CHAPTER – IV

SUMMARY

AND

CONCLUSIONS
Currently transparent conducting oxides (TCO) are playing an important role in most of the optoelectronic applications. The TCOs are the materials which exhibit high optical transmittance in the visible region with high electrical conductivity. Several pure and doped TCOs have been found in various applications such as flat panel displays, solar cells, light emitting diodes, heat mirror coatings, gas sensors, liquid crystal displays, energy efficient windows, optical memories, electrochromic windows, ultrasonic oscillators, touch panels etc. Indium oxide (In$_2$O$_3$) is one of the promising TCOs which exhibit high transmittance (> 80%) and low electrical resistivity (< 2x10$^{-3}$ $\Omega$cm). The physical properties of the materials in thin film form mainly depend on the method of preparation and preparation parameters maintained during the film growth.

In the present investigation, thin films of pure In$_2$O$_3$ were prepared using flash evaporation and activated reactive evaporation methods by systematically controlling the deposition parameters such as substrate temperature, oxygen partial pressure. Then Mo-doped In$_2$O$_3$ thin films were prepared under various doping levels, substrate temperatures and oxygen partial pressures using activated reactive co-evaporation method. The quality and usefulness of the experimental films were studied by analyzing the chemical composition, structure, and surface morphology, electrical, optical and photoluminescence properties. The thickness of the films has been measured using the optical interference method. The composition of the films was estimated using the X-ray photoelectron spectroscopy (XPS). The structure, grain size and lattice parameters of the films have been analyzed by X-ray diffraction (XRD). The RMS roughness and surface morphology of the films were measured by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The electrical properties of the films were measured using the van der Pauw technique. The optical transmittance, absorption and reflectance of the films have been recorded using the double beam spectrophotometer.

**Indium oxide (In$_2$O$_3$) films**

In order to study the usefulness of deposition method, the In$_2$O$_3$ thin films have been prepared using flash evaporation method and studied the effect of substrate temperature on the structural, optical and electrical properties of the films. The substrate...
temperature of the films increased from 303 K to 673 K. The films were oriented along (321) plane and the intensity of the diffracted peaks increased with the increase of substrate temperature. The films were cubic bixbyite in structure and the lattice constant of the films decreased from 0.10 nm to 0.098 nm with the increase of substrate temperature from 373 K to 673 K. The grain size of the films increased from 18 nm to 48 nm with the increase of substrate temperature from 303 K to 573 K. The AFM data demonstrated that the In$_2$O$_3$ films were homogeneous and uniform with regard to surface topography. The films exhibited dense packing of fine grains at lower substrate temperatures and the grain size increased with increase of substrate temperature.

The electrical resistivity of the films decreased from $2.1 \times 10^3$ $\Omega$cm to $1.11 \times 10^3$ $\Omega$cm with the increase of substrate temperature from 373 K to 573 K. The Hall mobility of the films increased from 18 cm$^2$/V.sec to 49 cm$^2$/V.sec with increasing the substrate temperature from 373 K to 573 K. The carrier concentration of the films increased from $3.7 \times 10^{19}$ cm$^{-3}$ to $1.1 \times 10^{20}$ cm$^{-3}$ with increase of substrate temperature from 373 K to 573 K.

The optical transmittance of the films decreased from 94% to 82% with the increase of substrate temperature from 373 K to 573 K due to the scattering of light by the charge carriers. The optical band gap of the films decreased from 3.71 eV to 2.86 eV. The figure of merit of the films decreased from $6.1 \times 10^3$ $\Omega^{-1}$ to $0.2 \times 10^3$ $\Omega^{-1}$ with increasing substrate temperate from 373 K to 573 K.

In order to achieve more adherent and uniform films with high optical transmittance and low electrical resistivities at lower substrate temperatures, a novel activated reactive evaporation method have been applied in which the films can be prepared in the presence of high density plasma. The effects of substrate temperature and oxygen partial pressure have been studied on structural, optical and electrical properties of the films. The substrate temperature and oxygen partial pressure of the films varied from 303 K to 573 K and $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar.

The films deposited at room temperature showed amorphous nature and the crystallinity of the films increased with the increase of substrate temperature from 373 K.
to 573 K. The films were predominantly oriented along (222) plane. The mean grain size of the films increased from 53 nm to 69 nm and lattice constant of the films decreased from 1.016 nm to 1.012 nm with the increase of substrate temperature from 373 K to 573 K. From the XPS analysis it is found that the In 3d_{5/2}, In 3d_{3/2} and O 1s levels of In_{2}O_{3} were located at the binding energy of 444.37 eV, 452.1 eV and 530.12 eV. From the SEM images, it is observed that the nuclei grew larger with the increase of substrate temperature indicating that the grain size of the films is highly influenced by the substrate temperature.

The films showed the low optical transmittance of 55 % at the low substrate temperature of 303 K. As the substrate temperature increased from 373 K to 573 K, the transmittance of the films increased from 75 % to 85 %. The optical absorption coefficient was determined and it was in the range (1.1 - 0.65) x 10^{4} cm^{-1}. The optical band gap of the films increased from 3.56 eV to 3.64 eV with increase of substrate temperature from 373 K to 573 K.

It is observed that the electrical resistivity of the films decreased from 2.5x10^{-3} \Omega cm to 9.7x10^{-4} \Omega cm with the increase of substrate temperature from 373 K to 573 K. The Hall mobility of the films decreased from 25 cm^{2}/V.sec to 18 cm^{2}/V.sec with the increase of substrate temperature from 373 K to 573 K. The carrier concentration of the films increased from 9.9x10^{16} cm^{-3} to 2.5x10^{20} cm^{-3} with the increase of substrate temperature from 373 K to 573 K. The figure of merit of the films increased from 0.56x10^{3} \Omega^{-1} to 5.09x10^{3} \Omega^{-1} with the increase of substrate temperature from 373 K to 573 K.

The effect of oxygen partial pressure in the range, 5x10^{-4} mbar to 5x10^{-3} mbar, was studied on the structural, optical, electrical and photoluminescence properties of the films. The films exhibited nearly stoichiometry at higher oxygen partial pressures. The films formed at lower oxygen partial pressures exhibited indium diffraction peak at 2\theta = 33.1° along with In_{2}O_{3}. As the oxygen partial pressure increased, single phase In_{2}O_{3} polycrystalline films were observed and all the films were predominantly grown along (222) plane. The grain size of the films calculated for the films formed at various
oxygen partial pressures and it varied from 36 nm to 53 nm with the increase of oxygen partial pressure from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar. The lattice constant increased from 1.0108 nm to 1.0115 nm with the increase of oxygen partial pressure from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar. From the AFM measurement the average roughness of the films was found to be 1.7 nm.

The films formed at lower oxygen partial pressures exhibited very low transmittance of about 65% then it increased to 87% with increase of oxygen partial pressure from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar. The films exhibited a higher absorption coefficient ($1.7 \times 10^{4}$ cm$^{-1}$) at a lower oxygen partial pressure ($5 \times 10^{-4}$ mbar). Then it decreased to $0.55 \times 10^{4}$ cm$^{-1}$ at higher oxygen partial pressures ($5 \times 10^{-3}$ mbar).

As the oxygen partial pressure increased from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar, the electrical resistivity of the films increased from $0.82 \times 10^{3}$ $\Omega$cm to $1.8 \times 10^{3}$ $\Omega$cm. From the Hall measurement it is found that the films were n-type and the Hall mobility decreased from 24 cm$^{2}$/V.sec to 16.34 cm$^{2}$/V.sec with the increase of oxygen partial pressure from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar. As the oxygen partial pressure increased from $0.5 \times 10^{-3}$ mbar to $5 \times 10^{-3}$ mbar, carrier concentration of the films decreased from $3.1 \times 10^{20}$ cm$^{-3}$ to $2.1 \times 10^{20}$ cm$^{-3}$. The films formed at lower oxygen partial pressure ($5 \times 10^{-4}$ mbar) exhibited the figure of merit of $0.42 \times 10^{3}$ $\Omega^{-1}$ and then it increased to $3.45 \times 10^{3}$ $\Omega^{-1}$ at higher oxygen partial pressure ($5 \times 10^{-3}$ mbar).

Two distinct peaks in the photoluminescence (PL) spectrum were observed in blue region at 415 nm and 440 nm wavelengths under the excitation of 375 nm at room temperature and the intensity of the photoluminescence (PL) peaks increased with the increase of substrate temperature.

**Mo-doped indium oxide (IMO) films**

In order to decrease the electrical resistivity, molybdenum was doped into $\text{In}_2\text{O}_3$ matrix. The Mo-doped $\text{In}_2\text{O}_3$ thin films (IMO) have been prepared using a novel activated reactive evaporation method and studied the effect of molybdenum doping level, substrate temperature and oxygen partial pressure on the chemical, structural,
surface topography, optical, electrical and photoluminescence properties of the IMO films.

The effect of Mo-doping level, from 0 at.% to 5 at.% was studied on the physical properties of the films by keeping substrate temperature and oxygen partial pressures at 573 K, 2x10^{-3} mbar, respectively.

As Mo-doping level increased from 1 at.% to 3 at.%, the (222) plane grew more predominately and intensity of peaks increased with the increase of Mo-doping level upto 3 at.%. The diffracted peaks as labeled coincide with cubic In$_2$O$_3$ structure. The grain size of the films increased from 25 nm to 35 nm with the increase of Mo-doping level increased from 0 at.% to 3 at.%. The chemical compositions of the Mo, In and O of the samples were identified as 2.92, 37.50 and 59.58 at.%, respectively. From the SEM images, it was found that the films formed at 573 K exhibited uniform, large grains with an average grain size of 36 nm. From the AFM studies, it is found that the surface became larger and more uniform and surface roughness of the films also increased with the increase of doping level.

The pure In$_2$O$_3$ films exhibited an electrical resistivity of 9.7x10^{-4} Ωcm and then it decreased to a value of 5.2x10^{-4} Ωcm when Mo doping level increased from 1 at.% to 3 at.%. The films exhibited lowers carrier concentration of 2.5x10^{20} cm$^{-3}$ at 0 at. %, then it increased to 4.5x10^{20} cm$^{-3}$ when the Mo-doping level increased from 1 at.% to 3 at.%. An increase in Hall mobility from 25 cm$^2$/V.sec to 26.58 cm$^2$/V.sec was observed for the films deposited in the dopant concentration from 0 at. % to 3 at.%.

Pure In$_2$O$_3$ films exhibited an optical transmittance of only 85 % after which it increased to 90 % with the increase of Mo-doping level from 1 at.% to 3 at.%. As the Mo-doping level increased from 1 at.% to 3 at.%, the optical band gap of the films was increased to 3.68 eV. The figure of merit increased from 5.09x10^{-3} Ω^{-1} to 16x10^{-3} Ω^{-1} with the increase of Mo doping from 1 at.% to 3 at.%. The intensity of the photoluminescence (PL) emission peaks increased with the increase of Mo doping content from 1 at.% to 3 at.%, after which, it decreased.
The effect of substrate temperature was studied in the range, 303 K to 623 K by keeping the oxygen partial pressure and Mo-doping levels at $2 \times 10^3$ mbar and 3 at.%, respectively. For the samples prepared with 3 at.% of Mo-doping level and substrate temperature of 573 K, the crystal structure was identified as cubic with lattice constant 1.0114 nm. The (222) plane grew more predominantly than the (400) plane and intensity of the diffracted peak increased with the increase of the substrate temperature from 473 K to 573 K. The variation of grain size of the films increased from 18 nm to 35 nm with the increase of substrate temperature from 473 K to 573 K. The XPS studies revealed that the binding energies of In $3d_{5/2}$, In $3d_{3/2}$, Mo $3d_{5/2}$, Mo $3d_{3/2}$ and $O1s$ levels are 444.40 eV, 452.3 eV, 232.3 eV, 235.8 eV and 530.12 eV, respectively. The measured mean grain size (statistical analysis of more than 100 grains on SEM image) was found as 34 ± 5 nm. From the AFM analysis it was found that the films were smooth with a root mean square (rms) of 1.8 nm.

The optimum electrical properties were observed for the films deposited from the 3 at.% of Mo-doping level. The 3 at.% Mo-doped films on glass substrate have electrical resistivity $\rho = 5.2 \times 10^{-4}$ $\Omega$cm with carrier concentration $n = 4.5 \times 10^{20}$ cm$^{-3}$ and mobility $\mu = 26.58$ cm$^2$/V.sec. As the substrate temperature increased from 473 K to 573 K, the resistivity and carrier concentration increased to $5.2 \times 10^{-4}$ $\Omega$cm, $4.51 \times 10^{20}$ cm$^{-3}$, respectively.

The films formed at lower substrate temperatures (< 473 K) showed only 75 % of transmittance in visible region of the solar spectrum while the films formed at a substrate temperature (> 573 K) exhibited the transmittance of 90 %. A higher value of band gap 3.68 eV was observed for the films formed at 573 K. The figure of merit increased from $1.8 \times 10^{-3}$ $\Omega^{-1}$ to $16 \times 10^{-3}$ $\Omega^{-1}$ with the increase of substrate temperature from 473 K to 573, after which it decreased to $5 \times 10^{-3}$ $\Omega^{-1}$ at higher substrate temperatures ($T_s = 623$ K). The intensity of the photoluminescence (PL) emission peaks decreased with the increase of substrate temperature from 473 K to 623 K.

The effect of oxygen partial pressure, in the range, 5$\times$10$^{-4}$ mbar to 5$\times$10$^{-3}$ mbar, was studied on the physical properties of the films. Polycrystalline films with cubic
structure were formed at all partial pressures oriented along (222) and (400) planes. From the AFM measurements, it was observed that the average roughness of the films as 1.9 nm.

The films exhibited a minimum electrical resistivity of $3.8 \times 10^{-4} \ \Omega \text{cm}$ with poor optical transmittance (70%) at lower oxygen partial pressures ($5 \times 10^{-4}$ mbar) at a constant Mo-doping level of 3 at%.

The films formed at lower oxygen partial pressure ($5 \times 10^{-4}$ mbar) exhibited higher mobility of $34 \ \text{cm}^2/\text{V}.\text{sec}$, which then decreased to $24 \ \text{cm}^2/\text{V}.\text{sec}$ at higher oxygen partial pressure ($5 \times 10^{-3}$ mbar).

The films formed at lower oxygen partial pressure ($5 \times 10^{-4}$ mbar) exhibited poor optical transmittance (70%). At an optimum pressure of $2 \times 10^{-3}$ mbar, the films exhibited the highest transmittance of 90%, which may be due to complete oxidation of the films. The optical band gap ($E_g$) of IMO films was determined from optical absorption coefficient ($\alpha$) and incident photon energy ($h\nu$) and it increased from 3.66 eV to 3.7 eV with the increase of oxygen partial pressure from $5 \times 10^{-4}$ mbar to $5 \times 10^{-3}$ mbar. The photoluminescence (PL) characteristics of the samples are found to be strongly dependent on the oxygen partial pressure in which the intensity of the PL peaks increased with the increase of oxygen partial pressure. The figure of merit increased from $1.8 \times 10^{-3} \ \Omega^{-1}$ to $16 \times 10^{-3} \ \Omega^{-1}$ with the increase of oxygen partial pressure ($P_{O_2}$) from $5 \times 10^{-4}$ mbar to $2 \times 10^{-3}$ mbar.

**Conclusions**

Thin films of pure In$_2$O$_3$ were prepared on glass substrates using the flash evaporation and activated reactive evaporation methods under various substrates, oxygen partial pressures and doping levels. The XPS and XRD studies revealed that the films were nearly stoichiometric.

Pure In$_2$O$_3$ thin films were prepared using flash evaporation method at different substrate temperatures. The films exhibited a minimum electrical resistivity of $1.1 \times 10^{-3} \ \Omega \text{cm}$, optical transmittance of 68% with optical band gap 3.51 eV.
In order to achieve more adherent, uniform, pin hole free films with enhanced optoelectrical properties, the films were prepared using an activated reactive evaporation method at various substrate temperatures and oxygen partial pressures. The films formed at a substrate temperature of 573 K and oxygen partial pressure of \(2 \times 10^{-3}\) mbar were single phase, polycrystalline with cubic structure and exhibited high optical transmittance of 85% with low electrical resistivity of \(9.7 \times 10^{-4}\) Ωcm with optical band gap 3.64 eV.

In order to decrease the electrical resistivity further, Mo was doped into In\(_2\)O\(_3\) matrix. Mo-doped In\(_2\)O\(_3\) (IMO) films were prepared using activated reactive evaporation method on the glass substrates at various doping levels, oxygen partial pressures and substrate temperatures. The films formed at a Mo-doping level of 3 at.%, substrate temperature of 573 K and oxygen partial pressure of \(2 \times 10^{-3}\) mbar, exhibited an optical transmittance of 90% with a minimum resistivity of \(5.2 \times 10^{-4}\) Ωcm along with wide band gap 3.68 eV. A visible photoluminescence at 416 and 440 nm wavelength was observed at room temperature for pure and Mo-doped In\(_2\)O\(_3\) films.

Such films are highly useful in the fabrication of flat panel displays, liquid crystal displays and window layers in solar cells. A systematic study will be taken in future for the effective utilization of these films in device applications.