Review Article

RF Sputtered Zinc Oxide (ZnO) Thin Films: A Review

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Abstract: Research groups around the world are investigating Zinc Oxide (ZnO) thin film via various deposition methods due to their potential applications in piezoelectric, optoelectronic and photovoltaic cells. This review evaluates ZnO thin films and its progress as a photovoltaic window layer. The impact of varied deposition parameters upon the ZnO thin film properties has also been elaborated.
Keywords: ZnO, RF sputtering, thin films, annealing, optical properties.

1. INTRODUCTION

Transparent conducting oxides (TCOs) are a class of materials which are having values of electrical conductivity, whilst maintaining a high light transmittance in the visible range of the electromagnetic spectrum. Since the realization of this type of material, vast amounts of research and development have gone into commercializing its thin film coatings. The current commercial products are based on n-doped metal oxide thin films, so-called transparent conducting oxides (TCO's). These films have a far-reaching range of applications from heat-mirror window-coatings, which control the transmission of infrared energy into and out of buildings, to their use as the transparent electrode materials in photovoltaic cells, touch-screen technology and flat panel displays: including, liquid crystal displays (LCD), organic light emitting displays (OLED) and plasma screen displays.

The II-VI compound semiconductors on the other hand had always been an interesting classification of semiconductors. For over a decade, II-VI semiconductors have attracted growing interest owing to their possible application in opto-electronics. The wide band gap II-VI semiconductors are efficient emitters in the blue to ultra-violet (UV) spectral range and are likely candidates to replace materials like gallium Nitride (GaN) in light emitting laser diodes. Despite some similarities, each of the II-VI semiconductors demonstrates its own unique and novel physical properties. These compounds mostly crystallize in the cubic (zinc blende) or hexagonal (wurtzite) structure (Caglar, M. *et al.,* 2006; Fatima, A. A. *et al.,* 2011). These structures occur in a wide range of various band gaps and lattice constants. The band gaps have a major influence on the properties of the material. This includes properties like optical absorption, electrical conductivity and refractive index. Materials are normally classified according to the type of band gap as direct or indirect band gap. The direct band gap semiconductors are found to be advantageous over indirect band gap semiconductors, as they do not require phonons to satisfy wave vector conservation. Most of the II -VI compounds are found to exist as direct band gap semiconductors and have been dominating the optical field for short wavelength applications (Haslinda, B. A. H. 2009). A common characteristic that all II-VI semiconductors share is an ability to form into the wurtzite crystal structure.

Zinc oxide as the name suggests is a compound semiconductor, for the fact that it is composed of two elements; it is sometimes referred to as a binary alloy (Loren, W. R. (2001). Zinc Oxide (ZnO) is a wide-band gap semiconductor material of the II-VI semiconductor group (since zinc and Oxygen belongs to the 2nd and 6th groups of the periodic table) (Yu, H. *et al.,* 2011). The native doping of ZnO is n-type due to oxygen vacancies. This semi-conductor (ZnO) has several favorable properties such as good transparency, high electron mobility, wide band-gap etc. It has direct and wide band gap (3.437 eV) in the near-UV spectral region, and a large free-exciton binding energy (60 meV) so that excitonic emission

processes can persists at or even above room temperature (Haslinda, B. A. H. 2009; Enrico, S. 2007; Chaitra, U. *et al.,* 2017). ZnO crystallizes in the Wurtzite structure as mentioned above and is available as large bulk singe crystals (Janotti, A. *et al.,* 2009).

As stated above ZnO crystals are almost always n-type (Sahal, M. *et al.,* 2008; Tazangi, F. E., & Rahmati, A. 2016), the cause of which has been matter of extensive debate and research [15]. Moreover, over the years, a significant improvement in the quality of ZnO single-crystal substrates has led to a revival of the idea of using ZnO as an optoelectronic or electronic material in its own right.

2. Thin Film Deposition Techniques

Deposition of high quality, uniform thin films, is an intensive area of research which has yielded many varied deposition techniques. Each technique falls into one of three broad categories: wet chemical deposition; physical vapour deposition and chemical vapour deposition. Careful selection of the appropriate deposition technique is essential for control over the properties of the resultant films. Different techniques can affect growth rates, crystallinity, substrate interaction (adhesion, line-of sight/non-line of sight coating) and morphology.

2.1 Wet Chemical Technique

This involve the use of a chemical precursor solution which reacts to produce a colloidal solution (sol), this then forms a continuous solid (gel) upon evaporation of the solvent. It includes chemical bath techniques and Sol–Gel techniques. Other types of wet chemical technique include;

2.1.1 Dip Coating: The immersion of the substrate into a precursor chemical solution followed by evaporation and annealing to yield the metal oxide layer.

2.1.2 Spin Coating: The precursor is dropped onto the center of a spinning substrate which then spreads out quickly and evaporates the solvent.

2.2 Physical Vapour Deposition (PVD)

This involves a range of techniques used to deposit thin films onto a substrate using purely physical processes, involving the condensation of a vaporized form of the material it includes;

2.2.1 Evaporative deposition - resistive heating is used to vaporize the material which is then allowed to deposit onto a substrate.

2.2.2 Electron beam Vapour deposition - a high energy beam of electrons bombards the sample material causing vaporization.

2.2.3 Sputter coating - Involves the use a plasma discharge to vaporize the material

2.2.4 Pulsed laser deposition - a high energy laser pulse causes evaporation of the material.

2.3 Chemical Vapour Deposition (CVD)

Chemical Vapour Deposition (CVD) is the most widely used technique to form thin film Transparent conducting oxides (TCO) materials, it involves deposition of the metal oxide film from the reaction of gas phase precursors on the substrate surface. The most common form involves the use of metal-organic precursor species and is thus named MOCVD (Metal-Organic CVD). Highly dense and pure materials can be produced with control over the deposition rate and a high number of possible precursors can be used. Common types of CVD are:

2.3.1 Atmospheric Pressure CVD: APCVD uses heating of the precursor to generate a vapour pressure which is transported using a carrier gas flow to a heated substrate for reaction (done at atmospheric pressure).

2.3.2 Low Pressure CVD: LPCVD uses the vapour pressure of the precursors under low pressure conditions, to aid transport to the reaction chamber.

2.3.3 Plasma Enhanced CVD: PECVD: uses APCVD conditions with a plasma generated in the reaction chamber, to enhance reaction of the precursors.

2.3.4 Flame Assisted CVD: FACVD uses an aerosol of the precursor solution which is injected into a flame to activate and accelerate precursors at the target substrate.

2.3.5 Aerosol Assisted CVD: AACVD is a modification of vapor deposition which uses a solution of the precursor in solvent, that is then transported to the substrate in an aerosol form using an inert carrier gas. The solvent then evaporates above the heated substrate allowing reaction of the precursors.

2.3.6 Spray Pyrolysis – Spray pyrolysis is considered a modification of vapor deposition, again using a fine spray of precursor solution (generated by a spray nozzle using compressed gas) which delivers the precursor metal organic molecules to the substrate surface for thermal reaction and film formation.

Chemical vapor deposition does have certain drawbacks, which include the possibility of carbon contamination from metal-organic precursors in the films, adhesion problems under certain conditions, limitations on temperature not compatible with the substrate, the shelf-life of the precursors, and possible side reactions.

3. Zinc Oxide Thin Film By Sputtering Technique

Sputtering is a process in which a target material is bombarded with energetic particles with the purpose of ejecting target atoms onto a substrate that is to be coated with a thin film. The process is dependent upon collisions between particles and electrons and the ensuing momentum exchange. A voltage is applied between the target material (cathode) and the substrate (anode). Due to the voltage, electrons are accelerated away from the target and collide with atoms of the gas (usually an inert gas like argon) occupying the space between the cathode and anode. The gas atoms are ionized and accelerated into the target material by the applied voltage. Collision of the gas ions with the target cause energy to be transferred from the gas ion to the target material. If this energy is greater than the binding energy of the target atoms, an atom will be ejected onto the substrate. In steady state, a constant flux of atoms leaves the target and deposits on the substrate. Sputtering performs high deposition rate, with no toxic gas emissions, is easy to expand to large scale glass substrates with no undesired layer formation problems and is low cost and simple method. It is also seen as one of the most preferred thin film deposition techniques due to its scalability, efficiency and film uniformity.

ZnO films were prepared on glass substrates by (Ahmad, R. *et al.,* 2017) using pulsed DC reactive magnetron sputtering technique. The glass substrates were ultrasonically cleaned in ethanol for 15 min, afterwards, washed out with acetone, and then rinsed in the de-ionized water. Pure Zn target was inserted inside the chamber at a distance of 7 cm from the substrate holder. The chamber was evacuated by using turbo-molecular pump up to 10^{-6} mbar. Argon (Ar) and oxygen (O_2) gasses were used as sputtering and reactive gasses respectively and these were filled inside the sputtering chamber at 50:50 ratio. The DC magnetron sputtering of Zn target was conducted at 60 W in Ar: O_2 environment at 1 mbar working pressure. The deposition time of ZnO film was varied by changing the sputtering time from 2 hours to 5 hours.

(Hammad, A.H. *et al.,* 2018) reported Structural and optical properties of ZnO thin films prepared by RF sputtering at different thicknesses. The Sputtered ZnO thin films with different thicknesses were deposited on glass substrate by RF- sputtering technique using ZnO (3 × 0.6 inch) target. Prior to the deposition, the glass substrates were cleaned using different cleaning steps with acetone and ethanol, then pressurized nitrogen gas was used to dry the glass

substrate. The base pressure inside the chamber was fixed at 6×10^{-6} Torr before inserting the argon gas with a fixed flow rate 20 SCCM. The plasma was generated by applying 200 W RF power for the ZnO target. The film thicknesses of the deposited films were varied from 31, 40, 107, 134 to 280 nm by changing the deposition time from 300, 600, 900, 1200 to 1500 seconds respectively. Other deposition parameters like operating pressure, substrate rotation, distance between target and the substrate were kept constant during the deposition at 5×10^{-3} Torr, 15 rpm and 14 cm.

In (Hassan, A. *et al.,* 2017) the N_2-doped ZnO thin films on glass substrate are deposited (by magnetron sputtering) with different N_2-inflow ratios varying from 0- 50sccm inflow. Before deposition, the glass substrates are cleaned firstly with detergent, and then given ultrasonic bath of acetone and IPA for 15 to 20 minutes, and then dried flowing with N_2. The ZnO target of 99.99% purity is used. Sputtering was carried out in the environment of (Ar + N_2) at room temperature and 10^{-5} Pa of pressure. Distance between target and substrate surfaces was maintained 72mm.

ZnO thin films were deposited on the thoroughly cleaned glass substrates by (Kumar, M. K. *et al.,* 2016). The glass substrates were soaked in Triton-X solution to remove the oily residues present on the surface of the substrates. After the deposition, the films were rinsed thoroughly in the running water followed by ultrasonication in the acetone and ethanol for 10 min. Zinc (99.99 % pure) metal target of 2" diameter and 3.2 mm thickness was used as the target. The substrate size was 2 × 1 cm. The target and the substrates were loaded in their respective positions and the chamber was evacuated to 2.5×10^{-5} mbar base pressure. Argon (Ar) and oxygen (O2) were used as the sputtering and reactive gas respectively. The working pressure of the chamber was kept at 3×10^{-3} mbar. All the depositions were carried out at room temperature. Sputtering was carried out for 15 min with power of 30 W keeping the distance between substrate and target as 50 mm.

(Zulkifli, Z. *et al.,* 2015) prepared three samples of ZnO thin films on glass substrate by RF sputtering. The substrate holder was heated up to 200^0C prior to the deposition process. The deposited ZnO thin films were then annealed in a quartz tube under hydrogen atmosphere for 60 minutes.

In (Senay, V. *et al.,* 2013), the ZnO thin films were deposited on glass substrates by RF magnetron sputtering system from a cylindrical Zinc target of 3N purity of 3 mm × 50 mm. The substrates were thoroughly cleaned by ethyl alcohol and deionized water before the deposition process. The substrates were then dried and placed in the chamber. The distance between the substrates and the target was kept constant at approximately 30 mm during deposition. In order to

generate the oxidation process of Zn, Ar/O$_2$ gas mixture in 1:1 ratio was employed. RF (13.56 MHz) power was adjusted to 125 W. Working pressure was approximately 300 mTorr and cooling water was circulated through the chamber to prevent overheating. The deposition was carried out for 60 minutes under these conditions.

Growth evolution of ZnO thin films deposited by RF magnetron sputtering was reported by (Rosa, A. M. *et al.,* 2012) in which ZnO films were deposited on $10\times30\times3mm^3$ rectangular glass substrates by RF magnetron sputtering technique. The glass substrates were ultrasonically cleaned in detergent diluted in deionized water, rinsed in new ultrasonic bath in deionized water and a final ultrasonic bath in isopropyl alcohol. Afterwards, the substrates were dried in a hot air flow and positioned in the sample holder. A metallic zinc target with 50 mm diameter and 99.99% purity was used as zinc source. The plasma was activated by a 13.56 MHz RF power of 70 W in argon pressure of 1.0×10^{-2} Torr and flow of oxygen of 0.10 sccm. In the lower electrode was mounted a set of magnets of Samarium- Cobalt (SmCo), with circular geometry, and on top of the set of magnets was placed the metallic zinc target. In the top electrode was placed the glass substrate and this was grounded while the lower electrode was applied of RF power. The substrate temperature was measured after the deposition by a thermocouple and it was maintained around 353 K. The ZnO thin film growth rate was approximately 5 nm/ min. In order to study the growth evolution, different ZnO films with thickness ranging from 0 up to 547 nm were deposited.

In (Liang, Z. *et al.,* 2011), the polycrystalline ZnO thin films were prepared on Si (100) substrates by magnetron sputtering method. The ZnO target purity is 99.99%. The intrinsic Si (1 0 0) wafers were cleaned by a standard procedure and transferred into the sputter chamber. The sputtering gas was Ar and the sputtering pressure was maintained at 1 Pa during deposition. The RF power was controlled at 80 W for 20 minutes and the thickness of the thin film is 500 nm.

3.1 Growth Process In Rf Sputtering
Once the sputtered material is deposited on the substrate, adatoms surface diffusion takes place which strongly depends upon the growth conditions such as the environmental energy that is related to substrate temperature. The adatoms surface diffusion results in the nucleation of islands on the substrate. The islands nucleate and grow with the passage of time that is related to adatoms surface mobility on the substrate. In the last step, the islands merge together to form a continuous film structure. Therefore, low crystalline quality of ZnO films may be related to low surface mobility of adatoms on the glass substrate that does not cause islands to grow sufficiently to form ZnO film with good crystalline quality. With increase in the

deposition time, more Zn material was sputtered from the Zn target that enhanced the surface diffusion of adatoms on the substrate. This promoted islands growth and thus the crystalline quality of the thin film.

3.2 Growth Mechanism
According to (Znaidi, L. 2010), there are two possible ways of describing the growth of ZnO crystals: Ostwald ripening and aggregation. As soon as the smallest stable molecular clusters are formed, they rapidly combine to give the next most stable aggregate. The primary aggregates would further rapidly combine to give the next most stable secondary aggregate and so on. It is therefore concluded that the Ostwald mechanism should be considered as only possible approach to the formation of bulk materials.

It has been found by observation of films evaporated directly in the viewing field of an electron microscope that film growth may be divided into certain stages. Namely:

- Nucleation, during which small nuclei are formed that are statistically distributed (with some exceptions) over the substrate surface.

- Growth of the nuclei and formation of larger islands, which often have the shape of small crystals (crystallites).

- Coalescence of the islands (crystallites) and formation of a more or less connected network containing empty channels.

- Filling of the channels.

It is important to note that after a certain concentration of nuclei is reached, additional impinging particles do not form further nuclei but adhere to the existing ones or to the islands formed already. The nucleation process and the growth and coalescence of separate islands have a fundamental importance for the formation of the film structure, i.e. the size of crystallites, their orientation, etc.

In the case of sputtering, the growth of the thin film starts when an atom with the energy of more than about 30 eV bombs the surface of the substrate, a small fraction of the energy and momentum of the incoming ion will, through lattice collisions, be reserved and may cause ejection of surface atoms. The sputtered atoms leave the target surface with rather high energies (~10eV) compared with evaporated atoms (~0.1eV). The average number of the atoms ejected from the surface per incident ion is called the sputtering yield. To reach a practical deposition on substrate, an ion source of sufficient high flux and a way for accelerating the ions are needed. The ion source is usually plasma generated by electron impact in a noble gas (e.g. Argon) at sub-atmospheric pressures. The ions are accelerated

in an electric field produced by applying a negative potential with regard to the plasma potential to an electrode absorbed in that plasma. When the accelerating ion comes within a few angstrom of the target surface, it is neutralized by an electron from the surface. The neutralized atom, upon interacting with the target surface, may cause the emission of target atoms and secondary electrons. These so-called γ electrons are necessary for generating and maintaining a direct current (dc) glow discharge.

The flow of electrons from the target constitutes an electric current that result in appreciable power dissipation at the target. This power must be dissipated within the chamber since there is no increase in the potential energy of the substrate or the deposited film. The only permanent changes that occur in the chamber are a transfer of material from the target to the substrate. Essentially all the electric power supplied to the chamber is converted into heat inside the chamber. Such heat must be controlled to provide stable, reproducible conditions for film deposition.

4. Role of Deposition Parameters on Optical, Structural and Electrical Properties

The most commonly studied deposition parameters in sputtering include but not limited to film thickness, rf power, substrate temperature, substrate rotation, target/substrate distance and process gases flow rate. In (Senay, V. *et al.,* 2013), the mean thicknesses of the samples were found to be approximately 80 nm and 190 nm. The measured refractive indices of the deposited films at =550nm are 2.03 and 2.05 for 80nm and 190nm thicknesses, respectively. A high transmittance (T = 91 and 89% at = 550 nm for 80 nm and 190 nm, respectively) and a very low absorbance (A = 0.04 at = 550 nm) were observed at wavelengths longer than 400 nm. The optical band gaps of the deposited ZnO films are found to be 3.5 eV and 3.3 eV for 80 nm and 190 nm thicknesses, respectively.

In (Ahmad, R. *et al.,* 2017), the XRD pattern of the 2-hour deposited film does not show any diffraction peak relating to ZnO. When the deposition time is increased to 3 hours, then ZnO diffraction peaks corresponding to (1 0 0), (0 0 2) and (1 0 1) planes are observed at 31.8°, 34.5° and 36.2° respectively. By increasing the deposition time to 4 hours, intensities of (1 0 0) and (0 0 2) diffraction peaks are decreased whereas the intensity of (1 0 1) peak is increased which indicates that the ZnO film shows preferred orientation towards (1 0 1) plane. The diffraction peaks corresponding to (1 0 0), (0 0 2) and (1 0 1) planes are observed at 32.1°, 34.9° and 36.5° respectively. With further increase of deposition time to 5 hours, structural quality of ZnO film is improved and the film shows preferred orientation along (0 0 2) plane. The diffraction peaks are shifted back towards lower angles as compared to the 4-hour deposition time. The

crystallite size D and strain ε in ZnO films along (0 0 2) plane were also analyzed. The average grain size at 2 hours, 3 hours, 4 hours and 5 hours deposition time was found to be ~45 nm, ~80 nm, ~105 nm and ~120 nm respectively. The increase of grain size with increase of deposition time suggests that more ZnO material is deposited on the substrate that enhances the islands growth and their coalescence forming the bigger grains. All the ZnO films show absorption of light in UV region between 300 nm and 380 nm. The absorption increases with increase in the deposition time. The 5-hour deposited ZnO film shows larger UV absorption as compared to the films deposited for lesser time. The band gap of ZnO was found to be 3.36 eV, 3.30 eV and 3.27 eV for the films deposited at 3, 4 and 5 hours respectively.

(Purohit, A. *et al.,* 2015) reported that the optical absorbance and transmittance spectra of as-grown and annealed ZnO thin films (thickness 50 nm grown on glass and indium tin oxide (ITO) coated glass substrates) were measured in the wavelength range 300 to 800 nm. The absorption coefficient is observed to increase with photon energy and found maximum in the high photon energy region which indicated band to band transition occurred in the high photon energy region (hv > 3 eV) while transitions between conduction band and ionized donor occurred in lower energy region. The absorption coefficient is also found to decrease with annealing in the lower energy region while vary slightly in the higher photon energy region. The optical energy band gap is varied from 3.30 eV to 3.52 eV and found to decrease with annealing. The optical absorption edge shows blue shift for annealing temperature 150 ^{0}C and red shift for higher annealing temperature. The extinction coefficient is found to be decreased with low temperature annealing and has an order of 10^{-1} except annealing temperature of 150 ^{0}C. It is found to be maximum at higher photon energy. The refractive index is found in the range 2.20 to 2.26 and observed to increase with annealing temperature except thin films annealed at 150 ^{0}C. The absorbance is found to be 1.58% in lower wavelength range and found to decrease with wavelength for as-grown and annealed thin films. The absorbance is observed to decrease slightly with annealing which indicated the band to band transition occurs between conduction band and ionized donor. The optical transmittance spectra of ZnO thin films show that the transmittance is increased in the lower wavelength range and found more than 40% in the visible range for as-grown and annealed films. The transmittance is also found to increase with annealing temperature. The diffraction peaks are observed in XRD pattern for the as- grown ZnO thin films at angular positions 31.61^{0}, 34.35^{0}, 36.89^{0}, 56.23^{0} and 67.91^{0} corresponding to orientations (1 0 0), (0 0 2), (1 0 1), (1 1 0) and (1 1 2) respectively. The pattern reveals that these films are crystallized in wurtzite structure of hexagonal phase having (1 0 0) preferred reflection and oriented along c-axis perpendicular to the substrate

surface. The calculated inter planner spacing is found in the range 2.807 to 2.827 Å and observed to decrease with annealing temperature. The lattice constants (a) and (c) are found in the range 3.241 to 3.265 Å and 5.614 to 5.655 Å respectively and these are observed to decrease with annealing. The FWHM and grain size are found in the range 0.7366 to 0.8063 and 10.69 to 11.71 nm respectively. The transverse current–voltage measurements were performed for as-grown and annealed ZnO films employing a source-meter. The variation in current with voltage for as-grown and annealed ZnO thin films is found to be linear and current is observed to increase with annealing temperature owing to realignment of the grains which indicated that the low temperature thermal annealing in air atmosphere created minor crystal growth. The resistivity of the films is found to decrease with annealing temperature. The electrical resistivity of pure ZnO films depends on the oxygen deficiencies or the presence of interstitial Zn in the ZnO lattice. The oxygen deficiencies or Zn interstitials in the ZnO lattice are increased with annealing temperature and may be attributed to the increase in free electrons.

In (Viswanathan, K. *et al.,* 2016), the Zinc Oxide (ZnO) thin films were deposited on n-type silicon (Si) by radio frequency magnetron sputtering at room temperature. The sputtering power was 80W and the experiment was performed for 1hour. The deposited films according to the XRD results were found to be well crystallized in the hexagonal system. The grain size of crystallites was found to be in the range of 30 to 50nm. The ZnO thin film thickness affects the electrical properties or the I-V characteristic of ZnO thin films. The reverse recovery time is 1nano second, forward drop voltage is less than 1V while the leakage current is 200 Na, corresponding to a current density of $10 Acm^{-1}$. The diode current can be determined from the forward bias characteristic. The Power factor reduces the cutoff voltage and functions even at high thermal affect. These films can be used for Hydrogen gas sensing.

Calcium doped zinc oxide (CZO) thin films were deposited by magnetron sputtering technique based nanocrystalline particles elaborated by sol-gel method in (Mahdhi, H. *et al.,* 2017). The films were deposited with different calcium concentrations. Three pronounced ZnO diffraction peaks, (100), (002) and (101) appeared at $2\theta = 31.87°$, $34.47°$ and $36.21°$ respectively. The surface morphology of the ZnO:Ca 3% nanoparticles has spherical particle structure with un-even grain size around 30 nm. The EDX analysis confirmed the presence of calcium in the matrix of ZnO and absence of other impurities. All the films are found to have the hexagonal wurtzite structure. The (002) peak intensity increases with the calcium concentration and reaches a maximum for a concentration of 3.0 at. % of Ca. The crystallite size was varied from 17 to 24 nm. A small displacement with the calcium concentration was observed, indicating that residual stress inside the

film may exist. The transmission spectra of ZnO:Ca thin films show strong interference fringes due to the multiple reflections at the interfaces; their observation indicates a fairly homogeneous film thickness. All samples exhibit a high transmittance (> 80%) in visible region, independently of the calcium concentration, indicating a good optical quality of the films with low scattering or absorption losses. The refractive index has a value which varies between 1.70 and 2.40, whereas the extinction coefficient of films is characterized by an increase but remains relatively low. The minimum value of the resistivity is about $5×10^{-3}$ Ω.cm, obtained for 3 atomic percentage (at.%) of Ca which correspond also to the maximum of the mobility (μ) $7.81 cm^2/V_s$ and the carrier concentration (n) $1.6×10^{20}$ cm^{-3}. A minimum resistivity is obtained at Ca doping concentration of 3.0 at. %, which correspond also to the maximum of the mobility and carrier concentrations. However, with further increase in Ca concentration, the resistivity is found to increase, and the Hall mobility of the films also decreases. The ZnO film generally grows as n-type semiconductor due to the presence of native defects in the form of either zinc interstitials or oxygen vacancies or both. The CZO films can be used as a transparent electrode.

In (Hassan, A. *et al.,* 2017), all the samples show high transparency >80% in visible region which drops to 0% at 350nm wavelength. It has also been observed that with the increase of N_2-inflow transmittance increases generally, with 20sccm flow of N_2 having the maximum transmittance of about 97%. In UV region, the absorbance is high and in visible spectrum it is found very low and goes to zero from infrared region and onward. A clear shift in absorption edge is observed with the function of doping concentration, which shifts the absorbance edge into visible region. With 50sccm inflow of N_2, the absorption edge falls to 440nm wavelength. And in pure ZnO thin films it falls to near 400nm wavelength. The band gap decreases with increase in the N_2-inflow ratio. The optical conductivity of ZnO thin films was also analyzed and results are found in such a way with 25sccm N_2 inflow the conductivity rose to the maximum value of about $1.4 × 10^7$ Ω^{-1} cm^{-1}, with 15sccm inflow of N_2 the conductivity value is $2.0 × 10^6$ Ω^{-1} cm^{-1} in the visible region after that it is decreasing exponentially. It is therefore concluded that the high doping of N_2 made these ZnO thin films very good UV absorber.

In (Hammad, A.H. *et al.,* 2018), the sputtered ZnO thin films show a polycrystalline nature with hexagonal structure. Two prominent peaks representing (002) and (103) planes are observed for all the thin film samples. The observed plane (002) is sharper and narrower than (103) plane. The sharper plane (002) was also observed for undoped ZnO sputtered films. The plane (002) is observed to increase in the intensity as the film thickness increases from 31 to 40 nm and

decreased when the film thickness exceeding 100 nm. The intensity of plane (103) is observed to increase as the film thickness increases. As the film thickness increase, the T_c (103) increases from 0.166 to 1.262 while T_c (002) varies from 1.834 to 0.735. The lattice parameter c values are observed to be higher than C_0 while the lattice constant a values are varied increasingly or decreasingly related to a_0 (a_0=3.248 Å) as the film thickness increases. For very low thickness of 31 nm, non-distinctive grains are presented. Major grains are of small size around 25.4 nm and few massive grains are detected with average size around 66 nm. The roughness of 31 nm ZnO film is recorded around 2.18 nm. For the film thickness of 40 nm, the grains appear distinctive with spherical shape. The massive grains disappeared, and the grain size is around 25 nm. The film roughness recorded 1.3 nm which means that films of 40 nm thickness are better in quality than 31nm. By increasing the film thickness to 107 nm, the grains are longitudinal shaped and become more identifiable than the previous thicknesses. However, the average grain size is still around 25 nm and the film roughness increase to 1.8 nm. ZnO Samples of thickness greater than 107 nm (134 nm and 280 nm) show larger grains and higher roughness. The grains increase from 30 to 40 nm, and the roughness varies from 1.82 to 2.44 nm respectively. The transmittance maxima increase with increase in the film thickness and the thickness at 280 nm behave good quality due to the presence of interference fringes. The Tauc plot for $(\alpha h v)^2$ vs. $h v$ give the value of E_g= 3.22 eV for direct transition, while the other curve gives E_g= 2.83 eV for indirect transition. The optical band gap increases as the film thickness increases.

The structure and morphology of ultra-thin zinc oxide (ZnO) films with different film thicknesses on confined polymer template were studied by (Singh, A. *et al.,* 2017). Zinc metal sputtering target was used for the deposition at 31 W, under Argon gas flow (~30 sccm) and oxygen partial pressure of 50 mPa (mean Oxygen gas flow ~10 sccm) with different deposition time to grow different thicknesses of ZnO films. Electron density profiles clearly indicate the presence of ZnO thin layers of different thickness, on top of confined polystyrene films for three different ZnO/PS (zinc oxide/polystyrene) samples. The sharpness of the air- ZnO and ZnO-PS interface suggest the formation of smooth (low roughness) ZnO thin films on confined polystyrene (PS) templates in a controlled manner (with fine precision of thickness), with a negligible diffusion of ZnO in PS films. All three systems with different ZnO film thickness show high coverage of ZnO, approximately 95%-100% as calculated from the bulk electron density of ZnO, which is 1.52eÅ^{-1}, irrespective of the ZnO film thickness for the ZnO deposition at 31 W. In between ZnO layer and Si substrate (along with a thin SiO$_2$ layer, of thickness <2 nm, on top of the Si substrate), there is a layer of thickness ~40 nm, with constant electron density, ~0.3 eÅ^{-3}, along the depth of the film, which corresponds to the polystyrene (PS) bulk electron density (0.31 eÅ^{-3}), confirming the negligible diffusion of ZnO into the PS film. The observation and precise thickness determination through X-ray reflectivity (XRR) indicate that the growth of ultra-thin ZnO films on confined PS template was achieved without causing any disruption in the polymeric system. ZnO exhibits two types of luminescence due to near band edge (NBE) and defects or deep-level (DLE) emissions in the UV and visible range respectively. Defect emissions (DLE) can originate from multiple defects and/or defect complexes involving oxygen vacancy (V$_0$), oxygen interstitials (O$_i$), oxygen antisite (Zn$_0$), zinc vacancy (V$_{Zn}$), zinc interstitials (Zn$_i$), and zinc antisite (O$_{Zn}$) in ZnO. These defects create deep levels in the bandgap and may act as recombination centers by capturing charge carriers during photoexcitation. In the emission spectra of ZnO/PS, the presence of two distinct deep-level peaks in visible region at~2.5eV and~3eV which correspond to green and blue/violet luminescence respectively, along with a significant NBE emission (~3.5 eV) of ZnO in UV range, which is blue shifted with respect to that of bulk ZnO were observed. With decreasing ZnO film thickness, photoluminescence spectra of ZnO/PS samples show relatively strong defect or deep-level emission that can be attributed to a significant enhancement of surface defects because of the greater surface to volume ratio.

5 CONCLUSION

Considerable progress has been made in the development of ZnO thin films by various deposition methods. We reviewed deposition methods that are most popular in the fabrication of ZnO thin films on different substrates. A complete section has been devoted to ZnO thin film deposition by RF sputtering technique. Influence of various process parameters upon the properties of ZnO thin films was also discussed. A comparative assessment of different deposition methods revealed that the RF sputtering is the simplest since all the deposition parameters can be controlled.

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