Chapter 1

Introduction

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1.1 **WHAT IS NANOTECHNOLOGY?**

The concept of nanotechnology was attributed from a lecture delivered by the famous Nobel laureate scientist Richard P. Feynman in the year of 1959 [1]. He had mentioned “there is plenty of room at the bottom”. In his famous lecture he had mentioned these famous words “I want to build a billion tiny factories, models of each other, which are manufacturing simultaneously........The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big”.

Drexler expanded Feynman’s definition in a most inspiring and lateral thinking way in his book, *Engines of Creation, the Coming Age of Nanotechnology* [2]. Drexler defined the term nanotechnology as “Nanotechnology is the principle of manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build molecular systems with atom-by-atom precision, yielding a variety of nanomachines.”

The word ‘nanotechnology’ is defined as the study, where matter is manipulated on an atomic and molecular scale at dimensions of roughly 1 to 100 nm enabling it to exhibit novel applications. A nanostructure/nanomaterial is reasonably defined as an object possessing at least one critical dimension less than 100 nm in extent with novel properties. It is an intermediate size between molecular and microscopic structure.
There are mainly two kinds of approach for synthesizing nanomaterials; Top down approach and bottom up approach. The initial one refers to slicing or successive cutting of a bulk material to obtain nano sized material whereas the later one refers to synthesis of material from the bottom i.e. atom by atom, molecule by molecule or cluster by cluster. Both approaches play very important role in modern industry and most likely in nano technology as well. High energy milling is a typical example of top down approach and the colloidal dispersion from solution is a good example of bottom up approach in the synthesis of nano particles.

In recent years the combination of biology and nanotechnology has led to a new generation of nanodevices that make it possible for biomedical applications in therapeutic, diagnostic and preventive medicine. It integrates interdisciplinary research and recent advances in instrumentation and methods for applying nanotechnology to various areas in biology and medicine.

It is true that the concept of nanotechnology had started from the early of 1960 but the real boom in this field came not before early of 1990. The beautiful ruby red colour of some glass is due to gold nanoparticles trapped in the glass matrix. This is the example of nanomaterial application. People used to make nanomaterial far before from that time era obviously unknowingly.
1.2 Why ZnO Nanomaterial?

The ZnO nanomaterial has various beneficial applications from optoelectronics device technology to biomedical application [3-6]. The ZnO nanomaterials have widely been used in the field of biological and biomedicine, such as tissue imaging, diagnosis, cancer therapy and antibacterial application. In recent years the ZnO nanomaterials are being incorporated rapidly into clinical medicine and particularly in the field of clinical oncology [7]. This nanomaterial is nontoxic and has UV blocking capacity [8]. The wide band gap around 3.37 eV and high excitonic binding energy ~ 60 meV, make this material an excellent candidate for a variety of applications such as UV lasers, light-emitting diodes, solar cells, sensors, thin-film transistor, and varistors [9-16]. There are a number of reasons for selecting ZnO nanoparticles for the study one of which is that ZnO is a metal oxide, which is structurally stable and has a longer life than organic-based disinfectants or antimicrobial agents.

1.3 Crystal Structure of ZnO

Zinc oxide is an inorganic amphoteric oxide with the formula of ZnO. It usually appears as a white powder, insoluble in water but soluble in most acids eg HCL. As because Zn and O are placed on the 2nd and 6th groups of the periodic table ZnO is often considered as II-VI semiconductor in materials science.
The group II–VI binary compound semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite (Wz) structure, where four cations at the corners of a tetrahedron surrounds each anion, and vice versa. The cubic rocksalt is another structure which is rarely observed. Though this material has a substantial ionic character that tends to increase the bandgap beyond the one expected from the covalent bonding inspite of the fact that tetrahedral coordination is typical of sp3 covalent bonding nature. ZnO is a II–VI compound semiconductor which lies at the borderline between the covalent and ionic semiconductors in terms of its ionicity. The wurtzite structure is most stable and common structure at ambient conditions whereas the zincblende structure can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide are tetrahedral. However the rocksalt NaCl-type structure is only observed at relatively high pressures ~10 GPa. The hexagonal and zincblende ZnO lattices have no inversion symmetry. The lattice constants are $a = 3.25 \text{ Å}$ and $c = 5.2 \text{ Å}$; their ratio $c/a \sim 1.60$ is close to the ideal value for hexagonal cell $c/a = 1.633$. As in most II–VI materials, the ZnO is strong piezoelectric due to the ionic bonding (17, 18). Due to this ionicity, a zinc and oxygen plane carries both positive and negative electric charge respectively. In most relative materials, those planes reconstruct at atomic level and therefore maintain its electrical neutrality. But in case of ZnO, its surfaces are atomically flat, stable and do not exhibit any reconstruction. The various crystal structures have been showed in Fig1.
1.3.1 Hexagonal Wurtzite

The wurtzite structure has a hexagonal unit cell with two lattice parameters a & c in the ratio of $c/a = \sqrt{8/3} \approx 1.633$ (in an ideal wurtzite structure) [19]. The structure is composed of two interpenetrating hexagonal close packed (hcp) sublattices, each of which consists of one type of atom displaced with respect to each other along the threefold c-axis by the amount of $u = 3/8 = 0.375$ (in an ideal wurtzite structure) in fractional coordinates. The internal parameter $u$ is defined as the bond length between the anion and the cation or the nearest neighbor distance divided by the c lattice parameter. Each sublattice includes four atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges of a tetrahedron.

Fig1: Three different Crystal structure of ZnO i.e Hexagonal wurtzite, Zinc blende, Rocksalt [19]
In a ZnO crystal, the wurtzite structure deviates from the ideal arrangement, either by changing the c/a ratio or the u value. The lattice parameters are commonly measured at room temperature by X-ray diffraction (XRD). The lattice parameter can be affected by free charge, impurities, stress, and temperature. There are three surfaces and directions are of special importance, which are (0 0 0 1), (1 1 0 0), and (1 Ti 0 0) planes among them, the (0 0 0 1) or the basal plane is the most commonly used surface for growth [20].

1.3.2 Cubic Zinc Blende

The zincblende ZnO structure is metastable. In the case of highly mismatched substrates, there is usually a certain amount of zincblende phase of ZnO separated by crystallographic defects from the wurtzite phase. There are four atoms per unit cell and every atom of one type (group II) is tetrahedrally coordinated with four atoms of other type (group VI), and vice versa. The 4 nearest neighbors and 12 next-nearest neighbors have the same bond distance in both structures due to the tetrahedral coordination of wurtzite and zincblende structures. The wurtzite and zincblende structures differ only in the bond angle of the second-nearest neighbors and, therefore, in the stacking sequence of close-packed diatomic planes [19].
1.3.3 **Rocksalt**

The rocksalt (NaCl) structure can be obtained when the wurtzite structure is subjected to external hydrostatic pressures. The reason behind this phenomenon is the reduction of the lattice dimensions which causes the interionic Coulomb interaction to favor the ionicity more than the covalent nature. The pressure-induced phase transition of ZnO from wurtzite to rocksalt phase occurs at a pressure of 10 GPa leading to a large decrease in volume of about 17% [21]. High-pressure cubic phase has been found to be metastable for long periods of time even at ambient pressure and above 100ºC [21]. Energy-dispersive X-ray diffraction (EDXD) measurements have shown that the hexagonal wurtzite structure of ZnO undergoes a structural phase transformation with a transition pressure of 10 GPa and completed at about 15 GPa [22, 23].

1.4 **Electronic Band Structure**

Several theoretical approaches have been employed to calculate the band structure of ZnO for its three different structures i.e. wurtzite, zinc blende, and rocksalt. A number of experimental data have been published regarding the band structure of the electronic states of wurtzite ZnO. X-ray or UV reflection/absorption or emission techniques have been used to measure the electronic states in solids. These methods basically measure the energy difference between electronic levels by inducing transitions from the upper valence band states to the upper conduction band states and vice versa. After the first theoretical work proposed in 1969 on band structure calculation of ZnO proposed by
Rossler using Green's function (Korringa–Kohn–Rostoker (KKR) method) [24], several experimental works [25-28] have been performed on the wurtzite ZnO. The first experimental data related to the energy levels of core electrons in ZnO were obtained by using X-ray induced photoemission spectroscopy [25]. An Angle-resolved photoelectron spectroscopy has been employed to study the electronic structure of the ZnO (0 0 0 1) [29]. The emission spectra give valuable information, which states that the normal emission spectra recorded at photon energies ranging from 20 to 50 eV, the binding energies were referred to the Fermi level and the intensities were normalized to the photon flux.

1.5 Growth of ZnO

The growth of zinc oxide (ZnO) thin films has been studied by a variety of techniques. The applications have been driven in part due to the excellent piezoelectric properties of ZnO and its tendency to grow along the fast growing plane (0 0 0 1) on various kinds of substrates, including glass [30], sapphire [31], and diamond [32]. The early reports dealt with deposition of ZnO utilizing various growth techniques such as magnetron sputtering [32, 33] and chemical vapor deposition [34–36] but the films were mainly polycrystalline. Later attempts leads to the formation of high-quality ZnO single-crystal films prepared by radio frequency (RF) magnetron sputtering [37, 38] and other growth techniques that allow fine control over the deposition procedure. Among the latter deposition techniques are molecular beam epitaxy (MBE) [39, 40], pulsed laser deposition (PLD) [41], organometallic vapor-phase epitaxy (OMVPE) [42], and hydride
or halide vapor-phase epitaxy (HVPE), depends on the chemistry [43, 44]. The sapphire substrate has been conventionally used for ZnO growth but the high dislocation density caused by the large lattice mismatch between the sapphire substrate and ZnO would deteriorate any device performance.

Growth of bulk ZnO crystals is mainly carried out by three methods: hydrothermal [45-48], seeded vapor transport [49-52], and melt growth [53, 54].

1.5.1. Hydrothermal Method:

The hydrothermal method is very well known as well as well established growth method. Therefore, its application to the large-area ZnO single crystals is quite suitable. The growth rate of ZnO through this method has been reported to be anisotropic. The ratio of the growth rates between the fast growing and slow growing direction is 3:1 [55]. The crystal shapes are depending upon the precursor and the solution basicity, and on the shapes of seed crystals. Actually ZnO exhibits a varied range of novel structures. The relative surface activities of various growth facets under given conditions determine the surface morphology of the grown structure. After an initial period of nucleation and incubation, a crystallite will commonly develop into a three-dimensional object with well-defined, low-index crystallographic faces. The hydrothermal method also faces some challenges; among them is the quality control of ZnO as semiconductor crystal, which is more demanding rather than other applications. The main impurities in
hydrothermal ZnO are Si, Cd, and Li. The source of Si and Cd are the mineralizer and the raw material, respectively. Their concentrations can be reduced by using higher purity starting materials. The main challenge is to reduce the Li concentration caused by the aqueous solution of LiOH, which is used as a mineralizer [45].

1.5.2. **Seeded Chemical Vapor Transport**

The seeded chemical vapor transport is the method that produces very high-quality bulk ZnO wafers. In this method, the reaction takes place in a nearly closed horizontal tube furnace [49]. Like all other growth techniques, the seeded chemical vapor transport technique also posses some disadvantages. The lower growth rate and the grain boundaries of the wafers are main problematic issues, which would undoubtedly result in high cost for wafers.

1.5.3. **Melt Growth**

Another method for producing bulk ZnO is that of melt growth. This method is based on a pressurized induction melting apparatus where the melt has been kept in a cooled crucible. Zinc oxide powder is used as the starting material. Compared to other growth techniques, melt growth offers some advantages as well as some disadvantages. The main advantages are the high-purity material, commercially viable growth rates, multiple crystal orientations, whereas the disadvantage of the pressurized melt growth method is
the low-angle grain boundaries. Furthermore, the residual impurity concentration is high, and currently, only a limited amount of 50mm wafers are available for growth due to small-angle boundaries. The primary impurities are Al, Si, Fe, Cd, and Pb, all of which come from metallic Zn as a source material used in the preparation of the ZnO [53, 54].

1.6 Properties

1.6.1. Mechanical Properties

The mechanical properties of ZnO materials involve various concepts such as hardness, stiffness, and piezoelectric constants, Young’s and bulk modulus, and yield strength [56]. Hardness and Young’s modulus of ZnO is 5.0±0.1\(^\circ\) (GPa), 111.2±4.7\(^\circ\) (E, GPa).

1.6.2. Vibrational Properties

Vibrational properties of ZnO were determined by Raman scattering technique [57-63]. The vibration modes, which are the heart of the mechanical properties, are very sensitive to crystalline defects, strain, and dopant. The mode and the broadening of phonon frequency can be used to reveal very crucial information about the semiconductor.
1.6.3 THERMAL PROPERTIES

The amplitude of the vibrations increases with temperature and the thermal properties of the semiconductor determine the response of the material to temperature changes.

1.6.4 ELECTRICAL PROPERTIES

As a direct and large bandgap material, ZnO is attracting much attention for a variety of electronic and optoelectronic applications. Advantages associated with a large bandgap include high-temperature and high-power operation, lower noise generation, higher breakdown voltages, and ability to sustain large electric fields. ZnO has a relatively large direct band gap of ~3.3 eV at room temperature; therefore, pure ZnO is colorless and transparent. It exhibits piezoelectric characteristics in thin film form. ZnO is multifunctional with uses in the areas as a piezoelectric, ferroelectric and ferromagnetic [64].

1.6.5 OPTICAL PROPERTIES

Zinc oxide is also luminescent and light sensitive material. The photoluminescence and photocatalytic property of ZnO nanostructures arises due to the crystal defect [65-73]. ZnO has large exciton binding energy i.e. ~60 meV.
1.7 **VARIOUS SYNTHESIS ROUTE AND STRUCTURES**

On the basis of synthesis method, different zinc oxide nanostructures can broadly classified into two types:- solution phase synthesis, gas phase synthesis.

➢ **SOLUTION PHASE SYNTHESIS** - In solution phase synthesis, the entire growth process is carried out in the presence of liquid medium. In general aqueous solution is used and then it is referred to as hydrothermal growth process. There are various solution phase synthesis route of ZnO nanomaterials like Sol–gel technique [74], Micro emulsion synthesis [75], Spray pyrolysis and drying [76], Hydrothermal processing [77], Direct precipitation [78] Homogeneous precipitation [79], Supercritical-water processing [80], Electrophoresis [81], Template assisted growth [82].

➢ **GAS PHASE SYNTHESIS**- The gas phase synthesis is carried out in the close chamber environment at high temperatures from 500-1500°C. There are various gas phase synthesis routes of ZnO nanomaterials like Thermal decomposition of organic precursor [83], RF plasma synthesis [84], Self-assembling [85], Vapor transport process [86].

The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O\(^2\) and Zn\(^{2+}\) ions, stacked alternately along the c-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. The three fastest growth directions <0001>, <0110>, &
<2110>, and the polar surface are main responsible for obtaining a diverse group of ZnO nanostructures.

1.8 APPLICATIONS

Zinc Oxide has proved the most effective activator to speed up the rate of cure with the new accelerators. In the curing process for natural rubber and most types of synthetic rubbers, the chemical reactivity of Zinc Oxide is utilized to activate the organic accelerator. ZnO and stearic acid are ingredients in the commercial manufacture of rubber goods. It serves as the accelerator with some types of elastomer. It is an effective co-accelerator in the vulcanization process. It is useful in the preservation of plantation latex as it reacts with the enzyme responsible for the decomposition. In high-voltage wire and cable insulation, Zinc Oxide improves the resistance to corona effects by its dielectric strength. In the production of latex foam rubber products, it is particularly effective in gelation of the foam with sufficient stability. It is outstanding among white pigments and extenders for its absorption of ultraviolet rays. Zinc compounds can provide a variety of properties in the plastics field. The variable properties of Zinc Oxide are capable of generating some of the newer applications such as in electronic glass, low-melting glass for metal-to-glass seals, thermistors. It can use as an Adhesives, Mastics, Sealants. Some of the unique electronic properties of Zinc Oxide are distinctively utilized in the photocopying process. Zinc Dithiophosphates which are prepared by reacting Zinc Oxide with organic Phosphates, are used as additives to lubricating oils for automotive engines, to reduce oxidation corrosion and wear. Zinc Oxide used as a constituent of cigarette
filters is effective in removal of selected ingredients from tobacco smoke. It is effective in removal of Sulfur and Sulfur compounds from a variety of fluids and gases, particularly industrial flue gases as well as it can use as a food packaging material and fire retardants. Zinc Oxide continues as an essential ingredient in the "soft" type of ferromagnetic materials for television, radio, and tele-communication applications. It can use in Batteries, fuel cells and photocells. It plays an important role in semiconductor ceramic elements for operation at elevated temperatures or High Voltages. It reacts with aqueous solutions of Silicates to form Zinc Silicate, a waterproof, fireproof refractory material, which is used as a binder in paintings [87-98].

### 1.9 ZnO NANOMATERIAL IN BIOAPPLICATION

ZnO nanomaterial has huge application in biological field. The oxide is also a fungistat, inhibiting the growth of such fungi as mold and mildew. ZnO as one of the multifunctional inorganic nanoparticles has drawn increasing attention in recent years due to its many significant physical and chemical stability, high catalysis activity, effective antibacterial and bactericide function, intensive ultraviolet and infrared adsorption. In recent years it is used in cosmetic industry as a sunscreen lotion. It is mainly used in Zinc soap, ointment, dental composite, food powders etc. In burn ointments it helps healing. Beside this it shows higher antimicrobial activity for gram +Ve & gram –Ve bacteria in both light and dark condition [99-109].
1.10 Bacterial Cell Wall Structure

The distinguishing characteristic of Gram positive bacterium with compare to that of Gram negative bacterium is the composition of the cell wall. Several peptidoglycan layers joined together forming a thick and rigid structure in case of Gram positive bacterium whereas gram-negative bacteria have only a thin peptidoglycan layer. Moreover, the cell wall of a Gram-positive bacterium has teichoic acids, which mainly consist of alcohols (like ribitol and alcohol) and phosphate. Teichoic acids have two types: lipoteichoic acid and wall teichoic acid. The initial one can travel across the peptidoglycan layer and is physically connected to the plasma membrane whereas the later one can physically connected to the peptidoglycan layer alone never touching the plasma membrane. Due to the presence of phosphate group in the molecular structure both types of teichoic acids bears negatively charged. Because of the nature of their charges, they play a role in binding and regulating the movement of positive ions into and out of the cell.

The presence of an outer membrane and the possession of only few peptidoglycan layers in the cell wall distinguish Gram-negative bacteria from Gram-positive ones. Lipids covalently linked to proteins called lipoproteins are the molecules that bind the peptidoglycan to the outer membrane. The peptidoglycan is located in the periplasm, a space filled with fluid located between the plasma membrane and the outer membrane. A high amount of degradative enzymes and transport proteins are found in the periplasm. Unlike Gram-positive cell walls it cannot find teichoic acids in the Gram-
negative cell walls. In addition, the cell walls of Gram-negative bacteria are more prone to mechanical breakage because of the low amount of peptidoglycan. The outer membrane is actually permeable to nutrients due to the presence of porins, proteins that form channels toward the cytoplasm. Porin allow the entry of valuable molecules like disaccharides, nucleotides, peptides, amino acids, iron, and vitamin B₁₂ but it prevents the entry of other molecules, especially the bigger ones [110-112].

![Cell wall structure of gram negative and gram positive bacteria](image-url)
11 REFERENCES


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