATIVITY AND ELECTRON AFFINITY

The electronegativity EN of In_2O_3 polycrystalline bulk material has been calculated by using the Mulliken's assumption, and Sanderson's concept of geometric mean. This is given by (section 4.15),

$$\begin{aligned} \text{EN}(\text{In}_2\text{O}_3) &= \left\{ \frac{1}{4} [A_F(\text{In}) + E_I(\text{In})]^2 \quad (1/6) [A_F(\text{O}) + E_I(\text{O})]^3 \right\}^{1/5} \\ &= 5.57 \text{ eV} \end{aligned}$$

For pure In_2O_3 semiconductor the electron affinity χ is therefore obtained as 3.81 eV corresponding to an optical band gap

of 3.53 eV. As the carrier concentration increases the electron affinity decreases accordingly. This value of χ is lower to that obtained experimentally by Wang et al⁽³⁵⁾. The experimental value is 4.45 eV for a sample of $E_g = 2.62$ eV. Our sample is of wider band gap and thus the electron affinity is low.

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CHAPTER - 5

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CHAPTER - 6

CONCLUSIONS AND FUTURE WORK

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It is mentioned in chapter-1 that the work presented in this thesis has been carried out with two major aims. One of them was to design an apparatus for the easy deposition of thin films by a spraying method and the other was to study the electrical and optical properties of some transparent conducting thin film samples of SnO_2 and In_2O_3 deposited by the designed apparatus. The following conclusions have been drawn from this work.

6.1 CONCLUSIONS

Undoped and doped SnO_2 and In_2O_3 thin films were prepared on glass substrates by a modified technique in the pyrosol process. The dopants in SnO_2 films were Sb and F while it was Sn for In_2O_3 films. The deposited films are found to show better electrical and optical properties and higher figure of merit in comparison to those of films prepared earlier by the spray pyrolysis method elsewhere. Moreover the present technique is found to be economic and very easy to control and operate.

Doped films of both SnO_2 and In_2O_3 are more conducting

than the undoped films. F-doped films of SnO_2 with HF acid as doping agent are preferable to Sb-doped SnO_2 films for use as transparent conducting layer on glass substrates.

Spray deposited SnO_2 and In_2O_3 thin films are polycrystalline semiconductors and show always n-type conductivity. These samples are normally degenerate in nature. The lower limit of the carrier concentration above which the samples remain as degenerate is $1.5 \times 10^{18} \text{ cm}^{-3}$ for SnO_2 films and about $1 \times 10^{18} \text{ cm}^{-3}$ for In_2O_3 films. The lower limit of the optical band gap E_g is about 3.45 eV for SnO_2 and about 3.53 eV for In_2O_3 films when direct allowed transitions are considered. The band gaps are undoubtedly very wide. The high conductivity and at the same time the high optical transparency of these films are due to the deviation from stoichiometry and also due to the presence of foreign impurities producing shallow donor levels just below the conduction band.

The valence band and the conduction band of these materials are probably curved in the same direction and are considered parabolic. Fermi levels are normally positioned inside the conduction band and they show a gradual pinning mode near the band edge with the decrease of carrier concentrations. Moss-Burstein shift is present with the fundamental absorption edges of both the In_2O_3 and SnO_2 films and thus the optical band gap widens upto 3.96 eV for $\text{SnO}_2\text{:Sb}$ films and upto 3.73 eV for $\text{In}_2\text{O}_3\text{:Sn}$ films at carrier concentrations $\sim 10^{20} \text{ cm}^{-3}$. The magnitude of the effective

mass of electrons in the conduction band is less than that of holes in the valence band for both In_2O_3 and SnO_2 films and are found to increase with the increase of carrier concentrations of the specimen. Since the holes are relatively heavier than the electrons, the conduction band curvature is probably greater than the curvature of the valence band and also that the extrema of the bands do not lie at the same wave vector $k_e = 0$.

The refractive indices of these films in the visible range of wavelengths lie between 1.69 and 1.8 for $\text{In}_2\text{O}_3\text{:Sn}$ film and between 1.75 and 2.18 for the SnO_2 films.

The Hall mobility in thin film samples of SnO_2 and In_2O_3 is substantially lower than that of the single crystal samples at the same carrier concentration limit. This may be due to the increased scattering of the charge carriers in the films. For thin film samples of spray deposited SnO_2 two distinct scattering processes are found to predominate in the two different ranges of carrier concentrations. From concentrations $\sim 10^{18}$ to $\sim 10^{20} \text{ cm}^{-3}$ the grain boundary scattering and from $\sim 10^{20}$ to $\sim 10^{21} \text{ cm}^{-3}$ the ionized impurity scattering mechanisms are found to predominate at room temperature. In the In_2O_3 films however the lattice scattering is predominant.

The resistivity of the as-deposited films of polycrystalline SnO_2 and In_2O_3 changes due to post-deposition heat treatment and is brought about by the oxygen chemisorption/desorption

mechanism at the grain boundaries, and the new values of resistivity and mobility remain almost unaltered for a long time if the sample is kept at normal temperature and pressure. Hall mobility in SnO_2 thin film having carrier concentration $\geq 10^{19} \text{ cm}^{-3}$ is thermally activated in the temperature range 27° to 250°C while the Hall coefficient remains almost temperature independent. In In_2O_3 film on the other hand mobility is thermally activated but the Hall coefficient is found to depend on temperature. It is believed that oxygen diffusion process in these films only modulates the inter-grain boundary barrier height and controls the carrier transport process. Heat treatment upto a temperature of 250°C in normal atmosphere could neither bring any fundamental structural change nor any gross change in the optical transmission of these films but it could only aid equilibrium of those oxygen states lying at the grain boundaries with oxygen present in the ambient of the film.

The empirical approach followed in this work for the determination of electron affinity and work function of SnO_2 and In_2O_3 films (and the way of representing them as a function of the carrier concentration of the sample) is only an approximate one. Although the estimated values of electron affinity and work function, as obtained for the SnO_2 thin films, are reasonably in line with the experimental values but still they can only be taken as a guide line for use. It is rather difficult to estimate here

the actual values because of the inherent structural defects in the extrinsic material that deviate the internal atomic distribution from ideality and produce uncertainties in the values of the electronegativity and in the position of intrinsic Fermi level.

It is observed that these materials (SnO_2 and In_2O_3) are fairly ionic in nature.

From all of the above calculated and experimental values of the energy band parameters of these two materials a tentative energy band picture of the samples can be obtained; but to have a detail energy band diagram more studies are required.

6.2 FUTURE WORK

We have studied the electrical and optical properties of SnO_2 and In_2O_3 thin films with special emphasis on their carrier concentration dependent behaviours. An important side of thin film research is to study the thickness dependent behaviour of the sample. As the present technique of film deposition is very much convenient to prepare films of various thicknesses from several angstrom to several thousand angstrom, the size effect studies could be made in detail for these samples.

To gain ideas about the true energy band picture of

the materials their characteristics only in the region of room temperature are not sufficient, their properties at low temperature limit down to the liquid nitrogen are also necessary. As regards the various electrical and optical properties of these materials we have studied here only some characteristics in the region of room temperature and above, therefore, a further study in this line at low temperature region would be interesting.

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