Chapter 2
Zinc Oxide thin film and its applications

2.1 Introduction

Zinc Oxide is a II-VI compound semiconductor. Most of the group II-VI binary compound semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite (Wz) structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa. This tetrahedral coordination is typical of sp$^3$ covalent bonding nature; but these materials also have substantial ionic character that tends to increase the band gap beyond the one expected from the covalent bonding. ZnO is a compound semiconductor whose ‘ionicity’ resides at the borderline between the covalent and ionic semiconductors. The crystal structures shared by ZnO are wurtzite (B4), zinc blende (B3), and rock salt (or Rochelle salt) (B1) as schematically shown in Fig. 1. At Room temperature, thermodynamically stable phase is wurtzite. The zinc-blende structure can be stabilized only by the growth on cubic structure while rock salt (NaCl) structure may be obtained at relatively high pressure.

Fig.1. ‘Stick and ball’ representation of ZnO crystal structures: (a) cubic rock salt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). The shaded gray and black spheres denote Zn and O atoms, respectively.
Wurtzite structure has hexagonal unit cell with two lattice parameters $a$ and $c$ in the ratio of $c/a=1.66$. The structure is composed of two interpenetrating hexagonal-close-packed (hcp) sub lattices, each of which consists of one type atom displaced with respect to each other along the three fold $c$-axis by the amount of $u=3/8=0.375$ (in ideal wurtzite structure) in fractional coordinate (the $u$ parameter is defined as length of the bond parallel to the $c$-axis, in unit of $c$). Each sub lattice includes four atoms per unit cell and every atom of one kind (group-II atom) is surrounded by four atoms of the other kind (group-VI) or vice versa, which are coordinated at the edges of a tetrahedron. In real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the $c/a$ ratio or the $u$ value.

2.2 Properties of ZnO

2.2.1 Direct and wide band gap

Band gap of ZnO is 3.44 eV at low temperature and 3.37 eV at room temperature [1]; for comparison, the respective values for wurtzite GaN are 3.50 eV and 3.44 eV [2]. This enhances applications in optoelectronics in the blue / UV region, including light-emitting diodes, laser diodes and photo detectors [3–7].

2.2.2 Large exciton binding energy

The free-exciton binding energy in ZnO is 60 meV [8, 9], compared with 25 meV in GaN [2]. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and higher. This makes ZnO a promising material for optical devices that are based on excitonic effects.

2.2.3 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 large electro-mechanical coupling in ZnO gives rise to strong piezoelectric and pyroelectric properties. Piezoelectric ZnO films, with uniform thickness and orientation, have been grown on a variety of substrates using different deposition techniques, including sol–gel process, spray pyrolysis, chemical vapour deposition, molecular-beam epitaxy and sputtering [10–17].

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2.2.4 Strong luminescence

Due to 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 which is broad [half-width of 0.4 eV] [18]. The n-type conductivity of ZnO makes it appropriate for applications in vacuum fluorescent displays and field emission displays. Origin of the luminescence center and luminescence mechanism is not really understood, being frequently attributed to oxygen vacancies or zinc interstitials, without any clear evidence [18]. It has been suggested that zinc vacancies are more likely the cause of green luminescence.

2.2.5 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 tyres). This 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) [19, 20]. High thermal conductivity translates into high efficiency of heat removal during device operation.

2.2.6 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. The possibility of low-temperature chemical etching adds great flexibility in the processing, designing and integration of electronic and optoelectronic devices.

2.2.7 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 [21, 22], even greater than that of GaN, the cause of which is still unknown.

2.2.8 Strong sensitivity of surface conductivity to the presence of adsorbed species

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 odour [23]. Mechanisms of the sensor action are poorly understood. Recent experiments reveal the
The existence of a surface electron accumulation layer in vacuum-annealed single crystals, which disappears upon exposure to ambient air [24–26]. This layer may play a role in sensor action, as well. 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.

2.3 Deposition Techniques

Growth technique played a significant role in controlling the properties of ZnO films, because the same material deposited using two different techniques, usually had different physical properties. This was due to the fact that the electrical and optical properties of the films strongly depended on the structure, morphology and the nature of impurities present. Moreover the films grown using any particular technique might have different properties due to the variation of various deposition parameters and hence the properties can be tailored by controlling the deposition parameters. The specific technique that has been used to grow the ZnO thin films include Chemical vapour deposition (CVD), Spray Pyrolysis, Pulsed Laser Deposition, Sputtering and evaporation of oxide materials. Each process has its own merits and demerits. The purpose of this part is to give the brief account of commonly used technique, particularly suitable for the growth of ZnO thin films.

2.3.1 Chemical Vapor Deposition (CVD)

CVD is one of the important techniques for producing thin film of semiconductor material. This technique involves reaction of one or more gaseous species reacting on a solid surface (substrate). In this process the metallic oxides are generally grown through the vaporisation of the organo-metallic compounds. Vapour containing the condensate material is transported to a substrate surface where it is decomposed usually by the heterogeneous process. Nature of the decomposition process varies according to the composition of the volatile transporting species. The decomposition condition should be such that the reaction occurs only at or near the substrate surface and not in the gaseous state to avoid formation of the powdery deposits which may result in haziness in the films. There are several modifications of this method depending on precursors used. When the metal–organic precursors are used the technique is called MOCVD, metal–organic vapour–phase epitaxy (MOVPE), or organo-metallic vapour–phase epitaxy (OMPVE). In the case of hydride or halide precursors, the technique is named as hydride or halide CVD or VPE.
In the CVD method, ZnO deposition occurs as a result of chemical reactions of vapour-phase precursors on the substrate. These vapours are delivered into the growth zone by the carrier gas. The reactions take place in a reactor where a necessary temperature profile is created in the direction of gas flow. For hydride VPE growth of ZnO, hydrogen (H\(_2\)) was employed as a carrier gas [27, 28]. In these cases, the typical pressure was \(\leq 133\) Pa and the flow rate was about 40 ml/min. Targets made from ZnO powder were placed in the evaporation zone in which the temperature was around 770 °C. High-quality homoepitaxial ZnO layers were grown on bulk ZnO substrates by using N\(_2\)O and diethyl zinc [29]. Two conditions, [proper thermal treatment of substrate prior to the growth to obtain a flat surface and high flow-rate ratios of source materials], were found to be important to obtain high quality layers.

Effect of oxygen partial pressure on the structural perfection as well as optical and electrical properties of ZnO films grown at 600 °C on Al\(_2\)O\(_3\) (0001) was studied by Ma et al. [30,31]. It was found that the conduction type in undoped ZnO layers could be controlled by adjusting the oxygen partial pressure during growth. The films grown under oxygen partial pressure lower than 45 Pa showed \(n\)-type conductivity. With increasing oxygen pressure, the crystallinity of the ZnO layers degraded to polycrystalline with additional (1012) orientation and intrinsic \(p\)-type ZnO (which should be treated with some caution) was produced as the oxygen partial pressure became higher than 55 Pa. The hole concentration and mobility reached \(1.59\times10^{16}\) cm\(^{-3}\) and 9.23 cm\(^2\)/V s, and the resistivity was 42.7 Ω cm. Transparent and conductive ZnO thin films were deposited over Si and InP substrates using CVD and characterized using X-ray diffraction (XRD), AFM, optical measurements etc [32]. The main observation was that the preferred orientation of the ZnO crystallite was along (112) for Si and (002) for InP substrates.

Sallet et al. [33] also reported growth of ZnO on (0001) sapphire substrates using MOCVD. Diethylzinc and tertiarybutanol were used as zinc and oxygen sources respectively. In this paper, the authors had given details of growth conditions such as substrate temperature and precursor’s partial pressure. Influence of the cleanness state of the MOCVD silica reactor was also emphasized, since it modified both layer quality and crystalline orientation. Moreover, it also affected growth process steps like sapphire thermal treatment and buffer layer deposition. ZnO epitaxial layers were characterized using
scanning electron microscopy [to assess the surface orientation and morphology], X-ray
diffraction and photo luminescence. Highly conductive polycrystalline ZnO films were
grown using MOCVD technique with dimethyl zinc, dimethyl zinc-triethylamine and
tertiary butanol as precursors [34]. Films grown using dimethyl zinc-triethylamine were
oriented with the c-axis in the growth direction. Resistivity was of the order of $3 \times 10^4$ ohm cm.

Stoichiometric ZnO films were grown on Si substrate using Plasma enhanced CVD
with a zinc organic source and carbon dioxide gas mixture [35]. Substrate temperature was
kept at 503 K initially with different gas flow rates and then keeping gas flow rate constant,
substrate temperature was varied. Films were oriented along (002) plane at higher substrate
temperature, while at low temperature, the films were polycrystalline with different
orientation. Room temperature exciton absorption peak was observed in these films, which
vanished at lower substrate temperature. This observation was correlated with the
crystalline quality of the film. PL studies were also done at room temperature.

Guotong et al. [36] reported growth of ZnO films on C-plane sapphire substrate
using plasma-assisted MOCVD. The experimental results show that the high-quality ZnO
films have been obtained by annealing. Furthermore, the films with better PL properties are
obtained by the final annealing, while the films with higher optical transmission are
obtained through annealing during the growth process. Low pressure chemical vapour
deposition (LP-CVD) of Al doped ZnO [AZO] thin film was investigated for transparent
electrode of thin film solar cell [37]. For LP-CVD, diethylzinc and trimethyl aluminium
were used as Zn and Al precursors respectively. Effects of trimethyl aluminium (TMA)
precursor flow rate on the structural and optical properties of transparent conducting
LPCVD ZnO film was analysed in this work. The haze factor of AZO films drastically
increased with the introduction of TMA precursor.

T.Sekiguchi et al. [38] deposited ZnO thin film on sapphire substrate using ‘remote
plasma-enhanced chemical vapour deposition’ with Zn($C_2H_5)_2$ and CO$_2$. In the ZnO films
grown under the oxygen-rich condition, broad emissions [peaked at 3.8 and 3.0 eV] were
observed.
2.3.2 Sputtering

Sputtering is one of the versatile techniques used for the deposition ZnO thin films. Compared to the chemical methods, samples will have better-controlled composition and homogeneity; also this permits to have better control of film thickness. Sputtering process involves the creation of gas plasma by applying voltage between a cathode and anode. Cathode is used as target holder and anode is used as substrate holder. Source material is subjected to intense bombardment by ions and particles are ejected from the surface of cathode. They diffuse away from it and deposit onto a substrate. Sputtering is normally performed at a pressure of $10^{-2}$ to $10^{-3}$ Torr. For conducting targets, DC voltage is applied between cathode and anode (DC Sputtering) and for non-conducting samples and insulators, a high frequency generator is connected between the electrodes (RF Sputtering). Magnetron sputtering is useful where high deposition rates and low substrate temperature are required. In magnetron sputtering, a magnetic field is applied to enhance the sputtering rate, which in turns, enhances the deposition rate also.

Highly conductive and transparent AZO thin films were grown using ‘off-axis magnetron sputtering’ on silica surface and effect of post deposition annealing was discussed in another paper [39]. Optimized ZnO film was having resistivity of $4.5 \times 10^{-4}$ ohm cm and optical transmittance of 85 %. Gupta et al. investigated the influence of post deposition annealing on the structural and optical properties of RF sputtered insulating ZnO thin films [40]. The as grown film, deposited over quartz substrate, was in a state of stress with orientation along c- axis. These films became stress-free after annealing in air at 673 K for 1hr. At higher temperature, a process of coalescence was observed which caused a major grain growth. This in turn resulted in the formation of ‘micro-crack’ and surface roughness. Packing density of 99% was observed for the film annealed at 673 K, which indicated almost a void free film.

Kook et al. [41] reported on the growth of very high quality Al doped n-type ZnO epilayer on sapphire substrate using a RF magnetron sputtering technique combined with a rapid thermal annealing. On increasing annealing temperature up to 900$^\circ$C, the PL Intensity (energy 3.2 eV) increased significantly. PL intensity ratio considerably enhanced with increasing the oxygen pressure. Annealing at 900$^\circ$C however resulted in improved carrier concentration and mobility about $10^{20}$ cm$^{-3}$ and 45-65 cm$^{-2}$/Vs.
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ZnO and AZO transparent thin films with different thicknesses were prepared using dc magnetron sputtering technique. Deposition was on silicon and Corning glass substrates [42]. Atomic force microscopic characterisation of the films surfaces revealed a granular, polycrystalline morphology with roughness decreasing as the oxygen partial pressure decreases. The films deposited at high O_2 ratio have shown bigger and better grains, whereas those deposited at higher Ar ratio had uniform grain distribution.

ZnO thin films deposited using RF magnetron sputtering method onto unheated glass, silicon, and kapton polymer foil substrates revealed a polycrystalline structure [43]. The influence of deposition arrangement and oxidation conditions on the structural, morphological, and optical properties of the ZnO films was discussed. The crystallites were preferentially oriented along (0 0 2) plane parallel to the substrate surface. Intensity of the (0 0 2) peak for ZnO deposited on kapton polymer foil substrate was higher than that of the other two substrates. This translates into bigger crystallites. All ZnO thin films showed a high transmittance in the visible region. Reflection spectrum of ZnO thin film deposited on Si showed interference maxima and minima due to reflections on the surface the film. Values of the energy gap calculated from the absorption spectra was 3.23 eV for ZnO sample deposited on glass substrate and 3.30 eV for the sample deposited on kapton polymer foil substrate.

AZO films were deposited on quartz substrates heated to 100 or 200°C under argon gas pressure between 0.08 and 2.7 Pa using RF magnetron sputtering [RF power of 100 W] from a ZnO target with 2 wt.% Al_2O_3. Structural, optical and electrical properties [such as electrical resistivity, carrier concentration and the Hall mobility] were studied as a function of argon gas pressure[44]. As argon pressure during deposition was increased, the grain size decreased and the surface roughness increased leading to higher electrical resistivity. The minimum resistivity of about 2.5× 10^{-4} \Omega \text{ cm} was obtained for film grown on quartz substrate heated at 100°C with RF power of 100 W at argon pressure of 0.13 Pa is comparable to that of ITO films.

Another report, AZO thin films with low resistivity and high transmittance were obtained through middle-frequency alternative magnetron sputtering using a ZnO target mixed with Al_2O_3 of 2 wt% [45]. Lowest resistivity obtained was 4.6 \times 10^{-4} \Omega \text{ cm} for the film with average visible transmittance of 90.0% and sheet resistance of
32 \Omega, deposited at 250°C and 0.8 Pa. Increase of conductivity and optical transmittance was attributed to the improvement of crystallinity with increasing substrate temperature. Resistivity increased and optical transmittance decreased due to deterioration of crystallinity resulting in an increase of surface roughness with the increase of argon gas pressure.

Piezoelectric ZnO film was deposited using RF magnetron sputtering to fabricate an LFE-mode SMR-type FBAR device [46]. Optimal conditions for ZnO deposition were 120 W of RF power and 10 m Torr pressure in the chamber. Suitable substrate rotation was very important for improvement of the c-axis-preferred orientation of the films. Electron temperature, plasma density and saturated ion current were approximately 5.5–5.8 eV, 1.0–1.3×10^{11} /cm^3 and 3.5–4.3 mA/cm^2, respectively. Piezoelectric- active area was 200×200 \mu m^2, and thicknesses of ZnO film and Au electrode were 1.25 \mu m and 110 nm, respectively. Series and parallel resonance frequencies of the FBAR device appeared at 1.68 and 1.71 GHz, respectively, which represent 68.4% of the values for a ZnO FBAR of the same thickness without a mass loading effect. Effective coupling coefficient was 0.0432, which corresponds to 54% of the theoretical value for an ideal ZnO FBAR device.

Rajesh Das et al. [47] reported that transparent conducting AZO thin films were prepared using RF-magnetron sputtering under different gas ambient at 300°C. The electrical resistivity varied from 1.23×10^{-1} to 2.8 ×10^{-4} \Omega cm on introducing O\textsubscript{2} and H\textsubscript{2} gas with Ar ambient. Hydrogen plays an important role for creation of oxygen vacancies due to its reducing action which causes the increase of carrier concentration of AZO films. Maximum carrier concentration and Hall mobility, as estimated from Hall effect measurement of the films, were 2.3 × 10^{21}/cm^3 and 44.4 cm^2 /V s respectively. Photoluminescence (PL) spectra peaks were mainly in the blue emission region; however there was a change from 432 nm (2.87 eV) and 541.5 nm (2.29 eV) with the change of gas ambient. From the X-ray diffraction (XRD) pattern exhibiting only the (002) peak of ZnO, all films were found to be c-axis-oriented. The crystallite size varies from 150 to 288Å for different films calculated from (002) orientation of XRD data. Y.B. Xiao et al. [48] studied the properties of Indium Zinc Oxide (IZO) thin films deposited on Polyethylene Terephthalate substrate room temperature with the help of dc magnetron sputtering. Preparation of IZO films were carried out under varying the O\textsubscript{2} concentration and deposition
parameters. As the \( \text{O}_2 \) concentration in \( \text{O}_2/\text{Ar} \) gas increased from 0.4\% to 3.5\%, the transmittance of the film increased from 70\% to 90\% and the resistivity decreased. With increase in dc power, the resistivity increased; but the transmittance decreased. For the variation of gas pressure and target-to-substrate distance, the transmittance showed little change; but the resistivity (5.1 \( \times 10^4 \) \( \Omega \) cm) decreased with decrease in gas pressure and increase in target-to-substrate distance.

### 2.3.3 Pulsed Laser Deposition (PLD)

Pulsed laser deposition (PLD) is one of the sophisticated techniques for depositing transparent semiconducting oxides. Recently PLD technique attained importance among the different techniques employed to fabricate crystalline thin films with good crystallinity. PLD technique involves evaporation of a solid target in a High Vacuum/Ultra High Vacuum chamber, by means of short and high-energy laser pulses. A pulsed laser beam vaporizes the surface of the target, and the vapour condenses on the substrate, producing a film with the same composition as the target. This is the result of the extremely high heating rate of the target surface (10\(^8\) K/s) due to pulsed laser irradiation. It leads to the congruent evaporation of the target irrespective of the evaporating point of the constituent elements or compounds of the target. Because of the high heating rate of the ablated materials, laser deposition of crystalline film demands a much lower substrate temperature than other film growth techniques. For this reason, the semiconductor and the underlying integrated circuit are not damaged from thermal degradation. Main components are a laser, optics, and a vacuum system. It not only involves the physical process of the laser-material interaction of the impact of high-power pulsed radiation on solid target, but also the formation of the plasma plume with high energetic species and even the transfer of the ablated material through the plasma plume onto the substrate surface. The targets used in PLD are small compared to the large size required for sputtering techniques. It is quite easy to produce multi-layered films of different materials by sequential ablation of assorted targets. Besides, by controlling the number of pulses, a fine control of film thickness down to even atomic monolayer can be achieved.

Highly transparent conductive AZO thin films have been deposited on the glass substrate using PLD [49]. Effect of substrate temperature and post deposition annealing treatment on structural, electrical and optical properties of the thin films was investigated.
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Resistivity of the film decreased from $1.3 \times 10^{-3}$ to $6.1 \times 10^{-4} \ \Omega \ \text{cm}$ with increase of substrate temperature from 170 to 240°C. Highest mobility value of $11.4 \ \text{cm}^2/\text{V} \cdot \text{S}$ was obtained for film deposited at 340°C. Resistivity of the film further reduced to $4.7 \times 10^{-4} \ \Omega \ \text{cm}$ by annealing at 400°C for 2 hr in argon.

The lowest resistivity of $8.54 \times 10^{-5} \ \Omega \ \text{cm}$ and average transmittance more than 88% in the visible range were obtained in a series of approximately 280 nm thick AZO films grown on glass substrate at a target-to-substrate distance of 25 mm in a magnetic field applied perpendicular to a plane generated by PLD using an ArF excimer laser[50]. To study the effect of thickness on structural, electrical and optical properties of AZO films, a set of polycrystalline AZO samples with different thicknesses were deposited using PLD [51]. XRD measurement showed that crystal quality of the film was improved with the increase of the film thickness. The optical band gap increased from 3.50 eV to 3.90 eV when AZO film thickness increased from 15 nm to 580 nm.

Choopun et al. [52] studied the influence of oxygen pressure on surface morphology and optoelectronic properties of ZnO films grown on sapphire (0001) by PLD. The films were grown at 750 °C under various oxygen background pressures ranging from $10^{-5}$ to $10^{-1}$ Torr. All the ZnO layers grown were found to be $c$-axis oriented. Samples grown under lower oxygen pressure regimes ($10^{-5}$–$10^{-4}$ Torr) had a $c$-axis lattice parameter 0.25% larger than that of the bulk material.

Preparation of highly conducting and transparent AZO films was reported by Singh et al. [53] which were deposited on quartz and Corning 7059 glass by focusing a XeCl ($\lambda=308$ nm and 20-ns pulse width) excimer laser onto a target rotating at 15 rpm. The ZnO target was 2 in. in diameter and doped with 2-wt % Al$_2$O$_3$. For all the experiments, a repetition rate of 5 Hz and an energy density of 1.5 J/cm$^2$ were used. The distance between the target and the substrate was 30 mm, and the deposition time was 30 min. Effects of substrate temperature (from room temperature to 400 °C) and oxygen pressure (from 0.1 to 5 m Torr) were investigated by analyzing the optical and electrical properties of the films. Average transmittance was found to be in the range of 86%–92%, and resistivity varied from $3.56 \times 10^{-3}$ to $7.0 \times 10^{-3} \ \Omega \ \text{cm}$. The lowest resistivity measured was $1.4 \times 10^{-4} \ \Omega \ \text{cm}$ for the films grown at 300 °C and 1 mTorr oxygen pressure.
Matsubara et al. [54] used oxygen radical-assisted PLD to grow highly transparent and low-resistivity AZO films at room temperature. A KrF excimer laser ($\lambda = 248$ nm, 30-ns pulse width, and 10-Hz repetition rate) was used for ablation. The oxygen partial pressure during deposition was $(0.7–1.4 \times 10^{-5}$ Torr) and the applied RF power was 150 W. Distance between the target and the substrate was approximately 6 cm. The minimum resistivity of the obtained transparent films was $5 \times 10^{-4} \Omega \cdot \text{cm}$, while average transmittance in the visible wavelength region was over 86% for ~0.7-μm-thick films.

Craciun et al. [55] deposited high-quality ZnO films on glass and silicon substrates using the PLD technique employing a KrF laser (=248 nm) and studied the influence of deposition parameters such as substrate temperature, oxygen pressure, and laser fluence on the properties of the grown films. All the films grown over a rather wide range of deposition conditions were found to be optically transparent, electrically conductive, and $c$-axis oriented. Investigations of the effect of different oxygen partial pressures showed that the best-quality films could be obtained in the higher pressure range.

### 2.3.4 Chemical Spray Pyrolysis (CSP)

Chemical Spray Pyrolysis (CSP) technique, one of the chemical methods for the preparation of thin films, is widely used one, to deposit variety of thin films. It involves spraying a solution, usually aqueous, containing soluble salts of the constituents of the desired compound, onto a heated substrate. It is quite suitable for depositing large area thin films with good reproducibility. The method has, for many years, been widely used for preparation of transparent conducting oxide films. Spray pyrolysis is based on the pyrolytic decomposition of a metallic compound dissolved in a liquid mixture when it is sprayed onto a preheated substrate. In CSP, doping process is rather simple; just by varying the concentration of the dopant in the solution, one can vary the percentage of doping in the sample. A major drawback of this technique is that it cannot be used for the deposition of very thin films. Another shortcoming lies in the selection of substrate since it is a high temperature process. Effects of substrate temperature on the structural, electrical and optical properties of ZnO films, prepared using CSP technique had been studied [56]. It was found that there was a critical temperature, $T_c = 180 \, ^\circ\text{C}$, below which the thermal decomposition to ZnO did not occur or was incomplete. Electrical resistivity was of the order of $10^3 \, \Omega \cdot \text{hm}$
cm in dark and it further reduced to $10^{-4}$ ohm cm after illumination. Band gap was nearly same (3.3 eV) for all samples prepared at different substrate temperatures.

Influence of substrate temperature on the properties of ZnO thin films was also a subject of detailed study and it has been found that resistivity and optical transmittance of the films very much depend on the temperature [57]. Substrate temperature was varied from 573 K to 773 K and spray rate was maintained at 6 ml/min. However films were found to be resistive. Effects of doping and annealing on the electrical, optical and structural properties of ZnO thin films prepared using this simple technique was also investigated [58]. Annealing in argon or vacuum reduced electrical resistivity substantially. The most pronounced change was observed in argon atmosphere. Highest figure of merit was obtained in the case of indium doped ZnO films.

Kuang–Che Hsiao et al. [59] synthesized AZO nano powder using spray pyrolysis technique. Aerosol droplets of the mixture of the zinc and aluminium nitrates [concentration varied from 0.06 to 3.0 M] were pyrolysed in air at temperatures ranging from 500 to 800 °C. The AZO powder had a primary and a secondary particle sizes in the range of 15–30 nm and 1–3 µm, respectively. Particle sizes increased with the reaction temperature and precursor concentration. Relative density of the particles increased with reaction temperature but decreased with precursor concentration. Particles synthesized from high precursor concentration had a tendency to form hollow and/or porous structure.

A.E.Manouni et al. [60] reported the structural, optical and electrical characterisation of AZO thin films prepared using CSP technique. The minimum resistivity was obtained for the sample with Al concentration of 1% [1 Ω cm]. All the films were polycrystalline with hexagonal wurtzite structure. The undoped ZnO films had preferred (002) orientation, while the doped samples with Al concentration higher than 2% had (101) and (102) reflection peaks indicating that Al causes a loss of preferential orientation in (002).

Jiwen Xu et al. [61] prepared the ZnO:Al films on glass substrate at relatively low temperature of 300°C by ultrasonic spray pyrolysis. Zinc acetate and Aluminum acetate acted as zinc and aluminium sources, which dissolved in ethanol–water solution. The results showed that ZnO: Al films exhibited stronger (1 0 1) preferred orientation and had lenticular-like grain morphology. Resistivity as low as $4.3 \times 10^{-1}$ Ω cm for as-deposited films.
was obtained at the 4 at.% doping concentration, which could be decreased to $1 \times 10^{-2}$ $\Omega$ cm level by post-deposited vacuum annealing. Average transmittance of as-deposited films was nearly 80% in the visible range while that of 4 at.% doped films was reduced to 60% after vacuum annealing at 550–600°C. AZO films were prepared using CSP technique of Zinc acetate and aluminium nitrate[62]. X-ray diffraction analysis showed that the sprayed AZO films were polycrystalline texture with hexagonal structure. All the films exhibited high optical transmission of over 90%. With increase in the film thickness, transmittance decreased. Dependence of the refractive index, n, and extinction coefficient, k, on the wavelength for the sprayed films was also reported. Optical band gap of AZO was between 3.30 and 3.55 eV, depending on the film thicknesses.

H. Gómez-Pozos et al. [63] deposited AZO thin films over sodocalcic glass substrates using CSP technique; in this work, zinc acetate and aluminum pentanedionate were the precursors. The group observed that addition of Al to the starting solution decreased the electrical resistivity of the films up to an optimum value between 2 and 3 at.%; further increase in the [Al/Zn] ratio lead to an increase in the resistivity. After a vacuum-thermal treatment, performed at 400 °C for 1 h, the films showed a resistivity decrease, reaching a minimum value, for the films deposited at 475°C, of $4.3 \times 10^{-3}$ $\Omega$ cm. X-ray diffraction studies showed that the films are polycrystalline and the peaks fit well to the hexagonal wurtzite structure with a preferred orientation along the (002) direction. Optical transmittance at 550 nm ranged between 85 and 90%, depending on the deposition temperature. Slight variations of the band gap were obtained when the substrate temperature was varied.

AZO ‘microrods’ with increasing [Al]/[Al+Zn] molar ratios up to 20 at.% were prepared on glass substrates[64]. X-ray diffraction studies revealed that all films had hexagonal wurtzite crystal structure with a strong (002) preferred orientation. Surface morphology of the films studied using scanning electron microscopy showed that the undoped ZnO film had hexagonal shaped microrods. Optical studies indicated that the band gap slightly decreased [from 3.23 eV to 3.15 eV as the doping increased from 0 at.% to 20 at.% Al] with increasing Al doping, which could be explained in terms of electron concentration dependence of band gap shift in the Al-doped ZnO films. Doping with Al resulted in the decrease of electrical resistivity (2.9 $\Omega$.cm) up to 15at.%.
Lokhande and Uplane discussed structural, optical and electrical studies on highly oriented (along 100 plane) sprayed ZnO films [65]. The resistivity of the film at room temperature was \( \sim 10^{-1} \) ohm cm and the band gap energy was 3.27 eV. Transparent conducting IZO thin films were prepared on soda-lime glass substrates using CSP technique [66]. Dependence of electrical, structural, morphological and optical properties on the preparation conditions was discussed in detail in this paper. Two main variables, viz., substrate temperature and molar concentration, were varied in the ranges of 425–525 °C and 0.05–0.5 M respectively in order to obtain films with low electrical resistivity and high optical transparency in the visible region. Minimum resistivity value of \( \sim 3 \times 10^{-3} \) Ω cm was obtained for films deposited from highly concentrated starting solutions, i.e. 0.4 and 0.5 M. Values of the free-carrier concentration and the electronic mobility were estimated using Hall effect measurements. XRD studies proved that the preferential orientation was along the (1 0 1) direction. Surface morphology was clearly affected by the variations in molar concentration, leading to a smoother appearance as the zinc concentration in the starting solution increased. Typical optical transmittance values in the order of 85% were obtained for all the films.

Indium doped ZnO thin films were grown on glass substrates using the CSP technique [67] and effect of acetic acid content in starting solution as well as the substrate temperature was studied. When the acetic acid content in the solution (\( C_{AA} \)) is extremely low, the resistivity becomes relatively high (4×10^{-2} Ω cm). When the \( C_{AA} \) was increased at fixed temperature, resistance of the film decreased as low as 4×10^{-3} Ω cm for the film deposited at 525°C. Another report, IZO thin films were prepared using spray pyrolytic decomposition of zinc acetate with indium acetate in an alcoholic solution [68]. The films were deposited onto soda lime glass substrate, alumina and sodium chloride crystals. Application of ‘Reitveld refinement’ method to analyse the XRD pattern has been proven to be effective method to obtain more detailed information about the crystallographic structure of the ZnO films. Another report, Indium doped ZnO [IZO] thin films were prepared on Corning glasses substrates again using CSP technique [69]. Doping concentration of 2 at.% was proved to be optimum for indium doped zinc oxide thin films. X-rays diffraction pattern showed that the IZO films were polycrystalline of wurtzite structure with preferential orientation of (0 0 2) direction. Samples having doping level of 2% exhibited
the lowest resistivity of $6 \times 10^{-3}$ (Ω cm) while undoped ZnO had 17 Ω cm. Optical gaps of the IZO thin films were determined using optical transmission spectra and band gap value increased slightly from 3.28 eV to 3.35 eV due to the indium doping.

Indium doped (2mol %) ZnO films on glass substrate were grown through the spray pyrolysis method at 500 °C [70]. Samples were annealed under N$_2$ atmosphere between 100 and 600 °C for 5min. The XRD spectra indicated that the c-axis became more prominent with increasing annealing temperature. Low resistivity of $4.0 \times 10^{-2}$ Ω cm with electron mobility of 3.0 cm$^2$ V$^{-1}$s$^{-1}$ and carrier concentration of $7.0 \times 10^{19}$ cm$^{-1}$ were obtained at annealing temperature of 450 °C. The PL indicated that five distinct peaks, [donor and acceptor bound exciton and its phonon replicas], could be observed in the undoped ZnO film. On the other hand, one broad peak was dominant in the In-doped ZnO film. This peak was due to donor bound exciton of the In interstitial (In$_i$) or In atom in the Zn site (In$_{Zn}$). No deep emission bands were observed in the undoped and In-doped ZnO films. This proved that the V$_O$ and/or Z$_{ni}$ defects were few in the ZnO films. The peak energy of the PL spectra was not changed with increasing annealing temperature. However, the PL intensity decreased with annealing temperature.

Gallium, aluminum, and indium-doped ZnO (ZnO:Ga, ZnO:Al, and ZnO:In) films have been deposited using the chemical spray method on sodalcalic substrates [71]. Best electrical properties were observed in the thickest indium-doped ZnO films; the lowest electrical resistivity was of the order of $10^{-3}$ Ω cm. Optical transmittance value in the visible spectrum was around 87% in the thinnest films. Structural and morphological properties of ZnO:Ga and ZnO:Al films were similar, as in both cases the (0 0 2) orientation was dominant. In the case of ZnO:In films, the (1 0 1) was the preferential growth orientation, and the surfaces seem to be smoother than the corresponding ZnO:Ga and ZnO:Al films.

Highly conducting and transparent gallium doped zinc oxide (ZnO:Ga) layers also were deposited [72]. The ZnO:Ga films grown at a substrate temperature of 350 °C with gallium concentration of 5.0 at.% had the best physical properties. These layers were highly oriented along the (002) planes and having n-type conductivity type [electrical conductivity ~ $1.32 \times 10^3$ Ω$^{-1}$ cm$^{-1}$]. Transmittance of these films was higher than 85% in the visible region with a high reflectance in the infra-red region.
ZnO and cerium-doped zinc oxide (ZnO:Ce) films were deposited using reactive chemical pulverization spray pyrolysis technique. Here chlorides of zinc and cerium were used as precursors [73]. All films were oriented preferentially along the (00 2) direction. Films doped with 0.8 at.% cerium had stronger c-axis orientation perpendicular to the substrate, larger grain, smoother surface morphology and higher transmittance than the others. Thicknesses of films grown from solution with 3.03% and 3.4% cerium concentration were 250 nm and 200 nm, respectively.

2.3.5 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy is a technique for the epitaxial growth via the interaction of one or several molecule or atomic beams that occurs on the surface of a heated crystalline substrate. The solid source materials are placed in evaporation cells to provide an angular distribution of atoms or molecular in beams. The substrate is heated to necessary temperature and, when needed, continuously rotated to improve the growth homogeneity. MBE takes place in the High Vacuum (10^{-8} \text{ Pa}). The most important aspect of the MBE is the slow deposition rate (typically less than 1000 nm per second), which allows the films to grow epitaxially. The term ‘beam’ means that evaporated atoms do not interact with each other or vacuum chamber gases until they reach the wafer, due to the long mean free path of the atom. MBE is also used for the deposition of some types of organic semiconductors. In this case, molecules, rather than atoms, are evaporated and deposited onto the wafer.

Highly transparent and conductive ZnO films were grown through atomic layer controlled growth on various substrates including glass, sapphire and polyethylene tetrathalate (PET) at different temperatures [74]. Effect of doping with Ga was also discussed in this report. Thermal annealing of ZnO layers was done in N\textsubscript{2} or O\textsubscript{2} atmosphere and their effects were also studied [75]. Annealing in O\textsubscript{2} atmosphere is necessary compared to N\textsubscript{2} atmosphere in order to suppress the generation of V\textsubscript{O} and Zn\textsubscript{i}. If the annealing is done in O\textsubscript{2} at temperatures higher than the growth temperature, the electron concentration increases while the annealing in O\textsubscript{2} at temperatures lower than the growth temperature, causes reduction in electron carrier density e.g., from 2.4\times10^{18} to 2.5\times10^{17} cm\textsuperscript{-3} by the 500°C annealing. Interestingly the crystallinity is improved.

M.A. Reshchikov et al. [76] observed strong shift of blue and yellow luminescence band with variation of excitation intensity in the ZnO film grown on sapphire using MBE...
with hydrogen peroxide as source of reactive oxygen. The group observed the Yellow Luminescence (YL) and Blue Luminescence (BL) bands with nearly Gaussian shape and positions of maxima in the ranges 2.1–2.3 and 2.85–3.15 eV, respectively. Both the PL bands were blue-shifted substantially with increasing excitation intensity. The shifts were attributed to screening of potential fluctuations created by random distribution of charged defects in regions with high degree of compensation. They suggested that BL and YL bands in studied ZnO were caused by diagonal transitions from the potential valleys in the conduction band (or shallow donors located there) to the potential humps in the valence band and to deep acceptor levels located in these humps, respectively. Tsukazaki et al. [77] reported the high-quality ZnO thin film deposition on close lattice-mismatched hexagonal ScAlMgO$_4$ substrate by laser MBE at high growth temperature up to 1000°C. The FWHM of (0002) XRD rocking curve is less than 18 arc sec for 1 µm thick ZnO films. By using the high quality undoped ZnO films, these authors also demonstrated ZnO p-i-n homojunction for light emitting diodes (LED) applications.

2.3.6 Summary of deposition techniques

Spray Pyrolysis can be employed for the growth of low-cost films for large area application. The technique has high growth temperature and poor uniformity compared to other deposition technique. Some of the major advantage of the spray technique than the others are 1) stoichiometry can be easily varied by varying the concentration of the constituents in spray solution 2) Easiness of doping 3) Spray solution contains soluble salt of constituents of desired compound. For the growth of reproducible device-quality films, CVD, PLD, sputtering have been extensively used in one form or another. The deposition rates of CVD are usually greater than those of sputtering. The sputter deposition technique, although more complex and more expensive, is preferred as it permits better control of film composition and thickness.
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2.4 Application of ZnO

2.4.1 Solar cells

There has been interest in recent years directed towards the development of conducting transparent oxide-based solar cell. These oxides offer the possibility of fabrication of solar cell with performance characteristics suitable for large-scale terrestrial applications. Transparent conducting oxides are particularly effective in solar cell applications because of the following advantages.

(a) The conducting transparent film permits transmission of solar radiation directly to the active region with little or no attenuation, so that solar cells based on these materials result in improved sensitivity in the high photon-energy portion of the solar spectrum.

(b) Ease of fabrication of the junction because of lower junction formation temperature.

(c) These films can serve simultaneously as low resistance contact to the junction and anti-reflective coating for the active region.

Oliver kluth et al [78] reported the suitability of the light scattering properties of different texture glass/ZnO surfaces for efficient light trapping in silicon thin film solar cells. AZO substrate with adapted surface texture for different applications and reduced absorption losses contributed to the development of μc-Si:H p-i-n, and a-si:H/μc-si:H stacked p-i-n cell with efficiencies of 9% and 12.1% respectively. J.A. Aranovich et al [79] investigated electrical and photovoltaic properties of heterojunction prepared using spray pyrolysed ZnO films on single crystal p-type CdTe. Under actual sunlight the optimum cell showed an open-circuit voltage of 0.54 V and short-circuit current of 19.5 mA/cm² with an efficiency of 8.8%.

CuInS₂/ZnO solar cell of 2% efficiency with Voc =280 mV, Isc=13.3 mA/cm² and FF=0.38 were prepared using spray pyrolysis [80]. The solar cell performance depends on the CuInS₂ deposition parameters and resistivity of CuInS₂ and ZnO thin films. Annealing is the most critical parameters for the improving junction behaviour. M.S.Tomer et al. [81] prepared thin film ZnO/CuInSe₂ heterojunction solar cell using CSP technique. The cell showed an open-circuit voltage 0.3 V, short circuit current of 23mA/cm², a fill factor of 0.29 and electrical conversion efficiency exceeding 2%.

M.C.Kao et al. [82] deposited Zinc Oxide nano crystalline thin film on Fluorine Tin Oxide(FTO) coated glass substrate using sol-gel spin-coating technology and rapid thermal
annealing for the use in dye sensitized solar cells. Efficiency of 2.5% with $J_{sc}$ and $V_{oc}$ 8.2 mA/cm$^2$ and 0.64 V respectively were obtained when the ZnO film were pre annealed at 300°C. ZnO layer was deposited as ‘diffusion barrier’ through DC Magnetron sputtering from pure ZnO target on stain steel substrate [83]. ZnO diffusion barrier had strongly reduced the diffusion of Fe from the stainless steel substrate into CIGS solar cells.

M.Berginski et al.[84] investigated the influence of doping level of the sputter target and substrate temperature on the post etching surface texture of ZnO:Al films and their light trapping ability in silicon thin film solar cells. Kerstin Schulze et al.[85] compared organic solar cell using different transparent conducting oxides as anodes [ITO and 3 kinds of AZO]. These anodes with different work functions were used for small molecule photovoltaic device based on as oligothiophene derivatives as donor and fullerene C60 as acceptor molecule. They concluded that the work function of the anode did not influence the $V_{oc}$ of the photovoltaic device.

S.Y.Myong et al. [86] developed hydrogenated ‘protocrystalline silicon’ (pc-Si:H)/Hydrogenated ‘microcrystalline silicon’ (μc-Si:H) double junction solar cell structure employing boron doped ZnO (ZnO:B) intermediate layer. Because the ZnO:B intermediate layer reduced the potential thickness for pc-Si:H absorber in the top cell, this double junction structure was promising candidate to fabricate highly stable Si- based thin film solar cell. T.Dittrich et al. [87] investigated the effect of annealing on the ZnO nanorods/In$_2$S$_3$/ CuSCN devices. They compared the charge selective contact of solar cells with extremely thin absorber based on ZnO- nanorod/In$_2$S$_3$/ CuSCN before and after thermal annealing by current-voltage measurements at varying temperature and light intensity.

A. Campa et al. [88] reported that the role of ZnO between the CIGS and the back metal contact in terms of optical improvement of the back contact. Simulation results showed significant increase in the reflectance of ZnO/Mo contact compared to Mo contact without ZnO layer. The analysis of improvements in simulated quantum efficiency (QE) and short circuit current ($J_{sc}$) of a thin film CIGS solar cell, related to TCO/metal indicated that significant amount of reflected light escaped from the substrate due to the insufficient light trapping in thin CIGS absorber.

U. Rau et al. [89] showed the role of i-ZnO layer in ZnO/CdS/CIGS solar cell. Authors proposed that the local series resistance provided by the i-ZnO prevented electrical
homogeneities from dominating the open circuit voltage of the entire device. Lin Ke et al [90] studied the degradation mechanism of ZnO dye sensitized solar cell (glass/ITO/ZnO/dye/electrolyte/Pt) using various characterisation techniques. Extremely Thin Absorber (ETA) cells with the structure of TCO/ZnO rod/In$_2$S$_3$/ CuInS$_2$ were prepared with the help of CSP technique [91]. Effects of buffer layer thickness and ZnO nano-rods of length 500–1000 nm were studied. Increasing In$_2$S$_3$ layer thickness reduced fluctuations of the cell output parameters and increased $V_{oc}$ and FF; however, certain thicknesses induce losses due to light absorption. The highest conversion efficiency 4.17% at AM1.5 was recorded from small contact area of the cell based on rods with length of 600 nm.

### 2.4.2 Light Emitting Diodes

One of the first [if not the first] ZnO-based hybrid hetero structure LEDs was fabricated by Drapak [92] in 1968 who used Cu$_2$O as the p-type layer. In all the other hybrid structures that followed, the emission observed under forward bias either originated in the p-type layer, or showed a very weak contribution at the ZnO band edge corresponding to extremely small external quantum efficiencies. When p-AlGaN was used to favour hole injection into ZnO thereby promoting emission in that material, strong Electroluminescence (EL) peaking at 390 nm due to excitonic recombination within ZnO has been observed [93,94]. Although these results show that p-AlGaN is a good candidate for fabricating efficient hybrid hetero-structure LEDs with ZnO active layers, ‘all-ZnO-based’ LEDs incorporating stable p-ZnO are needed for light emitters to compete with those based on nitrides. Reports on ‘all-ZnO-based’ light-emitting devices have also started to appear [95,96] as p-type ZnO became available. However, production of stable and device-quality p-type ZnO has not been realized despite a large number of publications reporting successful demonstration of p-type ZnO samples, as discussed in detail in the reference [97]. Incorrect interpretation of the van der Pauw–Hall measurements has been suggested [98] as one of the reasons for the controversial reports of p-type conduction in ZnO. In wide band gap semiconductors, doped with a high density of acceptor-type impurities, localization is an endemic problem: carriers are trapped and cannot follow the Lorentz force and the electric force induced by the low fields employed in Hall measurements. High carrier concentrations in p-type ZnO, which are often reported in the literature, are caused by very low Hall voltages. Correspondingly low-mobility values measured are usually indicative of
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Zinc Oxide thin film.

strong localization in the material which, if present, brings the applicability of conventional Hall measurements under question, particularly at low temperatures. Therefore, the interpretation of Hall effect measurements should be made very carefully.

2.4.3 Photodiodes

There have been many reports regarding the photo response properties of the ZnO-based hetero-junctions. Jeong et al. [99] reported the photoelectric properties of $n$-ZnO/$p$-Si photodiode (PD) which detect UV photons in the depleted $n$-ZnO and simultaneously detect visible photons in the depleted $p$-Si by employing two related photoelectric mechanisms. I-V measurements obtained while the photodiodes are exposed to radiation in a wavelength range of 310–650 nm showed a linear increase in photocurrent with reverse bias. In the visible range, the photocurrent rose rapidly with bias but saturated beyond a critical voltage. The diodes exhibited high response of 0.5 and 0.3 A/W for UV (310-nm) and red (650-nm) photons, respectively, under a 30-V bias with a minimum near 380 nm which corresponds to the band gap of ZnO.

Ohta et al. [100] also reported on transparent $p$-$n$ hetero-junctions composed of $p$-ZnRh$_2$O$_4$ and $n$-ZnO thin layers grown using reactive solid-phase epitaxy technique. Polycrystalline ZnRh$_2$O$_4$ was deposited on a ZnO epitaxial layer at room temperature. Thermal annealing of the bilayer sample at 950 °C in air converted the polycrystalline ZnRh$_2$O$_4$ layer to what was reported to be an epitaxial single-crystalline layer. The resultant $p$-$n$ hetero-junctions had an abrupt interface and exhibited distinct rectifying $I$-$V$ characteristics with a threshold voltage of ~2 V that is in agreement with the band-gap energy of ZnRh$_2$O$_4$. Photo voltage originating mainly from the $n$-ZnO layer was also observed.

$n$-ZnO/$p$-Si heterojunction photodiodes have been fabricated through sputter deposition of $n$-ZnO films on $p$-Si substrates [101]. The substrate temperatures were in the range 300, 400, 480 and 550°C with Ar and O$_2$ in the ratio of 6:1. All the diodes showed typical rectifying behaviour as characterized by the current–voltage ($I$–$V$) measurement in dark; the photoelectric effects from the diodes were observed under illumination using monochromatic light of wave length of 670 nm. Maximum amount of photo-current was obtained under reverse bias condition from $n$-ZnO/$p$-Si heterojunction when the ZnO film was deposited at 480°C while the ZnO films deposited at 550°C show the best
stoichiometric and crystalline quality. H. Y. Kim et al. [102] fabricated the n-ZnO/p-Si and n-ZnO/n-Si hetero-junction photodiode using RF sputtering technique varying the substrate temperature and Ar : O\textsubscript{2} ratio. The photoelectric effect was very promising at for the n-ZnO/p-Si structure while the n-ZnO/n-Si showed large dark current.

An optically transparent tin-doped indium oxide/ZnO/NiO n–i–p hetero-structure photodiode was fabricated using ion beam assisted e-beam evaporation [103]. The diode clearly demonstrated rectifying current–voltage (J–V) characteristics with current rectification ratio up to 104 at bias ±2V and low reverse current of \(\sim\) 100 nA/cm\textsuperscript{2} at −5 V. H.T. Hsueh et al [104] reported the deposition of Cu\textsubscript{2}O onto vertically aligned ZnO nanowires using DC sputtering. The average length, average diameter and density of these VLS-synthesized ZnO nano-wires were 1\(\mu\)m, 100 nm and 23 wires/\(\mu\)m\textsuperscript{2} respectively. With proper sputtering parameters, the deposited Cu\textsubscript{2}O could fill the gaps between the ZnO nanowires with good step coverage to form coaxial p-Cu\textsubscript{2}O/n-ZnO nano-wires having rectifying current–voltage characteristic. Furthermore, the fabricated coaxial p-Cu\textsubscript{2}O/n-ZnO nano-wire photodiodes exhibited reasonably large photocurrent to dark current contrast ratio as well as fast responses.

### 2.4.4 Gas Sensors

Semiconductor material whose conductance is modulated directly by interaction with an active gas has been studied for many years. There is reversible chemisorption of reactive gases at the surface of the certain metal oxides. The electron concentration in semiconductor sensors varies more less linearly with pressure up to eight decades, while the variation in the mobility was less than a factor of two over the same pressure range. This suggests that gas chemisorption into the surface of the semiconductor materials is useful for the fabrication of gas sensing electronic devices.

ZnO has been widely used for sensing application because of high sensitivity to the chemical environment. The sensing process is governed by oxygen vacancies on the surface that influence the electronic properties of ZnO. Upon oxidation, via adsorption of molecules such as NO\textsubscript{2} at vacancy sites that accept electrons, electrons are withdrawn and effectively depleted from the conduction band, leading to a reduction of conductivity. On the other hand, reducing molecules such as H\textsubscript{2} can react with surface-adsorbed oxygen, leaving behind an electron and hence higher conductivity. The challenge is to sense certain gases
selectively. All experimental result demonstrate that ZnO nano-wire owing to the large surface area, have potential for detecting \( \text{NO}_2 \)[105] \( \text{NH}_3 \)[106], \( \text{NH}_4 \)[107], \( \text{CO} \)[107], \( \text{H}_2 \)[108], \( \text{H}_2\text{O} \)[109], \( \text{O}_3 \)[110] \( \text{H}_2 \text{S} \)[111] and \( \text{C}_2\text{H}_5\text{OH} \)[112].

The key in the most biological process is the need for a small change of pH created by the release of H\(^+\) ions during the biological reactions. Determination of pH is a prerequisite for many processes. Sensing mechanism for the pH is the polarization induced bound charge by interaction with the polar molecule in the liquids. Application of ZnO nano-rods as the pH sensor for intracellular chemical sensing is under development and room temperature sensitivity as high as \( \sim 59 \) mV per decades change in the pH value has been reported [113].

There are two different types of contacts between the particles of sensing materials [114]: the two-dimensional (2-D) contact between “necked particles” and point-to-point contact between ordinary particles. When the particles are necked together significantly and the sizes of the necked part become comparable to the thickness of the resistive electron depleted layer, the conductive channel through the neck determines the total resistivity (neck model). When the particle sizes are significantly larger than the thickness of the electron depleted layer, the conductive channel through the neck becomes too wide for the channel to control the electrical resistivity of the particles chain. In this condition, the point-to-point contacts between the grain boundaries dominate the total resistivity, giving rise to gas sensitivity independent of the particle sizes (grain-boundary model). The sensitivity of a gas sensor is closely related to the degree of diffusion of the gas molecules into the sensing material used to adsorb and desorb them [115,116] as well as to the latter’s specific surface areas. In order to maximize its sensitivity, many attempts have been made recently to design the structure of the resistive channels so as to enhance the gas diffusion. Although channels with two-dimensional (2-D) film structures have been widely investigated [117,118] their small specific surface areas limit their adsorption efficiency. Recently, channels with one-dimensional (1-D) structures, such as nano-wires, nano-rods and nano-belts, were proposed [119–121] since they offer a greater degree of diffusion for gas molecules as well as relatively larger specific surface area compared with 2-D structured films. These 1-D structures provide well-defined channels without any grain boundaries which might obstruct the flow of electrons through the channels. Due to these favourable properties, gas sensors
with channels made of 1-D nano-materials have been widely investigated. In addition, sensing materials with zero-dimensional (0-D) structures such as nano-particles (NPs) have also been studied for the use in the channels, due to their larger specific surface area compared to those of the other dimensional structures. However, the relatively high temperature (600 °C) of the heat treatment used to stabilize the NPs brings about their agglomeration [122] which causes two critical problems for the gas sensors: the sensitivity decreases, since the gas sensing reaction occurs mainly at the surface of the agglomerates, and the response slows down, since the diffusion of gas molecules into the agglomerates becomes more difficult and slower. Thus, the application of NPs as gas sensing materials has been limited.

Controlling and monitoring ethanol is important in some fields [123], such as testing alcohol levels of drivers, monitoring chemical synthesis, etc. SnO$_2$, ZnO [124,125], $\gamma$-Fe$_2$O$_3$, $\alpha$-Fe$_2$O$_3$ [126], and other oxides are being investigated widely because of their high sensitivity to ethanol. However, much work needs to be done to improve the sensitivity of those materials to ethanol and further to explore new ethanol-sensitive materials. As the present research results on all kinds of semiconductor metal oxides have shown, ZnO may be one of the most hopeful candidates due to its matured fabrication technology, which can produce all kinds of ZnO nanostructures, such as nano-wires, nano-rods, nano-belts, nano-ribbons.

2.4.5 Transparent Thin Film Transistors [TTFT]

The most important electrical parameters in quantifying TFT performance are the ‘drain-current on-to-off ratio’ and ‘active channel mobility’. In terms of these parameters, the best TTFT performance has been reported by Hoffman et al. [127] Highly transparent ZnO-based TTFT’s with optical transmittance (including substrate) of ~75% for visible light have been fabricated by using RF sputtering method. Carcia et al. [128] fabricated ZnO thin film transistors using RF magnetron sputtering on heavily doped n-type Si substrates held near room temperature. In this structure, the substrate side was coated with a thermal oxide layer of ~100 nm thick. Ti–Au source and drain electrodes 200 µm wide with a 20µm gap (10-nm Ti followed by 100-nm Au) were deposited and patterned directly on the thermal silicon oxide layer applying traditional photolithography.
J. H. Chung et al. [129] investigated the electrical characteristics of ZnO thin film transistors with respect to the thickness of ZnO active layers. ZnO layers with thicknesses 30 nm to 1500 nm were deposited on bottom gate patterned silicon substrate using RF sputtering at room temperature. The leakage current was $9.97 \times 10^{-8}$ A, channel mobility was $0.16 \text{cm}^2/\text{Vs}$ and threshold current was 12.7 V. L. Zhang et al [130] also reported the performance of ZnO-TFTS with different thicknesses of the active layer and optimised the conditions. The leakage current of devices increased from $10^{-10}$ to $10^{-8}$ A and on/off ratio decreased from $1.2 \times 10^7$ to $2 \times 10^5$. Atomic force microscope measurements indicated that as the thickness increased, the surface morphology of the active layer improved noticeably at first and then deteriorated.

R. Navamathavan et al. [131] fabricated the ZnO based thin film transistor using RF magnetron sputtering with and without NH$_3$ plasma treatment. The electrical properties were observed to be significantly improved for the ZnO TFT with NH$_3$ plasma treatment. NH$_3$ plasma treated ZnO TFT exhibited excellent electrical characterisation as evident from sub threshold swing of 0.44 V/dec, minimum off-current of $10^{-11}$ A, threshold voltage of 14 V, field effect mobility of 34 cm$^2$/Vs, and on/off ratio of $10^5$.

H. Faber et al. [132] compared two different solution based techniques to fabricate ZnO TFTs. Nano-particle dispersions were processed through spin coating with thermal treatment of the semiconductor at 100 $^\circ$C. Precursor solutions were deposited and converted in to ZnO layers using spray pyrolysis at a temperature of 370 $^\circ$C. Thin film transistor devices (TFTs) based on spray pyrolysis films exhibit higher electron mobility up to 24 cm$^2$/V s compared to 0.6 cm$^2$/V s for nano particle based TFTs. The increased mobility is clearly due to improved crystalline arrangement in the spray coated films.

### 2.4.6 ZnO Nanostructures

One-dimensional semiconductor nano-wires and nano-rods have attracted increasing attention due to their physical properties arising from quantum confinement (such as electronic quantum transport and enhanced radiative recombination of carriers). Nano-wires have promising potential in extensive applications and are the fundamental building blocks for fabricating short-wavelength nano-lasers, field-effect transistors, ultrasensitive nano-sized gas sensors, nano-resonators, transducers, actuators, nano-cantilevers, and field emitters (FEs). These nano-structures are the ideal for studying transport mechanisms in one
dimensional (1D) systems, which are of benefit not only for understanding the fundamental phenomena in low-dimensional systems but also for developing new generation nano-devices with high performance.

Li et al. [133] prepared ZnO nano-needles on a silicon wafer through chemical-vapour deposition. The diameters of the needle tips were in the range of 20–50 nm. High-resolution transmission electron microscopy revealed that the nano-needles were single crystals growing along the (0001) direction and exhibiting multiple tip surface perturbations, and were just 1–3 nm in dimension. Field Emission measurements on the prepared nanostructures showed fairly low turn-on and threshold fields of 2.5 and 4.0 V/mm, respectively. The nano-size perturbations on the nano-needle tips are assumed to cause such excellent field-emission performance. High emission current density, high stability and low turn-on field make the ZnO nano-needle arrays one of the promising candidates for high brightness field-emission electron sources and flat-panel displays.

Park et al. [134] reported on the metal-organic vapour-phase epitaxial (MOVPE) growth of ZnO nano-rods which were well aligned vertically, showing uniformity in their diameters, lengths, and density as revealed from electron microscopy. The mean diameter of the nano rods is ~25 nm. In a study by Kong et al. [135], ‘single-crystal nano-rings’ of ZnO were grown using the solid-vapour process. The raw material was a mixture of ZnO (melting point of 1975 °C), indium oxide, and lithium carbonate powders at a weight ratio of 20:1:1. It was placed at the highest-temperature (1400 °C) zone of a horizontal tube furnace. ZnO decomposes at such a high temperature into Zn$^{2+}$ and O$^{2-}$ and this decomposition process is the key step for controlling the anisotropic growth of the nano-belts. Zhang et al. [136] reported formation of ZnO tubes by MOCVD at temperatures of 350–450 °C. The tubes obtained were grown epitaxially on sapphire (0001) substrates with the growth along c axis parallel to the substrate normal. All of the tubes had hexagonal cross section. Nature of the tubes was found to depend strongly on both the growth temperature and reactor pressure. Growth temperature also greatly influenced the tube formation. In the temperature range of 350–450 °C, density of the tubes increased from 0.04 to 1 µm$^{-2}$ and the outer sizes of the tubes decreased from 1.0 to 0.4 µm with increasing temperature.

T. Devoda et al. [137] presented the results on formation of ZnO nano-rods prepared by spraying aqueous solution containing ZnCl$_2$ and thiourea in different molar
ratios on to SnO$_2$ covered glass substrate. They observed that addition of thiourea into spray solution has great impact on the size, shape and phase composition of ZnO crystals. Thiourea addition generally leads to the formation of thinner rods with higher aspect ratio compared to those deposited from the ZnCl$_2$ solution. According the XRD, well crystallized (002) oriented pure wurtzite ZnO crystals have been formed. When the content of the thiourea was increased, weak reflection at 2$\theta$ of 28.5 °C was detected in the XRD pattern which could be attributed to the (111) reflections of ZnS sphalerite phase.

M. Krunks et al. [138] reported the growth of ZnO nano-rods arrays from Zinc Chloride solution with pH=2 and 5 on glass/ITO substrate at 480°C and 550°C through CSP technique. ZnO nano rods deposited at substrate temperature of 550°C from aqueous solution indicated the concentration of carriers in the range of $10^{14}$-$10^{15}$ cm$^{-3}$ irrespective of the spray solution acidity. Heo et al.[139] measured the temperature and the gas/ambient dependence of current-voltage characteristics of single ZnO nano-rods grown through catalyst-driven MBE on Au-coated Sapphire substrates. Individual nano-rods were removed from the substrate and placed between ohmic contact pads, kept 3.7 $\mu$m apart. Conductivity of the nano-rods increased after a post-growth annealing in hydrogen gas at 400 °C. In the temperature range from 25 to 150 °C, resistivity of nano-rods, treated in H$_2$ at 400 °C prior to measurement, showed an activation energy of 0.089±0.02 eV and was insensitive to the ambient used (C$_2$H$_4$,N$_2$O,O$_2$ or 10% H$_2$ in N$_2$).

M. Shahjahan et al. [140] reported the fabrication of undoped and Al-doped ZnO nano-wall structures on ordinary glass substrate by low cost spray pyrolysis technique at low deposition temperature of 350 °C. Structural study revealed that the fabricated ZnO nanostructures were polycrystalline in nature and crystallinity of the samples depends on the Al doping concentration. For undoped ZnO, the band gap was obtained as 3.27 eV and the band gap decreased up to 3.06 eV with the increased in Al doping concentration up to 4%.

Yuan-Chung Wang et al. [141] reported a novel method for preparing uniform and aligned ZnO nano-wire arrays embedded in anodic alumina membranes (AAM) through electrophoretic deposition (EPD). EPD is a simple and powerful method to obtain arrays of fibrils and tubules just by controlling the applied voltage. XRD and luminescence results indicated that the prepared ZnO arrays can have similar properties to those prepared by other methods. Shu-Cheng Chin et al. [142] compared the nano-structures of three samples
of ZnO thin film on sapphire under different growth temperature conditions. Although disconnected domain structures (on the scale of 100nm in size) were observed in the samples grown under high-temperature (450°C) their crystal quality was generally better than the one grown at a low temperature (200°C). Lattice misfits and threading dislocations were observed within a domain with the separation of around 8 nm.

Nano-crystalline ZnO thin films were grown on inexpensive Soda-lime Silica Glass substrates using ‘Chemical Solution Deposition’ process with zinc acetate - 2 thoxyethanol - MEA solution [143]. XRD analysis proved that the films were amorphous even when annealed at 100°C- 200 °C for 60 minutes, while c-axis oriented ZnO were obtained by pre-firing at a high temperature [400 °C and 500°C]. A relatively high transmittance in the visible region and clear absorption edges of the films were observed except for the film annealed at 100°C.

Z. W. Liu et al. [144] synthesized the ZnO nano-rods with various diameters using PLD technique at the relatively high background pressure of 5–20 Torr and substrate temperature 550 °C– 700°C without a catalyst. The PL properties of the nano-rods produced using various processes have been investigated. Thus, c-axis oriented ZnO nano-rods were easily synthesized on the sapphire substrate with the help of the laser ablation technique without using a catalyst. The size control could be accomplished by adjusting the temperature and pressure in the range of 550 °C–700 °C and 5–20 Torr.

2.5 Conclusions

A review of properties, deposition techniques and device applications of ZnO is presented in this chapter. ZnO has some unique properties and some advantages over other wide – gap materials such as GaN which is widely used today for production of short-wavelength light emitting devices. Regarding solar cells, already this material has received some attention, although competition is very stiff; however further studies are required to improve the current density and efficiency. As for the nanostructures, ZnO nano-structures (nano wires and nano-rods) provide a path to a new generation of device, but deliberate efforts have to be expended for ZnO nano-structures especially for large-scale device applications, and to achieve high device density with accessibility to individual nano-devices.
References


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