Chapter 2

Properties and Applications of ZnO

2.1 Introduction

ZnO has been investigated in 1912, with the beginning of semiconductor age after the invention of transistor [1], systematic investigation of ZnO as a binary compound semiconductor was performed. In 1960 the good pizo-electrical properties of ZnO were discovered [2], which lead to the first electronic application of zinc oxide as a thin layer for surface acoustic wave device [3]. Currently, research on ZnO as a semiconducting material sees a renaissance after intensive research periods in the 1950 and 1970 [4, 5]. The results of these earlier activities on ZnO were summarized by Heiland, Mollwo, and Stockmann (1959) [6], Hirschwald (1981) [7], and Klingshiran ad Haug (1981) [8]. Since, from 1990 to up to till date an enormous increase of the number of publications on ZnO due to its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, broad range of radiation absorption and high photo stability, therefore ZnO is called multifunctional material. Zinc oxide is an oxidic compound naturally occurring as the rare mineral zincite, which was discovered in 1810 by Bruce Franklin. Zincite is usually colored red and orange by manganese impurities. ZnO is a II–VI semiconductor material and it is a very promising material for semiconductor device applications due to its wide range of useful properties. ZnO has a direct wide band gap of 3.44 eV at low temperature and 3.37 eV at room temperature, which enables some applications in optoelectronics such as light [29]
emitting diodes, laser diodes and photo detectors, it has relatively large exciton binding energy (60 meV), which makes ZnO a promising material for excitonic effects based optical devices and due to the lack of a center of symmetry in the wurtzite structure combined with a large electromechanical coupling, ZnO possesses large piezoelectric and pyroelectric properties. These make the ZnO generally used for sensors, transducers and actuators. In addition, ZnO is also biocompatible, and it can be used in biomedical applications without modification such as phototoxic intracellular, which attracts ZnO for chemical sensor and biosensors applications [9-13]. Moreover, properties of ZnO can be changed with doping of transition metal ions because transition metal ion have intrinsic donor defects, which contribute to carrier and it enhanced ferromagnetic properties at room temperature, which makes the transition metal doped ZnO nanomaterial useful for spintronic applications [9, 11, 14-16]. Hence, ZnO nanostructures are attractive and promising material for some future nanotechnology applications [17-19]. However, most of these advantages are definitely utilized due to the fundamental properties of ZnO nanomaterial. Therefore, the fundamental properties and its selected application of ZnO nanostructures have been introduced in this chapter.

2.2 Crystal structure of ZnO

ZnO exhibits three crystallize structures, namely, Wurtzite, Zincblende and Rock salt [11, 20] are shown in Fig. 2.1, ZnO crystallizes in the wurtzite structure and has a hexagonal unit cell with two lattice parameters a = 0.3296 nm and c = 0.52065 nm in the ratio of c/a = 1. 633 (in an ideal wurtzite structure) and belongs to the space group C\(^4\) 6\(v\) in the Schoenflies notation and (P6\(_3\)mc) in the Hermann–Mauguin notation. Every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which means that one zinc ion (cation) is surrounded tetrahedrally by four oxygen ions (anions) and vice versa. Its structure is arranged by alternating planes of
tetrahedrally coordinated $\text{O}^{2-}$ and $\text{Zn}^{2+}$ ions stacking alternatively along the c-axis, which makes the entire structure to lack central symmetry. The surfaces can be terminated either with cations or anions, which leads ZnO possesses positively or negatively charged on the surfaces [21]. Additional to the wurtzite phase, ZnO is also known to crystallize in the cubic Zincblende and Rock salt (NaCl) structures, which are illustrated in Fig. 2.1. Zincblende ZnO is stable only by the growth on cubic structures, while the rocksalt structure is a high-pressure metastable phase forming at ~10 GPa, and cannot be epitaxially stabilized. The theoretical calculation indicates that fourth phase, cubic cesium chloride, may be possible at extremely high temperature.

![ZnO Crystal Structures](image)

**Fig.2.1** Stick-and-ball representation of ZnO crystal structures: (i) hexagonal wurzite (ii) cubic Zincblende (iii) cubic rock salt (Shaded gray and black spheres denote Zn and O atoms, respectively. (Images adapted from Hadis Morkoç and Umit Ozgur et al. (2009).
Another important characteristic of ZnO is the polar surfaces (refer Fig. 2.2) [11]. 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 ± (0001) are exceptions: they are atomically flat, stable and without reconstruction. Efforts to understand the superior stability of the ZnO ± (0001) polar surfaces are at the forefront of research in today’s surface physics.

Fig.2.2 Zinc oxide wurtzite structure and its polar surfaces. Zinc atoms are represented by the smaller white balls and oxygen atoms by red colour (Image adopted from: N. Rajeswari Yogamalar et al. (2013)).
The other two most commonly observed faces for ZnO are \{2\overline{1}10\} and \{01\overline{1}0\}, which are non-polar surfaces and have lower energy than the \{0001\} face. Aside from causing the inherent polarity in the ZnO crystal, the tetrahedral coordination of this compound is also a common indicator of sp³ covalent bonding. However; the Zn-O bond also possesses very strong ionic character, and thus ZnO lies on the border line between a covalent and ionic compound, with an ionicity of \( f_i = 0.616 \). On the other hand, each oxygen (or zinc) ion is tetrahedrally surrounded by four zinc (or oxygen) ions in the wurtzite structure. Further, each ion has twelve next-nearest neighbors of the same type of ions. The oxygen and zinc atom (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 covalent bond 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. A schematic representation of the wurtzite ZnO structure without tetrahedral coordination and with tetrahedral coordination is shown in Fig. 2.3 (a) and (b). The structure is composed of two interpenetrating hexagonal close packed (hcp) sub lattices, each of which consists of one type of atom displaced with respect to each other along the three fold 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 length of the bond parallel to the c-axis (anion–cation bond length or the nearest-neighbor distance) divided by the c lattice parameter. The basal plane lattice parameter (the edge length of the basal plane hexagon) is universally depicted by \( a \); the axial lattice parameter (unit cell height), perpendicular to the basal plane, is universally described by \( c \). Each sub lattice includes four atoms per unit cell, and every atom of one kind (group II atom) is surrounded by four atoms of the other kind (group VI), or vice versa, which are coordinated at the edges [33].
of a tetrahedron. The crystallographic vectors of wurtzite are $a' = a(1/2, 3^{1/2}/2, 0)$; $b' = a(1/2, -3^{1/2}/2, 0)$ and $c' = a(0, 0, c/a)$. In Cartesian coordinates, the basis atoms are $(0, 0, 0)$, $(0, 0, uc)$, a $(1/2, 3^{1/2}/6, c/2a)$ and a $(1/2, 3^{1/2}/6, [u+1/2] c/a)$.

**Fig 2.3 (a).** A schematic representation of a hexagonal wurtzite ZnO structure with lattice constants $a$ in the basal plane and $c$ in the basal direction. (Image adopted from: Zinc Oxide: Fundamentals, Materials and Device Technology. ISBN: 978-3-527-40813-9) Hadis Morkoç and Umit Ozgur et al. (2009).

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 \( u \cdot c/a = (3/8)^{1/2} \), where \( c/a = (8/3)^{1/2} \) and \( u = 3/8 \) for an ideal crystal.

\[ \text{Fig. 2.3 (b). The tetrahedral coordination of Zn–O. (Image adopted from: http://en.wikipedia.org/wiki)} \]

ZnO crystal structures deviate from this ideal arrangement by changing both of these values. This deviation occurs such that the tetrahedral distance is kept roughly constant in the lattice. Experimentally, for wurtzite ZnO, the real values of \( u \) and \( c/a \) were determined in the range \( u = 0.3817-0.3856 \) and \( c/a = 1.593-1.6035 \) \([22-24]\).

2.3 **Electronic band structure of ZnO**

The band structure is a very important property of a semiconductor material, because many important properties and parameters are derived from it, e.g. band gap and effective masses of electrons and holes. For this reason, understanding of the band structure of ZnO is crucial to explain the electrical and optical properties and many other
phenomena. The band structure provides the electronic one-particle (i.e. electron or hole) states. The electronic band structure of ZnO has been calculated by a number of groups [25-30]. ZnO is a direct band gap semiconductor which crystallizes in the wurtzite symmetry because the uppermost valence band (VB) and the lowest conduction band (CB) are at the same position in the Brillouin zone, namely at \( k = 0 \), i.e. at the \( \Gamma \)-point [31, 32]. The lowest CB is formed from the empty 4s states of \( \text{Zn}^{2+} \) or the anti-binding \( \text{sp}^3 \) hybrid states and the VB originates from the occupied 2p orbitals of \( \text{O}^{2-} \) or the binding \( \text{sp}^3 \) orbitals. The band structure of wurtzite ZnO structure is shown in Fig 2.4 (a). Under the crystal field and spin orbit interaction, the valence band is split into three sub-VB of symmetries, which are labeled in all wurtzite-type semiconductors from high to low energies as A, B, and C bands.

**Fig. 2.4 (a)** The LDA band structure of bulk wurtzite ZnO calculated using dominant atomic self-interaction-corrected pseudo potentials (SIC-PP). (Image adopted from: D. Vogel, P. Kruger et al., (1995).)
In most cases, the ordering of the bands is $A \Gamma_9$, $B \Gamma_7$, $C \Gamma_7$. However, for ZnO there is a long debate whether the ordering as usual or $A \Gamma_7$, $B \Gamma_9$, $C \Gamma_7$. Therefore, the ordering $A \Gamma_7$, $B \Gamma_9$, $C \Gamma_7$ have been selected [31-33] and have been shown in Fig. 2.4 (b).

![Fig. 2.4 (b). The valence band (VB) and conduction band (CB) of ZnO. (Image adopted from: Verma, M. Singh et al. (2005).)](image)

As mention earlier, nanotechnology applications are partly relying on the fundamental properties of the nanomaterial. Therefore, understanding the fundamental physical properties of ZnO is important to the rational design of functional devices. It should be noted that as the dimension of the semiconductor materials shrink down to nanometer scale, some of their physical properties undergo changes due to “quantum size effects”. However, some of these parameters of ZnO are not well demonstrated, e.g. hole mobility and effective mass are still under debate. Table 2.1 shows some of the basic physical parameters for wurtzite ZnO [34-36]. However, investigation of the properties of individual ZnO nanostructures is essential for developing their nanoscale devices.

[37]
2.4.1. Direct and wide band gap

The band gap of ZnO is 3.44 eV at low temperatures and 3.37 eV at room temperature[4]. For comparison, the respective values for wurtzite GaN are 3.50 eV and 3.44 eV [37]. As mentioned above, this enables applications in optoelectronics in the blue/UV region, including light-emitting diodes, laser diodes and photo detectors [38-41]. Optically pumped lasing has been reported in ZnO platelets [42], thin films [43], clusters consisting of ZnO nanocrystals [44] and ZnO nanowires [45]. Reports on p–n homo junctions have recently appeared in the literature [46-48], but stability and reproducibility have not been established.

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>ZnO</td>
</tr>
<tr>
<td>Molar mass</td>
<td>81.408 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>White solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Stable phase at 300K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1950°C (decomposes)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>1950°C (decomposes)</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>0.16mg/100ml (30°C)</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
</tr>
<tr>
<td>a=b</td>
<td>3.249 Å</td>
</tr>
<tr>
<td>c</td>
<td>5.206 Å</td>
</tr>
<tr>
<td>a/c</td>
<td>1.602</td>
</tr>
<tr>
<td>Lattice</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Space Group</td>
<td>P6_3mc</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.3 eV (direct)</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.008-2.029</td>
</tr>
</tbody>
</table>

Table.2.1. Basic physical and chemical properties of ZnO semiconductor
### 2.4.2. Large exciton binding energy

The free-exciton binding energy in ZnO is 60 meV [42, 43], compared with, e.g., 25 meV in GaN [49]. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and higher [42, 50]. Since the oscillator strength of exciton is typically much larger than that of direct electron–hole transitions in direct band gap semiconductors [51], the large exciton binding energy makes ZnO a promising material for optical devices that are based on excitonic effects.

### 2.4.3. Large piezoelectric constant

In piezoelectric materials, an applied voltage generates a deformation in the crystal and vice versa. These materials are generally used as sensors, transducers and actuators. The low symmetry of the wurtzite crystal structure combined with a large electromechanical coupling in ZnO gives rise to strong piezoelectric and pyroelectric properties.

Piezoelectric ZnO films with uniform thickness and orientation have been grown on a variety of substrates using different deposition techniques, including sol–gel process; spray pyrolysis, chemical vapor deposition, and sputtering [52-55].

### 2.4.4. Strong luminescence

Due to a strong luminescence in the green–white region of the spectrum, ZnO is also a suitable material for phosphor applications. The emission spectrum has a peak at 495 nm and a very broad half-width of 0.4 eV [56]. The n-type conductivity of ZnO makes it...
appropriate for applications in vacuum fluorescent displays and field emission displays. The origin of the luminescence center and the luminescence mechanism are not really understood, being frequently attributed to oxygen vacancies or zinc interstitials, without any clear evidence [57]. The defects cannot emit in the green region, and it has been suggested that zinc vacancies are a more likely cause of the green luminescence. Zn vacancies are acceptors and likely to form in n-type ZnO.

2.4.5. Large non-linear optical coefficients

ZnO crystals and, in particular, thin films exhibit second- and third-order non-linear optical behavior, suitable for nonlinear optical devices. The linear and non-linear optical properties of ZnO depend on the crystallinity of the samples. ZnO films grown by laser deposition, reactive sputtering and spray pyrolysis show strong second-order non-linear response. Third-order nonlinear response has recently been observed in ZnO nanocrystalline films [58]. The nonlinear optical response in ZnO thin films is attractive for integrated non-linear optical devices.

2.4.6. High thermal conductivity

This property makes ZnO useful as an additive (e.g. ZnO is added to rubber in order to increase the thermal conductivity of tires). It also increases the appeal of ZnO as a substrate for homoepitaxy or heteroepitaxy (e.g. for growth of GaN, which has a very similar lattice constant) [59, 60]. High thermal conductivity translates into high efficiency of heat removal during device operation.

2.4.7. Radiation hardness

Radiation hardness is important for applications at high altitude or in space. It has been observed that ZnO exhibits exceptionally high radiation hardness [61, 62], even greater than that of GaN, the cause of which is still unknown.

[40]
Zinc oxide is widely used in many areas. It plays an important role in a wide range of application such as spintronic device applications, ranging from tyres to ceramics, from pharmaceuticals to agriculture, and optoelectronic devices and biomedical, sensors etc.

### 2.5.1 Cosmetic

Due to its antibacterial, disinfecting and drying properties [63, 64], zinc oxide is widely used in the production of various kinds of medicines. It was formerly used as an orally administered medicine for epilepsy, and later for diarrhoea. At the present time it is applied locally, usually in the form of ointments and creams, and more rarely in the form of dusting powders and liquid powders. ZnO has properties which accelerate wound healing, and so it is used in dermatological substances against inflammation and itching. In higher concentrations it has a peeling effect. In addition, it is used in dentistry, chiefly as a component of dental pastes, and also for temporary fillings. ZnO is also used in various types of nutritional products and diet supplements, where it serves to provide essential dietary zinc [65]. For many years, before sun creams began to contain nanoparticles of ZnO or TiO2, they contained thick preparations which did not rub easily into the skin and which were cosmetically un-attractive. Due to their ability to absorb UVA and UVB radiation, these products began to be used in creams. A new cream formula, containing a combination of ZnO and TiO2, solved the problem of an insufficient white layer and produced a new medium which is more transparent, less adhesive and much more easily rubbed into the skin [66]. A number of studies have shown that titanium and zinc oxides are extremely good media in sun creams, since they absorb UV radiation, do not irritate the skin, and are easily absorbed into the skin [67-69].
2.5.2 Textile

The textile industry offers a vast potential for the commercialization of nanotechnological products. In particular, water repellent and self-cleaning textiles are very promising for military applications, where there is a lack of time for laundering in severe conditions. Also in the world of business, self-cleaning and water repellent textiles are very helpful for preventing unwelcome stains on clothes. Protection of the body from the harmful UV portion of sunlight is another important area. Many scientists have been working on self-cleaning, water repellent and UV-blocking textiles [70, 71]. For textile applications, not only is zinc oxide biologically compatible, but also nanostructured ZnO coatings are more air-permeable and efficient as UV-blockers compared with their bulk counterparts [72]. Therefore, ZnO nanostructures have become very attractive as UV-protective textile coatings [73].

2.5.3 Electronics

Zinc oxide is a new and important semiconductor which has a range of applications in electronics and electro technology. Its wide energy band (3.37 eV) and high excitonic binding energy (60 meV) at room temperature mean that zinc oxide can be used in photoelectronic [74] and electronic equipment[75], in devices emitting a surface acoustic wave [76], in field emitters [77], in sensors[78], in UV lasers[79], and in solar cells [80]. ZnO also exhibits the phenomenon of luminescence (chiefly photoluminescence-emission of light under exposure to electromagnetic radiation). Because of this property it is used in FED (field emission display) equipment, such as televisions. It is superior to the conventional materials, sulfur and phosphorus because it is more resistant to UV rays, and also has higher electrical conductivity. The photoluminescent properties of zinc oxide depend on the size of crystals of the compound,
defects in the crystalline structure, and also on temperature [81]. ZnO is a semiconductor and thin films made of that material display high conductivity and excellent permeability by visible rays. These properties mean that it can be used for the production of light-permeable electrodes in solar batteries. It also has potential uses as a transparent electrode in photovoltaic and electroluminescent equipment, and is a promising material for UV-emitting devices [82, 83].

2.5.4 Sensors

Zinc oxide is also used in gas sensors. It is a stable material, whose weak selectivity with respect to particular gases can be improved by adding other elements. The working temperature of ZnO is relatively high (400–500 °C), but when nanometric particles are used this can be reduced to around 300 °C. The sensitivity of such devices depends on the porosity and grain size of the material; sensitivity increases as the size of zinc oxide particles decreases. It is most commonly used to detect CO and CO₂ (in mines and in alarm equipment), but can also be used for the detection of other gases (H₂, SF₆, C₄H₁₀, C₂H₅OH). The zinc oxide used in the production of such equipment is obtained by a variety of methods (chemical vapour deposition, aerosol pyrolysis or oxidation of metallic zinc); it is important to control the process temperature, since this determines the properties of the product [84, 85].

2.5.5 Pigmentation

Through its high brightness, refractive index, and optimum particle size, Zinc Oxide provide a high degree of whiteness and tinting strength of such rubber products as tire sidewalls, sheeting and surgical gloves [86, 87].

2.5.6 Miscellaneous applications

Apart from the applications mentioned above, zinc oxide can also be used in other
branches of industry, including for example concrete production. The addition of zinc oxide improves the process time and the resistance of concrete to the action of water. Also, the addition of ZnO to Portland cement slows down hardening and quenching (it reduces the gradual evolution of heat), and also improves the whiteness and final strength of the cement.

Zinc oxide reacts with silicates (e.g., sodium silicate) to produce zinc silicates, which are water- and fire-resistant materials used as binders in paints. These fire-resistant and adhesive substances are used in the binding of cements used in the construction industry.

Methanol, the third most-important chemical product of the chemical industry, is produced using a Cu/ZnO/Al₂O₃ catalyst, with small Cu particles promoted by their interaction with the ZnO substrate as the active component [88].

ZnO is also used for the production of typographical and offset inks. It imparts good printing properties (high fluidity). The addition of ZnO means that the inks have better covering power, pure shade and high durability, and prevents darkening. Zinc oxide is also used in pigments to produce shine.

It is added to many food products, including breakfast cereals. ZnO is used as a source of zinc, which is an essential nutrient. It has special chemical and antifungal properties, zinc oxide and its derivatives are also used in the process of producing and packing meat products (e.g., meat and fish) and vegetable products (e.g., sweet corn and peas)[89, 90].

As mentioned above, ZnO and its derivatives suppress the development and growth of fungi and moulds. Zinc oxide is added to fungicides to improve their effectiveness. Zinc oxide is also being used increasingly often as an animal feed additive, as it supports the correct growth of animals. It is also used as an artificial fertilizer. Zinc oxide also has uses in criminology, in the mechanical fingerprint analysis. It is also an ingredient in cigarette filters, as it selectively removes certain components of tobacco smoke. Filters
are made of charcoal impregnated with ZnO and Fe$_2$O$_3$, which remove significant quantities of HCN and H$_2$S from tobacco smoke without producing a smell. It also removes sulfur and its compounds from various liquids and gases, particularly industrial waste gases. ZnO and its derivatives are also used as an additive to car lubricating oils, reducing consumption and oxygen corrosion. Zinc oxide has also been used in various types of lubricants, such as those with EP additives, vibration-resistant lubricants and solid lubricants. In the future, advantage may also be taken of the adhesive properties of ZnO [91]. Because the compound is nontoxic, cheap, and chemically stable in the air, nanoparticles of zinc oxide can be used to make new eco-friendly substances for cell marking [90]. Recent advances in electrochemical bio-sensing based on a wide variety of nanostructures such as ZnO nanowires, nanotubes and nanoporous materials have attracted great interest in biosensor applications due to their remarkable properties such as non-toxicity, bio-safety, excellent biological compatibility, high electron transfer rates, enhanced analytical performance, increased sensitivity, easy manufacture and low cost [92, 93]. Moreover, ZnO has a high isoelectric point (IEP) of about 9.5, which can be expected to provide a positively charged substrate for immobilization of low-IEP proteins or enzymes such as uricase (IEP ~ 4.6) at a physiological pH of 7.4 [94]. In addition, ZnO has high ionic bonding (60%), and it dissolves very slowly at biological pH values [95]. Many researchers have attempted to correlate the biological activity of inorganic antibacterial agents with the size of the constituent particles [96, 97]. Inorganic nanocrystalline metal oxides are particularly interesting because they can be prepared with extremely high surface areas, and are more suitable for biological molecular applications [98, 99]. ZnO semiconductors have been extensively studied as antimicrobial agents due to their photocatalytic activity under UV light [100, 101]. These antimicrobial substances based on inorganic chemicals have been found to be effective
for therapy [102, 103]. Padmavathy et al. [100] showed that ZnO nanoparticles were more abrasive than bulk ZnO (particle sizes in the range 0.1–1 μm), and this contributes to the greater mechanical damage to the cell membrane and the enhanced bactericidal effect produced by ZnO nanoparticles.
References


[49]


[75] Y. Yamauchi, T. Fukunaga, EL display device, driving method thereof, and electronic equipment provided with the EL display device, Google Patents, 2002.


[51]