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**INKJET-PRINTED ZNO THIN FILM SEMICONDUCTOR
FOR AM OF ELECTRONIC DEVICES**

TRAN VAN THAI

2019

**NANYANG
TECHNOLOGICAL
UNIVERSITY**
SINGAPORE

**INKJET-PRINTED ZNO THIN FILM SEMICONDUCTOR
FOR ADDITIVE MANUFACTURING
OF ELECTRONIC DEVICES**

TRAN VAN THAI

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

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FOR ADDITIVE MANUFACTURING
OF ELECTRONIC DEVICES**

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in the fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

15 March 2019

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Date

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Authorship Attribution Statement

*(B) This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

1. Chapter 4 is published as **Van-Thai Tran**, Yuefan Wei, Hongyi Yang, Zhaoyao Zhan, Hejun Du, "All-inkjet-printed flexible ZnO micro photodetector for wearable UV monitoring device," *Nanotechnology*, vol. 28, p. 095204, 2017. (**Highlighted paper 2017**)

The contributions of the co-authors are as follows:

- A/P Du Hejun gave initial idea and revised the manuscript
 - Dr Yuefan Wei assisted in preparation of ink formular and revised the manuscript
 - Dr. Hongyi Yang assisted in printing experiment and interpreting of XRD results
 - Dr. Zhaoyao Zhan assisted in design experiment for characterization of printed device
 - I did all of experiments, analysed data and wrote the manuscript
2. Appendix B contains materials which are published as **Van-Thai Tran**, Yuefan Wei, Wei Jing Liao, Hongyi Yang, Hejun Du, "Preparing of interdigitated microelectrode arrays for AC electrokinetic devices using inkjet printing of silver nanoparticles ink," *Micromachines*, vol. 8, p. 106, 2017.

The contributions of the co-authors are as follows:

- A/P Du Hejun, Dr. Yuefan Wei, Dr. Hongyi Yang and I conceived and designed the experiments
- I and Mr. Wei Jing Liao performed the experiments, including fabrication and testing of the devices.

- I and Dr. Yuefan Wei and Mr. Wei Jing Liao analyzed the data
- I wrote the manuscripts

A/P Du Hejun and Dr. Yuefan Wei read and provide input for revising manuscripts.

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The contributions of the co-authors are as follows:

- A/P Du Hejun gave initial idea and revised the manuscript
- Dr Yuefan Wei assisted in conducting and interpreting of XPS results, and revised the manuscript
- Dr. Zhaoyao Zhan assisted in characterization of printed device
- I performed experiments, analysed data and wrote the manuscript

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- A/P Du Hejun gave initial idea and revised the manuscript
- Dr Yuefan Wei assisted in conducting and interpreting of Mott-Schotky plot
- I performed experiments, analysed data and wrote the manuscript

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Abstract

Additive manufacturing, which is commonly known as three-dimensional (3D) printing, is a potential technology that possesses many advantages comparing with traditional fabrication technologies. The creative idea of additive manufacturing, which converts digital designs to physical objects via depositing material layer-by-layer, introduces many benefits such as capable of making complex structures, obtaining satisfactory material properties, prototyping rapidly and saving materials. Printing functional devices is an even more promising approach to utilize the benefits of additive manufacturing for micro-fabrication.

Zinc oxide (ZnO) is a well-known wide bandgap semiconductor which has numerous applications in electronics, optoelectronics, piezoelectric, and piezotronics. Hence, inkjet printing of ZnO thin film is of significant interest for producing functional devices using additive manufacturing. In addition, the electrical properties of ZnO are essential to the performance of devices, such as responsivity of UV photodetector. Thus, it is important to develop an inkjet printing manufacturing process for producing ZnO thin film of desired electric properties.

This thesis aims to develop and investigate the additive manufacturing process of ZnO thin film for electronic applications, and specifically to engineer the electrical properties of printed ZnO film to enhance the performance of printed UV photodetector. Owing to its fascinating features such as non-contact printing, high resolution, low cost and low-temperature process, inkjet printing is adopted as the main additive manufacturing method in this thesis. Inkjet printing process of a zinc precursor solution was successfully

developed for the additive manufacturing of ZnO thin film. It was also found that inkjet-printed ZnO possesses a polycrystalline structure.

To investigate the practicality of the proposed process, micro-sized flexible ZnO UV photodetectors were thoroughly prepared by a facile inkjet printing scheme. The fabricated devices can be potentially used for real-time monitoring of the UV intensity and warning users for health and safety purpose. Moreover, this additive manufacturing method can be applied to fabricate ZnO thin film on various flexible substrates, which makes the device more suitable for applications that require flexibility such as wearable devices.

Electrical properties of printed UV photodetectors were characterized and studied under varied thermal annealing temperatures of up to 350 °C. It was found that both conductivity and responsivity of the printed ZnO film significantly increase along with the increase of annealing temperature. The enhancement of electrical conductivity and responsivity was attributed to band bending modification, which was reduced due to the fusing of grain boundaries under heat treatment.

To explore and demonstrate the capability of integrating the inkjet printing of ZnO films with other 3D printing process, silver micro-heater was fabricated and employed to heat zinc precursor locally and form ZnO. Subsequently, electrical properties of printed ZnO films were further investigated by using localized Joule heating effect through the integrated fabrication of ZnO films and a silver microheater. The fabricated UV photodetector showed that the input power of microheater has a significant effect on the performance of the printed device.

The successful inkjet printing of micro-sized ZnO thin films and the integrated photodetector has demonstrated the feasibility and great potentials of fabricating sophisticated semiconductor devices using additive manufacturing technology.

Chapter 1: Introduction

Disadvantages in the conventional subtractive fabrication of ZnO and other functional materials, such as time-consuming, requiring complex equipment and material wasting, might limit them from advanced applications. Additive manufacturing provides a novel approach to deposit material in a controlled manner. Fabrication of multi-functional materials such as ZnO using additive manufacturing could overcome the limitation on the potential applications of such materials and boost up the fabrication technology.

1.1 Background

Along with the utilization of semiconductor materials, micro-fabrication process has become fundamental for the development of technology in the second half of the 20th century, where it has been applied for fabrication of sophisticated miniaturized electronic and electrical-mechanical devices. Up to now, photolithography is one of the essential tools of micro-fabrication. Photolithography working principle is the process that transfers the digital designs to physical features via an optical mask to create patterns on a photosensitive polymer. The patterns are then continuously transferred to underlying substrate via etching or deposition and lift-off of required material [1]. Although the ultra-high precision has been reached using photolithography, the prolonged processing time and wasting of material are the main drawbacks of this process [2].

The surge of additive manufacturing, which is also known as 3D printing, for many applications has motivated the development of printing technologies and materials. In 1984, the first three-dimensional (3D) printing system was launched [3]. It is a new fabrication approach which is expected to reduce fabrication cost and to enhance the

performance of the manufactured goods. It is no doubt that the traditional manufacturing process, which is based on removing excessive part of the material, provides high precision and high quality of material through an intensive development of cutting tools and techniques. However, as mentioned above, the traditional fabrication process has drawbacks such as time-consuming and wasting material via cutting or etching. On the other hand, 3D printing uses different methods to gradually add material onto an existing surface to build the object layer-by-layer. Therefore, this fabrication method is capable of constructing complicated structures which are difficult, or even impossible, to be built by conventional subtractive technologies [4, 5].

Many printing methods, such as powder bed, material jetting and bath polymer curing, have been developed to meet the demand of printing various materials, e.g., metal, ceramic, polymer and even living cells. Owing to various advantages of printing technique, 3D printed parts were used not only for prototyping purpose but also for practical applications. Besides, the resolution of additive manufacturing has reached microscale [6], and even approximate to nanoscale [7]. It is expected that 3D printing will play a significant role in the fabrication of goods in the near future. As a result, the demand for printed functional devices has been raised to fulfill the need for printed consumable products, which are composed of multi-materials. Hereby, the printed functional devices are not only basic electrical elements, such as resistors, capacitors, and transistors, but also advanced electric devices, such as sensor, solar cells and batteries.[8-10].

1.2 Motivation

Additive manufacturing provides a promising approach for material patterning in the fabrication of electronic devices. Additive manufacturing has proved its advantages, such

as throughput, low cost, and less wasting of material [11]. Hence, 3D-printing has a significant impact on how do we plan for manufacturing, especially by reducing the cost of small-lot production [12]. Recent progress has shown that the resolution and quality of the printed object have been continuously improved.

Many advanced applications of additive manufacturing base on the ability to directly create physical structures from computer-generated models. For example, 3D printing technologies have been utilized in houses building, creating limbs for people with disabilities[13] and studying the structure of the human brain [14]. Interestingly, studies of printing cells and tissues bring the hope that we will soon witness patients are implanted with 3D-printed organs instead of waiting in long queue for donated organs [15]. Making of the 3D electronic device is also possible by using 3D printing technology [16].

The idea of using additive manufacturing for micro-fabrication was proposed to improve the MEMS fabrication process, such as using less material, reducing setup time, and probably improving the device performance [5]. For example, the utilization of 3D printing in micro-fabrication has reduced the fabrication time by up to 80 % [2]. The construction of a product using 3D printing requires a combination of structural material and functional material. To accomplish the fully additive manufacturing process, printing of functional materials, such as conductor and semiconductor, is crucial.

Figure 1.1. Annual number of papers published with topic words (“additive manufacturing” or “3D printing”) and (“electronic” “sensor” or “actuator”). Literature search was implemented using Web of Science (<http://apps.webofknowledge.com>)

There have been approximately 1000 papers with the topic words “additive manufacturing”, “3D printing” for electronic, sensor and actuator. The first papers in the field appeared in 2002. Although during the next ten years, there were only a few publications on this topic, the number of related papers significantly increased to 64 publications in 2014. In 2018, at the moment of this search (8/12/2018), there have been 291 publications in the field. This literature statistic shows that the topic is of widely and actively interested by researchers.

ZnO is a metal oxide semiconductor of the II-VI group. Due to its interesting properties such as spontaneous poling of crystallinity structure, wide bandgap, and high excitation energy, ZnO has many applications in optoelectronics, electronics, sensors and piezoelectric devices [17, 18]. Also, ZnO nanostructure is suitable for flexible device application [19]. Moreover, alignment and patterning of ZnO crystals are critical in device

fabrication [20]. Alignment of ZnO nanostructure could be conducted using one-by-one fabrication process such as self-aligning [21], dielectrophoresis aligning [22, 23], manual aligning [24, 25]. Despite the high performance of those devices, these fabrication processes are not suitable for large-scale manufacturing.

ZnO thin film and nanostructures can be deposited by vapor deposition processes such as pulse laser deposition [26, 27], metal-organic chemical vapor deposition [28, 29], reactive electron beam evaporation [30, 31] and radio-frequency magnetron sputtering [32, 33]. As a substitute, sol-gel deposition is an inexpensive process in term of necessary equipment, and it is very suitable for large-scale manufacturing via different coating technologies such as dip coating [34], spin coating [35], and spray coating [36]. Nevertheless, patterning of the deposited film is required using micro-fabrication process such as photolithography to achieve design requirement [37].

As a consequence, printing of small size pattern of ZnO semiconductor will significantly benefit the fabrication of electronic device and promote advanced applications, such as wearable devices [38]. Moreover, the new fabrication approach may enhance the performances of the devices by modifying the structures and improve the properties of the films. Because of the elimination of etching chemical, additive manufacturing of ZnO is also applicable to polymer substrates which is suitable for flexible device fabrication.

Printing of ZnO using common 3D printing techniques is a relatively difficult task because ZnO is a metal oxide which is brittle and has a very high melting temperature. Therefore, the conventional method which melts and ejects the liquid material through a nozzle such as fused deposition modeling (FDM) is unlikely to be practical. On the other hand, localized heating approaches such as selective laser melting (SLM) or selective laser

sintering (SLS) produce internal stress and cause cracking in this brittle material. Hence, the most suitable approach to print ZnO is inkjet printing of ZnO precursor solution.

Another concern is the electrical properties of printed ZnO, which has a significant role in device performance. It is likely that the inkjet printing of ZnO will create a film with intrinsic defects which change the properties of printed material via phenomenon such as band bending. In a polycrystalline semiconductor, band bending at grain boundary has a remarkable influence on device properties and performance because it affects the electron transportation through grain boundary. Engineering the band bending is necessary to improve the performance of the printed device. Understanding the mechanism of the electrical properties modification becomes essential for the research in the printing of ZnO. This becomes the motivation of this work, where the inkjet printing of ZnO and the electrical properties of the printed film are studied.

1.3 Objectives

The promising additive manufacturing method for fabrication of ZnO-based devices has motivated the development of printing ZnO. This thesis presents a work toward the development of additive manufacturing process to fabricate ZnO thin films for semiconductor application. In addition, studying the electrical properties of printed ZnO thin films and how to enhance such properties could add further benefit for the development of printed electronic devices.

On the other hand, photodetector is an elementary semiconductor device which converts the light signal to electrical signal. Photodetector has a simple structure and very easy to be constructed using metal-semiconductor-metal (MSM) structure. Hence it is usually

utilized to study properties of semiconductor material. Furthermore, it has many practical applications, which are to be further discussed in Chapter 4. The working principle of photodetector is based on the interaction of semiconductor with photon with energy equal to or larger than bandgap elevates electron from valence band to conduction band, and create a hole [39]. These generated charge carriers cause an increase in conductivity of semiconductor film which could be converted to an electric signal. Transportation of the electron through the grain boundaries is significantly driven by band bending, which directly affects the electronic and optoelectronic device application [40].

Therefore, the objectives of this work are:

- To print ZnO thin film using inkjet printing as an alternative for photolithography process
- To fabricate the micro-sized ZnO pattern using additive manufacturing, i.e., inkjet printing, and demonstrate the semiconductor property through UV photodetector application.
- To investigate the effect of the low-temperature annealing process on the electrical properties of printed ZnO thin film and the underlying mechanism.
- To develop a process to additively fabricate the ZnO device which can be integrated with the other 3D printing process.

1.4 Research scope and structure

To achieve the objectives, the scopes of this work are:

- To prepare a facile ink formula and perform inkjet printing of ZnO
- To print ZnO micro-sized UV photodetector on polyimide substrate and to test the device performance under bending.

- To print ZnO micro UV photodetector on Si/SiO₂ substrate and investigate the influence of different thermal annealing temperature of up to 350 °C on the electric properties.
- To measure device current under dark and UV illumination and determine the device's responsivity.
- To observe and explain the change of responsivity under different annealing temperatures.
- To print and use microheater to perform calcination of printed zinc precursor to form ZnO film.

Consequently, this thesis includes four major parts. The first part is devoted to develop and investigate a suitable ink formula for the inkjet printing of ZnO film. The second part presents the printing of small-sized ZnO pattern for advanced applications in electronic and MEMS device. The third part investigates the influence of heat treatment on the properties of printed ZnO. The last part is devoted to the integration of heating element onto the device to introduce thermal annealing locally.

In details, Chapter 2 provides background knowledge of this research. It includes a review of additive manufacturing, ZnO properties, applications and approaches for additive manufacturing of ZnO. A major factor that affects the performance of the device such as band bending of polycrystalline semiconductor is also discussed.

Chapter 3 presents the method to fabricate ZnO film by inkjet printing and discusses some factors that could affect the printing. The influence of thermal annealing on the structure of the thin film is also discussed.

Chapter 4 presents the patterning technique of micro-sized ZnO thin films through inkjet printing. The effect of inkjet printing process parameters on the patterned structure is also discussed. Performance of fabricated devices is evaluated under different bending conditions to demonstrate that the printed ZnO thin film is suitable for flexible device applications.

Chapter 5 presents the investigation of the performance of UV photodetector fabricated under different annealing temperatures. It is found that the band bending plays a main role in the improvement of the device's responsivity.

Chapter 6 presents a novel design of an inkjet-printed micro heater for localized heating of zinc precursor to form ZnO UV sensor. The design is aimed at developing semiconductor devices by integrating inkjet printing process with other 3D printing methods.

Chapter 7 summaries the work and discusses future works, which will seek further understanding of the unique properties and potential applications of inkjet-printed ZnO patterns.

Chapter 2: Literature review

This chapter reviews zinc oxide (ZnO) properties and applications. The exciting features have gained many attentions and efforts to deposit ZnO thin film and nanostructure. Merits of additive manufacturing, such as ease of fabrication and integration, are strong motivation to study inkjet printing of ZnO.

2.1 Overview

2.1.1 ZnO properties

2.1.1.1 General properties

ZnO is a well-known compound II-IV semiconductor (metal oxide semiconductor) due to its versatile applications. The dominance crystallinity of ZnO is hexagonal wurtzite structure with spontaneous polar along c-axis, which has been observed in various ZnO nanostructures such as thin film [41, 42], nanorods [43, 44], nanowires [45, 46], nano tetrapods [47, 48] and nanobelts [49, 50]. Owing to its direct wide bandgap ($E_g=3.37$ eV at room temperature), large exciton binding energy (60 meV) and efficient radiative recombination, ZnO is an exciting material for electronic and optoelectronic applications [17, 18]. The direct wide bandgap is the reason why ZnO is widely utilized for UV photodetector application because of high selectively in wavelength. In addition, the large excitation binding energy is essential for an efficiency excitonic emission and laser operation based on excitonic transitions at room temperature [51].

2.1.1.2 Native defects of ZnO

The rich defect states of ZnO creates a wide range of properties depending on the preparation condition [52]. The intrinsic native defects in ZnO are oxygen vacancies (V_O),

zinc vacancies (V_{Zn}), zinc interstitials (Zn_i) oxygen interstitials (O_i), antisite oxygen (O_{Zn}) and antisite zinc (Zn_O) [53]. However, oxygen interstitials (O_i), antisite oxygen (O_{Zn}) and antisite zinc (Zn_O) are rarely present in normal condition because of their high formation energy [54]. While zinc interstitials are not stable at room temperature, oxygen vacancies have low formation enthalpies [55]. Hence, oxygen vacancies natively exist in ZnO material and could be the main root of n-type doping [56].

Spontaneous emission of ZnO has been studied using photoluminescence (PL) spectroscopy, which shows the UV emission and the other emissions in the visible band [57]. At room temperature, the PL spectra peaks are different between the nanostructures. It is believed that different concentration of the native defects is the main reason for the shifting of band-edge emission in ZnO nanostructures. Because the native defects likely happen on the surface, nanostructure with different surface-to-volume ratio would have different band-edge emission. In the visible spectra, ZnO has different emission peak of PL spectra such as 405, 420, 446, 466, 485, 510, 544, 583, and 640 nm [58]. Green emission is widely observed which is related to anti-site oxygen, oxygen vacancies and zinc interstitials. However, the singly ionized oxygen vacancy is the most commonly accepted hypothesis, whereby single ionized oxygen vacancy Vo^+ is proposed as the main root for deep donor level-green (510nm-540nm) PL emission [59]. There is evidence proving that the blue emission originates from the surface of nanorods. Furthermore, yellow emission and red emission are also observed. However, the origin of most of these defect emissions is still a controversial issue [57].

2.1.1.3 Electrical properties

ZnO is an intrinsic n-type semiconductor which has electron as a majority charge carrier [56]. However, the origin of n-type semiconductivity of ZnO is still a controversial issue. A theory of Kohan et al. proposed that native defects such as oxygen vacancies and zinc vacancies are a deep donor and deep acceptors, respectively [60]. Although, it is generally believed that oxygen vacancy is the primary cause for n-type semiconductor of ZnO because of its stability at room temperature [54]. On the other hand, Van de Walle et al. theoretically proved that hydrogen is an active shallow donor which is very hard to be removed during the deposition process, so they concluded that origin of that native n-type doping of ZnO is hydrogen [61].

Despite the difficulties in preparation, p-type doping of ZnO has gathered many research efforts because of its importance for the light emitting diode, where the p-n junction is established between p-type ZnO and n-type GaN [62]. The possible doping agents that could be used as acceptors in ZnO are nitrogen [51], arsenic [63], phosphorus [64] and antimony [65]. The defect density in those doped ZnO crystals could be reduced by growing the crystal on a lattice matched substrate such as scandium aluminum magnesium oxide (SCAM) [66]. However, it is widely reported that p-type ZnO is not stable and could turn to n-type after a few days [54].

The carrier mobility of a semiconductor is the speed of charge carrier moving in that material in a given direction under the effect of an electric field. Carrier mobility is an important parameter that decides the performance of the semiconductor device. The mobility of $205 \text{ cm}^2/\text{V s}$ at 300K of bulk material was reported, and the peak mobility was about $2000 \text{ cm}^2/\text{V s}$ at 50K [67]. The electron mobility of ZnO thin film and nanostructures

is usually lower than the bulk material. For example, pulse laser deposition ZnO thin film mobility was reported in the range of 115 and 155 cm²/Vs [26]. Also, a mobility value of 75 cm²/Vs was observed in ZnO nanorod [68].

2.1.2 ZnO with device applications

2.1.2.1 Piezoelectric

ZnO thin film and nanostructures with c-axis preferred orientation have the piezoelectric property thanks to the spontaneous poling of crystalline. These ZnO crystals can generate a voltage under an applied pressure and vice versa. With this feature, ZnO could be applied to sensor and actuator applications. For example, ZnO was used as both an integrated actuator and sensor in atomic force microscopy [69]. Jenkins et al. demonstrate a wide bandwidth micro-actuator made with sputtered ZnO thin film [70]. Deposited ZnO on a flexible substrate such as polyimide was used for flow sensor [71]. Yanhui et al. fabricated microcantilever with deposited ZnO thin film with high sensitivity, i.e., 12.09 nm/V [72, 73].

ZnO thin film has a sufficient surface-wave coupling of greater than 95%, which was investigated carefully by Yamamoto et al. [74]. Because of its ease of deposition on various substrates, ZnO is considered as a suitable material for SAW applications that can integrate with electronic circuits and microfluidics, bio-sensing applications [75]. Thin film ZnO SAW with coated graphene oxide also being used as a humidity sensor [76]. Also, flexible SAW device is fabricated by depositing ZnO onto PET flexible substrate [77].

Another application is energy harvesters by utilizing of reverse piezoelectric effect, where a voltage is generated when the crystal is deformed. These systems convert mechanical

energy into electrical energy. Usually, the device was fabricated using a cantilever structure with ZnO thin film sandwiched by two electrode layers. The efficiency of the device could be enhanced by employing p-n junction [78], changing the substrate [79], or matching the proof mass with resonance frequency [80]. On the other hand, ZnO nanowires can work as nanogenerator with efficiency in the range of 17%-30%, which is very promising for application in self-powered nanodevices [79, 81, 82].

2.1.2.2 Electronic applications

To prepare the diode device, p-type doping of ZnO is usually employed to create the p-n junction. The diode was fabricated by creating a p-type ZnO layer on the n-type substrate using laser doping [83]. Also, doping of aluminum in single ZnO nanowire was introduced to make a rectifying junction [84]. As discussed in the previous section, the p-type doping ZnO is not stable in normal condition. Hence, some studies directly employ n-type ZnO with either a high work-function noble metal [85] or another p-type semiconductor [86] for making diode device.

Owing to its compatible properties for liquid-crystal display (LCD) application, such as transparent, flexible and low-cost, ZnO has become a suitable candidate for thin film transistor (TFT) [87]. Solution-processed ZnO was used to prepare TFT which had the mobility of $0.35 \text{ cm}^2/(\text{V.s})$ [88]. A flexible ZnO TFT, which employed a polymer dielectric layer, reached mobility of $0.71 \text{ cm}^2/(\text{V.s})$ [89]. Very high mobility of $32.7 \text{ cm}^2/(\text{V.s})$ was achieved by employing hybrid ZnO thin film/graphene [90].

Coupling the piezoelectric with semiconductor properties of ZnO has led to some novel applications such as piezotronics and piezo-phototronics [91]. Proposed by Zhong et al.,

piezotronics in ZnO nanowire is the phenomenon that the strain-induced piezoelectric along c-axis, so-called piezopotential, will create a potential that change the height of Schottky barrier of semiconductor-metal contact, leads to the changing of transport behavior of the charge carriers [92]. Meanwhile, the piezo-phototronics employs the piezopotential to enhance the functionality of optoelectronic devices [93].

2.1.2.3 Optoelectrical application

Recently, the development of perovskite solar cell has shown an extraordinary potential for using ZnO as a transporting layer in a flexible solar cell, whose efficiency is comparable to a silicon-based solar cell. The advances in perovskite solar cell could be contributed to ZnO as an electron-transport layer which also blocks the holes [94]. The efficiency limit of perovskite solar cells has been estimated to be 31%, which makes it become a potential candidate for replacing silicon-based solar cell [95].

UV emission has been observed in ZnO nanowires grown by physical vapor deposition (PVD) [96]. By introducing p-type ZnO doping with nitrogen, ZnO homostructure light-emitting diode (LED), which emitted in the region of 400–1000 nm, was fabricated [97]. Also, UV-light emitting ZnO homojunction LED was fabricated by sequentially growing n-type ZnO (Ga-doped) and p-type ZnO (P-doped), and the emitting peak of 380 nm was obtained [98].

Under the illumination of UV light with photon energy larger than the bandgap of the crystal, the conductivity of ZnO hugely increased, which leads to the electrical current through the photodetector if there is an applied bias voltage. This phenomenon has been applied in UV photodetector application, which converts the light signal to an electrical

signal. The photoresponse of ZnO thin film strongly depends on the ambient environment [99]. A slow decaying of photocurrent is commonly observed, which could take hundreds of seconds to drop to a half of the maximum value [100]. The root of the slow response of ZnO nanowire under UV illumination could be contributed to the exchanging of oxygen and water at the oxygen defect site [101].

2.1.3 Physical and chemical vapor deposition of ZnO

ZnO could be grown using vapor deposition processes whereby ZnO is converted to the vapor phase by a high energy beam to be able to deposit on the substrate. Molecular beam epitaxy (MBE) deposits ZnO by delivering constituents along with a thermal beam to a heated substrate. The elemental zinc is evaporated to generate zinc flux while the active oxygen radicals are supplied by an RF plasma source. For example, ZnO with high quality could be grown on the sapphire substrate at a temperature up to 650°C [102].

Pulse laser deposition (PLD) is a technique that employs an excimer laser pulse to do flash evaporating of a target, such as ZnO powder, and form a plasma plume. These reactive species are then impinging onto the substrate [26, 27]. By employing this method, epitaxial ZnO thin film was grown on a sapphire substrate by PLD with a temperature range of 200°C-800°C [103]. Also, ZnO nanorods were grown on Si(001) wafer with a substrate temperature of 600°C [104]

Radio frequency (RF) magnetron sputtering of ZnO is carried out in low-pressure argon and oxygen gas mixture, where argon plays a role as a sputtering gas. The plasma yields sputtered ion from ZnO target and deposit onto the substrate. This deposition process could

be conducted at low temperature, typically from 200°C to 800°C. The obtained films usually have polycrystalline structure with highly c-axis preferred orientation [32, 33].

Metal-organic chemical vapor deposition (MOCVD) using reaction between precursors, such as diethyl-metal component, and oxygen or water or N₂O flow at high temperature [28, 29]. Different structures such as thin film and nanoneedles can be grown using different buffer layer [28].

2.1.4 Sol-gel method

On the contrary with the vapor deposition methods, solution-processing of ZnO is usually considered as a relatively cheap, highly controlled, and simple method for depositing large area of ZnO thin film [105]. In this process, a zinc salt compound precursor was dissolved in a suitable solvent with the aid of a stabilizer, such as diethanolamine (DEA) and monoethanolamine (MEA). These additives prevent the precipitation of zinc hydroxide and stabilize the precursor solution [105]. The precursor solution was coated on a large area by different techniques such as dip coating [34], spin coating [35], and spray coating [36]. Then, a suitable heat treatment was applied to decompose the compound and sinter the ZnO film.

Organic salt, such as acetate, is more preferred as a precursor because it is easy to decompose the acetate group and there is no residual after the process finish because the byproducts are combustion volatile. In contrast, the utilizing of inorganic salts, such as nitrate, introduces difficulties in removing of residual after treatment [106]. Alcohols, which have low carbon numbers, such as methanol, ethanol, isopropanol, and 2-methoxyethanol, are the most used solvent for ZnO sol-gel. However, some studies

employed ethylene glycol because it has some features such as high dielectric constant and high boiling temperature.

Figure 2.1. Preparation routes for ZnO sol-gel, starting with the precursor solution to colloidal sol and gelation of (a) film; and (b) powder (ref. [105])

Figure 2.1 describes the preparation of ZnO thin film and powder from the sol-gel method. In details, the thin film preparation process could be summarized by three steps: solution preparation, film coating, and heat treatment of xerogel film to produce a dense film [105]. On the other hand, ZnO powder could be prepared by heat treatment of condensed sol particles.

There are two possible routes of ZnO crystallinity growth, i.e., Ostwald ripening and aggregation [107, 108]. In the first route, it is believed that large particles are grown by combining of smaller particles. In the later route, the formation of ZnO colloidal particles includes two stages, i.e. the formation of small oligomers and the aggregation of those oligomers to form the crystalline wurtzite [109]. The synthesis of ZnO colloids includes two main steps, precursor preparation by reaction between zinc acetate in the early step and the alcohol and hydrolyzing the precursor to form the colloids by utilizing hydroxide [110].

A simplified reaction scheme was proposed by Jagan et al., which describes the formation of ZnO by three main step: hydrolysis, condensation, and pre-treatment [111]:

The film obtained from the sol-gel method usually has a wurtzite structure, which is the most thermodynamically stable crystal structure of ZnO. Depends on many parameters during deposition, the film could have a preferred orientation along (002) axis [112] and (100) axis, although the orientation along the (100) is rarely observed [113]. Those factors include the chemical system parameters such as precursor, solvent, additive and aging time. Also, film structure is affected by the coating parameters such as coating method, the thickness of film and nature of the substrate and the heat treatment conditions [105].

The vapor deposition processes are capable of preparing high-quality ZnO thin film and nanostructures thanks to the precisely controlled environment inside the reaction chamber. However, they require complex systems, expensive equipment and specific working space for material deposition. Hence, the solution process is a suitable alternative deposition process for fabrication of the ZnO thin film.

2.1.5 3D printing technologies

Additive manufacturing, or 3D printing, transforms digital designs to physical objects through a variety of methods. Although there are many available commercial systems, the printing methods could be classified into seven categories such as material extrusion, powder bed fusion, vat photopolymerization, material jetting, binder jetting, sheet lamination and directed energy deposition [114].

In short, the material extrusion method such as fused deposition modeling (FDM) melts the solid material and extrude via an orifice to a predefined shape. The powder bed fusion, such as selective laser sintering (SLS), selective laser melting (SLM) and electron beam melting (EBM), use high energy beam to fuse powder material dispersed in a coated layer. The vat photopolymerization technology, such as stereolithography, create an object by selectively hardening a liquid polymer in a vat. The material jetting method, such as inkjet printing and polyjet, deposit the material in the form of liquid droplets. The binder jetting technology selectively deposit liquid binder to link the discrete particles together [115]. The sheet lamination technology is a combination of additive and subtractive manufacturing by bonding sheets of material to form 3D structure. The directed energy

deposition technology, such as laser engineered net shaping (LENS), is similar to powder bed fusion technology, but the thermal energy selectively melts the streaming of material powder instead of powder bed [116].

Stereolithography is the method that selectively solidifies material from a liquid photopolymer. Although it was invented in the 1980s, this very first 3D printing technology is still widely applied. Very high-resolution 3D structure with the smallest feature of 0.6 μm was achieved using a digital micro-mirror dynamic mask [117]. Furthermore, stereolithography technology is compatible with biodegradable material for biomedical applications [118].

Patented by S. Scott Crump et al. in 1989, fused deposition modeling (FDM) heats materials to their melting state and extrudes them through a mobilized nozzle [119]. The extruded filament creates the 3D shape by the trajectory of the nozzle in 3 dimensions. FDM is widely applied because of its simple structure. Capable of printing thermoplastic polymer, FDM was used to create porous scaffolds for tissue engineering [120]. The mechanical strength of the printed object might be enhanced using a polymer-ceramic composite [121].

Selective laser sintering (SLS) employs a high energy laser beam to sinter the metal or polymer powder by raising the temperature to the softening state [122]. On the other hand, the selective laser melting (SLM) technology heats the metal powder to the melting temperature so the density of the printed part could reach nearly 100 % [123]. Electron beam melting (EBM) works on the same principle with SLM but it employs an electron beam instead of the laser beam to melt the powder [124]. Furthermore, laser engineered net shaping (LENS) ejects the powder to a melt pool created by a focused laser beam [125].

LENS technology has the capability to fabricate complex shape item, and various metals and alloys have been printed using this process [126, 127].

Laminated object manufacturing (LOM) technology bonds sheets of material that were already trimmed to a required shape. These layers are glued together to create 3D structures [128]. The precision of this method could be affected by process variables such as surface angle, layer thickness, the shape of the layer and penetration depth [129]. Because different materials could be employed, the LOM process can be applied for manufacturing of composite material to enhance mechanical strength [130].

Polyjet is the technique that deposits photocurable liquid polymer by inkjet printing, following by UV illumination to harden the material. The liquid polymer is continuously deposited and hardened layer-by-layer to create 3D structures [131]. Thanks to the utilization of inkjet nozzle and curing step after each layer, polyjet is suitable for printing multiple materials such as supporting material, which is typically wax, structural material and rubble-like material [132].

2.1.6 Inkjet printing

Unlike gravure printing which creates a pattern on the substrate through an engraved cylinder, inkjet printing is a non-contact depositing technology that jets material through the nozzle in the liquid form. Then, the generated droplets create characters or images on paper, textile or the other surface [9]. The information of the object is created and stored on a computer, before transferring the pixel information to the printer for printing as the droplet. The advantages of inkjet printing include low-temperature process and capable of

multi-material depositing. However, the requirement on the characteristics of ink is stringent, such as it must be prepared in the liquid form, either a solution or a suspension.

Figure 2.2. Inkjet printing technologies: Continuous inkjet printing and Drop-on-demand Inkjet printing and electrohydrodynamic inkjet printing [133]

Inkjet printing could be categorized into three methods, such as drop-on-demand (DOD), continuous inkjet printing and electrohydrodynamic (EHD) inkjet printing (Figure 2.2) [133, 134]. Although there are some different technologies, the principle of inkjet printing is generating small droplets to be deposited on targeting substrate. In case of continuous inkjet printing technology, the droplet is produced by nozzle continuously. An electric field will be applied to deflect the droplet to either the printing surface or the recycling reservoir. Electrohydrodynamic inkjet printing technology uses two electrodes: one is immersed into the ink chamber, and the other electrode is the substrate. The applied electric field between

the two electrodes will create a pressure that forms the droplets. On the other hand, the drop-on-demand technology only generates a droplet at the required position. Hence it is a material saving technology comparing with continuous inkjet printing. The droplet could be produced by either boiling the ink to create a bubble or pushing the ink by a piezoelectric actuator [133].

Some problems may occur in a DOD inkjet printing system, such as unstable droplet generation, unable to jet droplet, and clogging the nozzles. The two most critical fluidic parameters of ink that directly affect the formation of the droplet are viscosity and surface tension. To prevent clogging of the nozzles, it is essential that the ink not contain large particles that might block the fluid channel in the orifices. Furthermore, the ink solution or suspension must be stable in sufficient time such that the particles would not aggregate during the printing. Usually, dispersants must be added to the ink system to prevent the agglomeration of the particles [135].

2.2 Additive manufacturing of ZnO

2.2.1 Screen printing of ZnO

Screen printing has been employed to prepare ZnO films for different applications. Nanostructures of ZnO were mixed with polyvinyl alcohol binder and deposited using screen printing [136]. An annealing step at 500 °C was introduced to remove the organic binder. A similar process was used to prepared ZnO thin film for solar cell application [137]. The screen printing process can also be applied to a flexible substrate such as paper to fabricate UV photodetector. However, poor performance, such as the small on/off ratio of smaller than ten times, could originate from the existence of the binder in ZnO paste [138].

2.2.2 Inkjet printing of nanoparticle suspension

Nanoparticle suspension has been utilized for inkjet printing of ZnO via special preparation of the ink. The prepared ink must satisfy two requirements, such as particles do not block the nozzle, and the ink must be stable. The first requirement can be achieved by employing relatively small particles such as nanoparticles. Because of their high surface energy, the bare ZnO nanoparticles in the suspension system tend to agglomerate quickly. Hence, to achieve the second requirement, the surface of ZnO nanoparticles must be treated using a surfactant with sufficient functional group that can attach to the surface of the nanoparticle and prevents them from agglomeration [139-141].

One of the most effective chemicals is silane because it can create a silica nano-network to cover the nanoparticle core [142]. In an aqueous system, ZnO nanoparticles have been modified by anchoring the polymer chain, i.e., polymethacrylic acid (PMAA). This modification results in a long-term stability of the colloidal dispersion [139]. In addition, polyvinylpyrrolidone (PVP) is also a suitable surfactant for capping ZnO nanoparticles [143]. Glycerin was used to aid dissolving solid particle induced by zinc precursor in ethylene glycol [144]. Besides that, high viscosity solvent such as ethylene glycol was tested for the ability to stabilize Al-doped ZnO nanoparticles, such as zeta potential reached the maximum at a concentration of 1.14wt% [145]. On the other hand, a physical method such as ultrasonic sonication was effective in reducing sedimentation rate, hence it improved the stability of the ink [146].

2.2.3 Printing of ZnO sol-gel

Some studies have utilized zinc precursor solution as the ink for inkjet printing of ZnO-based materials. For example, 2D patterns of In_2O_3 -ZnO were deposited using inkjet

printing with a precursor of indium (III) isopropoxide and zinc acetate dihydrate (ZHD) dissolved in 2-methoxyethanol [147]. A bi-functionality device for sensing ferromagnetism and UV, made of pristine ZnO and Mn-doped ZnO film, were printed via a sol-gel containing ZHD and ethanolamine in isopropanol solvent [148].

An indirect approach has been utilized whereby inkjet printing is utilized for printing of the seeding layer for growing ZnO nanowires [149]. This approach could be described as a two steps process. Firstly, a ZHD solution was inkjet-printed to create precise precursor patterns. Secondly, the printed precursor patterns were used as a seeding layer to grow ZnO nanowires by hydrothermal process (Figure 2.3a) [150]. This digital fabrication process was applied to fabricate ZnO nanowires transistor and UV photodetector [151]. The advantages of this method are the ease of changing the design and the ability to grow ZnO nanowires on the plastic substrate.

Figure 2.3. Additively fabricated ZnO nanostructures. (a) Selectively grown ZnO nanowire from inkjet-printed pattern [151]. (b) Electro-spinning ZnO nanowire (ref. [40]).

2.2.4 Electrospinning

Electrospinning was employed to create ZnO nanowires with a small grain size [40]. The zinc salt solution, with the addition of polyvinyl alcohol (PVA) as a surfactant, was ejected through a nozzle under the effect of high voltage field to create a very thin nanowire in the flexible substrate. Upon calcination by a temperature of 400°C, the additive polymer was decomposed, and the ZnO nanowires were sintered. This nanostructure results in a giant responsivity and signal to noise ratio due to the extremely low dark current (Figure 2.3b). Although the electrospinning technique in this report is not capable of creating intricate patterns yet, the process is claimed as a printable process. The multi-grains structure has benefitted in creating of band edge modulation and minimizing of the dark current, hence, the printed devices have superior performance with detective up to 3.3×10^{17} Jones [40].

2.3 Band bending in polycrystalline semiconductor

In a semiconductor, the electron states exist at two energy level, such as valence band and conduction band. The valence band is the lower energy, and the conduction band is the higher energy. The energy gap between the two bands is called bandgap. Fermi level is the state of energy where all electron energy is below it at absolute zero temperature (0 K). Fermi level lies in between the conduction band and valence band. The excitation of an electron from the valence band to the conduction band by high energy source results in the generation of electron-hole pairs.

The surface of ZnO is susceptible to absorbed species which can change its electronic properties by band bending [24]. Band bending in semiconductor interfaces happens when

there is electron exchanging between the interface of semiconductor and the absorbed species which shifts the equilibrium of electron density and makes a change of energy band edges. In native n-type semiconductor such as ZnO, there is an interaction with electron acceptor absorbed on ZnO surface by receiving a free electron from the semiconductor. At equilibrium state, the lack of electron near the surface of semiconductor, due to absorbed species, forms a depletion layer. Hence, there is an upward bending of the band near the surface due to the charge-induced electric field [152].

The surface band bending is expressed by the following equation [153]:

$$\phi_B = E_g - (E_F - E_{V,S}) - \xi \quad (2.4)$$

where ϕ_B is the surface band bending, E_g is band gap of the semiconductor, E_F is Fermi level, $E_{V,S}$ is the valence band minimum at the surface and ξ is the difference of E_C and E_F .

Figure 2.4. Band diagram of a single nanowire with the width of the depletion layer D , conduction band (E_C), valence band (E_V), Fermi level (E_F), the potential barrier at the surface ϕ_B . The picture is redrawn from Ref. [153]

The Poisson equation describes the relationship of electric potential and charges concentration in semiconductor material for one-dimensional assumption [154]:

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\varepsilon\varepsilon_0} \quad (2.5)$$

where ϕ is the potential energy, x is the distance from the surface into the grain, ρ is the space charge density, ε is the relative dielectric constant of ZnO and ε_0 is the vacuum permittivity. From the Poisson equation, the depletion layer width can be determined by the equation [155]:

$$D = \left(\frac{2\varepsilon\varepsilon_0\phi_B}{q^2N_d} \right)^{\frac{1}{2}} \quad (2.6)$$

where D is the width of the depletion layer, ϕ_B is the potential barrier at the surface of the grain and N_d is the carrier concentration. It could be seen that the width of the depletion layer is dependent on the potential barrier and carrier concentration.

Conductivity and photoconductivity of polycrystalline semiconductor are strongly affected by the grain boundaries [156]. It is because the trapping states at the boundary capture free carriers cause potential barriers which repel the transportation through grains. Based on the grain-boundary trapping model, Baccarani et al. proposed that the dependence of dark conductivity by barrier height can be described by the equation [157]:

$$\sigma_d = \frac{q^2N_d d}{(2\pi m^* kT)^{1/2}} \exp(-qV_d / kT) \quad (2.7)$$

where N_d is the free carrier concentration, q is the electronic charge, d is the grain size, m^* is the effective mass for electron, V_d is the dark diffusion potential.

2.4 Photoconductive mechanism of ZnO

The generation of the electron-hole pair which causes the changing in carrier concentration is the fundamental mechanism of photoconductive response phenomenon in semiconductor [158]. ZnO surface is well known for its chemical sensitivity [159]. Hence, the response of ZnO to light illumination is affected by surface conditions such as Fermi-level pinning, surface band bending and depletion layers [160, 161].

The photocurrent under UV illumination originates from two phenomena: the separation of electron-hole and the absorption/desorption of oxygen species. In the first phenomenon, when semiconductor lattice absorbs a photon with energy higher than the semiconductor bandgap, an electron-hole pair is generated. In the latter phenomenon, generated holes migrate to the surface, and receive electron captured by oxygen species. The oxygen species are released from the surface of the semiconductor and make the depletion layer narrower. Hence, the electrical current increases thanks to both the increasing amount of charge carrier and broader conducting channel. The photocurrent decays due to the recombination of the generated electron-hole pair after turning off the illuminating light [101].

The reactions follows these equations [24]:

Figure 2.5. Photoconduction mechanism of ZnO nanowires: (a) generation of electron-hole due to high energy photon; (b) the absorbed oxygen species causes band bending at the surface of nanowire; (b) desorbing of oxygen by migrating hole [24]

In case of single crystalline nanowire photodetector, under certain circumstances, there is still a continuous conductive channel in the core of the nanowire because the band bending only happen on the surface of the nanowire. Hence the dark current of this single crystalline nanowire is very high, and it reduces the detectivity of the device. On the other hand, polycrystalline semiconductors witness the band bending between the grains because of the grain boundaries. Because of the band bending, there are energy barriers existing at grain boundaries that affect the carrier transport via tunneling and thermionic emission, which result in a minimal dark current of the photodetector [40].

Table 2.1 and Table 2.2 presents some representative studies of ZnO-based photodetectors, regarding preparation technique and performance. It is found that different preparation technique and crystal structure result in different performance in term of responsivity. Nanowires array show a poor performance in term of responsivity, which is in range of

0.5-40 A/W [162-164]. Although single nanowire usually has the best performance in term of responsivity [165], the difficulty in fabricating device could limit its practical application. Epitaxial films prepared by magnetron sputtering usually have a poor responsivity [166], when porous film prepared by sol-gel have relatively high responsivity, such as in range of 1-100 A/W [167]. Some advanced techniques have also been employed to improve the photodetector performance, such as rapid thermal annealing [168], plasma surface treatment [169].

Table 2.1. Comparison of photoresponse of the ZnO photodetectors with different material structures and preparation technique

Material structure	Preparation technique	Device structure	Light intensity (mW/cm ²)	Bias voltage (V)	Rise time (s)	Decay time (s)	Responsivity (A/W)	I _{ph} / I _{dark}	Notes	Ref.
Nanowires	Hydrothermal	MSM	0.5	5; 10	0.67; 3.77**	1.02; 14.16* *	1.2; 40	>10	Dielectrophoresis deposition	[162]
	Hydrothermal	Schottky contact	4.9	0.5	43x10 ⁻⁶	54x10 ⁻⁶	22.1	10.04		[163]
	Chemical vapor deposition	MSM	14	5	0.59; 6.2**	1; 10.1**	0.5	4		[164]
Nanorods	Thermal evaporation	MSM	300	5	0.035*	0.85*	1.6	-	Plasmonic enhanced	[170]
Single nanowire	Thermal evaporation	Schottky contact	33	5	-	1	4.5x10 ⁴	1.4x10 ⁷	Piezophotonic effect	[165]
Poly-crystalline nanowire	Electro-spinning	MSM	0.5x10 ⁻⁶ - 115.5 x10 ⁻⁶	1	0.56	0.32	7.5x10 ⁶	10 ⁵		[40]
Epitaxial thin film	Chemical vapor deposition	Schottky contact	0.1x10 ⁻³ (N2 laser pulse 2ns)	5	12x10 ⁻⁹	50x10 ⁻⁹	1.5	-		[171]
	Magnetron sputtering	MSM	-	3V	-	-	1.306		Plasmonic enhanced	[172]
	Sputtering	MSM	-	3V	-	-	3.8x10 ⁻²	1.6x10 ³		[166]

*Time constant of exponential function

**Time constant of bi-exponential function

MSM: Metal-semiconductor-metal

Table 2.2. Comparison of photoresponse of the ZnO photodetectors with different material structures and preparation technique

Material structure	Preparation technique	Device structure	Light intensity (mW/cm ²)	Bias voltage (V)	Rise time (s)	Decay time (s)	Responsivity (A/W)	I _{ph} / I _{dark}	Notes	Ref.
Poly-crystalline thin film	Sol-gel	MSM	1.06	120	<0.1	1.3*	61	10 ⁶		[167]
	Flame spray pyrolysis	MSM	0.1	5	250	150	12	3.4x10 ⁵		[173]
	Flame spray pyrolysis	MSM	0.086	1	145	181	7	9.3x10 ⁶		[174]
	Sol-gel	MSM	0.1	6	9.4	13.5	95.4	3.1x10 ⁵	Nano-junction	[168]
	Sol-gel	MSM	0.003	5	3.4	5	2.5	1270	Plasma surface activation	[169]
Pomegranates	Solvothermal	MSM	150	9	4.3	14	0.06	10 ³		[175]

*Time constant of exponential function

**Time constant of bi-exponential function

MSM: Metal-semiconductor-metal

2.5 Remarks

The exciting properties, as well as the significant importance of ZnO on various applications, have been reviewed. Disadvantages of the current deposition, patterning and alignment processes of ZnO for device applications were discussed. Novelty aspects of additive manufacturing, especially in the fabrication of MEMS device could be helpful for ZnO device development, such as simple fabrication process and better device performance. Inkjet printing is a promising technique which is suitable for additive manufacturing of ZnO material. Beside investigation on a suitable method for additive manufacturing of ZnO nanostructure, there is a lack of study about engineering inkjet-printed micro-sized ZnO thin film for electrical applications. Also, solution-processed ZnO usually produces intrinsic defect film which may turn its properties via band bending due to air absorption. The band bending has substantial effects on the electrical properties of the printed film. Modification of the band bending could improve the printed device performance. This gap has become one of the motivations for this work.

Chapter 3: Ink preparation and inkjet printing of ZnO thin film

Ink preparation is vital for inkjet printing because the internal feature of the orifice is typically complicated, and the physical size of the orifice is usually smaller than 100 μm , in particular the standard ten picolitres cartridge which employed in this project has an orifice feature size of 21 μm . Hence, the agglomeration of ink could easily stick in the nozzle and causes failure during printing. Therefore, a stable and printable ink is required to deposit ZnO film successfully using inkjet printing. This chapter discusses the preparation and characterization of ink for printing of ZnO thin film. The hydrolysis reaction occurs during storing of the ink is the main cause of cluster formation and jamming nozzle. Also, it was found that printed ZnO using sol-gel method creates a polycrystalline film which composes of nano-sized grains. This finding is essential in defining the electrical properties of printed ZnO thin film.

3.1 Introduction

Owing to its long-term stability of the solution, the sol-gel method is an appropriate approach to prepare the ink for printing ZnO. In this method, stabilizers such as MEA and DEA are usually employed to control the pH of sol-gel and prevent the agglomeration of ZnO nanoparticles [105]. However, these stabilizing substances might pose health hazards to operators, especially when the solvent vaporizes during printing. Therefore they are not suitable for our printing condition which requires an unarmful ink recipe.

It is worth noticing that zinc salt can be dissolved at a low concentration in common solvents such as water and ethanol. Hence, the stabilizer is not necessary for a low concentration ink formula. However, the low concentration material might result in a thin

and discontinuous printed film, which is not suitable for fabrication of electronic device. It can be compensated by printing multi-layers and utilizing small droplet space to achieve overlapping of droplets. In this work, zinc acetate dihydrate, $(\text{Zn}(\text{COOH})_2 \cdot \text{H}_2\text{O})$, was selected as a zinc precursor, and ethanol was used as a solvent to prepare ink for inkjet printing. Some challenges in the printing of ZnO will also be addressed. Printed films were examined using FE-SEM and XRD to confirm that the ZnO thin film has been successfully printed.

The dimensionless figure of merit Z , which is defined by Reynolds number divide by the square root of the Weber number, is one standard to estimate the ink's compatibility [176]:

$$Z = \frac{Re}{We^{1/2}} = \frac{(\gamma \rho a)^{1/2}}{\eta} \quad (3.1)$$

where γ , η , and ρ are surface tension, viscosity, and density, respectively, and a is feature dimension of the orifice. From physical parameters of ethanol, such as surface tension is $\gamma=21.93 \times 10^{-3}$ N/m, viscosity is $\eta=1.0606 \times 10^{-3}$ Pa.s, density is $\rho=0.7813 \times 10^3$ kg/m³ at room conditions [177], and the feature size of the nozzle is $a=21 \times 10^{-6}$ m, the Z value of ethanol could be determined as 17.9. Although it is generally believed that the value of Z must fall in the range from 1 to 10, there is experimental evidence showing inkjet systems with the value of Z from 1 to 14, and even inkjet systems with $Z=91$ were stably printed [178-180]. Therefore, it is reasonable to use the ethanol to prepare the ink. Furthermore, ethanol has a low boiling temperature of 78 °C at room conditions, so it is easy to remove ethanol from the printed material by applying heat to the substrate during printing. The next section is discussing some factors that might affect the formation of the ink droplet.

3.2 Experiment

3.2.1. Preparation of ink for inkjet printing ZnO

Zinc acetate dihydrate ($\text{Zn}(\text{COOH})_2 \cdot \text{H}_2\text{O}$, Sigma-Aldrich) was dissolved in ethanol at different concentrations, such as 10 mM, 50 mM, and 100 mM, by magnetic stirring the mixture on a hot plate at 60 °C in one hour. The inks were filtered by 0.22 μm polytetrafluoroethylene (PTFE) filter and stored at room temperature before printing. The stability was observed by loading the ink into the cartridge to conduct printing and examining the generation of droplets using a high-speed camera installed in the printer (Figure 3.1d).

3.2.2. Printer and setup

A multi-material inkjet printer (Dimatix 2831, Fujifilm USA) was used for deposition of the material. The inkjet printer is equipped with a standard cartridge (DMC-11610), which has 16 piezoelectric nozzles. Figure 3.1a and Figure 3.1b show the schematic and the optical picture of the printer, respectively. The printer has two motorized horizontal axes, such as x-axis and y-axis, to control the relative position of the cartridge with the substrate to precisely deposit the ink droplets to the substrate. Also, the vertical axis aims to change the height of the cartridge to match the thickness of the substrate. The inkjet printer employs piezoelectric-driven nozzle cartridge, which can be moved in a horizontal plane during printing by two motorized axes. Optical image of this cartridge is shown in Figure 3.1c, which includes an ink container, electrical connecting pads, and piezoelectric nozzles. Besides, there are two cameras which are integrated into this system, such as one high-speed camera to support for the adjustment of the droplet formation and one standard

camera to align the coordination origin. In details, the high-speed camera helps to observe and optimize the droplet formation before and after printing. Hence, the stability of the printing process could be improved, and the amount of defective product could be reduced. The schematic of this system, which is depicted in Figure 3.1d, includes three main components such as the background light for highlighting the droplets, the nozzles which generate the droplets and the high-speed camera to capture the image of the droplets. Printing substrate can be held onto a platen whose temperature is controllable. In this chapter, the platen temperature was set at 40 °C, 50 °C and 60 °C when observing the coffee effect.

Figure 3.1. Printer structure and printing process to prepare the thin film. (a) Printer structure shows the main components and three-axes of the printer. (b) Optical photo of the printer. (c) Optical picture of the cartridge, including ink container and nozzles. (d) The schematic of the droplet watcher, which is the system to observe the generation of droplet before running the printing.

The piezoelectric element inside each nozzle can be controlled independently by applying a predefined electrical pulse. The dispersing waveform and voltage applied to the nozzles were manually adjusted to obtain a stable generation of the droplets. Although the distance between nozzles is fixed, the relative distance between droplets is adjustable by changing the saber angle, which is the angle between the nozzles array and the x-axis of the printer. The input design was prepared as a bitmap file, which each pixel represents for one droplet to be deposited, on a computer using the Microsoft Paint software (Microsoft). Controlling parameters such as the distance between droplets and the number of layers were adjusted in the controlling software of the printer.

3.2.3. Printing film and heat treatment

Figure 3.2. Printing process and thermal annealing for ZnO film: (a) printing zinc salt solution; (b) pre-heat treatment at 200 °C; (c) post-heat treatment at different temperatures, such as 400 °C, 600 °C and 800 °C

The printing process is described in Figure 3.2. The silicon/silicon dioxide (Si/SiO₂) substrate and the glass substrate were cleaned in acetone and isopropanol (IPA) before the printing. The distance between droplets was set at 10 μm. For printing of large area film, the multiple-nozzles mode was chosen to reduce the printing time. The substrate temperature was set at 60 °C when printing film for characterizations. After printing, the printed films were heated on a hotplate at 200 °C for 10 minutes for calcination to form ZnO. The post thermal annealing was conducted in a furnace at 400 °C, 600 °C and 800 °C for one hour to improve the film crystallinity.

3.2.4. Characterization

Formation of droplets was examined using attached high-speed camera which comes along with the printer. Coffee effect of a single droplet was studied using optical microscope and profilometer (PGI 2540, Form Talysurf). Morphology of printed film was studied using

FE-SEM (JOEL 7600F). All thin film sample was coated with a thin layer of platinum to improve the conductivity and image quality using sputtering in 60 seconds. Film crystallization and average grain size at different annealing temperature were characterized by XRD (PANalytical Empyrean). Thermogravimetric analysis was employed to study the formation of ZnO from zinc salt by the thermal decomposition process.

3.3 Results and discussion

3.3.1 Ink concentration effect

Figure 3.3. Droplet formation stability after 1 hour of different concentration inks: (a1) 10 mM ink, (b1) 50 mM ink, (c1) 100 mM ink at beginning of the test; (a2) 10 mM ink, (b2) 50 mM ink, (c2) 100 mM ink after about 1 hour shows the clogging of some nozzle. Scale bar is 400 μm .

The ink stability was tested directly by conducting the droplet generation in one hour, and the results are shown in Figure 3.3. It was found that the inks with a concentration of 10 mM and 50 mM were still stable after one hour of printing (Figure 3.3a₂ and Figure 3.3b₂). However, the ink with a concentration of 100 mM got clogging, such as some nozzles could not further generate droplet without manual cleaning (Figure 3.3c₂).

The nozzle jamming could be due to the agglomeration of material inside the orifice. The transmittance of the inks after preparing in Figure 3.4a shows that the 100 mM solution has a lower transmittance in the visible wavelength range comparing with the 10 mM solution and 50 mM solution. The lower transmittance of the 100 mM solution is due to the formation of agglomeration inside the liquid system, which can also be observed as the white color cluster inside the 100 mM solution, while the other solution is entirely transparent (Figure 3.4b). Hence the 100 mM solution is not suitable for the printing. On the other hand, considering that a higher concentration is better in the sense that it could make a thicker film within a same amount of time, the 50 mM solution is a suitable concentration of ink for inkjet printing of ZnO.

Figure 3.4. (a) The transmittance of the inks after preparing, the 100 mM solution shows lowest transmittance value. (b) Optical picture of zinc solution with different concentration, the 100 mM solution shows white clusters, and the others solution is transparent.

It is worth noting that the ink prepared from 100 mM solution is a highly concentrated solution of zinc salt, which quickly forms a white cluster after preparation. The possible mechanism is the hydrolysis reaction of zinc acetate. In details, the hydrolysis of zinc acetate in ethanol solution with the presence of water results in the formation of polynuclear zinc hydroxide clusters [181]. The proposed mechanism could be described by Equation 2.1 and Equation 2.2 (Chapter 2). Therefore, the agglomeration will appear during the storing of the ink, which could be observed in the case of 100 mM solution. It is because of the higher concentration of this ink might facilitate the hydrolysis reaction. Although complexing agent such as diethanolamine (DEA) and monoethanolamine (MEA) could be employed to retard the Zn(II) condensation and stabilize the solution [107], they are hazardous materials and their utilization could be harmful to the user of the printer, hence the employment of such complexing agents was avoided in this project. Instead, a lower concentration of zinc salt such as 50 mM solution, which can be stable for a few hours, was employed as an ink for inkjet printing.

3.3.2 Coffee effect in printing ZnO

When an ink droplet touches a surface, and the solvent vaporizes, it usually leaves a ring of material on the substrate; this phenomenon is well known as coffee effect [182]. The coffee effect is a commonly observed phenomenon of printed patterns made by inkjet printing. Figure 3.5a₁-c₁ shows the optical microscopic images of the printed single droplet with different substrate temperature, and the Figure 3.5a₂-c₂ shows the 2D profile of these droplets. The white ring caused by coffee effect could be clearly observed in all the samples. Because the temperature of the substrate is lower than the temperature required for decomposition of zinc acetate, which is about 150 °C as will be discussed in the Section 3.3.4, those white ring could be the remaining of zinc acetate after solvent vaporization and zinc hydroxide complexes as a product of hydrolysis reaction [181].

The increment of substrate temperature led to the decreasing diameter of the spreading droplet as can be seen in Figure 3.5d. When the substrate temperature was set at 40 °C, the average diameter of the droplet is about 58 μm. Increase the substrate temperature to 50 °C results in a significant decrease of mean diameter to 49 μm. The average size of spreading droplet slightly reduce to 44 μm when the substrate temperature is 60 °C.

Figure 3.5. The coffee effect with different size of the spreading droplet. (a₁), (b₁), (c₁): Microscopic image of droplets; and (a₂), (b₂), (c₂): profile of the droplets printed at different substrate temperature (a) 40 °C; (b) 50 °C; (c) 60 °C. (d) Effect of surface temperature on droplet spreading size. Scale bar is 20 μm.

It is worth to investigate the coffee ring effect because printing resolution is an important factor for the fabrication of the small-sized device. Furthermore, many studies have addressed this coffee effect as a cause of poor printing quality, such as it could reduce the spatial precision of printed patterns [101, 183]. It is because the spreading droplet could make the printed patterns larger than expectation, so it might reduce the resolution of printed patterns. Hence, reduce the size of printed patterns is crucial for improving the resolution of the printed pattern.

Dot per inch (DPI) is defined by the number of the droplet that can be printed on an inch of the substrate [184]. The DPI could be determined using equation $DPI = 25400/d_{\text{droplet}}$, where d_{droplet} is the size of the spreading pattern. The mean DPI of the printed droplet with substrate temperature at 40 °C, 50 °C and 60 °C could be calculated as 438 DPI, 518 DPI, and 577 DPI, respectively. Therefore, increase the substrate temperature could improve the resolution of printed products and it can benefit the fabrication of small size device.

It is worth noting that this inkjet printing could not form a homogeneous pattern due to the coffee effect. Such unevenness should be considered when employing inkjet printing for fabrication of the electronic device because of the engineering constraints of shape and size of the printed pattern [183]. Therefore, the prohibition of coffee effect has been widely studied.

Generally, the coffee effect is the result of the flow toward the edge of the droplet due to the higher evaporation rate at the edge. This convective flow could be counteracted by Marangoni effect, which is induced by the surface tension gradient of vaporizing mixture solvent [185]. Also, the coffee effect could be reduced by adding a polymer binder to change the surface tension of the ink [186]. However, the additive polymer could cause a reduce the quality of the printed film due to polymer residue and poor performance of the fabricated device such as low on/off ratio of UV photodetector [138]. It is because the existence of the polymer at grain interfaces could prohibit the electron transportation between the semiconductor grains. Normally, the additive polymer must be decomposed using high-temperature heat treatment which is not suitable with the polymer substrate. Hence, this method is not preferred in this project. Instead, the approach which was employed in this project is using the heating substrate to reduce the spreading size of the

droplet, therefore the size of the printed pattern could be reduced. Although this approach could not completely suppress the coffee ring effect, the size of the printed pattern could be reduced which means the precision of the printed pattern could be improved. This approach is applied in Chapter 4 to improve the spatial precision of the printed pattern.

3.3.3 Pre-heat treatment induced film wrinkling

Figure 3.6. Optical property changing of printed material as-printed and after preheating. (a) Transmission spectra. (b) Optical images show the significant change after the annealing was applied

The transmittance spectrums of the film before and after pre-heat treatment are shown in Figure 3.6a. Figure 3.6b₁ and Figure 3.6b₂ are the optical images showing the transparency of film before and after pre-heat treatment, respectively. The as-printed film has transparency of about 70% in the visible range. The transparency remarkably dropped to 10-20% after the pre-heat treatment was applied. Hereby, the pre-heat treatment has transformed zinc precursor to ZnO and created a rough surface which turns the optical properties.

Some studies have reported the same structure of wrinkle surface of ZnO thin film prepared by sol gel method and it could bring certain benefits to the performance of the functional

devices. For example, enhanced light scattering by wrinkle film could increase light harvesting efficiency [187]. Also, the wrinkle structure was proved to help improving photovoltaic efficiency of dye-sensitized solar cells [188]. It could be explained that a wrinkle surface could absorb more light by the scattering of light when approaching the surface, therefore wrinkle surface could obtain a higher efficiency comparing with flat surface semiconductor.

Figure 3.7. FE-SEM image of the film (a) before and (b) after pre-heat treatment. Corresponding confocal microscopic images show the surface profile of films (c) before and (d) after pre-heat treatment, which shows a significant change in surface roughness. Scale bars are 10 μm

The morphology of as-printed film and the pre-heated film is shown in the FE-SEM images in Figure 3.7a and Figure 3.7b, respectively. The film before pre-heat treatment exhibits a flat surface with many aggregated particles. Meanwhile, the film after pre-heat treatment shows a wrinkled surface. The film wrinkling is the primary cause of reducing of film

transparency after pre-heat treatment because wrinkle structure could increase the light absorbance of the thin film. From the confocal microscopic scanning results, the surface roughness of as-printed film could be found to be $R_a=0.4107\text{ }\mu\text{m}$, and that of the pre-heat-treated film is $R_a=0.6577\text{ }\mu\text{m}$. Although these results are not as precise as atomic force microscope measurement due to the limiting resolution of the optical system, they are evidence for the appearance of the uneven surface along with the FE-SEM images. This rough surface makes the film opaque because light is scattered by the ununiform surface.

During the drying of the solvent, compressive stress appears in the solution-processed film because of the mismatch of thermal expansion of the film and the substrate [189]. It is also because the withdrawal of the solvent introduces the converting of the film from viscous to viscoelastic [188]. This internal stress of the film during the heat treatment makes the film being bent. Therefore, the wrinkle structure is formed by the pre-heat treatment process. Also, it is proposed that the pre-heat treatment temperature which is higher than the solvent boiling point is critically important to form the wrinkle of the film because it could promote the rapid withdrawal of the solvent [189]. Hence, with the pre-heat treatment temperature of $200\text{ }^{\circ}\text{C}$, the printed film exhibits a wrinkle structure. The potential benefit of the structure with semiconductor film will be discussed in the next sections.

3.3.4 Crystallinity of film by different annealing temperatures

Figure 3.8. (a) XRD patterns, (b) Full width at half maximum (FWHM) values of three main peaks, i.e. (100), (002) and (101), and (c) grain sizes of printed ZnO films.

XRD analysis was employed to study the effect of heat treatment to film crystallinity, and the results are shown in Figure 3.8. The peaks located at 31.8° , 34.4° , 36.3° , 47.5° , 56.6° , 62.9° , 66.4° , 68.0° , 69.1° can be indexed to planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively, of ZnO (JCPDS no. 36-1451), which are corresponding to the hexagonal wurtzite structure [190]. These results prove that ZnO thin film has been successfully deposited by inkjet printing.

Table 3.1. Crystallinity parameters of printed films on Si/SiO₂ substrate at different annealing temperatures

Temperature (°C)	FWHM (°)			Grain size (nm)		
	(100)	(002)	(101)	(100)	(002)	(101)
200	1.28	1.28	2.25	6.8	6.8	3.9
400	0.56	0.57	0.62	15.5	15.1	14.1
600	0.47	0.50	0.54	18.4	17.3	16.1
800	0.42	0.42	0.45	20.5	20.8	19.4

The average crystallite size D could be estimated from the XRD result using the well-known Scherrer equation [191]:

$$D = \frac{k\lambda}{\beta_D \cos \theta} \quad (3.2)$$

where k is shape factor equal to 0.94, λ is the radiation's wavelength equal to 0.1540598 nm, β_D is the FWHM value by radian, and θ is the diffraction angle. The unannealed sample has an average estimated grain size of 6.8 nm, 6.8 nm and 3.9 nm which are according to (100), (002) and (101) plane, respectively. The grain size is very small which is in the range of quantum size. Figure 3.8b-c show that the average grain size increase when a higher annealing temperature was applied. For example, the crystallite sizes for the printed ZnO along the (002) planes are 15.1 nm, 17.3 nm, and 20.8 nm for the sample annealed at 400

°C, 600 °C, and 800 °C, respectively. These results show that the thermal annealing from 400 °C to 800 °C is sufficient for sintering of printed ZnO thin film to sinter nanoparticles into larger particles and improve film crystallinity.

The main process to form ZnO in this scheme could be simply described by two steps: the solvent vaporization process and thermal decomposition of the zinc acetate dihydrate. The vaporization takes place during printing due to heating from the substrate holder and the thermal decomposition happens during pre-heat treatment and annealing. ZnO was formed during a well-known thermal decomposition of zinc acetate dihydrate process [192]. To understand the thermal decomposition process of the zinc salt, thermogravimetric analysis (TGA) of zinc acetate dihydrate is given in Figure 3.9. Under thermal heating in air, the water removing took place at a temperature from 60 °C to 100 °C, which resulted in a weight loss of about 15% (Equation (3.3)). Then, the decomposition of the zinc acetate took place at a temperature higher than 150 °C and the process completely finished at around 350 °C with the remaining weight of 22.6 %. Therefore, heat treatment at higher than 350 °C is required to completely decompose zinc salt to form ZnO. In this step, basic zinc acetate, $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$, was formed, as can be seen from equation (3.4). This compound then takes part in the reaction with water to produce ZnO (Equations (3.5) and (3.6)). The other products of the reaction are water (H_2O), carbon dioxide (CO_2), acetone ($(\text{CH}_3)_2\text{CO}$) and acetic acid (CH_3COOH) [193]. These results are well matched with those reported in XRD analysis and they could explain for the reaction to form ZnO in this inkjet printing scheme.

Figure 3.9. Thermogravimetric analysis result of zinc acetate dihydrate in air show the effect of temperature to formation of ZnO

Besides that, as discussion in the ink preparation section, when zinc acetate dihydrate was dissolved in alcohol, a series of reactions including hydrolysis and polymerization result in the formation of zinc hydroxide complex, $\text{Zn}(\text{OH})_2$, which exists as residual after solvent vaporizing as shown in XRD pattern of the sample ZnO-200 [181]. Under thermal annealing, zinc hydroxide was also decomposed to ZnO, as can be clearly seen in XRD pattern of samples with thermal annealing of above 400 °C, which does not exhibit peaks related to this residue.

3.3.5 Optical bandgap shifting of printed film

Figure 3.10. (a) Optical transmittance. (b) Optical absorbance. (c) Representative Tauc plot of the printed films

The transmittance and absorbance of printed films are shown in Figure 3.10a, b, respectively. The film without annealing has low transmittance from 4 % to 20 % in the range from 300 nm to 780 nm. The transmittance of annealed films has increased to the range of 5 % - 27 % and 5 % - 30 % for film annealed at 400 °C and 600 °C, respectively. A reverse trend is observed for the absorbance value, which decreases when thermal treatment was applied.

The Figure 3.10c shows the Tauc plot, which describes the relationship between optical absorption strength $\alpha h\nu$ and the difference of photon energy $h\nu$ and optical bandgap E_g .

The Tauc plot can be determined by the following equation [194]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (3.7)$$

where α is the absorption coefficient, and A is a proportionality constant. The Tauc plot can be used to estimate the optical bandgap of printed film.

The unannealed samples exhibit bandgap values from 3.01 eV to 3.03 eV. Meanwhile, the samples annealed at 400°C show bandgap values from 3.08 eV to 3.09 eV, and the samples annealed at 600°C show bandgap values from 3.05 eV to 3.09 eV. Although there are fluctuating values of the optical bandgap of the annealed samples, there is an increasing trend of the optical bandgap after thermal treatment. However, the difference between samples is minor which shows that thermal annealing does not significantly turn the optical bandgap of printed film.

It was reported that the sol aging time has a significant effect on optical bandgap of the sol-gel derived ZnO thin film. In details, a short aging time results in a small bandgap of the film [195]. Because the ink employed in this study is not stable for a long-time aging procedure due to the aggregation, it must be printed within a few hours which leads to the smaller bandgap of the printed film comparing with bulk material.

Although quantum confinement effect causes the blue-shifting of bandgap when particle size in the range of a few nanometers [196], the smaller bandgap of the printed film comparing with bulk material could be contributed to the defects and residues. The optical bandgap value is similar to reported sol-gel prepared ZnO thin film, which also observed the increasing optical bandgap [195]. Hereby, the increasing of the bandgap of annealed samples could be contributed to the reducing of defects and the increase in carrier concentration [197].

3.4 Conclusion

ZnO film was successfully deposited using inkjet printing via tuning of the ink composition and printing conditions. The zinc precursor solution with 50 mM concentration is compatible with inkjet printing. XRD results show that inkjet-printed ZnO thin film has a polycrystalline structure with nano-sized grains. The film with pre-heat treatment shows a small average grain size from 3.9 nm to 6.8 nm, depending on the crystal direction. Heat treatment at higher temperature induces a better crystallinity of inkjet-printed ZnO, such as increasing the grain size up to 20.8 nm at 800 °C. The film without annealing exhibits an optical bandgap value of about 3.01 eV. The optical bandgap slightly increases which probably due to the reducing of residue and increasing carrier concentration because of high annealing temperatures. This success of printing using the facile recipe presented in this chapter could encourage the development of additive manufacturing of ZnO for further applications.

Chapter 4: Printed small-size flexible ZnO thin film for UV photodetector

Fabrication of small-size patterns of inorganic semiconductor onto flexible substrates is a major concern of manufacturing wearable devices for measuring either biometric or environmental parameters. Using an approach proposed in the previous chapter, the ZnO sol-gel method was employed to prepare the ink for inkjet printing sub-millimeter size patterns. The printing of ZnO film and the effect of printing parameters on film morphology are presented. Bending test proved that the printed device could works as a flexible sensor, and mechanism of this bendable film was discussed. The results show that inkjet-printed ZnO is applicable for the fabrication of miniaturized flexible electronic devices.

4.1 Introduction

UV light has been commonly known for its harmful effect on human health, and it is the primary cause of skin cancer, such as causing the mutation in p53 tumor suppressor genes [198]. Therefore, monitoring of UV exposure in sunlight is vital in preventing skin illness, and personal monitoring is required because the received UV dose varies by each person [199]. Recent developments in wearable technology provide an advantaged solution for real-time monitoring and warning users about surrounding threat or even their biometric parameters [200]. Hence, a flexible UV photodetector can provide an adequate solution for individual UV monitoring by the capability of easily embedding into a wearable device, which is capable of working under inherent bending due to normal user activities.

In this chapter, an all-inkjet-printing method is introduced, which is an additive manufacturing process, for the deposition of flexible inorganic semiconductor thin film patterns with a high precision shape. The inkjet printing was employed for both fabrications of conductive material and semiconductor such as silver and ZnO, respectively. Inheriting from the previous chapter, ZnO ink was prepared using a facile sol-gel recipe, which contains only the zinc salt dissolved in ethanol. Following sufficient heat treatment forms semiconductor thin film pattern for fabrication of flexible ZnO UV photodetector.

The device response to UV light was characterized to evaluate the functionality of printed material. Also, the operation of the sensor was observed under bending of the film. Printed film crystallinity and morphology are characterized to unveil the photosensitive mechanism. The robust mechanical flexibility of the device, which was proven by the ability to work under high bending ratio and multiple cycles, shows it is a suitable candidate for wearable device for in-situ monitoring UV exposure which is potential for preventing the risk of skin cancer by sunlight.

4.2 Experimental section

4.2.1 Printing of the ZnO thin film pattern

Construction of the printed flexible device, which employs a metal-semiconductor-metal (MSM) structure, is depicted in Figure 4.1a. The entire printing process of ZnO thin film using a simple sol-gel recipe, including printed silver electrodes for UV photodetector, is schematically described in Figure 4.1b.

Figure 4.1. The schematically structure of photo-detecting sensor fabricated by inkjet printing. (a) The device structure of metal-semiconductor-metal. (b) The all-inkjet-printing fabrication process of the UV sensor.

A 25 μm -thick Kapton® polyimide film (Dupont) was utilized as the substrate for fabrication because it is highly chemical stable and high-temperature resistance of up to 400 °C. Before printing, the polyimide substrate was cleaned with acetone, then rinsed with isopropanol and blown up with a hand blower. Zinc precursor solution (50 mM) was prepared by dissolving zinc acetate dihydrate (Sigma-Aldrich) into ethanol (99.5%, Merck) using magnetic stirrer at 60 °C for 1 hour until obtaining a transparent solution. The

solution was then filtered by 0.22 μ m PTFE filter to eliminate large particles which might block the nozzles during jetting of ink droplets.

Effect of substrate temperature during printing on the film morphology was studied by applying different substrate temperatures of 40°C, 50°C, and 60°C, respectively. Since the ink concentration is low, the thickness of a single spreading droplet is estimated as thin as tens of nanometers. The spacing between droplets was set at 10 μ m, and the printing of ZnO thin film was repeated for ten times to increase the thickness of the film. The designed dimension of the rectangle pattern is 200 μ m by 400 μ m (20 pixels by 40 pixels). Drop-casting of the zinc precursor ink onto polyimide substrate was used to prepare samples for XRD characterization for investigating the film crystallinity.

4.2.2 Heat treatment

After the printing, the substrate with the printed film was immediately put on a hotplate at 200°C for 10 minutes for total vaporization of solvent and transformation of zinc salt into ZnO. The post heat treatment was conducted in a furnace at 400°C for 1 hour to sinter the printed ZnO. This temperature ensures the survival of the polyimide substrate.

4.2.3 Printing of the silver electrodes

The pair of silver electrodes was then printed over ZnO pattern, creating the metal-semiconductor-metal structure of photo sensor device as described in Figure 4.2a. The printing was conducted with the substrate heated at 60°C. The silver electrode was aligned using the built-in camera of the printer. The printing silver electrodes have a gap of about 100 μ m (Figure 4.2b). Printed electrodes were then cured in an oven at 150°C for 1 hour to improve the conductivity. Details of printing silver process are given in Appendix B.

The whole process is based on an additional material process, which does not involve any removing of material. The patterns, including conductive electrodes and functional semiconductor material, has been formed via a digital design and implemented by a single Dimatix inkjet printer. Figure 4.1c, which is the optical photo of the as-fabricated micro-sensor, illustrates the device flexibility. Optical microscopy image of the sensor is shown in Figure 4.1d, which depicts the structure of the printed sensor with printed ZnO pattern and two silver electrode.

4.2.4 Characterization of the printed device

Schematic of electrical characterization is described in Figure 4.2c. The light sensing performance of the all-inkjet-printed device was tested under UV light illumination using a UV lamp as the light source (Lightningcure LC5, HAMAMATSU). The light intensity is set at 47.5 mW/cm^2 and 4.7 mW/cm^2 for high and low light intensity scenario, respectively. The printed sensor was powered by a DC power source, and the device current was measured by a multimeter (Agilent 34410A) connected with a computer to synchronize data. A UV LED (S5050, Intelligent LED Solutions), which has an emitting peak at 370nm, was utilized in I-V characterization as a portable and low-intensity light source. I-V characteristic of the device was measured by a semiconductor analyzer (HP 4156B) and probe station under the dark condition and UV illumination by the UV LED. Morphology of printed film was characterized by SEM (JEOL JSM 5600), FE-SEM (JOEL 7600F) and profilometer (Form Talysurf PGI 2540). Film crystallinity was studied by XRD (PANalytical Empyrean).

Figure 4.2. (a) The optical image illustrates the flexibility of the printed sensor. (b) Enlarged optical microscopic image shows the printed ZnO sensor on the polyimide substrate. (c) The schematic of the testing setup for measuring device response to UV illumination.

4.3 Results and Discussion

4.3.1 Film morphology and structure

Figure 4.3. Characterization of the printed film structure. (a) Low magnification image shows the device with Metal-Semiconductor-Metal structure. (b) High magnification FESEM image shows a flat surface in the center area of the printed pattern. (c)(d) Wrinkled film in the coffee effect ring.

The structure of printed ZnO thin film pattern used in UV photodetector after heat treatment is presented in Figure 4.3. Figure 4.3a shows the SEM image of the ZnO deposited on the flexible substrate. It can be clearly seen that the patterns were printed with proper alignment, and they have relatively sufficient precision at a small size. Figure 4.3b-d show the surface morphology of printed ZnO pattern. The central area of the printed pattern is very flat (Figure 4.3b). Due to the coffee effect, most of the material focus in the

outside area, such as there is a ring of crumpled ZnO film in the boundary of the pattern (Figure 4.3c-d), which also features a hollow part in the middle area.

Rectangle patterns were printed with a dimension of 20 droplets by 40 droplets on glass substrates at 40°C, 50°C, and 60°C. The coffee effect is clearly demonstrated by surface profile of the printed ZnO patterns on the glass substrate (Figure 4.4a), which shows a much thicker material section in the outer area with the peak height range from 100nm to 400nm. This coffee effect ring is due to a lower temperature of the substrate causes a lower vaporization rate of the droplet when touching the surface as discussed in Chapter 3. This is not a result of single droplet but a composed of many droplets gathering to form a bigger droplet which is easier to spread over the substrate. Due to the heat from the platen, the solvent vaporizes and leaves behind the spreading pattern of the coffee effect, which is mostly composed of zinc salt. In fact, most of the printed material settle at this ring pattern.

Figure 4.4. Effect of substrate temperature on shape and profile of printed pattern. (a) The surface profile of the printed patterns at different depositing substrate temperature. (b)(c)(d) Printed pattern on the glass at different substrate temperature: 40°C (b), 50°C (c), 60°C (d). (e)(f)(g) The printed sensor on polyimide at different substrate temperature: 40°C (e), 50°C (f), 60°C (g). The scale bar is 200 μm . The dashed line rectangles show designed pattern, and the white shapes are printed pattern which are larger than designed pattern.

The effect of substrate temperature during deposition on the morphology of the film was investigated. As can be seen in Figure 4.4a, the film deposited at 60°C has a better dimensional precision, while those of the film deposited at 40°C is twice as big as the

designed pattern, which is a rectangle size of 200 μm by 400 μm . Also, the same conclusion is applicable in Figure 4.4b-d, which are the optical microscope images of printed patterns on glass substrates.

The ZnO film printed on the flexible substrate possessed similar effect of temperature as the patterns printed on the glass substrate (Figure 4.4e-g). It could be due to a higher evaporation rate of the droplet when it touches a hotter substrate. On the other hand, at a lower substrate temperature, the droplets have more change to spreading out on the surface and reduce the precision of printed pattern. The higher substrate temperature, the faster the vaporization of solvent and lesser spreading of the droplet which leads to a precise pattern dimension. Therefore, the precision of the printed pattern could be improved by increasing the temperature of the substrate during printing.

XRD measurement was employed to study the effect of heat treatment on the crystallinity of the film. Similar to the previous chapter, peaks corresponding to the wurtzite structure of ZnO were observed in printed samples. The obtained results show that ZnO thin film patterns were successfully deposited on polymer substrate. Figure 4.5a shows an increase in peak intensity by increasing the substrate temperature during the depositing. Also, the (002)/(101) peak ratio of films deposited at 40°C, 50°C and 60°C are 1.66, 1.87 and 3.25, respectively. While that value of the randomly oriented film is 0.44, our observed values show that there is a slightly preferred orientation of c-axis (002) [201]. Figure 4.5b shows that the film which had been treated in hotplate at 200°C had already transformed to ZnO crystallinity which has peaks of hexagonal wurtzite structure while the film as-deposited at 60°C does not show any peak belong to ZnO structure. The film with annealing at 400°C

has the (002)/(101) peak intensity ratio of 3.25, higher than that of the film only treated at 200 °C, which is 2.99.

Figure 4.5. The X-ray diffraction (XRD) patterns of deposited ZnO film. (a) XRD patterns of different depositing temperature of the substrate, at 40°C, 50°C, 60°C, after being treated at 200°C and 400°C. (b) XRD patterns of different heat treatment temperature, at 200°C and 400°C, of the film deposited at 60°C. The blue patterns from two figures are from the same sample for comparing purpose.

The c-axis preferred orientation is widely observed in solution-processed ZnO thin film, which could be contributed to the smallest surface energy when the film is growing in this orientation [202]. However, the difference in film structure could be explained by the effect of the vaporization process of solvent during preheat treatment. During this process, the remaining solvent is drawn from the film [189]. This drying process happened at the same time with thermal decomposition of zinc acetate to create the thin film, which started to take place at about 150 °C.

In details, when printing at a lower substrate temperature, there could be more solvent remaining in the gelled film. Hence, in case of the film printed at 40 °C, there was a higher rate of evaporation during the preheat treatment which caused a violent disturbance on the film structure. Printing at 60 °C, which is near the boiling point of ethanol, might result in a lesser remaining solvent inside the film. Hence, the printed film structure was less

disturbed by the vaporization during pre-heat treatment process comparing with the film printed at a lower temperature. Therefore, the c-axis preferred orientation was obtained due to the growth in this direction consumes lesser energy comparing with the other direction.

However, by testing of drop-casting samples prepared at different substrate temperature, it was found that the substrate temperature has a minor effect to the electrical performance of the deposited sample, such as photocurrent are on the same level between samples prepared at different substrate temperature. In details, under the same illumination condition, the photocurrent of devices prepared at 40 °C, 50 °C, and 60 °C are $1.50 \pm 0.53 \times 10^{-7}$ A, $1.50 \pm 0.52 \times 10^{-7}$ A, and $2.0 \pm 0.65 \times 10^{-7}$ A, respectively. Although the difference between samples is small, the larger photocurrent of samples prepared at 60 °C could be contributed to the better of crystal quality, such as the film suffers less disturbance during the pre-heat treatment process.

Also, the obtained c-axis preferred orientation of ZnO thin film is of interest because c-axis preferred orientation is the critical criteria for piezoelectricity of ZnO [41]. It is due to the hexagonal wurtzite structure ZnO is a polar crystal along the c-axis because of its arranging of atomic [203]. For the film preparing by sputtering, only c-axis preferred orientation film shows piezoelectricity [41]. Furthermore, the sol-gel prepared thin film which shows c-axis preferred orientation also exhibits piezoelectricity [204]. It is because the piezoelectricity of grains could cancel each other which results as a nonpiezoelectric film in a random orientated structure. Meanwhile, when the film exhibits c-axis preferred orientation, the grains have the same polarization and the film have piezoelectricity [41]. Hence, this result is promising for further studied to investigate the piezoelectric properties of printed ZnO thin film.

4.3.2 Photoresponse of device

Because of the better precision over lower printing temperature, the sample printed with substrate set at 60 °C was chosen for testing of electronic properties. The linear I-V characteristic (Figure 4.6a) proves that the contact between printed ZnO film and the silver electrode is the Ohmic contact. It could be explained by the close value of ZnO electron affinity ($E_a=4.5$ eV) and the work function of silver ($\phi_{silver}= 4.2$ eV) is supposed to form an Ohmic contact [81]. Also, it is possible that the printing of silver suspension promotes the spreading of silver onto ZnO crystallinity and create a firm contact between two materials. In the I-V characterization, a low-intensity light, which is about 3.3 mW/cm² is employed. The measured dark current was as low as $I_{dark}= 4 \times 10^{-12}$ A, and the current under UV light was $I_{light}=1.41 \times 10^{-8}$ A at a 5 V bias voltage. Despite such a low-intensity UV illumination, the changing level of current is enormous, such as the on/off ratio is 3525.

Figure 4.6b shows the multiple operations of the printed sensor when the UV illumination was toggled every 5 seconds with a bias voltage of 5V. Under high-intensity UV illumination of 47.5 mW/cm², the printed ZnO thin film photodetector showed its capability of fast response and recovery upon turning UV light on and off, respectively. Upon illumination, the photocurrent boosted to a very high value of 10 μ A following by a rapid decaying even under high-intensity UV illumination. However, this trend was inverted in the case of applying a low-intensity UV. In which, under low light intensity at 4.7 mW/cm², there is no decaying of photocurrent under UV illumination has been observed. We believe that the high-intensity UV illumination causes the degrading and slow recovery of photocurrent. In other words, response speed depends on light intensity.

For further investigation of the response/decay time of the sensor, we conducted one cycle operation of the sensor under the two light intensity illumination conditions. In the case of high-intensity UV, the rise time of light response of printed ZnO film is about 0.3s (Figure 4.6c). The decaying photocurrent is fitted using bi-exponential function equation with decay time constants were $\tau_{d1}= 0.104\text{s}$ and $\tau_{d2}= 0.537\text{s}$. However, in the case of low-intensity UV light, the response/decay time is much longer, i.e., the rise time is about 8.5s, decay time constants by bi-exponential fitting are $\tau_{d1}= 0.756\text{s}$ and $\tau_{d2}= 4.110\text{s}$, as can be seen in Figure 4.6d. Generally, response/reset time of the previous study is in the range of seconds [164, 205] or even hundreds of seconds [206]. Our fastest results, where the high-intensity light was applied, are comparable to the other reported response/reset time enhanced ZnO-based photodetectors. For example, a 0.8s reset time was obtained by employing ZnO nanowire with Schottky contact, although the best reset time of 20 ms could be reached when surface treatment of the nanowire is applied [207], and the other works that employ nanostructures [208]. Based on the experimental result, it can be concluded that the fabricated device has high performance in term of response and decaying time under high UV intensity illumination. These experimental results show that our printing precursor is a suitable candidate for digital fabrication of UV photodetectors device base on thin film developed from ZnO sol-gel.

Figure 4.6. The performance of the printed UV photodetector and effect of light intensity. (a) I-V characteristic in the dark and under UV illumination (measurement after 10 minutes under illumination). (b) Multi-operations of the printed device by 5 seconds on and off UV light, under low intensity and high intensity, the bias voltage was set at 5V. The rise and decay time of device current under (c) high-intensity UV light and (d) low-intensity UV light.

Many studies have suggested that the photoconduction of ZnO originates from the photo-generated electron-hole pair as well as the adsorption and desorption of surface trapped oxygen in the ambient air [209-211]. At a normal condition, oxygen in ambient air is trapped on the surface of the metal oxide semiconductor by receiving a free electron from the lattice, $O_2 \text{ (gas)} + e^- \rightarrow O_2^- \text{ (absorbed)}$ (Figure 4.7a). Hence, the concentration of free charge carrier at the surface of the grain reduces, and a depletion layer is formed near the surface of the grain [24]. Therefore, the band bending occurs at the grain-grain interface as shown in Figure 2.5. This energy barrier limits the transportation of electrons through grain interface, therefore it lowers the dark current of the device under applied external electrical field [40].

Under UV illumination, the separation of electron-hole pairs occurs when high-energy photons are absorbed by semiconductor lattice. These photo-generated electron-hole pairs increase the concentration of charge carrier in ZnO crystal. The holes migrate to the surface and recombine with the trapped electron. Hence, the oxygen species are released, O_2^- (absorbed) + h^+ $\rightarrow$ O_2 (desorbed). Therefore, the depletion layer at the grain surface is narrowed (Figure 4.7b). As a result, the energy barrier at the grain boundary is lowered and the conduction channel is widened which promotes the transportation of electrons [24]. Both processes, the charge carrier generation and the oxygen desorption, increase the conductivity of the film, therefore increase the current running through the device under the applied electric field. At the same time, electron-hole pairs recombine at recombination centers such as defect states and oxygen species reabsorbed to grain surface. When these processes balance under steady UV illumination, the photocurrent will reach an equilibrium state.

Figure 4.7. Schematic of the photoresponse mechanism of the printed photodetector. (a) Under dark condition: oxygens are absorbed to the surface by receiving an electron, creating a depletion layer. (b) Under UV illumination: electron-hole pairs are generated, then holes migrate to the surface and receive trapped electron, release absorbed oxygen; therefore, the depletion layer is narrowed, and the conduction channel is widened.

When the UV light is turned off, the generation of electron-hole pairs is ceased, which reduce the concentration of charge carrier in the semiconductor crystal. Furthermore, the oxygen species in the surrounding environment are reabsorbed to the surface of the grain and increase the band bending at the interface of the grains. Both processes enlarge the film resistance and cause the photocurrent to reduce gradually [101].

In case of strong intensity illumination as shown in Figure 4.6b-c, the response of sensor is different with weak intensity illumination, such as after reaching the maximum value, the photocurrent notably reduced even under steady UV illumination. This phenomenon is known as anomalous photocurrent decay and it strongly relates to defects of ZnO [212]. This phenomenon is common for metal oxide semiconductor which is widely reported by many studies [170, 213-215]

This phenomenon could be explained by the interaction of the material with ambient air. Under UV illumination, the photocurrent initially increases to the maximum value. Then, instead of reaching equilibrium, the photocurrent decreases even under steady UV illumination. It was proposed that there are two processes involving in this phenomenon: the surface trapping and charge carrier recombination at defect states creating the reduce of charge carrier concentration [212]. In this case, it is proposed that because of strong UV illumination, most of the oxygen species have quickly desorbed from the surface of the material which results in a high-speed response sensor by rapidly increasing photocurrent. These molecular is reabsorbed to the surface of the material and this process reduces the photocurrent. However, because of most of oxygen species have been desorbed, there is no counterbalance of absorption and desorption process. Therefore, the photocurrent tends to decrease after a short rising under high-intensity UV light.

There is an evidence for this hypothesis, such as after UV light is turned off, the photocurrent in the next cycle is recovered comparing with its value when UV light is turned off in the previous circle. It is because when UV light is turned off, the oxygen species have more time to be reabsorbed to surface of ZnO film. Hence the properties of ZnO film is partially recovered, so it exhibits a similar response in the next cycle.

The coffee ring with crumple surface could play an essential role in photoresponse of the printed device because the thickness of the wrinkled area as measured from profilometer is significantly larger than the center area. Hence, the photocurrent could be mainly contributed by this wrinkled ring. It is also possible that the wrinkled film area could have effects on the performance of the device by increasing light scattering in wrinkled structure. The extraordinary surface area of polycrystalline structure could increase the active area to absorbed species, such as oxygen and water. A likely mechanism for this is the interconnecting-interpenetrating of nanostructure which affect the potential barrier via depth of depletion layer [47]. These discussions are going to be further investigated in the next chapter, where electrical properties of printed film were studied.

The UV light sources using in this project are UV LED and xenon lamp, which generate a lot of heat during their activation. Therefore, the output light might be not stable. Due to the complexity of the experiment, such as the instability of UV light sources, the response of the sensor might be affected. Furthermore, because the thin film absorbs oxygen in air ambient, its property could vary with air conditions, such as moisture and pressure.

4.3.3 Bending testing

Further tests on the device bending are conducted to confirm the flexibility of the printed device. The printed sensor was mounted in a micro-positioner with one fixed and one moving stage which allow adjusting the bending radius of the flexible device (Figure 4.8a). Various range of bending was applied, and the performance of the printed device is shown in Figure 4.8b. The small bending radius, such as 1 mm and 2 mm, slightly affect the photocurrent; whereby, the more the sensor is bent, the lower the photocurrent. The result shows that critically bending in the way that stretching the film will decrease the photocurrent of the printed device.

Figure 4.8. Bending testing for the printed flexible device (a) The experiment setup for testing that allows adjusting bending radius of the printed sensor. (b) Different response of device according to different bending radius. (c) Stability tests for multiple bending cycles.

However, it is observed that the photocurrent was almost stable when it was bent within a larger radius, i.e., from 3mm to 10mm. Therefore, the device performance is independence with regular deformation. Also, bending the device multiple times will not weaken the operational stability of the device as shown in Figure 4.8c. The bending was repeated more than 500 times, and no degrading in device performance could be spotted. The above results prove that our device is capable of working as a wearable device.

Figure 4.9. Morphology of the film with (a) no bending and (b) under bending show a minimal change to film structure under bending. Possible mechanism of the minimal damage caused by bending: (c) the cross-sectional picture of printed film on silicon substrate show the structure of wrinkles; (d) the wrinkle response to bending like a spring which reduces the damage to the film.

By studying the morphology of film before and after bending, the root of the notable performance under bending was proposed. Small cracks with size of a few micrometers were found in unbend film as can be seen in Figure 4.9a-b. These cracks could be the result

of handling and pre-heat treatment of the sample during the fabrication process and could not be totally prevented. Interestingly, under bending, there is no observable developing of these cracks to cause film rupturing. Also, there was no destruction of the film due to bending. Therefore, the printed film has sufficient mechanical rigidity to overcome bending which is the reason for the stable performance of the device under bending.

Furthermore, the cross-sectional image shows that the wrinkle film assembles a spring-like structure with crumples and air gaps between the film and substrate (Figure 4.9c). This structure could work as a spring under deformation and reduce damage to the film by tolerating the strain caused by bending as demonstrated in Figure 4.9d. In addition, the benefit of wrinkle structure to good bending performance was investigated in a recent study by Wang et al., which shows that wrinkle film has a better tolerance to bending comparing with flat film [187]. In short, the film is still intact could be the main reason for the stable performance of the printed device under bending.

4.4 Conclusions

In summary, we demonstrated a full inkjet printing process for the fabrication of micro-sized flexible visible-blind UV sensing device. The deposition process is digitally implemented by a single inkjet printer, which is a process without the removal of material. Firm Ohmic contacts were created between the printed silver electrode and ZnO thin film. The depositing condition such as substrate temperature has a significant effect on shape precision and crystallinity of the film. The shortest response time and highest on/off ratio that we can achieve were 0.3s and 3525, respectively. Degradation of the device was observed under high UV intensity illumination but does not appear in low-intensity illumination. The effect of bending radius on the performance of the device was observed.

The device workability can withstand mechanical bending, such as multiple deforming cycles. These results suggest that the inkjet printing process of ZnO is applicable for semiconductor device fabrication, and the facile method might be applied to prepare wearable in-situ monitoring UV sensor.

Chapter 5: Effect of annealing on electrical properties of printed ZnO film

Study of the electronic structure of printed ZnO film is fundamental for printed electronic devices. In this chapter, the electronic properties of printed ZnO film were tuned by annealing at low temperature. The modification of printed material was investigated and demonstrated with a UV photodetector, and critical parameters such as conductivity and photoconductivity were measured. The changing of device performance after the annealing process is correlated with the nanostructure modification and surface defect. The results are essential for further development of printed materials for electronic devices, especially polycrystalline material.

5.1 Introduction

The performances of the inkjet-printed devices were strongly influenced by the properties of their functional material, i.e., ZnO. Generally, the inkjet-printed ZnO procedures a polycrystalline structure, therefore, the characteristics of the crystals determine the electrical transport properties of ZnO. On the one hand, the grain size of ZnO could significantly affect its performance in three perspectives, including the magnitude of band bending, the quantum size effects and the surface to volume ratio [152]. On the other hand, the electrical properties could be significantly altered by the grain boundary [216], as well as the surface states through the exchanging electron with trapping species such as oxygen and water [101, 167]. Hence, performance modifications of devices could be achieved via the modification of grain boundaries [40, 153]. For example, by controlling the

nanojunction of ZnO nanostructure, the band bending can be modified, and it effectively enhances the performance of UV photodetector [47]. The plasma treatment was applied to remove residues at the boundary of ZnO nanoparticle and magnify the surface depletion effect [169]. Furthermore, ultra-fast thermal annealing is effective in reducing the grain boundary barrier and contributes to the improvement of optoelectrical properties [168].

In this chapter, the effect of low-temperature annealing on electrical properties of inkjet-printed ZnO thin film for UV sensing was investigated. In order to study the effect of the annealing on charge transport of the printed ZnO, different factors such as grain size, carrier concentration and band bending between grain boundaries were examined. It was found that the photocurrent and responsivity increase significantly with the annealing temperature. The near-surface band bending of prepared ZnO thin film was studied by assessing the flat band potential value, which is reduced when annealing is applied. In addition, the interaction of printed film with ambient air was studied by observing the response and decay time variation, such as the persistence of photoconductivity dependence on the annealing temperature. The results are well correlated with the surface states study using X-ray photoelectron spectroscopy (XPS). This work demonstrates the effect of low-temperature heat treatment on the enhancement of responsivity and the role of band bending in the performance of nanoparticles-based UV photodetector, which is critical for inkjet-printed electronic devices.

5.2 Experimental section

5.2.1 Printing of ZnO thin film and preparing the device

Si/SiO₂ substrate was cleaned in acetone and rinsed with IPA before printing. The interdigitated electrodes (the active area is 110 μm by 600 μm) were firstly printed using a commercial silver nanoparticle suspension onto the Si/SiO₂ substrate, which is kept at 60 °C during printing, and then sintered at 150 °C for one hour to improve the conductivity and the adhesion with the substrate. The zinc precursor ink was printed over the silver electrodes. All printed samples were undergone a pre-heat treatment at 200 °C for 10 minutes on a hot plate to allow the zinc precursor to decompose into ZnO polycrystalline thin film.

5.2.2 Thermal annealing

The annealing process was conducted using a quartz tube furnace (Thermo scientific) in ambient air at temperatures of 250 °C, 300 °C and 350 °C for 30 minutes. The sample without annealing is denoted as ZnO-200. The samples annealed at 250 °C, 300 °C, and 350 °C are denoted as ZnO-250, ZnO-300, and ZnO-350, respectively.

5.2.3 Characterization

The morphology of printed ZnO thin film was studied with Field Emission Scanning Electron Microscope (FE-SEM, JEOL 7600). X-ray diffractometer (XRD, PANalytical Empyrean) was used to analyze the average grain size of the printed material before and after heat treatment. The XRD uses CuK α radiation (40 kV, 30 mA) as X-ray source with a wavelength of 0.1540598 nm. X-ray photoelectron spectroscopy (XPS, Kratos Analytical) equipped with a monochromatized Al K α X-ray source (1486.6 eV photons) was employed to study the elemental composition under different annealing temperatures.

A xenon arc lamp with a 365 nm bandpass filter was used as a UV light source, and the light intensity was 1.08 mW/cm². A homemade-mechanical shutter was used to control the light illumination on the sensor. Time-resolved photocurrent and current-voltage characteristics were recorded using a potentiostat (CHI 760D, CH Instrument) and a source metering unit (SMU B2902A, Agilent), respectively.

To determine the flat band potential (V_{fb}) and donor concentration (N_d) of ZnO thin films, Mott-Schottky plots were constructed by measuring the impedance of printed film under different potential. The samples for electrochemical testing was prepared by printing ZnO thin film on ITO coated glass substrate as a working electrode with an exposure area of 10 x 10 mm². A platinum plate and silver/silver chloride (Ag/AgCl) electrode were used as counter electrode and reference electrode, respectively. A Na₂SO₄ solution (0.5M) was used as an electrolyte. The measurement was performed using the potentiostat with Impedance-Potential mode. The frequency was set at 463 Hz during the test.

5.3 Results and discussion

5.3.1 Morphology

Figure 5.1. (a) and (b) Scanning electron microscope (SEM) images of printed ZnO films before and after annealing, respectively. (c) and (d) Transmission electron microscope (TEM) images of printed ZnO films, showing the film is composed of nanoparticles.

The morphologies of printed ZnO films are shown in Figure 5.1a-b, ZnO films composed of wrinkles are obtained by inkjet printing which is identical with the results in previous chapter. The film with crumpled structure is widely reported for sol-gel derived ZnO thin film [217]. It is believed that the wrinkles formed in ZnO film is induced by the stress generated during pre-heating of film [218]. It could be observed that the annealed film (sample ZnO-350) does not show a noticeable change in morphology, comparing with the unannealed sample (ZnO-200). Figure 5.1c-d are TEM images of printed ZnO, which

shows both samples are composed of nanoparticles with size smaller than 10 nm. However, due to low quality of TEM images, it is difficult to quantify the difference in particle size from these images. Therefore, we employed XRD analysis to estimate the grain size of printed ZnO thin film.

5.3.2 Crystallinity of the film

Figure 5.2a shows the X-ray diffraction patterns of printed films on glass substrate. The peaks located at 31.8° , 34.4° , and 36.3° can be indexed to planes (100), (002), and (101), respectively, of ZnO (JCPDS no. 36-1451), revealing a wurtzite structure.[190] These wide peaks are typical for a polycrystalline thin film as observed in TEM images (Figure 5.1c and d). Besides, the wide peak at $2\theta = 39^\circ$ could be assigned to the peak (021) of the residue zinc hydroxide, ϵ -Zn(OH)₂ [219]. The intensity of the peak gradually decreases when a higher heating temperature is applied which indicates the transition of zinc hydroxide residues to ZnO due to the thermal annealing reaction [220].

Figure 5.2. (a) XRD patterns, (b) Full width at half maximum (FWHM) values of three main peaks, i.e. (100), (002) and (101), and (c) estimated grain sizes of printed ZnO films.

The full width at half maximum (FWHM) values of the three main peaks are shown in Figure 5.2b. The grain size was calculated using Scherrer equation [191]. The FWHM value of the peak (002) exhibits a small variation around 1.3 degrees for all samples, which is according to an average grain size of about 6.8 nm. The other two peaks show a continuous decreasing of FWHM value, such as that of the peak (100) decrease from 1.22°

to 0.86° ; and that of the peak (101) decreases from 2.32° to 1.05° . The calculated grain size according to these peaks increases from 7.1 nm to 10.1 nm and from 3.8 nm to 8.3 nm for peak (100) and (101), respectively. The XRD results suggest that the low-temperature annealing has partially merged the particle boundary. This modification might benefit the electron transportation of the polycrystalline film. The estimated grain size values are in agreement with TEM result, which shows the grain size is in range of smaller than 10 nm.

5.3.3 Electrical and optoelectrical turning by temperature

Figure 5.3. Effect of annealing temperature on (a) dark current and light current and (b) responsivity with a bias voltage of 5 V.

The electrical current of printed ZnO photodetectors under the dark condition and UV light are shown in Figure 5.3a. Both dark current and light current have been significantly influenced by the annealing temperature. In details, the dark current has increased from 3.86×10^{-11} A to 8.50×10^{-11} A, 1.60×10^{-9} A and 3.03×10^{-9} A for the samples with heat treatment at 250°C , 300°C and 350°C , respectively. Notably, the light current has increased by a maximum of three orders of magnitude, from 1.89×10^{-8} A to 1.31×10^{-6} A, 1.58×10^{-6} A and 2.62×10^{-5} A for the sample with heat treatment at 250°C , 300°C and 350°C , respectively. In short, the dark current and light current increases by 78 times and 1386

times, respectively, after thermal annealing at 350°C, compared with the sample without heat treatment.

The responsivity of the photodetector could be determined using the equation:[40]

$$R = \frac{J_{ph}}{PS} \quad (5.1)$$

where J_{ph} is the photocurrent determined by the difference between light current and the dark current, P is the light intensity, and S is the effective area of the sensor. The average responsivity is described in Figure 5.3b. It is found that the responsivity has dramatically increased by more than 10^3 times, from 2.45×10^{-2} A/W to 33.9 A/W for the ZnO-200 and ZnO-350 sample, respectively (Figure 5.3b). The responsivity values are determined at a bias voltage of 5 V, so they can also be expressed as 4.89×10^{-3} A/(W V) and 6.78 A/(W V) for the sample ZnO-200 and sample ZnO-350, respectively. These results confirm that the heat treatment has enhanced the responsivity via increasing photocurrent. Furthermore, the rising of dark current shows that the conductivity of the printed film has increased as a result of annealing.

Table 5.1 compares our results with some representative studies. For comparison with the other additive manufacturing method, the previous works which digitally prints the seed layer for growing of ZnO nanowires have an I_{light}/I_{dark} ratio of 20 [151], while that of our device is 8646 at a light intensity of 1.08 mW/cm^2 . However, this result is still smaller than the result achieved from polycrystalline nanowire made from electrospinning [40]. Furthermore, when comparing with traditional fabrication method such as magnetron sputtering [166] and sol-gel [169], the result achieved by inkjet printing is better, such as

higher responsivity and on/off ratio, which is mainly contributed to the polycrystalline structure of inkjet-printed film.

Table 5.1. Comparing responsivity and on/off ratio of ZnO UV photodetector by different additive manufacturing methods and conventional method

Reference	Preparation technique	Illumination intensity (mW/cm ²)	Bia voltage (V)	Responsivity (A/W)	I _{light} /I _{dark}
Nanowires [151]	Additive manufacturing-Hydrothermal	N.A.	1	N.A.	>20
Polycrystalline nanowire [40]	Additive manufacturing-Electrospinning	0.5x10 ⁻⁶ – 115.5 x10 ⁻⁶	1	7.5x10 ⁶	10 ⁵
Thin film (This work)	Additive manufacturing-Inkjet printing	1.08	5V	33.9	8646
Thin film [166]	Sputtering	N.A.	3V	3.8x10 ⁻² , 2.63x10 ⁻³	1.61x10 ³ , 1.35x10 ³
Thin film [172]	Magnetron sputtering	N.A.	3V	1.306	N.A.
Thin film nanoparticles [169]	Sol-gel	0.003	5	2.5	1270

Following discussion in Chapter 4, the performance of ZnO thin film is significantly influenced by ambient air via absorption to the surface of the semiconductor. Especially, the printed ZnO film with nanosized grains would have a large surface to interact with air. Also, there are grain interfaces existing in the film. The grain interfaces of polycrystalline structure could have a strong effect on electrical properties of the printed film because the transportation of electron through these grain interfaces bases on tunnelling and thermionic emission [40]. Therefore, the electrical properties printed film with polycrystalline structure is studied with the consideration of the effect of grain interfaces.

The defect sites at the surface of ZnO can play the role of adsorption sites for oxygen and water molecules [221]. Band bending between semiconductor grains is due to the absorption of these species to the surface of the grains by capturing free electrons in the crystal which causes a depletion layer near the surface of the grain [153]. The conductivity of the polycrystalline semiconductor film is described by the equation:[157]

$$\sigma_d = \frac{q^2 N_d d}{(2\pi m^* kT)^{1/2}} \exp(-qV_d / kT) \quad (5.2)$$

where N_d is the free carrier concentration, q is the electronic charge, d is the grain size, m^* is the effective mass for electron, V_d is the barrier between the grains. From this equation, it could be noted that the conductivity of the film depends on grain size, carrier concentration, and band bending. Hence, in order to explain the turning of device performance, these factors are going to be probed in the following sections.

5.3.4 Mott-Schottky plot

In this work, the band bending modification was studied via the charge properties at printed film surface by capacitance analysis. Similar to the surface band bending caused by oxygen absorption in air, when the ZnO thin film semiconductor contacts with electrolyte, there is a transfer of electrons from semiconductor to acceptors in solution until there is an equivalent state of Fermi level and as a result, forming a band bending. By changing the potential between the semiconductor electrode and the counter electrode, the level of the band bending could be altered. The value of applied potential where there is no band bending is called flat band potential, V_{fb} [154]. Because of the exchanging of electron also

depends on the charge properties at the surface of the semiconductor, the magnitude of band bending could be correlated to the level of band bending in air ambient.

Derived from Poisson's equation, the Mott-Schottky equation describes the relation of the capacitance of the depletion layer and voltage applied to the film (V):[222]

$$\frac{1}{C^2} = \frac{2}{eN_d A^2 \epsilon \epsilon_0} \left(V - V_{fb} - \frac{kT}{e} \right) \quad (5.3)$$

where C is the capacitance of the depletion layer, A is the area of the working electrode, N_d is the electron concentration, and the thermal voltage, i.e., kT/e , is 0.0257 V. The Mott-Schottky plot was constructed by plotting $1/C^2$ versus the potential of the working electrode using a traditional RC model [223].

Figure 5.4. The Mott-Schottky plots to determine the flat band potential, the intersections of the linear fitting of the plots with the x-axis indicate the flat band potential of the printed ZnO films annealed at different temperatures.

The flat band potential value could be found by $V_{fb} = V - kT/e$, where V is the interception of the linear section of the curve with the potential axis. From the plots shown in Figure 5.4,

the flat band potential of ZnO-200, ZnO-250, ZnO-300, and ZnO-350 are -0.430 V, -0.324 V, -0.224 V and -0.108 V, respectively. All samples show a positive slope, which indicates that the major carrier of printed ZnO is electron and confirms the n-type semiconductivity of printed ZnO film. Because the value of flat band potential represents the magnitude of voltage where there is no band bending in the film, the reducing of the absolute value of V_{fb} demonstrates the decreasing of the band edge bending. In other words, annealed films exhibit a lower height of band bending, which facilitates the electron transportation through grain boundaries.

The free carrier concentration, N_d , could be estimated from the slope of the linear section of the Mott-Schottky plot: [222]

$$N_d = \frac{2}{meA^2 \epsilon \epsilon_0} \quad (5.4)$$

where m denotes the slope of the linear fitting. The free carrier concentration values were calculated to be $3.37 \times 10^{20} \text{ cm}^{-3}$, $3.51 \times 10^{20} \text{ cm}^{-3}$, $3.31 \times 10^{20} \text{ cm}^{-3}$ and $4.23 \times 10^{20} \text{ cm}^{-3}$, for sample ZnO-200, ZnO-250, ZnO-300 and ZnO-350, respectively. Although there is an increasing trend of carrier concentration along with increasing annealing temperature, the value of N_d did not change significantly when different treatment temperatures were applied except for the sample ZnO-350, the free carrier concentration of which has increased by 25 %. These calculated results are much higher than most of the reported references [222], and only approximate to the result reported by Allagui et al., whose group measured the carrier concentration of nanoflower ZnO [223]. The possible reason is the high surface to volume ratio of the nanostructure film which makes the effective area of the film larger than the nominal area.

The width of the depletion layer (D) can be estimated from the equation:[222]

$$D = \frac{A\epsilon\epsilon_0}{C} \quad (5.5)$$

At the potential of the working electrode $V = 0$ V, the average width of the depletion layer of sample ZnO-200, ZnO-250, ZnO-300, and ZnO-350 are 0.82 nm, 0.77 nm, 0.74 nm and 0.43 nm, respectively. Hence, the annealed samples have a thinner depletion layer, and it decreases when increasing the temperature to 350 °C. These results are essential evidences supporting the band bending modification model of printed films which will be discussed in the next section.

5.3.5 Mechanism of the band bending modification

Figure 5.5. Schematic of the band diagram shows the modification of the band bending of the printed ZnO polycrystalline film.

From the equation describing the conductivity of polycrystalline film, it can be seen that the effect of grain size and the carrier concentration is linearly proportional, while the effect

of band bending effect is more significant due to its exponential relationship with the conductivity. Furthermore, as discussed in the previous sections, the changing of grain size and the carrier concentration is minor. Hence, their contribution to the increase of dark and photocurrent is small, comparing with that of the surface band bending. The increasing of the device current could originate from band edge modification by the merging of the grains at the surface. Hereby, Mott-Schottky analysis has shown that the magnitude of upward band bending is reduced after annealing. The simplistic model of the energy band diagram of the printed film before and after heat treatment was applied is shown in Figure 5.5, which assumes the film structure as a serial of nanograins. The film before annealing composes of small grain size nanoparticles. The annealing introduces the sintering of these nanoparticles at their boundary to form larger particles as suggested by analyzing XRD patterns. Because of these merged boundaries between nanoparticles, the energy barriers between these grains are lowered. This discussion is well supported by the reducing of the calculated thickness of the depletion layer in the previous section.

In addition to the energy barrier between grains influences the transport of photo-generated carriers within the film, the recombination of photo-generated electrons and holes affects the concentration of the free carriers, which in turn affects the light current [224]. Hydroxide group (OH^-) has been widely known as a recombination center in solution-processed ZnO material [225]. The ZnO film which was not subjected to the annealing process (ZnO-200) produced the lowest photocurrent due to its high concentration of residues and defects, i.e., more recombination centers existed, comparing with the samples prepared with a post-annealing process.

Furthermore, the post-annealing treatment facilitates the conversion of residues, such as zinc hydroxyl complexes and basic zinc acetate, to ZnO via thermal decomposition process. Therefore, the annealing process increases the content of the active materials, i.e., ZnO, resulting in the enhancement of the generation of electrons and holes. Also, the reduction of residues helps improve the crystallinity quality because the existence of residues could limit the transportation of electron in the printed film. Hence, removal of these residues by thermal annealing could facilitate the charge carrier transportation and improve the electronic properties of the printed film.

5.3.6 Time-resolved photocurrent

Figure 5.6. Time-resolved photocurrent analysis using bi-exponential function. (a) Sample ZnO-200. (b) Sample ZnO-250. (c) Sample ZnO-300. (d) Sample ZnO-350.

Figure 5.6 shows the time response of all samples under UV illumination. As a typical process, the current increases when the UV light is turned on and followed by a decrease when the UV light is turned off. The bi-exponential function was used to fit the rising curve and decay curve of all samples, respectively are:[47]

$$I = I_0 + A_1 \left(1 - e^{-(t-t_0)/\tau_{r1}}\right) - A_2 \left(1 - e^{-(t-t_0)/\tau_{r2}}\right) \quad (5.6)$$

$$I = I_0 + A_3 e^{-(t-t_0)/\tau_{d1}} - A_4 e^{-(t-t_0)/\tau_{d2}} \quad (5.7)$$

where I_0 is dark current, A_1, A_2, A_3, A_4 , are fitting constants; τ_{r1} , τ_{r2} , τ_{d1} and τ_{d2} are time constants. The fitting gives the rise time constants for the sample ZnO-200 are $\tau_{r1} = \tau_{r2} = 9.3$ s. These time constants are equal which means that the rise curve of this sample can also be fitted using the exponential function, but the bi-exponential function is employed for comparing with the other samples. The decay time constants of this sample are $\tau_{d1} = 1.3$ s and $\tau_{d2} = 9.1$ s.

Meanwhile, the ZnO-250 sample exhibits higher time constants, such as $\tau_{r1} = 12.2$ s, $\tau_{r2} = 41.2$ s for the rise curve and $\tau_{d1} = 9.0$ s and $\tau_{d2} = 62.1$ s for the decay curve. These time constants slightly reduce in case of the sample ZnO-300. Finally, the sample ZnO-350 shows the most massive set of the time constants, such as $\tau_{r1} = 12.2$ s, $\tau_{r2} = 41.2$ s, $\tau_{d1} = 9.0$ s and $\tau_{d2} = 62.1$ s. The fast response component and the slow response component could be attributed to the reabsorption of water and oxygen, respectively [226].

In Figure 5.6a, anomalous photocurrent could be observed from sample ZnO-200. The response of the sample is different from that of the other samples, such as photocurrent

decay even under the steady UV illumination. Only a part of the response curve could be fitted with bi-exponential function. It could be explained by a high concentration of defects of this sample. As suggested from a previous study [212], anomalous photocurrent originates from defect states which play the role of recombination centres for electron-hole. As shown in the XRD result, the ZnO-200 sample exhibits a high content of residues, which act as recombination centres for photon-generated charge carriers, such as free electron and hole. Therefore, under UV illumination, the photo-generated charge carriers are easily recombined. This process causes a decrease of carrier concentration; therefore, the photocurrent is reduced. The relatively large time constants of printed devices are the evidence for the interacting with ambient air of the semiconductor because the absorption and desorption of gas molecules are relatively slow compared with the photo-induced charge carrier generation.

Overall, the analysis of time constants shows that the annealed samples show a longer time for response and recovery when UV light is turned on and off, respectively. The difference in time response will be discussed in the surface defect study.

5.3.7 Surface defect study

Figure 5.7. O1s spectra and their fitting results of printed ZnO thin film at different heat treatment temperature of (a) 200 °C, (b) 250 °C, (c) 300 °C and (d) 350 °C.

By analyzing the oxygen scanning spectra from XPS results, we can study the effect of thermal annealing on the chemical states of printed film. The O1s spectra exhibit asymmetric line shapes for all of the printed ZnO films (Figure 5.7a-d). Each O1s spectrum can be deconvoluted into three distinct sub-peaks. The sub-peak located at 530.1 eV corresponds to oxygen atoms within the ZnO lattice and is denoted as O1. The sub-peak at 531.0 eV is associated with oxygen vacancies and is denoted as O2. The sub-peak located

at the highest binding energy is associated with surface-adsorbed oxygen-containing species and is denoted as O3 [111, 227].

The percentage of lattice oxygen (O1) increases from 33.8 % to 36.0 % when treatment at 250 °C was applied to the printed ZnO film, as shown in Figure 5.7a-b. The percentage of lattice oxygen drops to 24.8% for sample ZnO-300, and it reaches to 41.0 % for sample ZnO-350, which is the highest value for all samples. Meanwhile, the percentage of oxygen vacancies (O2) slightly rises from 26.1 % to 31.0 % with the annealing at 250 °C before reducing to 24.9 % and 25.0 % for treatment at 300 °C and 350 °C, respectively. The excess oxygen generally decreases when a higher temperature was used, such as from 40.1 % to 28.8 % at 350 °C, except at 300 °C where the percentage of excess oxygen is 50.3 %. This result is complied with previous study [227]. It is suggested that the excess oxygen mainly converts to oxygen vacancies at a temperature lower than 300 °C. At the temperature higher than 300 °C, oxygen vacancies convert to lattice due to the oxygen vacancies are filled by free oxygen. It could be because high temperature could increase the atom gaps of ZnO crystal, which allows more oxygen atoms to enter the gaps [227].

It is worth noting that the time-resolved analysis in the previous section shows the sample ZnO-300 has faster response/recovery speed, comparing with the other two annealed samples at 250 °C and 350 °C. This result could be explained by the analyzing of XPS result of sample ZnO-300, which has a higher concentration of excess oxygen comparing with the other annealed samples. The higher excess oxygen promotes the interacting with air, so the sample exhibits a rapid response and recovery with UV illumination. In general, the annealing process could alter the chemical states of printed ZnO thin film, which results in different behavior of the fabricated photodetectors.

5.4 Conclusion

In summary, low-temperature heat treatment was utilized to modify the electrical properties of the inkjet-printed ZnO UV photodetector. Both dark and light current rose when annealing was applied. The responsivity of the printed UV photodetector had increased by three orders when the thermal annealing at 350 °C was performed. It was found that band bending at the grain boundaries play an important role in electrical properties of the printed film. The fusing of nanoparticle boundaries reduces the band bending at the interface and facilitates electron transportation through the boundaries. Furthermore, the removing of residues could enhance photocurrent current under UV light illumination by increasing the photo-generated charges. The annealing effect on the surface states was also studied, and it is found that the response and decay time of the photodetector is remarkably influenced by these surface states. This result contributes to the understanding of the electronic structure of inkjet-printed ZnO thin film from the precursor solution and provides a facile approach to improve the performance of the inkjet-printed electronic device.

Chapter 6: Printed micro heater for Joule effect annealing ZnO sensor

Previous chapters have presented the fabrication process as well as the effect of annealing to the inkjet-printed ZnO-based device. Meanwhile, integration of electronic device to conventional products is a big concern for the development of 3D printing products. In this chapter, instead of using external heating equipment, silver microheater was employed for the heat treatment process of the printed zinc precursor. The Joule heating effect shows that it can modify the electrical properties of the printed film. The integrated micro-heater could benefit additive manufacturing of ZnO, such as no external heating equipment is required.

6.1 Introduction

Owing to the saving energy feature and the ability to concentrate heat, the resistive micro heater has been utilized in applications such as local growth of functional material nanowires to obtain proper assembling of the material [228] and activating the gas sensing effect [229]. Resistive micro heater working principle is based on the Joule effect where heating is generated in an electrically resistive material by electric current runs through it. Because of the photolithography process is a complicated and time-consuming process, additive manufacturing approach such as selective laser sintering was employed to pattern the micro-heater [230]. The advantage of inkjet printing in the fabrication of ZnO-based device has been discussed over the last chapters. However, the annealing process using

bulky furnace could limit the developing of the integrated device into the 3D printed device and wasting energy.

In this chapter, a novel fabrication process based on the inkjet printing and localized thermal annealing is introduced. A micro-heater was printed along with the micro-electrodes of the UV sensor. Then, the zinc precursor is printed over as a thin film pattern. Instead of using external heating equipment such as hot plate and furnace, this method employs printed micro-heater to turn zinc precursor to ZnO by Joule heating effect when the heater is powered by a DC power source. The synthesized ZnO thin film was applied for UV photodetector application. The formation of ZnO thin film was studied by investigating the atomic percentage of zinc and oxygen using energy-dispersive X-ray spectroscopy (EDS). It was found that the input power significantly influences the temperature. Consequently, the performance of the photodetector was also impacted by the input power via the different generated temperatures, which is consistent with results in the previous chapter.

6.2 Experimental section

6.2.1 Printing of the micro-heater

Figure 6.1. Printing process to prepare the UV photodetector and microheater. (a) Printing the silver electrodes and micro-heater. (b) Powering the micro-heater by electric current to induce sintering of silver electrodes. (c) Printing of zinc precursor pattern. (d) Powering the micro-heater by electric current to induce the formation of ZnO.

Silicon wafer was chosen as a substrate because it has high thermal conductivity of $148 \text{ Wm}^{-1}\text{K}^{-1}$ [231], and it does not fracture when exposing to localized heating. Printing of metal electrodes and micro heater in this chapter was conducted by employing the same silver ink and procedure reported in previous chapters. The fabrication process of the Joule heating sensor is described in Figure 6.1. Firstly, the silver ink was printed onto the Si/SiO₂ substrate (Figure 6.1a). There are two main components with different functionalities of silver patterns, such as the two common electrodes serving as electrical contacts for the

semiconductor and the micro-heater serving as a local heat source. Before the next printing step, 4W DC power supply was applied to the micro-heater to induce the sintering of silver for 5 minutes (Figure 6.1b). This first heat treatment step helps to sinter the silver electrode and prevent the washing of silver nanoparticle when printing the zinc precursor ink.

6.2.2 Printing of zinc precursor and localized heat treatment of the ZnO

Zinc precursor ink was prepared and printed following the same procedure reported in previous chapter. A rectangle pattern of zinc precursor was printed over the silver contact with a heated substrate at 60 °C (Figure 6.1c). The active area between two electrodes is 200 μm by 500 μm . Then, the micro-heater was connected to a DC power source for 5 minutes to generate local heat (Figure 6.1d). The electrical power was set at 4 W and 5 W for different samples which are denoted as sample 4W and sample 5W, respectively. The temperature of the micro-heater was observed using a thermal camera (NEC F30W) located at the back of the substrate.

6.2.3 Photodetector characterization

UV LED with a central wavelength of 365 nm was used as a light source to test the optoelectronic properties of the device. The light intensity was adjusted by controlling the electric current and calibrated by a power meter (FieldMax II Coherent). Morphology of films was studied by FE-SEM. Element composition was studied by Energy Dispersive X-ray spectroscopy (EDS).

6.3 Results and discussion

6.3.1 Morphology of printed silver

Figure 6.2. (a) Array of printed silver patterns before printing zinc precursor. (b) Structure of the printed sensor with printed zinc precursor pattern. (c) Enlarged photo shows the zinc precursor overlap micro silver electrode.

The optical image of the printed sensor is shown in Figure 6.2. In details, Figure 6.2a shows as-printed silver electrode array. Single device was separated from the wafer before conducting heating, and the external electrical connections were done using conductive silver epoxy as shown in Figure 6.2b. Figure 6.2c shows the device with printed zinc precursor pattern over the silver electrode to create the metal-semiconductor-metal structure.

Figure 6.3. Sintering of one-layer printed silver by Joule heating. (a) Before annealing. (b) The micro electrode after annealing. (c) The micro-heater after annealing.

The changing of silver electrode nanostructure due to resistive heating was noticed. As can be seen in Figure 6.3, sintering of one-layer printed silver by Joule heating effect could be clearly observed. The as-printed silver pattern shows discrete particles with a diameter of about 50 nm (Figure 6.3a). Figure 6.3b shows sintered silver at the electrode section, which is separated from the heater. The particle size grew to about 80 nm to 100 nm. At the heater section, the agglomeration is more significant, such as the silver particles merged to form larger particles with the size of some grains could reach 200 nm (Figure 6.3c).

The strong sintering effect at the heating silver track is a result of heat generated from the resistive heating effect of the electrical current run through the silver pattern. Meanwhile, because the common electrodes section is far from the heat source, it suffered a lower temperature than the micro heater position. Therefore, the sintering effect is weaker but still visible, and it would improve the conductivity of the printed silver electrodes as well as improve the adhesiveness with the substrate. However, because of the strong agglomeration of the silver particles, the silver track will rupture at a high input power and cause the open circuit. In case the micro-heater was printed with four layers of ink, the agglomeration effect was weaker as can be seen in Figure 6.4b, compared with the one layer of ink in Figure 6.4a.

The sintering of silver nanoparticles could happen at a temperature which is much smaller than the melting point of bulk silver, i.e. 960 °C [232]. Under heat treatment, the wetting effect of silver nanoparticle leads to the merging of nearby nanoparticles and create larger grains. Therefore, if the film is too thin, it would create some gap in the film because there is not enough material to fill in. Hence, the breakdown of the micro-heater due to the agglomeration when it is powered could be prevented by printing a thicker micro-heater. However, at high temperature, the oxidation of silver could happen which also damages the electrode.

Figure 6.4. Effect of the number of layers to the morphology of printed film after annealing (a) The one-layer printed micro heater after annealing. (b) The four-layers printed micro heater after annealing.

6.3.2 Resistive heating effect by DC electricity

Figure 6.5. Thermal imaging shows temperature by different input power to the micro-heater. (a) Input power is 4 Watts. (b) Input power is 5 Watts.

It was proposed that the relationship of input power and temperature of the micro-heater could be described by the equation [233]:

$$P = a(T - T_0) + b(T - T_0)^2 + c(T^4 - T_0^4) \quad (6.1)$$

where P is the input electrical power, T is the temperature of the heater, T_0 is the ambient environment, a , b and c are physical constants. The equation shows that the micro-heater

temperature is proportional to input power and could be adjusted by changing the input power [234].

The thermal images of the micro-heater and the substrate under different input power are shown in Figure 6.5. In the case of using 4 Watts DC power, the temperature at the heater position could reach 175.5 °C, while the temperature at the printed zinc precursor pattern is measured at 162.5 °C. A noticeable increase of temperature was observed when using 5 Watts electric power to heat the substrate, such as temperature of 250.3 °C and 225.0 °C were measured at the micro-heater and the zinc precursor pattern, respectively. Hence, heating temperature of device could be adjusted by turning the input power of the heating element.

6.3.3 Formation of ZnO from zinc precursor

Figure 6.6. FE-SEM images of the printed ZnO thin films at different heating power. (a) Without heating power (0 W). (b) A film with 4 W heating power. (c) A film with 5 W heating power.

Formation of ZnO thin film by local heat treatment was investigated using FE-SEM and EDS. Morphology of the printed film with different Joule annealing condition is presented in Figure 6.6. The film without annealing has many cracks on the surface (Figure 6.6a). The cracks might be formed due to the slow vaporization of remaining solvent at room conditions, it leaves the zinc salt which is brittle and could be easily cracked. Meanwhile, the morphologies of the films annealed with power of 4 W and 5 W have significantly changed, such as the surface does not appear visible crack (Figure 6.6b-c). Also, wrinkle in the films due to the stress during heating can be clearly observed, and it is similar to the morphology of printed films using conventional annealing process in previous chapters.

Figure 6.7. EDS results of the printed ZnO thin films at different heating power. (a) Printed film without heating power (0 W). (b) Printed film with 4 W heating power. (c) Printed film with 5 W heating power.

Energy dispersive X-ray spectroscopy (EDS) analysis, which is shown in Figure 6.7, has unveiled the mechanism of the resistive heating formation of ZnO thin film. In details, the weight percentage of zinc and oxygen in the unannealed sample is 53.98 % and 30.73%, respectively, which is according to the Zn:O atomic ratio of 0.43. For the sample 4W, the weight percentage of zinc and oxygen is 56.82 % and 25.96 %, respectively, which is according to the Zn:O atomic ratio of 0.54. The increasing of Zn:O ratio is the evidence for

the converting of zinc precursor to ZnO. The Zn:O ratio of the sample 5W is 0.55. The rising of Zn:O ratio prove that more ZnO had been formed as the result of the higher temperature due to higher input electric power.

The reaction to form ZnO from zinc precursor was discussed in previous chapters, which is the decomposition of zinc salt under high temperature which starting from 150 °C. The reaction could be completely finished at a temperature of higher than 350 °C. Therefore, by-products are expected to present in this sample, which is only annealed at a lower temperature. The by-products could be zinc acetate and basic zinc acetate, $\text{Zn}_4\text{O}(\text{CH}_3\text{COO})_6$. The final products, along with ZnO, are water, carbon dioxide, acetone and acetic acid [193].

6.3.4 UV sensor performance

Figure 6.8. Performance characterization of the sensors. (a) Time-resolved photoresponse of the sensor. (b) The responsivity of each sample at different light intensity.

Figure 6.8 shows the performance of the sensors with different Joule heating condition. In Figure 6.8a, the time-resolved current of the sample 0W is colored in black which does not

exhibit any response to the UV light turning on and off. On the other hand, both sample 4W and sample 5W show a noticeable response to the UV light illumination, such as the current rise upon the UV light is turned on and the current decay when the UV light is turned off. Furthermore, there is a substantial difference of photocurrent between the two sample, such as the maximum value of the current of sample 4W is about 1.5×10^{-8} A at 5V bias voltage, and that of the sample 5 W is about 1.6×10^{-7} A, which is ten times larger than the sample 4W. Figure 6.8b shows the responsivity of the heated devices as a function of the light intensity. Both devices show a decreasing of responsivity with the increasing of UV illumination intensity which is in agreement with previous reports [168]. The responsivity value of the sample 5W is 0.029 A/W at 5.42 mW/cm^2 , which is much larger than the responsivity value of 0.0027 A/W of the sample 4W.

Sample 0W was not suffered from Joule thermal treatment, therefore ZnO could not be formed by the thermal decomposition reaction. Hence, this sample does not exhibit the photoresponse properties. On the other hand, applying the electric power to micro-heater creates heat to introduce the decomposition of the zinc precursor. When using input power of 4 W, the temperature at the printed precursor position could reach $162.5 \text{ }^{\circ}\text{C}$. This obtained temperature is higher than the starting temperature of decomposition reaction, such as about $150 \text{ }^{\circ}\text{C}$ as discussed in Chapter 3. Therefore, the formation of ZnO is facilitated but not completely finished because the temperature is still lower than the maximum temperature of the reaction. Similarly, using 5 W input power could generate a temperature of $225.0 \text{ }^{\circ}\text{C}$ as shown in the previous section, which is much higher the temperature when using 4W input power. Therefore, there are more ZnO could be formed by the decomposition process.

However, the performance of the devices, such as the responsivity, is much lower than the annealed devices reported in Chapter 5. It is because the temperature generated by 5 W Joule heating is not sufficient to fully decompose the zinc precursor and effectively sinter the printed ZnO film. Hence, the residues are still presenting in the film and they could reduce the electrical quality of the device.

Also, the previous discussion in EDS result has shown that a higher percentage of ZnO could be formed by a stronger electrical input power during Joule heating process. This observation could be the reason for a better performance for the UV sensing application. Furthermore, higher temperature annealing improves the responsivity of ZnO UV photodetector due to the reducing of band bending as discussed in Chapter 5. The better performance of sample 5 W suggests that electrical input power during Joule heating treatment has a vital role in the formation of ZnO thin film for the electronic and optoelectronic applications.

6.4 Conclusion

Inkjet printing of silver microheater for the localized heating synthesis of ZnO thin film is introduced. ZnO thin film was formed from inkjet-printed zinc precursor by locally heating using silver micro-heater. The single layer printed silver film morphology is strongly affected by thermal annealing, and it causes the agglomeration of silver which then results in an open circuit. Printing four layers of silver have helped to reduce the agglomeration due to high temperature and keep the micro-heater works at high input power. It is found that the input electrical power has a significant effect on UV detecting performance, such as a higher the input power would result in a higher responsivity of the photodetector. Although the responsivity of the device prepared by this method is much smaller than that

has been reported in the previous chapter using conventional annealing process, the proposed approach for fabricating the sensor in this chapter is suitable for integrated 3D printing product, which could be composed by multi-materials.

Chapter 7: Conclusions and future works

7.1 Conclusions and contributions

This work is dedicated to develop the additive manufacturing of ZnO thin films for miniaturized electronic applications, particularly UV photodetector, and enhance the performance of the printed device via modification of the electrical properties of the printed films. The additive manufacturing of ZnO thin films was carried out using inkjet printing of a zinc precursor solution. Modification of printed films was carried out using thermal annealing, which resulted in the decrease of band bending at the grain boundary of nanocrystalline film. These works present some crucial foundations for future 3D printing of more sophisticated ZnO based semiconductor devices. In summary, the following conclusions can be drawn:

1. A facile sol-gel based formula was prepared for inkjet-printing of ZnO thin film with special consideration of ink concentration. Printing of ZnO was conducted with a systematical investigation of many processing factors such as driving voltage and waveform. Inkjet-printed ZnO thin film has nanocrystalline structure which could alter the electrical properties of the film. Annealing at high temperatures, such as 400 °C, 600 °C and 800 °C, was carried out. It is found that the high-temperature thermal annealing has a substantial influence on the crystallinity structure of the printed film, such as increase of the grain size from 6.8 nm to 20.9 nm and an increase of optical bandgap.
2. Micro-sized flexible ZnO UV photodetectors have been thoroughly developed and fabricated using inkjet printing technology. The facile ink recipe of zinc acetate precursor

solution was utilized. The relatively sufficient precision of ZnO film patterns was achieved via the tuning of substrate temperature. The printed device has many outstanding features such as robust flexibility, Ohmic contact and short response time. It was found that the substrate temperature during the deposition of zinc precursor ink has a significant effect on ZnO pattern shape, film morphology, and crystallization. It was also found that the response/decay time of the printed UV sensor is strongly affected by the illuminating light intensity. This additive manufacturing fabrication process has many advantages such as saving material, environmentally friendly, high-resolution patterns and could be used for rapid prototyping. The compatibility of the processing with flexible substrate makes the process ideal for fabrication of wearable devices, which require certain bendability. The process is also of potential for printing other ZnO film devices that need flexibility such as transistor and solar cell in small size for wearable devices or artificial skins. In addition, the simplicity of the fabrication process could support the idea of the customer-made device or in-situ fabrication by combining our process with other 3D printing processes.

3. Inkjet-printed ZnO thin film for UV photodetector was prepared with the adoption of low-temperature thermal annealing. The effect of annealing temperature on the UV sensing performance was investigated. Band bending modification was evaluated using flat band potential measurement. Electrical properties such as film resistance and responsivity witnessed a significant improvement with heat treatment. It was found that the increase of film conductivity is strongly influenced by the band bending modification. Thermal annealing induces the fusing of nanoparticle boundaries and reduces the band bending. Hence, electron transportation through the boundaries is facilitated. Thermal annealing also reduces residues, which helps enhance the photocurrent. The results illustrate the

significance of band bending in printed electronics, which benefits the fabrication of wearable electronic devices.

4. Local heating was used to produce ZnO thin film from printed zinc precursor. The micro-heater was inkjet-printed using commercial silver nanoparticle ink. During the Joule effect heating, the temperature of the substrate reached 162 °C and 225 °C with input power was set at 4 W and 5 W, respectively. Resistive heating using a DC electric current induced the formation of ZnO, and the UV photodetector was fabricated by this method. The responsivity of the UV photodetector was notably influenced by the input power during the resistive heating process. It was found that a higher percentage of ZnO could produce a better performance of the printed UV photodetector. Also, the higher temperature could reduce the band bending and promote the electron transportation at grain boundaries.

The main contributions of this thesis are: (1) the development of a facial ink formula for printing of ZnO thin film using inkjet printing; (2) the development and demonstration of the inkjet printing process to fabricate micro-sized ZnO patterns; (3) development and characterization of a inkjet-printed flexible UV photodetector via employing flexible substrate; (4) investigation of the effect of low-temperature process on electrical properties of printed ZnO thin film; (5) study and elaboration on the mechanism of band bending modification that facilitates electron transportation; (6) development of a process to fabricate ZnO device by integrated and localized heat treatment.

7.2 Recommendations

Although relatively low-temperature treatment is effective in enhancing the performance of the ZnO-based UV photodetector, the annealing process is not compatible with many

plastic substrates which have lower melting temperatures. Plasma treatment could be applied to treat inkjet-printed ZnO thin film via the reaction of ionized oxygen with residues on the surface of ZnO. Hence, it could improve the crystal quality and benefit the electron transportation.

Due to the nature of metal oxide semiconductor, the performance of printed ZnO-based device is strongly affected by ambient air, which exhibits the degrading of photocurrent under strong UV illumination. This is common for solution-processed ZnO thin film, which might be overcome by encapsulating the printed film with suitable material. On the other hand, many studies utilized this property as a gas sensor, where electrical conductivity of film changes along with surrounding air.

Also, because the deposition of the ink droplet to the substrate strongly depends on substrate properties such as contact angle and previously deposited material which could reduce the precision of printing. Hence, the precision of the inkjet-printed device is limited. However, a smaller droplet volume could help increase the printing precision because liquid can vaporize quickly, therefore the spreading size is smaller.

The porous property of printed film introduces difficulty for printing electrode in a sandwich-structure because the conductive ink could penetrate through printed ZnO film and create a short-circuit. Therefore, printing of the electronic device that requires multiple-layer electrodes, such as transistor, might be difficult. In this case, surface treatment of printed ZnO film which changes the contact angle might help to prevent the penetration of conductive ink. This could be done by plasma treatment which changes the surface charge properties of printed ZnO film.

The poor performance of the photodetector prepared by microheater is due to the low temperature generated by Joule heating. However, if the input power is adjusted to increase the temperature, the wetting effect of the silver electrode and the oxidation might cause its rupture. Therefore, the future studies could use the other materials for microheater, such as graphene oxide, to improve the heating efficiency and quality of printed ZnO thin film.

Recent studies have found the wrinkled structure could be able to help improving the photovoltaic efficiency of dye-sensitized solar cells [188]. The enhanced light harvesting efficiency could help in improving the performance of photonic devices. Further investigation of physical properties of printed ZnO thin films, such as photoluminescence and Hall measurement should be conducted. Also, because of its large surface to volume ratio, printed ZnO thin film could be used for surface enhanced Raman scattering chemical sensing application by depositing metal nanoparticles on the film surface.

Self-powered sensor is an interesting topic of functional nano-systems where the service is self-sufficient. The independence of power supply leads to a simpler system and reduces consumed power which extends the working time for the system. Meanwhile, the junction of semiconductors has interesting properties such as internal field and self-power device. ZnO- PEDOT:PSS could be utilized to make self-powered photodetector. We have successfully conducted inkjet printing of PEDOT:PSS. Hence, it is possible to design and develop self-powered UV photodetectors by solely inkjet printing.

Appendix A: Optimizing printing conditions

The printer has capable of controlling the nozzle separately using different peak voltage and waveform. Figure A.1 shows the effect of the voltage to the formation of the droplet. Low voltage setting, such as 10 V, could not create the droplet; and high voltage, such as 18 V and 20 V, would create the satellite or tale of drops, which might result in the uncontrolled splashing of the small droplet in the substrate.

Figure A.1. Effect of peak voltage to the droplet formation: at low voltage waveform, droplets could not be generated (10 V) or not stable (12 V); at medium voltage waveform (14 V and 16 V), droplets are generated stable; at high voltage waveform (18 V and 20 V), satellite droplets are formed.

The slew rate, which is the slope of the ramping voltage curve in the waveform, is also important to the formation of the droplet. Figure A.2 shows the slew rate value of 0.14

cannot generate proper droplet. The droplet is unstable and contains satellite droplet when the slew rate is set at 0.35. The droplet can be very stable with the slew rate of 0.18.

Figure A.2. Effect of the slew rate to the droplet formation. (a) Slew rate is 0.14: droplet could not be generated. (b) Slew rate is 0.15: droplet is generated but not stable. (c) Slew rate is 0.18: droplet is generated stably. (d) Slew rate is 0.35: droplet is generated along with satellite droplets.

Appendix B: Printing of silver ink

All printed silver in this thesis was printed using a commercial ink (Silver dispersion 736465, Sigma-Aldrich) which contains silver particles dispersed in triethylene glycol monomethyl ether (TGME) solvent. The nanoparticles have diameter smaller than 50 nm. According to the supplier datasheet, the ink viscosity is 10×10^{-3} - 18×10^{-3} Pa.s, surface tension is 35×10^{-3} - 40×10^{-3} N/m, and the density of the ink is 1.45×10^3 kg/m³.

Figure B.1. Printing process. (a) Photo of generated droplet (b) relationship of the velocity of generated droplets with the voltage applied to the piezoelectric-driven nozzle; (c) the spreading droplet array; (d) pattern printing with droplet space at 50 μm; (e) pattern printing with droplet space at 40 μm; (f) surface profile of the printed line.

Figure B.1 shows some feature images regarding the printing of silver. During printing, the substrate temperature was set at 60 °C to boost the vaporization of solvent. Hence, the spreading of ink to the substrate was reduced, helping to make smaller features. In order to obtain stable droplet generation, cartridge temperature was selected to be 35 °C. Firing

voltage was varied from 17 V to 23 V to observe the droplet velocity. For printing of the demonstration device, a peak voltage of 19 V was utilized. The resolution was set at 40 μm . Because the horizontal speed of the printing head during printing depends on the jetting frequency, a higher jetting frequency would result in a faster movement of the nozzles while jetting the nozzle. Hence, maximum jetting frequency was set at 2 kHz to reduce the horizontal velocity of the cartridge.

After printing, the substrate was kept in the printer platen for 10 minutes. Even with a heating temperature as low as 60 $^{\circ}\text{C}$, the solvent of the deposited ink vaporized, and nanoparticles had partially sintered, appearing as a shiny surface. The printed pattern was then kept in an oven at higher temperatures such as 100 $^{\circ}\text{C}$, 150 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ for 1 hour to enhance the sintering of the printed metal and improve the adhesion to the substrate. These heat treatments were conducted in ambient air.

Figure B.2. Morphology of printed silver film which is undergone different annealing temperature.

Figure B.2 shows the sintering of silver nanoparticles ink under different annealing temperature. Figure B.2a is the printed silver at 60°C which is composed of particles with diameter smaller than 50nm. The film annealed at 100°C did not show a significant change in size of nanoparticle. However, it is notice that the particles were starting to build-up to larger particles (Figure B.2b). The sintering effect increased significantly with the treatment temperature. Such as 150°C annealing could result in particle size of 100 nm (Figure B.2c). In Figure B.2d, the clear agglomeration effect was observed with treatment at 200°C with particle size of 200 nm. This result is matching well with the XRD result and could explain for the conductivity improvement of printed silver film by thermal sintering.

Publications list

Journal papers

Van-Thai Tran, Yuefan Wei, Hongyi Yang, Zhaoyao Zhan, Hejun Du, "All-inkjet-printed flexible ZnO micro photodetector for wearable UV monitoring device," *Nanotechnology*, vol. 28, p. 095204, 2017. (**Highlighted paper 2017**)

Van-Thai Tran, Yuefan Wei, Wei Jing Liao, Hongyi Yang, Hejun Du, "Preparing of interdigitated microelectrode arrays for AC electrokinetic devices using inkjet printing of silver nanoparticles ink," *Micromachines*, vol. 8, p. 106, 2017.

Manuscripts submitted or under preparation

Van-Thai Tran, Yuefan Wei, Hejun Du, "Enhanced responsivity of inkjet-printed zinc oxide UV photodetector by band bending modification via low-temperature annealing", submitted

Van-Thai Tran, Yuefan Wei, Hejun Du, "Printed micro heater for Joule effect annealing ZnO sensor", in preparation

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