Fabrication of zinc nitride thin films using RF magnetron sputtering deposition for optoelectronic applications

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The University of Toledo
A Dissertation

entitled

Fabrication of Zinc Nitride Thin Films using RF Magnetron Sputtering Deposition for Optoelectronic Applications

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Doctoral of Philosophy Degree in Mechanical Engineering

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An Abstract of

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Zinc nitride thin films possess a small optical band gap with direct transition, low resistivity, high mobility and carrier concentration. Therefore, it may be suitable as an optoelectronic material for infrared sensors, smart windows and energy conversion devices. The objective of this work is to grow zinc nitride thin films using RF magnetron sputtering, understand its mechanical, optical, and electrical properties, and investigate its performance as light sensing devices.

Synthesis and characterization of zinc nitride thin films has been investigated in this work. An RF magnetron sputtering deposition was employed to synthesize zinc nitride thin films using pure metal zinc target in either N₂-Ar or N₂-Ar-H₂ mixtures. The microstructural, optical and electrical characterizations of the representative films were investigated with stylus profilometry, XRD, AFM, SEM, TEM, UV-VIS-NIR double beam spectrometry, and Hall effect measurement. The photoresponse of the zinc nitride photoconductors was also studied under the irradiation of white light and NIR light.

The as-deposited zinc nitride thin films were relatively soft and densely packed with smooth surface. It possesses a narrow optical band gap in the NIR range with direct
transition. The zinc nitride showed n-type conductivity with low resistivity and high carrier concentration. To study the RF discharge power effect, the zinc nitride thin films were synthesized at different discharge powers densities. With discharge power density increasing, the film deposition rate increased, and the zinc nitride films acquired better crystalline structure, smaller optical band gap and less oxygen contaminations.

After thermal annealing at moderate temperatures in either air or O₂, the annealed zinc nitride thin films were photoconductive under irradiation of both NIR light and white light. The largest photoresponse and fastest response times were measured at the room temperature for the zinc nitride thin films annealed at 300°C in the air.

Hydrogen inclusion can modify the electrical and optical properties of crystalline semiconductor films by introducing impurity donor states. The ZnNx:H films deposited in N₂-Ar-H₂ mixture acquired less oxygen contamination and higher relative nitrogen atom concentration than the ZnNx films deposited in N₂-Ar mixture. The as-deposited ZnNx:H films showed a clear photonic behavior under white light irradiation, and the annealed ZnNx:H films exhibited a pronounced change in resistance under both white light and NIR light irradiation comparing to the annealed ZnNx films. This was the first time to report photoresponse of zinc nitride thin films fabricated by reactive sputtering method. The photoconductivity was gradually improved by optimization of deposition conditions, annealing conditions and film compositions.
This dissertation is dedicated to my parents, Mingzhe Wen and Ailan Jin. Thank you for bringing me to this world and give me unconditional love and support.
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List of Abbreviations

AFM..........................Atomic Force Microscope
a.u............................Arbitrary unit

CVD..........................Chemical vapor deposition

EDS..........................Energy dispersive spectroscopy

FWHM.........................Full width at half maximum

LED..........................Full width at half maximum

MOCVD.......................Metal oxide chemical vapor deposition
MBE..........................Molecular beam epitaxy

NIR..........................Near infrared

PECVD.......................Plasma enhanced chemical vapor deposition
PVD..........................Physical vapor deposition
PFCVAD......................Pulsed cathodic vacuum arc deposition technique
PL............................Photoluminescence

RMS..........................Root mean square
RF............................Radio frequency
RTA..........................Rapid thermal annealing

SEM..........................Scanning electron microscopy

TEM..........................Transmission electron microscopy
TFT..........................Thin film transistor

UV............................Ultra-violet

VIS..........................Visible

XRD..........................X-ray diffraction
List of Symbols

ZnN_x..................Zinc nitride sputtered in N_2-Ar plasma
ZnN_x:H...............Zinc nitride sputtered in NH_3-Ar or N_2-Ar-H_2 plasma
ZnO:N..................Nitrogen doped zinc oxide
T.........................Transmittance
R.........................Reflectance
G.........................Gauss
d.........................Film thickness
α.........................Absorption coefficient
hv........................Energy of photon
µm.......................Micrometer
ρ.........................Electrical resistivity
Ω.........................Ohm
KΩ.......................Kiloohm
GPa......................Gigapascal
θ.........................Angle
h.........................Hour
ms.......................Millisecond
R.........................Resistance
nm..................Nanometer
Å..................Angstrom
cm..................Centimeter
s..................Second
O..................Oxygen
N..................Nitrogen
Ar..................Argon
H..................Hydrogen
Au..................Gold
I..................Current
V..................Voltage
$V_G$.................Gate voltage
eV..................Electron volt
$E_g$..................Optical band gap
t..................Time
t$_1$..................Transient response
W..................Watt
Chapter 1

Introduction

1.1 Motivation

Zinc nitride is a relatively unstudied II-V semiconductor material, and most of its properties have yet not been investigated in detail yet. It is considered as a material for applications in electrical, optoelectronic and electronic applications. The low cost of its elements and synthesis procedure makes zinc nitride an excellent choice for mass production in electronic systems. Moreover, it has been demonstrated the possibility of transforming zinc nitride into p-type ZnO:N by high temperature thermal oxidation, which enables the fabrication of cheap and reliable transparent optoelectronic devices.

Zinc nitride thin films have been grown by various methods including direct reaction between evaporated Zn and NH$_3$, reactive RF magnetron sputtering, RF-PAPLD, molten salt electrochemical process, pulsed filtered cathodic vacuum arc deposition, etc. However, each of those yields different properties. There is a large dispersion of its band gap reported from 0.9 eV to 3.2 eV. Morphology was reported as smooth columnar-like nano scale grains, nanowires and empty balls. These contradictory reports were
presumably due to different crystalline qualities and the vacancy and interstitial defects generated during film growth. Therefore, further investigations on the synthesis and characterizations of zinc nitride thin films are needed.

In this research project, the investigation was made to grow zinc nitride thin films by reactive RF magnetron sputtering of metal zinc target in N$_2$-Ar, NH$_3$-Ar or N$_2$-Ar-H$_2$ mixtures, respectively. The microstructure, optical, and electrical properties of the as-deposited and thermal annealed zinc nitride thin films were characterized. The applications were investigated by applying zinc nitride thin films in optoelectronic devices.

1.2 Objectives

The overall objectives of this research were:

1. to fabricate zinc nitride thin films by reactive RF magnetron sputtering deposition;
2. to characterize the micro-structural, surface, electrical and optical properties of zinc nitride thin films;
3. to modify the zinc nitride thin films by changing deposition parameters (discharge power density and plasma source gas) and post-annealing process (Air, O$_2$, N$_2$); and
4. to apply the zinc nitride thin films for optoelectronic device (photoconductor).
1.3 Overview of the Dissertation

In this chapter, some background information related to this research is presented, including synthesis mechanisms and properties of zinc nitride. The applications of zinc nitride in thin film transistor, p-type ZnO:N and P-N junctions fabrications are discussed at the end of this chapter.

Chapter 2 includes experimental methods used in this research. The reactive RF magnetron sputtering deposition system used in this work is introduced. The processes of synthesis, thermal annealing and zinc nitride based photoconductor production are described in detail. Characterization techniques including XRD, AFM, SEM, TEM, Vickers hardness test, UV-VIS-NIR double beam spectrometry, Hall effect and photoresponse measurement are also discussed.

In Chapter 3, the zinc nitride thin films deposited in N$_2$-Ar mixture at different discharge power densities are presented. The discharge power density effect on deposition rate, microstructural, optical, and electrical properties is discussed.

Chapter 4 describes the effect of thermal annealing the as-deposited zinc nitride thin films in either air or O$_2$ at moderate temperatures was covered. The important photoconduction phenomenon of the annealed zinc nitride thin films is presented for the first time.

Chapter 5 is devoted to thermal annealing effect, presented by annealing an as-deposited zinc nitride film in air, N$_2$, air and N$_2$ at 300° C, alternately. The influence of nitrogen atom concentration in zinc nitride is discussed based on the results of the research.
In Chapter 6, the zinc nitride thin films deposited with atomic hydrogen inclusion are presented. The NH$_3$-Ar and N$_2$-Ar-H$_2$ mixtures are applied as working gas, respectively. H$_2$ to total gas ratio dependence is also investigated. The microstructural, optical, and electrical properties and photoconduction behaviors of the zinc nitride thin films are studied in relation to hydrogen inclusion.

The conclusions of this research and recommendations for future research are given in Chapter 7.

1.4 Synthesis of Zinc Nitride

1.4.1 Direct Chemical Reaction Process

Zinc nitride has been fabricated by nitridation reaction of Zn with NH$_3$ gas at 410°C for 4 h [1] and at 600°C for 120 min [2-10]. The chemical reaction of the fabrication process is as follows:

$$3Zn(s) + 2NH_3(g) \rightarrow Zn_2N_3(s) + 3H_2(g)$$  \hspace{1cm} (1)

It was reported that nitridation was incomplete at 550°C and zinc nitride was decomposed at 650°C. The optimum nitridation temperature was at 600°C. Compact ZnO or Zn$_x$O$_y$N$_z$ layers were formed on zinc nitride surface after annealing between 200°C and 500°C [4]. Interior of zinc nitride was oxidized fast when the annealing temperature was higher than 500°C. All the zinc nitride turned into zinc oxide when the annealing temperature was over 750°C.
Molten salt electrochemical process has been experimentally confirmed to form various metal nitrides films [11-15]. Zinc nitride thin films were also synthesized using a zinc electrode at 1.6 V (vs. Li+/Li) in a LiCl-KCl-Li₃N melt at 400°C [16-17]. The surface of the zinc nitride films contained a small amount of Zn(OH)₂ and ZnO observed by X-ray photoelectron spectroscopy analysis.

1.4.2 Chemical Vapor Deposition

Chemical vapor deposition is used to produce high-purity, high-performance solid materials, especially semiconductor thin films [18]. MOCVD is a highly complex CVD process for growing semiconductor multilayer structures. It has become a major process in the manufacture of optoelectronics. Polycrystalline zinc nitride films were synthesized by MOCVD using Zn[N(SiMe₃)₂]₂ and NH₃ as precursors [19]. Dimethylzinc (DMZ) and NH₃ were also employed as zinc and nitrogen source [20, 21]. The NH₃ gas was cracked at 800°C for decomposition. The growth rate increased with the growth temperature up to 575°C.

PECVD is a CVD process that utilizes plasma to enhance chemical reaction rates of the precursors [22]. It can perform a fast deposition rates at low temperature while maintaining film quality. Zinc nitride thin films were deposited at a low temperature of 140°C by PECVD using diethylzinc (DEZ), NH₃ and H₂ as zinc source, nitrogen source and carrier gas respectively [23].
1.4.3 Epitaxial Processes

Epitaxial growth is one of the most important techniques to fabricate electronic and optical devices. It mostly depends on the parameters of the thermodynamic driving force and the misfit between substrate and layer, which characterizes the film nucleation. Molecular beam epitaxy (MBE) is widely used in the manufacture of transistors for cellular phones. And the world's most efficient solar cells are commercialized by MBE fabrication. Polycrystalline zinc nitride has been synthesized by rf MBE, in which Zn flux was produced using a conventional Knudsen cell, while nitrogen radicals were generated by decomposing N₂ gas in rf plasma cell 13.56 MHz at 250 W [24]. The growth rate decreased from 7 nm/min to 0.5 nm/min, while the grain size increased from about 1 to 3.5 um as the growth temperature increased from 200 to 450°C.

1.4.4 Plasma-based Deposition Processes

In a plasma-based deposition, the target surface is sputtered by the bombardment with energetic ions in the plasma. It is useful technique for large-area coating of uniform thin films of compound semiconductors in electronic industry. Therefore, coating of zinc nitride thin films by plasma-based deposition methods can be beneficial for application of zinc nitride in electronic industry. In reactive RF magnetron sputtering, once the plasma is initiated, positive gas ions bombard on the target surface and sputter the target atoms out through momentum transferring. Powerful magnets are used to encourage the atoms to settle on the substrate in the form of a thin film. Zinc [25-29] and zinc nitride [30-35]
targets were employed to synthesize zinc nitride thin films. The zinc nitride targets were made out of the direct nitridation between zinc and ammonia. Pure argon [30, 35, 38], pure nitrogen [32, 29, 39-41] or a mixture of argon and nitrogen [26, 27, 33, 34, 42-51] were applied as sputtering gas. Mn [36] and Tb [37] metal flakes have also been put on top of target to introduce dopants during deposition.

Pulsed filtered cathodic vacuum arc deposition (PFCVAD) is an ideal source for the production of good quality (harder, denser, and cleaner) thin films at low temperature. It uses an electric arc to vaporize the target material. The impact energy of the target ions can be controlled using electric fields. Zinc nitride films have been synthesized by PFCVAD with an arc current of 650 A [51].

1.5 Properties of Zinc Nitride

1.5.1 Structural Properties

Zinc nitride was first synthesized by Juza and Hahn in 1940 [52]. It remained a relatively unstudied material until 1993; Kuriyama et al. obtained the polycrystalline zinc nitride films through direct reaction between evaporated Zn and NH$_3$ [1]. In 1997, Partin et al. reported that Zn$_3$N$_2$ adopts the cubic anti-bixbyte structure (anti Mn$_2$O$_3$ type) by time-of-flight power neutron diffraction [53]. The space group is Ia-3, and lattice parameter is equal to 9.7691(1) Å. In 2007, O-defective zinc nitride was theoretically investigated [55]. Figure 1-1 shows the simulated zinc nitride model in a cubic structure with an 80-atom supercell, and the defective models were optimized for only the atoms
around the O atom. It was reported that the formation of substitutional and interstitial O defects is easy during the synthesis of zinc nitride films. The solid with substitutional O is more stable than that with interstitial O. The electronic band structure shows that the oxygen defect plays an important role in the n-type character of the synthetic zinc nitride films.

Figure 1-1 Supercell and partial geometry of the Zn$_3$N$_2$ models for (a) supercell, (b) one substitutional O atom to N(1) (O$_{N(1)}$), (c) one O atom substituting N(2) (O$_{N(2)}$), (d) one O atom substituting Zn (O$_{Zn}$), and (e) one interstitial O atom (O$_{In}$). The bond length is in angstroms [55].
Zinc nitride power with nanoneedles and hollow spherical shell particles microstructure was fabricated by direct nitridation between zinc powder and ammonia gas [2-5, 9, 10]. The deposition mechanism is illustrated in Fig. 1-2. Empty-balls and nanowires microstructures detected in the SEM micrographs are illustrated in Fig. 1-3.

Figure 1-2 Schematic illustration of the growth mechanism for the formation of zinc nitride (a) nanoneedles [9] (b) hollow structures [10].
In situ high-pressure energy dispersive x-ray diffraction with synchrotron radiation was employed to study the structural stability of zinc nitride powder under high pressure [56]. It was stable in the pressure range up to 25.2 GPa and the bulk modulus $B_0$ was found to be 228(2) GPa.

For zinc nitride synthesized by reactive RF magnetron sputtering, M. Futsuhara et al. reported that the crystalline microstructure was affected by the nitrogen concentration in the plasma [25]. When the nitrogen concentration in the gas mixture was lower than 5 %, only zinc metal film was achieved. With the nitrogen concentration increasing to 15 %, both zinc nitride and zinc textures were detected in the film. Pure zinc nitride film was deposited when the nitrogen concentration was higher than 20 %. Similar phenomenon was presented by Kambilafka et al. that zinc nitride was opaque in color due to excess Zn in the structure as revealed by XRD analysis [54]. Zinc nitride films were also reported to adopt a single crystalline microstructure on (400) plane [27]. The crystal structure of zinc nitride films was characterized by high temperature x-ray diffraction.
under vacuum [42]. The results showed that the gradual transformation of zinc nitride phase occurred at temperature higher than 320°C.

In 2012, Nunez et al. reported substrate temperature dependence on the microstructure of zinc nitride films synthesized by reactive RF magnetron sputtering [43]. Figure 1-4 shows SEM viewgraphs of the zinc nitride samples grown at 200 W RF power, 30 sccm nitrogen gas flow and two different temperatures: 298 and 473 K. It is clear that sample grown at 473 K shows larger grain size and grain-to-grain disorientation.

![SEM viewgraphs of zinc nitride samples](image)

Figure 1-4 EM images of samples grown at deposition temperature of (a) 298 K and (b) 473 K [43].

Figure 1-5 shows that the position of the two diffraction peaks corresponding to (400) and (440) directions changed to a higher value with substrate temperature increasing. Calculated lattice constants were $a = 0.978 \pm 0.001$ nm and $a = 0.973 \pm 0.001$ nm for 298 K and 473 K, respectively. The reduction of the lattice constant is attributed to the mismatch between the thermal expansion coefficients of the substrate and the nitride film.
1.5.2 Optical Properties

The real value of the energy gap, consequently determining whether zinc nitride is a narrow or wide band gap material, is of paramount importance if it is to be used either as a passive or active layer on devices for optoelectronic applications.

The optical band gap of zinc nitride powder and films grown by direct reaction between Zn and NH$_3$ was reported in the range of 2.71 eV – 3.2 eV [1, 3, 4, 8, 9]. The PL spectrum of zinc nitride with hollow structure was illustrated in Fig. 1-6 and exhibited UV emission band at 384 nm and defect related yellow emission band at 605 nm [9]. Oxygen impurities may be incorporated in nitrogen vacancy sites due to the high reaction temperature and the oxygen and water contamination, which generated the deep level yellow emission and explained the wide band gap similar to that of zinc oxide.
The optical band gap value of the zinc nitride films fabricated by rf plasma assisted reactive pulsed laser ablation deposition was found to be 3.2 eV with direct transition by spectroscopic ellipsometry measurement, and the refractive index was in the range of 1.7 to 2.4 as a function of wavelength from 200 nm to 1600 nm [58].

It has been reported that the zinc nitride films can be prepared by PFCVAD and annealed up to 500°C [51]. The optical energy band gap of the films for assuming direct transition increased from 2.91 eV to 3.24 eV with annealing.

It was also reported that zinc nitride films had a narrow optical band gap in the range of 1.01 eV – 1.06 eV with direct transition [19, 20]. The films were deposited by MOCVD and rf-MBE. The optical band gap as a function of carrier concentration for zinc nitride films is illustrated in Fig 1-7 [20]. A strong blue shift of the optical band gap

Figure 1-6 PL spectrum of zinc nitride powder with hollow structure [9].
is observed with increasing carrier concentration. It was claimed that oxygen existed as a donor and caused a larger optical band gap due to the Burstein-Moss effect. Consequently, the high carrier concentration was a result of the oxygen contamination. It is found that oxygen contamination without an intentional doping in zinc nitride films can produce a high carrier concentration, leading to a broader optical band gap due to the Burstein-Moss effect.

Figure 1-7 Optical band gap as a function of carrier concentration. The solid line shows the calculated Burstein-Moss shift. The inset represents absorption coefficient squared plotted as a function of photon energy [20].

As regards the zinc nitride films deposited by reactive RF magnetron sputtering, a wide range of optical band gap with different transition type was reported. Zinc nitride films deposited using zinc target in N₂-Ar mixture was reported to have a narrow direct
optical band gap of 1.01 eV - 1.46 eV [25, 29, 43]. Figure 1-8 shows that the optical band gap was found to be increasing from 1.25 eV to 1.46 eV with substrate temperature decreasing [43]. PL spectrum of the zinc nitride films deposited using zinc target in pure N₂ working gas showed one well-defined peak at 582 nm (2.13 eV), which was considered to be the emission peak of ZnₓOᵧNₜ formed on the surface of the zinc nitride films due to the substitutional incorporation of oxygen for nitrogen [27]. According to the analysis of the photon energy dependence of absorption coefficients, the zinc nitride films prepared using zinc nitride targets in pure N₂ working gas at room temperature had obtained an indirect optical band gap about 2.11(2) eV [31].

![Optical band gap calculations from the Tauc model as a function of the deposition temperature. Inset: results from the Davis-Mott model [43].](image)

In summary, depending on the deposition technique and/or the oxygen impurities, the optical band gap of zinc nitride has been reported to be ranging from 0.9 eV to 3.4 eV.
Zinc nitride thin films were reported to show a dark blue color in appearance. In general, dark blue color semiconductor cannot have a band gap in the UV/visible range of spectrum. Therefore, it is very important to avoid oxygen contamination during fabrication of zinc nitride. This fact indicated that the reported band gap values should be purified to get the actual optical band gap of Zn$_3$N$_2$.

1.5.3 Electrical Properties

Zinc nitride was reported to be n-type conductive despite different synthesis methods and conditions. According to the theoretical study in 2007, O defects can easily be formed during synthesis of zinc nitride or deterioration when left in air, and the unintentional substitutional O defect was responsible for the n-type conductivity of zinc nitride films [55].

Zinc nitride films deposited by reactive RF magnetron sputtering of zinc target in N$_2$-Ar mixture atmosphere were reported with high electron mobility of $\sim$ 100 cm$^2$V$^{-1}$s$^{-1}$. Depending on the nitrogen concentration in the plasma, the carrier concentration was in the range of $1.2 \times 10^{20}$ to $6 \times 10^{18}$ cm$^{-3}$ [25]. However, zinc nitride films deposited using ZnN target in Ar plasma were reported to exhibit low mobility of $\sim$ 10$^{-1}$ cm$^2$/Vs [33]. In 2012, zinc nitride films were prepared in N$_2$-Ar mixture ambient at different deposition temperature [43]. Fig 1-9 shows the dependence of electric properties on substrate temperature. Resistivity reached a minimum, and mobility was also maximized at 423 K.
Zinc nitride films grown by rf-MBE and MOCVD exhibited n-type conductivity with carrier concentration of $1.0 - 1.6 \times 10^{20} \text{ cm}^{-3}$ and $0.15 - 1.6 \times 10^{20} \text{ cm}^{-3}$, and mobility of $24 - 156 \text{ cm}^2/\text{Vs}$ and $8.6 - 118 \text{ cm}^2/\text{Vs}$ at room temperature, respectively [20]. The high carrier concentration of $\sim 10^{20} \text{ cm}^{-3}$ was attributed to the plasma cell employed, consisted of a quartz tube, which easily produced oxygen. The slightly higher mobility was due to the larger grain sizes obtained by the deposition techniques.
1.6 Applications of Zinc Nitride

1.6.1 Channel Layer for Thin Film Transistors

Zinc nitride films were deposited by reactive RF magnetron sputtering and annealed inflowing nitrogen in a rapid thermal annealing system for 1 min [30]. Annealing in nitrogen at high temperatures deteriorated the electrical properties and the film became transparent. It was reported that the channel layer in a TFT must have high mobility and low carrier concentration [60]. Therefore, the nitrogen annealed transparent zinc nitride thin layer was employed as the channel for the transparent TFT. The structure of the TFT was shown in Fig. 1-10.

![TFT structure configuration](image)

Figure 1-10 The TFT structure configuration [30].

The device gave transistor characteristics illustrated in Fig. 1-11. The gate voltage after annealing at 300°C was ~ 14 V, and after annealing at 400°C it decreased to ~ 6 V.
This can be attributed to the higher transparency, resistivity and mobility with the increase in annealing temperature.

![Graph](image)

Figure 1-11 Output characteristics (IDS-VDS) after annealing at 300°C and 400°C [30].

In the year of 2012, as-deposited zinc nitride film was directly applied for TFT [59]. The polycrystalline zinc nitride thin film of thickness ~ 200 nm was deposited onto insulating ATO/IOT (~50 nm) coated corning glass by PLD technique of a zinc target in nitrogen plasma. Figure 1-12 shows that the transistor transfer characteristics were found to be nonlinear in a linear plot. This is a well-known phenomenon in transistors and has been addressed previously in a-Si TFT technology as well as in organic TFTs [61, 62].
Figure 1.12 Transfer characteristic of the zinc nitride transistor, which is used to estimate the field effect mobility (0.073 cm$^2$/Vs) and threshold voltage shift (-6.8 V) [59].

1.6.2 P-type ZnO:N Fabrication

It has been demonstrated the possibility of transforming zinc nitride into p-type ZnO:N by high temperature thermal oxidation, which enables the fabrication of cheap and reliable transparent optoelectronic devices. It is known that the realization of reproducible and controllable p-type ZnO:N will lead to the new era of cheap and reliable transparent optoelectronic devices. It was pointed out that the oxidation temperature is a critical parameter to obtain a good quality p-type ZnO:N.
P-type ZnO:N films was achieved by annealing zinc nitride films deposited by DC magnetron sputtering at an oxidation temperature between 350°C to 500°C [66]. N-type conductivity was observed when oxidation temperature reached 550°C or higher.

A ZnO phase was detected in the zinc nitride films fabricated by PECVD from a DMZn and NH₃ gas mixture at the annealing temperature of 500°C [21, 23]. And p-type ZnO:N films with a carrier density of ~ 4.16x10¹⁷ cm⁻³ was obtained when annealing temperature increased to 700°C.

As regarding the zinc nitride films grown by reactive RF magnetron sputtering, p-type ZnO:N was also achieved by annealing at an oxidation temperature between 400°C and 550°C [33, 34, 44]. The ZnO:N films were transparent, having high resistivity and low carrier concentration [33, 34]. Neutral acceptor bound excitons at 3.36 eV and high transmittance in the visible light range was observed [44].

In 2008, the as-deposited ZnNx:Mn films were thermally oxidized in flowing O₂ at 550°C and turned into p-type Mn doped ZnO:H thin films with a hole concentration of ~ 2.8x10¹⁶ cm⁻³ [36].

1.6.3 Fabrication of P-N Junctions

N-type zinc nitride films were deposited on n-type Si wafer by PECVD using dimethyl zinc and NH₃ at 450°C [21]. The zinc nitride films were oxidized and turned into p-type conductive at annealing temperature of 500°C, 600°C and 700°C. Figure 1-13 shows the I–V characteristics of the p-ZnO:N/n-Si annealed at different thermal oxidation
temperatures. Maximum value of a rectifying characteristic with a turned-on voltage of 2.44 V was observed in the zinc nitride annealed at 700°C.

Figure 1-13 The I–V characteristics of the p-ZnO:N/n-Si annealed at different thermal oxidation temperatures [21].

A P-N junction between p-type ZnN:O film and n-type ZnN film was also fabricated. The zinc nitride films were grown by RF magnetron sputtering at 30 W. The p-type ZnN:O was achieved by annealing the zinc nitride films at 300°C for 3 h. It was reported the carrier concentration increased from ~10^{17} cm^{-3} to ~10^{19} cm^{-3}, since the heat treatment would active the carriers. The mobility decreased from ~10^2 cm^2/Vs to ~2.05 cm^2/Vs due to the impurity scattering caused by the increased carrier concentration.
The rectification characteristic of p-n junction was shown in Fig. 1-14. In the dark environment, the leakage current was about -15 μA under reserve bias and did no breakdown under -3 V. The light generated hole-electron pairs in the depletion region. The hole-electron pairs were separated by the reverse bias and generated extracted leakage current. The increased carrier concentration decreased the resistivity, which resulted in the increased current under forward bias.

![Graph showing the electrical property of zinc nitride p-n junction measured in the dark (1) with the lighting (2) [94].](image)

Figure 1-14 The electrical property of zinc nitride p-n junction measured in the dark (1) with the lighting (2) [94].
1.7 Summary

In this chapter, the motivation of this research, historical background, and up-to-date progress have been summarized. Zinc nitride has mix properties reported by different researchers. In order to apply this material in optoelectronic devices, the fundamental properties of zinc nitride must be well understood and accurate.
Chapter 2

Experimental and Characterization Details

The synthesis of zinc nitride thin films by reactive RF magnetron sputtering is presented in this chapter. The reactive RF magnetron sputtering system is illustrated in detail. The growth processes of zinc nitride thin films are described step by step. Thermal annealing processes and zinc nitride photoconductors fabrications are also introduced. XRD, AFM, SEM, TEM, Vicker hardness tester, double beam spectrometry, and Hall effect measurement are applied to characterize the samples of zinc nitride thin films. The measurement mechanism of photoconduction behavior of zinc nitride photoconductors is also presented.

2.1 Experimental Procedures

2.1.1 Deposition Mechanism

Reactive RF magnetron sputtering is one of the most widely used methods for semiconductor fabrication; it has the advantages of simple implementation, high deposition rate, and large film area. This technique is also used to fabricate thin film
sensors, photovoltaic thin films, metal cantilevers and interconnects etc. Here, magnets are used to increase the percentage of electrons that take part in ionization of events and thereby increase the probability of electrons striking the Ar atoms, increase the length of the electron path, and hence increase the ionization efficiency significantly. The deposition was performed under vacuum to reduce the particle density so that the mean free path for collision is long. The substrate can be heated up to 300°C to improve the film adhesion to the substrate. The deposition rate for any given material depends on the operating parameters such as deposition pressure, discharge power level, substrate temperature, and distance between target and substrate et al.

Figure 2-1 shows the schematics of simplified RF magnetron sputtering system. The zinc nitride thin films were deposited on non-alkaline glass using a zinc target (purity 99.995 %) in N$_2$-Ar, NH$_3$-H$_2$, or N$_2$-Ar-H$_2$ mixtures. The distance between the cathode and the anode was 4 cm. The substrates were ultrasonically cleaned in acetone and isopropanol, rinsed in deionizer water, and subsequently dried in flowing nitrogen gas before they were introduced into the sputtering system. A rotary pump is used to achieve a low to medium vacuum. A turbo pump is used to achieve high vacuum. The base pressure was in the range of $2 \times 10^{-6} - 5 \times 10^{-6}$ Torr, and the deposition pressure was around $5 \times 10^{-3}$ Torr. Once the vacuum reached to $2 \times 10^{-5}$ Torr, introduce Ar gas to the chamber by opening the argon inlet valve gradually. Sputtering starts when a negative charge is applied to the target material, which will ionize the Ar and N source working gas. Positive charged Ar ions generated in the plasma region are attracted to the negatively biased zinc target plate at a very high speed. This collision creates a momentum transfer and ejects atomic size zinc particles from the target. These Zn particles react with the
negatively charged N atoms in the plasma and are ultimately deposited as a thin film on the surface of the substrates. To prevent RF signal returning to the RF power supply, a matching box is used for tuning the impedance of the system. Although the substrate temperature would increase with the bombardment, it was controlled below 35°C from the starting substrate temperature of 22°C during the deposition processes.

Figure 2-1 Schematic of simplified reactive RF magnetron sputtering system [72].
2.1.2 Thermal Annealing Process

Figure 2-2 Top: Cartoons of P3HT thin films with representative scattering patterns for each morphology. Bottom: The crystallographic directions are shown relative to the molecular structure [84].

Thermal annealing is a method widely used to improve the structural properties and repair damages in materials (illustrated in Fig 2-2). Diffusion would also occur and drive-in the dopant deeper into the structure. Furthermore, the physical and chemical properties, and phase transition of semiconductors are usually temperature dependent [80]. Therefore, thermal annealing is also performed to investigate the thermal stability of the materials. For instance, the electronic and structural properties of p-μc-Si:H can be changed by thermal annealing to make an optimal design of solar-cell structure and its
fabrication process [81]. The photoresponse of the anodic TiO$_2$ nanotube layers would be strongly enhanced by at least a factor of 100 by annealing in air or in argon [82]. It is also investigated that nanoparticle grew larger in size with thermal annealing, which can help to improve the conversion efficiency of solar cells if metal nanoparticles are included in the photovoltaic devices [83].

Therefore, a key point for a full understanding of zinc nitride is the availability of a clear picture showing its properties and evolution upon thermal annealing. In this work, the as-deposited zinc nitride films were annealed using a Lindberg/Blue tube furnace in air, O$_2$, and N$_2$ at 300°C to study the moderate temperature thermal annealing effect.

2.1.3 Fabrication of Zinc Nitride Photoconductors

Photoconductivity is an optical and electrical phenomenon in which a semiconductor becomes more conductive due to the absorption of light, such as visible light, ultraviolet light, infrared light, or gamma radiation. To cause excitation, the light that strikes the semiconductor must have enough energy to raise electrons across the band gap, or to excite the impurities within the band gap. The most common application of photoconductors is a photodetector, which measures light intensity.
According to earlier results in this project [87], zinc nitride forms very good ohmic contacts with gold (illustrated in Fig. 2-3) and therefore 200 nm thick gold film contacts (in a Van der Pauw configuration) were deposited at four corners of square-shaped samples using thermal evaporation.

In order to fabricate zinc nitride photoconductors, Au electrodes were patterned by standard optical lithography technique and etching of Au with an aqueous KI/I₂ solution. The width and spacing of Au electrodes were 6 mm and 4 mm, respectively. Therefore, the light irradiated area was 0.24 cm² for each optical sensor.
2.2 Characterization Techniques

2.2.1 Microstructure and Surface Properties

The crystal structure of the zinc nitride thin films was determined by XRD using a PANalytical X’Pert Pro MPD and Scintag XDS-2000 x-ray powder diffractometer with a Cu Kα radiation source in a 2θ range of 30° to 60°. The RMS surface roughness and grain size of the zinc nitride thin films were studied with AFM and SEM. SEM images were obtained using a Carl Zeiss field-emission scanning electron microscope (SMT AG Supra 35VP) operating at an accelerating voltage of 15 kV and using an in-lens ion annular secondary electron detector. In order to obtain quantitative information on chemical composition in the zinc nitride thin films, EDS measurements were performed at a voltage of 20 kV. The hardness of the zinc nitride films was measured using a Vicker hardness tester (CM-400AT) with a diamond indenter under a load of 10 g.

2.2.2 Electrical and Optical Properties

Hall effect measurements were performed by an H-50 system at room temperature to determine the resistivity, carrier type, mobility, and carrier density in the zinc nitride thin films by applying an electric field and a magnetic field. The magnetic field was set at 2500 G, and the optimal current, being sample dependent (i.e. carrier concentration dependent) was determined automatically by the Hall effect system.

To characterize how molecules in the zinc nitride thin films react with photons of varying wavelengths, the optical transmittance and reflectance were measured at room
temperature with a UV-VIS-NIR double beam spectrometer over the wavelength range from 200 to 1800 nm. The absorption coefficient, $\alpha$, was calculated by inserting transmittance $T$, reflectance $R$ and film thickness $d$ into the following equation [89]:

$$T = [(1 - R)^2 \exp (-\alpha d)]/ [1 - R^2 \exp (-2\alpha d)]$$

(2)

Then, the optical band gaps of the zinc nitride thin films were calculated by using the Tauc model (plotting $(hv\alpha)^2$ versus energy $(hv)$, for direct electron transition) and the Davis-Mott model (plotting $(hv\alpha)^{1/2}$ versus energy, for indirect electron transition).

**2.2.3 Optoelectronic Properties**

Figure 2-4 shows the schematic diagram of the zinc nitride thin film photocurrent measurement system. The zinc nitride photoconductor was tested in a vacuumed glass chamber (200 cm$^3$, 10$^{-3}$ Torr) with Au connecting by measuring the resistance of zinc nitride layer between Au electrodes or the current flowing through the circuit using a high mega ohm multimeter (Keithly Model: 22-816). The films will be irradiated with both 850 nm light beam using an array of LED with an intensity level of 2.16 $\mu$W/mm$^2$ and simulated solar light (Newport 92251A-1000). The change in electrical conductivity of the zinc nitride thin films varies the current flowing through the circuit. The data was collected using a commercial software package (LabView) available from the National Instruments Company.
The experimental data of the dynamic response behavior of the annealed zinc nitride films for the change in conductivity were fitted well into the exponential form as [95]:

$$I = I_0 + A \exp\left(\frac{-t}{t_1}\right) \quad \text{or} \quad R = R_0 + A \exp\left(\frac{-t}{t_1}\right)$$

Here, the current $I$ (or resistance $R$) is measured as a function of time ($t$). $I_0$ (or $R_0$) is the saturation current (saturation resistance), and $A$ is the amplitude of the response, and $t_1$ is the constant.
Chapter 3

Discharge Power Density Effect

Radio frequency (RF) discharge power level plays an important role and can influence the physical and chemical properties of the zinc nitride films. During the sputtering process, the acceleration of the positive ions towards the substrate in the plasma was primarily determined by the excitation frequency of the discharge. This positive ion bombardment would be intensified with discharge power increasing, resulting in a rise of the substrate temperature [73, 74]. Due to the different energetic and thermal circumstances, zinc nitride films with different final quality and structures would be achieved. Therefore, in this section, the discharge power density effect on the properties of the zinc nitride thin films was investigated. The depositions were processed at discharge powers density from 1.08 to 1.51 W/cm$^2$.

3.1 Structural Properties

Figure 3-1 shows the XRD spectra of the zinc nitride films sputtered at different discharge power. The zinc nitride film deposited at 1.08 W/cm$^2$ was amorphous. Whereas the 1.29 W/cm$^2$ deposited zinc nitride film exhibited polycrystalline structure with no
preferred orientation. Zn$_3$N$_2$ (222), (321), (400) and (440) peaks were visible at 2θ = 30.76°, 33.8°, 36.97°, and 53.87°, respectively (JCPDS card no 01-088-0618). When the discharge power density reached to 1.51 W/cm$^2$, the zinc nitride thin film obtained preferred orientation on (400) plane. The intensity of the XRD peaks is also found to increase with increase in discharge power. This is in accordance with the temperature measurements, because it can be assumed that when the temperature of the film is high enough, the lattice gets enough energy to crystallize. Therefore, it can be concluded that higher deposition power might be attributed to the better crystalline structure.

The deposition rate was estimated by dividing the film thickness by the deposition times. Table 3-1 shows the deposition rate at different discharge power density. The deposition rate increased with the increase of discharge power. The RF power influence on the deposition rate can be explained like this: when increasing the RF power, the ionic current bombarding the target is expected to increase too. The ionic current increase enhances the Zn sputtering rate from the target and this increase, in turn, increases the deposition rate on the substrate. It was also supported by the increased zinc element concentration measured by EDS, which will be explained in detail in section 3.3.

<table>
<thead>
<tr>
<th>Discharge power density (W/cm$^2$)</th>
<th>1.08</th>
<th>1.29</th>
<th>1.51</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition rate (nm·s$^{-1}$)</td>
<td>7.89</td>
<td>8.52</td>
<td>15.4</td>
</tr>
</tbody>
</table>
Figure 3-1 X-ray diffraction spectra of the zinc nitride films deposited at 1.08, 1.29 and 1.51 W/cm$^2$.

### 3.2 Optical Properties

Figure 3-2 shows the optical transmittance and reflectance spectra of the zinc nitride thin films measured by spectrophotometer as a function of the photon wavelength from 200 to 1800 nm. The deposited films were dark in appearance. A characteristic shoulder was observed at around 650 nm in the transmittance spectra of the zinc nitride film deposited at 1.08 W/cm$^2$, and it drastically increased to 990 nm when the discharge power increased to 1.29 W/cm$^2$. 

Figure 3-2 Optical transmittance and reflectance spectra of the zinc nitride films deposited at 1.08, 1.29, 1.51 W/cm².

The optical band gap can be obtained as shown in Fig. 3-3. It is seen that the values of optical band gap energy drastically decreased from 2.3 eV to 1.4 eV with the discharge power increased from 1.08 W/cm² to 1.29 W/cm². However, the band gap just slightly decreased to 1.3 eV when the discharge power increased to 1.51 W/cm². On the basis of experimental results, it may be concluded that band gap of the zinc nitride films is also discharge power dependent. Here we observed that the band gap of the zinc nitride thin films decreased on increasing the discharge power, and narrow band gap could be achieved at discharge power higher than 1.29 W/cm². The decrease in optical band gap
was probably attributed to the decrease in oxygen content and increase in zinc and nitrogen concentration analyzed using EDS.

Figure 3-3 \((a\nu)^2\) as a function of photon energy for the zinc nitride films deposited at 1.08, 1.29, 1.51 W/cm².

3.3 Surface Morphology and Chemical Composition

Figure 3-4 shows the SEM micrographs of the representative zinc nitride thin films. The SEM micrographs illustrated lower grain sizes at low growth discharge power. The corresponding film roughness measured using atomic microscope is given in Table 3-2. Results suggested smoother surface morphology at low growth discharge power. It is
clear that larger grain size would result in rougher surface. Therefore, the change in grain size observed by SEM was in accordance with surface roughness measured by AFM.

Figure 3-4 Plane-view images of the zinc nitride thin films deposited at (a) 1.08, (b) 1.29 and (c) 1.51 W/cm$^2$. 
EDS measurements indicated that the zinc nitride film deposited at low discharge power had more defects and could be more easily oxidized during storage. On opposed to the lower oxygen contamination with higher discharge power, zinc and nitrogen concentration was increased, and the Zn:N ratio was closer to the stoichiometric value of 1.5 with the discharge power increasing. This also explained the better crystalline structure achieved at higher discharge power observed by XRD measurement.

Table 3.2 Zn, N and O atomic concentration and surface roughness of the zinc nitride films deposited at 1.08, 1.29 and 1.51 W/cm².

<table>
<thead>
<tr>
<th>Discharge power density</th>
<th>Surface roughness (nm)</th>
<th>Zn (%)</th>
<th>N (%)</th>
<th>O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08 W/cm²</td>
<td>7.89</td>
<td>51.99</td>
<td>21.67</td>
<td>26.34</td>
</tr>
<tr>
<td>1.29 W/cm²</td>
<td>8.52</td>
<td>53.56</td>
<td>28.6</td>
<td>17.85</td>
</tr>
<tr>
<td>1.51 W/cm²</td>
<td>15.4</td>
<td>59.65</td>
<td>35.13</td>
<td>5.22</td>
</tr>
</tbody>
</table>

Figure 3-5 shows the TEM image of the as-deposited zinc nitride film synthesized at 1.51 W/cm². It can clearly see the arrangement of atoms inside the thin film, with the bright points being the interspaces inside the crystal and the dark thread being the shadow of the atom inside the crystal. The interplanar distance was measured to be 2.43 Å, which was close to the theoretical value of the predominant phase (400) in the zinc nitride thin film.
Figure 3-5 TEM image of the zinc nitride film deposited at 1.51 W/cm².

Figure 3-6 Cross-section SEM image of the zinc nitride film deposited at 1.51 W/cm².
Crack-free hardness indentations were achieved on the surface of the as-deposited zinc nitride film synthesized at 1.51 W/cm² under the load of 10 g. The penetration depth was ~1.36 um. Figure 3-5 shows the cross section SEM image of the zinc nitride film. It indicated that the film thickness (~2 um) was sufficient for the surface roughness measurement. The hardness was measured to be ~410HV, indicating that zinc nitride is a relatively soft material.

3.4 Electrical Properties

The zinc nitride films exhibited n-type conductive and low resistivity. With the increase in discharge power, the resistivity and carrier concentration of the zinc nitride films decreased, whereas the mobility increased. The lower resistivity and carrier concentration might be due to the increased zinc concentration, decreased oxygen defects and improved crystallinity. The zinc nitride film sputtered at higher discharge power embrace bigger crystallites (grains), which are closer to bulk crystalline zinc nitride. Bigger grain sizes results in larger unfilled inter-granular volume. Furthermore, the higher discharge power increased the plasma temperature near the substrate, and provided atoms with higher energy level. Both might be the underlying reason for the higher mobility.
Table 3.3 Resistivity, mobility, and carrier concentration of the zinc nitride thin films deposited at 1.08, 1.29 and 1.51 W/cm².

<table>
<thead>
<tr>
<th></th>
<th>Resistivity (Ω·cm)</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
<th>Carrier Density (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.08 W/cm²</td>
<td>1.63×10⁻²</td>
<td>3.95</td>
<td>9.70×10¹⁹</td>
</tr>
<tr>
<td>1.29 W/cm²</td>
<td>5.55×10⁻³</td>
<td>10.40</td>
<td>1.08×10²⁰</td>
</tr>
<tr>
<td>1.51 W/cm²</td>
<td>2.16×10⁻³</td>
<td>24.71</td>
<td>1.17×10²⁰</td>
</tr>
</tbody>
</table>

3.5 Summary

The zinc nitride thin films obtained polycrystalline structure at the discharge power density higher than 1.29 W/cm². The deposition rate and crystallinity was increased with the discharge power density increasing, and the Zn:N ratio of the films were closer to the stoichiometric value of 1.5. The zinc nitride film deposited at 1.51 W/cm² obtained narrow optical band gap of ~ 1.4 eV and low oxygen contamination. The zinc nitride thin film obtained good adhesion with the non-alkaline glass substrates. The surface of zinc nitride thin films was smooth and densely packed, and the grain size increased with discharge power density. The zinc nitride thin films exhibited n-type conductivity and low resistivity of ~10⁻³ Ω·cm and high carrier concentration of ~ 10²⁰ cm⁻³. With discharge power density increasing, zinc nitride thin films obtained lower film resistivity with higher carrier mobility and density.
Chapter 4

Air and Oxygen Thermal Annealing Effect

It was reported that the zinc nitride films prepared by RF magnetron sputtering was converted into p-type ZnO upon oxidation at 400°C [33]. Further annealing up to 550°C deteriorated the electrical properties. Zinc nitride thin films were unstable and could absorb oxygen easily. Therefore, high temperature thermal annealing process would convert it into zinc oxynitride or nitrogen doped zinc oxide upon annealing [35]. In this section, the as-deposited zinc nitride films were annealed in either air or O₂ at 300°C for 1 h to study the thermal annealing effect on the microstructure, optical characterization, surface morphology, chemical composition, electrical properties and photo-conducting behavior.

4.1 Structural Properties

Figure 4-1(a) shows the XRD spectra of the zinc nitride films. The as-deposited and annealed zinc nitride films were polycrystalline and had a dominant peak located at 36.96°, which was the (400) plane of cubic anti-bixbyite zinc nitride structure (JCPDS
card no 01-088-0618). In addition to the (400) plane, other zinc nitride structures were also observed on the (222), (321), (440) and (442) plane, which were located at 31.7°, 34.2°, 53.7° and 56.4°, respectively. There were two important observations from the XRD patterns shown in Fig. 4-1 (a). First, one small XRD peak at 2θ = 36.25° found in the as-deposited zinc nitride film corresponded to Zn (002) phase (JCPDS card no 04-831). The presence of Zn diffraction peak indicated the excess of Zn into the zinc nitride sub-lattice, which was normally found in deposition with high percent of Ar in the plasma [27, 30, 33-35, 96]. The excess Zn in the structure of the as-deposited zinc nitride films was responsible for higher surface roughness and high conductivity (~10⁻³ Ω). Secondly, after annealing in either air or O₂ environments, the Zn phase was removed and no zinc oxide crystalline structure was observed. However, there might be some insignificant zinc oxide or zinc oxynitride phases because the concentration of oxygen increased after thermal annealing effect as seen in the energy dispersive spectroscopy (EDS) analysis (section 4.3). Figure 4-1(b) showed that the full width at half maximum (FWHM) of the (400) plane obtained from XRD spectra of the zinc nitride films increased in the annealing process. The increase in FWHM indicated that the crystallinity was decreased after thermal annealing process. The decrease in crystallinity of the zinc nitride films might be due to oxidation peripheral of crystallites or doping of oxygen in the crystalline structure. A slight increase of oxygen concentration in the film was also confirmed by EDS analysis. However, the doping levels were not large enough to produce a significant zinc oxide phase.
Figure 4-1 (a) X-ray diffraction patterns of the as-deposited, air-annealed, and O₂-annealed zinc nitride thin films and (b) XRD spectra magnified around (400) reflection.
4.2 Optical Properties

Figure 4-2 (a) shows the optical transmittance and reflectance spectra of the as-deposited and annealed zinc nitride thin films. The as-deposited zinc nitride thin film showed an absorption onset at around 800 nm. Although the annealed zinc nitride films were as opaque as the as-deposited zinc nitride film, the optical transparency decreased significantly in the NIR region.

Figure 4-2 (b) shows the plot of $(\alpha h \nu)^2$ versus photon energy. The optical band gap of the annealed zinc nitride films narrowed down to $\sim 1.15$ eV from $\sim 1.3$ eV. Previous studies reported that the band gap of annealed films was wider than the as-deposited zinc nitride film [6, 35]. This was due to the high annealing temperature in the range of 500 - 800°C, which might turn the zinc nitride film into either zinc oxynitride or nitrogen doped zinc oxide. As the annealing temperature in this study was moderate (300°C), chemical doping by oxygen was not high enough to change the zinc nitride film into zinc oxynitride. Chemical composition analysis obtained from EDS spectra for annealed films also revealed that there was only a slight increase in the oxygen concentration of the annealed zinc nitride films. However, further theoretical investigations are required to understand such a behavior.
Figure 4-2 (a) Optical transmittance and reflectance spectra and (b) $(ahv)^2$ as a function of photon energy of the as-deposited, air-annealed, and O$_2$-annealed zinc nitride thin films.
4.3 Surface Morphology and Chemical Composition

Figure 4-3 and 4-4 show the surface and cross section microstructure of the zinc nitride films, respectively. It was seen that the annealed zinc nitride films were smooth and densely packed as the as-deposited film. There was no significant change in the microstructures of the bulk due to thermal annealing process. However, by means of the Scherer formula [85, 86], the average grain size of the annealed films was estimated to decrease slightly due to the increased FWHM of the predominant phase (400). The surface roughness obtained by AFM and the atomic percentage of Zn, N and O atoms derived from EDS analysis is listed in Table 4-1. The surface roughness of the zinc nitride films was slightly decreased after thermal annealing process. The smaller grain size and the removed excess Zn in the structure of the annealed zinc nitride films might be responsible for the lower surface roughness. After thermal annealing process, the oxygen concentration in the zinc nitride film increased, whereas the nitrogen concentration decreased. It can be attributed to the fact that the removal of excess nitrogen and the doping of oxygen in the zinc nitride films occur simultaneously during thermal annealing process.
Figure 4-3 Plane-view SEM images of the (a) as-deposited, (b) air-annealed, and (c) O$_2$-annealed zinc nitride thin films.

Figure 4-4 Cross-section SEM images of the (a) as-deposited, (b) air-annealed, and (c) O$_2$-annealed zinc nitride thin films.

Table 4.1 Zn, N and O atomic concentration and surface roughness of the as-deposited and annealed zinc nitride thin films.

<table>
<thead>
<tr>
<th></th>
<th>Surface roughness (nm)</th>
<th>N/Zn (%)</th>
<th>O/(O+Zn+N) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>26.9</td>
<td>58.89</td>
<td>5.22</td>
</tr>
<tr>
<td>Air-annealed</td>
<td>25.0</td>
<td>57.12</td>
<td>5.68</td>
</tr>
<tr>
<td>O$_2$-annealed</td>
<td>25.8</td>
<td>57.02</td>
<td>5.83</td>
</tr>
</tbody>
</table>
4.4 Electrical Properties

The values of resistivity, carrier concentration, and mobility are shown in Table 4-2. The as-deposited films exhibited n-type conductivity with a carrier mobility of \(~35\, \text{cm}^2\, \text{V}^{-1}\, \text{s}^{-1}\). Although the values of mobility reported in different literatures were in the range of \(0.1 \sim 100\, \text{cm}^2\, \text{V}^{-1}\, \text{s}^{-1}\) [20, 25, 30, 43], the mobility obtained in this work still demonstrated the as-deposited zinc nitride film as a potential candidate in opto-electronic devices because of its low band gap energy. Lower mobility for the as-deposited film might be due to the low substrate temperature and high nitrogen content in the sputtering mixture [87].

The zinc nitride films were not turned into p-type zinc oxynitride after thermal annealing process as reported by different researchers [21, 23, 33, 66, 90, 96]. Insignificant increase in oxygen concentration analyzed by EDS also indicated that the annealed films didn’t turn into p-type zinc oxynitride. The underlying reason for this would be the moderate annealing temperature. The zinc nitride films were reported to turn into zinc oxynitride or nitrogen doped zinc oxide at relatively high temperature [33, 35]. On the other hand, the conductivity, carrier concentration and mobility decreased after thermal annealing process. This can be attributed to the fact that the loss of zinc phase and the decrease in crystallinity of the annealed film may have deteriorated the electric property. Kambilafka et al. reported similar behavior, when the zinc nitride films were annealed at \(550^\circ\text{C}\) in air [33].
Table 4-2 Resistivity, conduction type, mobility, and carrier density of the as-deposited and annealed zinc nitride films.

<table>
<thead>
<tr>
<th></th>
<th>As-deposited</th>
<th>Air-annealed</th>
<th>O₂-annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (Ω cm)</td>
<td>8.05×10³</td>
<td>2.08×10¹</td>
<td>1.962</td>
</tr>
<tr>
<td>Conduction type</td>
<td>n-type</td>
<td>n-type</td>
<td>n-type</td>
</tr>
<tr>
<td>Mobility (cm² V⁻¹ s⁻¹)</td>
<td>32.33</td>
<td>4.77</td>
<td>5.26</td>
</tr>
<tr>
<td>Carrier Density (cm⁻³)</td>
<td>2.60×10¹⁹</td>
<td>6.29×10¹⁸</td>
<td>8.24×10¹⁸</td>
</tr>
</tbody>
</table>

4.5 Behavior of Photoconductivity

No photo-conducting behavior was observed from the as-deposited zinc nitride films with the spectral region including ultra-violet (UV), visible and near infra-red (NIR) light. However, the spectral response consisted of two distinct observable peaks with the zinc nitride films annealed in air and oxygen. Figure 4-5 (a) shows the spectral response of the device containing the zinc nitride films annealed in oxygen environment at 300 °C. Two main peaks were at around 760 nm and 970 nm corresponding to 1.63 and 1.29 eV, respectively. The sharper peak at 1.29 eV might correspond to the emission from nitrogen bound excitations. When the as-deposited films were annealed in air, it produced a very similar behavior with the O₂-annealed device. There was no significant change in the optical spectra from different devices fabricated at different times. Voulgaropoulou et al. reported the photo luminescence (PL) spectra of the zinc nitride films annealed in
different conditions [35]. A sharper peak at around 3.3 eV was observed for the films annealed at 800°C in air. As reported, the peak at around 3.3 eV was also consistent with the transmission spectra. Kambilaflka and et al. also reported that the zinc nitride films annealed at 550°C exhibited the excited related emission between 3.10 – 3.38 eV [33]. The observations revealed that the elevated annealing temperature produced ZnO phases, giving rise to the PL peaks associated with ZnO. However, the zinc nitride films in this study showed no ZnO phase in thermally annealed films. The absence of ZnO phase might have shifted the emission peaks towards higher wavelength region. However, a detailed chemical and electronic implication about the significant difference in the spectral response needs further theoretical investigations.

The devices produced by air and oxygen annealed films were also tested for photo-conducting behavior. Figure 4-5 (b) shows the response and recovery of the device with zinc nitride films annealed in O₂ at 300°C when NIR light of 850 nm wavelengths was used as a step function. Figure 4-5 (c) shows the baseline of the device for the current measured in dark. For ten consecutive cycles of response and recovery, the response of the device exhibited the behavior of reproducibility. The device was also tested at different times. The cycles of response and recovery of the device investigated at different times showed similar behavior and agreed well within 1 % signifying the reliability of the device. The net change in the current due to the presence of IR light was relatively small. It was due to the fact that the intensity of IR light was in the order of microwatt per square centimeter.

The as-deposited zinc nitride films exhibited excellent band-gap matching for the adsorption layer of thin film solar cells having theoretical maximum efficiency. Although
numerous efforts were made to improve the photoconductivity though optimization of deposition parameters, it was difficult to achieve photoconducting characteristics to a measurable level. However, it was observed that the annealing of zinc nitride for shorter period ether in air or O$_2$ ambient improved the photoconductivity of zinc nitride. The results presented in this work are the conclusion obtained from many repeated experiments. On the other hand, it is generally believed that the zinc and copper nitrides are unstable materials in air hence these materials cannot be used in solar cells and other electronic devices. The experimental results obtained from this investigation contradicts these believes and they indicated that the optical absorption edges have a red shift and improved photoconductivity after annealing in either air or O$_2$. 
Figure 4-5 (a) Spectral response, (b) photoconducting behavior, and (c) baseline (current in dark) of the $O_2$-annealed zinc nitride film under the irradiation of NIR light.
4.6 Annealing Temperature Dependence on Zinc Nitride Photoconductor

To further study the dependence of annealing temperature on photoconductivity, the as-deposited zinc nitride films were annealed in air at 275°C, 300°C, and 350°C for 2 h. Figure 4-6 shows the effect of annealing temperature on photoconductivity at room temperature. The vertical axes of this set of graphs were set at the same magnitude for comparison of the effect of photoresponse magnitude. As discussed earlier, these films exhibited photoresponse only after annealing at a temperature above 275°C. The results indicated that the highest photoresponse was seen for the film annealed at 300°C for NIR light. On the other hand, fast response was shown by the zinc nitride thin film annealed at 275°C, but the recovery time increased. At 350°C, the response was drastically reduced. Although the exact reason for this phenomenon is unknown at present, this phenomenon can be dependent on the content of nitrogen in the films. It is anticipated that the annealing process resulted in the formation of stoichiometric Zn$_3$N$_2$ materials by removal of nitrogen inclusion from the films. When the films were annealed at a temperature higher than 300°C, the film loses nitrogen at a rapid rate and therefore, these films exhibit poor electronic properties.
Figure 4-6 Dependence of annealing temperature on photoconductivity of zinc nitride.

The measurement temperature is 24°C. The annealing temperature is indicated in the figures. The full scales of vertical axis are set at the same magnitude.
Figure 4-7 (a) shows the response and recovery of the Zn$_3$N$_2$ film annealed at 300°C when NIR light was turned on and off for several cycles while (b) is for one cycle. Since the intensity of the NIR light was low, the resistance change due to the NIR light was low but the signal was very clear.

Figure 4-7 Photoresponse of the zinc nitride thin film annealed at 300°C due to NIR light for (a) eight cycles and (b) one cycle.
Figure 4-8 shows the exponential rise and fall patterns when NIR light was turned on (a) and off (b). The time responses were ~ 441 ms and ~ 640 ms, respectively. The recovering time is longer than the response time partly due to the thermal effect of NIR light.

Figure 4-8 Photoresponse (a) and recovery (b) of the zinc nitride thin film annealed at 300°C with exponential fitting due to NIR light at room temperature.
4.7 Measurement Temperature Dependence on Zinc Nitride Photoconductor

Figure 4-9 Photo response of the zinc nitride thin film annealed at 300°C with exponential fitting due to NIR light at 24°C, 50°C and 100°C.
Figure 4-9 shows the photo-response at room temperature, 50˚C and 100˚C. The film was heated for 30 min to attain the thermal equilibrium. It can be seen that the resistance of the device decreases under the irradiation of IR light for a given temperature whereas the photo-response was reduced with the increase in temperature. This behavior was in accordance with the photoconductivity of many semiconductors. The data was also fitted with the equation (1) to evaluate the rise time and fall time. Comparing the data taken at the room temperature with 50˚C and 100˚C, the rise time increased to ~ 514 ms and ~ 570 ms, the corresponding fall time increased to ~ 648 ms and ~ 714 ms, respectively.

4.8 Summary

After thermal annealing in either air or O₂ at moderate temperature (300˚C), the crystallinity of the zinc nitride thin film was slightly weakened, and the optical band gap, conductivity, and carrier mobility were decreased. The annealed zinc nitride films exhibited a photo-conducting behavior with a stronger peak at around 1.30 eV corresponding to the emission of nitrogen bound excitations. Therefore, the thermal annealing process in either air or O₂ of zinc nitride films at moderate temperature can be used to tune the band gap without changing the crystal structure significantly.
Chapter 5

Nitrogen Thermal Annealing Effect

Due to N vacancy defects and O interstitial and substitutional defects in zinc nitride, contradictory properties were reported. The results in Chapter 4 show that atomic nitrogen concentration decreased and oxygen contamination slightly increased in the zinc nitride films after thermal annealing in either air or O$_2$ at moderate temperatures. In this chapter, to study the dependence of atomic nitrogen concentration on the properties of zinc nitride, diffusion of atomic nitrogen into the zinc nitride films structure was approached by thermal annealing an as-deposited zinc nitride film in air, N$_2$, air, N$_2$ alternately for 1 h at 300°C.

5.1 Structure Properties and Chemical Composition

Figure 5-1 (a) and (b) shows the XRD spectra and the FWHM of the predominant peak of the zinc nitride film right after deposition and each annealing process. The as-deposited zinc nitride film was polycrystalline and had three phases on (400), (321), and (440) plane of cubic anti-bixbyite zinc nitride structure. Same as the air and O$_2$ annealing
experiments in Chapter 4, the FWHM of the preferred orientation (400) increased after thermal annealing in air. It indicated that the crystallinity was decreased after air annealing process. The reason might be that the nitrogen atoms escaped from the crystalline structure, which was in accordance with the decrease in atomic nitrogen concentration in the film analyzed by EDS illustrated in Figure 5-2.

However, after annealing the air-annealed zinc nitride film in flowing N$_2$ at 300°C for 1 h, the FWHM of the predominant zinc nitride peak was decreased, and nitrogen concentration was increased in the zinc nitride film. Therefore, it could be interpreted that the improvement in crystallinity of the zinc nitride film was due to the atomic nitrogen incorporated into the crystalline structure.
Figure 5-1 (a) X-ray diffraction patterns of the zinc nitride film annealed in air, N₂, air and N₂ at 300°C alternately for 1 h, (b) XRD spectra magnified around (400) reflection.

Figure 5-2 Ratio of N and Zn atoms concentration of the zinc nitride film annealed in air, N₂, air and N₂ at 300°C alternately for 1 h.
5.2 Optical Properties

Figure 5-3 shows the optical transmittance and reflectance spectra of the same zinc nitride thin film right after deposition and each annealing step. It was observed that the transmission intensity decreased in the NIR wavelength region each time annealing in air, and it increased back after annealing the air-annealed film in N$_2$. On the basis of experimental results it may be conclude that band gap of the zinc nitride films is nitrogen concentration dependent. Here it was observed that the band gap of the zinc nitride thin films decreased on decreasing the nitrogen concentration by annealing in air at 300°C, and increased on increasing the nitrogen concentration.
Figure 5-3 (a) Transmittance and reflectance and (b) optical band gap of the zinc nitride film, which was annealed in air, N₂, air and N₂ at 300°C alternately for 1 h.

5.3 Electrical Properties

The zinc nitride film behaved n-type conductivity after deposition and each annealing process. Figure 5-4 shows the change of resistivity, mobility and carrier concentration with annealing, respectively. Similar to the behavior reported in section 4.4, air annealing increased the resistivity, and both the mobility and carrier concentration decreased. The underlying reason for this would be the decrease in nitrogen concentration analyzed by EDS discussed in section 4.3. After annealing the air-annealed zinc nitride thin film in flowing N₂, the resistivity, mobility and carrier concentration regained similar value as the as-deposited film, and the nitrogen concentration also increased reflected in the EDS analysis. Therefore, it can be concluded that the air annealing process reduced the nitrogen ions, however the N₂ annealing introduced nitrogen ions back into the film.
Figure 5-4 Resistivity, mobility and carrier concentration of the zinc nitride film, which was annealed in air, N₂, air and N₂ at 300°C alternately for 1 h.
5.4 Behavior of Photoconductivity

Similar to the behavior reported in section 4.4, no photo-conducting behavior was observed from the as-deposited zinc nitride films with the irradiation of NIR light. The film became photoconductive after annealing in air as seen in Figure 5-5. The resistance decreased to ~ 670 Ω after nitrogen annealing process on the air-annealed and (air +N2+air)-annealed zinc nitride film. It indicated that the resistance was increased with air annealing and decreased with nitrogen annealing. And air-annealing process decreased the nitrogen concentration, whereas N2-annealing process incorporated nitrogen into the zinc nitride film according to the increased N/Zn ratio. The experimental results indicated that zinc nitride films were not photoconductive due to the high nitrogen concentration. Either air or O2 annealing, which decreases the nitrogen concentration and introduces atomic oxygen into the lattice, would activate the photoconductivity of zinc nitride films under the irradiation of infrared light.
Figure 5.5 Photo-conducting behavior of the zinc nitride film under the irradiation of infrared light, which was annealed in (a) air, N\textsubscript{2}, (b) air and N\textsubscript{2} at 300°C alternately for 1 h.

5.5 Summary

Thermal annealing the air-annealed zinc nitride film in the flowing N\textsubscript{2} at moderate temperature (300°C) introduced atomic N into the vacancies of the zinc nitride films, which improved the crystallinity, resulting in the increased carrier mobility. The increase in atomic nitrogen concentration increased the film conductivity and carrier density, and deteriorated the photoconductivity of the air-annealed zinc nitride thin films.
Chapter 6

Effect of Addition Hydrogen in Reactive RF Magnetron Sputtering

The incorporation of atomic hydrogen into polycrystalline semiconductors causes significant changes in both the electrical and optical properties of these materials [75, 76]. An interesting example is the copper nitride films deposited in N₂-Ar-H₂ atmosphere showed unexpected structure and properties by changing the H₂/N₂ ratio [77]. H doping was reported to generate higher ionic conductivity with low activation in Li₃N [78]. The Zn₃N₂ with N vacancy defects is not stable and may decompose and oxidized during storage in the ambient air. Hydrogen in crystalline semiconductor can passivate the electrical activity of dangling or defective bonds [75]. Therefore, It is anticipated that zinc nitride would also be modified by atomic hydrogen inclusion. The ZnNₓ:H films were deposited in NH₃-Ar and N₂-Ar-H₂ mixture working gas for 1 h at 1.51 W/cm² with substrate temperature kept below 35°C. The content of the N₂ and NH₃ in the N₂-Ar-H₂ and NH₃-Ar mixture was 80 %. H₂ to total gas ratio dependence was also investigated. The effect of hydrogen ion implantation on the properties of zinc nitride films has not been studied in other published works and is first clarified in this work.
6.1 NH$_3$-Ar Mixture Working Gas

6.1.1 Structural Properties

The XRD patterns illustrated in Fig. 6-1 shows that the two zinc nitride thin films were polycrystalline with cubic anti-bixbyite Zn$_3$N$_2$ structures. The ZnN$_x$ film prepared in N$_2$-Ar mixture working gas has a preferential Zn$_3$N$_2$ growth on the (400) plane. While no preferential orientation was observed in the ZnN$_x$:H film deposited in NH$_3$-Ar plasma, and the film exhibited low intensity XRD reflections. It can be considered that using NH$_3$ as nitrogen source gas significantly decreased the negatively charged nitrogen concentration in the plasma. Therefore, the deposition rate and N concentration in the zinc nitride was decreased, resulting in the weakened crystallinity.
6.1.2 Optical Properties

The optical transmittance and reflectance of the zinc nitride thin films were plotted in Fig. 6-2 as a function of the photon wavelength from 200 to 1800 nm. As seen in Fig. 6-3, the N$_2$-Ar prepared film was opaque and black in appearance with a characteristic shoulder at 800 nm, while the NH$_3$-Ar prepared film was transparent and white-yellow in color with the absorption edge lying at around 370 nm. Thus it is quite reasonable that 80% of the visible and infrared light was transmitted through the NH$_3$-Ar prepared film and absorbed by the N$_2$-Ar prepared zinc nitride film.

The thickness of the zinc nitride thin films, $d$, is calculated using the formula [97, 98]:

![X-ray diffraction patterns](image)
Where $n$ is the refractive index, $\lambda_1$ and $\lambda_2$ are the wavelength of adjacent peaks in the transmittance spectrum. With $n = 2.0$, the film thickness was calculated and shown in Table 6-1. For the same deposition time, the film prepared in NH$_3$-Ar was much thinner, which explained the color difference between the two films. The thinner thickness can be interpreted as that the deposition rate was decreased due to decreased atomic N concentration in the plasma.

Figure 6-4 plots $(ahv)^2$ versus photon energy. The band gap energy was obtained by the extrapolation of the linear portion to the energy axis. With atomic hydrogen inclusion, the optical band gap increased to 2.37 eV, which was in accord with the smaller absorption edge. On the contrary, the optical band gap of N$_2$-Ar prepared zinc nitride thin film was narrow as $\sim$ 1.35 eV. The estimated band gap values were in good agreement with Futsuhara et al.’s conclusion that the band gap of zinc nitride would be decreased with increasing nitrogen concentration in the film [25].

Table 6.1 Film thickness of the zinc nitride thin films prepared in N$_2$-Ar and NH$_3$-Ar mixtures.

<table>
<thead>
<tr>
<th></th>
<th>N$_2$-Ar</th>
<th>NH$_3$-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness (nm)</td>
<td>1980</td>
<td>350</td>
</tr>
</tbody>
</table>
Figure 6.2 Optical (a) transmittance and (b) reflectance spectra of the as-deposited zinc nitride thin films prepared in N$_2$-Ar and NH$_3$-Ar mixtures.

Figure 6.3 Images of the zinc nitride thin films deposited in (a) NH$_3$-Ar and (b) N$_2$-Ar mixtures.
Figure 6-4 \((ahv)^2\) as a function of photon energy for the zinc nitride thin films prepared in NH\(_3\)-Ar and N\(_2\)-Ar mixtures.

6.1.3 Surface Morphology and Chemical Composition

The AFM and SEM images in Fig. 6-5 shows the surface microstructure of the zinc nitride thin films prepared in N\(_2\)-Ar and NH\(_3\)-Ar working gases. Table 6-2 lists the corresponding RMS surface roughness. In the higher magnification analyzed by AFM, it is observed that triangular grains coarsely covered the top surface with small round densely packed grains beneath for the NH\(_3\)-Ar prepared ZnN\(_x\) film, and the N\(_2\)-Ar prepared film was compact with larger round grains. It is clear that larger grain size results in rougher surface. However, the roughness of the NH\(_3\)-Ar prepared film was twice large as that of the N\(_2\)-Ar prepared film. The likely reason is that the triangular grains and the micro holes between the triangular grains drastically increased the surface roughness.
Figure 6-5 AFM (a) and SEM (b) images of the zinc nitride thin films prepared in N$_2$-Ar and NH$_3$-Ar mixtures.
Table 6.2 RMS surface roughness of the zinc nitride thin films prepared in N$_2$-Ar and NH$_3$-Ar mixtures.

<table>
<thead>
<tr>
<th></th>
<th>N$_2$-Ar</th>
<th>NH$_3$-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface roughness (nm)</td>
<td>17</td>
<td>36.5</td>
</tr>
</tbody>
</table>

6.1.4 Electrical properties

The resistivity of the zinc nitride thin films prepared in NH$_3$-Ar and N$_2$-Ar mixtures is shown in Table 6-3. The resistivity significantly increased with the replacement of N$_2$ as NH$_3$ as nitrogen working gas. It can be interpreted that less atomic zinc was incorporated into the zinc nitride structure due to the significantly decreased atomic nitrogen in the plasma.

Table 6.3 Resistivity of the zinc nitride thin films prepared in NH$_3$-Ar and N$_2$-Ar mixtures.

<table>
<thead>
<tr>
<th></th>
<th>N$_2$-Ar</th>
<th>NH$_3$-Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity ($\Omega \cdot \text{cm}$)</td>
<td>$7.74 \times 10^{-3}$</td>
<td>$5.61 \times 10^{3}$</td>
</tr>
</tbody>
</table>
6.2 N$_2$-Ar-H$_2$ Mixture Working Gas

6.2.1 Structural Properties

As seen in fig. 6-6, the ZnN$_x$ and ZnN$_x$:H films were polycrystalline with cubic anti-bixbyite Zn$_3$N$_2$ structure and no ZnO phases, even though oxygen contamination was observed through subsequent EDS analysis in Table 6-4. Figure 6-6 (a) showed that the ZnN$_x$ film exhibited a dominant (400) texture and very weak (321) peak of Zn$_3$N$_2$ structure (JCPDS card no 01-088-0618). As seen in Fig. 6-6 (b), the ZnN$_x$:H (0.5 % H$_2$) film exhibited the same preferred orientation on (400) plane, and the FWHM value was lower than that of the ZnN$_x$ film. It indicated that the zinc nitride film crystallinity was improved by introducing 0.5 % H$_2$ in the deposition. On the other hand, the ZnN$_x$:H (2 % H$_2$) film acquired very low degree of the XRD reflections with no preferred orientation as shown in Fig. 6-6 (c). It was considered that the preferred orientation depended mainly on the ratio of Zn:N atoms and kinetic energies of these atoms reaching the substrate during the film growth. The light weighted hydrogen ions would not strongly influence the kinetic energies of Zn and N atoms. And the bombardment of hydrogen ions toward the zinc target and the quartz surface was close to zero. However, the hydrogen flow rate diluted the argon content and subsequently changed the Ar:N ratio in the plasma, which changed the growth orientations and prohibited the crystallization of zinc nitride films.
Figure 6-6 X-ray diffraction patterns of the (a) ZnN$_x$, (b) ZnN$_x$:H (0.5 % H$_2$) and (c) ZnN$_x$:H (2 % H$_2$) thin films.
6.2.2 Optical Properties

As can be seen in Fig. 6-7 (a), (b), and (c), the plot of $(\alpha h\nu)^2$ versus photon energy was linear, consistent with direct transition. The optical band gap values were obtained by the extrapolation of the linear portion to the energy axis. The optical band gap of the ZnN$_x$ film was estimated to be $\sim$ 1.32 eV. The optical band gaps of the ZnN$_x$:H films were wider comparing to the ZnN$_x$ film, and it increased with the H$_2$ to total gas ratio. According to the subsequent EDS results in Table 6-4, the atoms ratio of (N+O):(N+O+Zn) was increased with hydrogen inclusion. The increase in $E_g$ was probably attributed to the increase in ionicity due to the stimulated formation of Zn-N and Zn-O bonds.
Figure 6-7 $(\alpha h\nu)^2$ as a function of photon energy for the (a) ZnN$_x$, (b) ZnN$_x$:H (0.5 % H$_2$) and (c) ZnN$_x$:H (2 % H$_2$) thin films.
6.2.3 Surface Morphology and Chemical Composition

The SEM images in Fig. 6-8 showed the surface microstructure of the ZnN\textsubscript{x} and ZnN\textsubscript{x}:H films. It was observed that the ZnN\textsubscript{x}:H film was smooth and densely packed as the ZnN\textsubscript{x} film. The atomic percentage of Zn, N, and O atoms in the as-deposited ZnN\textsubscript{x} and ZnN\textsubscript{x}:H films was derived from EDS analysis and listed in Table 6-4. The stoichiometric value of nitrogen atomic percent in zinc nitride is 1.5. As can be seen from the Zn:N ratio, Zn-rich zinc nitride film prepared in an atmosphere of N\textsubscript{2} and Ar was turned into N-rich zinc nitride with hydrogen ion implantation. In such case, the hydrogen diluted the argon concentration in the deposition atmosphere and lowered the bombardment towards the target and the substrate. Oxygen was also observed in both films due to the water contamination, and the amount was comparable or less than that reported by other groups [1, 10, 20, 25, 31, 43]. It was noticed that the oxygen content was lower in the as-deposited ZnN\textsubscript{x}:H film. The reason might be that more Zn-N was formed with the increase of N content and the hydrogen in zinc nitride would also compensate defect states. Due to the special structure of hydrogen atoms, the hydrogen content in the ZnN\textsubscript{x}:H film cannot be detected from EDS analysis.
Figure 6-8 SEM images of the (a) ZnN$_x$, (b) ZnN$_x$:H (0.5 % H$_2$) and (c) ZnN$_x$:H (2 % H$_2$) thin films.
Table 6.4 EDS results of the ZnN_x and ZnN_x:H films (2 % H_2).

<table>
<thead>
<tr>
<th></th>
<th>ZnN_x</th>
<th>ZnN_x:H (2% H_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (%)</td>
<td>34.14</td>
<td>43.83</td>
</tr>
<tr>
<td>Zn (%)</td>
<td>59.46</td>
<td>51.34</td>
</tr>
<tr>
<td>O (%)</td>
<td>6.4</td>
<td>4.83</td>
</tr>
</tbody>
</table>

6.2.4 Electrical Properties

The numerical values are shown in Table 6-5. All the films exhibited n-type conductivity even after low temperature thermal oxidation. For the as-deposited ZnN_x film, the carrier density was in the range of ~ 10^{19} cm^{-3}, the mobility was ~ 22.63 cm^2 V^{-1} s^{-1} and the resistivity was ~ 10^{-3} Ωcm. These values are in agreement with the data published by the other groups [27, 33, 43]. The conductivity, mobility, and carrier density was decreased in the annealed ZnN_x film. Such behavior due to thermal annealing in air at moderate temperature was presented in Chapter 4.

In contrast, by introducing H ion in the zinc nitride film, the electrical conductivity and the mobility decreased to ~ 10^{-2} Ωcm and ~ 6 cm^2 V^{-1} s^{-1}, and the carrier density was slightly decreased. It can be explained that the hydrogen in zinc nitride compensated defect states by increasing the N atom concentration and decreasing the Zn atom concentration. Similar to the annealed ZnN_x film, the conductivity and carrier density was deceased in the annealed ZnN_x:H films, however, to a higher extent. The mobility increased with the decrease in carrier density, indicating that the impurity scattering mechanism was attributed to the increase of mobility. Further theoretical
investigations are required to understand such a behavior. It was also observed that the change in electrical properties increased with the $H_2$ to total gas ratio.

Table 6.5 Resistivity, mobility, and carrier density of the as-deposited and annealed $\text{ZnN}_x$ and $\text{ZnN}_x:H$ films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity ($\Omega \cdot \text{cm}$)</th>
<th>Mobility (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Carrier Density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AD ZnN}_x$</td>
<td>$2.81 \times 10^{-2}$</td>
<td>22.63</td>
<td>$9.38 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Ann ZnN}_x$</td>
<td>$9.11 \times 10^{-2}$</td>
<td>2.78</td>
<td>$2.46 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{AD ZnN}_x:H (0.5% H_2)$</td>
<td>$5.78 \times 10^{-2}$</td>
<td>6.32</td>
<td>$1.73 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Ann ZnN}_x:H (0.5% H_2)$</td>
<td>$1.82 \times 10^{-2}$</td>
<td>18.70</td>
<td>$1.89 \times 10^{15}$</td>
</tr>
<tr>
<td>$\text{AD ZnN}_x:H (2% H_2)$</td>
<td>$1.80 \times 10^{-2}$</td>
<td>5.47</td>
<td>$6.34 \times 10^{19}$</td>
</tr>
<tr>
<td>$\text{Ann ZnN}_x:H (2% H_2)$</td>
<td>$1.19 \times 10^{1}$</td>
<td>24.67</td>
<td>$2.12 \times 10^{14}$</td>
</tr>
</tbody>
</table>

The IV characteristics of the as-deposited and annealed $\text{ZnN}_x$ and $\text{ZnN}_x:H$ (2 % $H_2$) films are plotted in Fig. 6-9 (a) and (b), respectively. The higher slope coefficient indicated that the film exhibited higher resistivity. The current of the as-deposited films and the annealed $\text{ZnN}_x$ film was in milli-ampere, and that of the annealed $\text{ZnN}_x:H$ film was in micro-ampere. Therefore, the IV characteristics had good accord with the Hall effect and resistivity measurement.
Figure 6-9 I-V characteristics of the (a) as-deposited and (b) annealed ZnN$_x$ and ZnN$_x$:H films.
6.2.5 Behavior of Photoconductivity

The as-deposited ZnN\textsubscript{x} film did not indicated any photoconductivity for both NIR light and white light. However by introducing H\textsubscript{2} in the deposition, as shown in Fig. 6-11 (a) and 6-12 (a), both the as-deposited ZnN\textsubscript{x}-H films became photoconductive under the irradiation of white light. The annealed ZnN\textsubscript{x} and ZnN\textsubscript{x}-H films acquired higher resistivity and exhibited clear photoconductive behavior for both NIR and visible lights as shown in Fig. 6-10 (a), (b), 6-12 (b), (c), and 6-14 (b), (c). Since the intensity of the NIR light was low, the change in the resistance due to the NIR light was lower compared to the visible lights. Although the response for the NIR light was small, both the transient response and recovery time was not observed in the order of microseconds as the generation and recombination of electron-hole pair should be very instant. As shown in Table I, the change in resistance of the ZnN\textsubscript{x}-H films was evidently larger with visible light illumination comparing to the air-annealed ZnN\textsubscript{x} film, and it increased with the higher H\textsubscript{2} to total gas ratio. Therefore, hydrogen inclusion yielded better photonic behavior than the ZnN\textsubscript{x} based optical sensors. Because of these interesting properties, the hydrogen included zinc nitride can be applied in photo detectors, smart window as well as the photovoltaic devices.
Figure 6-10 Photo-response curves of the annealed ZnN$_x$ film due to (a) NIR light and (b) white light at room temperature.
Figure 6-11 Photo-response curves of (a) the as-deposited ZnN\textsubscript{x}:H (0.5 % H\textsubscript{2}) film due to white light and annealed ZnN\textsubscript{x} (0.5 % H\textsubscript{2}) film due to (b) NIR light and (c) white light at room temperature.
Figure 6-12 Photo-response curves of (a) the as-deposited ZnN$_x$:H (2 % H$_2$) film due to white light and annealed ZnN$_x$ (2 % H$_2$) film due to (b) NIR light and (c) white light at room temperature.
Table 6.6 Change in resistance of the annealed ZnNₓ and ZnNₓ:H films under the irradiation of white light.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔR/R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ann ZnNₓ</td>
<td>3.31</td>
</tr>
<tr>
<td>Ann ZnNₓ:H (0.5% H₂)</td>
<td>21.88</td>
</tr>
<tr>
<td>Ann ZnNₓ:H (2% H₂)</td>
<td>48.09</td>
</tr>
</tbody>
</table>

6.3 Summary

The ZnNₓ:H (0.5 % H₂) film acquired better crystalline structure and slightly wider direct band gap comparing to the ZnNₓ film. However, with atomic hydrogen concentration increasing in the plasma (80 % NH₃ or 2 % H₂), the ZnNₓ:H film achieved polycrystalline structure with low degree of Zn₃N₂ reflections and no preferential growth, and the optical band gap was broadened. Oxygen contamination was decreased and N-rich zinc nitride was achieved with 2 % H₂ in the plasma. The resistivity of ZnNₓ:H film exhibited increased with atomic hydrogen concentration. The as-deposited zinc nitride film became photoconductive under the irradiation of white light by introducing H₂ into the plasma. The annealed ZnNₓ:H film exhibited more and faster change in resistance for both NIR light and white light comparing to the annealed ZnNₓ film, and more evitable photoconductive behavior was observed with the higher H₂ to the total gas ratio.
Chapter 7

Conclusions and Future Work

7.1 Conclusions

The investigation including the synthesis, characterization, and light sensing applications indicated that the zinc nitride thin films synthesized by reactive RF magnetron sputtering using zinc target in N\textsubscript{2}-Ar and N\textsubscript{2}-Ar-H\textsubscript{2} mixture working gas have either similar or better properties compared with other deposition methods, and the zinc nitride thin films have a potential to be used as an optoelectronic material for infrared sensors, smart windows and energy conversion devices.

The ZnN\textsubscript{x} films were n-type conductive, opaque with low resistivity of \(~10^{-3}\) Ω cm and high carrier concentration of \(~10^{20}\). The surfaces of the ZnN\textsubscript{x} films were smooth and densely packed. With discharge power density increasing to 1.51 W/cm\textsuperscript{2}, rougher surface roughness and larger grain size were achieved; the ratio of Zn to N atoms in the ZnN\textsubscript{x} films was closer to the stoichiometric value of 1.5; oxygen contamination was less; the optical band gap decreased to the NIR range. The hardness of the ZnN\textsubscript{x} films deposited at 1.51 W/cm\textsuperscript{2} was approximately 410HV, indicating that zinc nitride is a
relatively soft material. No photo-conducting behavior was observed for the as-deposited ZnN$_x$ films with the spectral region including ultra-violet, visible and near infrared light.

After thermal annealing the ZnN$_x$ films in either air or O$_2$ at moderate temperature, the crystallinity was slightly weakened, and the transmittance spectra revealed a decrease in optical band gap. The ZnN$_x$ films annealed at a temperature above 275°C exhibited photoresponse under both the illumination of NIR light and white light. The annealed zinc nitride films exhibited a photoconducting behavior with a strong peak at ~ 1.30 eV corresponding to the emission of nitrogen bound excitations. Both the annealing temperature and measurement temperature dependence on photoconductivity were studied. The results indicated that the highest photoresponse and fastest transient response time were seen for the ZnN$_x$ film annealed at 300°C measured at room temperature. After thermal annealing the air-annealed ZnN$_x$ film in the flowing N$_2$ at moderate temperature (300°C), atomic nitrogen concentration in the film was increased close to the value of the as-deposited ZnN$_x$ film. The film crystallinity was improved, resulting in the increased carrier mobility. However, the photoconducting behavior of the air-annealed ZnN$_x$ film was deteriorated.

The ZnN$_x$:H thin films deposited in N$_2$-Ar-H$_2$ mixture working gas had slightly wider direct optical band gap in the NIR region, lower mobility, higher resistivity and less oxygen contamination. The Zn-rich ZnN$_x$ film was turned into N-rich ZnN$_x$:H with H$_2$ inclusion. The as-deposited ZnN$_x$:H film was photoconductive under the illumination of white light. After thermal annealing in air at 300°C, the ZnN$_x$:H films became photoconductive for both NIR light and white light, and the photoresponse was more evitable comparing to the annealed ZnN$_x$ film.
7.2 Future Work

There are still some spaces to improve the reactive RF magnetron sputtering system although it is better than the other methods to grow zinc nitride thin films. There are some drawbacks for the application of zinc nitride in optoelectronic devices. More research should be done for more applications of zinc nitride.

During this research, very encouraging results of the IR sensing experiments have been reported, notably the sensing of NIR light on the air annealed zinc nitride thin films. In a future project, the properties of the low temperature air annealing should be further characterized in order to ascertain the performance as NIR sensing device. It was found that the zinc nitride film prepared with \( \text{N}_2-\text{Ar}-\text{H}_2 \) performed better photoconductivity for both NIR and solar light than the films prepared with \( \text{N}_2-\text{Ar} \). Further experiments to find the influence of hydrogen on the zinc nitride should be explored. Other sensing properties, such as gas or pressure may also be investigated.

P-type doping by oxidation is still an important topic both in application and scientific view. It was reported that some zinc nitride films became p-type during annealing due to diffusion of oxygen dopant. In this project, the zinc nitride films still performed n-type conductive after thermal annealing up to 550\( ^\circ \)C and after oxygen plasma treatment. Therefore, it would be prudent to repeat and expand these experiments to confirm the most suitable method.

With this study, the synthesis and properties of zinc nitride could be better understood. It is anticipated that this material will have some applications in photonics and solar cells in the future.
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