

# Basics of Zinc oxide as a semiconductor : Theoretical explanation

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## **Abstract**

As Zinc oxide (ZnO) is a wide bandgap semiconductor. So it has earned significant attention in the last few years due to its versatile properties and potential applications in various electronic devices. ZnO has the properties like high electron mobility, high thermal conductivity, wide and direct band gap and large excitation binding energy which make ZnO very suitable for making a wide range device like transparent thin-film transistors, photodetectors, Light emitting diodes and laser diodes that operates in the blue and UV region of spectrum. It is a cheap, transparent, conductive oxide and is used as a material for electronic circuits that is optically transparent for semiconductor spintronics and thus as an alternative to gallium nitride (GaN). This chapter firstly discusses the effect of defects and impurities on the electrical and optical properties of ZnO, secondly the practical applications of ZnO semiconductors in various fields such as nanotechnology, sensors, etc.

## 1.INTRODUCTION:

In recent few years, the field of semiconductor has witnessed significant advancements, which is driven by the quest for efficient, versatile, and eco-friendly alternatives for electronic and optoelectronic applications. Due to remarkable properties including high electronic mobility, wide band gap, and excellent optical and piezoelectric characteristics of ZnO semiconductor, it is widely used for application ranging from transistors and sensors to light –emitting diodes and solar cells.

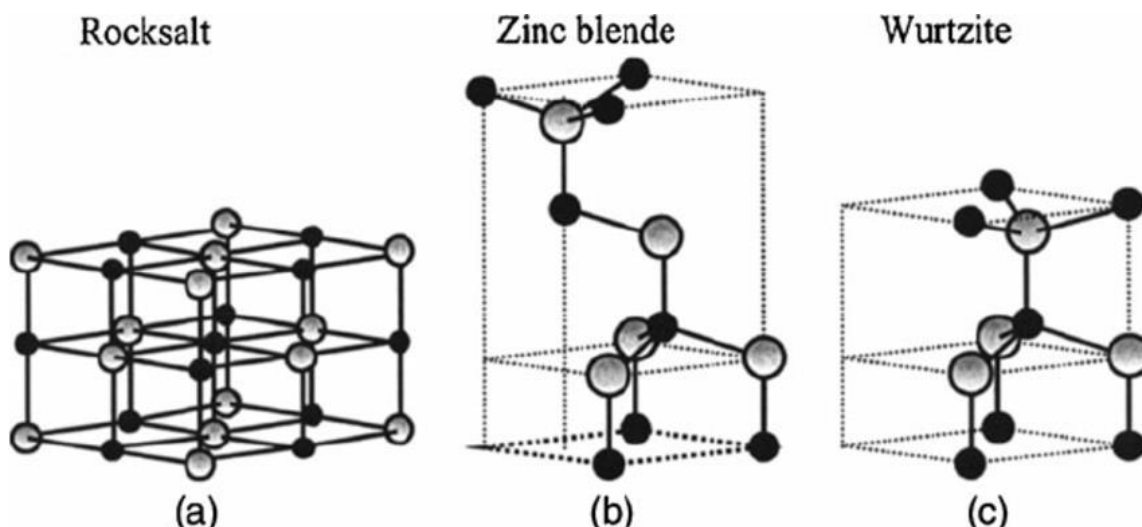
In this chapter the unique properties of ZnO semiconductor has highlighted that set it apart from other semiconductors. We will explore the crystal structure of ZnO , its electronic band structure, and the intrinsic and extrinsic factors that influences its electrical and optical properties.

By laying a solid foundation of knowledge about ZnO as a semiconductor, this chapter aims to provide readers with a comprehensive introduction to the key concept that will be described in details in this chapter. As we embark on this exploration, we invite readers to delve into the intricate world of ZnO, where scientific curiosity meets technological innovation in the realm of semiconductor materials.

## 2. Crystal Structure and Properties of ZnO semiconductor :

Zinc Oxide (ZnO) is a wide-bandgap semiconductor. It posses hexagonal wurtzite structure. Its lattice consists of alternating layers of zinc and oxygen atoms. ZnO's unique crystal structure imparts various properties that make it a significant material for semiconductor applications.

**2.1. Crystal Structure:** ZnO crystallizes in the hexagonal wurtzite structure. It consists of close-packed hexagonal layers of Oxygen atoms with Zn atom sandwiched in between. The arrangement influences its electronic properties. It has huge optoelectronic applications, such as light –emitting diodes (LEDs) and lasers due to its direct bandgap which is around 3.37 eV at room temperature. Its wide bandgap also enables ZnO to withstand high-temperature environment , expanding its utility in various scenarios.



**Fig 1: ZnO crystal structures: cubic rocksalt ( a ), cubic zinc blende ( b ) and hexagonal Wurtzite ( c ). The shaded gray and black spheres represent zinc and oxygen atoms.**

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## 2,2 Properties:

**2.2.1. Bandgap:** ZnO has a wide direct bandgap of approximately 3.37 eV at room temperature. This bandgap allows ZnO to absorb ultraviolet (UV) light, making it suitable for optoelectronic applications like UV detectors and light-emitting devices. The electronic band structure of ZnO determines its electronic behaviour. The valence band of ZnO is mainly composed of oxygen 2p orbitals, while the conduction band is formed primarily by Zinc 4s orbitals. The energy gap between these bands, the bandgap, dictates the energy required for an electron to transition from the valence to conduction band, influencing the material's electrical conductivity.

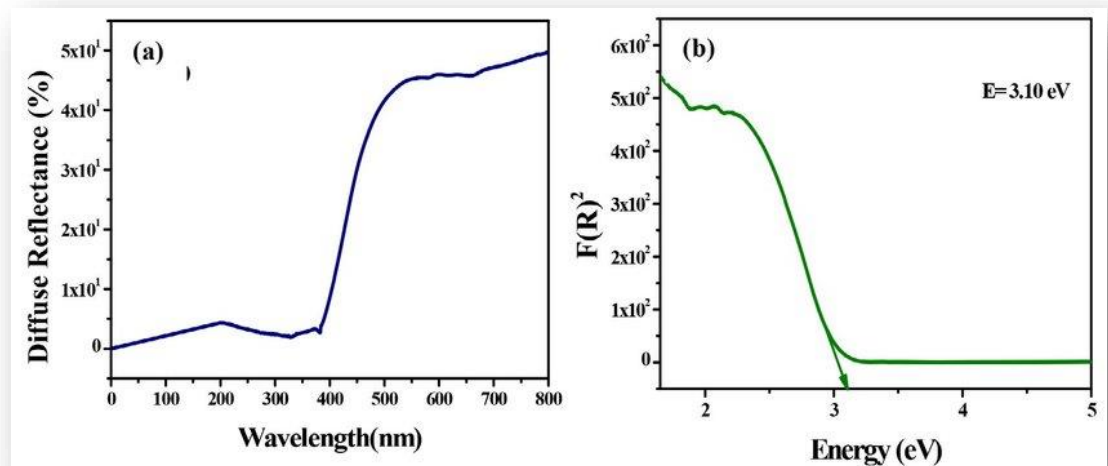
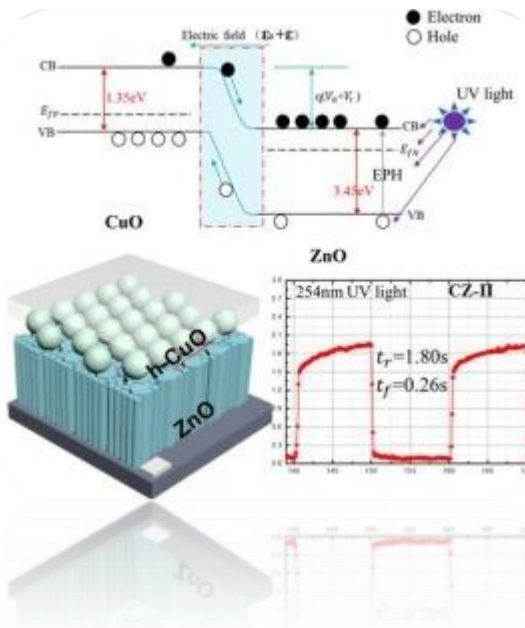


Fig 2 : Diffuse reflectance spectrum (a) and direct band gap energy of ZnO (b).

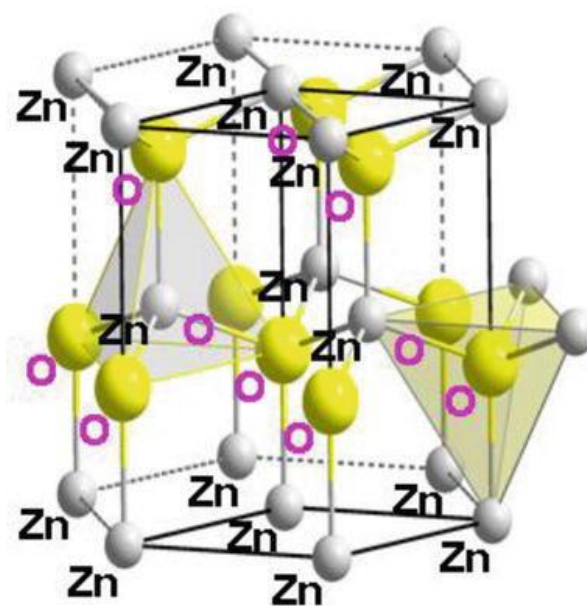
**2.2.2. Optoelectronic properties:** Zinc oxide (ZnO) is an attractive material for making UV light-emitting devices, UV detectors and LASER diodes due to its wide bandgap and high excitation binding energy. It can efficiently emit and detect UV light due to its direct bandgap transition.

When excited by UV light or electrons, ZnO emits light through photoluminescence (PL). The high excitation binding energy in ZnO results in efficient excitation formation and emission, contributing to its strong photoluminescence. These photoluminescent properties are advantageous for applications like LEDs, where ZnO can emit UV light for various purposes, including sterilization and communication.



**Fig 3: Ultraviolet photodetector using hollow N-ZnO nanorods with a PN junction structure.**

**2.2.3. Electrical Properties:** ZnO can exhibit both n-type and p-type conductivity depending on the growth condition and doping elements. Intrinsic ZnO is usually n-type due to oxygen vacancies, which act as donor defects. Doping with element like aluminium, gallium, or Indium introduces acceptors states , leading to p-type behaviour. The control of doping levels and type is essential for designing ZnO based electronic device.



**Fig 4 : Doped ZnO**

**2.2.4. Piezoelectricity:** Piezoelectricity is also an important property of ZnO. An electric polarization is created by its crystal structure which is subjected to mechanical stress or strain. By using this property sensors, resonators, and energy harvesting device can be generated.

**2.2.5. Transparent Conductive Film :** ZnO thin films have excellent transparency and good electrical conductivity. So, it has huge application in transparent conductive electrodes for displays, solar cells, and touchscreens.

**2.2.6. Gas sensing :** Various gases can be absorbed on the surface of ZnO and its electrical properties are altered. By using this property gas sensors are generated , where changes in conductivity due to gas absorption are used to detect and quantify specific gases.

**2.2.7. Photoelectrochemical application:** ZnO can be used as a photoanode material which is very useful to produce dye-sensitized solar cells and photocatalytic systems. As ZnO has efficient electron transport properties and also it has suitable band edge positions , so it is effective for light-driven conversion process. Another prominent application of it is water splitting, so that Hydrogen gas is produced by utilizing solar energy.

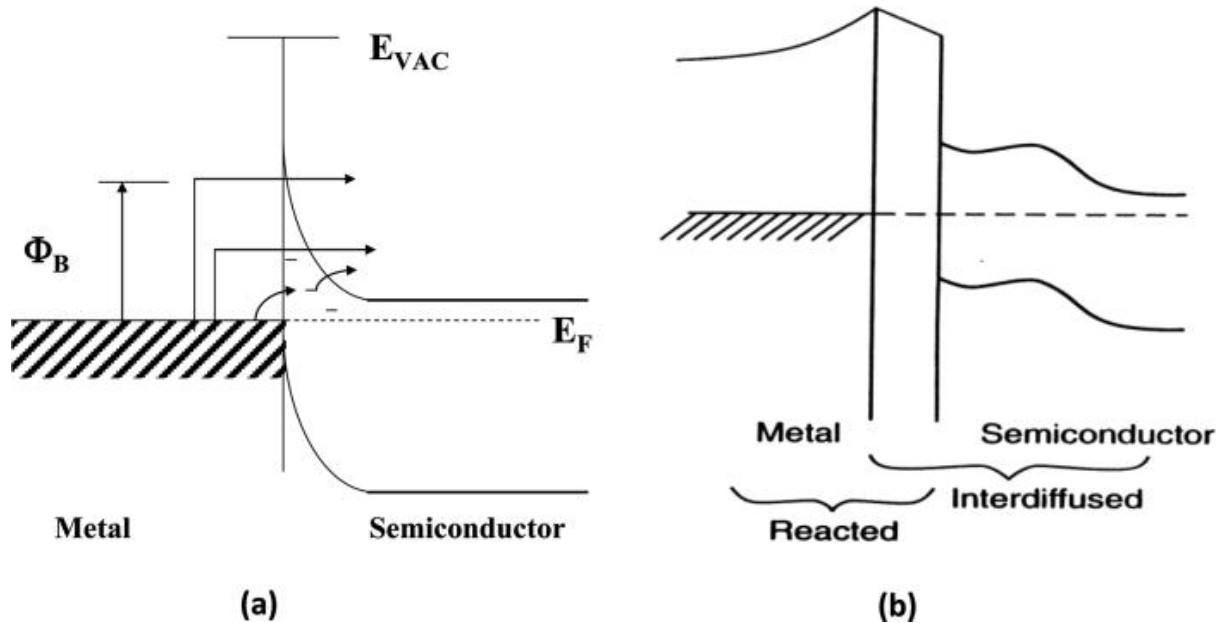
Despite of its potential, there are many difficulties related to ZnO to be applied for photoelectrochemistry . It has issues related to charge carrier recombination and stability under prolonged light exposure . Researcher have taken many strategies to enhance ZnO's performance, such as surface modification , heterojunction formation with other semiconductors, and are trying to improve charge separation and transport .

In summary, these unique properties of ZnO make it promising material for a wide range of technological application., from optoelectronics and sensing to energy conversion and beyond.

### **3. Electronic Transport Mechanism of Zinc oxide:**

Various charge character including electrons, holes , ionized donors or acceptors governs the electronic transport in ZnO . Some factors such as doping , defect states and temperature influence the intrinsic carrier concentration , mobility and conductivity . Here are some discussion about electronic transport mechanism in ZnO.

- **Intrinsic Carrier Concentration** : An electron –hole pair is created due to a small fraction of valance electrons of ZnO are excited to the conduction band at room temperature . This intrinsic carrier concentration is also known as equilibrium carrier concentration .



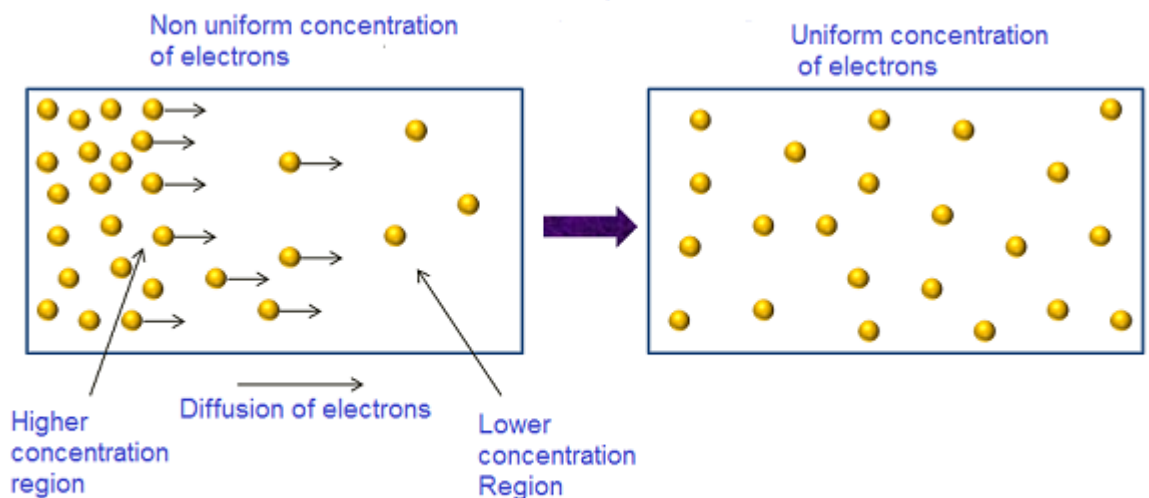
**Fig 5: (a) Complementary charge transport mechanisms in ZnO including thermionic emission, tunneling, and hopping transport through defect levels in the bandgap. (b) An extended metal-semiconductor interface that illustrates reacted and/or interdiffused regions that are possible along with associated changes in band bending and interface dielectric phases.**

- **Conduction mechanism** :
  - **Intrinsic Conduction** : This is the phenomenon of ZnO where charge carrier namely electrons and holes, are generated within the material without the introduction of deliberate impurities or dopants. These electrons gained sufficient thermal energy as temperature increases, and their transition occurs from valance band to conduction band, which creates electron –hole pairs also known as exciton . With the rise of temperature the intrinsic carrier concentration , which is actually the result of thermal excitation , leads to higher intrinsic conductivity . The energy gap between the valance and conduction bands play a crucial role in determining the energy required for this transition.
  - **Extrinsic conduction** : This is actually an intentional introduction of impurities or dopants to modify its electronic property . Extrinsic conduction aims to increase the concentration of charge carrier ( electrons or holes ) by selectively adding atoms of different valance , and in this way the material’s conductivity has altered .
- **Drift** : Drift mechanism of ZnO refers to the movement of charge carriers in response to an electric field. Charge carrier experience a force by applied electric field across a ZnO crystal., that drives them to move through the crystal lattice . The drift current is constituted by the

movement of charge carrier . The rate at which charge carriers move in response to the electric field , characterised by their mobility , which is a measure of their ability to move per unit electric field .

- **Diffusion** : It is another important electronic transport mechanism of ZnO as semiconductor . It involves a movement of charge carrier in response to a concentration gradient rather than applied electric field. In this type of semiconductor , charge carrier tends to move from region higher concentration to lower concentration . This movement occurs due to random thermal motion of carriers. The rate of diffusion depends on following factors :-

- **Concentration gradient**
- **Drift current**
- **Carrier mobility**
- **The presence of crystal defects.**
- **Impurities**
- **Material's unique crystal structure**



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**Fig 6: Diffusion current**

- **Scattering mechanism** : Various scattering mechanism obstruct s the movement of charge carrier. Lattice scattering (interaction with lattice vibration), impurity scattering i.e interaction with impurities and defects are included with these . These scattering events can reduce carrier mobility and increase resistance, affecting the overall transport properties of material.
- **Temperature Dependence** : The electronic transport mechanism in ZnO is strongly temperature – dependent . As the temperature increases , carrier mobility tends to

decrease due to increased scattering from lattice vibrations and defects. However at high temperature , more carriers are thermally excited into the conduction valance bands , leading to increased carrier concentration and conductivity .

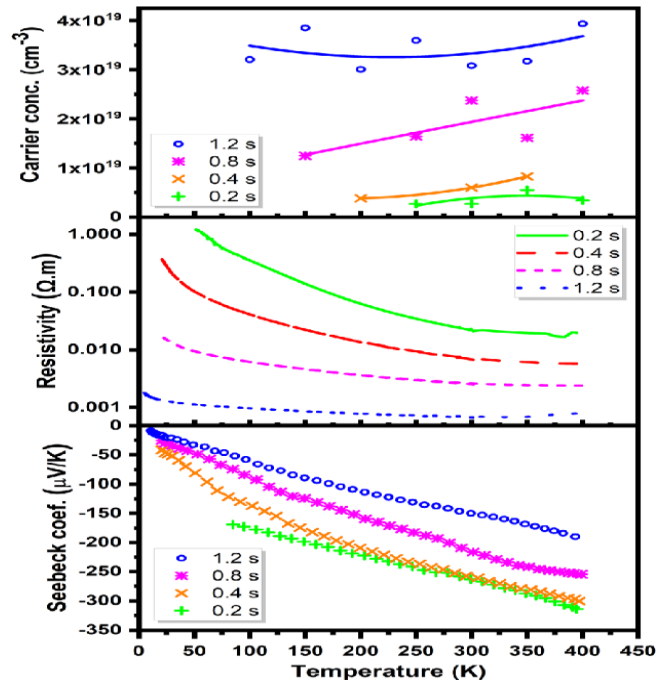


Fig 7 : Temperature dependence of electrical transport properties of ZnO films.

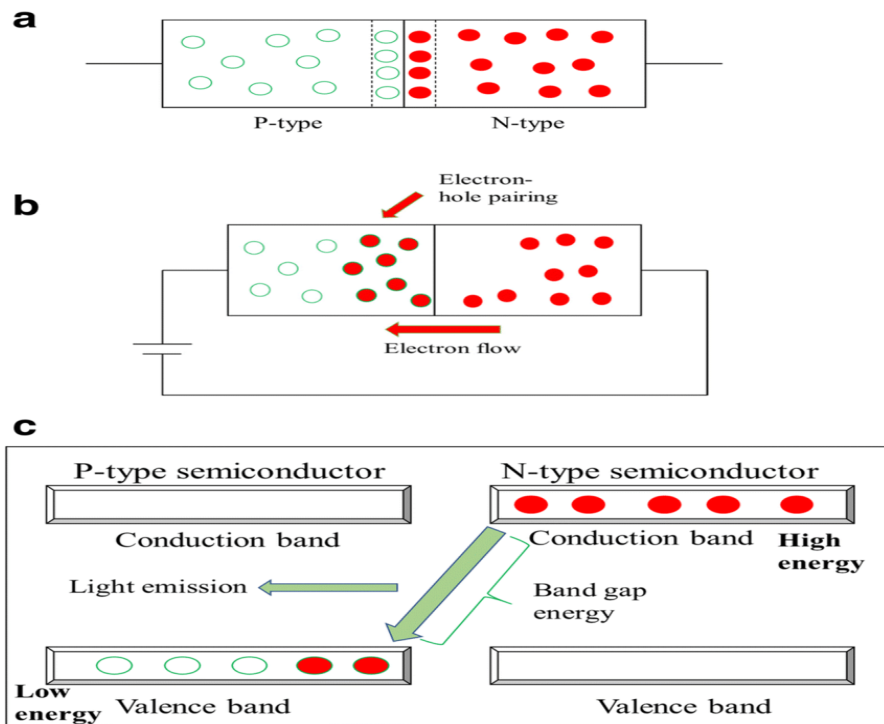
In summary , the electronic transport mechanism in ZnO semiconductor involves a combination of drift and diffusion processes. The mobility and concentration of charge carriers, as well as the influence of scattering mechanisms and temperature, dictate the material's electrical conductivity and overall transport properties . Understanding these mechanism is crucial for designing and optimizing ZnO based electronic device .

#### 4. Carrier mobility and conductivity:

ZnO is good conductor of both electrons and holes as its carrier mobility is relatively high . This properties can be seen due to its crystal structure and the presence of free charge carrier . ZnO can be doped with different **elements** to control its conductivity .

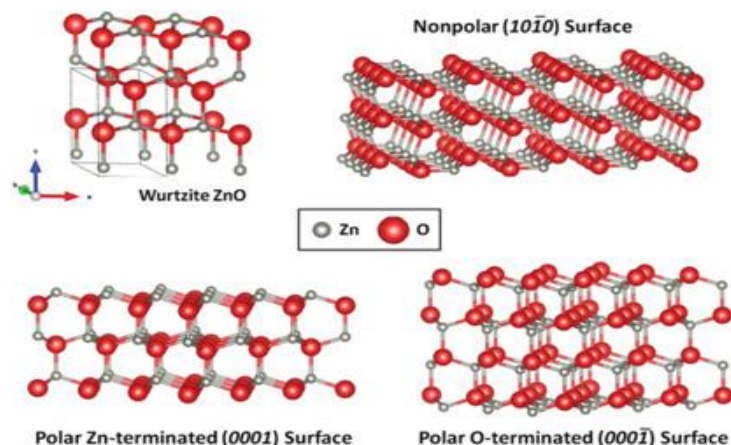
- Doping Mechanism :** In order to modify the electrical and optical properties of ZnO , foreign atom into the crystal lattice has to be introduced for which doping of ZnO is a fundamental process. Conductivity of ZnO , carrier concentration are significantly influenced by this mechanism . There are two types of doping mechanism : **n-type** and **p-type** doping . In n-type doping group (vi) elements like Phosphorus and Nitrogen are introduced into the ZnO lattice , which can create extra electrons or donors , which has enhanced the electron concentration , conductivity and overall electrical performance . On the other hand, in p-type doping , group(iv) elements like aluminium or gallium are added , generating “ acceptor” states that promote the formation of electron vacancies or “holes”. These holes lead to improve hole concentration , conductivity ,and p-type behaviour.





**Fig 8 : The electrons on the n-type semiconductor and holes in the p-type semiconductor forms a depletion region at the p-n junction without external current (a). Forward-biased diode resulting in the recombination of electrons and holes (b).Light emission with energy equivalent to the band gap energy(c)**

- Surface and interface properties** : The surface and interfaces properties of ZnO semiconductor play a pivotal role in determining its behaviour and performance in various applications. Surface of ZnO and interface characteristics are influenced by its wurtzite crystal and the termination of atoms at its surface . These properties of ZnO are critical, especially in nanoscale application. ZnO surfaces are often terminated by oxygen atoms, creating a stable surface structure . These surface can be modified to control the interaction with other materials , such as organic molecules or metals , leading to enhance device performance in various application .



**Fig 9 : Surface and interface effects : properties of nanostructured ZnO**

## 5. Applications of ZnO as semiconductor :

Zinc Oxide (ZnO) semiconductor has vast applications across various fields due to its unique properties . Some applications like optoelectronics , transparent conductive films , gas sensors , piezoelectricity are discussed before . Here are more notable applications:-

- **Photovoltaics:** In thin –film solar cells ZnO can be used as a transparent electrode. Its conductivity , transparency , and ease of fabrication make it suitable for improving the performance of solar cells by enhancing light absorption and electron collection .
- **Biomedical applications:** ZnO nanoparticles has vast applications on drug delivery , imaging , and photodynamic therapy due to their biocompatibility and tunable optical properties . They hold potential for targeted drug delivery and cancer treatment.
- **Optoelectronics and Photonics:**
  - I. Light Emitting Diodes (LEDs): ZnO can be used to create efficient blue and ultraviolet LEDs, thanks to its wide bandgap. These LEDs find applications in displays, lighting, and medical devices.
  - II. Laser Diodes: ZnO-based laser diodes emit ultraviolet light and have applications in areas such as medical diagnostics, high-density data storage, and photolithography.
- **Transparent Conductive Films:**

Transparent Conductive Oxides (TCOs): ZnO can be doped with elements like indium to create transparent conductive films. These films are used in touch screens, solar cells, and displays.
- **Solar Cells:**

Dye-Sensitized Solar Cells (DSSCs): ZnO nanoparticles are often used as photoanodes in DSSCs, helping to convert solar energy into electricity. They are cost-effective and can be used in flexible or transparent solar cell applications.
- **Water Splitting and Hydrogen Generation:**

**Catalysis:** ZnO can serve as a photocatalyst in water splitting reactions, producing hydrogen gas from water using sunlight. This has implications for renewable energy storage.
- **Antibacterial Coatings:**

**Antimicrobial Properties:** ZnO's antibacterial properties make it suitable for coatings on surfaces like textiles, plastics, and ceramics to inhibit the growth of bacteria and other microorganisms.

- **UV Photodetectors:**

ZnO-based photodetectors are highly sensitive to ultraviolet light and can be employed in UV sensing applications, such as flame detection, UV exposure monitoring, and water purification.

- **Nanogenerators:**

ZnO nanostructures can be utilized in nanogenerators that convert mechanical energy into electrical energy. These devices can be integrated into wearable electronics, self-powered sensors, and energy harvesting systems.

In conclusion, the wide range of applications for ZnO semiconductor highlights its significance in modern technology. Its unique combination of electronic, optical, and mechanical properties makes it a valuable material in various industries, from electronics and energy to healthcare and environmental monitoring. Ongoing research and development are likely to uncover even more innovative applications for ZnO in the future.

## **6. Challenges and future directions for ZnO semiconductor:**

Though it has huge potential, ZnO faces challenges such as doping efficiency, stability under operating conditions, and control over defect states. Researchers are actively exploring strategies to formation and defect engineering.

## **7. Conclusion:**

In conclusion, the exploration of Zinc Oxide (ZnO) as a semiconductor material has illuminated a realm of possibilities that intersect the realms of electronics, photonics, materials science, and beyond. The fundamental properties of ZnO have positioned it as a unique and versatile platform for technological innovation. From its wide bandgap, exceptional piezoelectric attributes, and optoelectronic capabilities to its compatibility with transparent conductive films and its ability to catalyze groundbreaking applications, ZnO stands as an emblem of the intricate interplay between materials science and the advancement of modern technology.

Throughout its journey from the laboratory to practical applications, ZnO has encountered its share of challenges and opportunities. Defect engineering and doping control have emerged as essential arenas for refining the material's properties, allowing researchers to fine-tune its behavior for specific applications. The pursuit of stable interfaces and the integration of ZnO with other materials have sparked novel directions in device design, promising innovative solutions in electronics and photonics.

The landscape of ZnO's applications stretches wide and far. From its role in optoelectronics, where it contributes to the development of UV light sources, LEDs, and photodetectors, to its pivotal position in transparent conductive films that enable the touchscreens and displays we interact with daily, ZnO's presence is ubiquitous. It finds its place in solar cells, enhancing energy conversion efficiency, and in gas sensors, acting as guardians of environmental and industrial safety. Its piezoelectric qualities resonate in the fields of sensors, actuators, and energy harvesting devices, while its

potential in biomedicine and quantum technologies holds the promise of ground breaking discoveries.

As we look toward the future, the path of ZnO as a semiconductor material will be defined by continued exploration and innovation. Overcoming challenges related to material defects, stability, and scalability will pave the way for its seamless integration into mainstream technologies. Collaborations across disciplines, from chemistry and physics to engineering and medicine, will amplify our understanding of ZnO's potential and lead to transformative breakthroughs.

In essence, the story of ZnO as a semiconductor material embodies the spirit of scientific inquiry and the relentless pursuit of harnessing nature's intricacies for human progress. Its journey stands as a testament to the harmonious symphony between scientific discovery and technological advancement. The saga of ZnO continues to unfold, and as it does, its influence will reverberate through the annals of innovation, enriching our lives and shaping the technological landscape of generations to come.

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