CHAPTER–I

1. Introduction & Review of literature

A. Introduction:

The Sun delivers 1,20,000 TW (approx. 1000 Wm$^{-2}$) of power to the surface of the Earth, which far exceeds present and future human demand. Giving the rising population and increasing demand for power, renewable energy sources must be implemented in order to reduce the detrimental effects of burning fossil fuels and reduce the pollution environment. Processing carbon fuels is not renewable and leads to increased pollution and speedup the global warming. Considering the prospect of growing energy usage in developing nations, renewable options that are robust and cost effective must be realized in order to preserve healthy ecosystems and stable economic growth.

1.1. Transparent conducting oxides:

TCOs comprise a class of materials that can be thought of as conjugate property in which one property, i.e. electrical conductivity, is strongly coupled to a second property, namely, the lossy part of the refractive index or the extinction coefficient. In this regard, materials, like metals, that are highly conductive, will not normally transmit visible light, while highly transparent media like oxide glasses behave as insulators. The challenge for achieving materials that are both conducting and optically transmissive is to understand the fundamental materials structure/property relationships that drive these properties so that they may be decoupled such that the material both retains transparency while becoming electrically conductive. To an extent, many phenomenological approaches based upon well-understood physical principles have been reported to achieve materials having these properties.
Chapter-I  Introduction & Review of literature

TCO with optical transmission exceeding 80% in the visible region (550 nm) and resistivity less than $10^{-3}$ Ω cm has been widely used in a variety of applications, for more than a half century. More recently, it has become the subject of intense investigation for applications as transparent electrodes for optoelectronic devices like flat panel displays [1], solar cells [2], or organic light emitting diodes [3]. Most of the previous research on TCOs has been focused on ITO and FTO. Nevertheless, TCO films based on ZnO are receiving much attention because of the advantages over the more commonly used TCO, like low cost, resource availability (about a factor of 1000 more abundant than indium), non-toxicity and high thermal/chemical stability [4].

The first realization of a TCO material occurred a century ago when a thin film of sputter deposited cadmium metal underwent incomplete thermal oxidation upon post-deposition heating in air [5]. While the electrical conductivity of this material did in fact change with time, the oxide was indeed representative of a free-carrier like conductor where a resident oxygen deficiency lends free carriers to associated metal defect energy levels near the bottom of the metal-like conduction band of the oxide. The generalization here is that certain slightly reduced metal oxide systems can show n-type electrical conductivity provided that charge-compensating electrons can be promoted to the conduction band of the metal oxide from defect energy levels lying close in energy to the conduction band minimum. Since this early discovery, appreciable values of electrical conductivity have been observed in many single, binary, ternary and quaternary metal oxide systems [6-9]. However, while transmission through these materials in the visible region of the spectrum can be quite good, electrical conductivities still remain considerably below those of metals.
In this thesis, ZnO, a novel optoelectronics material which is very promising in future LEDs, sensors and solar cell applications, and its variant, CdZnO, were grown, studied and characterized.

ZnO is an interesting II-VI compound semiconductor material with wide direct band gap. Its band gap of 3.37eV at room temperature [10] is very close to that of GaN, which is now widely used in UV, blue, green and white LEDs. Although the development of ZnO is lagging far behind GaN, ZnO has some superior properties over GaN that make it a very promising candidate in next generation wide band gap optoelectronics devices, such as LED and LD. First of all, ZnO is cheaper and Zinc is quite abundant in Mother Nature while gallium is rare metal. Secondly, ZnO is not only cheaper in material cost, it is also cheaper in fabrication. ZnO can be easily etched by acid while GaN is chemically inert. In industry, people have to use plasma etching on GaN device fabrication, which largely increases the production cost. Lastly but most important, ZnO has a high exciton binding energy of 60meV, while the counterpart in GaN is around 25meV [11]. The large exciton binding energy in ZnO makes it potentially higher in emission efficiency, and also provides a possible path in exciton induced laser emission.

1.2. History of ZnO:

The research on the properties of ZnO started as early as 1930s [12], when scientists and researchers studied the lattice parameters, electron distribution and electron diffraction patterns, etc. Later on, the studies on Raman scattering [13] and optical properties [14] were also reported. And then over the years, with the development of optoelectronics industry, more and more efforts have been put on the study of ZnO properties.
Controlling the conductivity in ZnO has remained a major issue. Even relatively small concentrations of native point defects and impurities (down to $10^{-14}$ cm$^{-3}$ or 0.01 ppm) can significantly affect the electrical and optical properties of semiconductors. Therefore, understanding the role of native point defects (i.e. vacancies, interstitials, and antisites) and the incorporation of impurities is a key toward controlling the conductivity in ZnO. For a long time, it has been postulated that the unintentional n-type conductivity in ZnO is caused by the presence of oxygen vacancies or zinc interstitials [15, 16]. However, recent state-of-the-art density-functional calculations confirmed by optically detected electron paramagnetic resonance measurements on high quality ZnO crystals have demonstrated that this attribution to native defects cannot be correct [17]. It has been shown that oxygen vacancies are actually deep donors and cannot contribute to n-type conductivity [18]. In addition, it was found that the other point defects (e.g. Zn interstitials and Zn antisites) are also unlikely causes of the observed n-type conductivity in as-grown ZnO crystals [19].

Band-gap engineering of ZnO can be achieved by alloying with MgO or CdO. Adding Mg to ZnO increases the band gap, whereas Cd decreases the band gap, similar to the effects of Al and In in GaN. Although MgO and CdO crystallize in the rocksalt structure, for moderate concentrations the $\text{Mg}_{1-x}\text{Zn}_x\text{O}$ and $\text{Cd}_{1-x}\text{Zn}_x\text{O}$ alloys
assume the wurtzite structure of the parent compound, while still leading to significant band-gap variation.

1.3. **Properties of ZnO:**

ZnO could form three different crystal structures: wurtzite, zinc blende and rocksalt, as shown in Fig. 1.1. However, under normal ambient condition, wurtzite structure ZnO is the most stable among the three [20]. Table 1.1 summarizes the properties of wurtzite ZnO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Hexagonal wurtzite</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Zn: 65.38, O: 16 and ZnO: 81.38</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>a = 0.3246 nm, c = 0.5207 nm</td>
</tr>
<tr>
<td>Density</td>
<td>$5.67 \text{ g/cm}^3$ or $4.21 \times 10^{19} \text{ ZnO molecules/mm}^3$</td>
</tr>
<tr>
<td>Cohesive energy</td>
<td>$E_{\text{coh}} = 1.89 \text{ eV}$</td>
</tr>
<tr>
<td>Melting Point</td>
<td>$T_m = 2250 \degree \text{K under pressure}$</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>4,470 cal/mole</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>25 W/mK at 20 °C</td>
</tr>
<tr>
<td>Thermal expansion coefficient</td>
<td>$4.3 \times 10^{-6} \rho/\text{K at 20 °C}$</td>
</tr>
<tr>
<td></td>
<td>$7.7 \times 10^{-6} \rho/\text{K at 600 °C}$</td>
</tr>
<tr>
<td>Band gap at RT</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008</td>
</tr>
<tr>
<td>Electron &amp; hole effective mass</td>
<td>$M_e^* = 0.28$, $m_h^* = 0.59$</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>370 °K</td>
</tr>
<tr>
<td>Lattice energy</td>
<td>964 kcal/mole</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>$\varepsilon_o = 8.75$, $\varepsilon_r = 3.75$</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>$E_b = 60 \text{ meV}$</td>
</tr>
<tr>
<td>Pyroelectric constant</td>
<td>6.8 Amp./sec/cm$^2$/°K $\times 10^{10}$</td>
</tr>
<tr>
<td>Piezoelectric coefficient</td>
<td>$D_{33} = 12 \text{ pC/N}$</td>
</tr>
</tbody>
</table>

A partial list of the properties of ZnO that distinguish it from other semiconductors or oxides or render it useful for applications includes:
• **Direct and wide band gap:** The band gap of ZnO is 3.44 eV at low temperatures and 3.37 eV at room temperature [10]. As mentioned above, this enables applications in optoelectronics in the blue/UV region, including light-emitting diodes, laser diodes and photo-detectors [22]. Optically pumped lasing has been reported in ZnO platelets [23], thin films [24], clusters consisting of ZnO nanocrystals and nanowires [25].

• **Large exciton binding energy:** The free-exciton binding energy in ZnO is 60 meV [10], compared with, e.g. 25 meV in GaN [11]. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and higher. Since the oscillator strength of exciton is typically much larger than that of direct electron–hole transitions in direct gap semiconductors, the large exciton binding energy makes ZnO a promising material for optical devices that are based on excitonic effects.

• **Large piezoelectric constants:** In piezoelectric materials, an applied voltage generates a deformation in the crystal and vice versa. These materials are generally used as sensors, transducers and actuators. The low symmetry of the wurtzite crystal structure combined with a large electromechanical coupling in ZnO gives rise to strong piezoelectric and pyroelectric properties.

• **Strong luminescence:** Due to a strong luminescence in the green–white region of the spectrum, ZnO is also a suitable material for phosphor applications. The emission spectrum has a peak at 495 nm and a very broad half-width of 0.4 eV [26]. The n-type conductivity of ZnO makes it appropriate for applications in vacuum fluorescent displays and field emission displays. The origin of the luminescence center and the luminescence mechanism are not really
understood, being frequently attributed to oxygen vacancies or zinc interstitials, without any clear evidence [26].

- **Strong surface sensitivity:** The conductivity of ZnO thin films is very sensitive to the exposure of the surface to various gases. It can be used as a cheap smell sensor capable of detecting the freshness of foods and drinks, due to the high sensitivity to trimethylamine present in the odor. The mechanisms of the sensor action are poorly understood. This layer may play a role in sensor action, as well. The presence of this conducting surface channel has been suggested to be related to some puzzling type-conversion effects observed when attempting to obtain p-type ZnO [27].

- **High thermal conductivity:** This property makes ZnO useful as an additive (e.g. ZnO is added to rubber in order to increase the thermal conductivity of tires). It also increases the appeal of ZnO as a substrate for homoepitaxy or heteroepitaxy (e.g. for growth of GaN, which has a very similar lattice constant) [28]. High thermal conductivity translates into high efficiency of heat removal during device operation.

- **Availability of large single crystals:** One of the most attractive features of ZnO as a semiconductor is that large area single crystals are available, and epi-ready substrates are now commercialized. Growth of thin films can be accomplished using MOCVD, MBE and laser ablation [29] or sputtering [30].

- **Amenability to wet chemical etching:** Semiconductor device fabrication processes greatly benefit from the amenability to low-temperature wet chemical etching. It has been reported that ZnO thin films can be etched with acidic, alkaline as well as mixture solutions. This possibility of low-
temperature chemical etching adds great flexibility in the processing, designing and integration of electronic and optoelectronic devices.

- **Radiation hardness:** Radiation hardness is important for applications at high altitude or in space. It has been observed that ZnO exhibits exceptionally high radiation hardness [31], even greater than that of GaN, the cause of which is still unknown.

Band-gap engineering of ZnO can be achieved by alloying with MgO or CdO. Adding Mg to ZnO increases the band gap, whereas Cd decreases the band gap, similar to the effects of Al and In in GaN. Although MgO and CdO crystallize in the rocksalt structure, for moderate concentrations the Mg$_{1-x}$Zn$_x$O and Cd$_{1-x}$Zn$_x$O alloys assume the wurtzite structure of the parent compound, while still leading to significant band-gap variation.

Band-gap engineering in ZnO can be achieved by alloying with MgO and/or CdO, in analogy to GaN which can be alloyed with AlN and/or InN. One of the differences between the nitride and the oxide families is that AlN and InN assume the same wurtzite crystal structure of GaN, whereas MgO and CdO assume the rock-salt structure, not the same as the ZnO wurtzite structure. This is indeed a problem for ZnO based alloys with high content of MgO or CdO, in which case phase separation is expected to occur. For moderate contents of MgO and CdO, however, MgZnO and CdZnO alloys assume the wurtzite crystal structure of the parent compound, still providing a wide range of band gaps (2.3–4.0 eV) and band offsets for practical device applications.

CdZnO alloys with Cd concentrations of 7% and band gap of 3.0 eV were grown on sapphire (0001) and glass substrates using PLD. While adding Mg to ZnO leads to an increase in the band gap, adding Cd leads to a decrease in the band gap,
similar to the case of addition of Al and In to GaN, respectively. In the case of CdZnO, both lattice parameters $a$ and $c$ increase with the Cd content, consistent with the larger atomic size of Cd compared with Zn. CdZnO films were also grown by metal-organic vapor-phase epitaxy on sapphire (0001). A large red shift of 300 meV in the band gap for a lattice mismatch of only 0.5% with respect to ZnO has been observed by Th. Gruber et al. [32].

Although there have been many studies on ZnO properties and devices, there have been very few on the counterpart on CdZnO research, which is critical in visible light emission. Few groups have demonstrated CdZnO with large band gap change (band gap smaller than 3.0eV), [33, 34]. However, there are very few studies on the properties of CdZnO itself, let alone the devices based on CdZnO. The study on the properties and light emitting devices will be the main topic of this dissertation.

1.4. Interaction of radiation with matter:

It is well known that all matter is comprised of atoms. But sub-atomically, matter is made up of mostly empty space. For example, consider the hydrogen atom with its one proton, one neutron, and one electron. The diameter of a single proton has been measured to be about $10^{-15}$ m. The diameter of a single hydrogen atom has been determined to be $10^{-10}$ m; therefore the ratio of the size of a hydrogen atom to the size of the proton is 1,00,000:1. Consider this in terms of something more easily pictured in your mind. If the nucleus of the atom could be enlarged to the size of a softball (about 10 cm), its electron would be approximately 10 km away. Therefore, when electromagnetic waves pass through a material, they are primarily moving through free space, but may have a chance encounter with the nucleus or an electron of an atom.
When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction or transmitted forward into the material. Let us first consider the interaction of visible light. Reflection and transmission of light waves occur because the light waves transfer energy to the electrons of the material and cause them to vibrate. If the material is transparent, then the vibrations of the electrons are passed on to neighboring atoms through the bulk of the material and reemitted on the opposite side of the object. If the material is opaque, then the vibrations of the electrons are not passed from atom to atom through the bulk of the material, but rather the electrons vibrate for short periods of time and then reemit the energy as a reflected light wave. The light may be reemitted from the surface of the material at a different wavelength, thus changing its color.

When an energetic particle such as $\alpha$-particle, ion or electron hits the atoms of a target, different mechanisms of energy or momentum transfer takes place. The most important primary effects are electronic excitation or ionization of individual atoms, collective electronic excitations, breakage of bonds or cross linking, generation of photons leading to heating of the target, displacement of atoms from the bulk of the target, sputtering of atoms from the surface, generation of ion tracks etc [35].

1.5. Swift heavy ions:

The ion having the velocity comparable to that of Bohr velocity of electron is called swift heavy ion also called heavy charged particle (HCP). The energy of SHI is ranging from few MeV to GeV. A single SHI induces a continuous trail of damage with a few nanometer (nm) width and typically several tens of micrometer ($\mu$m) length. Such ion track consists of material with properties that are drastically different from the surrounding virgin bulk. The high energy ions have no significant definition
of the ion path and makes cylinders of radii ranging from 1 to 20 nm depending on the nature of target and types of the ion. In particular, close to ion path, extremely high energies are deposited in a very small volume of some hundreds of eV/cm³ with in an extremely short time difficult to reach by any other radiation source. The high electronic excitation density in the core region has strong influence on the resulting defect creation, whereas the damage in larger halo is similar to effects induced by conventional radiation [36].

1.6. Theory of ion matter interaction:

When energetic ions pass through matter they collide with the atoms and a number of processes can also takes place. These ions lose their energy in two ways: direct collisions with lattice atoms called elastic scattering corresponds to nuclear energy loss ($S_n$) and electronic excitations and ionizations called inelastic scattering correspond to electronic energy loss ($S_e$). The nuclear energy loss by ions predominates at low energies (keV/$\mu$) where as electronic energy loss predominates at higher energies (MeV/$\mu$) [37]. Both electronic and nuclear energy losses of an ion depend on the ion species, ion energy and columbic interaction. When an ion moving in a given path $\Delta x$ it lose an energy $\Delta E$, the mean value of the energy loss $\Delta E/\Delta x|_{\Delta x \to 0}$ for a large number of particles is termed as stopping power ($S$) or range of ion. Range is the sum of the energy losses and is given by

$$S = - \frac{dE}{dx} = S_e + S_n$$  \hspace{1cm} (1.1)

The energy of the projectile is of particular importance since it leads to creation of various types of defects and ion tracks. The mass of the ion is much higher than the mass of the electron the initial direction of the ion in solid remains almost unchanged. Fig. 1.2 shows the schematic representation of the two mechanisms that occur during the ion solid iteration. The detailed mechanisms of $S_e$ and $S_n$ are discussed in section
1.6.1 and 1.6.2 respectively. It is also customary to speak of the stopping cross section $\varepsilon$ which is defined as

$$\varepsilon_{e,n} = -\frac{1}{N} \frac{dE}{dx_{e,n}}$$

where $N$ is the atomic density.

**Fig. 1.2** Schematic representation of ion solid interaction: Demonstration of electronic and nuclear energy loss.

### 1.6.1. Nuclear stopping power:

Let a moving ion with an energy range of few keV/$\mu$ interacts with nuclei of the target atoms. The energy loss $dE$ of an ion by elastic collision in a layer $dx$ is proportional to the atomic density $N$ as well as the total energy transferred in all individual collisions [38]. Consider the interactions between particles with energy $(E)$ and the amount of energy transferred to the target atom between $T$ and $T+dT$ is given by [39]

$$\frac{dP(E)}{dT}dT = Nd\sigma(E)\frac{d\sigma(E)}{dT}dT \quad \text{------- (1.3)}$$

where $\sigma(E)$ is differential scattering cross section. The average energy loss by the moving particle in the distance $dx$ is obtained

$$<dE> = \int T \frac{dP(E)}{dT}dT = N\int T \frac{d\sigma(E)}{dT}dTdx \quad \text{------- (1.4)}$$

-for infinitesimal $dx$, the nuclear stopping power is given by
\[ \frac{dE}{dx} = N \int_{T_{\text{min}}}^{T_{\text{max}}} T \frac{d\sigma(E)}{dT} dT \]  

--- (1.5)

-and it is known as nuclear stopping power. The power limit in the integration \( T_{\text{min}} \) is the minimum energy transferred and need to be zero. \( T_{\text{max}} \) is maximum energy transferred and is given by

\[ T_{\text{max}} = 4 \frac{M_I M_T}{(M_I + M_T)^2} E \]  

--- (1.6)

where \( M_I \) and \( M_T \) are the masses of the ions and target respectively. The differential scattering cross section \( \sigma(E) \) depends on the inter atomic potentials. For heavy particles of low velocity and in the case of relatively distinct collisions the scattering effect of the electrons cannot be neglected and resulting scattering potential can be written as

\[ V(r) = \frac{Z_I Z_e}{r} \left( \phi \left( \frac{r}{a} \right) \right) \]  

--- (1.7)

where \( \phi \left( \frac{r}{a} \right) \) is the screening function, \( a \) is the screening parameter of the order of Bohr radius and \( r \) is the distance between center of mass of the system. In the higher energy regime, the contribution of nuclear stopping power is insignificant as shown in fig. 1.3.

1.6.2. Electronic stopping power:

In general, despite the wide attention given to radiation damage due to nuclear stopping, most of the ion energy is lost to electronic stopping. The interactions between a charged particle and bound electrons are very complex and therefore rather difficult to describe theoretically. That is to say, electrons in the target can both collide elastically with a projectile and be excited or ionized, and the same processes can take place for the electrons of the energetic ion [37].

The electronic energy loss for ions has a peak at intermediate energies (Fig. 1.4). At high projectile energies, the ion is stripped of its electrons and the situation
can to a good approximation be seen as Coulomb scattering between the ion and electrons in the target. The stopping power is consequently found by solving the scattering integral for the Coulomb potential without screening, and using \( N \rho \) as the electron density, which gives

\[
\frac{dE}{dx} = N \rho \pi Z^2 e^4 \frac{m_e}{m_T} \ln \left( \frac{\gamma E}{I} \right)
\]

where \( \gamma \) is the kinematic factor \( 4m_m + m_T \) and \( I \) is the average ionization energy.

Equation 1.8, which arises only from analysis of elastic collisions, is almost identical to the Bethe equation for electronic stopping at high energies, except for the absence of a factor 2 that arises when a quantum mechanical treatment is carried out. The Bethe formula gives a good approximation for the electronic stopping at relatively high energies but below the regime in which relativistic effects need to be accounted for.

![Electronic Stopping Regimes](image)

**Fig. 1.3** Electronic stopping regimes. The electronic stopping for slow ions is proportional to the velocity of the ion, while for fast ions the electronic stopping decreases with increasing kinetic energy.

At low projectile energies, the ion is close to neutral and the conduction electrons contribute more to the electronic energy loss. This is because lower energies are needed to excite such electrons compared to inner shell electrons, for which the closest energy levels might be filled. Simple considerations regarding an elastic collision between a projectile and an electron and the proportion of electrons available
for excitation [38] give that the stopping power at low energies is proportional to the ion velocity:

\[
\frac{dE}{dx} = 8\sigma N \left( \frac{m_e}{m_i} \right)^{1/2} E^{3/2} = kE^{3/2}
\]

This expression gives a reasonable approximation in the low ion energy regime.

1.6.3. Range of ions in solid:

The projected ion range in solid is defined as the mean depth from the target surface at which the ion comes to halt. The range of ion (R) in solid can be expressed by the rate of energy loss \((dE/dx)_{\text{total}}\) along with the trajectory of the ion [39],

\[
R = \int_{E_t}^{0} \frac{1}{dE/dx_{\text{total}}} dE
\]

The main parameter governing the range is the energy and the atomic number of the ion \((Z_i)\) and the atomic number of target \((Z_f)\). Range along the path is the total distance of ion traversed along the trajectory. Since the collisions which lead to deceleration is random process.

1.7. Chapters’ arrangement:

This Thesis is organized as following chapters: **Chapter I** includes the basic concepts and current status of TCO materials, introduction and motivation of ZnO and CdZnO materials for device applications and discusses the irradiation effect on the physical properties of the CdZnO thin films followed by the thorough review of literature. **Chapter II** is about growth of CdZnO with different deposition techniques with their importance and also discusses the irradiation equipments to perform the irradiation studies. Then the characterization techniques utilized to study the structural, surface, optical and electrical properties are introduced. The techniques include X-ray diffraction (XRD), field emission scanning electron microscope.
(FESEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscope (AFM), UV-vis NIR Spectrophotometer and Hall Measurement system. Chapter III focuses on the results and discussion of the CdZnO thin films with various sputter parameters like substrate temperature, post sputter annealing temperature, oxygen flow rate and Cd sputter power and also demonstrate the effect of swift heavy ion (SHI) irradiation on CdZnO thin films. Finally Chapter IV focuses the summary and conclusions of the thesis.

B. Review of literature:

C.G. Granqvist [40] reviewed the transparent conductors (TCs) have a multitude of applications for solar energy utilization and for energy savings. The largest of these applications, in terms of area, make use of the fact that the TCs have low infrared emittance and hence can be used to improve the thermal properties of modern fenestration. Depending on whether the TCs are reflecting or not in the near infrared pertinent to solar irradiation, the TCs can serve in “solar control” or “low-emittance” windows. Other applications rely on the electrical conductivity of the TCs, which make them useful as current collectors in solar cells and for inserting and extracting electrical charge in electrochromic “smart windows” capable of combining energy efficiency and indoor comfort in buildings.

H. Hosono [41] reviewed recent research progress on new TCO materials and electronic and optoelectronic devices based on these materials. The materials including p-type materials, deep-UV transparent TCO(β-Ga2O3), epitaxially grown ITO with atomically flat surface, transparent electrochromic oxide (NbO2F), amorphous TCOs, and nanoporous semiconductor 12CaO·7Al2O3. TCO-based electronic/optoelectronic devices realized to date, UV/blue LED and UV-sensors based on transparent p-n junction and high performance transparent TFT using n-type TCO as an n-channel. Finally, unique optoelectronic properties originating from 2D-electronic nature in p-type layered oxychalcogenides are summarized along with the fabrication method of epitaxial thin films of these materials.
B. Szyszka et al. [42] reviewed transparent and conductive films are key components for optoelectronic devices. They are applied as n-type transparent electrical contacts for inorganic and organic light emitting diodes, solar cells and flat panel displays as well as p- and n-type active semiconductive oxides to setup wide band gap p–n junctions and devices for the emerging field of transparent and radiation hard electronics. The demand for these films is strongly increasing due to the extensive market growth in these areas but the solutions available today only partially fulfill the requirements on low resistivity, high transmittance, large area deposition, low cost manufacturing, and ability for fine patterning, light scattering and precise alignment of the electronic structure to surrounding semiconductors.

G.J. Exarhos and X.-D. Zhou [43] reviewed the properties of TCO materials derive from the nature, number, and atomic arrangements of metal cations in crystalline or amorphous oxide structures, from the resident morphology, and from the presence of intrinsic or intentionally introduced defects. An enormous body of literature can be accessed from which empirical relationships among structure, composition, charge transport, and transparency have been developed and reviewed by G.J. Exarhos and X.-D. Zhou [43].

Single-phase rock-salt CdZnO films were synthesized on r-plane sapphire substrates by metal–organic chemical vapor deposition. Evolutions in growth orientations have been investigated by T. C. Zhang and A. Yu. Kuznetsov [44] in CdZnO films as a function of Zn content and film thickness. The preferred orientation is found to black (thick) and red (thin) lines depend on the balance between the surface and strain energy accumulated in the films in accordance with the so-called overall energy model. Specifically, (100) orientation dominates below a critical Zn content and/or a critical film thickness, otherwise (111)-oriented grains nucleate on top of the (100) planes.

W. F. Yang et al. [45] reported on high quality ZnCdO alloy epilayers and ZnCdO/ZnO single quantum well structures on sapphire substrates by pulsed laser deposition. The Cd concentration in the ZnCdO alloy can be systematically adjusted
via the substrate temperature and single-phase ZnCdO alloy with a band gap at room temperature extended to 2.94 eV is achieved. The single quantum well structures exhibit strong photoluminescence from the well layer with extremely weak emission from deep level defects and the ZnO barrier, indicating the high quality of ZnCdO/ZnO single quantum well structures.

_Th. Gruber et al. [46]_ developed the ternary Zn$_{1-x}$Cd$_x$O allows reduction of the band gap relative to ZnO, which would be necessary for devices emitting visible light. _Th. Gruber et al. [46]_ have analyzed the structural and optical properties of Zn$_{1-x}$Cd$_x$O layers grown by metalorganic vapor-phase epitaxy. A narrowing of the fundamental band gap of up to 300 meV has been observed, while introducing a lattice mismatch of only 0.5% with respect to binary ZnO. PL, high-resolution XRD, and spatially resolved cathode luminescence measurements revealed a lateral distribution of two different cadmium concentrations within the Zn$_{1-x}$Cd$_x$O layers.

_L. Li et al. [47]_ reported the CdZnO thin films have been grown on Si (100) substrates by plasma-assisted molecular beam epitaxy. As-grown samples show near band edge emissions at 1.87, 2.03, and 2.16 eV, respectively, while the emission peak energy dramatically increases to up to ultraviolet region with increasing rapid thermal annealing temperature. Room temperature PL and temperature dependent PL show phase separations in the samples after the annealing process. Secondary ion mass spectroscopy measurements show redistribution of Cd in the as-annealed sample, which is believed to be the reason of PL peaks shift.

_S. Vijayalakshmi et al. [48]_ investigated the thin films of Cd:ZnO with different Cd concentrations have been prepared by the spray pyrolysis method on different substrates at 400 °C. The XRD analysis revealed that the films are polycrystalline in nature having a hexagonal wurtzite type crystal structure with a preferred grain orientation in the (002) direction. Due to Cd doping, the degrees of polycrystallinity increased simultaneously and the orientation of the grains in the (002) axis is found to be deteriorated. AFM measurements reveal that the surface morphology of the films changes continuously with a decrease in the grain size due to
Cd doping. Both PL and optical measurements showed that the band gap decreases from 3.12 to 2.96 eV with increasing Cd concentration. Increasing the Cd concentration also leads to the broadening of the emission peak and degrading the crystalline quality.

*J. Ishihara et al.* [49] studied the Zn$_{1-x}$Cd$_x$O films in the range of the content $x$ from $x=0$ to $x=1$ have been grown by remote-plasma-enhanced metal organic chemical vapor deposition. The crystal structure of Zn$_{1-x}$Cd$_x$O film changed with increase of the content $x$ from wurtzite structure to rocksalt structure around $x=0.7$. The relationship between the cadmium content and axis length in the Zn$_{1-x}$Cd$_x$O films was studied. PL spectra were observed from the wurtzite Zn$_{1-x}$Cd$_x$O films in the range of 3.3–1.8 eV at room temperature. Stokes’s shift in the restricted composition range was compared with the previous results.

*M. Lange et al.* [50] reported on (Zn,Cd)O thin films, grown by PLD on a-plane sapphire substrates with high Cd-contents up to 0.25. By incorporating Cd in ZnO and by applying a low growth temperature of about 300 °C, the (Zn,Cd)O related luminescence red shifts to an energy of 2.46 eV as a result of the large Cd-content of 0.25. The red shift of the band gap energy was additionally proven by transmission measurements. By fitting the transmission curves, the spectra of the absorption coefficient and the index of refraction are calculated. The (Zn,Cd)O thin films are single phase and exhibit the wurtzite crystal structure. An increasing a- and c-lattice constant is observed with increasing Cd-content.

*D. M. Detert et al.* [51] have been synthesized Cd$_x$Zn$_{1-x}$O alloys across the full composition range. The structural mismatch of the two endpoint compounds splits the alloy into two regions of distinct optical and electrical behavior. The wurtzite phase alloys at compositions $0<x<0.69$ exhibit a decrease in the absorption edge across the visible range and an increase in the conductivity with increasing Cd content. A phase transition to the rocksalt structure is observed above $x=0.69$ along with a step increase in the electron mobility and the absorption edge. The intrinsic band gap of these
alloys was determined taking into account the carrier filling and renormalization effects.

A. Schleife et al. [52] investigated the fourfold (wurtzite structure) and sixfold (rocksalt structure) coordination of the atoms. By means of density-functional theory, we study a total number of 256 16-atom clusters divided into 22 classes for the wurtzite structure and 16 classes for the rocksalt structure for each of the alloy systems. From the cluster fractions, we derive conclusions about the miscibility and the critical compositions at which the average crystal structure changes. Thermodynamic properties such as the mixing free energy and the mixing entropy are investigated for the three different statistics. We discuss the consequences of the two different local lattice structures for characteristic atomic distances, cohesive energies, and the alloys’ elasticities. The differences in the properties of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) and \( \text{Cd}_x\text{Zn}_{1-x}\text{O} \) are explained and discussed.

Band gap tuning of ZnO by Cd and Mg doping has been investigated by S. Gowrishankar et al. [53]. Cd and Mg doped ZnO thin films of different concentrations (0, 3, 10 & 20 mol%) were grown on Si (100) substrates by rf. magnetron sputtering. The corresponding targets were prepared by the conventional solid-state reaction route. XRD studies showed that all films are preferentially oriented along (002) plane. AFM studies showed that decrease of grain size with the increase of doping concentration. Electrical studies indicate that the resistivity of the films increased by the increase of Cd and Mg concentration. UV–vis–NIR studies showed that the optical band gap of ZnO (3.35eV) was reduced to 2.74eV upon Cd alloying while increased to 3.94eV upon Mg alloying. Red and blue shift in NBE emission observed from PL studies for Cd and Mg alloying respectively, well acknowledged this modulation of band gaps. From modified Vegard's law, the bowing parameter has been estimated to be 1.9eV and 2.59eV for Cd and Mg alloyed ZnO films, respectively. The incorporation of dopants (Cd and Mg) in the films has been confirmed by EDS analysis.
Chapter-I

Introduction & Review of literature

R. Zhang et al. [54] investigated the hexagonal Cd$_x$Zn$_{1-x}$O films with low and high Cd contents ($x=0.10$ and 0.52) deposited by magnetron sputtering. The as-deposited Cd$_x$Zn$_{1-x}$O films hardly exhibit detectable PL. Once subjected to RTA at sufficiently high temperatures, the Cd$_x$Zn$_{1-x}$O films exhibit pronounced PL. For the Cd$_{0.10}$Zn$_{0.90}$O films subjected to RTA at 500 °C and above, they are of single hexagonal phase. The enhanced NBE emission is somewhat blue-shifted with the increase of RTA temperature. While for the Cd$_{0.52}$Zn$_{0.48}$O films, they are transformed into hexagonal (Cd-incorporated ZnO) and cubic (Zn-incorporated CdO) phases due to the RTA at 500°C and above. The NBE emissions from the two above-mentioned phases are well revealed in the PL spectra.

I. Shtepliuk et al. [55] investigated the Cd behavior in the ZnCdO alloys, where Cd content exceeds the solubility limit, is of importance due to possible impurity segregation and second phases’ formation in this material. The Cd behavior in the Zn$_{1-x}$Cd$_x$O films deposited by dc magnetron sputtering on different substrates: c-plane Al$_2$O$_3$, bare Si (100) and Au (45 nm)/Si (100) was reported. It is revealed that Cd content of 10 at.% in the target results in average 6–8 at.% of Cd in the films, depending on the substrate type. Structural analysis based on XRD revealed the absence of Cd-related secondary phases. TRPL and high-resolution EDX help to understand the recombination dynamics of spontaneous emission and to establish correlations between cadmium content and radiative lifetime.

Cd$_x$Zn$_{1-x}$O films in a wide range of Cd contents have been grown by reactive direct-current magnetron sputtering. At $x \leq 0.66$, the sputtered Cd$_x$Zn$_{1-x}$O films are of single hexagonal phase. The optical band gap energies of the Cd$_x$Zn$_{1-x}$O films decrease from ~3.3 eV at $x=0$ to ~1.8 eV at $x = 0.66$. Correspondingly, the near-band-edge photoluminescence is tuned in a wide visible region from ~378 to 678 nm. Moreover, the ultraviolet irradiation enhanced PL from the Cd$_x$Zn$_{1-x}$O films has been reported by X. Ma et al. [56].

T.K. Subramanyam et al. [57] reported the dc magnetron reactive sputtering of cadmium in an oxygen and argon atmosphere. The dependence of cathode potential
on the oxygen partial pressure has been explained in terms of cathode poisoning effects. The cadmium oxide films formed during this process have been studied for their structural, electrical and optical properties. At an optimum oxygen partial pressure of $1 \times 10^{-3}$ mbar, the films were single phase with polycrystalline in nature. The films showed resistivity of $4.6 \times 10^{-3}$ V cm, Hall mobility of $53 \text{ cm}^2/\text{V s}$, carrier concentration of $3.5 \times 10^{19}$ cm$^{-3}$, with an optical transmission of 85% in the wavelength range 600–1600 nm and with a band gap of 2.46 eV.

Thin films of ZnO and CdO are prepared by the simple, economical and versatile method of chemical spray pyrolysis reported by N. Benramdane et al. [58]. This method is based on the preparation of solutions of some salt of the material whose thin films is to be prepared. The thin films obtained by this method are suitable for many scientific studies and technological applications. For the ZnO and CdO thin films, the optical properties are investigated, the energy gaps are estimated, the absorption coefficient, index refraction, extinction coefficient and real and imaginary dielectric constants as well as the lattice parameters were studied and calculated.

A. Kumar et al. [59] studied the influence of growth temperature on electrical and optical properties of polycrystalline ZnO thin films on sapphire substrates grown by atomic layer deposition technique. Dimethylzinc and de-ionized water were used as precursors by varying the growth temperature ranging from 70 to 130 °C. X-ray diffraction pattern confirms the formation of hexagonal wurtzite phase of ZnO with preferred (103) orientation. AFM results infer the growth of good quality films with root mean square roughness ~1 nm for all these films having same thickness. The free carrier concentration and mobility of samples is found to increase whereas resistivity decreases with increasing growth temperature. The electrical results are well corroborated on the basis of photoluminescence and X-ray photoelectron spectroscopy.

J. H. Yu et al. [60] investigated the Cd$_{1-x}$Zn$_x$O alloy layers have been grown by using a rf magnetron co-sputtering system. From the XRD measurement, the Cd$_{1-x}$Zn$_x$O layers were observed to have a cubic structure until a single phase for $x \leq$
0.21. However, a polycrystalline form having mixed phases was observed at x = 0.29. It seems that the high miscibility of Zn in CdO leads to a large fluctuation in phase segregation caused by the hexagonal ZnO and cubic CdO structures within CdZnO. The band gap energies of the Cd\(_{1-x}\)Zn\(_x\)O layers for values of x between x = 0 and x = 0.21 were distributed from 2.574 to 2.892 eV, respectively, while the band gap energy for x = 0.29 was a value of 2.834 eV due to the polycrystallinity. Thus, a sensor with x = 0.21 showed a sensitivity of S = 1.31 at 100 ppb. Furthermore, the response and the reduction times of the sensor were found to be 184 and 210 sec, respectively. From these results, we found that the Cd\(_{1-x}\)Zn\(_x\)O layer has a capability for use as a new material for ozone sensing.

*M.D. Uplane et al.* [61] reported the thin films of cadmium oxide are prepared on a glass substrate by a spray pyrolysis technique from an aqueous solution of cadmium acetate. The XRD studies show that the films are polycrystalline. The room temperature resistivity is of the order of 10\(^{-2}\) \(\Omega\) cm. From optical absorption data the band gap energy of CdO is estimated to be 2.5 eV. Thermoelectric power measurement is carried out to understand the conduction mechanism.

*L. B. Duan et al.* [62] reported the 1 at.% Al-doped Zn\(_{1-x}\)Cd\(_x\)O (x = 0–8 at.%) thin films have been prepared on glass substrates by sol–gel method. The co-doping films retained the hexagonal wurtzite structure of ZnO, and showed preferential c-axis orientation. The transmittances of the co-doping films were obviously degraded by vacuum annealing to 50–60 %, but enhanced to 70–80 % after nitrogen annealing. The carrier concentration and Hall mobility both increased and resistivity decreased with narrowing band gap of Al-doped Zn\(_{1-x}\)Cd\(_x\)O, below different critical concentrations x = 4 % (in vacuum) and x = 6 % (in nitrogen). It is revealed that the conductivity is also improved by Cd doping along with band gap modification. The variations in optical and electrical properties are ascribed to both the changes of the crystallinity and concentration of oxygen vacancies under different ambient.

*R. Vinodkumar et al.* [63] investigated the CdO doped (doping concentration 0, 1, 3 and 16 wt.%) ZnO nano-structured thin films have been grown on quartz
substrate by pulsed laser deposition and the films are annealed at temperature 500 °C. The XRD patterns suggest a hexagonal wurtzite structure for the films. The crystallite size, lattice constants, stress and lattice strain in the films are calculated. The presence of high-frequency E$_2$ mode and the longitudinal optical A$_1$ (LO) modes in the Raman spectra confirms the hexagonal wurtzite structure for the films. The presence of CdO in the doped films is confirmed from the EDX spectrum. AFM picture suggests a porous network structure for 3% CdO doped film. The porosity and refractive indices of the films are calculated from the transmittance and reflectance spectra. Optical band gap energy is found to decrease in the CdO doped films as the CdO doping concentration increases.

Numerical calculations of the excitonic absorption spectra in a strained Cd$_x$Zn$_{1-x}$O/ZnO quantum dot are investigated for various Cd contents by A.J. Peter and C.W. Lee [64]. A.J. Peter and C.W. Lee [64] calculated the quantized energies of the exciton as a function of dot radius for various confinement potentials and thereby the inter-band emission energy is computed considering the internal electric field induced by the spontaneous and piezoelectric polarizations. The optical absorption as a function of photon energy for different dot radii is discussed. Decrease of exciton binding energy and the corresponding optical band gap with the Cd concentration imply that the confinement of carriers decreases with composition x.

P.M. Devshette et al. [65] reported the thin films of Zn$_x$Cd$_{1-x}$O have been deposited by spray pyrolysis technique. The preparative parameters were optimized to obtain good quality of thin films. The as-deposited thin films were characterized for structural, compositional, surface morphological and optical properties. An XRD pattern shows polycrystalline nature. As $x$ varies from $x = 0.0$ to 1.0, it was observed that the crystal structure changes from rock salt cubic (CdO) to wurtzite (ZnO) structure. EDX spectra were used to study the composition of the ternary semiconductor compound (Zn$_x$Cd$_{1-x}$O) thin films. Uniform grain distribution over entire glass substrate was seen from the SEM micrographs. A significant change in
optical absorption edge with variation in composition was observed. Nearly, linear
variation of band gap was seen with respect to the change in the composition \( x \).

R.K. Gupta et al. [66] studied the CdZnO thin films with different ratio of
CdO and ZnO (3:1, 1:1, and 1:3) have been grown on glass substrate using sol–gel
spin coating method. The morphology of the CdZnO films depends on the amount of
ZnO and CdO in the films. The optical band gap of the CdZnO films depends on the
compositions of CdO and ZnO. Films having higher amount of CdO shows the
presence of grains along with the fiber nature of ZnO, whereas the film with lower
percentage of CdO shows fiber nature of the film very similar to pure ZnO film. Other
optical properties such as refractive index, extinction coefficient, and dielectric
constants were calculated using the optical data. The volume and surface energy loss
functions were also calculated and observed to increase with increase in the photon
energy.

P. Samarasekara et al. [67] reported the thin films of ZnO have been
deposited on conductive glass substrates by dc sputtering. The sputtering parameters
have been varied to obtain ZnO films with maximum open circuit photo-voltage
measured in the electrolyte KI/I\(_2\). A photo-voltage as high as 40.66 V/m\(^2\) could be
obtained for the film synthesized at the pressure of 6 mbar for a duration of 23.75
hours. These ZnO thin films can be used to absorb the short wavelengths in the
ultraviolet (UV) region of the solar spectrum.

Y. Lee et al. [68] reported the effects of thermal treatments on the electrical
conduction properties for the unintentionally doped ZnO thin films were investigated.
Despite the decreased carrier density in the annealed ZnO thin films, the conductivity
was increased because the contribution of the effective carrier mobility to the
conductivity of the unintentionally-doped ZnO thin films is greater than that of the
carrier density. The resistivity exponentially decreased with increasing RTA
temperature, and this result was confirmed to come from the enhanced effective
carrier-mobility, which originated from the increased crystallite size in the annealed
ZnO thin films.
O. Vigil et al. [69] have been prepared (ZnO)$_x$(CdO)$_{1-x}$ thin films by spray pyrolysis. Mixed thin film oxides with different compositions of cadmium and zinc were deposited on glass substrates and exposed to different annealing treatments at a fixed temperature. The crystalline structure was studied by XRD. We found the presence of CdO XRD patterns for low Zn concentrations, and a mixing of CdO (cubic) and ZnO (hexagonal) phases for low Cd concentrations. In all cases, the crystallite sizes increased with the annealing. In addition, the band-gap and the resistivity vary between those found for pure CdO and ZnO. The changes of the latter parameters with the post-thermal annealing are also studied.

H. Tabet-Derraz et al. [70] reported the Zn$_x$Cd$_{1-x}$O thin films have been prepared on glass substrates by spray pyrolysis technique. The precursor solutions were obtained by varying the concentration of Zn(NO$_3$)$_2$.6H$_2$O and Cd(NO$_3$)$_2$.4H$_2$O in bi-distilled water. All the structures include the basic compounds, i.e. ZnO and CdO. The orientation and the crystalline phases of the deposited films were specified. The electrical measurements have performed using method of four contacts. Thin films transmittances, in the 1.5–4.3 eV range, for different compositions have been measured and the optical gaps have been determined. The variations are explained considering the gaps of the two pure films. The influence of increased Cd concentration in the films on the structural, electrical and optical properties is investigated in this study.

M.S. Kim et al. [71] investigated the Cd$_x$Zn$_{1-x}$O thin films with different Cd contents ranging from 0 to 0.75 have prepared by the sol–gel spin-coating method. The optical parameters, such as optical band gap, absorption coefficient, Urbach energy, refractive index, dispersion parameter, and optical conductivity, were studied in order to investigate the effects of Cd content on the optical properties of the Cd$_x$Zn$_{1-x}$O thin films. The optical band gap and Urbach energy decreased as Cd content increased. The dispersion energy, single-oscillator energy, average oscillator wavelength, average oscillator strength, and refractive index at infinite wavelength of
the Cd$_{x}$Zn$_{1-x}$O thin films were affected by Cd incorporation. The optical conductivity of the Cd$_{x}$Zn$_{1-x}$O thin films also increased with increasing photon energy.

The structural properties of annealed (ZnO)$_x$(CdO)$_{1-x}$ thin films are studied by F. Cruz-Gandarilla et al. [72]. The films were obtained by spray pyrolysis using different values for the nominal composition ($x$), and then they were annealed at 450°C from 0 to 120 min. The structural analysis confirms previous results on the formation of a homogeneously mixed oxide semiconductor, but in which crystalline and amorphous phases co-exist for both CdO and ZnO. In this work, F. Cruz-Gandarilla et al. [72] showed that for annealed films, there is a strong interaction between the amorphous, the hexagonal ZnO and the cubic CdO phases regarding the lattice constants and the crystallite growth rate. In the annealed films, for $x \leq 0.5$ the optical behavior is mainly controlled by the CdO phase, so that there is a reduction of the effective band-gap of the material when the CdO crystallite size is increased, possibly due to grain size effects.

R. Jayakrishnan and G. Hodes [73] reported the ZnO films have been electrodeposited from a dimethylsulfoxide bath containing dissolved gaseous oxygen. Variations in deposition parameters and their effects on the structural (crystal size, growth direction), optical (band gap variations, photoluminescence) and electrical (conductivity) properties are described. The technique was extended to give highly-conducting films of CdO.

Z. Bi-Ju et al. [74] investigated the ZnO/CdO composite films with different CdO contents are obtained by pulse laser deposition technique. The structural, optical and electrical properties of the composite films are investigated by x-ray diffraction, photoluminescence and electrical resistivity measurements, respectively. The results show that the UV emission is at a constant peak position in the photoluminescence spectra. Meanwhile, their electrical resistivity decreases to very low level approaching to the value of the CdO film, which can be explained by the Matthiessen composite rule for resistivity. The peculiarity of low resistivity and high transmittance in the visible region enables these films suitable for optoelectronic device fabrication.
S. Mondal and P. Mitra [75] reported the Cadmium-doped zinc oxide (Cd:ZnO) thin films have been deposited from sodium zincate bath following a chemical dipping technique called successive ion layer adsorption and reaction (SILAR). Structural characterization by X-ray diffraction reveals that polycrystalline nature of the films increases with increasing cadmium incorporation. Particle size evaluated using X-ray line broadening analysis shows decreasing trend with increasing cadmium impurification. The average particle size for pure ZnO is 36.73nm and it reduces to 29.9 nm for 10% Cd:ZnO, neglecting strain broadening. The strong preferred c-axis orientation is lost due to cadmium doping and degree of polycrystallinity of the films also increases with increasing Cd incorporation. Incorporation of cadmium was confirmed from elemental analysis using EDX. The optical band gap of the films decreases with increasing Cd dopant.

A. Singh et al. [76] reported the Zn$_{1-y}$Cd$_y$O ternary alloyed thin films with different Cd volume ratios ($y = 0.01$ to 0.35) have been successfully deposited by sol-gel spin coating method on p–Si (100) and quartz glass substrates. XRD results revealed that the thin films were polycrystalline in nature and their crystallinity was reduced with Cd content. Phase segregation as cubic CdO was observed for Cd content $y \geq 0.15$. Residual stress in the films was strongly influenced by Cd concentrations and its maximum value was observed near the phase segregation limit. Raman results also confirmed that the higher Cd contents distorted the wurtzite structure. UV–Vis transmission spectra exhibited reduction in band gap of ZnCdO films with increase of Cd incorporation. The Hall measurements were performed to estimate the carrier concentration and mobility as a function of Cd doping.

W.E. Mahmoud and A.A. Al-Ghamdi [77] studied the Cadmium doped zinc oxide thin films have been prepared using a thermal decomposition technique. A deep correlation has been found between the surface roughness and the optical properties. The roughness is found to deteriorate the non linear response, such that the highest non linear susceptibility $\chi^{(3)}$ is obtained for the smoothest layer. The third-order non linear susceptibility $\chi^{(3)}$ has been calculated using the Frumer model, and is estimated
to be $3.37 \times 10^{-10}$ esu. The dispersion of the refractive index of the prepared thin film is shown to follow the single electronic oscillator model. From the model, the values of oscillator strength ($E_d$), oscillator energy ($E_o$) and dielectric constant ($\varepsilon$) have been determined. The conductivity has been measured as a function of the energy of the photons, revealing marginal change at energies below 3.15eV, while above this value there is a large increase in the conductivity. This suggests that CdZnO is a potential candidate for applications in optical devices such as optical limiter and optical switching.

*O. Vigil et al.* [78] reported the mixed thin film oxides of cadmium and zinc with different compositions were deposited on glass substrates by spray pyrolysis. The effect of the various parameters on the growth and on the film properties is presented. The sample structure was studied by XRD having found the presence of a cubic phase resembling that of pure CdO XRD pattern for low Zn concentrations. For $x=0.75$ a low crystallinity of the ZnO structure was observed. Optical band-gap was also studied from optical transmittance measurements. As expected, the band-gap values change between those of pure CdO and those of ZnO.

*R. L. Call et al.* [79] showed that CdS, CdO and ZnO films can be deposited on glass, aluminum, copper, nickel, molybdenum, steel, tin and zinc substrates from aqueous solution using reagent grade chemicals. Their structural properties have been investigated and these values found compared well with values for the bulk form showing that equilibrium phase has being deposited. A short-circuit current of 2.7 mA and an open-circuit voltage of 0.2 V was obtained for the best cell under an illumination of AM-1 and an area of 1 cm$^2$. The characteristic curve is a straight line showing that improvements could possibly be made in these devices to obtain greater efficiencies.

*G. Santana et al.* [80] reported the thin films of $(\text{ZnO})_x(\text{CdO})_{1-x}$ oxides have been deposited on glass substrates by spray pyrolysis and annealed in air at 450°C. The structural and optical properties of the as-grown and thermally annealed thin films are presented. The crystalline structure was studied by XRD having found the
presence of the CdO cubic phase pattern for low Zn concentrations and a mixing of cubic-CdO and hexagonal-ZnO phases for low Cd concentrations. The crystallinity of all samples improves with the thermal annealing. The optical band-gap was also studied from the optical transmittance for the as-grown and annealed samples. As expected, the band-gap changes between that for pure CdO and that for ZnO.

M. Tortosa et al. [81] studied the ternary single-phase Zn$_{1-x}$Cd$_x$O alloy semiconductor films have been obtained by means of cathodic deposition. Crystalline thin films with cadmium concentrations ranging from about 0.4% to 9% were electrodeposited onto glass conductive substrates and subsequently annealed in air at 300°C. XRD studies confirm a hexagonal wurtzite structure for the ternary alloy compounds. The amount of cadmium incorporated in the electrodeposited films, which was measured by EDS, produces a red shift of the absorption edge of the alloy semiconductor films proportional to the cadmium content. A linear relationship has been found between the width of the film and the deposited electric charge.

Y.-S. Choi et al. [82] investigated the thin films of zinc oxide, cadmium oxide, and their compounds have been deposited by the sol-gel process. The ZnO and CdO films are found to have different crystallographic structures and their compounds are found to be simple mixtures of the two different crystallographic structures for the constituent materials. The electrical resistivity of the compounds, Zn$_x$Cd$_{1-x}$O thin films decreases as the composition $x$ decreases, so that pure CdO thin films have the lowest electrical resistivity of $3 \times 10^{-3}$ Ω cm. Although the optical transmittance and band gap of the Zn$_x$Cd$_{1-x}$O films also decrease as the value of $x$ decreases, all the films prepared in this study have a fairly high transmittance reproducibly in the visible spectral range at room temperature. The electrical resistivity of the films is found to have significant dependence on the post-deposition annealing environments. This dependence is more pronounced for the films which contain higher percentages of Zn among all the Zn$_x$Cd$_{1-x}$O films prepared in this study. The dependence of the electrical resistivity on the aluminium impurity concentration in the Zn$_x$Cd$_{1-x}$O films is also examined.
L.N. Bai et al. [83] studied the Zn$_{1-x}$Cd$_x$O thin films are deposited on quartz substrate by pulse laser deposition. Their band structure and optical properties are experimentally and theoretically investigated. By varying Cd concentration, the band gap of Zn$_{1-x}$Cd$_x$O films can be adjusted in a wide range from 3.219 eV for ZnO to 2.197 eV for Zn$_{0.5}$Cd$_{0.5}$O, which produces different emissions from ultraviolet to Kelly light in their photoluminescence spectra. Simultaneity, the electronic structure and band gap of Zn$_{1-x}$Cd$_x$O are investigated by the density functional theory (DFT) with a combined generalized gradient approximation (GGA) plus Hubbard U approach, which precisely predicts the band-gaps of ZnO and Zn$_{1-x}$Cd$_x$O alloys. Both the experimental results and theoretical simulation reveal that with increasing Cd concentration in Zn$_{1-x}$Cd$_x$O alloys, their absorption coefficients in visible light range are evidently enhanced.

Z. Wang et al. [84] reported the nitrogen-doped p-type zinc oxide films have been realized by radio frequency (rf) magnetron sputtering and post-annealing techniques. The nitrogen-doped p-type zinc oxide film with good structural, electrical and optical properties can be obtained at an intermediate annealing temperature region (e.g., 650°C). The nitrogen-doped p-type zinc oxide had the lowest resistivity of 2.9 Ω cm, Hall mobility of 18 cm$^2$/V s and carrier concentration of 1.3 $\times$ 10$^{17}$ cm$^{-3}$. The p-type conduction behavior of the nitrogen-doped zinc oxide film was confirmed by the rectifying I–V characteristics of a ZnO homo-junction. The chemical bonding states of nitrogen doped in ZnO film were examined by XPS analysis.

The microstructure and the electrical and optical properties of ZnO and CdZnO) films deposited by a sol-gel method have been investigated by F. Yakuphanoglu et al. [85]. The films have a polycrystalline structure with hexagonal wurtzite ZnO. SEM images indicated that the films have a wrinkle network with uniform size distributions. The elemental analyses of the CZO films were carried out by EDS analysis. The fundamental absorption edge changed with doping. The optical band gap of the films decreased with Cd dopant. The optical constants of the films such as refractive index, extinction coefficient and dielectric constants changed with
Cd dopant. A two-probe method was used to investigate the electrical properties, and the effect of Cd content on the electrical properties was investigated. The electrical conductivity of the films was improved by incorporation of Cd in the ZnO film.

C. Karunakaran et al. [86] investigated the nanocrystalline Cd-doped ZnO has been obtained by hydrothermal synthesis and characterized by powder XRD, EDS, high resolution SEM and UV–visible diffuse reflectance, PL and electrochemical impedance spectra. Cd-doping by hydrothermal method decreases the grain size and destroys the microstructure. Although doping does not modify the band gap it suppresses the deep level emission, decreases the charge-transfer resistance and increases the capacitance. Cd-doping enhances the photo-catalytic and bactericidal activities.

Z. Wang et al. [87] reported the nitrogen doped zinc oxide (ZnO:N) film has deposited on a quartz substrate at 773 K by reactive rf magnetron sputtering using mixture of nitrogen and oxygen as sputtering gas. Hall measurement results indicate that the ZnO:N film behaves p-type conduction after annealed at 923 K, which has the lower room temperature resistivity of 2.9 Ω cm, Hall mobility of 18 cm²/V s and carrier concentration of $1.3 \times 10^{17}$ cm⁻³, respectively. Compositional analysis confirmed the nitrogen (N) is incorporated into the ZnO and the N occupies two chemical states in the ZnO:N. The ZnO:N film has high optical quality and displays the stronger NBE emission in the temperature-dependent photoluminescence spectrum, the acceptor energy level was estimated to be located 110 meV above the valence band.

X. Tang et al. [88] studied an ab initio calculation based on density functional theory is applied to study the formation energy and transition energy level of defects and complexes in Cd-doped ZnO. The calculation shows that the incorporation of Cd into ZnO leads to the increase of the O vacancies ($V_O$). $V_O$ exists in the form of Cd$_{Zn}$-$V_O$ complex, which can balance the strain caused by Cd$_{Zn}$ and $V_O$. Due to high formation energy of the Zn interstitials (Zn$_i$) and deep transition energy level of $V_O$, Zn$_i$ and $V_O$ cannot serve singly as the source of the n-type carriers in Cd-doped ZnO.
It is also found that the Zn$_{i}$-Cd$_{Zn}$-$V_{O}$ complex is a shallow donor like Zn$_{i}$, but has lower formation energy. Thus, the source of n-type carriers is believed to be a complex with Zn$_{i}$-Cd$_{Zn}$-$V_{O}$ structures in Cd-doped ZnO.

J. Song et al. [89] reported the Y and Cd co-doped ZnO nano powders have been prepared via chemical precipitation method in order to modify the band gap and increase the luminescent intensity. The effects of Y and Cd ions on the optical properties of the samples were studied. Doping of Y into ZnO evidently increases the intensity of UV emission, or co-doping of Y and Cd enhances the UV emission, narrows the band gap of ZnO and hence red shifts the UV emission at the same time. Therefore, Y and Cd co-doped ZnO nano powders exhibit an intense violet emission in the room temperature PL spectrum, which could be a potential candidate material for optoelectronic applications.

W. Gao and Z. Li [90] investigated the ZnO thin films have been deposited onto glass substrates with direct current (dc) or rf magnetron sputtering using Zn or ZnO target. SEM and XRD analysis demonstrated that the type of deposition mode, plasma excitation, working pressure and oxygen partial pressure, bias, working distance, and doping could significantly change the quality and microstructure of the films. The electrical conductivity of ZnO films is strongly affected by the deposition mode (dc or rf), crystal structure, chemical composition and microstructure. Photoluminescence of these films were also studied, and the relationships of processing parameters, microstructure, and properties were explored.

T.K. Subramanyam et al. [91] investigation, zinc oxide films have been prepared by DC reactive magnetron sputtering. A systematic study has been made on the structure and electrical and optical properties of ZnO films as a function of substrate temperature in the range 548-723 K. The X-ray diffraction studies revealed that the films were polycrystalline in nature with wurtzite structure. Films with a minimum resistivity of $6.9 \times 10^{-2}$ $\Omega$ cm and high transparency of 83% have been achieved at a substrate temperature of 663 K.
M. Suchea et al. [92] pure and aluminum (Al) doped zinc oxide (ZnO and ZAO) thin films have been grown using dc magnetron sputtering from pure metallic Zn and ceramic ZnO targets, as well as from Al-doped metallic ZnAl2at.% and ceramic ZnAl2at.%O targets at RT. The effects of target composition on the film's surface topology, crystallinity, and optical transmission have been investigated for various oxygen partial pressures in the sputtering atmosphere. It has been shown that Al-doped ZnO films sputtered from either metallic or ceramic targets exhibit different surface morphology than the un-doped ZnO films, while their preferential crystalline growth orientation revealed by XRD remains always the (002). More significantly, Al-doping leads to a larger increase of the optical transmission and energy gap ($E_g$) of the metallic than of the ceramic target prepared films.

Effects of variation of the oxygen partial pressure on the structural and optical properties of zinc oxide (ZnO) thin films prepared by reactive radio-frequency sputtering have been investigated by J.P. Zhang et al. [93]. Analyses by XRD and SE revealed that the oxygen partial pressure had effect on the orientation of the ZnO films, the surface morphology, the packing density, and the interfacial layers. And the relationship between crystallinity and interfacial layer, as well as the relationship between surface roughness and packing density was discussed. All these had a significant impact on the optical properties illustrated by SE analysis.

Wurtzite Cd$_x$Zn$_{1-x}$O epilayers with cadmium concentrations ranging from $x=0.02$ to 0.30 have been investigated by J.W. Mares et al. [94] using photoluminescence, transmission/reflection spectroscopy, and atomic force microscopy. The Cd$_x$Zn$_{1-x}$O photoluminescence peak was found to shift through the visible region from 421 (2.95eV) to 619 nm (2.0 eV) as the cadmium concentration was increased from 2% to 30%. An additional broad photoluminescence peak was observed and is attributed to deep levels – the center of the broad peak was found to shift from 675 to 750 nm as the cadmium concentration was increased. RMS roughness of the epilayers increased from 1.5 nm ($x=0.02$) to 9.2 nm ($x=0.30$), as determined from atomic force microscopy. The demonstrated visible wavelength
tunability throughout the visible range verifies the viability of using wurtzite \( \text{Cd}_x\text{Zn}_{1-x}\text{O} \) compounds for visible light emission in future optoelectronic devices.

The structural and optical properties of \( \text{Cd}_x\text{Zn}_{1-x}\text{O} \) films have been studied by C.Y. Liu and Y.C. Liu [95]. The films have been deposited using pulse laser deposition (PLD). The Cd concentration was changed in the range from \( x=0 \) to 0.2. The optical band gap of the films was measured by using transmission and PL spectra. The exciton recombination dynamics was investigated by means of the TRPL spectra of the films at 77 K.

S. Ilican et al. [96] reported the \( \text{Cd}_x\text{Zn}_{1-x}\text{O} \) films have been deposited by sol–gel spin-coating method onto glass substrates. The Cd/Zn ratio in solution was changed from 0 to 1. Zinc acetate dehydrates, cadmium acetate dehydrates, 2-methoxyethanol and monoethanolamine were used as a starting material (zinc and cadmium), solvent and stabilizer, respectively. XRD patterns show that the films are polycrystalline nature. As \( x \) varies from 0 to 1, it was observed that the crystal structure changed from wurtzite (ZnO) to cubic (CdO) structure. The optical properties of these films have been investigated by means of the optical transmittance and reflectance spectra. A significant change in optical absorption edge, optical band gap and optical constant with variation in composition was observed.

D. Zhao et al. [97] reported the \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) thin films have been successfully fabricated by the sol–gel method on n-type Si (001) and quartz substrates. The \( \text{Mg}_{0.05}\text{Zn}_{0.95}\text{O} \) and \( \text{Mg}_{0.15}\text{Zn}_{0.85}\text{O} \) alloys with wurtzite structure show high thermal stability up to 1000°C. However, when \( x \) is 0.36, phase separation will occur at 800°C. The optical band gap of \( \text{Mg}_x\text{Zn}_{1-x}\text{O} \) alloys (0≤\( x \)≤36) ranges from 3.4 to 3.93 eV.

M. Chen et al. [98] investigated the high preferred (002) orientation Al-doped ZnO (ZAO) films have been prepared by dc magnetron reactive sputtering from a Zn target mixed with Al of 2.0 wt%. The dependence of spatial distributions of resistivity on substrate temperature indicates that the spatial distribution of resistivity across
substrate placed parallel to the target was improved by increasing substrate temperature. XPS analysis indicates Al-enrichment on the film surface.

*W.E. Mahmoud et al.* [99] investigated the ZnO and Cd-doped ZnO nanostructures have been prepared by new facile method at 80°C. XRD measurement indicated that both samples had typical hexagonal wurtzite structures. Transmission electron microscopy (TEM) measurement shows that rod-like crystals have been formed. EDX measurement confirms the incorporation of the cadmium ion into the crystalline lattice of ZnO and indicated that cadmium ions uniformly distributed on the surface of the rods. The doping with cadmium ions has a great influence on the optical properties of the ZnO. The electrical measurements of Cd-doped ZnO nanorod were measured. The current–voltage (I–V) characteristic curve revealed that the charge transport above 4V is mainly nonlinear due to grain boundary contribution. The complex impedance spectroscopy was confirmed that the grain boundary effect controls the charge transport mechanism through CdZnO ceramic material.

*M. Lange et al.* [100] studied the thermal stability of ZnO/Zn$_{1-x}$Cd$_x$O/ZnO double hetero structures grown by pulsed-laser deposition has been studied by annealing them for 30 min in air at temperatures from 620 to 970°C. In photoluminescence spectroscopy measurements on the as-grown samples emission with energies between 3.122 and 3.044 eV were observed, corresponding approximately to Cd-contents between 2.7% and 3.6%. Due to the annealing a monotonic blue-shift of the Zn$_{1-x}$Cd$_x$O-related luminescence has found with increasing annealing temperature. The shift has small for annealing temperatures of up to 720 °C, thus a stability of the hetero structures up to this temperature was concluded. The underlying diffusion process was investigated to determine the diffusion coefficient for the different annealing temperatures. The temperature dependence of the diffusion coefficient shows an activation enthalpy in the range between 2.1 and 3.5 eV, depending on the growth conditions.

ZnCdO thin films with different Cd contents have been deposited on quartz substrate by *J. Jiang et al.* [101] using pulsed laser deposition. All the obtained films
have a hexagonal wurtzite ZnO structure with a highly c-axis orientation without any Cd related phases from the XRD patterns. The band gap energy of ZnCdO films extending to 2.88 eV can be achieved by incorporating 9.6% Cd content. The bound excitons emission at 2.925 eV in the ZnCdO thin film can be found in the low temperature photoluminescence measurement.

A.D. Acharya et al. [102] investigated the Cd doped ZnO (Cd:ZnO) thin films on the glass substrate prepared by chemical spray pyrolysis technique have been characterized for their optical and electrical properties. The X-ray diffraction and atomic force microscopy results indicate that the crystalline quality degrade due to higher Cd doping in ZnO. The activation energy was found to be decreased when Cd concentration increased. The absorption edge of Cd:ZnO film was found to be red shifted. The direct modulation of band gap caused by Zn/Cd substitution is responsible for the red shift effect in absorption edge of ZnO. The low temperature conduction has been explained by variable range hoping mechanism, which fits very well in the temperature range from 108 K to 301 K.

Y. Caglar et al. [103] reported the CdZnO films have been deposited by the sol–gel spin coating method onto glass substrates. ZnO, Cd(0.25)Zn(0.75)O, Cd(0.50)Zn(0.50)O, Cd(0.75)Zn(0.25)O, CdO films have been deposited using different rates of cadmium acetate dehydrate and zinc acetate dehydrate solutions. These values in parentheses refer to the ratio in solution. The dried and annealing temperatures were selected to be 300 °C and 500 °C in air, respectively. The XRD patterns show polycrystalline nature. It was observed that the crystal structure changes from wurtzite (ZnO) to cubic (CdO) depending on the Zn and Cd proportions in the CdZnO structure. The optical properties of these films have been investigated by means of the optical transmittance measurement. The absorption band edges of films shift from 3.26 to 2.31 eV. The morphological characterizations of the films have been performed by SEM and AFM. The electrical measurements show that the CdZnO films have semiconducting behaviour and are very sensitive to light.
A. Singh and P. Kumar [104] reported the Cadmium doped zinc oxide has been the potential candidate for the fabrication of low-cost transparent conductors having applications in energy conversion devices such as thin-film solar cells and light-emitting diodes. The XRD study has revealed the hexagonal wurtzite crystal structure with crystallite size ranging from 45 to 49 nm for these films. All the prepared films show the larger values of optical transparency (>80%) along with the shift in the fundamental absorption edge and the direct optical gap was found to be between 3.14 and 3.19 eV. The highly intense band edge emission for the sample was synthesized using the 2-ethoxyethanol while the presence of other defect-related bands in the other samples has been observed.

Structural, optical and electrical properties of Cd$_{y}$Zn$_{1-y}$O ($y=0–0.1$) ternary alloy thin films have been investigated by B.K. Sonawane et al. [105] for the films prepared using the spin coating method on the glass substrate. XRD pattern confirmed the nano-size polycrystalline hexagonal wurtzite structure for all the samples. The size of nano-crystals was found to be varied in between 21 and 30 nm. Optical band gap calculated from the absorption coefficient signifies the shift in direct band gap from 3.2 to 2.97eV with cadmium composition. Through EDAX spectrum, it was confirmed that cadmium was successfully incorporated into ZnO. SEM studies make clear that even after cadmium incorporation; the surface morphology of the films remained smooth. Our investigations lead to the applicability of CdZnO as an active layer in CdZnO/ZnO hetero structure for light emitting devices.

A.A. Ziabari and F.E. Ghodsi [106] reported the nanocrystalline Cd$_{x}$Zn$_{1-x}$O thin films with different Cd volume ratios in solution ($x=0$, 0.25, 0.50, 0.75 and 1) have been deposited on glass substrate by sol-gel dip-coating method. The as-deposited films were subjected to drying and annealing temperatures of 275°C and 450°C in air, respectively. The results show that the samples are polycrystalline and the crystallinity of the films enhanced with x. The average grain size is in the range of 20–53 nm. The atomic percent of Cd:Zn was found to be 9.50:1.04, 6.20:3.77 and 4.42:6.61 for x=0.75, 0.50 and 0.25, respectively. It was observed that the
transmittance and the band gap decreased as x increased. All the films exhibit n-type
electrical conductivity. The resistivity ($\rho$) and mobility ($\mu$) are in the range of
$3.3 \times 10^2 - 3.4 \times 10^{-3}$ Ω cm, and $1.5 - 4.5$ cm$^2$ V$^{-1}$ s$^{-1}$ respectively. The electron density
lies between $1.26 \times 10^{16}$ and $0.2 \times 10^{20}$ cm$^{-3}$.

*D.-H. Lee et al.*[107] have been fabricated the ZnCdO transparent TFTs with
a back-gate structure using highly p-type Si (001) substrate. For the active channel, 30
nm, 50 nm, and 100 nm thick ZnCdO thin films were grown by pulsed laser
deposition. The ZnCdO thin films were wurtzite hexagonal structure with preferred
growth along the (002) direction. All the samples were found to be highly transparent
with an average transmission of about 80% in the visible range. We have investigated
the change of the performance of ZnCdO TFTs as the thickness of the active layer is
increased. The carrier concentration of ZnCdO thin films has been confirmed to be
increased from $10^{16}$ to $10^{19}$ cm$^{-3}$ as the film thickness increased from 30 to 100 nm.
Based on this result, the ZnCdO TFTs show a thickness-dependent performance which
is ascribed to the carrier concentration in the active layer. The ZnCdO TFT with 30
nm active layer showed good off-current characteristic of below $\sim 10^{11}$, threshold
voltage of 4.69 V, a subthreshold swing of 4.2 V/decade, mobility of 0.17 cm$^2$/V s,
and on-to-off current ratios of $3.37 \times 10^4$.

*M. Lange et al.*[108] reported the (Zn,Cd)O thin films have been grown by
pulsed laser deposition on a plane sapphire substrates with high Cd-contents up to
0.25. By incorporating Cd in ZnO and by applying a low growth temperature of about
300 °C, the (Zn,Cd)O related luminescence red shifts to an energy of 2.46 eV as a
result of the large Cd-content of 0.25. The red shift of the band gap energy was
additionally proven by transmission measurements. By fitting the transmission curves,
the spectra of the absorption coefficient and the index of refraction are calculated. The
(Zn,Cd)O thin films are single phase and exhibit the wurtzite crystal structure. An
increasing a- and c-lattice constant is observed with increasing Cd-content.

*D.M. Detert et al.*[109] have been measured the band edge energies of
Cd$_x$Zn$_{1-x}$O thin films as a function of composition by three independent techniques.
The three techniques find consensus in explaining the origin of compositional trends in the optical-band gap narrowing upon Cd incorporation in wurtzite ZnO and widening upon Zn incorporation in rocksalt CdO. The conduction band minimum is found to be stationary for both wurtzite and rocksalt alloys, and a significant upward rise of the valence band maximum accounts for the majority of these observed band gap changes. Given these band alignments, alloy disorder scattering is found to play a negligible role in decreasing the electron mobility for all alloys. These band alignment details, combined with the unique optical and electrical properties of the two phase regimes, make CdZnO alloys attractive candidates for photo-electrochemical water splitting applications.

Single-phase rock-salt CdZnO films have been synthesized on r-plane sapphire substrates by metal–organic chemical vapor deposition reported by T. C. Zhang and A. Yu. Kuznetsov [110]. Evolutions in growth orientations were investigated in these films as a function of Zn content and film thickness. The preferred orientation is found to black (thick) and red (thin) lines depend on the balance between the surface and strain energy accumulated in the films in accordance with the so-called overall energy model. Specifically, (100) orientation dominates below a critical Zn content and/or a critical film thickness, otherwise (111)-oriented grains nucleate on top of the (100) planes.

D.W. Ma et al. [111] reported the highly (002)-oriented Zn$_{0.8}$Cd$_{0.2}$O crystal films have been prepared on different substrates, namely, glass, Si(111) and a-Al$_2$O$_3$(001) wafers by the dc reactive magnetron sputtering technique. The Zn$_{0.8}$Cd$_{0.2}$O/a-Al$_2$O$_3$ film has the best crystal quality with a FWHM of (002) peak of 0.37°, an average grain size of about 200 nm and a root-mean-square surface roughness of about 70 nm; yet the Zn$_{0.8}$Cd$_{0.2}$O/glass holds the worst crystal quality with a much larger FWHM of 0.6281°. SIMS depth profile shows that the Zn and O compositions change little along the film depth direction; the Cd incorporation also almost holds the line towards the top surface other than an accumulation at the
interface between the film and the substrate. The Cd content in the film is nearly consistent with that in target.

Here G.-R. Li et al. [112] explored a novel and facile electrochemical route for the preparation of \( Zn_{1-x}Cd_xO \) (x is atomic percentage of Cd) nanorods with controllable optical properties. The \( Zn_{1-x}Cd_xO \) nanorods can be routinely obtained when the electrochemical deposition was carried out in solution of \( Zn(NO_3)_2 + Cd(NO_3)_2 + \) citric acid at -1.0 V (vs SCE). EDS results demonstrated that Cd, Zn, and O elements existed in the deposits, and ternary \( Zn_{1-x}Cd_xO \) compounds were obtained. XRD results showed that \( Zn_{1-x}Cd_xO \) nanorods were pure ZnO wurtzite structures. HRTEM and SAED analyses confirmed that \( Zn_{1-x}Cd_xO \) nanorods were single-crystalline. The optical properties of \( Zn_{1-x}Cd_xO \) nanorods were investigated.

Using first-principles calculations, H. Rozale et al. [113] investigated the structural and electronic properties of two binaries: ZnO in wurtzite structure and CdO in wurtzite and rock-salt structures. In addition several compositions with various ordered structures of \( Zn_xCd_{1-x}O \) alloys were studied within the theory of order–disorder transformation. The full potential linearized augmented plane wave method was used and the d orbitals of Zn and Cd were included in the valence bands. In this investigation of alloying ZnO with CdO, the fundamental band-gap of the alloys is shown to be direct and to decrease versus the Cd composition.

F. Wang et al. [114] reported the ZnCdO nanorods and ZnCdO nanoneedles have been synthesized simultaneously by evaporating Zn and Cd powders using Au as a catalyst. The synthesized ZnCdO nanorods have uniform hexagonal crystallographic planes, and their diameters are about 150 nm. The Cd content of quasi-aligned ZnCdO nanorods was as high as (about) 16.7 at%. Notably, the UV NBE emission was red-shifted from 386nm (3.21 eV) to 408nm (3.04 eV) due to the direct modulation of band gap caused by Zn/Cd substitution. Temperature is deemed as a critical experimental parameter for the formation of different morphologies of ZnCdO nanostructures.
J. Ishihara et al. [115] investigated the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films were successfully grown by remote plasma enhanced metalorganic chemical vapor deposition (RPEMOCVD) with diethyl zinc, dimethyl cadmium, and oxygen plasma. The Cd composition $x$ in the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films was tuned by changing a flow rate of group-II sources. With increasing the Cd composition $x$, the crystal structure was changed from wurtzite (WZ) to rock-salt (RS). The optical band-gap of the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films with the wurtzite structure up to $x \leq 0.7$ varied from 3.3 eV down to 1.9 eV.

L. Chen et al. [116] demonstrated the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ ($x = 0.1, 0.2$) thin films with highly (002)-preferred orientations were deposited on glass and Si (111) substrates by DC reactive magnetron-sputtering method in the atmospheres with different Ar/O$_2$ ratios. When the Ar/O$_2$ ratios change from 1:4 to 1:1, the FWHM of the films deposited on glass substrates of $\text{Zn}_{0.9}\text{Cd}_{0.1}\text{O}$ films decreases (from 0.361$^o$) gradually and reaches a minimum value of 0.291$^o$ at the ratio of 1:1; the band gap ($E_g$) decreases (from 3.149 eV) gradually and reaches a minimum value of 3.099 eV at the same ratio of 1:1. When the Ar/O$_2$ ratios continue to increase up to 2:1, the FWHM increases to 0.351$^o$; the band gap ($E_g$) increases to 3.114 eV. The variations for $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{O}$ films are the same as for $\text{Zn}_{0.9}\text{Cd}_{0.1}\text{O}$ films. A mechanism for the influence of Ar/O$_2$ gas ratios on the band gap of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ thin films is proposed.

The optical and structural properties of textured ZnCdO films that exhibit a newly found distinct blue luminescence have been investigated by K. Sakurai et al. [117]. Microscopic compositional fluctuations of Cd, associated with hexagonal grain structures, were observed. Models for the blue-luminescence process are proposed.

Using the dc reactive magnetron sputtering method D.W. Ma et al. [118] have successfully deposited completely (002)-oriented ternary $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ ($0 \leq x \leq 0.6$) alloy crystal films without Cd segregation on Si(111) substrates. The Zn and Cd exist only in oxidized states, no evidence of metallic Zn or Cd was observed by XPS measurements. The O/(Cd+Zn) atomic ratios of the films are in the range of 0.89–0.98. Transmission electron microscopy measurements show that for the (002)-oriented films the grains are columnar structures with the c-axis perpendicular to the
Si substrate. By post-annealing treatments in O\textsubscript{2} ambient, the crystal quality of the Zn\textsubscript{1-x}Cd\textsubscript{x}O films can be improved.

A common misconception is that the irradiation of solids with energetic electrons and ions has exclusively detrimental effects on the properties of target materials. In addition to the well-known cases of doping of bulk semiconductors and ion beam nitriding of steels, recent experiments show that irradiation can also have beneficial effects on nanostructured systems. Electron or ion beams may serve as tools to synthesize nanoclusters and nanowires, change their morphology in a controllable manner, and tailor their mechanical, electronic, and even magnetic properties. Harnessing irradiation as a tool for modifying material properties at the nanoscale requires having the full microscopic picture of defect production and annealing in nanotargets. In this article, A. V. Krasheninnikov and K. Nordlund [119] reviewed recent progress in the understanding of effects of irradiation on various zero-dimensional and one-dimensional nanoscale systems, such as semiconductor and metal nanoclusters and nanowires, nanotubes, and fullerenes. We also consider the two-dimensional nanosystem graphene due to its similarity with carbon nanotubes. We dwell on both theoretical and experimental results and discuss at length not only the physics behind irradiation effects in nanostructures but also the technical applicability of irradiation for the engineering of nanosystems.

A. Yu. Azarov et al. [120] investigated the thin films of wurtzite Mg\textsubscript{x}Zn\textsubscript{1-x}O (x\leq0.3) grown by molecular beam epitaxy and wurtzite Cd\textsubscript{x}Zn\textsubscript{1-x}O (x\leq0.05) grown by metal organic chemical vapor deposition were implanted at room temperature with 150 keV Er\textsuperscript{+} ions and 200 keV Au\textsuperscript{+} ions in a wide dose range. Damage accumulation was studied by Rutherford backscattering/channeling spectrometry. Results show that the film composition affects the damage accumulation behavior in both MgZnO and CdZnO dramatically. In particular, increasing the Mg content in MgZnO results in enhanced damage accumulation in the region between the bulk and surface damage peaks characteristically distinguished in the pure ZnO. However, the overall damage accumulation in MgZnO layers, as well as in pure ZnO, exhibits saturation with
increasing ion dose and MgZnO cannot be amorphized even at the highest ion dose used ($3 \times 10^{16}$ Er/cm$^2$). Increasing the Cd content in CdZnO affects the saturation stage of the damage accumulation and leads to an enhancement of damage production in both Cd and Zn sublattices.

*S. Kraft et al.* [121] have been investigated the irradiation induced interface mixing in ZnO/SiO$_2$ ($\alpha$-quartz) and Sb/Ni/Si thin layer systems under swift heavy ion irradiation in the electronic stopping power regime. The irradiations were carried out at 77 K using 100 MeV Ar, 260 MeV Kr, and 200 MeV Xe ions. For the ZnO/SiO$_2$ system experiments were also carried out at lower ion energies (300, 600, and 900 keV, respectively) where nuclear stopping dominates. The alterations of the interface concentration profiles were determined by means of Rutherford backscattering spectrometry performed subsequently at the irradiated and the nonirradiated parts of the samples. While for the semimetal/metal Sb/Ni interface almost no mixing could be found after high-energy irradiation (mixing efficiency for Xe ions: $k/Se<0.02$ nm$^5$/keV) the ceramic system ZnO/SiO$_2$ strongly reacts upon high energy ion irradiation (Xe: $k/Se=2.1$ nm$^5$/keV). The Ni/Si interface shows an intermediate effect (Xe: $k/Se=0.2$ nm$^5$/keV). The mixing behavior found at high ion energies is in contrast to that found in the nuclear stopping regime, where Sb/Ni shows very strong mixing and phase formation while ZnO/SiO$_2$ exhibits only weak ballistic mixing. As was previously observed for the formation of ion tracks, interface mixing due to electronic energy deposition also sets in only if the electronic stopping power exceeds a threshold value.

*P.M.R. Kumar et al.* [122] have been prepared the spray pyrolyzed ZnO films using solution containing ethanol and water, exhibited optical transmission of 85% in the visible range and electrical resistivity of 78 $\Omega$ cm. These samples were irradiated using 120 MeV Au ion beam and then characterized using optical absorption and transmission, XRD, electrical resistivity measurements, XPS, and PL studies. It appears that irradiation does not affect absorption edge while optical transmittance was slightly reduced. But intensities of peaks of XRD and photoluminescence were
found to decrease continuously with increasing ion fluence. Electrical resistivity of the films decreased considerably (from 78 to 0.71 V cm) with increase in ion fluence. Atomic concentration from XPS analysis showed that Zn/O ratio is getting increased due to ion beam irradiation. Variations in carrier concentration were also measured using Hall measurements.

R. Kumar et al. [123] reported the low temperature PL and optical absorption studies on 200 MeV Ag$^{+15}$ ion irradiated Co-implanted ZnO thin films were studied. The Co clusters present in as implanted samples were observed to be dissolved using 200 MeV Ag$^{+15}$ ion irradiation with a fluence of $1 \times 10^{12}$ ions/cm$^2$. The PL spectrum of pure ZnO thin film was characterized by the $I_4$ peak due to the neutral donor bound excitons and the broad green emission. The Co-doped ZnO films show three sharp levels and two shoulders corresponding to $3t_2g$ and $2e_g$ levels of crystal field splitted Co $d$ orbitals, respectively. The ultraviolet-visible absorption spectroscopy also shows the systematic variation of band gap after 200 MeV Ag$^{+15}$ ion irradiation.

Al-doped ZnO (AZO) films are known as n-type transparent semiconductors. We have investigated the effects of 100 MeV Xe ion irradiation on the optical and structural properties of AZO films, which were prepared on SiO$_2$ glass at 400 °C by using a rf-magnetron sputtering deposition method. O. Fukuoka et al. [123] discussed the relationships between these property modifications and the recent observations of the conductivity increase by ion irradiation. It is suggested that the band-gap modification has more close relation with the conductivity increase than the structural modification.

Metal organic chemical vapour deposition (MOCVD) grown n-type GaN on sapphire substrates has irradiated with 100 MeV Au$^{7+}$ ions, varying the fluence as $1 \times 10^{12}$, $1 \times 10^{13}$ and $5 \times 10^{13}$ ions cm$^{-2}$ at room temperature reported by V.S. Kumar et al. [125]. XRD analysis reveals a huge lattice disorder for fluence beyond $1 \times 10^{13}$ ions cm$^{-2}$. This is observed from the increase in the FWHM and decrease in the intensity of the GaN (0002) peak. AFM images show the roughness of GaN increases with increasing ion fluences. At a fluence of $5 \times 10^{13}$ ions cm$^{-2}$, a new type of ditch
and dike structure was observed. These structures were distributed over the irradiated GaN surface. UV–visible absorption spectrum shows that the band gap energy decreases with increasing ion fluences and also that the band edge is broadened. The results are discussed by the complementary use of these studies.

The temperature dependant photoluminescence of the Co-doped ZnO thin films, prepared by ion implantation on the MBE grown ZnO thin films followed by swift heavy ion irradiation, have been investigated by B. Angadi et al. [126]. The phenomenon of negative thermal quenching (NTQ), where the PL intensity increases with temperature, in contrast to the usual behavior of decrease in intensity with temperature, has been observed. The NTQ temperature range 35–45 K observed in un-doped ZnO shifts towards lower temperature with the Co doping.

Modifications in the structural and optical properties of 100 MeV Ni$^{7+}$ ions irradiated cobalt doped ZnO thin films ($\text{Zn}_{1-x}\text{Co}_x\text{O}$, $x = 0.05$) prepared by sol–gel route have been studied by S. Kumar et al. [127]. The films irradiated with a fluence of $1 \times 10^{13}$ ions/cm$^2$ were single phase and show improved crystalline structure with preferred c-axis orientation as revealed from XRD analysis. The spectrum shows no change in bonding structure of Zn–O after irradiation. Optical absorption spectra show an appreciable red shift in the band gap of irradiated $\text{Zn}_{1-x}\text{Co}_x\text{O}$ thin film due to sp–d interaction between Co$^{2+}$ ions and ZnO band electrons. Transmission spectra show absorption band edges at 1.8 eV, 2.05 eV and 2.18 eV corresponding to d–d transition of Co$^{2+}$ ions in tetrahedral field of ZnO. The AFM study shows a slight increase in grain size and surface roughness of the thin films after irradiation.

N.G. Deshpande et al. [128] reported the spray pyrolysis deposited ITO thin films were fabricated and irradiated using Au$^{8+}$ SHI (100MeV energy), at different fluency doses ranging between $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{13}$ ions/cm$^2$. After irradiation, significant changes have been observed in surface morphology and crystallographic structure pertaining to increase in grain size, change in surface roughness, crystallographic disorders of large crystallites, and noticed a net decrease in optical transmittance and electrical resistivity of these films.
M. G. Abraizov et al. [129] presented the effects of ion irradiation and irradiation alternated with heat treatment on the properties of 10%Fe-4%Ni-86%Si resistive alloy thin films manufactured by flash evaporation. It is shown that structural changes which occur in the films at an irradiation temperature of 573 K are similar to those which occur under heat treatment. The extrema which are absent on the dose vs. temperature coefficient of resistance curves are found on dose vs. resistance curves. The stability of the resistance and temperature coefficient of resistance of irradiated films depends on the dose and temperature of the irradiation. Alternation of irradiation and heat treatment causes a drop in resistance under irradiation and a rise in resistance under annealing. The electro-physical properties are influenced by the mode of deposition.
References:


Chapter-I  Introduction & Review of literature


