Chapter 1

Introduction

1.1 Transparent conducting oxides

Semiconducting materials have been the subject of great interest due to their numerous practical applications. One of the most important fields of current interest in materials science is the fundamental aspects and applications of semiconducting transparent thin films. The characteristic properties of such coatings are low electrical resistivity and high transparency in the visible region. Materials like metals, that are highly conductive, will not normally transmit visible light, while high transparent media like oxide glasses behave as insulators. Transparent Conducting Oxide (TCO) films exhibit both these properties. They have high electrical conductivity combined with high optical transparency and high infrared reflectivity. This combined property of TCO makes it useful for several applications. As the areas of the major applications of TCOs increases, the demand will grow for materials having lower sheet resistance while retaining good optical properties.

In general thin films of metals (Au, Ag, Cu) are not very stable and their properties change with time. TCOs stability and hardness are superior to thin metallic films. TCO is a wide band gap semiconductor that exhibit transparency over wavelength range from 0.4 \( \mu \)m to 1.5 \( \mu \)m. The ultraviolet (UV) wavelength corresponds to the fundamental band gap of the material, whereas the Infrared (IR) edge corresponds to the free carrier plasma resonance frequency. In general, for a material to be transparent across the visible spectrum, its band gap must be greater than 3 eV to enable transmission up to the near UV (0.4 \( \mu \)m) wavelength, and its free carrier plasma resonance absorption must lie in the near infrared (1.5 \( \mu \)m) or longer wavelengths. In the IR their metallic property leads to reflectance and at sufficiently shorter wavelengths (UV), they become absorbing due to excitation across an energy gap [1].

TCO has high concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of
which lie near the conduction band edge. TCOs must necessarily represent a compromise between electrical conductivity and optical transmittances; a careful balance between the properties is required. Reduction in the resistivity is possible either with increase in the carrier concentration or mobility. But, increase in carrier concentration will lead to an increase in the visible absorption and thus will reduce optical transmittance. The high electron carrier concentration causes absorption of electromagnetic radiation in both the visible and infrared regions of the spectrum. Increasing the mobility has no deleterious effect and is probably the best direction to follow. This can only be achieved by making material with longer electron relaxation times (i.e. by permitting the electrons to travel further between the successive randomizing collisions) or by identifying materials with lower electron effective masses [2].

The mobility of the semiconductor is directly proportional to the carrier relaxation time and inversely proportional to the effective mass of the carriers; so the only option available is, to increase the carrier relaxation time or to decrease the effective mass of the carriers. The carrier relaxation time is limited by extrinsic factors, such as a high concentration of defects in the film, which may possibly be related to film fabrication. Defects in the film can cause charge scattering that reduces the relaxation time. On the other hand, the effective mass is intrinsic to the specific semiconductor and may not be changed unless a different semiconductor is used. The quality of transparent conducting films can be judged by the figure of merit ($\varphi_{TC}$), calculated from the transmittance ($T$) and sheet resistance ($R_{sh}$) (which are inversely proportional to each other data) data [3].

$$\varphi_{TC} = \frac{T^{10}}{R_{sh}}$$

The higher values of the figure of merit represent the better performance of the transparent conducting film. The optical and electrical performance of TCO is intimately tied to the fundamental band structure of the material and therefore, periodic distribution of potential in the crystal [1].
It might appear reasonable to ask which transparent conducting material is the best. However, this question does not have a unique answer, since different TCOs are best suited for different applications. Also, a given application may constrain the method of preparation and thereby affect the choice of material. The properties of a TCO layer depend not only on its chemical composition, but also on the method used for its preparation. For mass application, low cost preparation technique and good quality TCO is preferable.

In general, when TCOs are deposited onto a substrate, the temperature of the substrate must be maintained at a sufficiently high in order to develop the required properties in the TCO. The required temperatures usually increase in the following order: ITO<ZnO<SnO₂<Cd₂SnO₄ [4]. The cost of producing transparent conducting materials depends on the cost of the raw materials and the processing of it into a thin layer. The cost of the raw materials generally increases in this order: Cd<Zn<Ti<Sn<Ag<In. The costs of the deposition methods typically increase in the following order: spray pyrolysis < atmospheric-pressure CVD < vacuum evaporation < magnetron sputtering < low-pressure CVD < sol-gel < pulsed laser deposition [4]. Therefore in the view of material and preparation aspect, cadmium and spray pyrolysis technique are cost effective. In this thesis work spray pyrolysis technique is employed to prepare cadmium based oxide films.

1.2 Classification of TCOs

TCOs can be classified into families by structure as shown in Fig. 1.1 [5]. The first family has cations tetrahedrally coordinated by oxygen and is n-type in character. ZnO is the only known oxide to posseses this coordination. The second family has cations in octahedral coordination (Fig. 1.2b) and is also n type character. This is the largest family of TCOs, including CdO, In₂O₃, SnO₂, CdIn₂O₄, Cd₂SnO₄ and most of the best n-type complex oxide materials. The third family of TCOs has cations in linear coordination with oxygen and is p type character. This family includes CuAl₂O₃ and related Cu and Ag based delafossites plus SrCu₂O₂.
1.3 General applications of TCOs

Practical application for the TCOs is limitless. In the following section some of the important applications of the TCOs have been given.

1.3.1 Photovoltaic technology

Harvesting energy directly from sunlight using photovoltaic technology is being increasingly recognized as an essential component of future global energy production. The finite supply of fossil fuel sources and the detrimental long-term sources and the detrimental long term effects of CO$_2$ and other emissions into our atmosphere (global warming) underscore the urgency of developing renewable energy resources. Photovoltaic (PV) technology is being increasingly recognized as part of the solution to avoid global warming and an essential component of future global energy production [6]. Using cadmium stannate TCO as front contact material, the world record efficiency of 16.5% has been obtained in CdTe solar cell research [7]. However, this cadmium stannate film has not been used for practical application due to difficulties in preparing the film with better quality. In this thesis work effort has been taken to prepare high quality cadmium stannate film using simple spray technique.

1.3.2 Display devices

TCOs have been extensively used as transparent electrodes in various display devices, e.g. liquid crystal displays (LCDs), electroluminescent (EL) devices, image sensors based on amorphous silicon, light emitting diodes (LED) etc. [8-11]. Indium tin oxide (ITO) has been widely applied to LCDs, organic light emitting diodes (OLEDs)
1.3.3 Transparent heat reflecting films

TCO films are used for heat insulation where unhindered light transmission is required. The films on the one hand efficiently reflect broadband infrared heat radiation in a manner similar to highly conductive metal-like materials; and on the other hand they transmit light effectively in the visible region as if they were insulators. Such spectrally selective films have wide applications in solar photovoltaic conversion, spectrally selective solar reflectors (TiO₂:Nb), window heater (ZnO:Ga), solar cell back reflectors (ZnO), window insulation and thermal insulation in lamps [15-18].

1.3.4 Gas sensors

Unlike metal films whose conduction modulation by gas adsorption is small and related to changes in surface scattering, the conductance changes in semiconductor materials are large and are caused primarily by changes in carrier concentration due to charge exchange with the species adsorbed from the gas phase. The electron concentration in semiconductor sensors can vary in the conduction band approximately linearly with pressure, over a range of up to eight decades, while variations in the carrier mobility are generally small [15]. It's large and reversible variation in conductance with active gas pressure that has made semiconductor materials attractive for the fabrication of gas sensing electronic transducers. The semiconducting properties of the transparent conducting films have been exploited for use of these films in the sensing of various gases, e.g. carbon monoxide, propane and hydrogen.

CdO is known to be sensitive to acetone (CH₃COCH₃), H₂, CO₂ and O₂ gases in the temperature range of 300 to 450 °C. CdO doped with Pt, Pd and RuO₂ is reported as excellent sensors for acetone and it is compatible with hybrid microcircuit fabrication [19, 20]. Effect of thickness on liquefied petroleum gas (LPG) sensing properties of CdO films were reported by Salunkhe et al. [21]. They observed that the response and recovery time decreases with increase in film thickness. It is a rare distinction that not
many sensors are available that are sensitive to this industrially important chemical vapor.

1.3.5 Protective coatings

It has been reported [22] recently that the application of a metallic oxide coating to glass containers reduces appreciably the coefficient of friction of the glass surfaces, facilitating the movement of containers through high speed fitting lines. It has now become common practice to apply these metallic oxide coatings to glass containers immediately after forging. The subsequent application of an organic lubricant to the cooled and annealed container gives a highly desirable change to the glass surface, particularly with respect to the abrasion resistance and lubricity.

1.3.6 Other applications

In addition to these main applications, these transparent conducting films are now being widely used in a variety of other applications, such as low-emissivity ("low-e") windows applications. TCOs also necessary for the advanced development such as flat panel displays (FPDs), touch screen, laser-damage resistant coatings in high power laser technology light transmitting electrodes in the development of optoelectronic devices, optical waveguide based electro-optic modulators, the photocathode in photoelectrochemical cells, antistatic surface layers on temperature control coatings in orbiting satellites and surface layers in electroluminescent applications etc. TCOs can also be formed into transparent electro-magnetic shields, invisible security circuits on windows and transparent radio antennas built into automobile windows [4, 23–31]

A large number of materials can be used for these applications, e.g. In$_2$O$_3$, CdO, ZnO, SnO$_2$, In$_2$O$_3$:Sn, CdSnO$_3$, Cd$_2$SnO$_4$, and CdIn$_2$O$_4$. ITO is one of the best TCOs due to its better optical and electrical properties with a typical electrical conductivity of $3-5 \times 10^3$ S/cm and 85-90% transparency in the visible region, is employed on a huge scale as a transparent electrode in many display technologies [32–38]. Recently, the demand for ITO thin film transparent electrodes has dramatically increased in the filed of optoelectronic devices. If the increase in usage of ITO films for flat panel displays and solar cells continues, not only will the price of ITO continue to rise but also the availability of In may be jeopardized in the near future. The development of alternative
TCO materials is necessary to resolve this problem. New materials must be developed with lower resistivities than previously achieved and with optical properties superior to those of the present generation of TCOs.

Recently, cadmium oxide (CdO) based TCOs have received much attention due to their exceptional carrier concentrations, nearly metallic conductivities and relatively simple cubic rocksalt crystal structure [39]. CdO contains broadly dispersed s-like conduction bands and a small carrier effective mass, which represent an ideal material to study the effects of doping on TCO band structure, crystal chemistry and charge transport [40, 41]. The optical band gap of undoped bulk CdO is only 2.28 eV [42], leading to relatively poor optical transparency in the short wavelength range, aliovalent metal doping (e.g. In\(^{3+}\) on Cd\(^{2+}\) site) offers the possibility of tuning the electronic structure and the optical band gap through a carrier concentration dependent Burstein-Moss energy level shift [43]. In the present study, a part of work reports the growth of Al, In doped CdO films and (CdO)\(_{1-x}(\text{PbO})_x\) thin films on glass substrates by spray pyrolysis technique. Their structural, optical and electrical properties are investigated as a function of doping concentration.

Solar cells need highly transparent and conducting TCO for the better cell performance. For example cadmium stannate (Cd\(_2\)SnO\(_4\)), a ternary TCO material, combines with many beneficial characteristics of both SnO\(_2\) and CdO. Cd\(_2\)SnO\(_4\) film possesses electron mobility up to 100 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with high electrical conductivity and low absorption in the visible region. These properties make it potentially suitable material for a wide range of applications [44–48]. In the case of wide bandgap semiconductors, addition of impurities often induced dramatic changes in their electrical and optical properties. Dou and Egdell [47, 48] have reported that In-doping in Cd\(_2\)SnO\(_4\) improves its electrical properties. However, a detailed study on the effects of In-doping on the properties of Cd\(_2\)SnO\(_4\) films remains to be clarified. Parts of this thesis focus to obtain better cadmium stannate films relatively at lower preparation temperature. An effort has been taken to improve the electrical properties of the cadmium stannate film by vacuum annealing and In doping. More details regarding CdO and cadmium stannate films have been given in the next section.
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Cadmium, like indium, derives from zinc ores. Although this thesis is actually concerned with cadmium-containing compounds, negative comments about these can be made on the grounds of the toxicity of cadmium [49]. Despite the fact that the cadmium-based oxide materials are toxic, they are successfully employed in several applications [50]. For example, the quantity of cadmium in the CdTe absorber layer is far greater than that in the TCO (Cd₂SnO₄) and the latter will not significantly affect the total amount used in a cell. It has been claimed that its hazards, when in the form of a solar cell, may be mitigated by prior recognition and appropriate management strategies [50]. The cells or modules are completely encapsulated and, even in the event of a fire, would not be expected to emit significant amounts of cadmium. Careful safety analyses have been conducted that support this assertion.

This work would form the basis of our understanding on the specific properties of cadmium compounds to make them more superior to be used for practical applications.

1.4 Swift heavy ion irradiation

The growing interest in studying the interaction of swift heavy ions (SHI) with energies of several hundreds of MeV up to GeV with solids is due to several aspects. The first one is a consequence of future technological requirements: the tendency to move to higher implantation energies in order to form buried layers with modified properties requires studying the influence of the increasing electronic energy deposition on the structural modifications connected with the irradiation. A way to investigate this influence is the use of swift heavy ions because at these high energies the depth regions of dominating electronic and nuclear interaction are clearly separated. The second point is the damage caused in devices of future super-high energy particle accelerators or in equipment used for space applications, which can also be studied using swift heavy ions. The use of swift heavy ions to produce nanostructures in various materials is a further stimulating aspect [51].

When an energetic ion penetrates any material, it loses energy mainly by two nearly independent processes: (i) elastic collisions with the nuclei known as nuclear energy loss \((dE/dx)_n\), which dominates at an energy of about 1 keV/amu; and (ii)
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Inelastic collisions of the highly charged projectile ion with the atomic electrons of the matter known as electronic energy loss \( (dE/dx)_e \) which dominates at an energy of about 1 MeV/amu or more. In the inelastic collision (cross-section \( \sim 10^{-16} \text{ cm}^2 \)) the energy is transferred from the projectile to the atoms through excitation and ionization of the surrounding electrons. The amount of energy loss in each collision varies from tens of eV to a few keV per Angstrom (Å). For a swift heavy ion moving at a velocity comparable to the Bohr velocity of the electron the inelastic collision is the dominant mechanism for transfer of energy to the material for producing tracks when its value crosses a threshold value for track formation. The diameter and length of the track depend on the type and energy of the beam and the electrical and thermal conductivity of the material. SHI is very useful for modification of the properties of films, foils and surface of bulk solids. It penetrates deep into the materials and produces a long and narrow disordered zone along its trajectory. The passage of SHI induces very rapidly developing processes which are difficult to observe during or immediately after their occurrence. The information about these processes is stored in the resulting damage, such as size, shape and structure of defects. The degree of disorder can range from point defects to a continuous amorphized zone along the ion path, commonly called latent track [52].

A growing concern about non-uniform electric charge build-up on the exterior surfaces of orbiting satellites has prompted investigations with the preparation and properties of electrically conducting transparent coatings for use as surface layers on temperature control coatings. Field intensity fluctuations in the earth's magnetosphere especially at geosynchronous orbital altitudes continuously irradiated with UV and charged particle radiation may differentially bias spacecraft areas to potentials as high as \( 10^4 \text{ V} \) [53].

In this work, we report the effects of swift heavy ion (SHI) beam of \( \text{Ag}^{9+} \) on the structure, optical and electrical properties of \( \text{CdO} \) and \( \text{Cd}_2\text{SnO}_4 \) thin films at the fluences of \( 1 \times 10^{12} \) and \( 1 \times 10^{13} \) ions cm\(^{-2}\).
1.5 Literature review of CdO thin films

1.5.1 Basic properties of CdO films

CdO is known to be an n-type semiconductor with non-stoichiometric composition due to the presence of either interstitial cadmium or oxygen vacancies, which act as doubly charged donors [54]. The optical band gap of bulk CdO is 2.28 eV [42], leading to optical transparency is relatively less as compared with other TCOs in the short wavelength range. CdO with a simple cubic rock salt structure, broadly dispersed s-like conduction band, and a small carrier effective mass, is considered to be an ideal model material in which to study the effects of doping on TCO band structure, crystal chemistry and charge transport and on searching for ITO alternatives that are less expensive and possess comparable or higher conductivity or wider optical transparency window.

Cadmium oxide was synthesized and characterized in bulk form as early as 1902 [55], five years later the first TCO was reported in 1907 by Baedeker, who used a primitive vapor deposition system to deposit thin film CdO that was both optically transparent and electrically conducting [56]. A number of research articles are available in the literature to explain the properties of the pure CdO films prepared by spray pyrolysis, rf sputtering, dc sputtering, pulsed laser deposition, vacuum evaporation and metal oxide chemical vapor deposition etc. Several researchers reported preparation of pure CdO thin films using different preparation techniques mentioned above [57–70]. They have analyzed structural, electrical and optical properties of the as deposited CdO thin film and after the heat treatment. The basic properties of the pure CdO films depending on the preparation conditions are reviewed briefly in this section.

The property of the CdO is mainly depending on the substrate temperature and the growth atmosphere. Effect of substrate temperature on CdO films have been investigated by many workers [58, 66, 71–75]. The films prepared by sputtering at low substrate temperature (75 °C) results unoxidized cadmium peak due to incomplete reaction during the time of film deposition and the crystalline film formed at 202 °C [66]. Further, the electrical resistivity decreased from $4.6 \times 10^{-2}$ to $5 \times 10^{-4} \Omega \text{cm}$ with the increase in substrate temperature from 75 to 450 °C. The decrease in resistivity with the increase in substrate temperature is due to the improvement in the degree of
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crystallinity of the sputtered films. The Hall mobility and carrier concentration also increased from 21 to 69 cm$^2$/Vs and $6.4 \times 10^{18}$ to $1.81 \times 10^{21}$ cm$^{-3}$ with increasing the substrate temperature. Further, the optical band gap value increased from 2.41 to 2.53 eV and the films grown at 200 °C show the highest optical transmittance of 85% [66]. Ramakrishna reddy et al. [76] observed that the films grown in evaporation method at substrate temperature of 200 °C have the resistivity of $1.5 \times 10^{-3}$ Ω cm and transmittance greater than 85% with a band gap of 2.42 eV. Barnes et al. [75] showed that the microstructure of the film improves by increasing the deposition temperature. They observed the film grown on low substrate temperature (150 °C) have high defect density while film grown at high substrate temperature (450 °C) have nearly perfect lattice structure with few defects and no dislocation.

The film growth atmosphere also plays an important role regarding the electrical properties of the film. In general, the variation in the resistivity of the CdO thin film is related to the variation in carrier concentration and mobility of the films, which in turn is related to the variation of oxygen vacancies and or interstitial cadmium. Change in film property in the growth atmosphere of different Ar/O$_2$ and O$_2$ partial pressure can be found in the literature [62, 63, 65, 66]. For the films prepared in low oxygen atmosphere there exists a large number of interstitial cadmium atoms and /or oxygen vacancies, which serve as donors and contribute to higher conductivity. The films prepared at optimized oxygen partial pressure of $1 \times 10^{-5}$ mbar and substrate temperature of 350 °C shows a resistivity of $8.2 \times 10^{-4}$ Ω cm and visible transmittance of 85% with a figure of merit value of $7.5 \times 10^3$ Ω$^{-1}$ [66]. Saha et al. [77] observed that the films prepared in pure argon atmosphere have higher conductivity (1000 S cm$^{-1}$) as compared to the film deposited at 75% oxygen flow rate (2.27 S cm$^{-1}$). Further, Eze [78] reported the effect of oxygen partial pressure on thermally evaporated CdO films. He varied the O$_2$ partial pressure from $1.33 \times 10^{-3}$ to 0.133 Pa at a substrate temperature of 160 °C and obtained a maximum transmittance of 80% and minimum resistivity of $9.1 \times 10^{-4}$ Ω cm at an optimum O$_2$ partial pressure of $4 \times 10^{-2}$ Pa.

In addition to the effect of preparation condition, post annealing modifies the electrical, optical and structural properties of the as deposited CdO films. Salunkhe, Santos-Cruz and Akshoy et al. [64, 68, 69] reported the annealing effect on CdO films.
Annealing improves the crystalinity of the films, further, the optical band gap value decreased from 2.47 to 2.29 eV when the film annealed at 400 °C [68]. Santos-cruz et al. [68] annealed the CdO films in the range from 200 to 450 °C in open atmosphere to improve the electrical property of the prepared film. They found that annealing effect reduce the film resistivity and increase the carrier mobility. Films prepared using SILAR method have the resistivity of $10^{-2} \, \Omega \, \text{cm}$, this value decreased to $10^{-3} \, \Omega \, \text{cm}$ when the film annealed at 350 °C [64]. Ueda et al. [62] reported that annealing the CdO films in N$_2$/H$_2$ atmosphere can increase the carrier concentration and mobility. Therefore literature review shows that post annealing procedure improves the CdO film quality.

The CdO film has been prepared by spray pyrolysis technique using different precursor materials of cadmium nitrate and cadmium acetate [57-60]. Only limited number of publications is available on preparation of CdO films by spray pyrolysis technique. The film deposition temperature is in the range of 100–400 °C depending on the precursor materials. Spray deposited CdO films have the resistivity in the range of $10^{-2} \, \Omega \, \text{cm}$ to $10^{-3} \, \Omega \, \text{cm}$ and the carrier concentration of the order of $10^{19}$–$10^{20} \, \text{cm}^{-3}$ [57–59]. The optical band gap of the prepared films is in the range of 2.2 to 2.54 eV [58–61].

Microstructural perfection improvement as a function of annealing time of spray deposited CdO films has been reported by Vigil et al. [70]. Annealing at 450 °C for 120 minute decreases the optical transmittance of the films and decreases the resistivity of the films from $7 \times 10^{-4}$ to $5 \times 10^{-4} \, \Omega \, \text{cm}$ and the band gap value decreased from 2.53 to 2.29 eV. Annealing the spray deposited film causes significant drop in film resistivity, it tends to saturate at larger annealing time [79]. The high value of figure of merit of annealed CdO films is $1.29 \times 10^{-2} \, \Omega^{-1}$.

1.5.2 Effect of doping on CdO films

To improve the film quality researchers tried to dope the CdO film using different dopants such as In [80–83], Sn [74, 40], F [71, 72, 84], Cu [85], Mg [86], Ti [87], Ga [88, 89], Y [90], Al [63, 73, 91–94], Sm [95] and Ti [96] etc. Doping the CdO film alters the electrical, optical and structural properties of the film. Suitable doping
material improves these film properties. Change in the preferred orientation due to the
doping has been reported by Yang et al. [90]. Annealing in N$_2$ has no considerable
effect on the crystalline parameters of Sm doped CdO films under nitridation. Yan et al.
[97] reported the epitaxial growth of pure and Sn doped CdO thin films on MgO
substrate. A maximum conductivity of 42000 S/cm with higher mobility of 609 cm$^2$/V s
is obtained when the film is doped with 2.5 % Sn. Barnes et al. [75] obtained a higher
mobility of 262 cm$^2$/Vs for the CdO:F films prepared by MOCVD method at a
substrate temperature of 450 °C. Ferro and coworkers [98] reported the effect of
fluorine on CdO films. For the optimum concentration of 2% F, the films shows the
Hall Mobility of $25.4 \times 10^{-4}$ m$^2$/Vs, carrier concentration of $3.66 \times 10^{26}$ m$^{-3}$ and
resistivity of $6.72 \times 10^{-6}$ Ω m. F doped CdO films prepared at three different
temperatures of 190, 210, 230 °C. The minimum resistivity of $3 \times 10^{-6}$ Ω cm has been
reported for the films prepared at a substrate temperature of 210 °C [71]. Further, Ferro
and Rodriguez obtained a maximum carrier concentration of $8.24 \times 10^{26}$ m$^{-3}$ at 210 °C
[72]. Ga doping decreased the resistivity from $1.33 \times 10^{-2}$ to $9.30 \times 10^{-3}$ Ω cm and the
mobility value increases from 8.85 to 28.38 for the 0 and 6% Ga doped CdO films
respectively [88, 89].

Gupta et al. [87] reported the effect of substrate temperature on the properties of
2 at.% Ti doped CdO films. They observed an increase in transmittance with increasing
substrate temperature and obtained a maximum band gap of 2.84 eV for the films
prepared at 300 °C. Further, the films prepared at 150 °C shows minimum resistivity of
$5.5 \times 10^{-5}$ Ω cm and high carrier concentration of $1.87 \times 10^{21}$ cm$^{-3}$ and high mobility of
61 cm$^2$/Vs. Ga and In doped CdO films on amorphous and single crystal MgO (100)
reported by Jin et al. [88]. The films show a high conductance of 11500 and 20000
S/cm at an optimum Ga and In doping level of 1.6% and 2.6%.

CdO with In and Y has been investigated by high resolution ultraviolet and X-
ray photoemission spectroscopy [99]. Band gap and band edge effective mass of single
crystal epitaxial cadmium oxide grown by MOVPE on r-plane sapphire substrates are
reported by Jefferson et al. [100]. They reported the band edge effective mass and band
gap values are 0.21 m$_o$ and 2.16 eV respectively.
Al doping increases the transmittance from 40 to 60% for the sol-gel prepared CdO films and the carrier concentration increases from $0.34 \times 10^{20}$ to $8.11 \times 10^{20}$ cm$^{-3}$ [92]. RF magnetron sputtered Al doped CdO films show an increase in carrier concentration from $0.34 \times 10^{19}$ to $1.06 \times 10^{20}$ cm$^{-3}$ and the mobility value decreased from 459 to 194 cm$^2$/Vs for 7% Al doped CdO films. Gupta et al. [73] observed an increase in resistivity when the Al doped CdO films is prepared at higher substrate temperatures (600 °C). The resistivity increased from $2.8 \times 10^{-5}$ to $1.1 \times 10^{-4}$ Ω cm and the electron mobility increased to 54 cm$^2$/Vs as compared to the room temperature mobility of 19 cm$^2$/Vs and the optical band gap value varied from 2.74 to 2.84 eV. Khan et al. [94] reported the nano crystalline Al-doped CdO films. The transmittance of the films increases with increasing Al doping except for 0.5 wt.% and the band gap value decreases from 2.49 to 2.34 eV for the doping concentration increases from 0 to 2.0 wt.%. They obtained a decrease in mobility from 36 to 22 cm$^2$/Vs$^{-1}$s$^{-1}$ and increase in carrier concentration from $4 \times 10^{20}$ to $1.7 \times 10^{21}$ cm$^{-3}$ as the doping concentration increased from 0 to 2 wt.%.

For the In doped CdO films the band gap value is in the range of 2.51 to 2.8 eV and exhibit an optical transmittance of ~80% in the visible region [80, 101, 102]. Gupta et al. [74] studied the effect of oxygen partial pressure on In doped CdO films. They found a decrease in carrier concentration from $1.97 \times 10^{21}$ to $1.56 \times 10^{21}$ cm$^{-3}$ as the oxygen pressure increases from $2.5 \times 10^{-4}$ to $1.0 \times 10^{-3}$ mbar and the mobility value increased to 155 cm$^2$/Vs.

Literature review shows that there are only a minimum number of reports available on the preparation of indium and aluminum doped CdO films using spray pyrolysis method. Further research work is necessary to understand the basic properties of the doped CdO thin films by using the low cost spray pyrolysis technique. Therefore, in this thesis work the effect of doping on the structural, surface, optical and electrical properties of CdO films was studied in detail. Further the effect of irradiation on the CdO film properties has been studied.

In addition with doping of CdO film, researchers are also reported a new kind of mixed films such as CdO+ZnO and CdO+PbO [103–107]. It is being tried out to mix with other oxides as well. Cadmium acetate and Zinc acetate was used to prepare mixed
films of (CdO)$_{1-x}$ (ZnO)$_x$ [103, 104]. Hosono et al. [105] reported amorphous semiconductor 2CdO-PbO$_x$ thin films with a novel information about the carrier generation through the formation of oxygen vacancies. Sarma and Srinivasan [106] explored the structural and optical properties of (PbO)$_x$(CdO)$_{1-x}$. Further, in our laboratory we have reported the preparation and characterization of spray deposited (CdO)$_{1-x}$(PbO)$_x$ mixed films with $x = 0.25$ [107]. In continuation with the work, a detailed investigation on (CdO)$_{1-x}$(PbO)$_x$ mixed films with $0 \leq x \leq 1$ has been done in this thesis work.

1.6 Literature review of Cd$_2$SnO$_4$ thin films

Cadmium stannate thin film has superior film quality when compared to other TCOs with high optical transmittance and low resistivity. The high conductivity of Cd$_2$SnO$_4$ films has been proposed due to the presence of defects and oxygen vacancies which contribute to the conductivity through the creation of free electrons [108]. The chemical [109] and thermal [110] stabilities of Cd$_2$SnO$_4$ films are very good and the films can be removed from the substrate only by strong acid etch. Cd$_2$SnO$_4$ and CdSnO$_3$ are the two known phases of cadmium stannate. Both of these compounds possess cubic and orthorhombic crystal structure and are wide band gap n-type semiconductors. The higher conductivity of the cadmium stannate films is mainly attributed to oxygen deficiency which provides the donor states in cadmium stannate thin films [111–115]. Due to these basic properties of the cadmium stannate films, it can be used for the military applications [110]. Also, Cd$_2$SnO$_4$ thin film is most suitable especially for CdTe solar cell application [116–118].

The major problem with cadmium stannate thin film is the film stoichiometry. Literature review shows that it is difficult to get stoichiometric cadmium stannate thin films [119]. Mainly the amount of cadmium is less in the film when the films prepared at higher substrate temperatures. Generally, the films prepared at room temperature are amorphous. Therefore, higher substrate temperature is necessary to obtain Cd$_2$SnO$_4$ phase.

By using spray pyrolysis technique it is easier to increase the cadmium content in the precursor solution to solve the stoichiometric problem in the film and doping of
the material is very simple. No expensive target preparation as like sputtering is necessary for the above mentioned trials. Therefore in this thesis work spray pyrolysis technique was used to deposit doped and undoped cadmium stannate thin films. In the following section preparation of cadmium stannate by different techniques reviewed briefly.

Nozik [44] first demonstrated the potential of this material as a transparent conductor when he sputtered amorphous (one film exhibited cubic symmetry) with conductivities exceeding 1300 S/cm, optical gap as high as 2.85 eV and with the carrier mobility of 100 cm²/Vs, which he attributed to low effective mass. In addition to films, Nozik prepared Cd₂SnO₄ powder above 900 °C in the orthorhombic form described by Smith [120] and below 900 °C in a cubic form tentatively identified as a spinel [44]. Higher conductivities than those reported by Nozik were obtained by Haacke et al. [121] who prepared thin films that were primarily crystalline spinel Cd₂SnO₄ with conductivities as high as 6700 S/cm. After this, several researchers tried to improve the film quality of cadmium stannate thin films by sputtering technique [121–129]. According to the literature review, in comparison with other preparation techniques sputtering technique results relatively better film quality [127]. The sputtered films generally contain CdO and CdSnO₃ phases, depending on the sputtering conditions. Heat treatment of sputtered Cd₂SnO₄ films in an Ar-CdS atmosphere at 600–700 °C results in a decrease in CdO content in the film, along with an increase in the lattice parameter (from 9.167 to 9.189 Å) [121]. A possible explanation is that cadmium dissociates from the CdO and diffuses into the Cd₂SnO₄ lattice to form interstitial donors; this is corroborated by an accompanying increase in carrier concentration [124]. Miyata and coworkers have reported reactive sputtering of mixed targets [127, 128] or Cd-Sn alloy [130] targets in an Ar-O₂ mixture, resulting in films with ρ ~ 6 × 10⁻⁴–10⁻³ Ω cm and transmittance (T) ~ 85%.

Post deposition heat treatment of Cd₂SnO₄ films is found to affect their electrical properties significantly [110, 111, 125, 127, 131–135]. In general as deposited films were annealed to improve the electrical and structural properties. Annealing in vacuum or inert gases causes recrystallization of the films and generates oxygen vacancies. Many authors has made investigation on the influence of post-deposition heat treatment in different ambient on the electrical properties of cadmium
stannate films. Miyata and co-workers [130] observed a decrease in resistivity and an increase in carrier concentration after annealing of DC reactive sputtered Cd$_2$SnO$_4$ films either in vacuum, Ar or N$_2$ atmosphere at 300 °C. Pisarkiewicz et al. [135] observed an increase in both carrier concentration and Hall mobility in DC reactive sputtered Cd$_2$SnO$_4$ films after annealing the film in vacuum at $10^{-4}$ Pa at 397 °C. Wohlmuth and Adesida observed decrease in resistivity after annealing the Cd$_2$SnO$_4$ films from $1.1 \times 10^{-3}$ to $5.2 \times 10^{-4}$ Ω cm [131]. Cd$_2$SnO$_4$ films prepared by r.f. sputtering of an oxide target in pure O$_2$, when heat treated in an Ar–CdS ambient, show an increase in carrier concentration from $10^{19}$ to $10^{21}$ cm$^{-3}$ [121, 124], mobility ($\mu$) is typically in the range 30–50 cm$^2$ V$^{-1}$ s$^{-1}$ leading to resistivity ($\rho$) ~ $1.5 \times 10^{-4}$ Ω cm [45, 136] along with $T \sim 85\%$ [110]. The increase in carrier concentration with annealing treatment is due to creation of oxygen vacancies. Mamazza et al. [132] reported the preparation of Cd$_2$SnO$_4$ films by RF magnetron co-sputtering at room temperature and subsequently subjected to heat treatment in inert or reducing (H$_2$) ambient. The H$_2$ annealing increased the band gap from 2.97 to 3.18 eV [132]. An increasing conductivity in Cd$_2$SnO$_4$ films, whether it is caused by adjusting the sputtering conditions or by a heat treatment, invariably results in a large shift in the fundamental absorption edge [44, 124] typically from 2.1 to 2.9 eV and improving the visible transmittance significantly. This large shift is attributed to the Burstein–Moss effect and appears most likely to be composed of contributions from Cd$_2$SnO$_4$ and CdO present in the films [121].

Researchers also tried to alter the sputtered film stoichiometry by altering the composition of the sputter target. Targets of various compositions ranging from 50% Cd–Sn to 75% Cd–Sn have been used to grow Cd$_2$SnO$_4$ films [111, 112, 121, 137]. Films sputtered from targets with Cd content 60–70% have in general results Cd$_2$SnO$_4$ phase. Schiller et al. [112] obtained a Cd:Sn ratio of 1.5–1.6. A high Hall mobility of 50–60 cm$^2$ V$^{-1}$ s$^{-1}$ and carrier concentration of $10^{20}$ cm$^{-3}$ were achieved in a wide Cd to Sn ratio [138]. As mentioned above, the film quality improves after post deposition annealing in a suitable atmosphere of Ar, O$_2$ or H$_2$–Ar at 400–500 °C [111–113]. Schiller et al. [112] reported that a reduction in pressure ratio ($P_{O_2}/P_{total}$) resulted in a reduction in the cadmium to tin ratio. The texture and composition of Cd$_2$SnO$_4$ films depend strongly on thickness, deposition rate and the target used [110, 126, 129, 130].
139]. In addition to the effect of deposition temperature on crystallinity of the film, Miyata and co-workers [137] in their extensive studies of Cd$_2$SnO$_4$ films observed that the films less than 800 Å thick were always amorphous irrespective of the rate of deposition.

Cadmium stannate thin films have also been prepared by other preparation techniques such as electroless [140], dip coating [114], chemical vapor deposition [138, 141, 142], ion exchange [143], and sol-gel [144, 145]. Using electroless deposition technique Raviendra et al. [140] obtained Cd$_2$SnO$_4$ phase after annealing the film. However the electrical properties of the films are poor. For CVD prepared films, the films exhibit a carrier concentration in the range of $10^{20}$ cm$^{-3}$ and the mobility of 50 cm$^2$/Vs. But the film have also contains CdO phase [138]. Electrochemical properties of sol-gel prepared nanocrystalline cadmium tin oxide electrodes were investigated by Valincius and coworkers [144]. Tahar et al. [145] deposited Cd$_2$SnO$_4$ films by sol-gel method with a grain size of 20 to 50 nm. They obtained a minimum resistivity of $3.3 \times 10^{-4}$ Ω cm, a carrier concentration of $1.55 \times 10^{21}$ cm$^{-3}$ and a mobility of 12 cm$^2$/Vs after annealing the film at 500 °C in nitrogen atmosphere.

There are only few reports available regarding preparation of cadmium stannate thin films using spray pyrolysis technique. Haacke et al. [45] was the first to report the preparation of the Cd$_2$SnO$_4$ films by spray pyrolysis method. They observed that the film preparation with substrate temperature in the range of 400–500 °C results translucent coatings. At higher substrate temperature of 500–700 °C the coatings consist of CdSnO$_3$ phase, whereas films deposited at temperatures higher than 800°C result in Cd$_2$SnO$_4$ phase. The Cd$_2$SnO$_4$ films have also been prepared using spray pyrolysis technique at low substrate temperatures. Ortiz [125] prepared the Cd$_2$SnO$_4$ film in the substrate range of 370 to 450 °C. At low substrate temperature the films are cluster like nature. When the substrate temperature increased the cluster disappeared and the surface became almost smooth. Further the transmittance of the film increased with increasing substrate temperature. They obtained a sheet resistivity of 400 ohms/sq and optical transmission of 83%. In order to reduce the electrical conductivity of the films, Agnihotri et al. [133] and Mohammad et al. [134] annealed their samples at about 300 °C under high vacuum to reduce the effect of oxygen traps created during...
film preparation. Agnihotri et al. [133] reported that if the cadmium stannate film is prepared in the normal air atmospheric conditions, the film can absorb excess amount of oxygen which can act as electron trap. Further, Zhu et al. [146] reported that the existence of adsorbed oxygen in films will trap a part of electrons, leading to the increase of resistivity. Annealing in vacuum atmosphere can help to reduce the effect of electron traps created during the film preparation by creating oxygen vacancies [124, 133, 140]. Abrutis and coworkers [147] reported the 80% transmission in the spray deposited films. The reflectivity minimum in the case of Cd$_2$SnO$_4$ films is observed [115] in the energy range of 0.55–0.72 eV, and depends on the carrier concentration of the samples tested.

In the case of wide bandgap semiconductors, addition of impurities often induced dramatic changes in their electrical and optical properties. The effects of n-type doping on the electrical properties of Cd$_2$SnO$_4$ thin [45] and thick films [148] have been studied. Only few reports are available in the literature on the preparation of doped cadmium stannate thin films [47, 48, 149, 150]. Dou and Egdell [47, 48] have reported that In-doping in Cd$_2$SnO$_4$ improves its electrical properties. Sb-doped Cd$_2$SnO$_4$ films are characterized by NMR, EPR and spectroscopic studies [47, 149, 150]. It is necessary to study the effect of In doping on the properties of Cd$_2$SnO$_4$ films.

Since, spray pyrolysis technique is simple and there are very limited publications available on the preparation of cadmium stannate thin films by spray pyrolysis technique, it is planned to study the spray deposited cadmium stannate film properties. Doped (indium) and undoped cadmium stannate thin films were deposited and their optical and electrical properties were analyzed. Further its stability with heavy ion irradiation has been studied.

1.7 Experimental techniques used in the present study

Methods of preparing thin films may be divided essentially into two main groups, namely, chemical methods and physical methods. The former includes electro deposition, spray pyrolysis, chemical solution growth, chemical vapor deposition, metal oxide chemical vapor deposition. Thermal evaporation, sputtering, e-beam evaporation and pulsed laser deposition are the most important physical methods. Spray pyrolysis is
the most widely used method for the deposition of thin films, which offers the large area coating, ease of adds doping and cost effective.

1.7.1 Spray pyrolysis experimental setup

The films studied in the present investigation are deposited by home made spray pyrolysis experimental setup [151]. Fig.1.2 shows the schematic diagram of the spray pyrolysis experimental unit used for the deposition of thin films. Spray pyrolysis is one of the relatively simple and inexpensive methods which can easily be employed for mass production of large area coatings for industrial applications. It is based on the pyrolytic decomposition of a metallic compound dissolved in a liquid mixture when it is sprayed on a heated substrate. The spray gun was made using a coaxial assembly of quartz tube. The inner capillary tube used for the solution and outer tube for passing carrier gas. Filtered compressed air was used as carrier gas. Microscope glass slides, quartz and Corning plates, cleaned with organic solvents, were used as substrates.

The substrate temperature was monitored with the help of chromel-alumel thermocouple fixed at the centre of the hot plate. Hence the substrate temperature referred in the present study is of the hot plate. The variation of substrate temperature during spray was maintained within ±5 °C with the help of temperature controller. The air pressure flowing through spray gun was controlled with pressure regulator. The flow rate of the carrier gas, 6 l/min at a pressure of 4.412 MPa, is used in the present study. A glass beaker was used as the solution container. Spray setup has been housed in the closed chamber with exhaust arrangement. The parameters such as distance between the spray nozzle and the substrate (35 cm), and spray angle (about 45°) were kept constant. The other parameters such as substrate temperatures, spraying time and spraying interval are varied. After completion of the deposition process, the films were allowed to cool down slowly to room temperature.
1.7.2 X-ray diffraction

X-ray powder diffraction is generally the first and perhaps the most widely used probe of crystal structure. Much information related to the crystal structure of the films, including lattice constants, grain size, preferred orientation of polycrystals, defects, stress, internal stress, etc. can be determined from the X-ray diffraction measurement. X-ray diffraction based on monochromatic radiation is generally more important because the ‘d’ spacing can be calculated from the observed diffraction angles [152]. The requirements to obtain a useful powder diffraction data set are conceptually straightforward: allow a beam of X-rays to impinge on the sample and record the diffracted intensity as a function of angle. Diffraction will occur whenever the Bragg law $n\lambda = 2d \sin \theta$ is satisfied [153]. Most laboratory powder X-ray diffractometer uses a sealed X-ray tube with a target of copper or molybdenum. About half of the X-rays from such a tube are in the characteristic Kα line ($\lambda=1.54056$ Å (Cu Kα)), and the remainder are in other lines and in a continuous bremsstrahlung spectrum. In these diffractometers, the diffracted radiation is detected by counter tubes, which move through the angular range of reflections. The most widely used X-ray detector today is the scintillation counter, in which X-rays are converted into visible light and then into electronic pulses by a photomultiplier tube. XRD is a nondestructive method, which makes it deal for in-situ studies.
1.7.3 Scanning electron microscopy (SEM)

This is one of the most useful and versatile instruments for the investigation of surface topography, microstructural feature, etc. It provides a pictorial display of the surface layer with a high depth of focus greater than that possible in an electron microscope thus providing better details than that by the conventional replica technique [154]. Thus a surface with a comparatively rough topography can be examined with resolution of about 30 to 150 Å. It is also possible to have a three dimensional view of the surface with a magnification as high as 80000 or even more.

The principle involved in imaging is to make use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the specimen. At the point of contact several processes may take place by which electrons, photons, etc. may be emitted. In SEM secondary electrons are primarily used. These generally have very low energy say <50 eV compared to 30 keV of the primary electrons and hence only those secondaries which are generated at the surface layers can leave the surface. These secondaries are formed by the interaction of the primary electron beam with the loosely bound electrons of the surface atoms and their emission is very much sensitive to the incident beam direction and the topography of the surface atoms and the contrast is primarily due to these factors rather than the compositional variation of the surface layer. The more oblique is the surface the greater will be the surface area from which secondary electrons can emit. The contrast hence depends on the rate of the secondary electron yields and the incident angle of the primary beam to the surface element. The secondary electron yield is not much affected by the compositional variation of the material, but may be so in the case of contaminations.
Fig. 1.3 Schematic diagram of scanning electron microscopic arrangement

The basic instrument (Fig. 1.3) consists of an electron source, a series of lens system to produce a finely focused electron beam on the specimen surface, two pairs of deflection coils at right angles to each other and connected to a saw tooth wave generator system so that a finely focused electron beam describes a rectangular zig zag raster i.e specimen scanning. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.

1.7.4 Atomic force microscopy (AFM)

The ability of the AFM to create three-dimensional micrographs with resolution down to nanometer scale renders it as an essential tool for imaging the surfaces. It provides nanoscale to atomic-scale microscopy by measuring the tip-surface interactions from forces and translating these to a sensor to provide information on the
topographic features of the surface. The forces involved can include van der Walls, electrostatic, frictional and magnetic. Typically, forces measured are in the range $10^{-3}$ to $10^{-6}$ N [155]. The small probe-sample separation makes it possible to take measurements over a small area. AFM operates by measuring attractive or repulsive forces between a tip and the sample [156].

In a typical instrument (Fig. 1.4), an atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezoelectric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from Si$_3$N$_4$ or Si, and extended down from the end of a cantilever. The nanoscope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photodetector measures the difference in light intensities between the upper and lower photodetectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezoelectric transducer monitors real-time height deviation. In the constant height mode the deflection force on the sample is recorded. The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01 nm vertical resolutions on all types of samples. Three-dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position. The way in which image contrast is obtained can be achieved in many ways. The three main classes of interaction are contact mode, tapping mode and non-contact mode.
Contact mode is the most common method of operation of the AFM. As the name suggests, the tip and sample remain in close contact as the scanning proceeds. As the tip is raster-scanned across the surface, it is deflected as it moves over the surface corrugation. In constant force mode, the tip is constantly adjusted to maintain a constant deflection, and therefore constant height above the surface. It is this adjustment that is displaced as data. However, the ability to track the surface in this manner is limited by the feedback circuit. Sometimes the tip is allowed to scan without this adjustment, and one measures only the deflection. This is useful for small, high speed atomic resolution scans, and is known as variable-deflection mode. Because the tip is in hard contact with the surface, the stiffness of the lever needs to be less than the effective spring constant holding atoms together, which is on the order of 1–10\text{nN/\text{nm}}. Most contact mode levers have a spring constant of \text{<1N/m}}.

Tapping mode is also frequently used in AFM. When operated in air or other gases, the cantilever is oscillated at its resonant frequency (often hundreds of kilohertz) and positioned above the surface so that it only taps the surface for a very small fraction
of its oscillation period. This is still contact with the sample, but the very short time over which this contact occurs means that lateral forces are dramatically reduced as the tip scans over the surface. When imaging poorly immobilized or soft samples, tapping mode may be a far better choice than contact mode for imaging. The advantage of tapping the surface is improved lateral resolution on soft samples.

In a non-contact mode, a stiff cantilever is oscillated in the attractive regime, meaning that the tip is quite close to the sample, but not touching it. The forces between the tip and sample are quite low, on the order of pico Newton (10^{-12} N). The detection scheme is based on measuring changes to the resonant frequency or amplitude of the cantilever. This is a very difficult mode to operate in ambient conditions with the AFM.

1.7.5 UV-Vis Spectrophotometry

A spectrophotometer is a device which detects the percentage transmittance of light of certain intensity and frequency range is passed through the sample. Thus the instrument compares the intensity of the transmitted light with that of incident light. It consists of a source, focusing optics, standard sample cuvette, wavelength isolation device, and a detector with amplifier and readout system. Fig. 1.5 shows the schematic representation of double beam UV-Vis spectrophotometer.

**Scanning double beam spectrophotometer**

Spectrophotometers of this type feature a continuous change in wavelength. One beam permanently accommodates a reference or blank, and the other the sample. An automatic comparison of transmittance of sample and reference is made while scanning through the wavelength region. The ratio of sample to reference after conversion to absorbance values is plotted as a function of wavelength on a recorder.
In an optical arrangement light from either visible or ultraviolet source enters the grating monochromator. Broad band filters contained in a filter wheel are automatically indexed into position at a required wavelength to reduce the amount of stray light and unwanted orders from diffraction grating. The optical beam is then directed alternatively through the sample and reference cells by a system of rotating sector mirrors (choppers) and corner mirrors. Each beam, a pulse of light separated in time by a dark interval, is then directed onto a photomultiplier tube in a time sharing procedure. After amplification, the reference signal is used to provide a signal to dynode voltage regulator. The dynode voltage is varied to maintain a constant reference signal and keep all amplifiers within required operating limits. The sample signal is either processed through a logarithmic converter for absorbance measurements or is used directly for transmittance measurements. The result is fed to recorder, meter or digital indicator [157].

1.7.6 Resistivity and Hall measurement

The van der Pauw method involves applying a current and measuring voltage using four small contacts on the periphery of a flat, arbitrarily shaped sample of
uniform thickness. This method is particularly useful for measuring very small samples because geometric spacing of the contacts is unimportant. Effects due to a sample’s size, which is the approximate probe spacing, are irrelevant.

\[ r^h \]

\[ 1 \quad 2 \]
\[ 4 \quad 3 \]

\[ H^h \]

\[ t \]
\[ 4 \quad 3 \]

Fig. 1.6 Van der Pauw Resistivity measurement

Resistivity derivation

Using this method, the resistivity can be derived from a total of eight measurements that are made around the periphery of the sample with the configurations shown in Fig.1.6. Once all the voltage measurements are taken, two values of resistivity, \( \rho_A \) and \( \rho_B \), are derived as follows:

\[ \rho_A = \left[ \frac{\pi}{\ln 2} \right] \times [f_A t] \times \left[ \frac{V_1 - V_2 + V_3 - V_4}{4I} \right] \quad (1.2) \]

\[ \rho_B = \left[ \frac{\pi}{\ln 2} \right] \times [f_B t] \times \left[ \frac{V_5 - V_6 + V_7 - V_8}{4I} \right] \quad (1.3) \]

where: \( \rho_A \) and \( \rho_B \) are volume resistivities (ohm-cm);

\( t \) is the sample thickness (cm);

\( V_1 \) through \( V_8 \) represent the measured voltages;

\( I \) is the current through the sample (amperes);

\( f_A \) and \( f_B \) are geometrical factors based on sample symmetry (\( f_A = f_B = 1 \) for perfect symmetry). The average resistivity (\( \rho_{AVG} \)) is simply \( \frac{\rho_A + \rho_B}{2} \).
Hall Voltage Measurements

Hall effect measurements are important to semiconductor material characterization, because from the Hall voltage the carrier density, mobility, and conductivity type can be derived [158]. With an applied magnetic field, the Hall voltage can be measured using the configurations shown in Fig. 1.7.

![Hall voltage measurement configuration](image)

**Fig. 1.7 Hall voltage measurement configuration**

Procedure

With a positive magnetic field of known flux B, applied to the sample, a current is sourced and voltages measured between the sample terminals as follows:

- Constant current is applied between terminals 1 and 3; voltage drop ($V_{24+}$) is measured between terminals 2 and 4.
- Reverse the current and measure the voltage drop ($V_{42+}$).
- Apply current between terminals 2 and 4; measure the voltage drop ($V_{13+}$) between terminals 1 and 3.
- Reverse the current and measure voltage drop ($V_{31+}$).
- Reverse the magnetic field, B, and repeat the procedure, measuring the four voltage drops ($V_{24-}$), ($V_{42-}$), ($V_{13-}$), and ($V_{31-}$).

Calculations

From the eight Hall voltage measurements, the average Hall coefficient can be calculated as follows:

$$R_{HE} = \frac{t(V_{4-2+} - V_{2-4+} + V_{2-4-} - V_{4-2-})}{BI}$$  \hspace{1cm} (1.4)

$$R_{HD} = \frac{t(V_{3-1+} - V_{1-3+} + V_{1-3-} - V_{3-1-})}{BI}$$  \hspace{1cm} (1.5)
where: $R_{HC}$ and $R_{HD}$ are Hall coefficients in $cm^3/C$;

$t$ is the sample thickness in cm;

$V$ represents the voltages measured by the voltmeter;

$I$ is the current through the sample in amperes;

$B$ is the magnetic flux in $VS/cm^2$ ($1 VS/cm^2 = 108$ gauss)

Once $R_{HC}$ and $R_{HD}$ have been determined, the average Hall coefficient ($R_{HAVG}$) can be calculated as $(R_{HC} + R_{HD}) / 2$. From the resistivity ($\rho_{AVG}$) and Hall coefficient ($R_{HAVG}$), the mobility ($\mu_H$) can be calculated:

$$\mu_H = \frac{|R_{HAVG}|}{\rho_{AVG}} \quad (1.6)$$

The carrier concentration ($n$) in the sample can be calculated from the relation

$$n = \frac{1}{\rho_{AVG}\epsilon\mu_H} \quad (1.7)$$

### 1.7.7 Operating principle–The 15 UD Pelletron accelerator

Ion beam irradiation was carried out using 15 UD Pelletron tandem type accelerator at Inter University Accelerator Centre, New Delhi, India. The 15 UD pelletron is a versatile, heavy ion tandem type of electrostatic (Van de Graaff) accelerator. The Pelletron accelerator can be operated up to 15 MV of terminal potential and can produce dc as well as pulsed beam of a variety of elements. Fig.1.8 shows the principle of acceleration of ions in the accelerator. The Van de Graaff accelerator can provide beams of higher energy than the single - stage Cockcroft-Walton accelerators with a very precisely defined energy. In the tandem Van de Graaff accelerator, negative ions are produced and preaccelerated to ~300 KeV in ion source and injected into strong electric field inside an accelerator tank filled $SF_6$ insulating gas. At the center of the tank is a terminal shell, which is maintained at a high voltage (~15 MV). The negative ions on traversing through the accelerating tubes from the column top of the tank to the positive terminal get accelerated. Inside the terminal the negative ions, which now have an energy in MeV equal to the terminal potential difference in mega volts times the charge of the ion, pass through either a foil or gas ‘stripper’ and are stripped of electrons, producing a positive ion-beam. These
positive ions are then repelled away from the positively charged terminal potential is used twice to accelerate the ions. On exiting from the tank, the ions are bent into horizontal plane by analyzing magnet, which also select a particular beam of ion. The switching magnet diverts the high-energy ion beams into various beam lines into the different experimental areas of the beam hall. The entire machine is computer controlled and is operated from the control room.

![Diagram of ion acceleration process in Pelletron](image)

**Fig. 1.8 schematic figure showing the principle of acceleration of ions in Pelletron**

**Irradiation Experiment**

The irradiation was performed at Materials Science beam hall with 120 MeV Silver (Ag$^{9+}$) ions produced in a way discussed above. The selection of Ag$^{9+}$ ions is to understand the effect of ions having different masses (heavy and light ions) on the properties of the films. The energy of the ions was selected based on the results obtained from the simulation program 'The stopping and Range of Ions in Matter
(SRIM) developed by Ziegler et al. [159]. The projected range and energy loss of Ag ions in CdO and Cd$_2$SnO$_4$ has been estimated using the program version SRIM -2009.

For irradiation purpose, films of dimension 1 cm x 1 cm were mounted on a rectangular copper target ladder. Silver paste was applied at the corner of the sample to achieve good charge collection and to avoid heating of target during irradiation. The irradiation chamber was evacuated to a pressure of $10^{-6}$ Torr prior to ion bombardment. The irradiation was performed for different ion fluencies in the range between $10^{12}$ and $10^{13}$ ions/cm$^2$. The beam current was maintained 1 pnA (particle nanoampere) to avoid heating effect during irradiation. The ion beam was focused to a spot of 10 mm diameter and then scanned over an area of 1 cm$^2$ using magnetic scanner to achieve dose uniformity across the sample area. The fluence values were measured by collecting the charge falling on the sample mounted on an electrically insulated sample ladder placed in secondary electron suppressed geometry. Ladder current was integrated with a digital current integrator and the charged pulses were counted using scalar counter.


References

Chapter 1

Introduction

[49] J. Plachy,
Chapter 1

Introduction