# Synthesis, Dopant Study and Device Fabrication of Zinc Oxide Nanostructures: Mini Review

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Abstract- The advantageous crystal structure properties along with the ease growth of one-dimensional (1-D) zinc oxide (ZnO) nanostructures define the material to possess wide technological applications. The ultimate goal of this review article is to provide an overview of research activities prevailing on ZnO nanostructures from the basic synthesis technique to world-wide scientific and industrial applications. The article covers the recent progress, growth of ZnO nanostructures with unique and dimensionality confined morphology through surfactant-assisted simple chemical precipitation methods and through newly emerging self assembly techniques. Much emphasis is showered on the growth of nanostructures with controlled size and shape, synthesized by means of precipitation of a solid phase from solution. It also highlights the superior physio-chemical properties including structural, optical, electrical, and magnetic properties with the addition and substitution of dopant atoms. The optical properties including UV absorption and luminescence studies are rigorously probed for samples in the form of nanostructures and thin film prepared by various methods and doped with different impurities. The review further outlines the implementation of material properties in opto-electronic device applications and their commercial availability. This article extensively explores the achievements, research prospects, limitations and updates upcoming in *n*-type and *p*-type ZnO nanostructures. Additionally, we devote our attention to the study of native defects, origin of surface defects, defect emissions and their role in producing unintentional ntype ZnO. Finally, the review concludes with the homo- and hetero-type junction formation, device characterization and the open challenges to stabilize the device construction. This article also includes the research work carried out in our nanomaterials laboratory on ZnO preparation (both powder and thin film) and their characterizations and property studies will be presented briefly. We trust this review will be beneficial to expand the practical applications and offer some inspirations to the researchers in the fields of engineering, biomedicine, and materials science.

Keywords- One-dimensional; Solid Phase; Dopant Atoms; Native Defects; Physio-Chemical Properties

# I. INTRODUCTION

Nanotechnology is a new science or technology bringing drastic changes in the properties of physical systems when their dimensions are approached to nanometer scale. The prefix "nano" does not merely mean small system (10<sup>-9</sup> m) but of high potency with large applications piercing through all discipline of knowledge thereby, leading to industrial and technological growth. Nanotechnology, abbreviated as "nanotech", has witnessed rapid and broad developments over the past decades. The National Nanotechnology Initiative (NNI) defines nanosized particles as roughly 1 nm

to 100 nm in dimensions and this range can extend to 1000 nm<sup>[1]</sup>. Nanomaterial displays novel optical, electronic and structural properties different from an individual molecules or bulk particles. Nanoscience is concerned with the synthesis, characterization and has found its way to high end applications and engineering in industrial sectors, such as electronics, communication, energy, advanced materials, space technology and biomedicine. Nanoparticles are subjects of interdisciplinary covering a large diversity of chemistry, physics and material science. Nanostructures with unique structural geometries can adopt wide technological applications in the fabrication of microelectronic to nanoelectronic circuits, effective sensors, piezoelectric devices, fuel cells for energy concern, coatings for the passivation of surfaces against mechanical wear and corrosion, and as reaction catalysts. The ultimate goal of nanotechnology is to grow nanostructures of self-assemblies with superior physio-chemical properties compared to those of bulk materials or single particle species. To achieve such material compound significant conditions are adopted and analyzed theoretically and experimentally from the initial synthesis stage to device fabrication.

The characteristic feature which decorates the nanocrystalline field or which lay a boundary between the discrete and continuum crystalline compound is the quantum confinement (QC)<sup>[2]</sup>. The QC enriches and manipulates the material performance by several factors such as establishing appropriate growth technique, having a control on the synthesis condition, tuning the distribution and concentration of atom, selective incorporation of foreign atoms, and many more. Among them, the two widely accepted methods to modify the electrical and optical properties of a semiconductor are the usage of optimized synthesis condition and addition of impurity atoms or doping  $[^{3-5}]$ .

In the first case, the synthesis of nanoparticles in large yield with novel properties remains a challenge for fundamental research. ZnO 1-D nanostructures have been one of the most studied families of nanostructures <sup>[6-8]</sup>. The one-atom thick structures represent the ideal physical system for studying size effects and low-dimensional physics. ZnO nanoparticles around the size of individual atoms and molecules exhibit both physical and chemical behavior, very different from that of bulk size materials. Number of synthesis techniques including physical and chemical methods have been adopted. In comparison, the chemical methods are much more effective than physical methods as they are cost effective and all the synthesis parameters are highly controllable and tunable. Many groups have successfully adopted new chemical growth techniques and chemistry to synthesize controlled structural and optical properties of ZnO nanostructures. ZnO nanopowders are produced in large scales by employing simple, cost effective surfactant-assisted hydrothermal and co-precipitation methods. Now a days, several reports have been appeared which explain the predictable nature of hydrothermal interactions with reactant during the synthesis of materials. However, the exact growth mechanism still remains unclear and speculative.

Secondly, the electronic band structure and their optimization are of great importance in designing semiconductor devices. It can be simulated by changing the material crystal structure and chemical composition. As the impurity atoms are introduced, the spatial geometries which are providing the lowest energy configuration in the bulk may not provide the same, as the surface atoms and surface bonds are altered <sup>[9,10]</sup>. The performance of the device is well tuned and tailored by the controlled addition of dopant atoms resulting in surface modification and property enhancement. Numerous dopants including transition metal ions, rare earth ions, magnetic ions and their co-doping are performed in ZnO. ZnO has been doped with Mn or rare earth elements in order to change their luminescence properties. The electrical and optical properties of ZnO are enhanced by doping with Groups III, IV, and V elements (eg. Li, Ga, In, Sn, Sb, N, and P)<sup>[11-13]</sup>. Spintronic devices such as magnetic-optic switches, magnetic sensors, spin valve transistors, spin light emitting diodes can be activated by implanting ferromagnetic Mn, Ni, Co and Cr in ZnO nanorods<sup>[14-17]</sup>.

Recently, property study of trivalent ions of transition metal elements trapped in host materials has attracted a great deal of attention in the present days. The aluminium doped ZnO (Al: ZnO) and yttrium doped ZnO (Y: ZnO) nanomaterials are powerfully implanted as sensor coatings for hazardous gas detection <sup>[18]</sup>. Doping ZnO with trivalent Al and Y reduces the optical energy bandgap and thus, improves the optical conductivity in ZnO. The enhanced conductivity in nonstoichiometric ZnO is due to the presence of oxygen vacancies  $V_O$  and interstitial zinc  $Zn_i$ . During the incorporation of trivalent ion in ZnO, the existence of interstitial metallic Zn increases with increase in  $V_{0}$  and thus, promotes a transition from semiconductor to metal-like behaviour <sup>[19]</sup>. As a result, Al:ZnO and Y:ZnO has been considered as transparent conducting oxides (TCO) and piezoelectric (PZT) materials for fabricating solar cells, electrodes, high electron mobility transducers and gas sensors. The enriched conductivity in Al:ZnO is regarded as an alternative candidate for indium tin oxide (ITO) materials.

Though many scientific achievements are established in ZnO, there are few hurdles to go ahead. ZnO are partially ionic in nature due to the natural existence of native defects such as zinc vacancy  $V_{Zn}$ ,  $Zn_i$  and  $V_O$  incorporated during their growth or synthesis. As a result there is a lack of stable reliable *p*-type dopant impurities for ZnO. In order to attain the potential offered by ZnO, both high quality *n*- and *p*-type ZnO are indispensable. However, difficulty in bipolar

carrier doping (both *n*- and *p*- types) is a major obstacle as seen in other wide bandgap semiconductors such as GaN and II-VI compound semiconductors including ZnS, ZnSe, and ZnTe  $^{[20-22]}$ . The difficulties in *p*-type doping can arise from a variety of causes. Dopants may be compensated by low-energy native defects, such as  $Zn_i$  or  $V_0$ , or background impurities (H). Low solubility of the dopant in the host material is also another possibility. Deep impurity level can also be a source of doping problem, causing significant resistance to the formation of shallow acceptor level. The ptype doping in ZnO may be possible by substituting either Group-I elements (Li, Na, and K) for Zn sites or Group-V elements (N, P, and As) for O sites. It has been believed that the most promising dopants for *p*-type ZnO are the Group-V elements, although theory suggests some difficulties in achieving shallow acceptor level. The achievements in ptype ZnO and their property studies including structure, morphology, optical, magnetic, and transport are updated periodically <sup>[23-25]</sup>. As the diffusion capability of Li is greater, the lithium doped ZnO (Li: ZnO) acts as an effective catalyst for the trans-esterification of soyabean oil with methanol <sup>[26]</sup>. A stable p-type Li: ZnO nanopowders utilized for dye sensitized solar cell exhibits an efficiency of ~53%, is synthesized by conventional method <sup>[27, 28]</sup>.

The limitation in conquering *p*-type doping in ZnO, switched the researcher to work on hetero- junctions <sup>[29-31]</sup>. The combination of organic and inorganic structures offers a variety of existing technological challenges that leads to a dramatic improvement in function and cost. The architecture of organic-inorganic LEDs consists of *p*-type polymer and *n*-type ZnO sandwiched between two metallic electrodes of varying work function namely ITO and aluminium. The organic material has high luminescence efficiency where as the inorganic material has high charge carrier density, high mobility, steady chemical properties, and high strength. These properties define a material compound with high performance electroluminescence device.

### II. GENERAL BACKGROUND

# A. About Zinc Oxide

The surface and quantum size confinement (QSC) are believed to be the key factors in determining the novel electrical, mechanical, optical, and chemical properties of reduced particle especially, in the quantum regime <sup>[32]</sup>. Quantum mechanical effects with reduced dimension (nanometric range) affect the band structure of semiconductors leading to changes in atomic structure. The emergence of nanotechnology and the study of 1-D ZnO nanostructures such as nanotubes, nanorods, nanocables, nanowires and nanoribbons stimulate considerable interests for scientific research due to the well establishment in understanding the fundamental physics and potential applications. The low processing temperature and full compatibility with large scale integrated circuit fabrication, ZnO nanostructures is recognized as a promising material for improving nanoscale optoelectronic devices, such as bandgap engineered solar cells, organic light emitting diodes (OLED's), Ultra-violet (UV) laser diodes etc. [33, 34].

Research works on ZnO material started as early as 1920s with the first utilization of ZnO for its semiconducting properties as a detector in build-your-own radio sets, in which a thin copper wire, known as "cat's whisker", is placed in contact to sensitive spots on a ZnO crystal <sup>[35]</sup>. ZnO is II-VI inorganic compound semiconductor; exhibiting a wurtzite structure with hexagonal unit cell. ZnO being a wide bandgap semiconductor with large exciton binding energy of 60 meV has emerged as a potential candidate in the field of research from the past to till date. The wide direct bandgap transition exhibited by ZnO is much advantageous over indirect bandgap semiconductor as they do not involve phonon transition for wave vector conservation. The wide optical bandgap has a major influence on physical properties of the material like optical absorption, index of refraction, band structure, electrical conductivity and also makes ZnO an efficient emitter and high transparency in the short wavelength applications from blue to UV spectral range. This property enables ZnO to fabricate LED's of various colours (green, blue, red and white), UV photodetectors, UV blue laser diodes, flat panel displays, optical waveguides, transparent electrodes, transistors, nano-generators, solar cells, and many more. 1-D ZnO nanostructures (rods, fibers, tubes, wires, ribbons) are of special interest due to their unique catalytic, electronic, optical, thermal, and photonic properties intrinsically associated with their low dimensionality and QSC effect. ZnO nanomaterials are subject of intense research as they are low cost, efficient and environmentally friendly semiconductor materials with wide application in gas sensing, catalysis, energy storage, optoelectronic devices, UV lasing action, surface acoustic wave devices, PZT transducers, blue LEDs, TCO, and many more. With these aspects, it is highly expected that 1-D ZnO with tuned aspect ratios would be a potential candidates for exhibiting several interesting phenomenon. The growth, properties and applications of nanosized ZnO are systematically reviewed and reported by [36-38].

### B. Fundamentals of zinc oxide

At ambient pressure and temperature, ZnO crystallizes in the wurtzite structure which is considered to be the relatively thermodynamically stable phase of ZnO. Wurtzite ZnO is a hexagonal lattice, belonging to the space group of  $P6_3mc$  with lattice parameters a = 0.3296 nm and c = 0.52065 nm. In an ideal wurtzite crystal, the axial ratio c/a and the *u* parameter (which is a measure of the amount by which each atom is displaced with respect to the next along the *c*-axis) are correlated by the relationship uc/a = $(3/8)^{1/2}$  where  $c/a = (8/3)^{3/2}$  and u = 3/8. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions, stacked alternatively along the c-axis. The tetrahedral coordination in ZnO results in non-central symmetric structure and consequently piezoelectric and pyroelectric properties. Additional to the wurtzite phase, ZnO is also known to crystallize in the cubic zinc blende and rocksalt (NaCl) structures, which are illustrated in Fig. 1<sup>[33]</sup>. Zinc blende ZnO is stable only by growth on cubic structures, while the rocksalt structure is a high-pressure metastable

phase forming at  $\sim 10$  GPa, and cannot be epitaxially stabilized. Theoretical calculations indicate that a fourth phase, cubic cesium chloride, may be possible at extremely high temperatures.



Fig. 1 Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt, (b) cubic zinc blende and (c) hexagonal wurtzite structure. The shaded gray and black spheres denote zinc and oxygen atoms respectively.

Another important characteristic of ZnO is the polar surfaces (refer Fig. 2) [33]. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(000-1) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO  $\pm$  (0001) are exceptions: they are atomically flat, stable and without reconstruction. Efforts to understand the superior stability of the ZnO  $\pm$ (0001) polar surfaces are at the forefront of research in today's surface physics. The other two most commonly observed facets for ZnO are  $\{2-1-10\}$  and  $\{01-10\}$ , which are non-polar surfaces and have lower energy than the {0001} facets. Aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also common indicator of  $sp^3$  covalent bonding. However; the Zn-O band also possesses very strong ionic character, and thus ZnO lies on the border line between a covalent and ionic compound, with an ionicity of fi = 0.616. On the other hand, each oxygen (or zinc) ion is tetrahedrally surrounded by four zinc (or oxygen) ions in the wurtzite structure. [0 0 0 1]



Fig. 2 Wurtzite ZnO and its polar surfaces.

Further, each ion has twelve next-nearest neighbors of the same type of ions. The O-Zn distance of the nearest neighbors is 1.992 Å in the direction parallel to the *c*-axis of the hexagonal unit cell and 1.973 Å in the other three directions of the tetrahedral arrangement. The tetrahedral

arrangement between the nearest neighbors indicates the Since 1960s, the S

covalent bod between the zinc and oxygen atoms. The covalent radii of zinc and oxygen are reported to be 1.31 Å and 0.66 Å, respectively.

# C. Open Challenges

□ Extended and oriented nanostructures are desirable for many applications. However, direct fabrication of complex nanostructures or device architecture with controlled crystalline morphology, orientation, and surface architectures remains a significant challenge.

□ The second main obstacle is the lack of reliable and stable *p*-doping for ZnO. Despite the successful demonstration of ZnO *p*-doping with P, As, and N, the hole concentration in the *p*- ZnO is still limited to  $2\sim3 \times 10^{17}$  cm<sup>-3</sup>, which is insufficiently high to provide efficient carrier injection into the active region of *pn* junction.

 $\Box$  The third challenge is to demonstrate radically new applications for 1-D ZnO nanostructures.

# D. Applications

ZnO with interesting material properties establishes numerous applications. The world usage of ZnO in 2004 is estimated to be over a million tons. The biggest markets are Asia and Europe (about 300,000 tons ZnO are used in Europe during 2004)<sup>[39]</sup>. ZnO is commercially used as varistor materials, PZT, sensors, surface acoustic wave devices, TCO (e.g. electrode of solar cells), glasses (reduces thermal expansion coefficient of glasses), rubber industry (effective activator of the curing process of natural rubber, increases heat conductivity in tires, retards devulcanization of many rubber types, stabilization of latex foam rubbers, rubber metal bonding), addition to plastics to tune properties like viscosity, fire-resistance, tensile strength, etc., paints, white pigment, phosphors (green phosphors in displays), pharmaceutical industry (antiseptic healing creams, suntan lotions, source of micronutrient zinc), agriculture (addition to fertilizers, source of micronutrient zinc for plants and animals), lubricant (reduce corrosion and wear of engines), photocopying process, anticorrosive coating of metals, constituent of cigarette filters (reducing amounts of HCN and H<sub>2</sub>S in the smoke). This demonstrates the wide usage of ZnO in industry.

The non-centrosymmetry and polarity developed along the *c*-axis make ZnO material inherently piezoelectric, which, in combination with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties useful in actuators, piezoelectric sensors, and nanogenerators. On the other hand, ZnO is also a biocompatible material with a high isoelectric point (IEP) of 9.5, which makes it suitable for adsorption of proteins with low IEPs, because the protein immobilization is primarily driven by electrostatic interactions <sup>[40]</sup>. Moreover, ZnO nanostructures have unique advantages including high specific surface area, low toxicity, chemical stability, electrochemical activity, and high conductivity. Hence, ZnO is a promising material for biosensor applications and can be directly used for biomedical applications without coating.

Since 1960s, the synthesis of ZnO thin films has been an active field because of their applications in sensors <sup>[41]</sup>. ZnO nanostructures with high surface area are used for sensing applications because of high sensitivity to the chemical environment. ZnO nanowires have demonstrated high sensitivity even at room temperature. The sensing process is governed by  $V_0$  on the surface that influence the electronic properties of ZnO  $^{[37]}$ . 5.1 µm long ZnO nanotube arrays are prepared by chemical etching of electrochemically deposited ZnO nanorods on FTO substrate <sup>[42]</sup>. By varying the deposition condition of Zn.Ac<sub>2</sub> precursor, a full-sun energy conversion efficiency of 1.18% is achieved. With this efficiency it can drive humidity sensor without 0 V external power (self-powered device). Recently high sensitivity enzymatic biosensor, as high as 201.12 mAM<sup>-1</sup> is demonstrated by complex multiple forklike ZnO nanostructure grown by citric acid assisted annealing process <sup>[43]</sup>. Here, the ZnO nanostructure grows from a thin base platelet whose width ranges from 60 nm to 230 nm, the diameter of the rod is about 16 nm to 60 nm and the length varies from 0.5 µm to 1.3 µm. Moreover, the biosensor displayed good stability, high sensitivity, and quick response to  $H_2O_2$ .

ZnO is the most extensively studied wide-bandgap material for both photo-voltaic (PV) and thin film transistor (TFT) applications. Being efficient electrical conductivity, optical transparency and TCO, ZnO are employed in many device applications. Suchea et al., suggested a simple, facile chemical route for the growth of ZnO thin films on rigid (glass) and flexible (PET) substrates for TFT applications . ZnO nanowire and nanosphere compound nanostructure are prepared by employing trisodium citrate in order to control the nucleation and growth rate thereby produces nanospheres in the interstices between the nanowires [45]. Filling the nanospheres in the interstices is mainly to increase the surface area of the photoelectrode and to promote light scattering and enhance the photon adsorption. In comparison, compound nanostructure DSSC exhibits a significant enhancement of the short-circuit current density than nanowires. ZnO:Al<sub>2</sub>O<sub>3</sub> ceramic targets are used to deposit transparent and conductive quasi-crystal Al-doped ZnO thin films <sup>[46]</sup>. The relationship between structure property and optical, electrical properties are investigated by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), optical transmittance and four probe point system. Thus, quasi-crystal Al-doped ZnO thin film with excellent crystallinity, grain size of 77 nm, optical transparency of 85% in the visible region and low resistivity can be used in PV devices either as front electrode or back side reflector. As the applications concerned with ZnO nanoparticles cover a wide range, several challenges must be overcome to utilize them in efficient manner and for mass commercialization.

# III. SOLUTION PRECIPITATION PROCESS

The synthesis of nanomaterials includes control of size, shape, and structure. Assembling the nanostructures into ordered arrays often becomes necessary for rendering the nanostructures to functional and operational performances. In the last decade, nanoparticles (powders) of metal oxides have been produced in large scales by employing both physical and chemical methods. Nanomaterials with narrow size distributions have been prepared by controlling the shape in some instances. All particle synthesis techniques fall into one of the three categories: vapour-phase, solution precipitation and solid-state processes.

Precipitation from colloidal solutions is evidently the first method of producing nanoparticles [47]. The conventional method of producing nanoparticles from colloid solutions is based on a chemical reaction between the components of the solution and interrupting the reaction at a specific time. Subsequently, the dispersed system is transferred from the liquid colloid state to the nanocrystalline solid state. The method of precipitation from colloidal solutions is characterized by high selectivity and thereby, produces stable nanoclusters with narrow size distribution. The main problem associated with the method of precipitation from colloidal solutions is the coalescence of nanoparticles. Precipitating clusters of inorganic compounds from a solution of chemical compounds have been an attractive intention for researchers, primarily because of the simplicity with which experiments can be conducted in a laboratory. A major advantage of solution processing is the ability to form encapsulated nanoparticles, specifically with an organic molecule, for providing functionality to the nanoparticles, improving their stability in a medium, or for controlling the shape and size. Solution processing can be classified into five major categories: solprocessing, precipitation method, water-oil gel microemulsions (reverse micelle) method, polyol method, and hydrothermal synthesis. Among various solution synthesis methods co-precipitation and hydrothermal methods are the most recognized and benefited.

The hexagonal faceted ZnO quantum dots about 3-4 nm are prepared by oleic acid assisted sol-gel route [48]. These quantum dots show an enhanced photocatalytic activity for photocatalytic decomposition of methylene blue than the spherical quantum dots. This is due to the small size with large surface and high crystalline nature. In addition, the Znterminated (001) and O-terminated (001-) polar faces are facile to adsorb oxygen molecules and OH ions, resulting in a greater production rate of H<sub>2</sub>O<sub>2</sub> and OH radicals, hence promoting the photocatalysis reaction. Recently, Elilarassi and Chandrasekaran synthesized Ni-doped ZnO of varying concentration by sol-gel (auto-combustion) method and reported the existence of room temperature ferromagnetism [49]. Such material compounds are dilute magnetic semiconductors (DMS) and hence find applications in Spintronics. Tetrapod like ZnO with legs length between 200 nm to 300 nm is prepared by microemulsion-mediated hydrothermal method [50]. FESEM, transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selective area electron diffraction (SAED) analyses are performed to understand the growth mechanism and formation of tetrapod-like morphology. Further, the electrochemical characteristics of as-synthesized tetrapod ZnO are investigated by constructing sensors. A facile polyol process is established to synthesize super paramagnetic Fe-doped ZnO nanoparticles in a liquid polyol <sup>[51]</sup>. At room temperature, the pure ZnO exhibits diamagnetic behaviour whereas, the Fe-doped ZnO are super paramagnetic explained on the basis of exchange interaction between local spin polarized electrons and conductive electrons.

# A. Co-precipitation method

Co-precipitation occurs when the solution is supersaturated with the substance forming the precipitate. The precursors for synthesizing these colloids consist of metal nitrates or metal chlorides, which can readily react with water medium. At the functional group level, two reactions are generally used to describe the co-precipitation process: hydrolysis and water condensation <sup>[52]</sup>. Hydrolysis is the process of formation of an insoluble hydroxide which can then be converted to its oxide by heat-assisted dehydration. However, the characteristics and properties of a particular co-precipitation reaction are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as pH, temperature and hydrolysis duration, reagent concentration, catalyst nature, aging temperature and time, and drying <sup>[53]</sup>.

In the co-precipitation method, an inorganic metal salt (e.g., chloride, nitrate, acetate, or oxychloride) is dissolved in water. Metal cations in water exist in the form of metal hydrate species. These species are hydrolyzed by adding a base solution, such as NaOH or NH<sub>4</sub>OH. The hydrolyzed species condense with each other to form either a metal hydroxide or hydrous metal oxide precipitate on increasing the concentration of OH<sup>-</sup> ions in the solution. The precipitate is then washed, filtered and dried. The dried powder is subsequently calcined to obtain the final crystalline metal oxide phase. The major advantage of this process is that it is relatively economical and is used to synthesize a wide range of single and multi-components oxide nanopowders. The processing parameters including solution concentration, pH, annealing temperature, and washing medium are controlled to synthesize ZnO nanoparticles with different morphologies <sup>[54]</sup>. The influence of annealing temperature on photoluminescence properties of Eu-doped ZnO nanowires synthesized by co-precipitation method is reported <sup>[55]</sup>. One of the major drawbacks of this process is the inability to control the size of particles and the subsequent aggregation.

# B. Hydrothermal Method

Hydrothermal method is a subset of solvothermal synthesis which involves water at elevated conditions <sup>[56]</sup>. The basic principle is that small crystals will homogeneously nucleate and grow from solution when subjected to high temperature and pressure. During the nucleation and growth process, water acts as catalyst and occasionally as solid-state phase component. Under the extreme conditions of the synthesis vessel (autoclave or bomb), water often reaches supercritical, thereby increasing the dissolving power, diffusivity and mass transport of the liquid by reducing its viscosity. In addition, the pressure of the vessel provides an avenue to tailor the density of the

final product. When compared to other methodologies, hydrothermal synthesis is an environmentally benign, inexpensive and allows for the reduction of free energies for equilibriums. Materials various that are made hydrothermally are generally high-quality, single crystals with a diversity of shapes and sizes. Although hydrothermal synthesis is an established synthesis route within the ceramics industry, it is recently been rekindled within the scientific community by synthesizing 1-D nanostructures, such as carbon nanotubes and oxide nanowires. Hydrothermal synthesis has been used to synthesize wellaligned pure and doped ZnO nanorods for optoelectronic applications <sup>[57] [38]</sup>. The term "hydrothermal" is purely of geological origin. It is first used by the British geologist, Sir Roderick Murchison to describe the action of water at elevated temperature and pressure, in bringing about changes in the earth's crust leading to the formation of various rocks and minerals. Byrappa and Yoshimura define hydrothermal as any heterogeneous chemical reaction in the presence of a solvent (whether aqueous or non-aqueous) above the room temperature and at pressure greater than 1 atm in a closed system <sup>[58]</sup>. Various additives are used in aqueous medium to synthesize ZnO nanostructures with different morphology and a detailed hydrothermal growth of ZnO nanostructures is reviewed as it is receiving a lot of attention<sup>[38]</sup>.

Hydrothermal synthesis is a common method to synthesize zeolite/molecular sieve crystals. This method exploits the solubility of almost all inorganic substances in water at elevated temperature and pressure, and subsequent crystallization of the dissolved material from the fluid. Water at elevated temperature plays an essential role in the precursor material transformation, because the vapour pressure is much higher and the structure of water at elevated temperature is different from that of room temperature. The properties of the reactants, including their solubility and reactivity, also changes at high temperature. The changes mentioned above define more parameters to produce different high-quality nanoparticles and nanotubes, which are not possible at low temperature. During the synthesis of nanocrystals, parameters such as water pressure, temperature, reaction time, and the respective precursor product system can be tuned to maintain a high nucleation rate and even size distribution. The solvent is not limited to water but also includes other polar or non-polar solvents, such as benzene, n-hexane, carbon tetra-chloride and hence, the process is termed as solvothermal synthesis <sup>[59]</sup>. The nanorods properties and the device performance are strongly dependent on the growth method. The hydrothermal growth of ZnO nanorods for hetero- junction LED's result in violet emission, while electrodeposition result in yellow emission [60]

### IV. UNIQUE MORPHOLOGY

Nanocrystalline materials are single-phase or multiphase polycrystals and the crystal size, atleast in one dimension is typically in the order of 1 nm to 100 nm <sup>[61]</sup>. Thus, nanocrystalline materials can be equiaxed and are termed as nanostructure crystallites (3-D nanostructures), or they can

have a lamellar structure and are termed as layered nanostructures (2-D nanostructures), or they can be filamentary (1-D nanostructures) <sup>[62]</sup>. Additionally, zerodimensional (0-D) are considered to be atom clusters and cluster assemblies. The length and width are much greater than the thickness in layered nanocrystals, and the length is substantially larger than the width or diameter in filamentary nanocrystals. Among nanocrystalline materials, in recent years, 1-D semiconductor nanostructures such as rods, wires, belts, and tubes have attracted and much attention is given due to their unique properties <sup>[63, 64]</sup>. 1-D nanostructures are probably considered as the building blocks for future electronics and photonics, as well as for life-science applications. It is generally accepted that 1-D nanostructures are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction. 1-D nanostructures are also expected to play an important role as both interconnects and functional units in fabricating optoelectronics, electrochemical, electronics. and electromechanical nanodevices <sup>[65, 66]</sup>.

The morphology of ZnO is a key factor in bringing a difference in the material properties, in comparison to bulk compound. With different morphologies and sizes, ZnO materials can bring various potential applications into many fields. For example, the luminescence property of ZnO is morphology-dependent. The relative intensity of the luminescence is the greatest for nanowire and the least for nanoparticle (nanowire > powder > nanoneedle > nanoparticle) <sup>[67]</sup>. Producing large-scale uniform ZnO nanostructures with unique morphology, oriented growth and crystalline structure remains a challenging mission. The small changes or modifications in synthesis and synthesis parameters including the precursor concentration, usage of structure directing agent, pH value, growth kinetics (polarity, reaction temperature and growth time), annealing, substrate variation etc. could generate nanostructures with totally different morphologies. The FESEM serves as a powerful image analyzer to characterize the various morphologies of ZnO nanostructures [68]. Figure 3(a) shows the shape controlled 1-D ZnO nanostructures synthesized on GaN thin films using metal organic vapour phase epitaxy (MOVPE) <sup>[69]</sup>. By adjusting the growth parameters from zinc rich at low temperature to oxygen rich at high temperature, morphology of ZnO nanostructures is tuned from non-polar smooth surfaced ZnO nanorods-nanowall networks to Opolar stacked pyramid structured ZnO nanorods. A selfcatalyzed vapour-liquid-solid (VLS) mechanism and classical nucleation theory are proposed to interpret the growth of ZnO nanowires <sup>[70]</sup>. According to the theory, zinc vapour supersaturation is considered for controlling the diameter and the areal density of the nanowires. The average diameter of the nanowires can be finely controlled in the range of 12-31 nm by regulating the oxygen flow rate and hence, the zinc vapour supersaturation (refer Fig. 3(b)). 1-D ZnO nanostructures with different morphologies are synthesized by round-to-round metal vapour deposition at 550 °C using a zinc powder covered with indium film as the source material. The formation of  $In_2O_3(ZnO)_m$  compounds

with different m values is deduced to explain the growth process <sup>[71]</sup>.



Fig. 3 Surface polarity and shape controlled ZnO nanostructures by (a) MOVPE, (b) VLS, and (c) thermal evaporation of solid powders.

Furthermore, ZnO is bio-safe and biocompatible, and is used for biomedical applications <sup>[72-75]</sup>. Intensive research has been focused on fabricating 1-D ZnO nanostructures and in correlating their morphologies with size-related optical and electrical properties. Figure 3(c) shows various kinds of ZnO nanostructures, such as nanorods, nanowires, nanobelts, nanotubes, nanobridges, nanonails, nanowalls, nanohelixes, seamless nanorings, mesoporous single-crystal nanowires, and polyhedral cages <sup>[76]</sup>. ZnO nanostructures with various distinct morphologies are obtained by varying the concentration of L(+) ascorbic acid (vitamin C) dissolved in the weak acidic and alkaline solutions Using controlled seeded growth and citrate anions that selectively adsorb on ZnO basal planes as the structuredirecting agent, large arrays of oriented ZnO nanorods with controlled aspect ratios are prepared. The advantages of the as-synthesized ZnO structures for photocatalytic decompositions of volatile organic compounds and studies on growth kinetics and crystallization of ZnO in water medium have been reported <sup>[78]</sup>. 1-D ZnO growth along the *c*-axis under hydrothermal conditions is related to both its intrinsic crystal structure and external factors. The overall shape and aspect ratio of crystals are determined by the relative rates of growth of its various faces. In general ZnO is a polar crystal and the growth rate of a face will be controlled by a combination of internal, structurally-related factors (intermolecular bonding preferences or dislocations), and external factors (supersaturation, temperature, solvents and impurities). Among the external factors, the growth rate also depends on the effect of solvents on the nucleation and the interface-solvent interaction. Hence, it is possible that morphologies of polar inorganic nanocrystals can be controlled by the interface-solvent interactions, which in turn, may be specified by choosing a suitable solvent <sup>[79]</sup>.

In addition, the surface plays an important role in determining the chemical properties including the solubility,

reactivity, stability, melting point, and electronic structure <sup>[80]</sup>. At the same time, the surface is the connection of the nanoparticles to other materials and objects and plays a vital role in the construction of superlattices in the fabrication of new devices and in the conjugation with target molecules for drug delivery applications. Thus, the chemical modification of the surface nanoparticles is a very important field. During the growth of the nanoparticles, stabilizing agents are present to prevent the nanoparticle aggregation and precipitation. Various organic and inorganic materials have been utilized as capping materials on the surface of nanoparticles through covalent or ionic interactions [81]. These capping groups can stabilize nanocrystals in solution and passivate surface electronic states in semiconductor quantum dots. For example, many nanoparticles are capped with inorganic materials to improve the photoluminescence quantum yield <sup>[82]</sup>. Besides modifying the properties of the bare nanoparticles, capping molecules also play a role as the connecting media of the nanoparticles to the outside world. For example, in the superlattices of nanoparticles, they define the space distances between nanoparticles <sup>[83]</sup>. On the other hand, in nanoparticles based drug delivery, they connect the nanoparticles to the therapeutic agents <sup>[84]</sup>. The techniques for tuning the surface capping materials of nanoparticles allow more methods to tailor the properties of these materials. For organic capping, the tail and head groups can be varied independently through wellestablished chemical substitutions by ligand exchange. This involves repeated exposure of the nanocrystals to an excess competing capping group, followed by precipitation to isolate the partially exchanged nanocrystals<sup>[85]</sup>.

## V. DOPING PROCESS

Doping of materials is the addition of foreign atoms or impurities purposely. The intention of doping is to modify the physical properties of the materials. For example, pure silicon has poor electrical conducting properties, but, it can be doped with boron or arsenic to make it a good hole or electron conductor respectively. This opened up a new class of doped-silicon materials, which is now the basis of perhaps the largest global electronics industry. It is well known from present semiconductor technologies that the incorporation of impurities or defects into the semiconductor lattices is the primary means of controlling electrical conductivity, optical, luminescent, magnetic, and physical properties <sup>[86]</sup>. For example, pure other stoichiometric ZnO is an insulator, the conductivity of ZnO can be tuned over 10 orders of magnitude with the small change in the concentrations of native or non-native defects such as  $Zn_i$  or Al dopant. Conventional semiconductor devices, such as the transistor, would not operate without such impurities.

### A. Hindrance in Doping

A long-standing mystery has been why impurities could not be incorporated into some types of semiconductor nanocrystals.

□ The findings by Naval Research Laboratory (NRL) and University of Minnesota (UMN) researchers establish the

underlying reasons for these difficulties, and provide a rational foundation for resolving them in a wide variety of nanocrystal systems <sup>[87]</sup>. "The key lies in the nanocrystals surface," said Dr. Steven Erwin, a physicist at NRL and lead theorist. "If an impurity atom can stick, or 'adsorb', to the surface strongly enough, it can eventually be incorporated into the nanocrystal as it grows. If the impurity binds to the nanocrystal surface too weakly, or if the strongly binding surfaces are only a small fraction of the total, then the doping will be difficult."

□ According to Dr. David Norris, an Associate Professor of Chemical Engineering and Materials Science at UMN, "nanocrystals are intrinsically difficult to dope because they somehow 'self-purify' by expelling impurities from their interior" <sup>[88]</sup>.

□ An additional problem is the lack of analytical techniques available to study small amount of dopant in nanocrystals<sup>[89]</sup>.

## B. Why Doping?

The significance, selection and incorporation of impurities are mainly studied and focused for specific applications. For example, solar cells and lasers could benefit from impurities that can induce an additional electrical charge to the nanocrystal. One of the main potential applications of doped materials is in the semiconductor industry, where intensive miniaturization has been taking place for the last 50 years and is now in the nanometer range. However, these semiconductors are poor electrical conductors, and in order to use them in electronic circuits, their conductivity must be tuned by the addition of impurities. Another major category of dopant for semiconductor nanocrystals is that of luminescence activators. Manipulation of the luminescent properties of the nanocrystals by doping with ions such as Mn or Eu, has the potential to broaden the range of useful spectroscopic properties <sup>[86]</sup>. The high quantum yields combined with narrow emission line shapes and broadband excitation profiles make these luminescent colloids interesting candidates for optical imaging applications. In addition, impurities will be chosen to explore the use of nanocrystals in spin electronics (or "spintronics"). Spintronic devices utilize the fact that electrons not only possess charge, but also a quantum mechanical spin. The spin provides an additional degree of freedom that can be exploited in devices to realize a host of new spintronic technologies, from nonvolatile "instant-on" computers to so-called

"reconfigurable logic" elements whose underlying circuitry can be changed on-the-fly<sup>[90]</sup>.

# C. Doping in Zinc OxideIntrinsic Defects

The intrinsic or native point defects concerned with ZnO are zinc interstitials  $Zn_i$ , oxygen interstitials  $O_i$ , zinc vacancies  $V_{Zn}$ , oxygen vacancies  $V_O$ , zinc antisites  $Zn_O$  and oxygen antisites  $O_{Zn}$ . In wurtzite ZnO there exist two different interstitial sites: the tetrahedrally and the octahedrally coordinated sites. In ZnO, the octahedrally coordinated interstitials  $Zn_i$  and  $O_i$  have lower defect formation energies than the tetrahedrally coordinated interstitials  $Zn_i$  and  $O_i$ .

The dominant native donors are the  $V_O$  and  $Zn_i$ . The  $Zn_O$ defect in ZnO may also be a relevant donor, although its formation energy is always higher than that of  $Zn_i$ . However, it is thermally more stable than  $Zn_i$ . So if ZnO is once created by a non-equilibrium process (e.g. irradiation), it is expected to be a relevant donor <sup>[91]</sup>. The formation of these donor levels is especially probable, if the Fermi energy (FE) is equal to the valence band (VB) maximum  $E_V$ . The  $V_O$  is a deep donor defect (predicted to be 0.5-1 eV below the conduction band (CB) minimum  $E_C$ ) and, therefore, do not contribute to the free electron concentration. The main native acceptor in ZnO is the  $V_{Zn}$ . Its transition level energy is with 0.11 eV above  $E_V$  or 0.8 eV above  $E_V$  depending on its transition state. The  $O_i$  is a deep acceptor defect and its formation energy is higher than that of  $V_{Zn}$ . Among the native point defects of ZnO,  $O_{Zn}$  has the highest defect formation energy even for oxygen rich conditions and it is considered as a deep acceptor.

At thermal equilibrium, the concentration of point defect is given by the relation

$$c = N_{sites} \exp\left(\frac{-E^f}{k_B T}\right) \tag{1.1}$$

In Eq. (1.1), the  $N_{sites}$  is the number of available sites for defect formations,  $E^f$  is the defect formation energy,  $k_B$  is the Boltzmann constant and T is the absolute temperature in Kelvin. From the relation it is clear that the defects with high  $E^f$  will occur at low concentration. The  $E^f$  of the point defects is not constant and it has a greater dependency on synthesis parameters and annealing conditions. Moreover, if the defects are charged then  $E^f$  depends on the position of FE. The order of intrinsic defect formation energy  $E^f$  in ZnO is  $V_{Zn} < V_O < Zn_i < Zn_O < O_i < O_{Zn}$ <sup>[92]</sup> and the energy levels are represented in Fig. 4(b).



Fig. 4 (a) Defect formation energies as a function of the FE at the oxygen poor and oxygen rich limits and (b) Defect thermodynamic transition levels

### D. Extrinsic Defects

*n*-type ZnO can easily be obtained by doping with Group III elements such as Al, Ga, In, transition metal elements such as Pb, Mn, Fe, Ni, Co and rare earth elements like Eu, Y, and Gd. The elements incorporate readily on the zinc lattice site and form shallow effective mass donors. Hydrogen, being an amphoteric defect in many semiconductors, is always a donor in ZnO. It is a shallow defect and can significantly contribute to the free electron concentration of *n*-type ZnO. The realization of *p*-type ZnO for practical applications has proven difficult and thought to be the bottleneck in the development of ZnO based devices due to the asymmetric doping limitations in ZnO. The difficulties in *p*-type doping can arise from variety of causes [93].

 $\Box$  Dopant may be compensated by low-energy native defects, such as  $Zn_i$  or  $V_O$  or the presence of hydrogen background impurities.

□ Large activation energy and low solubility of the dopant in the host material is also another possibility. Deep impurity level can also be a source of doping problem, causing significant resistance to the formation of shallow acceptor level.

 $\Box$  Inspite of achieving *p*-type ZnO, with the period of ageing there is a slow transition from *p*-type conductivity to *n*-type conductivity. It is probably assigned to the acceptor migration from the substitutional sites to interstitial sites.

Even with all above difficulties *p*-type conductivity is achieved by incorporating Group I (Li, Na) and Group V (N, As, Sb, P) elements<sup>[11]</sup>.

### E. Transition Metal Ions

The transition metal elements belongs to d-block, grouped under 3-12 of the periodic table with an incomplete

d orbital. The exceptions are zinc, cadmium and mercury, as they have filled d shell with the electronic configuration of  $\begin{bmatrix} 93 \end{bmatrix}^{2} d^{10} s^{2}$ . The melting and boiling point of these elements are lower and they are paramagnetic since their filled d subshells prevent the *d*-*d* bonding. However, the substitution or alloying of other transition metals may result in ferromagnetism, when the spin vectors are aligned parallel to each other in a crystalline compound. Thus, the incorporation of Fe-, Co-, Ni- in the zinc sites of ZnO can result in room temperature ferromagnetism which finds a wide application in spintronics, DMS, magnetic switches, magnetic sensors, and many more. The research work on the transition metal ion doped ZnO ( $Zn_{1-x}M_xO$ , M = transition metal ion, x = dopant concentration) for the enhancement of ferromagnetism and understanding the spin exchange concept is under developing <sup>[94]</sup>. In 2006, Benjamin et al. reported the production of anisotropic  $Zn_{l,r}M_rO$  nanowires by the thermal decomposition of zinc acetate and dopant acetate in refluxing trioctylamine <sup>[95]</sup>. Here, the average nanowire diameter is about 35 nm and the length ranges from 80-160 nm for Co-doped ZnO nanowires. The substitution of Co for Zn cations results in complex magnetic behavior that cannot be modeled by a simple paramagnetic and ferromagnetic mechanism. Recently, Anghel et al. correlates the saturation magnetization, bandgap and lattice volume of  $Zn_{l-x}Mn_xO$  (M = Cr, Mn, Fe, Co and Ni) nanoparticles synthesized by chemical process for x = 0.02 and 0.05 <sup>[96]</sup>. Among the various dopant, the Fe doping with maximum unit cell volume determined by XRD and bandgap determined by diffuse reflectance spectroscopy exhibits strong ferromagnetic saturation (DRS) magnetization of 6.38 memu/g. Similarly, the relation between Fe dopant concentration and magnetic behavior and their dependence on structure and optical properties are studied by [97]. Thus, the introduction of transition metal ions into the ZnO lattice will exhibit ferromagnetic behavior due to the partially filled d shells, which give rise to unpaired electrons.

MOVPE is used to deposit 8 µm thick Ga-doped ZnO film on GaN-based LED as a transparent conducting layer (TCL). Here, the intensity value of the LED is improved by 23.6% as compared to that of the LED with an ITO TCL <sup>[98]</sup>. The addition of Cu and Mn (0.015 wt.%) on the catalytic and photocatalytic activities of ZnO is influenced by admixtures on the electronic band structure parameters and also by the alteration of the sorption ability on the semiconductor surface <sup>[99]</sup>. Pd-doped ZnO nanofibers exhibit considerable sensitivity, rapid response and good selectivity to low concentration carbon monoxide (1 ppm - 20 ppm) at 220°C. The prominent sensing properties are attributed to the geometry of nanofibers and the promoting effects of Pd <sup>[100]</sup>. The inhomogeneous Co distribution analyzed by scanning TEM is helpful for manipulating the states of the Co ions and the ferromagnetic coupling in Zn<sub>1-x</sub>Co<sub>x</sub>O by post-treatment, which could account in future DMS studies <sup>[101]</sup>.

### F. Rare Earth Ions

Rare earth doped ZnO are technically significant materials in optoelectronic devices and have received great

research interest especially, for an efficient energy transfer from ZnO host to rare earth ions. The doping of rare earth ions into ZnO lattice is difficult due to:

 $\hfill\square$  large differences in ionic size and charge between the rare earth dopant ion and  $Zn^{2+}$ 

 $\Box$  an inappropriate energy level position of rare earth ion relative to the VB and CB of ZnO

However, different growth mechanism and growth techniques (both physical and chemical) are systematically studied and experimented to obtain rare earth doped ZnO with specific morphology. Dan-dan et al. synthesized and studied the  $Eu^{3+}$  related red emission in Eu-doped ZnO nanosheets <sup>[102]</sup>. Here, Eu-doped ZnO nanosheets are obtained by pyrolyzing Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub> and subsequent annealing at 250°C in air. In addition, the rare earth doped ZnO exhibit intrinsic ferromagnetism due to the magnetic moment borne on 4f and 4d electrons. Recently, Assadi et al. investigated the structural, electronic and magnetic properties of Eu and Pd-doped ZnO by ab initio density functional theory methods based on gradient approximation <sup>[103]</sup>. The investigation concluded that the ferromagnetism in Eu-doped ZnO can be induced by creating excess Zn interstitial sites, whereas Pd-doped ZnO possesses no ferromagnetism. Eeckhout recently reviewed on the significance, methods of synthesis and mechanism involved in persistent luminescent materials based on Eu<sup>3+</sup> emission <sup>[104]</sup>. The morphological, optical, electrical and magnetic properties of Ho and Y-doped ZnO nanoparticles having same ionic radii are compared. It revealed that the difference in properties is due to the magnetic behaviour of Ho whereas, Y is non-magnetic <sup>[105]</sup>. The luminescence properties of Nd<sup>3+</sup> ions in ZnO recorded at 10 K, provided the evidence for the existence of multiple luminescence centers, defect mediated energy transfer and host to Nd<sup>3+</sup> energy transfer [106].

In general, the rare earth ions with different electron and hole concentrations doped into the ZnO can enhance the ferromagnetic coupling. Moreover, the presence of native defects such as  $V_{Zn}$  and  $V_O$  will also affect the ferromagnetism. This phenomenon is verified by firstprinciples calculations for Gd- and Nd- doped ZnO nanoparticles and their results are in agreement with the earlier experiments <sup>[107]</sup>. The influence of rapid thermal annealing on the mechanism of implantation, diffusion and substitution of rare earth ions (Eu and Pr) on Zn site is characterized by Rutherfor backscattering and PL spectroscopy <sup>[108]</sup>. Here, nearly 90% of the rare earth ions are substituted on Zn sites, however, by the process of annealing at 1000°C for 20 min, the diffusion of rare earth ions towards the surface occurs thereby damaging the implantation. This in turn increases the non-radiative recombination rates and suppresses the optical activation of rare earth ions. Houabes and Metz demonstrated that the addition of rare earth oxides such as Pr<sub>6</sub>O<sub>11</sub>, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>O<sub>3</sub> of 0.01-0.5 wt.% to standard ZnO, allows large energy absorption capability and 30% increase in threshold voltage for ZnO-based varistors <sup>[109]</sup>. Here, a new ceramic composition is proposed and the increase in

absorption capability and conductivity are explained by the presence of pyrochlore phase  $Zn_2Bi_3Sb_3O_{14}$ , where less bismuth oxide resides at the grain boundaries (refer Fig. 5).



Fig. 5 Proposed model for the bismuth continuous phase at the grain boundaries.

### G. Group I and V elements

Recently, N has proven to be a suitable acceptor for making *p*-type ZnO and hence, the synthesis and property studies of N-doped ZnO are increasing <sup>[110, 111]</sup>. High mobility of 20 cm<sup>2</sup>/V.s <sup>[112]</sup> and dopant activated luminescence emission <sup>[113]</sup> are observed in Sb-doped ZnO nanoparticles synthesized by RF magnetron sputtering and molecular beam epitaxy (MBE). P-doped ZnO nanowires from single source precursor Zn<sub>2</sub>P<sub>3</sub> is synthesized and time-resolved PL measurement is conducted to characterize the recombination dynamics <sup>[114]</sup>. Thus, doping by means of intrinsic and extrinsic, have a greater impact on semiconductor nanocrystals and undergoes a critical step for tailoring the material properties for specific applications.

# H. Codoping

A process of codoping Group V elements and Group III elements of the periodic table is also realized to achieve *p*type conductivity in ZnO and thereby, to construct homojunction devices. Balakrishnan et. al reported the fabrication of ZnO based *pn* homo- junction using codoped AlN as *p*type material by RF sputtering <sup>[115]</sup>. Hall measurement shows that 1 mol% AlN codoped ZnO exhibit a high hole concentration of the order of  $10^{19}$  cm<sup>-3</sup> and low resistivity of 0.545  $\Omega$ cm. With this electrical properties and device configuration, a high rectification ratio of 13.4 and excellent junction parameters is attained. Further, to enhance the magnetization and their utilization in DMS and spintronics, codoping of transition metal ions such as Ni, Co, Mn, and Ni are also established. Yu and Li investigated the magnetic properties of Al and Ni codoped ZnO and Mn and Co codoped ZnO nanostructures respectively <sup>[116, 117]</sup>. Here, the ferromagnetism is induced only due to the *s*-*d* exchange interaction between the conducting electron and the localized spin of transition metal ion. Thus, the significance and modification of ZnO nanomaterial properties with impurity atoms paves the way towards the manufacture of improved semiconductor devices.

### VI. OPTICAL TRANSITIONS

Optical transitions in ZnO have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photoreflection, spectroscopic ellipsometry, photoluminescence (PL), cathodoluminescence (CL), calorimetric spectroscopy, etc.

### A. Band Structure

The electronic band structure of ZnO is theoretically predicted and stimulated by many research groups. The results of an electronic band structure of ZnO calculated using Local Density Approximation (LDA) along with atomic self-interaction corrected pseudo potentials (SIC-PP) <sup>[118]</sup> is shown in Fig. 6. The band structure is shown along high symmetry lines in the hexagonal Brillouin zone. Both the VB maxima and the lowest CB minima occur at the  $\Gamma$ point k = 0 indicating that ZnO is a direct bandgap semiconductor. The bottom 10 bands (occurring around -9 eV) correspond to zinc 3d levels. The next 6 bands from -5 eV to 0 eV correspond to oxygen 2p bonding states. The first two CB states are strongly zinc localized and correspond to empty 4s states of  $Zn^{2+}$  or anti-bonding  $sp^3$ hybrid states, whereas the higher CBs (not illustrated in Fig. 6) are free electrons. The oxygen 2s bands (also not illustrated) associated with the core-like energy states, appears around -20 eV. The bandgap of ZnO is estimated to be 3.77 eV and correlates reasonably with the experimental value of 3.37 eV.



### B. Excitons

The absorption of a photon by an interband transition in a semiconductor creates an electron in the CB and a hole in the VB. The oppositively charged particles are created at the same point in space and can attract each other through mutual Coulomb interaction. This attractive interaction increases the probability of the formation of an electronhole pair called exciton and therefore, increases the optical transition rate. The excitons are of two types Wannier-Mott or free excitons and Frenkel or tightly bound excitons.

Figure 7 schematically represents the two types of excitons. Here, an electron and hole are orbiting around each other within a crystal. The Wannier-Mott excitons have a large radius that encompasses many atoms, and they are in delocalized states that can move freely throughout the crystal and hence, referred as free excitons. Frenkel excitons have a much smaller radius comparable to the size of the unit cell. This makes them to be in localized states and tightly bound to the specific atoms or molecules. Tightly bound excitons are much less mobile than free excitons, as a result they move through the crystal by hopping from one atom side to another. Bound excitons are extrinsic transitions and are related to dopants or defects, which usually create discrete electronic states in the bandgap, and therefore influence both optical absorption and emission processes. The electronic states of the bound excitons depend strongly on the semiconductor material, in particular, the band structure.

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Fig. 7 Schematic illustration of free and tightly bound excitons.

### C. Bandgap Engineering

To design new semiconductor materials for new device applications, the tuning and engineering of bandgap is started effectively. Modern growth techniques, tuning the transport properties of electrons and hole, and new generation of devices from solid state photomultipliers to resonant tunneling are emerging through bandgap engineering advancement. Alloying, doping, strain-tuning and band edge warping are the commonly used methodologies for bandgap engineering and to control the location of charge carriers. The optical bandgap is defined as the minimum energy required to excite an electron from the VB to the CB. In the pure crystalline materials, the bandgap equals the energy separation between the band edges, as illustrated for the case of isotopic and parabolic bands in Fig. 8(a). The tuning and tailoring of the bandgap in ZnO are usually performed by the process of doping. In principle, the material can be doped until the critical Mott density is reached. In a heavily doped semiconductor or at the Mott density [119, 120],

$$n_c^{1/3} a_H^* \sim 0.25 \tag{1.2}$$

where,  $a_H^*$  is the effective Bohr radius, the doped atoms are ionized. For *n*-type doping, the associated electrons occupy the bottom of the CB. Since the Pauli exclusion principle prevents states from being doubly occupied and optical transitions are vertical, the optical bandgap can be larger or smaller in comparison to the original host crystal. Figure 8(b) shows the widening of the bandgap, due to the blocking of the low-energy transitions and is known as the Burstein-Moss (B-M) shift. The bandgap narrowing is usually associated with many body effects on the CB and VB. It is caused by the correlated motion of the charge carriers and by their scattering against ionized impurities. Figure 8(c) illustrates the bandgap narrowing observed in an indirect semiconductor.



Fig. 8 Schematic band structure with (a) parabolic CB and VB separated by bandgap, (b) widening caused by B-M shift and (c) narrowing due to many body interactions.

Room temperature luminescence from ZnMgO nanowires shows a blue shift of the near band edge (NBE) emission and is attributed to the diffusion mechanism of Mg from the shell into the core ZnO of the nanowires to form a ternary ZnMgO alloy <sup>[121]</sup>. The energy shift due to B-M effect and the bandgap narrowing effect are calculated by using a self-consistent approach based on the band-anticrossing model in InAsN alloy <sup>[122]</sup>. The B-M shift in *p*type doped ZnO nanostructures is clearly illustrated and discussed by Rajeswari et. al. <sup>[123]</sup>. Here, B-M shift serves as a qualitative tool to interpret the widening of the optical bandgap and to study the shape of the NBE luminescence in Li-doped ZnO nanopowders synthesized by hydrothermal method. In Li-doped ZnO, the bandgap widens to 3.20 eV from 2.60 eV concerned for pure ZnO nanostructures.

The influence of Al, Y and Sc on bandgap modification of *n*-type ZnO are analyzed by bandgap narrowing and bandgap widening phenomena <sup>[124]</sup>. Further, the bandgap tuning of ZnO by the substitution of ferromagnetic ions such as  $Mn^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  are studied by energy absorption spectroscopy <sup>[125]</sup>. Similarly, bandgap bowing due to the inclusion of *p*-type dopant (Mg and Be) on ZnO is studied by first principles <sup>[126]</sup>.

### D. Luminescence

The origin of luminescent transitions including both intrinsic and extrinsic luminescence in ZnO is always one of the central investigation topics. The energy levels of the donor and acceptor occur near the CB edge and VB edge respectively, while the deep centers lie in the forbidden bandgap region of the semiconductor. The room temperature PL spectrum of ZnO nanorods/nanowires with diameters larger than 20 nm is similar to the PL spectra of bulk ZnO. This spectrum is normally characterized by NBE UV emission and at least one broad band emission due to deep levels called deep level emission (DLE). DLE refers to the broad band extending from 400 nm to 750 nm of the visible spectrum. The broadness of the band results from the fact that it represents a superposition of many different deep levels emitting at the same time. The NBE emission band of ZnO is related to the recombination of the free excitons. The DLE band is attributed to several defects in the crystal structure.

TABLE I THE EMISSION COLOURS FROM ZNO AND THE ASSOCIATED DEFECT LEVELS  $% \left( {{{\left[ {{L_{\rm{E}}} \right]} \right]}} \right)$ 

Emission colour	Proposed deep level transition
Violet	Zn <sub>i to VB</sub>
Blue	$Zn_i$ to VB or CB to $V_{Zn}$
Green	$V_O$ to $V_{Zn}$
Yellow	$CB to O_i$
Orange	$\begin{array}{c c} & O_i & Zn_i & O_i \\ \hline CB & to & O_i & Tn_i & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i & Tn_i \\ \hline CB & to & Tn_i \\ \hline $
Red	Lattice disorder along the c-axis

The common bands observed in ZnO are green luminescence, yellow luminescence and red luminescence DLE bands <sup>[33]</sup>. The green luminescence band, which appears at energies of 2.4 eV - 2.5 eV is the most investigated DLE band in ZnO and their origin remains unexplored. Though the mechanism of green luminescence is elaborated and discussed by Baskar et al., it fails to establish a confidential work <sup>[127]</sup>. The origin of violet and blue-green luminescence from Ti-doped ZnO films deposited by RF reactive magnetron sputtering is investigated by Chen et al <sup>[128]</sup>. The green emission is probably due to the energy transition from shallow donor levels  $(Zn_i)$  to shallow acceptor levels  $(V_{Zn})$  and the violet emission is from shallow donor level  $(V_0)$  to VB. The origin and controllability of blue emission of ZnO nanoparticles through non-equilibrium process is highlighted by Zeng et al <sup>[129]</sup>. According to him, the blue emission originates from transitions related to  $Zn_i$  defect states. The non-equilibrium process along with low annealing temperature provides enough ionization energy for the formation of  $Zn_i$  with different charges, including single, double and neutral.

The yellow luminescence (2.19 eV) at 10 K in pure and N-doped ZnO layers grown on sapphire substrate is reported by Reshchikov. Yellow band is attributed to a transition between a shallow donor and an acceptor with an energy level of 0.4 eV above the VB. The yellow emission band that appears at 2.2 eV is first observed in Li-doped ZnO layer <sup>[130, 131]</sup>. Li is located 0.8 eV above the VB and constitutes a deep acceptor level in ZnO. Yellow emission is also attributed to the native deep level defects in ZnO, namely to  $O_i$  <sup>[132, 133]</sup>. Similarly, electron-proton resonance (EPR) and PL spectroscopy studies are performed to confirm that the deep Li acceptor with an acceptor energy of 800 meV is only responsible for the yellow luminescence at 2.2 eV <sup>[134]</sup>. In-doping in ZnO introduces a negatively-charged  $O_i$ , which contributes to the yellow luminescence [<sup>135]</sup>. Depending on the In dopant concentration occupying the lattice sites or interstitial sites, the shift and intensity of the PL emission can be tuned.

Orange, orange-red and red emission bands have also been observed in ZnO  $^{[136]}$ . The orange emission, which is not very common in ZnO, is proposed to be due to the transitions related to  $O_i$  <sup>[137]</sup>, the orange-red emission is attributed to transitions associated with  $V_{Zn}$  complexes <sup>[138]</sup> and the red emission is proposed to be due to the transitions associated with  $Zn_i$  <sup>[139]</sup>. Blue-green emission, green emission and yellow-orange-red emission are observed for ZnO nano-flowers synthesized by microwave assisted hydrothermal method<sup>[140]</sup>. The PL emission bands are deconvoluted by using a Guassian response function and Fourier decomposition or filtering algorithm. Here, the visible emissions originate from the intrinsic mixture of  $ZnO_x$  (x = 3 and 4) clusters formed before the recrystallization of ZnO. Many other literatures also reviews and reports the origin and defect related PL emissions of various colours <sup>[141, 142]</sup>. Table 1 summarizes the different colours observed in PL spectrum of ZnO and their associated deep level defects <sup>[92]</sup>. Thus, the origin of the different observed colours, due to the different defect configurations in ZnO, provides the potential for creating white LEDs [143].

To scale the importance of ZnO in optoelectronic and optophotonic applications, PL studies associated with electronic energy level transitions and band structure modifications are recognized systematically. Thus, PL emission study can correlate the optical and electrical properties of nanostructures. Usually, PL measurements are performed by dispersing the nanoparticles in suitable solvent medium or by growing the nanostructures on suitable substrate. In both the cases, the individual structure parameters such as distribution in the shape and orientation of the particles, difference in the structure along the nanostructure length, width, and diameter are not considered. To mark a new dimension, Li et al. reported angular dependent (length-wise and perpendicularly) micro PL measurements on individual suspended ZnO nanorods attached to sharp metal tips <sup>[144]</sup>. By this measurement, he is able to interpret that nearly 99% of the near band emission can be confined effectively in the nanorods and emitted from the end facets. In addition, PL imaging revealed that the angular resolved PL can yield quantitative information on the waveguide property of semiconductor nanorods. In 2007, Mu Oh et al., correlated the optical and electrical properties of ZnO nanostructures with the aid of CL emission <sup>[145]</sup>. Here, two different types of ZnO devices are produced by varying the charge carrier density (depletion

width). Further, the paper confirms that the origin of green luminescence is only due to the existence of charge carrier density variation and not with the size or nanostructures. Another paper as a supportive to Mu Oh conclusion is published by Young Park and Sub Kim in the year 2008 <sup>[146]</sup>. According to them, the PL properties of vertically and laterally well-oriented ZnO nanorods arrays, synthesized by MOCVD on Al<sub>2</sub>O<sub>3</sub> substrate are the same irrespective of the different sizes obtained by changing the precursor ratio.

An article by Tainoff et al., says that the crystallinity of the sample products are a prime factor than the stoichiometric in deciding the luminescence efficiency [147]. In this paper, the quality or the crystallinity of the ZnO nanostructures along with the growth kinetics are non-equilibrium experimented under and thermodynamically stable state. Unipolar self assembly of ZnO along negative or positive polar ends leads to distinct optical emission pattern<sup>[148]</sup>. Here, the significance and the growth mechanism of Zn-polar and O-polar spatial organization of the individual nanorods on optoelectronic properties are distinguished by luminescence properties. The Zn-polar rods have stronger UV emission at the tips and at the base. The visible emission is stronger in the middle region. In the case of O-terminated rods, the UV emission is stronger at the base, whereas the visible emission is almost uniform. This variation in emission intensity is attributed to the difference in growth kinetics on the Zn and the O faces and also due to the surface adherents of the growing crystal on the substrate (refer Fig. 9).



Fig. 9 (A) Crystal structure of wurtzite ZnO. The unit cell is dominated by four lowMiller index surfaces: nonpolar (10-10) and (11-20) surfaces and the polar Zn-terminated (0001)-Zn and oxygen-terminated (000-1) surfaces. Arrows indicate the polar direction of Zn-O bonds. (B) (i and ii) Schematic showing the orientation of polarity in two ZnO rods grown along the [000-1] and [0001] directions within the c-crystallographic axis, respectively. (C) Schematic representation of two possible assemblies of ZnO rods. Besides a possibility of being randomly oriented, all rods in an assembly may also orient along (i) the negative or (ii) positive polar direction, making the two identical looking assemblies intrinsically different.

The pressure-induced phase transition from wurtzite ZnO/MgO to rock salt ZnO/MgO nanocomposites leads to remarkable changes in the luminescent properties. Here, the blue luminescence in the range of 410-446 nm due to donor-acceptor pair transition is reported <sup>[149]</sup>. Many literatures also reported the improvement or declination of luminescence efficiency in doped ZnO nanostructures synthesized under different methods and synthesis conditions. The PL spectra of sol-gel derived Cu-doped ZnO films revealed that the excitonic peak intensity increased by many fold, compared to that of defect related emission with increasing Cu concentration <sup>[150]</sup>. The incorporation of Li<sup>+</sup> ions during the synthesis combustion process can effectively enhance the characteristic luminescence of Dy<sup>3+</sup> ions (fluorescence originating from 5*d*-4*f* transitions) <sup>[151]</sup>. The

defect related visible emission in Al-doped ZnO nanostructures synthesized by hydrothermal method is studied with the aid of absorption-emission study <sup>[152]</sup>.

### VII. FILM PROCESSING

### A. Zinc Oxide Thin Films

ZnO thin films have been studied extensively due to their potential applications, such as PZT, optical waveguides, acousto-optic media, surface acoustic wave devices, conductive gas sensors, transparent conductive electrodes, solar cell windows and varistors. ZnO crystallites with preferential orientation are desirables for applications, where crystallographic anisotropy is a prerequisite for UV diode lasers and piezoelectric surface acoustic wave or acousto-optic devices. Many methods have been broadly used for the oriented ZnO films synthesis, including MBE, pulsed laser deposition (PLD), metal-organic chemical deposition, cathodic sputtering, vapour magnetron sputtering, reactive electron beam evaporation, spray pyrolysis, and electrodeposition (refer Table 2). However, solution-route processes are particularly adapted to produce ZnO colloids and films in a simple, low-cost and highly controlled way.

TABLE II METHODOLOGIES FOR ZNO DEPOSITION AND GROWTH

	Thermal evaporation						
	Electron-beam						
	RF induction						
Physical Vapour	Resistive						
Deposition (PVD)	Sputtering						
	Focused ion beam						
	Radio frequency						
	Magnetron						
	Pulsed Laser Deposition						
	Thermal CVD						
	Thermal CVD Low pressure CVD (LPCVD)						
Chemical Vapour	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD)						
Chemical Vapour Deposition (CVD)	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD)						
Chemical Vapour Deposition (CVD)	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD) Molecular beam epitaxy (MBE)						
Chemical Vapour Deposition (CVD)	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD) Molecular beam epitaxy (MBE) Atomic layer deposition (ALD)						
Chemical Vapour Deposition (CVD)	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD) Molecular beam epitaxy (MBE) Atomic layer deposition (ALD) Precipitation						
Chemical Vapour Deposition (CVD) Solution-based	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD) Molecular beam epitaxy (MBE) Atomic layer deposition (ALD) Precipitation <i>Co-prcipitation</i>						
Chemical Vapour Deposition (CVD) Solution-based Chemistry (SBC)	Thermal CVD Low pressure CVD (LPCVD) Plasma enhanced CVD (PECVD) Metal-organic CVD (MOCVD) Molecular beam epitaxy (MBE) Atomic layer deposition (ALD) Precipitation <i>Co-prcipitation</i> <i>Hydrothermal</i>						

A review on sol-gel deposited ZnO thin films by Lamia Znaidi summarizes the main chemical routes involved in sol-gel process and highlights the influence of various synthesis parameters on structural properties <sup>[153]</sup>. The influence of annealing temperature on the structure and optical properties of ZnO films synthesized by sol-gel

method is investigated <sup>[154]</sup>. With the increase in annealing temperature, the orientation of (002) peak along *c*-axis is highly improved and hence, the optical transmittance and the optical bandgap decreases.

ZnO thin film synthesis involves several parameters:

- $\Box$  Nature of the precursor and its concentration;
- □ Type of solvent and the acidity of the medium;
- □ Type of additive species and their concentrations;
- $\Box$  The aging time of the early mixture ;
- $\Box$  The method of coating of substrates and its speed;
- □ Nature of the substrate and pre- and post-heat treatment of the materials.

All these parameters play a key role on the evolution of fine texture in ZnO films.

# B. Spin Coating Technique

The starting point for much of the spin coating modeling is published by Emslie, Bonner and Peck <sup>[155]</sup>. Spin coating has been used for several decades for the application of thin films. A typical process involves depositing a small puddle of a fluid resin (viscous fluid) onto the center of a substrate and then spinning the substrate at high speed (typically around 3000 rpm).

Centripetal acceleration will cause the resin to spread to, and eventually off the edge of the substrate leaving a thin film of resin on the surface. Final film thickness and other properties will depend on the nature of the resin, viscosity, drying rate, percent solids, surface tension, etc. and the parameters chosen for the spin process. Factors such as final rotational speed, acceleration and heating contribute to the properties of coated films. Figure 10 displays the photographic view of programmable spin coating unit.



Fig. 10 Apex programmable spin coating unit.

### C. pn Junction

*pn* junction is discovered by Ohl in 1940 when he observed the PV effect when light is flashed onto a silicon rod. He also noticed that when a metal whisker is pressed against different parts of the crystal, opposite behaviors are observed. He coined the material *p*-type when "positive" bias is put on the crystal relative to the whisker to produce a large current, and conversely, *n*-type when "negative" bias is needed to conduct similar current <sup>[156]</sup>. The theory for the *pn* junction diode is developed by Shockley in 1949 <sup>[157]</sup>. The *pn* junction is the most common rectifier and has many

circuit applications. Many devices are the special forms of pn junction. Examples are LED, laser, solar cell, and photodiode. A pn junction also serves as a building block for many other devices, such as the bipolar transistor, junction field effect transistor (FET), metal oxide semiconductor FET (MOSFET), etc.

Surface directed VLS process for the planar growth of 1-D hetero junction of ZnO on single crystal GaN is hierarchically assembled to form LEDs. An abrupt and epitaxial np hetero junction is formed as depicted in Fig. 11(a). The collective light emission study suggests that the combination of II-VI and III-V semiconductor can offer their integration to photonic and lab-on-chip platforms with applications in energy generation and light detection<sup>[158]</sup>. A combined hydrothermal and PLD method is used to grow vertically aligned ZnO/MgZnO coaxial nanorods arrays by [159] shadow effect (refer Fig. 11(b)) Core/Shell heterostructures with high-quality interfaces and coherent epitaxial develops nano LEDs and their aligned orientation facilitates the "bottom-up" integration of nano devices.



Fig. 11 (a) SEM image of a group of ZnO nanowires horizontally grown at the border of a Au pattern, (b) Schematic diagram of the growth process and structure of coaxial nanorod arrays and (c) Energy band diagram of *pn* homo junction.

Recent advances in the synthesis of *p*-type ZnO allow ZnO to be viewed as a semiconductor material capable of competing with GaN in UV optoelectronic applications [160]. To date, *p*-type conduction in ZnO has been obtained through doping with Group V ions (N, As and P) by a variety of techniques [161, 162]. This has enabled the fabrication of ZnO based light emitting *pn* homo junctions. Catalyst-free pn ZnO nanowire arrays are epitaxially synthesized by utilizing P and Zn as p-type and n-type dopant [163]. The width of doping transition region in this pn homojunctions can be scaled down to sub-50 nm along the [0001] ZnO nanowire growth direction. The observation of CL emission peak at 340 nm from n-type ZnO:Zn nanowire is presumably due to the B-M effect in the high electron carrier concentration regime as shown in Fig. 11(c). As a result, the synthesis of the ZnO pn homo junctions is a promising strategy to create the building blocks for short wavelength UV LEDs and photoelectronics applications. Thus, the ability to produce commercially viable ZnO based

*pn* junction nano devices depends crucially on detailed knowledge of the properties of doped layers.

### VIII. CONCLUSIONS

In summary, the review initially focused on the basic structure, properties, open challenges, crvstal and applications of ZnO. We have discussed the number of available solution synthesis techniques and investigated the influence of synthesis parameters (pH, annealing temperature, growth duration, growth temperature, and precursor concentration) for the growth of ZnO with 1-D nanostructures. We also analyzed the growth mechanism and surface growth kinetics involved in the formation of ZnO nanostructures with unique morphologies. Further, the enhancement of ZnO material properties including structural, optical, magnetic, and electrical either by the substitution of dopant atoms on ZnO lattice or by alloying process is examined. The intentional addition of impurity atoms and their influence on the modification of electronic band structure and bandgap engineering are also appreciated. The significance of ZnO towards the optoelectronic device applications such as color LEDs, photodetectors, solar cells, laser diodes etc. are recognized by the addition of luminescent materials. Thus, this review article has briefed the synthesis, dopant study and device fabrication based on ZnO.

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