ROLES OF ZNO NANORODS AS ARRAYS, FILLER MATERIAL AND HOST MATERIAL FOR ENHANCING PHOTODETECTOR APPLICATIONS USING METAL-SEMICONDUCTOR-METAL AND HETEROJUNCTION CONFIGURATIONS

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by

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LIST OF SYMBOLS

A	Absorbance
A_{PD}	Area of Photodetector
A	Ampere
α	Absorption coefficient
c	Speed of light
°*C*	Degree Celcius
D	Detectivity
d	Crystallite Size
e	Electron charge
ε	Microstrain
E_g	Band gap energy
eV	Electron Volt
h	Planck's constant
h,k,l	Miller Indices
I-V	Current-Voltage
I_{dark}	Dark current
I_{light}	Photocurrent
k	Boltzmann's constant
θ	Bragg's angle
σ-bond	Sigma bond
π-bond	Pi bond
R	Responsivity, Reflectance
S	Sensitivity

V	Volt
W	Watt

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
APS	Ammonium Persulphate
CB	Conduction Band
CBD	Chemical Bath Deposition
DI	Deionized
DLE	Deep Level Emission
DRS	Diffuse Reflectance Spectroscopy
DUV	Deep Ultraviolet
EDX	Energy Dispersive X-ray
EQE	External Quantum Efficiency
FESEM	Field Emission Scanning Electron Microscopy
FWHM	Full Width at Half Maximum
GIXRD	Grazing Incidence X-ray Diffraction
HCl	Hydrochloric Acid
HMT	Hexamethylenetetramine
HOMO	Highest Occupied Molecular Orbital
ITO	Indium Tin Oxide
LED	Light Emitting Diode
LSPR	Localized Surface Plasmonic Resonance
LUMO	Lowest Unoccupied Molecular Orbital
MSM	Metal-Semiconductor-Metal
NBE	Near Band Edge
NIR	Near Infrared
NP	Nanoparticle

NR	Nanorod
PANI	Polyaniline
PD	Photodetector
PFO	Poly (9,9-di-n-octylfluorenyl-2,7-diyl)
PL	Photoluminescence
QD	Quantum Dot
RCA	Radio Corporation of America
RF	Radio Frequency
RMS	Root Mean Square
TEM	Transmission Electron Microscopy
UV	Ultraviolet
VB	Valence Band
XRD	X-ray Diffraction

PERANAN NANOROD ZNO SEBAGAI TATASUSUNAN, BAHAN PENGISI DAN BAHAN HOS UNTUK MEMPERTINGKATKAN APLIKASI FOTOPENGESAN MENGGUNAKAN KONFIGURASI LOGAM-SEMIKONDUKTOR-LOGAM DAN HETEROSIMPANG

ABSTRAK

Nanorod zinc oksida (ZnO NRs) telah digunakan secara meluas dalam bidang optoelektronik dan aplikasi fotopengesan. Meskipun begitu, fotopengesan masih mempunyai beberapa kekangan. Kekangan ini termasuk struktur berlapis yang terlalu banyak, kestabilan bahan organik yang rendah, dan kecacatan dalam struktur ZnO NRs. Kekangan ini boleh diatasi melalui penggunaan dan pengubahsuaian ZnO NRs. Tesis ini mengkaji peranan ZnO NRs dalam pelbagai konfigurasi untuk aplikasi fotopengesan kos rendah. ZnO NRs disintesis melalui kaedah hidroterma dan tiga konfigurasi yang dikaji ialah sebagai tatasusunan, bahan pengisi dan bahan hos. Konfigurasi tatasusunan ZnO NRs telah digunakan dalam struktur fotopengesan sandwic yang menggunakan substrat silikon jenis-n (n-Si), oksida stanum indium (ITO) dan polyaniline (PANI). Bagi penggunaan ZnO NRs dalam konfigurasi pengisi, ZnO NRs telah dicampurkan ke dalam Poly (9,9-di-n-octylfluorenyl-2,7-diyl) atau polimer PFO melalui kaedah calar dan gaul mudah untuk membentuk nanokomposit PFO-ZnO NRs. Nanokomposit kemudiannya dititiskan ke atas substrat Si dan ZnO/ITO untuk menghasilkan fotodiod PFO-ZnO NRs. Untuk mengkaji ZnO NRs sebagai konfigurasi bahan hos, perak (Ag) telah didopkan ke dalam ZnO NRs dengan tiga kepekatan (1.7, 3.4, and 5.1 mol %) semasa pertumbuhan hidroterma dan kepingan mikro Ag telah dienapkan ke atas ZnO NRs terdop Ag melalui fotoenapan, untuk menghasilkan fotopengesan logam-semikonduktor-logam (MSM) kepingan mikro Ag/ZnO NRs terdop Ag. Bagi aplikasi fotopengesan sandwic, fotopengesan

ITO/PANI/n-Si menunjukkan prestasi yang lebih tinggi berbanding fotopengesan ITO/n-Si. Walau bagaimanapun, penambahan PANI dalam fotopengesan dengan ZnO NRs menghasilkan keputusan yang tidak begitu baik. Meskipun fotopengesan yang menggabungkan PANI menunjukkan prestasi yang lebih baik pada voltan pincang 0, prestasinya menurun pada voltan yang lebih tinggi, dari -2 hingga -8 V. ITO/PANI/ZnO NR/nSi mencatatkan kepekaan tertinggi iaitu 43300% pada voltan pincang 0. Fotopengesan sandwic ITO/ZnO NR/nSi pula memperoleh nilai responsiviti tertinggi iaitu 0.258 A W^{-1}, pengesanan tertinggi pada 1.56×10^{10} Jones dan kecekapan kuantum tertinggi pada 83 %. Fotodiod nanokomposit PFO-ZnO NR memberi nilai arus foto, responsiviti, pengesanan, dan kecekapan kuantum yang jauh lebih tinggi berbanding fotopengesan PFO tulen. Fotodiod nanokomposit PFO-ZnO NR memperoleh prestasi tertinggi untuk kepekaan iaitu 3900 %, responsiviti pada 1.45 A W^{-1}, pengesanan pada 1.38×10^{11} Jones, dan kecekapan kuantum pada 468 %. Prestasi yang dipertingkatkan ini dikaitkan dengan peningkatan keluasan permukaan aktif dalam nanokomposit, yang memudahkan disosiasi eksiton dan pengumpulan cas yang lebih cekap. Akhir sekali, bagi fotopengesan MSM kepingan mikro Ag/ZnO NR terdop Ag, fotopengesan yang menggunakan ZnO NR terdop Ag menunjukkan peningkatan kepekaan berbanding fotopengesan yang menggunakan ZnO NR tidak terdop. Fotopengesan yang terdop 1.7 mol % Ag mempunyai kepekaan tertinggi iaitu 105 %. Fotopengesan yang terdop 5.1 mol % Ag mempunyai responsiviti tertinggi iatiu 2.70 A W^{-1} dan kecekapan kuantum tertinggi pada 341 %.

ROLES OF ZNO NANORODS AS ARRAYS, FILLER MATERIAL AND HOST MATERIAL FOR ENHANCING PHOTODETECTOR APPLICATIONS USING METAL-SEMICONDUCTOR-METAL AND HETEROJUNCTION CONFIGURATIONS

ABSTRACT

Zinc oxide nanorods (ZnO NRs) have seen many uses in the field of optoelectronics and photodetector applications. Despite that, photodetectors have certain limitations such as too many layered structures, poor stability of organic materials, and defects within ZnO NRs itself that can be improved by using and modifying ZnO NRs. This thesis thus explores the role of ZnO NRs in different configurations for low-cost photodetector applications. The ZnO NRs were synthesized via hydrothermal growth and the three configurations studied were arrays, filler material, and host material. ZnO NRs array configurations have been utilized in novel sandwiched photodetector structures using n-type silicon substrate (n-Si), indium tin oxide (ITO) glass, and polyaniline (PANI). For the usage of ZnO NRs in filler configuration, ZnO NRs were mixed into Poly (9,9-di-n-octylfluorenyl-2,7-diyl) or PFO polymer via simple scratching and mixing method to form PFO-ZnO NRs nanocomposite. The nanocomposite was then drop-casted onto Si and ZnO/ITO substrates to fabricate novel PFO-ZnO NRs photodiodes. To study ZnO NRs as host material configuration, silver (Ag) was doped with three concentrations (1.7, 3.4, and 5.1 mol %) into ZnO NRs during hydrothermal growth, and Ag microflakes were deposited onto the Ag-doped ZnO NRs via photodeposition, to fabricate Ag microflakes/Ag-doped ZnO NRs metal-semiconductor-metal (MSM) photodetectors. For sandwiched photodetector applications, ITO/PANI/n-Si photodetectors displayed superior performance compared to ITO/n-Si devices, highlighting the effectiveness of

the n-Si/PANI heterojunction. However, the inclusion of PANI in devices with ZnO NRs produced mixed results. While the PANI-incorporated device outperformed at zero bias voltage, its performance declined at higher voltages. ITO/PANI/ZnO NRs/nSi recorded the highest Sensitivity of 43300 % at 0 V bias. ITO/ZnO NRs/nSi sandwiched device obtained the highest Responsivity, Detectivity, and EQE values at 0.258 A W^{-1}, 1.56×10^{10} Jones, and 83 % respectively. The PFO-ZnO NRs nanocomposite photodiodes displayed significantly higher photocurrent, Responsivity, detectivity, and External Quantum Efficiency (EQE %) compared to the pristine PFO device. The devices obtained the highest Sensitivity at 3900 %, Responsivity of 1.45 A W^{-1}, Detectivity of 1.38×10^{11} Jones, and EQE of 468 %. This enhanced performance is attributed to the increased active surface area within the nanocomposite, which facilitates more efficient exciton dissociation and charge collection. Lastly, for the Ag microflakes/Ag-doped ZnO NRs MSM photodetectors, photodetectors incorporating Ag-doped ZnO NRs exhibited enhanced sensitivity compared to those with undoped NRs. The photodetector doped with 1.7 mol % Ag obtained the highest Sensitivity at 105 %. The photodetector doped with 5.1 mol % Ag obtained the highest Responsivity and EQE at 2.70 A W^{-1} and 341 % respectively.

CHAPTER 1 INTRODUCTION

1.1 Introduction

This chapter provides the background of the thesis, which serves as the foundation of the research presented here. Following that, the problem statement identifies any research gaps that will be filled by this research. Research objectives and scope of study serve to focus the research efforts presented, based on the problem statement. Lastly, the thesis organization gives an overall view of the structure of this thesis.

1.2 Background

In a fast-paced world, there is a necessity to create efficient and high-performing devices while at the same time reducing the cost required for fabrication [1-3]. Photodetectors are one of the simplest yet quite important optoelectronic devices playing a robust role in our world. They have been in use for many applications, ranging from climate observation, flame detection, light signal processing, medical imaging, memristor, space exploration, and many others [4]. The commercial industry for photodetectors has demanded photodetectors with high sensitivity, fast response time, easy to process, and lastly, low-cost [5, 6].

One of the most common materials studied for photodetector applications is zinc oxide (ZnO). ZnO is well-researched for its amazing properties, such as having a wide direct band gap of 3.37 eV and exciton binding energy of 60 meV, suitable for the fabrication of ultraviolet (UV) photodetectors [7-9]. Not only that, ZnO is

versatile, environmentally friendly, and can easily be processed into many types of microstructures and nanostructures [10].

ZnO is a commonly used electron acceptor in polymer/inorganic nanocomposites [11]. The previous studies on polymer/ZnO nanocomposites have shown photoluminescence (PL) quenching, which was suggested to be due to efficient charge transfer [12]. Efficient charge transfer is an essential characteristic of good photoelectric materials and depends on comparable band structures. ZnO can be fabricated with different organic semiconductors to create new device configurations for various applications using inorganic-organic hybrid heterostructures. Among the devices being fabricated are multi-level memory cells [13], color-tunable light-emitting diodes [14], and color-dependent photodiodes [15].

Polyaniline or PANI is one of the most studied polymers due to its conductivity properties. This conductivity gives rise to electronic and optical properties that enable it to be developed as a photodetector. PANI has four main structures: general, leucomeraldine, emeraldine, and pernigraniline. Among the four structures, the emeraldine form of PANI is useful for it is the structure that enables conduction and also serves as a p-type semiconductor [16]. Recent research trend focuses on the formation of organic-inorganic heterojunctions, as they are superior to pure organic or inorganic heterojunctions due to increased chemical stability and cost-effectiveness. PANI has been used in conjunction with inorganic materials to fabricate photodetectors, such as zinc oxide (ZnO) [17], titanium dioxide (TiO_2) [18], and gallium nitride (GaN) [19].

Poly (9,9-di-n-octylfluorenyl-2,7-diyl) or PFO is a well-researched conjugated polymer with good optoelectrical properties, among them are high photoluminescence

and electroluminescence, high optical gain, and good charge-carrier mobility, and good thermal stability [20]. These properties make PFO attractive in many optoelectronic applications such as light-emitting diodes (LEDs) [21], lasers [22], and photodetectors [23]. This makes PFO an ideal p-type organic material for hybrid photodiodes.

ZnO, being very versatile, can also be doped with other elements to improve its properties. Many types of elements have been doped with ZnO nanostructures, such as manganese (Mn), cobalt (Co), copper (Cu), nickel (Ni), iron (Fe), fluorine (F), and silver (Ag) [24-29]. Ag is an attractive dopant as Ag improves the ultraviolet (UV) and gas-sensing mechanisms of ZnO nanorods by acting as a catalyst for the ionization of oxygen molecules on the surface of ZnO [30]. Ag is also a good acceptor in ZnO and can become an interstitial dopant [31]. Many researchers have previously studied the effect of Ag doping on ZnO nanostructures by varying the concentration of the Ag dopant [29, 32, 33]. In addition to doping of foreign elements into ZnO nanostructures, ZnO can be deposited with metals such as Ag and gold (Au), via photodeposition.

Therefore, being given a glimpse at the versatility of ZnO nanostructures, particularly in photodetector applications, ZnO nanostructures can be used in various capacities: either undoped/ in array formations, mixed with other materials as composites, and being doped with other elements.

1.3 Problem Statement

Looking back at the various uses of ZnO microstructures and nanostructures in photodetector applications, there are inherent weaknesses that warrant further study and thus identify research gaps that will be presented in this thesis.

Standard photodetectors currently contain many layered structures, typically 5 layers: anode, hole transport material (HTM), an active layer, electron transport material (ETM), and cathode to facilitate charge transport and increase the efficiency of said devices [34-36], but these result in increased processing cost and time to manufacture. To justify the earlier statement, current organic photodetectors uses vacuum thermal evaporation [37] or by inkjet printing [38] to deposit organic layers as the active layer. For the deposition of electrodes, a thin layer of metal was deposited via thermal evaporation or by sputtering process [39]. These fabrication processes require significant amount of money to obtain them and maintain their machineries. In the quest for simplicity yet cheap devices, research is focused on fabricating as few layers as possible in a device without employing expensive machineries or equipments. An important consideration needed to satisfy this goal is the need for transparent, conducting electrodes to allow photons to pass through them to reach the active materials. Ultra-thin layers of metals can also serve perfectly well as transparent electrodes but require further deposition steps to obtain them [40].

To remedy this, an innovative way is to fabricate devices using materials that are easy to synthesize such as ZnO and PANI in a sandwiched configuration, whereby the active layers are in between two electrodes, which reduces the number of layers to 3 or 4. One of the electrodes should be a transparent electrode such as indium tin oxide (ITO)

glass glass to allow light to be transmitted to the active area. To the best of my knowledge, there are no studies published on sandwiched ZnO or ZnO/PANI photodetectors.

Organic materials such as PFO have shortcomings that do not allow the semiconductor industry to make a complete shift to organic electronics, such as being fragile, easy to degrade via moisture and oxygen exposure, and having low charge carrier mobility compared to their inorganic counterparts [41]. Despite the setbacks, another path that is explored to reduce the weakness of organic semiconductors is to form hybrid electronics with inorganic materials, due to their thermal and chemical stabilities [42].

Therefore, hybrid electronics with an organic-inorganic interface make excellent use as a photodiode, usually by combining the p-type organic material with the n-type inorganic material [43]. The p-n heterojunction will create a built-in electric field at the interface, resulting in the separation of photon-generated electron-hole pairs when photons reach the interface, to be channelled to the electrodes as photocurrent [43]. An attractive material that can be used with PFO is ZnO. To the best of my knowledge, there are no studies regarding the synthesis of PFO-ZnO nanocomposites being utilized as active materials in n-type Si and ITO/ZnO substrates for photodetector applications.

Despite the many advantages of ZnO, ZnO has weak optical properties that arise from point defects such as oxygen vacancy and/or interstitial zinc [44]. One of the ways to improve ZnO nanostructures is to dope ZnO with other materials.

In addition to doping ZnO nanorods with Ag via the solution method, metal nanoparticles can be directly deposited onto the nanostructures by pulsed electro-depositions, microemulsions, sputtering, and electrospinning methods [45]. These

methods have some major shortcomings, being expensive and requiring high-temperature processing. High-temperature processing could result in the oxidation of the metal nanoparticles. The photodeposition technique is a low-cost and easy solution to this dilemma whereby the samples are immersed in an $AgNO_3$ solution under the illumination of a UV lamp.

The deposition of Ag on the nanorods gives an improvement in the performance of UV photodetectors, due to the localized surface plasmonic resonance effect [45]. This effect extends the range of the light absorption wavelength and enhances the incident electric field [46]. To the best of my knowledge, no known studies have been published concerning the fabrication of Ag microflakes being photodeposited onto Ag-doped ZnO nanorods for photodetector applications.

1.4 Research Objectives

The objectives of this thesis are:

1) To investigate ZnO NRs arrays for ZnO NRs/PANI sandwiched photodetectors based on the heterojunction configurations (n-type Si/ITO, n-type Si/PANI/ITO, n-type Si/ZnO NRs/ITO, and n-type Si/ZnO NRs/PANI/ITO).
2) To assess ZnO NRs as filler material for PFO-ZnO NRs nanocomposite deposited on n-type Si and ITO/ZnO substrates for heterojunction photodetectors.
3) To evaluate ZnO NRs as a host material for Ag-doped ZnO NRs/Ag microflakes metal-semiconductor-metal (MSM) photodetectors.

1.5 Scope of Study

In the scope of the study, ZnO NRs are utilized in three different roles:

The first role is as arrays. The ZnO NRs are hydrothermally grown as arrays on n-type Si substrates and sandwiched with ITO glass and PANI/ITO glass electrodes to form sandwiched photodetectors. Following synthesis and fabrications, both characterization and photodetector performance measurements are carried out.

The second role is as filler material. ZnO NRs were grown via the hydrothermal method on glass substrates and scratched into PFO solution to form PFO-ZnO NRs nanocomposites. Following that, the nanocomposites are then characterized. Later on, the fabrication of PFO-ZnO NRs nanocomposite-based photodetectors on n-type Si and ITO/ZnO substrates are done and their photodetector performances are measured.

The third and last role is as host material. Ag-doped ZnO NRs were synthesized via the hydrothermal method in different Ag doping concentrations. Following that, the characterizations of the Ag-doped ZnO NRs are undertaken. Ag photodeposition was then done on the Ag-doped ZnO NRs to deposit Ag microflakes, with subsequent characterization. Finally, the samples are fabricated under MSM configuration and their photodetector performance is measured.

1.6 Thesis Organization

This thesis is organized into seven chapters:

Chapter 1 is the Introduction. In it, the background that serves as the foundation of this thesis is given. Problem statements, research objectives, and scope of study are given to identify and focus the research output presented in this thesis.

Chapter 2 is the Theoretical Background and Literature Review. Theoretical background on ZnO, PANI, PFO, and photodetectors is given, as well as other knowledge needed to understand the results and discussion section later on. Recent works on similar photodetectors presented in this thesis are given.

Chapter 3 is the Methodology and Instruments. The characterizations used, as well as their equipment and working principles are given. Furthermore, emphasis is given on how the characterizations help understand and analyse the prepared samples and photodetectors.

Chapter 4 is the ZnO Nanorods As Arrays For Sandwiched Photodetector Applications. The results and discussion of ZnO NRs as Arrays are presented here.

Chapter 5 is the ZnO NRs As Filler Material For Nanocomposite-Based Photodetector Applications. The characterization of PFO-ZnO NRs nanocomposite and its utilization as photodetectors are presented here.

Chapter 6 is the ZnO NRs as Host Material For Ag Doping For Metal-Semiconductor-Metal Photodetector Applications. The characterizations of Ag-doped ZnO NRs and the photodeposited Ag microflakes onto the Ag-doped ZnO NRs are

presented here. Photodetector performance of Ag microflakes/Ag-doped ZnO NRs MSM is also given.

Chapter 7 is the Conclusion and Recommendations. The overall conclusion of the three previous Results and Discussion Chapters are given here. The novelties obtained from the results are also presented. Lastly, recommendations for future studies are given.

CHAPTER 2 THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

In this chapter, the theoretical background related to the thesis is given. Firstly, zinc oxide (ZnO) is introduced and explained, along with a focused view of ZnO nanorods (NRs). Various synthesis methods of ZnO NRs are given with an emphasis on the hydrothermal method. Later on, an introduction is given regarding the role of ZnO NRs as arrays, filler, and host material, especially in optoelectronic applications. Modification of ZnO NRs by doping and photodeposition of metallic NPs onto ZnO NRs was explained. The next subchapter focuses on p-type organic polymers, with an emphasis on polyaniline (PANI) and Poly (9,9-di-n-octylfluorenyl-2,7-diyl) (PFO). Their properties, synthesis methods, and applications are presented here. The final subchapter is dedicated to photodetectors. In it, the general working principle of a photodetector is explained, along with their figures of merit. Lastly, recent literature reviews were given on photodetectors based on ZnO NRs/PANI, ZnO/PFO, and doped ZnO NRs.

2.2 Zinc Oxide (ZnO)

This subchapter will give a brief introduction on ZnO. This is followed by a deeper explanation on the morphological, optical, and electrical properties of ZnO. Finally, a bried introduction is provided on the various nanostructures of ZnO.

2.2.1 Introduction

Zinc oxide (ZnO) is an inorganic compound that has been utilized by mankind since ancient times, albeit mostly for medical and additive purposes. It is a white powder that is insoluble in water. In ancient India, it served to heal wounds and was termed *pushpanjan*, cited in the Indian medical text *Charaka Samhita* dated around 500 BC [47]. ZnO is also acknowledged by other leading researchers of the ancient era such as Ibn Sina and Galen for treating cancer [48]. Technological progress has allowed mankind to experiment with ZnO, resulting in ZnO being used in many other applications such as cosmetics, food supplements, rubbers, plastics, ceramics, lubricants, and many others [49]. It was only in the middle of the 20^{th} century during the silicon boom when semiconductors were widely researched that ZnO, with its amazing properties, is being seriously considered as an alternative material for semiconductor applications.

2.2.2 Morphological and Structural Properties

ZnO has two crystalline forms; namely the hexagonal wurtzite and the cubic zincblende. The hexagonal wurtzite structure of ZnO is the most stable and hence the most common form found in nature. The wurtzite structure is characterized by a hexagonal closed-packed structure (hcp) arrangement of atoms, whereby the atom of zinc (Zn) is surrounded by 4 atoms of oxygen (O) and vice versa, thus they are tetrahedrally coordinated. According to the Schoenflies notation, the hexagonal lattice of ZnO belongs to the space group of C^4_{6v}.

The hexagonal wurtzite structure of the ZnO crystal lattice consists of a hexagonal unit cell. In that cell, the lattice parameters *a* and *b* lie on the x-y plane and have a degree of 120° with equal length and *c* is parallel to the z-axis. The lattice parameters of $a = b = 3.2495$ Å and $c = 5.2069$ Å at room temperature [50]. The tetrahedral arrangement of the Zn and O atoms resulted in a polar symmetry along the hexagonal axis, imbuing ZnO with properties such as piezoelectricity and polarization. It also causes defect states present in ZnO during crystal growth.

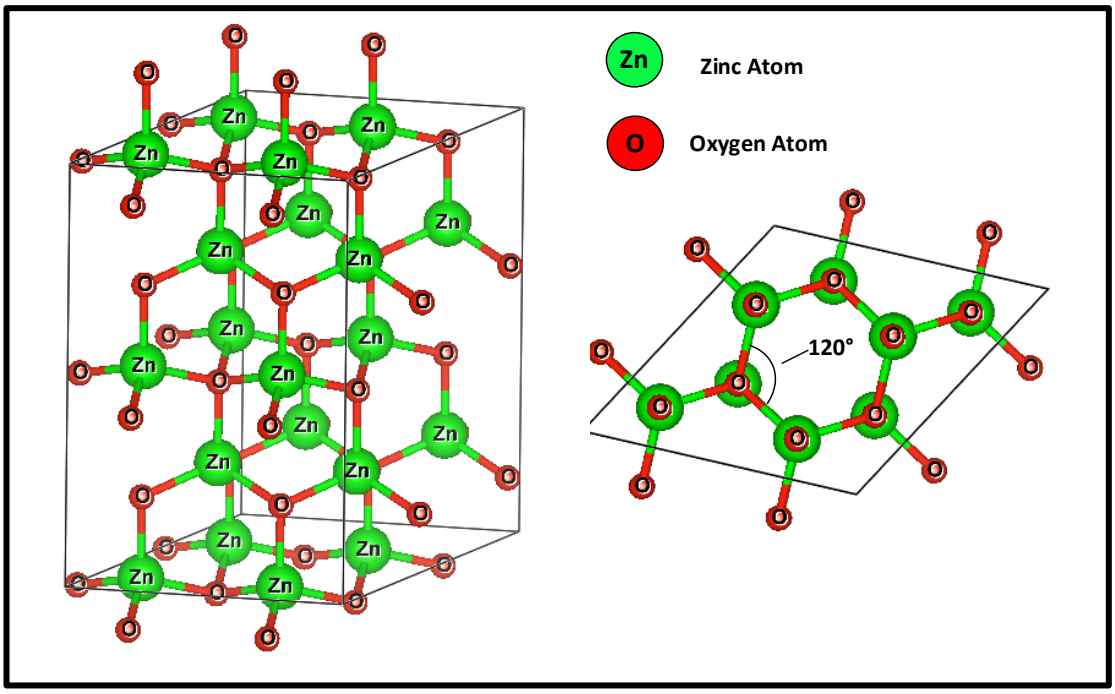

Figure 2.1: Hexagonal wurtzite structure of ZnO (left) and the structure when viewed from the top (right), drawn using the software VESTA.

2.2.3 Optical Properties

ZnO has a wide band gap of 3.37 electron Volts (eV). This makes ZnO transparent to visible light and able to absorb ultraviolet (UV) light, in other words, ZnO is optically active in the UV region [51]. ZnO also has a high excitonic effect due to its high band gap and high exciton binding energy of 60 meV. This helps ZnO in having efficient exciton generation and recombination [7-9]. Furthermore, ZnO exhibits non-linear optical properties, such as second harmonic generation and optical parametric amplification that make ZnO attractive in non-linear optical applications [52].

Photoluminescence (PL) spectra analysis has been commonly employed to study the optical properties of ZnO. The PL spectra typically feature a UV emission peak at around 380 nm, attributed to the near band edge (NBE) free exciton recombination [53], complemented by a visible broadband emission peak at approximately 550 nm, as shown in Figure 2.2. This visible broadband emission peak arises from the many defects present in the ZnO crystal structure and is generally termed as deep level emissions (DLE) [54, 55].

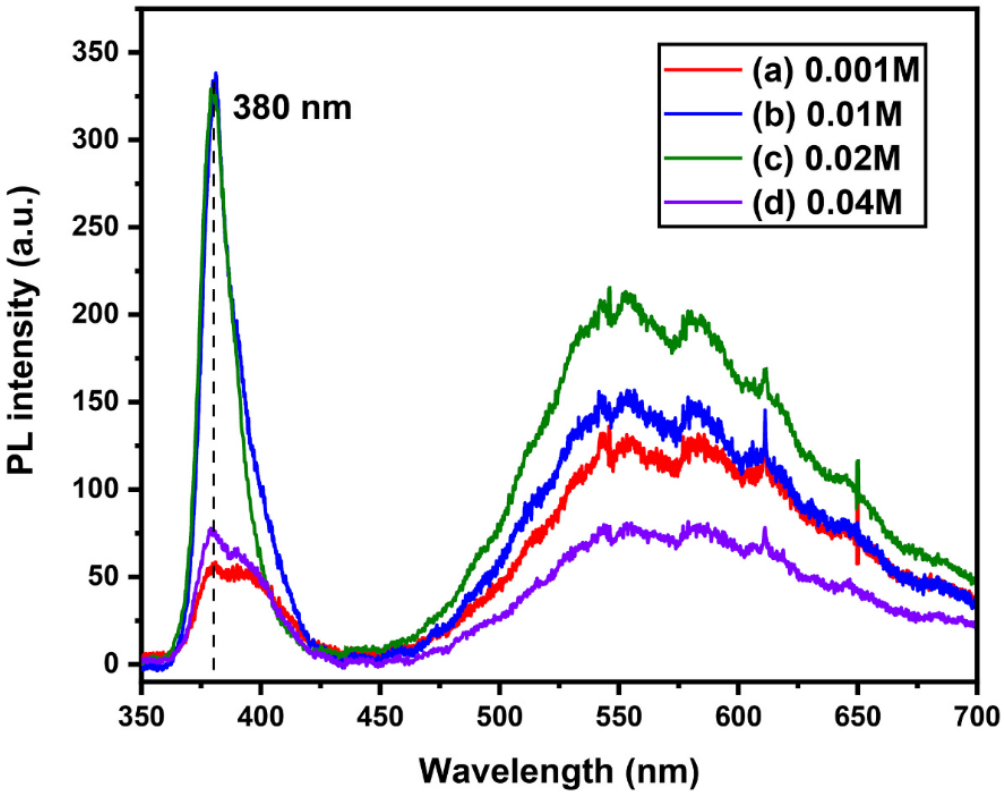

Figure 2.2: PL spectra of ZnO NRs grown on glass slides using different concentrations of zinc acetate dihydrate solution [56].

Distinct shifts in the position of the UV emission peak across ZnO nanostructures of varying sizes have been observed in PL spectra. This phenomenon, often termed a blue shift, is commonly attributed to quantum confinement effects [57].

Additionally, differences in native defect concentrations between nanostructures of differing dimensions are speculated to contribute to variations in UV emission positions [58]. The density of defects on the surface tends to exceed that in the bulk, consequently influencing the position of PL spectra peaks due to differing surface area-to-volume ratios. Thus, both the shape of the PL spectrum and the position of the UV emission may be influenced by defect density in nanostructures.

2.2.4 Electrical Properties

ZnO, with a wide band gap (3.37 eV) can be classified as an intrinsic semiconductor, and thus its semiconductor property can be modified by changes in temperature, doping, and defects present in it. ZnO has high electron mobility, of roughly 145 $cm^2 V^{-1} s^{-1}$ [59], possibly due to defects [60]. This makes ZnO attractive in applications requiring fast electronic transport, such as in high-frequency and high-power electronic devices [61].

With its high electron mobility, ZnO can also function as a transparent conducting electrode [62]. As stated earlier, due to the wurtzite crystal structure of ZnO, ZnO also exhibits piezoelectric properties, allowing ZnO to generate electric current from changes in mechanical stress or deformation. This allows ZnO to function as piezoelectric sensors, actuators, and energy harvesting devices [63].

Not only that, ZnO has a varistor behaviour. A varistor behaviour occurs when a material exhibits different values in electrical resistance as a response to changes in voltage applied to it. This is characterized by a non-linear current-voltage (I-V) relationship. Therefore, ZnO has applications as surge protectors and voltage

regulators in circuits [64]. Finally, ZnO is also sensitive to gases. When gas molecules come into contact with ZnO, ZnO's electrical conductivity changes, therefore it can function as gas sensors in industrial and healthcare applications [65].

2.2.5 Nanostructures of ZnO

ZnO nanostructures are structures made of ZnO that have at least one dimension that is within the nanometer scale (1-999 nm) [66]. Various methods have been developed by scientists to synthesize ZnO nanostructures and the methods can be broadly classified into vapor-based and solution-based techniques. Vapor-based methods encompass metal-organic chemical vapor deposition (MOCVD), physical vapor deposition (PVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), and sputtering [10].

While vapor-based techniques can yield high-quality ZnO nanostructures under meticulously controlled high-vacuum conditions, they entail drawbacks such as high temperatures, equipment cost, and complexity, and are unsuitable for growth on substrates that are not able to withstand high temperatures, which diminishes ZnO usage on flexible substrates [67].

The solution-based technique encompasses methods such as solvothermal, hydrothermal, chemical bath deposition (CBD), and electrochemical deposition [68]. This approach has found widespread use for mass production of oxide nanomaterials, semiconductors, and metals due to its advantages of low-temperature processing, environmentally friendly chemicals, simplicity, lower cost, and scalability [69].

In solvothermal reactions, either organic or inorganic solvents are employed under high pressure and temperature to synthesize materials. Hydrothermal processes utilize water as a solvent within a closed vessel, operating at pressures between 106 Pa to 108 Pa and temperatures from 100 °C to 1000 °C [70]. Chemical bath deposition, on the other hand, utilizes water as a solvent at ambient pressure and temperatures below 100 °C. Electrochemical deposition, similar to CBD, involves applying electricity to deposit materials onto a substrate placed on an electrode. Unlike vapor-based methods and electrochemical deposition, CBD can be performed at low temperatures and is compatible with a wide range of substrates, including non-conductive surfaces, plastics, and polymers, due to their low heat resistance.

CBD is widely employed for fabricating various ZnO nanostructures, including nanoparticles [71], nanobelts [72], nanotubes [73], nanoflowers [74], nanowires [72], and nanorods [75], offering control over their morphology, structure, and optical properties through manipulation of growth parameters such as precursor type, concentration, duration, and temperature. Figure 2.3 shows the common ZnO nanostructures that can be synthesised: tetrapods, nanosheets, nanoshells, nanowires, and NRs [76]. Among all the aforementioned nanostructures, ZnO NRs are an attractive nanostructure.

NRs hold a distinct advantage over other structures as they can be fabricated from a wide range of elements, including metals, nonmetals, and compounds, with fabrication requirements being relatively straightforward [77]. Consequently, a multitude of researchers are drawn to NRs due to their exceptional chemical and physical characteristics and their extensive utility in electronic devices [78]. Fundamental investigations into the behavior of materials at the nanoscale have revealed markedly different properties compared to their bulk counterparts. However,

the fabrication of electronic nanodevices remains a challenging endeavor. Despite this, recent advancements suggest that electronic devices previously considered unattainable may now be within reach.

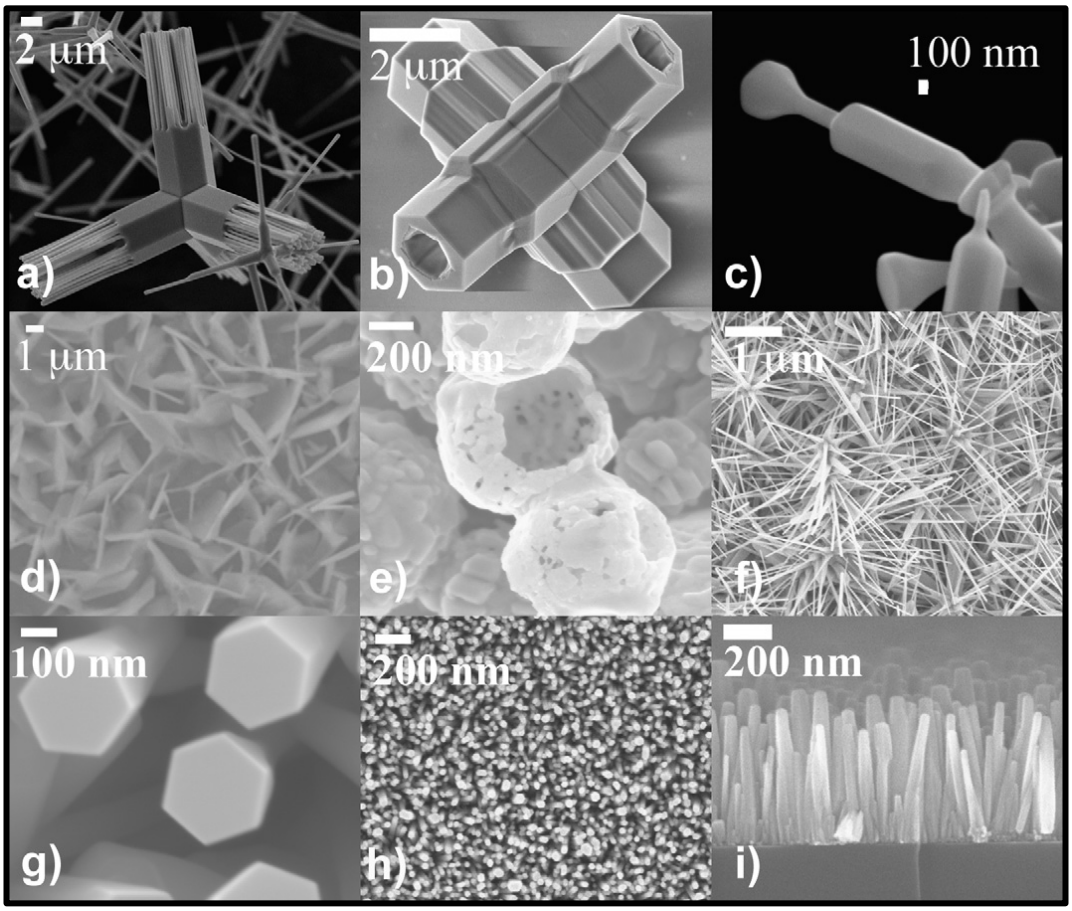

Figure 2.3: SEM images of some of common ZnO nanostructures (a), (b), (c) tetrapods with different diameters, (d) nanosheets, (e) nanoshells, (f) nanowires, (g), (h) and (i) NRs [76].

2.3 ZnO Nanorods (NRs)

This subchapter will first provide an introduction to ZnO NRs. This is followed by presenting the unique properties of ZnO NRs. The subchapter then leads on to the hydrothermal synthesis of ZnO NRs and an overview of ZnO NRs utilized as arrays, filler and host material for photodetector applications. The last subsections gives description on doping and photodeposition of ZnO NRs.

2.3.1 Introduction

Simply put, ZnO NRs are ZnO nanostructures that look like rods, in the nanometer scale and are termed as 1-dimensional (1-D) nanostructures. 1D nanomaterials exhibit elongation in a single precise direction, distinguishing them from their 2D and 3D counterparts, and offering unique optical and electronic properties. ZnO NRs garner significant attention for their role in various applications, including nano-electronics, chemical and biological sensing, energy conversion and storage, photovoltaic cells, batteries, capacitors, hydrogen-storage devices, light-emitting diodes, catalysis, drug delivery, and piezoelectric energy generation [79].

Research has shown that the morphology of one-dimensional ZnO nanostructured materials significantly influences their optical and electrical properties [80]. Therefore, it can be concluded that 1D nanostructured ZnO holds the highest potential among different dimensions, primarily due to its straightforward fabrication process and its applicability in electronic devices.

2.3.2 Unique Properties of ZnO NRs

ZnO NRs, being nanostructures exhibited unique properties due to its 1-D structures. As for its mechanical properties, ZnO NRs have a higher yield strength compared to its bulk counterpart. This can be explained by the Hall-Petch effect. This effect states that as the grain size of a material decreases, its yield strength increases [81, 82]. In 1D nanostructures, such as ZnO NRs, a notable decrease in the melting point of solid materials is evident. This phenomenon arises due to the unique characteristics of nanocrystalline materials, where the high specific boundary area results in significant stored interface energy. As a result, 1D nanostructures can be precisely tailored based on their thermal properties, including parameters such as synthesizing and annealing temperatures [83].

For ZnO NRs, the grain size and boundaries primarily influence the electron mean free path and resistance. It is observed that numerous physical properties of 1D nanostructures, such as optical and electrical properties, undergo significant enhancement as the material's size or dimension decreases to the nanoscale due to quantum effects and their high surface-to-volume ratios [84]. Additionally, ZnO NRs often exhibit a higher incidence of surface defects, as well as oxygen and cation vacancies, owing to their low formation energy within nanoscale materials [83, 85].

When the diameter of a nanorod decreases to a critical length (Bohr radius), the confinement of size significantly influences its energy levels. The bulk ZnO exciton Bohr radius is 2.34 nm from the literature [86]. In the case of silicon nanowires, for example, the absorption edge is notably blue-shifted due to the narrow bulk silicon indirect bandgap of only 1.1 eV. The absorption spectra exhibit sharp and discrete

characteristics, particularly in the relatively strong "band-edge," as observed in photoluminescence (PL).

For ZnO NRs, this effect is also observed. Cathodoluminescence (CL) spectroscopy has been utilized to investigate the electronic and optical characteristics of well-aligned ZnO NRs spanning various diameters from 50 to 180 nm. Single-nanorod CL investigations indicate that the emission peak shifts towards higher energy levels as the diameter of the ZnO nanorod reduces, despite the sizes extending beyond the quantum confinement regime. Observations reveal a blueshift of several tens of meV in the CL peak of these NRs. Furthermore, this anomalous energy shift demonstrates a linear correlation with the inverse of the rod diameter [87]. Furthermore, emitted light along the longitudinal axes of the ZnO NRs demonstrates high polarization [83, 88, 89].

ZnO NRs exhibit natural n-type electrical conductivity owing to the presence of intrinsic defects [90]. These defects primarily include oxygen vacancies, characterized by the absence of an oxygen atom from the crystal structure, and zinc interstitials, where an additional zinc atom is incorporated into the crystal lattice [91]. However, certain studies propose that the inadvertent absorption of impurities from the environment, acting as shallow donors—such as hydrogen—may contribute to the observed n-type conductivity in ZnO nanostructures [92]. Figure 2.4 shows some of the defects inherent in ZnO NRs [93]. From the figure, the ZnO NRs are being bombarded with H+ ion beam irradiation, and the stages I to IV represent the increase of H+ ion fluence increasing from 0 to 1.0×10^{15} ions/cm^2. Among the defects observed during the bombardment are surface defects, Zn and O ion interstitials, and isolated Zn and O vacancies.

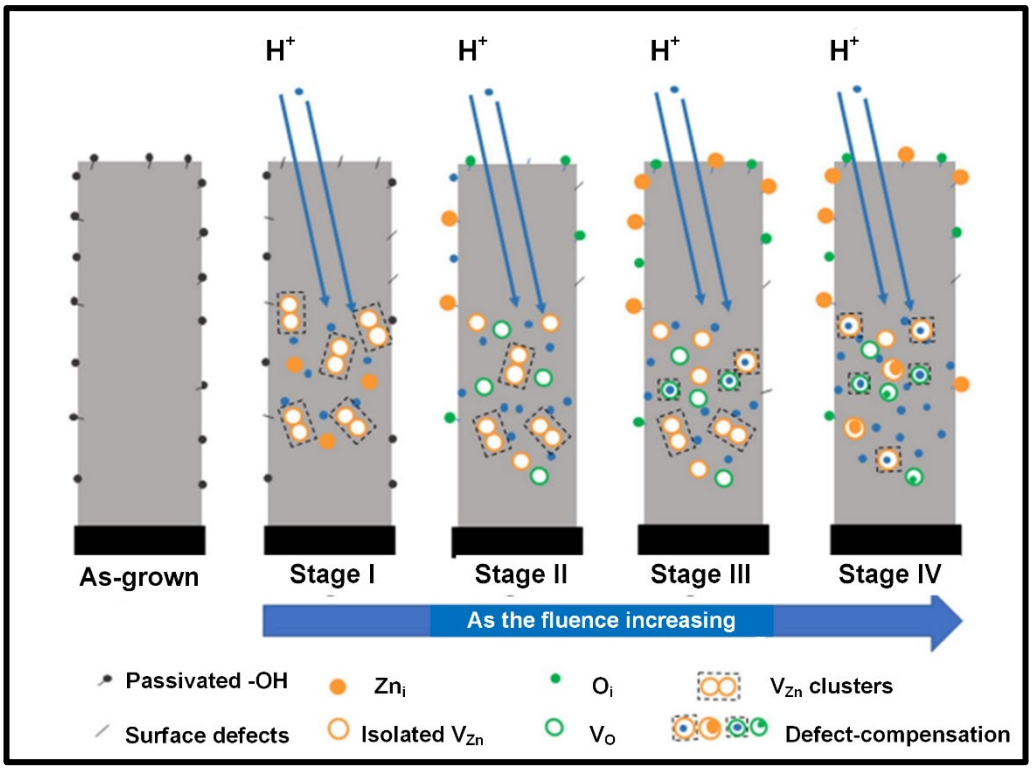

Figure 2.4: Schematic diagram indicating the generation, evolution, and annihilation of defects in ZnO NRs arrays under 180 keV H+ ion beam irradiation [93].

While ZnO is typically diamagnetic, ZnO NRs produced in some experiments exhibited magnetic properties. Analysis of magnetic susceptibility revealed an increase in susceptibility with decreasing temperature, characteristic of paramagnetic materials [94, 95]. Additionally, the magnetization curve or hysteresis curve (B–H curve) exhibited no hysteresis, which would have suggested ferromagnetism. Consequently, it was concluded that the synthesized NRs demonstrated super-paramagnetic properties [94, 95]. This finding holds significance for numerous potential medical applications, as the magnetic nature of the NRs could prove beneficial for drug delivery or magnetic-field-induced hyperthermia in cancer treatments.

2.3.3 Hydrothermal Growth of ZnO NRs

When a substrate, seeded with a ZnO layer is placed in a chemical solution containing the aqueous solution of zinc nitrate hexahydrate or $Zn(NO_3)_2.6H_2O$ and hexamethylenetetramine ($C_6H_{12}N_4$) in deionized (DI) water and heated, growth of ZnO NRs occurs. The following chemical reactions (Equations 2.1 to 2.5) then occur on the seeded substrate [96]:

$$C_6H_{12}N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3 \quad (2.1)$$

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \quad (2.2)$$

$$Zn(NO_3)_2.6H_2O \longrightarrow Zn^{2+} + 2(NO_3)^- + 6H_2O \quad (2.3)$$

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2 \quad (2.4)$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO\ (nanorods) + H_2O \quad (2.5)$$

When zinc nitrate hexahydrate and HMT are dissolved in DI water, both chemicals undergo decomposition to produce Zn^{2+} and OH^- ions respectively. Both these ions will combine to form zinc hydroxide $Zn(OH)_2$ when their ionic concentrations have reached supersaturation levels. Due to high temperature, $Zn(OH)_2$ will dissolve into their respective ions and will form fine ZnO NPs in the aqueous solution.

These ZnO NPs will now act as the nuclei for further growth and they merge with the nucleation layer prepared earlier from the thermal decomposition of zinc acetate to reduce interfacial free energy. From a thermodynamic viewpoint, larger particles are easier to form than smaller particles resulting in smaller particles merging to form larger particles due to Ostwald ripening [97]. This merging process is the

growth process of the ZnO that happens. The Wurtzite structure of ZnO NRs exhibits two distinct crystal planes, comprising a polar (0 0 1) plane alongside nonpolar planes such as (1 0 1) and (1 0 0). Differential surface energies among these crystal planes result in varying growth rates, with higher surface energy planes exhibiting faster growth.

Consequently, the growth rate of planes aligned with the [0 0 1] direction surpasses that of planes aligned with the [1 0 0] direction. This discrepancy firstly results in the NRs mostly growing in the [0 0 1] direction and giving their rod-like appearance. Not only that, the rate of growth in the [0 0 1] versus the [1 0 0] direction determines the aspect ratio of the resulting ZnO NRs [98, 99].

2.3.4 Overview of ZnO NRs as Arrays, Fillers, and Host Material

ZnO NRs, with their amazing properties, are generally synthesized in three main settings, especially in conjunction with other materials. The first way is as arrays. ZnO NRs arrays are NRs grown without being tampered with by other materials. They can, for example, be grown on any substrates to fabricate metal-semiconductor-metal (MSM) photodetectors and the mechanism of the photodetector is solely based on ZnO NRs. Not only that, they can be grown above or below p-type materials to form heterojunctions, either as photodetectors, light-emitting diodes (LEDs), or others. Figure 2.5 shows the application of ZnO NRs as arrays, firstly on (a) polypropylene carbonate (PPC) substrate for MSM photodetector applications and (b) on p-GaN layer as LEDs.