Chapter 3

Novel method for enhancing the electrical conductivity of ZnO thin film

3.1 Strategies to enhance the conductivity of ZnO thin film

3.1.1 Doping

Doping of ZnO films not only improves their electrical and optical properties, but also makes them highly stable. High quality Gallium doped Zinc Oxide (GZO) films were deposited quartz glass substrate using PLD itself [1]. The film formed at substrate temperature of 300°C showed electrical resistivity of 8.25×10^{-5} ohm cm, carrier concentration of 1.46 ×10^{22} cm^{-3} and carrier mobility of 30.96 cm²/Vs at an oxygen pressure of 0.67Pa. T. Prasada Rao et al.[2] discussed the structural, electrical and optical properties of the transparent conducting GZO prepared using spray pyrolysis; the film had lowest resistivity of 6.8×10^{-3} Ohm cm. Saraswathy et al. [3] deposited ZnO and Indium doped ZnO (IZO) with different indium composition on corning glass substrate. Resistivity decreased initially with doping concentration and subsequently increased. IZO with 1% showed the lowest resistivity 2.41×10^{-2} Ohm cm. Lokhande et al. [4] discussed the structural, optical and electrical studies on highly oriented (along 100 plane) sprayed ZnO film. Resistivity of the film at room temperature was 10^{-1} ohm cm. In one report, it was reported that transparent conducting IZO films were prepared on soda-lime glass substrate having resistivity of 3×10^{-3} ohm cm and transmittance of 80% [5].

A. Suzuki et al. [6] deposited Al doped ZnO (AZO) using PLD, having resistivity of 1.4×10^{-4} ohm cm and average transmittance of 90%. In another report, on AZO films studies on the effect of variation of Al content in the film was reported. Here-lowest resistivity of 8.54 ×10^{-4} ohm cm and average transmittance of >88% were obtained for the best film [7]. Magnetron Sputtering was used to deposit transparent conducting AZO. The lowest resistivity obtained in this work was 4.6×10^{-4} ohm cm with average transmittance of 90% in the visible range and sheet resistance of 32 ohms for samples deposited at 250°C and 0.8 Pa [8]. In another report, it was shown that the electrical resistivity of the AZO thin film
decreased after H\textsubscript{2} plasma treatment; the resistivity decreased from 1.23\times10^{-3} ohm cm to 8.23\times10^{-4} ohm cm and average optical transmittance in the visible region increased slightly from 89.5\% to 91.7\% \cite{9}. Y. Igasaki and H. Kanma prepared AZO films on amorphous substrate, [heated up to 200\(^\circ\)C with rf power of 100W] using rf magnetron sputtering from a ZnO target mixed with Al\textsubscript{2}O\textsubscript{3} of 2wt\% \cite{10}. Resistivity of the film deposited at argon gas pressure of 0.31Pa was \sim 2.5\times10^{-4} Ohm cm.

AZO films were also deposited using electron beam evaporation technique \cite{11}. Transmittance measurement showed that the best optical and structural properties were achieved for samples deposited at 200\(^\circ\)C. Electrical resistivity was 2.5\times10^{-4} ohm cm. AZO films were prepared using RF Plasma evaporation \cite{12} and the influence of the O\textsubscript{2} flow rate and Zn concentration on the properties of the film was investigated. Electrical resistivity decreased with decreasing O\textsubscript{2} flow rate and minimum resistivity of 9\times10^{-4} Ohm cm was obtained at O\textsubscript{2} flow rate of 30ml/min, which corresponds to a ratio of 0.069 \% of total gas flow rate.L.Dghoughi et al. \cite{13} prepared AZO films again using spray pyrolysis on glass substrate at 450\(^\circ\)C using anhydrous Zinc Chloride(ZnCl\textsubscript{2}) and Aluminum Chloride (AlCl\textsubscript{3}). Film had minimum resistivity of 1.4\times10^{-3} ohm cm. C. M. Muiva et al. achieved \cite{14} the lowest resistivity of 2\times10^{-2} ohm cm and high transmittance of over 85\% at 550 nm. Doping percentage of the films was 2at\% of Al.

3.1.2 Post deposition treatment

Influence of substrate temperature and post deposition treatment on the properties of AZO films prepared using PLD technique, was also reported \cite{15}. The experiment result showed that when deposited at 240\(^\circ\)C, resistivity of the film was 6.1\times10^{-4} ohm cm which was further reduced to 4.7 \times10^{-4} ohm cm, by post deposition annealing at 673K, for 2 hours in argon atmosphere. M.de la L.Olevera et al discussed the structural, electrical and optical properties of ZnO film using different dopant like Gallium, Aluminium and Indium \cite{16}. The best electrical property was observed in the thickest sample doped with indium. Lowest electrical resistivity was of the order of 10^{-3} ohm cm. Here Major et al. also reported the deposition of low resistive ZnO films doped with indium \cite{17}. Spray pyrolysis technique has been used for the deposition and they could attain a resistivity of 8 to 9 \times 10^{-4} ohm cm.

Another study of the effect of annealing of AZO films revealed that minimum electrical resistivity [1.7\times10^{-2} ohm cm] was obtained for the sample containing 3 at\% of Al.
and which had undergone annealing at 500°C in nitrogen with 5% hydrogen [18]. P. Nunes et al. [19] reported the effect of annealing treatment on the performance of IZO samples prepared using spray pyrolysis. The most significant improvement was obtained after annealing in ‘forming gas’ at 200°C for 2 hrs. These samples exhibited resistivity of 5.2×10⁻² ohm cm and high transmittance (T=86%). ZnO were also prepared with the help of Ultrasonic Spray Pyrolysis on indium films [deposited using evaporation] and subsequently subjected to rapid thermal annealing (RTA) in air or vacuum [20]. The resistivity of these samples was 2×10⁻³ ohm cm.

Influence of post deposition annealing on structural and optical properties of RF sputtered [insulating] ZnO films has been investigated by Gupta et al. [21]. The ‘as grown’ films, deposited on quartz substrates, were highly c-axis oriented. These films became almost stress free after a post deposition annealing at 673K for 1 hr in air. Above 673K, a process of coalescence was taking place which caused major grain growth resulting in ‘microcracks’ formation and surface roughness. Grain size increased drastically [from ~18 nm to ~28 nm] with the increase in annealing temperature above 673 K. Studies using SEM showed that ‘as- grown’ films were columnar in nature. All the film exhibited high transmittance (>75%) in visible region with fundamental absorption edge at about 0.38µm. Aghamalyan et al [22] investigated effect of post deposition annealing in air on the physical properties of ZnO thin films, deposited on sapphire substrates using electron beam evaporation technique. The increase of intensity and decrease of FWHM of the diffraction peak (002) with annealing treatment are related to the improvement of crystal quality of ZnO films after annealing. The unannealed samples have very low resistivity of about 10⁻² Ω cm. After annealing, electrical resistivity of the films increased from 10⁻² to 36 Ω cm.

Effect of thermal annealing [in different ambient conditions] on structural and optoelectrical properties of ZnO thin films deposited using sol-gel technique were also studied [23]. The samples were annealed in nitrogen, vacuum and open air. The highest carrier concentration was observed for the film annealed at 500°C for nitrogen and vacuum. The lowest resistivity measured in this study was 2.25×10⁻⁴ Ω cm only in the case of vacuum annealed samples. Interestingly samples annealed in nitrogen, vacuum and air, were highly transparent in the visible region. Properties of ZnO films were investigated as the function of annealing temperature in H₂/Ar and vacuum. Resistivity and mobility of ZnO films
decreased with increase of annealing temperature in vacuum and H$_2$/Ar ambient. Resistivity of the films annealed [at 300 °C] in H$_2$/Ar and vacuum ambient was $\approx$2186 Ω cm and $\approx$ 798 Ω cm respectively, while annealing in vacuum and H$_2$/Ar ambient [at 600 °C] resulted in resistivities of $\approx$0.040 Ω cm and $\approx$0.035 Ω cm, respectively. Average optical transmission was >82% and an orientation of the samples was [0 0 2] for all annealed in vacuum and H$_2$/Ar ambient [24]. Various stages have been employed to increase the mobility of TCO film while maintaining high transparency and conductivity as reviewed by Exarhos and Zhous[25].

In yet another paper, the effect of thermal annealing of ZnO thin film in N$_2$ or O$_2$ atmosphere and their effects were studied [26]. Electron density increased due to annealing in N$_2$ atmosphere. But optical properties are improved when annealed in O$_2$ atmosphere at lower temperature. Crystallinity also improves with the annealing. Mobility of the film increased up to 51 cm$^2$/V s as annealing temperature increased; but it is low at lower temperatures.

Effects of Al doping and an annealing treatment on electrical and optical properties of ZnO thin films were studied [27]. Here Zinc acetate dihydrate, 2-methoxyethanol were used as the precursor solution and aluminium chloride was used as the dopant material. Electrical conductivity of ZnO films was improved by Al doping and by annealing in a reducing atmosphere. Minimum electrical resistivity was obtained for the doping concentration of 3 at.% Al-doped film, annealed at 500 °C in nitrogen with 5% hydrogen and its value was $1.71 \times 10^{-2}$ Ω cm. Optical transmission was higher than 80% in the visible range. Musat et al. reported [28] the effect of post-deposition heating temperature and atmosphere on the electrical and optical properties of ZnO: Al thin films, prepared using sol-gel method. For the film doped with 2 wt% Al, the resistivity of $2.9 \times 10^{-3}$ Ω cm has been achieved after annealing under reducing atmosphere of forming gas. The optical transmission spectra of post – heated and annealed film showed a good transmittance within visible wavelength region.

Post deposition treatment in vacuum or in other ambient conditions can be used to improve the properties of films, which is due to the following reasons. 1) Recrystallization of the amorphous portions of the film. 2) Reorientation of existing crystallites 3) Chemisorption
/ desorption of oxygen at the grain boundaries. The conductivity of the film enhanced after the post deposition treatment of the film.

3.2 Experimental details

3.2.1 Chemical Spray Pyrolysis (CSP)

[CSP] technique is based on the pyrolytic decomposition of a metallic compound dissolved in a liquid mixture when it is sprayed onto a preheated substrate. Typical CSP equipment consists of an atomizer, substrate heater, temperature controller and solution container. Additional features of like solution flow rate control, improvement of atomization using electrostatic spray or ultrasonic nebulisation can be incorporated into this basic system to improve the quality of the films. To achieve uniform large area deposition, arrangements for moving either nozzle or substrate or both are used. The schematic diagram of typical spray unit is given below. The atomization of chemical solution into spray of fine droplets is accomplished through spray nozzle with the help of filtered carrier gas.

Due to simplicity of the apparatus and good repeatability of this technique on a large area, it has already become most attractive technique to produce thin films of oxides and sulfides of metals, binary / ternary / quaternary compound semiconductors and superconducting compounds. In addition to its simplicity CSP has a number of advantages; for example it offers an enormously easy way to dope films with any element in any proportion [by just diluting the solution we can go even to concentration which cannot be weighed] which help us to change structural, optical and electrical properties.
Fig 3.1. Schematic Diagram of chemical spray pyrolysis unit

ZnO thin films can be deposited on soda-lime glass substrates using CSP technique. Spray solution is prepared by dissolving Zn (CH$_3$COO)$_2$.2 H$_2$O in the solvent usually deionized water (1:1 volume ratio). This salt of Zn is used due to its high vapour pressure at low temperature. Molarity of this solution can be as low as 0.3M. A few drops of acetic acid are to be added to the aqueous solution to prevent the formation of hydroxides. Substrate temperature is usually around 450 to 500 $^\circ$C and movement of the spray head is required for uniformity of film. [29]. Air can be directly compressed from the atmosphere; filters are used to remove water vapour and oil particles in order to avoid contamination. Pressure of the gas fed into the nozzle has to be measured using the mechanical gauge and the pressure can be varied in the range 0-100 psi. The carrier gas pressure and nozzle to substrate distance are held constant. Through this arrangement it is possible to have consistency in the results as well as large area deposition.

The formation of ZnO thin film given by the following equations [30]
3.2.2 An innovative and original post deposition treatment (Zero- Energy Process) for obtaining low resistive films from CSP technique

Usually in CSP technique, the thin film samples after deposition are left for cooling. It takes about an hour for the samples to come down to room temperature and during this time sample is in open atmosphere with the film surface facing the air. In the case of ZnO films the deposition temperature is of the order of \(~500^\circ C\) and there is every chance that oxygen from air will be getting into the films at this high temperature. Unfortunately diffusion of oxygen into the ZnO film will be very much detrimental as far as its electrical properties are concerned. This is because, in order to have highly conducting ZnO films, there should be excess of zinc atoms or oxygen vacancies in the sample and diffusion of oxygen into the film during cooling will naturally damage this condition. For rectifying this we should anneal the ZnO samples in high vacuum for long time-say one hour. But this process is again energy consuming and is not preferred by industries where they require a process which can be easily adapted for the ‘production line’. Hence it was felt that during the cooling time, a different process should be incorporated so that the film surface should not come into contact with air.

After the deposition of the ZnO films using CSP technique, the film is kept in the open atmosphere for cooling. It was felt that the cooling of the samples in open atmosphere just after deposition may enhance incorporation of oxygen in the film. Quenching the sample after spraying can reduce the oxygen adsorption. If we avoid air contact while cooling, it can decrease the oxygen adsorption. After the deposition, the samples were quickly removed from the hot plate using a mechanical holder and placed on a plane surface, which is kept at room temperature. In this process the sample was cooled with zinc oxide film surface kept open to the atmosphere. Another set of the samples were prepared and cooled with the film surface in direct contact with the surface of the “base material”.

\[
\begin{align*}
Zn(CH_3COO)_2 & \xrightarrow{\text{Heat}} 4Zn(CH_3COO)_2 + H_2O \xrightarrow{\text{Adsorption}} 4ZnO \ (\text{Film}) + 6CH_3COOH \ (\text{Gas}) \\
Zn_4O(CH_3COO)_6 & \xrightarrow{\text{Adsorb/substr}} \xrightarrow{\text{Solid near substrate}} Zn_4O(CH_3COO)_6
\end{align*}
\]
The former set of samples were named as ‘zinc oxide-regular cooling (Z-R)’ and the latter as ‘zinc oxide-inversion cooling (Z-I)’ respectively.

<table>
<thead>
<tr>
<th>No</th>
<th>Base material</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Metal Sheet</td>
<td>Glass breaks</td>
</tr>
<tr>
<td>2</td>
<td>Cardboard</td>
<td>Carbon adsorbed to the surface</td>
</tr>
<tr>
<td>3</td>
<td>Thick Chart paper</td>
<td>Air expansion make the base Zig-Zag</td>
</tr>
<tr>
<td>4</td>
<td>New wood Material</td>
<td>Uniform Thickness of the film</td>
</tr>
</tbody>
</table>

Table 3.1. Different base materials used for post deposition cooling of ZnO thin film.

We used different base materials for the standardisation of the method and also for the obtaining of good film. Table 3.1 gives the results from the different base materials used for the post deposition cooling. After all these trials, “New wood” was found to be the best base material for the ‘inverting the process’. This made the cooling process carried out keeping ZnO film surface in isolation from air atmosphere through a non-vacuum process. This process is relatively “environmental friendly” and is quite useful for large area samples. Moreover, this can be easily incorporated into the production line in any large scale unit. Thus it is a ‘zero-energy process’ and requires no additional cost.

3.3 Results and discussion

3.3.1 Structural Studies

XRD technique was used here to study the structural changes of the samples taking place after the ‘zero-energy process’. XRD is an extremely important technique in the field of material characterization especially to distinguish between crystalline and non-crystalline (amorphous) materials. It can be also used to determine the phase content in many minerals and materials. It requires no elaborate sample preparation and is essentially non-destructive. Generally, it gives whole range of information about the crystal structure, orientation, crystallite size, composition (with the help of standards), defects and stresses in thin films. Experimentally obtained diffraction pattern of the sample is compared with ‘Joint Council Powder Diffraction (JCPDS)’ data for Standards. This gives information of different crystallographic phases, the relative abundance and preferred orientations. From the width of the diffraction peak, average grain size in the film can also be estimated.
Inter-planar spacing \( d \) was calculated from the X-ray diffraction profiles using the formula,

\[
2d \sin \theta = n\lambda 
\]

where \( \theta \) is the Bragg angle, \( n \) is the order of the spectrum and \( \lambda \) is the wavelength of X-rays. Using the \( d \)-values the set of lattice planes \((h k l)\) were identified from the standard data and the lattice parameters were calculated using the following relations.

For the tetragonal systems,

\[
\frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \quad \text{................................ (3.2)}
\]

and for hexagonal systems,

\[
\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad \text{........................... (3.3)}
\]

where \( a \) and \( c \) are lattice parameters. The grain size \( (D) \) can be evaluated using Scherrer’s formula,

\[
D = \frac{k\lambda}{\beta \cos \theta} \quad \text{............................................ (3.4)}
\]

where \( k \) is a constant which is nearly equal to one and \( \beta \) is the “Full Width at Half Maximum (FWHM)”, usually measured in radians.

In the present study, XRD analysis was done using Rigaku (D.Max.C) X-Ray Diffractometer, with Cu K\(_\alpha\) (\( \lambda = 1.5405 \) Å) radiation and a Ni filter operated at 30 kV and 20 mA. X-ray diffraction pattern of the sample Z-R and Z-I are depicted in the Fig.3.2. Both the films are polycrystalline having hexagonal wurtzite structure (\( a=3.250, c=5.206\) Å), with peaks appearing at \( 2\theta = 31.62^0, 34.42^0, 36.25^0 \) corresponding to (100), (002) and (101), orientations respectively [JCPDS data card (36-1451)]. When the (002) plane is dominant in the XRD pattern, axis is mainly found to be perpendicular to the surface of the film. The 2-dimensional zinc atom population is highest in the (002) plane of the wurtzite structure [31].
3.3.2 X-ray Photoelectron Spectroscopy (XPS)

‘X-ray photoelectron spectroscopy (XPS)’ which is also called ‘Electron Spectroscopy for Chemical Analysis (ESCA)’ is the technique that uses x-rays to knock electrons out of shells / orbitals. The kinetic energy ($E_k$) of these photoelectrons is determined from the experiment; as the energy of the x-ray radiation ($h\nu$) is already known, the electron binding energy ($E_b$) can be calculated as,

$$E_k = h\nu - E_b \quad \text{(3.5)}$$

The electron binding energies are dependent on the chemical environment of the atom. XPS is therefore useful to identify the oxidation and / or compound state of an atom. Binding energy of the valance electrons is affected by the chemical environment of the atom. When atomic environment of an atom changes, it alters the local charges surrounding the atom. This charge, in turn, reflects itself as a variation in the binding energy of the valence electrons of the atom. Thus binding energies of valence electrons experience a characteristic shift and this can give important information regarding the valence states/compound formation of the atoms in the sample and one can use this technique to find out whether an element present in a sample is in pure or in compound form. XPS technique is generally a surface analysis technique. However, with facility for physically etching using
sputtering technique, ‘depth profile’ is also achieved. In XPS spectra, ‘intensity’ [or ‘count’] of the emitted photoelectron signal is plotted as a spectrum of binding energies.

Fig. 3.3 XPS of the sample (a) Z-I (b) Z-R

Depth profiling of samples Z-I and Z-R were carried out in the XPS analysis and the results are depicted in Fig. 3.3(a) & 3.3(b) respectively. XPS spectra of the sample were recorded using an ULVAC-PHI unit (model: ESCA 5600 CIM) employing argon ion sputtering (Voltage=3kV, Raster size=3×3 mm², pressure 10⁻⁸ m bar). Al Kα X-ray (1486.6eV) with a beam diameter of 0.8mm and power of 400 W was used as the incident beam. Bottom portion of the figures [near the X-axis] gives the results from surface of the films and the top portion gives results from the substrate-film interface. From the depth profile analysis, one gets details on the variation of atomic percentage as well as atomic states of Zn and O along the thickness of the sample.
A very clear and interesting observation is that when the samples were cooled in the ‘inversion process’ concentration of oxygen incorporated into the sample decreased considerably and this occurs along the whole thickness of the sample. Similar results have been observed in vacuum annealed ZnO samples [32]. This proves beyond doubt that the new process of cooling the sprayed samples is just equivalent to vacuum annealing.

Binding energy values are clearly indicating the formation of zinc oxide (1022.95 eV for Zn3p3/2 and 531.02 eV for O1s) only even on the surface which is in contact with the ‘base material’. Atomic concentrations of zinc and oxygen were determined for the Z-R and Z-I films (Fig 3.4 (a) & 3.4 (b)). In the case of Z-R, atomic concentrations of Zn and O are not having uniform distribution throughout the thickness of the sample. At the surface of the film, the atomic concentration of zinc is lower as compared to that of oxygen and probably due to this layer, the resistivity of this sample is found to be high. Interestingly towards the interior of the sample [i.e., after sputtering out the sample for 20 min], atomic concentration of zinc [~ 55%] was higher than that of oxygen [~45%]. This is because in this cooling process, incorporation of oxygen from the atmosphere is rather easy in the surface layers of the film and this diffusion goes up to one-fourth of the sample thickness.
[i.e. up about 120 nm]. Near the surface of the Z-R sample, [i.e. after sputtering out for ~10 min] the Zn/O ratio was 0.72 while in the depth of the sample [i.e. for sputtering time > 20 min], the Zn/O ratio was 1.71. Thus the Zn/O ratio varied from 0.72 to 1.71 from the surface to the depth of the sample which is not desirable for good electrical properties. But in the case of films which have undergone inversion cooling (Z-I), atomic concentration of zinc was found to be 62% and that of oxygen 35% (Zn/O ratio - 1.77) throughout the whole thickness of the samples. The large decrease in the resistivity of the Z-I samples might be due to the reduction of oxygen concentration in the film [33].

The XPS depth profile study also proved that there is no diffusion of sodium in to the samples from the soda glass substrates even though the ZnO films were deposited at high temperature (Fig 3.3(a) and 3.3 (b)).

3.3.3 Scanning Electron Microscopy (SEM)

SEM is one of the most useful and versatile instruments for the investigation of surface topography, microstructure features, etc. The principle involved in imaging is to make use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the specimen. The electrons are produced by a thermal emission source, such as heated tungsten filament, or by using field emission cathode. To create SEM image, the incident electron beam is scanned in a raster pattern across the sample surface. Secondary electrons are produced due to the interaction of the primary electron beam. The emitted electrons are detected at each position in the scanned area by an electron detector. Intensity of the emitted electron signal is displayed as brightness on a cathode ray tube. There are two modes of imaging- one is by using Secondary Electrons and the other is by using Backscattering Electrons. Secondary electron imaging provides high resolution imaging of fine surface morphology and for this the samples must be electrically conductive. From the scanning electron microscopic analysis it was found that the crystallite size of the sample increased after the inversion process (Fig.3.5).
Fig. 3.5 SEM micrograph of Z-R and Z-I samples

3.3.4 Stylus profilometer

Thickness of the films measured using stylus profilometer (Dektak 6 M). This instrument takes measurements electro-mechanically, by moving the sample beneath a diamond tipped stylus. The stylus is mechanically coupled to the core of an LVDT (Linear Variable Differential Transformer). The high precision stage moves the sample beneath the stylus according to the user programmed scan length, speed and stylus force. As the stage moves with the sample, the stylus rides over the sample surface. Surface variation causes the stylus to be translated vertically. Electrical signal corresponding to the stylus movement are produced as the core position of the LDVT changes. The LDVT scales an AC reference signal proportional to the position change, which in turn, is conditioned and converted to digital format through a high precision, integrating, analogue to digital converter.

Fig. 3.6 given below shows the thickness data plot of Z-I samples deposited over an area, 30cm$^2$. Thickness was measured from thirty points using thickness profiler and surface mapping was done. It is observed that the thickness variations are prominent only at the edges and the variation is just 10%. Major portion (80% of the sample area) of the film has thickness within the range of 535 nm.
Fig. 3.6 Two dimensional surface mapping of Z-I sample thickness (nano meter scale) over an area of 6 cm ×5 cm.

3.3.5 UV- Vis- NIR Spectroscopy

The most direct and probably the simplest method for determining the band structure of semiconductors is by measuring the optical absorption spectrum. Absorption is expressed in terms of a coefficient ($\alpha h\nu$), which is related to the energy gap $E_g$ according to the equation,

$$\alpha h\nu = A(h\nu - E_g)^n$$ ............................ (3.6)

where $A$ is a constant, $h$ is the Plank’s constant, $\nu$ the frequency of the incident beam and $n$ is equal to $\frac{1}{2}$ for a direct gap and 2 for an indirect gap.

Fig.3.7 ($\alpha h\nu)^2$ vs. $h\nu$ plot of Z-R and Z-I samples
Absorption and transmission spectra of all the samples were recorded using UV-Vis -NIR spectrophotometer (JASCO -V-570 model). Optical band gap was determined using the \( (\alpha h\nu)^2 \) versus \( h\nu \) plot by extrapolating the linear portion of the curve to \( h\nu \) axis. Practically there is no variation of the band gap after the ‘inversion process (Fig.3.7).

Optical transmission spectra were recorded for both samples in the wavelength range 200 – 1200 nm (Fig.3.8). Interestingly the percentage of transmission increased in the visible range, after the inversion process. Interference fringe like pattern of transmittance curve established the smooth reflecting nature of the film.

![Transmission curves for Z-R and Z-I samples](image)

Fig.3.8 Transmission curves for Z-R and Z-I samples

### 3.3.6 Photoluminescence (PL)

PL measurement is a standard technique to observe defects and impurities in semiconductors. Study of luminescence processes can, not only show the content as well as the behaviour of the defects and impurities in semiconductors, but also can give information on different paths for the radiative recombination. The PL spectrum and its dependence on the irradiation intensity and device temperature can deliver important information for the device characterisation.
PL spectra can be used to determine the band gap energy as well as the energy levels of different defect levels in the band gap region. Hence it can be used for determining the impurity levels and/or activation energy of impurity levels and to study the radiative recombination taking place in semiconductors. Photoluminescence in solids can be classified according to the nature of the electronic transitions producing it. We can have mainly intrinsic and extrinsic emissions. Intrinsic luminescence is further divided into band to band luminescence, exciton luminescence and cross luminescence. In ‘band-to-band luminescence’, the emission occurs when an electron in the conduction band recombines with a hole in the valence band. This emission can be observed in very pure crystal at higher temperatures while at lower temperature this gets transformed into ‘exciton luminescence’. If there are some impurities having their levels in the forbidden gap, electrons or holes are trapped by them and these recombine with each other via such levels, either radiatively or nonradiatively. ‘Cross luminescence’ is usually observed in alkaline and alkaline earth halides. Luminescence caused by intentionally incorporated impurities (in most cases metallic impurities) is classified as “extrinsic luminescence”. In semiconductors, most important impurities are donors and acceptors that control semiconductor property and these can also act as luminescence activators.

In the present work, the PL studies were performed using 325 nm line of Kimmon He-Cd laser [output power of 20mW] as the excitation wavelength and the emissions were analyzed with the help of Ocean Optics [USB 2000] spectrophotometer.

Fig.3.9 Room temperature PL spectra of Z-I and Z-R samples.
Photoluminescence properties depend on the growth conditions including temperature and ambient. In our case the growth temperature was kept constant. The only important parameter here is the ambient condition. In CSP technique, there is strong possibility of samples becoming O-rich as oxygen can easily get incorporated in the sample from the atmosphere. The PL spectra of ZnO have both UV and blue-green emission (Fig.3.8). The green emission is located at ~2.38 eV. In the case of ZnO, majority donors are ‘oxygen vacancy’ \([V_o]\) and zinc interstitial \((Z_{ni})\). When the sample is kept in the open atmosphere, the oxygen concentration related to Zn-O bonding increases, reducing concentration of oxygen vacancies. Hence it is rather easy to have higher concentration of Oxygen antisite \((O_{zn})\) because the Oxygen antisite has relatively low formation energy [34]. In CSP method, air is used as the carrier gas and hence the concentration of oxygen antisite in ZnO prepared using this technique is higher in comparison with samples prepared using other techniques. This results in an intense PL emission due to the transition from the conduction band to antisite oxide \((O_{zn})\) [35] and this is the blue-green emission, centred around 503 nm. Interestingly the intensity of this emission is very low in the samples which have undergone the “Inversion” process while the ‘near band edge’ emission [in the UV region] is higher in these samples. It had been reported that the blue-green emission is due to the transition from conduction band to the acceptor level corresponding to the oxygen antisite\([O_{Zn}]\) [36]. Hence it becomes evident that the newly introduced ‘cooling under inversion process’, reduces the density of the levels due to the antisite of oxygen is considerably.

### 3.3.7 Electrical properties

The resistivity of some of the ZnO films was determined using the ‘two probe’ method with the electrodes in planar geometry. Electrical measurements were done after giving electrical contacts using silver paint in the form of two end contacts, having a distance of 1cm between them. In this study, the sheet resistance was calculated by the following equation,

If \(l\) and \(b\) are the length and breadth of a rectangular film between the two electrodes and \(t\) is its thickness then sheet resistance is given by the equation,

\[
R_s = \frac{\rho l}{bt}
\]

Where \(\rho\) is the resistivity in Ohm cm.
If we measure l=b
\[ \rho = R \frac{b}{l} \]
\[ \rho/t = R_s \]

Rs- Sheet resistance, which is expressed in Ohm per square is given by the above equation

Then resistivity can be calculated as,
\[ \rho = R_s d \]  \hspace{1cm} (3.7)

Electrical resistivity values of these two samples are given in the Table. 3.2. The conductivity enhanced by 3 orders of magnitude after the “Inversion- cooling” and the significant enhancement in the electrical conductivity might be due to the increase in the Zn/O ratio after the ‘cooling through inversion’ process.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-R</td>
<td>80</td>
</tr>
<tr>
<td>Z-I</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table.3.2 Resistivity variation of Z-R and Z-I

3.4 Effect of vacuum annealing

In the present study, both Z-R and Z-I films were annealed at 450°C for 2h in vacuum (2×10^{-5} m bar) and samples named as Z-R-A and Z-I-A respectively.

3.4.1 Result and discussion

X-ray diffraction patterns of the Z-R-A and Z-I-A are shown in the Fig 3.10. Both the films are polycrystalline having hexagonal wurtzite structure (a=3.250, c=5.206Å), with peaks appearing at 2θ= 34.42° corresponding to (002) orientation [JCPDS data card (36-1451)]. Among the two types of samples, Z-R-A film was higher intensity peak of (002) plane than Z-I-A.
Fig. 3.10 XRD patterns of Z-I-A and Z-R-A.

Fig. 3.11 \((\alpha h)^2\) vs. \(h\nu\) plot of Z-R-A.
Optical band gap was determined [using the \((\alpha h\nu)^2\) versus \(h\nu\) plot] for the Z-R-A and Z-I-A samples. There is not much variation in the band gap after the vacuum annealing (Fig.3.11). Transmission of both the sets of samples increased after the vacuum annealing. Fig 3.12 shows transmission curve of Z-I-A and Z-R-A. Resistivity of Z-R-A decreased from 80\(\Omega\) cm to 1.8\(\times10^{-2}\) \(\Omega\) cm. But for Z-I-A sample, there is only insignificant decrease of resistivity [from 2\(\times10^{-2}\) \(\Omega\) cm to 1.5\(\times10^{-2}\) \(\Omega\) cm]. In the case of Z-R samples, after the deposition the film was kept open to the oxygen rich condition. Hence films have absorbed more oxygen atoms during the cooling process. When these samples were annealed in vacuum, desorption of oxygen occurs leading to the annihilation of oxygen acceptor states at the grain boundaries. So there is a drastic decrease of resistivity of the film [37]. Now in the case of Z-I, these are quickly removed from the hot plate and the process of ‘Inversion cooling ‘is carried out. This process actually isolates the sample from atmospheric oxygen leading to lesser chance of oxygen being incorporated in the film. Further annealing this sample in vacuum condition, only causes the release of remaining few adsorbed oxygen within the film thereby causing a small decrease in resistivity. From the
present electrical study it is clear that the inversion process is one of the best alternatives of vacuum annealing and is very suitable for large area deposition of the samples.

3.5 Conclusions

The newly introduced process of ‘cooling under inversion’ for ZnO films deposited using CSP technique is capable of reducing resistivity of the ZnO samples by three orders [i.e., from $10^1$ to $10^2$ Ohm.cm] and is a “zero-energy process” as it does not require any external energy supply. Hence it becomes much useful in industrial applications. The process could also enhance the crystallinity and the optical transmittance. X-ray photo-electron spectroscopy analysis showed that Zn/O ratio increased after inversion and is uniform throughout the thickness of the samples. Room temperature photoluminescence revealed that the intensity of the blue-green emission decreased considerably, indicating the reduction of Oxygen antisite defects. Vacuum annealing does not bring any change in electrical properties of Z-I samples. Thus the process resulted in samples of high electrical conductivity and optical transmission avoiding the post deposition [and energy consuming] processes like vacuum annealing.

References

[8] En-Gang Fu, Da-Ming Zhuang, Gong Zhang, Zhao Ming, Wei-Fang Yang and Jia-Juan
Chapter 3

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