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LIST OF SYMBOLS

| | |
|----------------------|--|
| A | Illuminated Area |
| a.u | Arbitrary unit |
| \AA | Angstrom |
| a, b, c | Lattice constant |
| c_0 | Lattice constant in z-axis for bulk material |
| $^{\circ}\text{C}$ | Celsius temperature |
| D | Crystallite size |
| d_{hkl} | Inter-plane distance |
| E_g | Energy Band Gap |
| E_f | Fermi level |
| E_v | Valance band upper level |
| eV | Electron volt |
| F | Faraday's constant |
| h | Plank's Constant |
| h,k,l | Miller indices |
| I | Intensity of the transmission light |
| I_o | Intensity of the incident light |
| I_{ph} | Photocurrent |
| I_{dark} | Dark Current |
| I_L | Current under Light |
| I-T | Current-Time |
| I-V | Current-Voltag |
| $I_{UV}/I_{visible}$ | Intensity ratio |

| | |
|--------------|----------------------------------|
| J_o | Diode saturation current density |
| m | Mass |
| P | The power of the light |
| P_{in} | Incident Optical |
| R | Responsivity |
| S | Photosensitivity |
| T | Temperature |
| V_o | Oxygen vacancy |
| θ | Bragg's angle |
| ΔH | Enthalpy of Transition |
| ϵ_c | strain |
| λ | Wavelength |
| ϕ_S | Semiconductor work function |
| ϕ_M | Metal work function |
| ν | Frequency |

LIST OF ABBREVIATION

| | |
|-------|---|
| CBD | Chemical Bath Deposition |
| CB | Conduction Band |
| DC | Direct Current |
| DIW | Deionized water |
| DLE | Deep Level Emission |
| DSC | Differential Scanning Calorimeter |
| EDX | Energy-Dispersive X-Ray |
| FESEM | Field Emission Scanning Electron Microscope |
| He-Cd | Helium Cadmium |
| ITO | Indium Tin Oxide |
| MBE | Molecular Beam Epitaxy |
| MOCVD | Metal-Organic Chemical Vapour Deposition |
| NSs | Nanostructures |
| NRs | Nanorods |
| NWs | Nanowires |
| NBE | Near Band Edge Emission |
| PECVD | Plasma Enhanced Chemical Vapour deposition |
| PVD | Physical Vapour Deposition |
| PET | Polyethylene Terephthalate |
| PDMS | Polydimethylsiloxane |
| PI | Polyimide |
| PL | Photoluminescence |
| PLD | Pulsed Laser Deposition |

| | |
|-------|--|
| PD | Photodetector |
| PET | Polyethylene terephthalate |
| RF | Radio Frequency |
| SL | Seed Layer |
| SILAR | Successive Ionic Layer Adsorption and Reaction |
| TPU | Thermoplastic Polyurethanes |
| TGA | Thermogravimetric Analyser |
| UV | Ultraviolet |
| VB | Valence Band |
| ZnO | Zinc Oxide |

**KAJIAN NANOSTRUKTUR ZINK OKSIDA DITUMBUHKAN ATAS
SUBSTRAT PTFE OLEH PEMENDAPAN RENDAMAN KIMIA UNTUK
APLIKASI PENGESAN FOTO**

ABSTRAK

Projek ini diperuntukkan untuk mengkaji ciri fizikal nanostruktur ZnO yang ditumbuhkan atas substrat fleksibel PTFE oleh pemendapan rendaman kimia. Substrat fleksibel (PTFE, nama dagangan Teflon) diperkenalkan untuk menumbuhkan nanostruktur ZnO buat pertama kali bagi tujuan mendapatkan satu substrat dengan takat lebur yang tinggi bagi penambahbaikan penhabluran bahan termendap di atasnya dengan proses sepuh lindap. Substrat fleksibel ini berkemungkinan membolehkan pasaran baru buat elektronik percetakan atau peranti pakai buang dengan kos rendah. Menggunakan substrat fleksibel untuk fabrikasi peranti elektronik menjanjikan kos pengilangan yang lebih rendah berdasarkan bahan tambahan, sifat tanpa-vakum teknologi ini serta kelebihan proses gulungan-ke-gulungan. Sifat termal substrat PTFE telah dicirikan menggunakan analisis Thermogravimetrik (TGA) dan teknik pembezaan imbasan kalorimetri (DSC). Substrat PTFE menunjukkan penurunan berat yang ketara pada suhu melebihi 530 °C menunjukkan pemecahan ikatan C-C apabila melebihi suhu ini. Takat lebur bagi PTFE ditemukan pada sekitar 338.29 °C. Kajian ini menggunakan substrat terbenih PTFE dan Si (substrat Si digunakan untuk tujuan perbandingan) untuk menumbuhkan nanostruktur ZnO menggunakan kaedah pemendapan rendaman kimia (CBD). Teknik percikkan frekuensi radio digunakan untuk memendapkan lapisan benih ZnO ke atas berbagai substrat di bawah tekanan serta kuasa percikkan pada 4.36×10^{-3} mbar dan

150 Watt (W), masing-masing. Lapisan benih ZnO yang dipercik kemudian telah disepuh lindap pada suhu 150, 200, 250, dan 300 °C. Didapati bahawa suhu sepuh lindap memberikan peningkatan ketara pada ciri fizikal (struktur dan morfologi) bagi benih ZnO. Apabila suhu sepuh lindap telah ditingkatkan kepada 300 °C, kehabluran benih ZnO telah meningkat dengan sewajarnya. Nanorod (NR) ZnO kemudian ditumbuhkan ke atas substrat terbenih yang disepuhlindap dengan teknik CBD menggunakan parameter penumbuhan yang berbeza seperti kepekatan precursor, suhu penumbuhan dan tempoh penumbuhan. Keputusan menunjukkan ciri-ciri ZnO NRs yang ditumbuhkan adalah terkesan dengan perubahan parameter penumbuhan. ZnO NRs yang ditumbuhkan menunjukkan ciri-ciri optimum dengan menggunakan kepekatan precursor Zn^{+2} pada 50 mM pada tempoh penumbuhan dan suhu 3 jam dan 95 °C, masing-masing. NRs yang ditumbuhkan didapati menjajar secara menegak kepada substrat dengan purata diameter 55 nm dan 104 nm atas substrat PTFE dan Si, masing-masing. Pungukuran fotopendarkilau (PL) bagi ZnO NRs yang ditumbuhkan mempamerkan pemancaran UV yang runcing dan sangat terang. Selain itu, nisbah pemancaran pinggir jalur dekat (NBE) ke pemancaran aras dalam (DLE), (I_{NBE}/I_{DLE}) yang sangat tinggi menandakan kualiti yang lebih baik pada ZnO NRs yang ditumbuhkan. Pengesan foto untra ungu (UV PDs) logam-semikonduktor-logam (MSM) Pd/ZnO/Pd difabrikasikan berasaskan penumbuhan ZnO yang dioptimumkan. UV PDs yang difabrikasikan mempamerkan nilai kesambutan foto 0.92 dan 0.61 A/W pada panjang gelombang 373 and 379 nm, masing-masing. Kesensitifan foto telah diukur bernilai 4068% dan 6045% untuk peranti yang di fabrikasikan menggunakan substrat PTFE dan Si, masing-masing. Keputusan menampakkan yang prestasi peranti UV PDs yang di fabrikasi berasaskan PTFE adalah hampir dengan peransi berasaskan

Si menandakan keboleharapan penggunaan bahan PTFE sebagai substrat untuk menumbuhkan ZnO NRs bagi aplikasi optoelektronik.

**STUDY OF ZINC OXIDE NANOSTRUCTURES GROWN ON PTFE
SUBSTRATE BY CHEMICAL BATH DEPOSITION FOR
PHOTODETECTOR APPLICATION**

ABSTRACT

This project devoted to study physical properties of ZnO nanostructure grown on PTFE flexible substrate by chemical bath deposition. A flexible substrate (PTFE, trade name Teflon) was introduced to grow ZnO nanostructure for the first time for obtaining a substrate with a high melting point to improve the crystallization of the material deposited on it by annealing process. This flexible substrate may enable new markets for large-area printed electronics or low-cost disposable devices. Using flexible substrates to fabricate electronic devices promises lower manufacturing costs because of the additive, non-vacuum nature of the technology. The thermal properties of PTFE substrate were characterized by Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) techniques. The PTFE substrate show sharp weight losses at temperature above 530 °C indicated the break of C–C bond beyond this temperature. The melting temperature of PTFE was found to be around 338.29 °C. The study employed PTFE and Si seeded substrates (Si substrate was used for comparison) to grow ZnO nanostructures using the chemical bath deposition (CBD). Radio frequency (RF) sputtering technique was used to deposit ZnO seed layers on to different substrates under a sputtered pressure and power of 4.36×10^{-3} mbar and 150 Watt (W), respectively. The sputtered ZnO seed layer was annealed at different temperatures of 150, 200, 250, and 300 °C. It has found that the annealing temperature has significantly improved the physical (structural and morphological) properties of

the ZnO seed layers. When the annealing temperature was increased up to 300 °C, the crystallinity of ZnO seeds was improved accordingly. ZnO nanorods (NRs) were grown onto the annealed seeded substrates by the CBD technique using different growth parameters namely, precursor concentration, growth temperature and growth time. Results revealed that the properties of the grown ZnO NRs were affected by varying the growth parameters. The grown ZnO NRs showed optimum characteristics using Zn⁺² precursor concentration of 50 mM at growth duration and temperature of 3 hrs and 95 °C, respectively. The grown NRs were found to be vertically aligned to the substrates with average diameters of 55 nm and 104 nm on PTFE and Si substrates, respectively. Photoluminescence (PL) measurements exhibited the sharpest and most intense UV emission for the grown ZnO NRs. Besides, the near band edge (NBE) emission to the deep level emission (DLE) ratio (I_{NBE}/I_{DLE}) was the highest, indicating better quality grown ZnO NRs. Metal-semiconductor-metal (MSM) Pd/ZnO/Pd ultraviolet photodetectors (UV PDs) were fabricated base on the optimized grown ZnO. The fabricated UV PDs showed photo-responsivity values of 0.92 and 0.61 A/W at wavelengths of 373 and 379 nm, respectively for Si and PTFE-based devices. The photosensitivity was measured to be 6045% and 4068% for the fabricated devices using Si and PTFE substrates, respectively. Results revealed that the performance for the fabricated PTFE-based devices was close to that for Si-based UV PDs indicating the reliability of using PTFE material as substrate to grow ZnO NRs for optoelectronic applications.

CHAPTER 1: INTRODUCTION

1.1 Introduction

Zinc oxide (ZnO) nanostructures (NSs) are intrinsically n-type semiconductors with a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV; thus, they have interesting properties such as high thermal and mechanical stabilities, unique optical and electronic properties [1]. ZnO NS is a versatile functional material that exists in various growth morphologies such as nanorings, nanobelts, nanotubes, nanospheres, nanowires, nanorods, and flowers-like structures.

One-dimensional ZnO NSs have drawn much attention in last decade because of their slow electron/hole recombination rate, faster response, high surface-to-volume ratio, specific crystalline orientation, and higher optical gain. Therefore, production of ZnO NRs characterized by diverse morphologies and diameter size is of major significance for the fundamental research and development of novel electronic and optoelectronic devices such as photodetectors [2], field-effect transistors [3], chemical sensors [4], next-generation UV sources, solar cells [5], light-emitting diodes [6], and nanogenerators [7]. Several techniques such as hydrothermal [8], electrochemical deposition [9], pulsed laser deposition [10], and chemical bath deposition [11], metal organic chemical vapor deposition [12], have been utilized to produce ZnO nanorods on various types of substrates.

Seed layer is very important factor for the growth of high-quality ZnO NRs. The crystal quality of the ZnO seed layer is the dominating factor that influences NR growth. The size of the nanoparticle on the substrate determines the size of the growing ZnO NRs, and the growth of the nanorods is enhanced by the presence of the seed materials [13]

The annealing of the ZnO seed layer improved adhesion on the substrate, which contributed to well-aligned ZnO nanorods. The annealing process is important to obtain desirable structural and optical properties. The main contributions of seed layer annealing may come from the improvement of the crystallinity and absorption which could give a significantly effect on the photocatalytic activity of ZnO nanorods [14].

ZnO NSs would be the most important material for future optoelectronic applications, such as nanoscale ultraviolet (UV) light emitting diodes [15] and UV optical detectors [16] Growth of patterned and aligned one-dimensional NRs is a very important aspect for nanodevices application. UV photodetector (PD) is an important application that can be utilized in a wide range of applications such as environmental and biological analysis, optical communication, civilian and military usages, and space applications [17].

Recently, UV PDs based on ZnO NRs have attracted much attention because of their unique characteristics such as wide direct band gap of 3.37 eV, high sensitivity to absorb oxygen on the surface, radiation hardness [18], high temperature resistance [19, 20], high optical gain [21, 22]. To date, several UV PDs based on ZnO nanostructure have been fabricated using various substrate such as silicon [23], sapphire [24], porous silicon (PS) [25], glass [26], and quartz [27].

However, for moving objects, flexible polymer substrates are a suitable substrate for the fabrication of UV photodetector based on ZnO nanorods because of low cost, high flexibility, lightweight, and portable characteristics. Among various polymer substrates, polyethylene naphtholate (PEN) is used most often because of its optical and mechanical properties [39]. Vertically well-aligned ZnO nanorod arrays on PTFE substrate are extremely demanded for the purpose of fabricating highly sensitive

fast response UV PDs. CBD method is an attractive, dominant and adaptable technique for the synthesis of ZnO NRs such as low cost, low processing temperature (lower than 100 °C), relatively safe (no hazardous chemicals and equipment), very easy operation to produce ZnO NRs. To the best of our knowledge, UV PDs based on ZnO NRs grown on flexible PTFE substrate has not been reported in any literature. In this study, the prospect of ZnO NRs for the fabrication of UV PD based on flexible PTFE substrates along with important related parameters were discussed.

Silicon substrate is very common for photodetector device. As the PTFE is used for the first time as a substrate for photodetector device, the silicon substrate PD is used as a reference to compare the quality level and performances.

1.2 Background of ZnO Material

Lately, intensive research efforts are directed towards the controlled synthesis of ZnO NRs with desirably reproducible properties useful for diversified applications. Certainly, ZnO is one of the most significant semiconductor compounds having direct wide band gap of 3.37 eV and large exciton binding energy of 60 meV beneficial for sundry room temperature operations. Besides, ZnO reveals good electrical conductivity and high optical transparency in the near UV region. On top, ZnO material is environmentally affable, abundant, bio-compatible and non-toxic [1]. These distinct attributes of ZnO make it prospective for broad array of optoelectronic applications particularly in the blue and UV-A (320–400 nm) wavelength regions including laser diodes, light-emitting diodes, high performance nanosensors, piezoelectric nanogenerators [28], photodetectors, etc. to cite a few.

Over the years, several methods are developed to synthesize ZnO nanostructures (ZnO NSs) with diverse morphologies (shapes and sizes) such as NRs,

nanodots, nanobelts, nanowires (NWs), nanotubes, nanobridges, nanoflowers, nanofibers, nanonails, nanowalls, nanohelices, nanoflakes, mesoporous single-crystal NWs, and polyhedral cages [29, 30]. Amongst these morphologies, ZnO NRs and ZnO NWs are most attractive due to their easy preparation, reproducibility and numerous applications [31]. Constant efforts are dedicated to creating innovative designs and fabrication methods of ZnO NRs with improved performance and applicability. These growth techniques include metal-organic chemical vapour deposition (MOCVD) and wet chemical methods [32], radio frequency (RF) and direct current (DC) sputtering [33, 34], thermal evaporation, physical vapour deposition (PVD) [35], laser ablation-catalytic growth [36], sol-gel spin coating [37], molecular beam epitaxy (MBE) [38] plasma enhanced chemical vapour deposition (PECVD) [39], template-induced growth [40], solution-liquid-solid growth in organic solvents [31] pulsed laser deposition [41], flux methods [42] and even top-down approaches [43].

It is realized that the structures, morphologies and overall properties of the synthesized ZnO NRs are growth method dependent, where the growth conditions and parameters play decisive role. For the growth of high quality ZnO NRs selection of synthesis method, substrate, and optimization of growth parameters are prerequisite. Furthermore, most of these conventional preparation techniques suffer from many shortcomings such as the requirement of complex vacuum conditions, very high temperature, prolonged growth time, supply of more energy and materials to deposit ZnO NRs in a narrow region. To surmount such limitations, an easy and economic method for large scale ZnO NRs synthesis with controlled morphologies, desirable properties and reproducibility is needed. Moreover, to meet the ever-increasing industrial demand a role-to-role production of ZnO NRs became mandatory. In this regard, growth of ZnO NRs on flexible substrates appears vital. Inspired by these

gamut research activities, present thesis takes the opportunity to realize the feasibility of growing ZnO NRs on soft Teflon substrate using a simple, inexpensive and yet accurate method called CBD as discussed hereunder.

1.3 Problem Statement

- Through comprehensive literature review it is noticed that earlier studies used two types of substrates for the growth of ZnO NRs. The normal type is the rigid solid substrates such as Si, Glass, and sapphire. These solid substrates possessed high melting points to allow the annealing of the precipitated material. This is required in order to achieve re-crystallization of the deposited material and strengthen the continuity with the substrate. The other type of substrates is the flexible substrates such as polyethylene terephthalate (PET) [44], polydimethylsiloxane (PDMS) [45], thermoplastic polyurethanes (TPU) [46], common paper, plastic and aluminium foil [47]. Recently, these are used for fabricating diverse ZnO NRs using different techniques. However flexible electronic devices are rapidly developing due to the need of the modern technology for the electrical applications that reduced in size, mechanically flexible, and light weight. The main problem of these substrates is associated to their low melting temperature (65-250 °C) which disallows the annealing process of the precipitated material on the substrate. To overcome this problem new types of flexible substrates with high melting point is targeted. Soft substrate with high melting point not only allows the annealing process and increases the adhesion of precipitated material to the substrate but also imparts more freedom to grow high quality ZnO NRs at large scale. Moreover, flexible substrates facilitate the re-crystallization of the deposited material, thereby produce a high quality NSs suitable for designing efficient optoelectronic devices.

- Amongst the entire wide band gap semiconductor ZnO NRs based application is escalating in the frequency spectrum. This demand of ZnO NRs generated renewed interest to achieve high performance, flexible, and low-cost substrates for roll-to-roll large scale production of ZnO NRs. It is very important and valuable to add a new flexible substrate with advanced specifications such as high melting point and high flexibility to the field of fabrication of the flexible electrical devices. So far, flexible devices are beginning to show great promises for technical or commercial interests. For instance, Polytetrafluoroethylene, known as Teflon or PTFE possess a good resistance to processing chemicals, negligible water absorption, high temperature resistance, and high melting point of 326.8 °C. On top, the coefficient of thermal expansion of conventional Teflon substrates is high which is typically about 180 to 205 ppm/°C, depending on the dielectric constant of the substrates [48, 49]. Thus, PTFE substrates are able to satisfy all the technical requirements of large scale production of ZnO NRs and design of flexible UV photodetectors. ZnO is one of the most suitable materials on flexible substrate, as ZnO can be prepared by low temperature processes. However, the characteristics of ZnO nanorods photodetectors on flexible substrates have seldom been addressed. In this view, present thesis intends to grow high quality ZnO NRs on Teflon substrates following CBD. The as-prepared ZnO NRs are used to design UV photodetectors.

1.4 Research Objectives

The objectives of this research are summarized as follows:

- To study the thermal, structural and morphological properties of PTFE substrate for ZnO nanostructures growth.

- To study the effect of annealing temperature on ZnO seed layers deposited on PTFE and Si substrates.
- To study the effect of growth parameters (precursor concentration, time, and temperature) on ZnO NRs grown on PTFE and Si substrates using CBD method.
- To fabricate and characterize UV PDs based on PTFE substrate.

1.5 Scope of the Study

Based on the proposed objectives the following scopes are projected:

- Characterization of Teflon substrates in terms of their thermal, structural and morphological properties.
- Synthesis of ZnO NRs on Teflon and Silicon substrates under different parameters (time, temperature and precursor concentration) via CBD technique and use the optimum values.
- Structural, optical and morphological characterizations using XRD, PL, FESEM, and AFM.
- Fabrication of the UV photodetector using the sample grown under optimum synthesis conditions.

1.6 Significance of the Study

Presently, the manufacturing cost of the conventional PDs and electronic devices is one of the main barriers. This proposed novel of nanotechnology route is expected to reduce the cost such devices without compromising with the quality. This study will elucidate fundamental knowledge on the growth mechanism of ZnO NRs on Teflon substrate. Definitely, the current systematic methods for the preparation and characterizations of the ZnO NRs would help to produce such materials at large scale

useful for the fabrication of UV PDs. ZnO NRs obtained via CBD method can be applied to varieties of industrial applications. The advances of nanotechnology in the semiconductor devices manufacturing have paved access to the production of devices at relatively cheaper and more efficient rate and the present study is a fair attempt towards that direction. Nanotechnology has been put forward as a viable alternative to the conventional techniques of manufacturing semiconductor devices, due to its potential ability to enhance the effective of semiconductor device as well as lower the manufacture expenses. In short, the production of ZnO NRs on flexible Teflon substrate has numerous advantages that need to be explored. This research will open up such avenues.

1.7 Contributions

The contributions of the proposed study can be listed in the following points:

- Introduction of outstanding thermal properties for a flexible substrate such as PTFE for the synthesis of ZnO nanostructures.
- Demonstrated the feasibility of large scale production of ZnO NRs on flexible substrate using CBD method.
- Optimized the annealing temperature of ZnO seed layers for the growth of ZnO NRs for optoelectronic applications.
- Optimized the preparation parameters for the growth of ZnO NRs using PTFE substrates.
- Fabrication of highly photosensitive and fast response flexible UV-photodetector based on ZnO NRs.

1.8 Originality of Thesis

The originality of this research work involves the following aspects:

- The PTFE flexible substrate has been studied and characterized in term of thermal, structural and morphological as used for the first time.
- The ZnO seed layer has been deposited on PTFE substrate by RF sputtering and the effect of annealing on ZnO seed layer has been studied used different temperatures.
- The growth of vertically aligned ZnO nanorods with high structural and optical qualities the first time on flexible PTFE substrate.
- The investigation of precursor concentration, growth temperature and growth time of ZnO NRs on PTFE substrate have been studied and got the optimum parameters values to fabricate the UV-Photodetector.

1.9 Thesis Organization

Chapter 1 presents a background on wide band gap ZnO semiconductor with different reported nanostructures. The synthesis of ZnO nanostructures using different approach was discussed along with CBD technique which was used to growth ZnO NRs on flexible substrates. Besides, this chapter highlights researches gap and the research objectives that would aim to bridge the gap based on previous reported studies. Scope of research, originality and the significance of the present study were also presented in chapter 1. Chapter 2 renders a comprehensive literature survey on the relevant research areas such as properties of ZnO, characterizations and properties of bulk as well as low dimensional ZnO structures. The growth of ZnO NRs on different substrates using the CBD method was discussed. Chemical and physical properties of Teflon as a flexible substrate were emphasized as well. Moreover, the working principles of UV photodetectors were also presented

Chapter 3 depicts the detailed research methodology that involved in the production of ZnO NRs on PTFE and Si substrates. The fabrication of MSM UV PD devices was also presented. Fundamental equations related to various characterization tools are enclosed as well. In chapter 4, PTFE thermal, structural and morphological properties were characterized by different techniques i.e., Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), XRD and FESEM. The properties of the as-deposited and annealed ZnO seed layers were studied and presented in chapter 4 for ZnO nanostructures growth suitable for optoelectronic applications. Chapter 5 discussed the growth of ZnO NRs under different conditions using the CBD method on PTFE and Si substrates. Besides, the fabrication of MSM-based UV PDs was also presented and discussed. Current-voltage (I - V) behaviour and photoresponse performance of the fabricated devices were examined and discussed in chapter 5 as well. Chapter 6 presents the conclusions based on the discussed results and shows the opening for future research. Some information from research results in the form of images and tables are appended in Appendix 1 and 2.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter provides a comprehensive literature survey on various concepts, past developments and theoretical background relevant to ZnO NRs research. These includes the information on ZnO semiconductor materials and their detailed chemical as well as physical properties. A description is given on the Teflon substrate in terms of its advantages, chemical, physical and thermal properties. In addition, the chemical reactions related to the growth mechanisms of CBD method are also emphasized. Finally, the basic operational principles of the UV photodetector together with various parameters and theoretical equations that are utilized to determine the PD performances are explained.

2.2 Properties of ZnO

ZnO is of large exciton binding energy (60 meV), exhibited exciton recombination mediated lasing action even above the room temperature. In the past decade global research interest in wide band gap semiconductors has been attracted towards zinc oxide (ZnO) due to its excellent properties as a semiconductor material. Features such as high electron mobility, high thermal conductivity, good transparency, wide direct band gap (3.37 eV), large exciton binding energy and easiness of growing it in the nanostructure form make ZnO suitable for optoelectronics, transparent electronics, lasing, sensing, and wide range of applications [50-52]. ZnO exhibits low thermal expansion, high heat capacity and high melting point. These thermal properties are prospective for alloying ZnO with different materials such as Mg and/or Cd (e.g. MgZnO and CdZnO) having same (wurtzite) crystal structure. Generally, the useful

properties of ZnO NRs are determined by their crystal quality, synthesis conditions and methods, surface morphology and chemical compositions. Table 2-1 summarizes some basic characteristics of standard ZnO material [53].

Table 2-1: Important properties of hexagonal ZnO [53].

| Parameters | | Values |
|------------------------------------|-------------|------------------------------|
| Lattices constants at 300 K | a_0 | 3.2495 Å |
| | c_0 | 5.2098 Å |
| | c_0 / a_0 | 1.6033 (ideal) |
| Density | | 5.606 g/cm ³ |
| Melting temperature | | 2248 K |
| Linear expansion coefficient (/°C) | | a_0 : 6.5×10^{-6} |
| | | c_0 : 3.0×10^{-6} |
| Static dielectric constant | | 8.656 |
| Refractive index | | 2.008 to 2.029 |
| Energy gap (T = 300 K) | | 3.37 eV |
| Exciting binding energy | | 60 meV |
| Electron mobility (T = 300 K) | | 200 cm ² /V. s |
| Hole mobility (T = 300 K) | | cm ² /V. s |

2.2.1 Electronic Structure Properties of ZnO

It is very crucial to understand the electrical properties of ZnO for applications in nanoelectronics. The electrical behavior of ZnO nanostructures is n-type and it is widely believed that it is due to native defects such as oxygen vacancies and zinc interstitials [54]. The electron mobility in ZnO nanostructures is not constant and it

depends on growth method and it is approximately $120\text{-}440\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [55]. At room temperature the mobility of electrons is $200\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the holes mobility is $5\text{-}50\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The effective mass of electrons is $0.24m_0$ and the effective mass of the holes is $0.59m_0$ and due to this difference in effective mass, the holes have very less mobility as compared to electrons [56] .

Being an n-type inorganic semiconductor belonging to the II–VI binary semiconductor group ZnO has a density of about 5.6 g/cm^3 [57]. It is verified that the n-type conductivity in the intrinsic ZnO is generated from point defects like oxygen vacancies and interstitials of Zn atom within the lattice structure. ZnO possesses a direct wide energy band gap of 3.37 eV at room temperature [58, 59] and large exciton binding energy around 60 meV . However, in ZnO super-lattices the exciton binding energy can be increased to over 100 meV [60]. The occurrence of extremely stable exciton offers the possibility of achieving highly efficient lasers operation at room temperature [61]. In addition, ZnO reveals stable UV emission at room temperature [62] and high energy radiation stability [63] which is suitable for space applications.

ZnO nanomaterials are advantageous for diverse optoelectronic applications due to their high luminescence, high transparency and good electrical conductivity. Using ZnO based NSs, it is possible to fabricate transparent thin film transistors (TFTs), solar cells, light emitting diodes and UV photodetectors [64-66]. Also, ZnO displays very high piezoelectric constants than existing AlN or GaN materials [67]. The presence of high piezoelectric constants that is responsible for the enhancement of electromechanical coupling is truly demanding for transducers, piezo-electrical sensors and actuators applications [68, 69]. The reduced solubility of ZnO in water is beneficial for numerous favourable usage such as an additive in the production of materials like glass, plastics, cement, ceramics, paints and rubbers.

2.2.2 Crystal Structure of ZnO

ZnO exists in two types of crystal structures such as hexagonal wurtzite and cubic zinc blend as shown in (Figure 2-1). The wurtzite form is the most common and stable at normal conditions (common phase at 300 K). In both structures, each anion (Zn^{2+}) in the middle is specified by four cations (O^{2-}) at the angles of a tetrahedron and vice versa, pending along the *c*-axis. It makes the whole structure to inherit lack of central symmetry.

The existence of tetrahedral organization flow the sp^3 covalent bonding structure provides a significant ionic property responsible for the enhancement of band gap and charging the surfaces by cations or anions. Subsequently, ZnO has usually negative but sometimes positive charge on the surfaces. The wurtzite structure consists a hexagonal unit cell with lattice parameters *a* and *b* lay in the *x*-*y* plane (which include an angle of 120° and have equal length), and *c* is parallel to the *z*-axis, which are revealed in Figure 2.1 (b) [50]. The lattice parameters values of the hexagonal unit cell at room temperature are $a = b \approx 3.2495 \text{ \AA}$ and $c = 5.2069 \text{ \AA}$. The axial ratio c/a of an ideal hexagonal wurtzite structure is $(8/3)^{1/2} = 1.633$, which changes in response to stress or strain [70]. Experimentally, for hexagonal wurtzite structure of ZnO, the real value of c/a was determined in the range $c/a = 1.593\text{--}1.603$ [71].

This tetrahedral coordination of wurtzite structure gives rise to polar symmetry along the hexagonal axis, chosen to be parallel to *z*. This polarity is responsible for a number of the properties of ZnO such as its spontaneous polarization and piezoelectricity and it is also an important factor in defect generation and crystal growth.

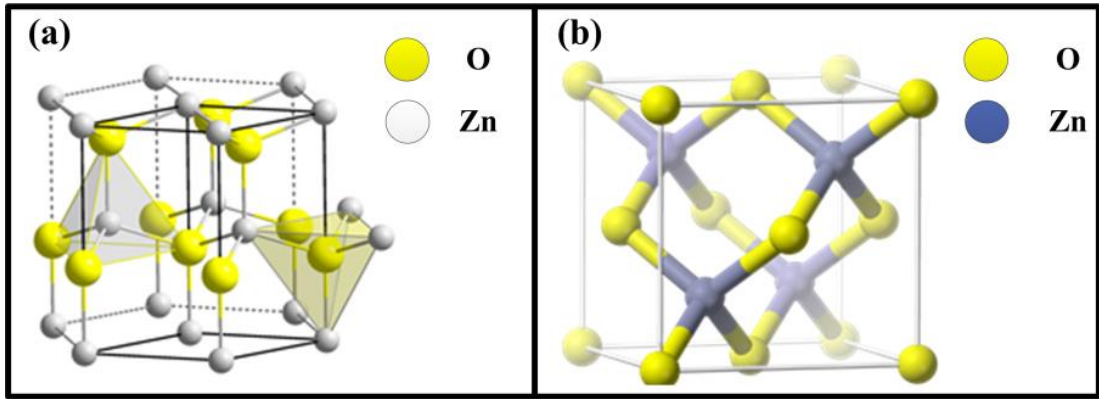


Figure 2-1: Crystal structures of ZnO: (a) hexagonal wurtzite, and (b) cubic zinc blend [72]

XRD pattern being the electron density map of the crystal structure are generated from the waves scattered by the electrons in the atomic shells (more precisely the valence electrons). The scattered waves constructively interfere to produce the diffraction pattern which is then recorded by a detector equipped in the diffractometer and finally plotted as intensity versus the scattered angles (2θ) of the diffracted X-ray beams.

2.2.3 Optical Properties of ZnO

ZnO material is characterized by several prominent optical properties such as wide optical band gap, large exciton binding energy for efficient excitonic emission at room temperature and strong radiative recombination [73]. These optical properties of ZnO make it as a potential candidate for photonic applications such as light emitting diodes (LEDs), ultraviolet (UV) lasers and photodetectors (PDs). Over the years, the optical transitions in ZnO are characterized via various spectroscopic measurements such as optical absorption, transmission, reflection, photo-reflection, photoluminescence (PL), and cathode-luminescence [50].

The PL spectra of ZnO NSs reveal an intense emission peak located at UV regions $\approx 365\text{-}381\text{nm}$ ($\approx 3.25\text{-}3.4\text{ eV}$) and a visible broad band emission centred around

550 nm (2.5 eV). The occurrence of UV emission peak is attributed to the near band-edge transition (NBE) of ZnO or the free excitons recombination [73]. Conversely, the visible band is ascribed to the several defects (deep level emissions ((DLE)) mediated mechanisms in ZnO crystal structure such as O-vacancy (V_O) [74], Zn-vacancy (V_{Zn}) [75], O-interstitial (O_i) [76], and Zn-interstitial (Zn_i) [77]. Because of the presence of higher defects in the surface (variation of surface to volume ratio), the position of the UV emission for 1D ZnO NSs could be shifted [78].

2.2.4 Growth of ZnO Nanostructures (NSs)

ZnO in the form of polycrystalline films was mostly grown using magnetron sputtering [79, 80] and chemical vapour deposition (CVD) [81, 82] methods. Presently, high-quality single crystalline ZnO can be prepared using molecular beam epitaxy (MBE) [83], plasma assisted molecular beam epitaxy [84], organometallic chemical vapour-phase epitaxy (OMVPE) [85], pulsed laser deposition (PLD) and there are also hydride or halide vapour-phase epitaxy (HVPE) [86, 87] techniques. So far, these ZnO structures were grown on different substrates such as sapphire [88], GaAs [89], GaN [90], Si [91] and SiO₂ [92]. ZnO NSs have been investigated extensively due to their unique physical and chemical properties that are prospective for broad array of technological applications. It is realized that by reducing the morphology (shape and size) of ZnO structure novel electrical, mechanical, chemical and optical properties can be controlled. These low dimensional emergent properties are attributed to the effects of surface states and quantum confinement. Meanwhile, 1D ZnO NRs have been widely used for different electronic, optoelectronic, energy storage electrochemical and bio-electrochemical applications [93]. These include light-emitting diodes LEDs [94], ultraviolet lasers [95], field emission devices [96], solar cells and dye-sensitized solar cell [97], piezoelectric nano-generators [98], and UV photodetectors [99-101].

Various methods were developed to synthesize such 1D ZnO NRs such as CBD [102], physical vapour deposition [103], pulsed laser deposition [104], metal–organic chemical vapour deposition [105], molecular beam epitaxy [106] and electro spinning [107]. Compared to other techniques, CBD is attracting considerable attention in the synthesis of nanostructured ZnO. It is a relatively inexpensive, simple, and convenient method for large area deposition. Furthermore, using the CBD method, a large number of different substrates in various shapes and sizes can be coated in a single run [108].

Using the CBD to grow ZnO NRs, seed layer material is essential to initialize the growth of crystal materials from the seed material because CBD is a low temperature process. Therefore, the existing of seed layer in CBD aims to achieve high-density ZnO NRs which can be promising for optical devices application. Besides, the annealing of seed layers at certain temperatures would enhance the properties of the grown ZnO NRs due to the re-crystallization of the deposited material and strengthen the continuity with the substrate [109].

Therefore, numerous reports focused on the annealing effect of seed layers on the properties of ZnO NWs grown by CBD. Wen Ji et al. [110] studied the effect of ZnO seed layer thickness on the morphology of ZnO NWs grown on glass substrates using low temperature chemical growth method. It has been found that, the average diameter of nanowires are increased from 50 to 130 nm and the nanowire density is decreased from 110 to 60 μm^{-2} while the seed layer thickness is varied from 20 to 1000 nm.

The improved control of the morphology of ZnO nanowire arrays may lead to an enhanced carrier collection of hybrid polymer photovoltaic devices based on ZnO. Wang et al. [111] studied the effect of ZnO seed layers crystal orientation on the properties of ZnO NR arrays grown on Si substrates. It has been found that, ZnO seed

layer with (1 0 3) preferred orientation, prepared using DC reactive sputtering, did not facilitate the formation of ZnO NRs in the solution grown process. Prior seeding of the surface by ZnO layer with (0 0 2) preferred orientation, deposited using RF magnetron sputtering, leads to nucleation sites on which ZnO NR arrays can grow in a highly aligned fashion. ZnO nanorods with well-defined hexagonal facets (0 0 2) were grown almost vertically over the entire substrate.

The uniformity and alignment of the NR arrays are strongly related to the properties of underneath ZnO seed layers. Tao et al. [112] reported that the sputtering parameters like oxygen partial pressure and annealing treatment of seed layers had a great influence on the morphology of ZnO NR arrays grown on Si substrates by hydrothermal method. NR arrays grown on seed layer deposited at magnetron sputtering parameters of argon/oxygen ratio of 20:7, had better alignment and crystallization compared with those grown on seed layer deposited at argon/oxygen ratio of 20:3. Further, the diameters increased, and the alignment gained further enhanced for the ZnO NRs grown on annealed seed layer.

The reactions involved in the CBD process can be controlled by adjusting the reaction parameters such as the precursor concentration, deposition temperature and time, pushing the reaction equilibrium forwards or backwards. Peterson et al. [113] reported the growth of an epitaxial ZnO column, which exhibited uniformity and reproducibility over a large surface area. It is mentioned that the nucleation is an important factor since column growth is observed only on ZnO seeded substrates where super saturation of the zinc species was attributed to the driving force for column deposition. It was further acknowledged that the pH level must be adjusted to maintain the degree of super saturation. Both the ZnO column length and the optimal deposition temperature can be controlled by increasing the Zn^{2+} ion concentration. Continual

stirring led to the promotion of the uniform columnar growth via the reduction of concentration gradients on the substrate surface.

Using CBD method, Yi et al. prepared aligned ZnO NRs arrays on a PET substrate at low temperature [114]. It was found that ZnO seed layer played vital role for the alignment of such ZnO NRs. Room-temperature PL spectra revealed a strong UV emission band at 378.3 nm. The XRD, field emission transmission electron microscope (FE-TEM), and selected area electron diffraction (SAED) patterns of ZnO NRs displayed single-crystal wurtzite structure as well as preferred growth orientation along [0001] lattice planer direction. Li et al. [115] have grown ZnO NRs arrays on Si substrate using CBD method and determined the effects of precursor concentration, deposition time and the growth temperature on the NRs morphology and aspect ratio. Results indicated that the aspect ratio of such NRs can be controlled by adjusting the precursor concentration, growth temperature and time. CBD has been comprehensively used to deposit various 1D ZnO NSs (NRs, NNs, NTs and NWs) using different Zn^{+2} precursors and complexion solution.

In this research, CBD technique was used to grow ZnO NRs on seeded substrates, thus, this technique will be further discussed in the subsequent sections.

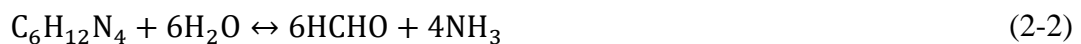
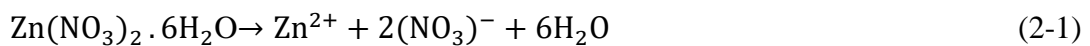
2.2.5 Growth Mechanism of ZnO NRs by CBD

The CBD method is largely associated with the fabrication of diverse ZnO NRs including high quality NRs, NWs, nanoneedles, etc. This method is greatly advantageous to grow high quality ZnO NRs because its uses ZnO seeds in the form of thin films or nanoparticles to deposit NSs on different substrates such as Si wafers [116], polydimethylsiloxane (PDMS) [117], thermoplastic polyurethanes (TPU) [118], paper [119], fibres [120], and carbon fibres [121]. The CBD method involves two steps

including nucleation and particle growth based on the formation of a solid phase from a solution. In this method, the substrate is immersed in a solution containing the precursors.

Vayssieres et al. [116] prepared ZnO micro-rods for the first time in 2001 using the CBD method. The reaction carried out at 95 °C using zinc nitrate $Zn(NO_3)_2 \cdot 4H_2O$ and hexamethylenetetramine (HMT) ($C_6H_{12}N_4$). It was acknowledged that in common cases the homogeneous nucleation of solid phases such as metal oxides involve a higher activation energy barrier. Therefore, hetero-nucleation is promoted and remained energetically more favourable (e.g., influence of seeding on crystal growth). This observation is supported by fact that the interfacial energy between the grown material and substrates is frequently lower than the one between grown material crystals and solvents (solutions). This in turn makes the hetero-nucleation more predominant onto a substrate at a lower saturation of homogeneous solutions [122].

The mechanism of growing 1D ZnO NRs using CBD can be described as four step processes. First, the $Zn(NO_3)_2$ compound provides Zn^{2+} ions required for the ZnO NRs growth process. Second, the HMT reacts with the water molecules to produce hydroxide molecules OH^- . Third, the Zn^{2+} ions react with the hydroxide to produce Zinc Hydroxide $Zn(OH)_2$. Finally, $Zn(OH)_2$ decomposes to ZnO and water. The growth processes involves the following chemical reactions pathways [123]:



2.3 Polymer Substrates for ZnO NSs

Recently, the interests in transparent, flexible, small and lightweight devices have significantly grown because of their portability and foldability. With this growing demand for convenient and portable applications, flexible substrates are increasingly more valuable for flexible devices than conventional rigid substrates. Despite the fact that flexible substrates are constrained by deposition temperature, applications of flexible substrate have drawn considerable attention because of their exceptional properties such as transparency, transportability, lightweight, and high resistance to impact damage in contrast to typical rigid substrates. Consequently, flexible substrates are widely studied as precursor materials in the manufacture of flexible-based optoelectronic devices such as LEDs [124], and solar cells [125]. Several substrates such as polyethylenenaphthalate (PEN), polycarbonate (PC), thermoplastic polyurethanes (TPU), and polyethylene terephthalate (PET) were used for the growth of different ZnO nanostructures.

Nadarajah et al. [124] reported the growth of single crystalline ZnO nanowires (NWs) on flexible PET substrate covered with a sputtered indium-tin-oxide (ITO) layer. The electrodeposition of ZnO NWs was carried out in an aqueous electrolyte at 80 °C. The grown NWs were used to fabricate a novel flexible LED. This flexible hybrid LED generates a broad emission spectrum covering most of the visible range and reaching to the near-ultraviolet.

Jiang et al. [125] reported a high-bendability flexible dye-sensitized solar cell based on a ZnO NWs. highly bendable ZnO-NW film on PET/ITO substrate was fabricated by low-temperature hydrothermal growth at 85 °C. The results demonstrate that modified ZnO nanowires fabricated by the low temperature hydrothermal method

are promising for efficient and flexible plastic solar cells. Pradhan et al. [126] demonstrated successful growth of both 1D (nanopillars) and 2D (nanowalls) ZnO nanostructures on In₂O₃-coated PET substrates at 70 °C by using electrodeposition technique. Albiss et al. [127] demonstrated the growth of ZnO-NRs grown on a flexible polydimethylsiloxane (PDMS) seeded by ZnO nanoparticles synthesised via simple low temperature hydrothermal method. This study claimed that ZnO-NR-based UV light detector can be fabricated using a simple process that only requires an organic flexible substrate, organic reducing agent.

Zainelabdin, A., et al.[128] fabricated white light-emitting diode (WLED) by growing well-aligned ZnO NRs at a temperature as low as 50 °C following chemical bath deposition strategy. The ZnO NRs were grown on multi-layered polymers spun coated on commercially available flexible Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) plastic substrate. The fabricated device was bent at large angles (>60°) and still retained its electro-optical characteristics. This WLED can fit well to wide varieties of lighting applications. Manekkathodi et al. [129] reported a direct growth of aligned ZnO NRs on paper substrates seeded by ZnO layers deposited by spin coating method. The NRs were grown using hydrothermal method for low-cost flexible p-n junction diodes.

Shabannia and Abu Hassan [130] reported the synthesis of vertically aligned ZnO NRs on a polyethylene naphthalene (PEN) substrate using a chemical bath deposition method at a low temperature. A 70 nm thick ZnO seed layer was deposited on the PEN substrates and was sequentially annealed in a furnace at 200 °C for 60 min. Liu al. [118] reported the synthesis of ZnO NRs on thermoplastic polyurethane (TPU) flexible substrate for biomolecules application. The NRs growth was carried out via an in-situ sol thermal process at low temperature (75 °C). In-depth literature survey did

not reveal the any use of Teflon as a flexible substrate to grow ZnO NRs. Thus, it may be a good choice to explore such feasibility. Table2-2 summarizes some fluoropolymer materials with general properties.

Table2-2: Summary of some fluoropolymer materials with their general properties [49].

| Fluoro-polymer | Melting temperature (°C) | Tensile modulus (MPa) | Break elongation (%) | Dielectric strength (kV/mm) |
|-----------------------|---------------------------------|------------------------------|-----------------------------|------------------------------------|
| PTFE | 317-337 | 550 | 300-550 | 19.7 |
| PFA | 302-310 | 276 | 100-250 | 19.7 |
| FEP | 260-282 | 345 | 300 | 19.7 |
| ECTFE | 235-245 | 240 | 250-300 | 80 |
| PCTFE | 210-215 | 60-100 | 100-250 | 19.7 |
| PVF | 190-200 | 2000 | 90-250 | 12-14 |
| PVDF | 155-192 | 1040-2070 | 50-250 | 63-67 |

2.3.1 Teflon as Substrate

Currently, diverse ZnO NRs are fabricated on varying substrates using different techniques. Most of the flexible substrates suffer from low melting temperature (200 – 250) °C that prohibits the annealing procedure of the precipitated material onto the substrate. On top, ZnO NRs deposited on these substrates reveal very large lattice mismatch. Thus, new types of flexible substrates with high melting point are demanded to overcome these problems. Flexible substrates with high melting point are suitable for annealing process which also enhances the precipitation of the material onto the substrate surface. This allows the growth of high quality ZnO NRs at commercial level [131]. Soft substrates not only aid the process of re-crystallization of the precipitated material it also achieves high quality NSs beneficial for competent optoelectronic devices fabrication.

Earlier, PTFE substrates were employed for numerous saleable and defense applications. This material is selected due to its extreme softness and other interesting properties. Basically, PTFE is not soluble in any organic solvents. PTFE exhibits high thermal stability without obvious degradation below 440 °C. Furthermore, the coefficient of thermal expansion of usual PTFE substrates is very high (180 to 205) ppm/°C depending on their dielectric constant. Interestingly, it is believed that soft Teflon as substrate can meet all the technological necessities of roll-to-roll manufacturing of ZnO NRs and the fabrication of flexible-based electronic devices.

2.3.2 Properties of PTFE

Compare to all established plastics, PTFE possesses very high molecular weight (100.02 g/mol) and is considered as the best chemically stable polymer compound. PTFE has many distinct properties such as good resistance to processing chemicals, negligible water absorption, high temperature resistance, high melting point and low coefficient of friction. The rigid polymer chain structure also caused a high melting temperature (~320 °C) and a high melt viscosity for PTFE, which made it difficult to process PTFE with the traditional methods for polymer materials. One of the most distinguishing properties of PTFE is its outstanding chemical resistance, except for some extreme conditions such as molten alkali metals or elemental fluorine.

PTFE has a helical chain confirmation due to the larger fluorine volume. The rigid helical polymer chains can crystallize very easily and result in a high crystallinity (up to 98%). Because of the compact crystalline structure and the dense fluorine atoms, PTFE is the heaviest polymer material with a density of 2.1 g/cm. Moreover, PTFE has high electronegativity and electrical insulation [132, 133]. The high electronegativity of PTFE does not allow the absorption of water, alcohols, and other greatly polarized oxygen and hydroxyl composition materials on its surface. The existence of highly