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Reactive Sputtering Deposition and Characterization of Zinc Nitride and Oxy-Nitride Films for Electronic and Photovoltaic Applications

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Engineering

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An Abstract of

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This dissertation presents a study on the fabrication of zinc nitride and zinc oxy-nitride films, and related hetero-structures on glass, silicon and other substrates. The goals of this study include gaining fundamental understanding on the electrical and optical properties, the chemical-bonding states and the micro-structure of these materials and examining their potential for photovoltaic and other electronic and optoelectronic applications.

Reactive radio-frequency (RF) magnetron sputtering was used as the deposition method, which potentially enables control of composition of the thin films, as well as fabrication of multilayer structures for the study of possible hetero-junctions between zinc nitride and zinc oxy-nitrides. Along with reactive sputtering, several other fabrication methods, such as thermal evaporation and solution (e.g. silver or carbon paste) painting, were used as auxiliaries where necessary. The characterization techniques employed include (i) x-ray based techniques (x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDXS)), (ii) optical based methods (spectroscopic ellipsometry (SE), optical spectrophotometry,
Raman spectroscopy), (iii) scanning electron microscopy (SEM), and (iv) electrical measurements (resistivity, Hall effect measurements, current-voltage and photovoltaic measurements).

The cross-correlation between the deposition/post-deposition conditions and the physical properties of the films was investigated. The deposition conditions, such as the nitrogen (or oxygen) partial concentration in the sputtering gas mixture, substrate temperatures, total deposition pressure, as well as the post-deposition treatments such as thermal treatment and/or oxidation in ambient, were studied in detail. Zinc nitride, with a small fraction of "naturally" incorporated oxygen, is found to be a promising candidate for photovoltaic applications because of its optical and electrical properties. Also, the capability of property tuning for the zinc oxy-nitride material system was demonstrated by intentionally introducing varied amount oxygen into zinc nitride.

In order to better understand the crystalline structure and the electronic band structure of these materials, first principle density functional theory (DFT) was used for computations of pure zinc nitride and the doping effects in it with both native elements (Zn, N) and copper family elements (Cu, Ag, Au) as possible p-type dopants. Atomic geometry, formation energy, as well as electronic structure of defects in zinc nitride were studied and a general consistency was observed between theoretically calculated and experimentally determined results. Defect density of states (DOS) suggest that among all three studied copper-family elements, copper is a good candidate for a p-type dopant.

Technological insight and approaches to the fabrication of device-relevant structures were the other important outcomes of this work. Our studies showed that the fabrication of device-relevant ohmic contacts, rectifying metal-nitride junctions and p-n
junctions was possible. Substantial photovoltaic action was observed in a single junction solar cell configuration that uses p-type zinc oxy-nitride as an absorber layer.
TO MY BELOVED FATHER,

Haohui Jiang

WHOSE GUIDANCE MAKES ME WHO I AM;

TO MY DEAR MOTHER,

Yuxian Wang

WHOSE DEEPEST LOVE ENCOURAGES ME;

TO MY SWEETHEART,

Weihu Xu

WHOSE UNDERSTANDING AND SUPPORT STRENGTHENS ME,

THIS DISSERTATION IS AFFECTIONATELY DEDICATED

BY THE AUTHOR.
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List of Abbreviations

AC ..............................Alternating Current
BE ..............................Binding Energy
CB ..............................Conduction Band
CP ..............................Critical Point
CVD ...........................Chemical Vapor Deposition
EDXS ..........................Energy Dispersive X-ray Spectroscopy
EV ...............................Electron Voltage
DC ..............................Direct Current
DEZ ............................Diethylzinc
DFT ............................Density Functional Theory
DMZ ............................Dimethylzinc
DOS ............................Density of States
FCC .............................Face-Centered Cubic
FF ...............................Fill Factor
FWHM ...........................Full Width at Half Maximum
GGA ...........................Generalized Gradient Approximation
GIXRD ........................Gazing Incidence X-ray Diffraction
HEMT ..........................High-Electron Mobility Transistor
ITO .............................Indium-Tin-Oxides
LED .............................Light Emitting Diode
LD ...............................Laser Diode
LDA ..............................Local Density Approximation
LDOS ............................Local Density of States
LPCVD ........................Low Pressure Chemical Vapor Deposition
MIS ..............................Metal-Insulator-Semiconductor
MISFET ........................Metal-insulator-semiconductor Field-effect Transistor
MOCVD ........................Metal Organic Chemical Vapor Deposition
MQW .............................Multiple Quantum Well
MS ..............................Metal-Semiconductor
PAMBE ........................Plasma-Assisted Molecular Beam Epitaxy
PECVD ........................Plasma-Enhanced Chemical Vapor Deposition
PLD ..............................Pulsed Laser Ablation Deposition
RF ...............................Radio Frequency
RT ...............................Room Temperature
SAXS ..........................Small Angle X-ray Scattering
SE ...............................Spectroscopic Ellipsometry
SEM..........................Scanning Electron Microscopy
TCO..........................Transparent Conducting Oxides
TFT..........................Thin Film Transistor
TTFT..........................Transparent Thin Film Transistor
UV...........................Ultraviolet
VB...........................Valence Band
XPS..........................X-ray Photoelectron Spectroscopy
XRD..........................X-ray Diffraction
List of Symbols

$\Delta$.................................Angle of ellipsometry
$\alpha$.................................Absorption coefficient
$\theta$.................................Bragg angle
$\lambda$.................................Wavelength of the incident x-ray beam
$\mu$.................................Chemical potential
$\rho$.................................Resistivity
$\tau$.................................Scattering time
$\nu$.................................Frequency of the electromagnetic wave associated with a photon
$\psi$.................................Angle of ellipsometry

$A^0X$.................................Acceptor bound exciton
$B$.................................Full width at half maximum
$E_F$.................................Fermi Energy
$J_{sc}$.................................Short circuit current density
$K$.................................Scherrer constant
$L$.................................Mean grain size
$P_{in}$.................................Incident power
$P_{max}$.................................Maxima power
$V_{oc}$.................................Open circuit voltage

$d$.................................Distance between atomic layers in a crystal
$h$.................................Planck constant
$k$.................................Extinction coefficient
$m_e$.................................Effective mass of electron
$n$.................................Index of refraction
$r_p$.................................Complex amplitude reflection coefficients for incident light with parallel polarizations
$r_s$.................................Complex amplitude reflection coefficients for incident light with perpendicular polarization
Chapter 1

Introduction

Nitride semiconductors have been recognized as one of the most promising class of materials for optical devices, high-speed and high-power electronic devices due to their unique optical and electrical properties. Group-III-nitride semiconductors, in particular, such as aluminum nitride (AlN), gallium nitride (GaN) and indium nitride (InN), have attracted significant research interest and have now become important materials for optoelectronic and electronic devices. The large and mostly direct band gaps of III-nitrides cover the visible region and extend into the ultraviolet (UV) range. The group-III-nitrides system (AlGaInN) contains a range of compounds, which, theoretically, allows the III-nitrides to achieve any band gap value within that range. This, combined with excellent luminescence properties, makes the III-nitrides suitable for solid state light applications, such as high brightness visible light emitting diodes (LEDs) and blue or violet laser diodes (LDs), as well as UV photo-detectors [1]. Besides the optoelectronic area, III-nitride semiconductors also find applications in the fields of high-speed and high-power electronics. Because of the wide band gap, great thermal stability and thermal conductivity, GaN/AlGaN based high-electron mobility transistor (HEMT) are well-known for its high break down voltage and high power performance [2].
The group-II-nitrides are also believed to offer great potential in many areas. However, group-II-nitrides are much less studied and understood. Research interest in zinc nitride (Zn$_3$N$_2$), in particular, appeared only in recent years, even though Zn$_3$N$_2$ powder was first synthesized by Juza and Hahn [3] in 1940. After remaining a relatively unstudied material for more than 50 years, zinc nitride films were first fabricated by Kuriyama et al. [4] through direct reaction between ammonia and metal zinc in 1993. Since then, different methods, like sputtering deposition, chemical vapor deposition (CVD), epitaxy deposition, pulsed laser ablation deposition and electrochemical processes, have been used to prepare Zn$_3$N$_2$ thin films and nanostructures.

Zinc nitride is a group-II-V compound semiconductor. It has an almost black color, and its prevailing crystalline structure is that of the cubic anti-bixbyite (space group of Ia$\bar{3}$). The Zn$_3$N$_2$ structure can be regarded as a face-centered cubic (FCC) arrangement of N atoms with the larger Zn atoms occupying three-fourth of the tetrahedral sites [4]. The absence of the Zn atoms in the unoccupied tetrahedral holes produces a slight distortion of the FCC structure. The lattice constant of Zn$_3$N$_2$ is 9.7691(1) Å [5]. Zinc nitride is considered a promising material, offering advantages such as relatively high electron mobility, environment-friendly processing and low fabrication cost. Although it is still a relatively new material, Zn$_3$N$_2$ has already been investigated in relation to various applications, for example, as the channel layer [6,7] in transparent thin film transistors (TTFTs), as an interesting negative electrode material exhibiting little irreversible capacity loss [8], and as a material in renewable energy storage processes [9]. Zinc nitride is also considered as a potential compound for electronic, photovoltaic and sensor applications [10-12].
Beyond what is mentioned above, zinc nitride also has attracted research interest because of its potential as a precursor in the fabrication of p-type ZnO:N, the success of which would have major implications for the semiconductor industry. Zinc oxide (ZnO), a transparent group-II–VI oxide semiconductor with a wurtzite crystal structure and a direct band gap of 3.37 electron voltage (eV) at room temperature, has attracted significant attention because of its good optical, electrical and piezo-electrical properties. However, ZnO thin films are usually n-type with high electron concentrations, resulting in difficult p-type doping due to self-compensation effects. From theoretical work, nitrogen is considered to be one of the most promising potential acceptors in ZnO [13]. In addition, if the fabrication of zinc oxy-nitrides could be fully controlled, one can expect that their band gap as well as other properties can be finely tuned by varying the composition. Epitaxial zinc oxy-nitride films can be grown on ZnO substrates which could be of significant importance to device development.

In very recent years, another group of materials based on zinc nitride, the Zn-IV-nitrides, is receiving an increasing amount of attention [14]. With the group-IV elements, silicon (Si), germanium (Ge), and tin (Sn), the Zn-IV-nitrides can be seen as a series of compounds which are very similar to III-nitrides. These ternary alloys are expected to provide advantages such as the possibility of forming promising hetero-junctions, better tunability of the band gaps and other properties, together with low cost due to earth abundant elements.

The potential opportunities, and even breakthroughs, mentioned above rely on expanding the currently limited understanding of the base material, zinc nitride. The physical properties of zinc nitride are not well studied or understood. In efforts to
understand this material, significant disagreements on the values of some of the key
physical parameters exist, such as the energy band gap and the type of the conductivity.
The energy band gap of zinc nitride reportedly ranges from 1.01 to 3.2 eV and has been
stated either as direct or indirect type, depending on deposition and characterization
methods, and microstructure (i.e., thin films, hollow nano-balls, etc.). Both n-type and p-
type zinc nitride, in either as-prepared or annealed forms, were reported. The respective
carrier concentration in this intrinsic material was in the range of $10^{15}$ cm$^{-3}$ to $10^{20}$ cm$^{-3}$.
Other challenges include the control and reproducibility of chemical composition and
electrical properties in the deposition process, stability of the composition and properties
under ambient conditions after deposition, and in particular, challenges related to the
undesired oxidation of films.

The main goal of this project was to identify the physical properties and film
structures dependencies of zinc nitride on the deposition conditions, such as nitrogen
partial concentration in the sputtering gas mixture, substrate temperatures during
deposition, and total deposition pressure. Zinc nitride thin films were prepared at
different deposition conditions, and then examined both before and after post-deposition
treatment, by various techniques including (i) x-ray based techniques (x-ray diffraction
(XRD), x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray spectroscopy
(EDXS)), (ii) optical based methods (spectroscopic ellipsometry (SE), optical
spectrophotometry, Raman spectroscopy), (iii) scanning electron microscopy (SEM), and
(iv) electrical measurements (resistivity, Hall effect measurements, current-voltage (I-V)
and photovoltaic measurements). The second goal of this project was to establish a way
for controllable incorporation of oxygen into zinc nitride films to obtain wider ability of
property tuning by, again, controlling the deposition conditions and with additional help from post-deposition treatments such as annealing and/or oxidation. The oxygen and nitrogen interaction is believed to be crucial for conducting type as well as other electrical properties. By varying oxygen and nitrogen concentration in the sputtering gas mixture, as well as other conditions, the properties of zinc oxy-nitride thin films can, in principle, be tuned and controlled. Annealing can also be helpful due to its potential of eliminating or reducing existing defects or facilitating other, leading to desirable electrical and optical properties. The third goal of this project was to gain understanding of the atomic and electronic structures of both pure and extrinsic zinc nitride by involving theoretical modeling, particularly first principles density functional theory (DFT) calculations. These theoretical calculations are an appropriate tool for examining fundamental physical properties of pure zinc nitride based on the crystal structure of its primitive unit cell. Information on native defects can also be obtained from DFT calculations. Other possible defects that are non-native (i.e., impurities and related) were also considered and their behavior was modeled. The fourth goal of this project was to use the acquired knowledge and understanding on controlling of the properties of zinc nitride and zinc oxy-nitride for the development of device-relevant structures, such as p-n junctions, metal-semiconductor (MS) junctions, and metal-insulator-semiconductor (MIS) junctions. Combinations of layers between semiconductors or semiconductors and metals were studied by electrical and photovoltaic measurements.
Chapter 2

Background and literature review

Beginning with a general review of nitride compounds, mainly III-nitrides, on their optical and electrical properties as well as the related applications, this section summarizes the research developments on zinc nitride, zinc oxy-nitride and nitrogen-doped zinc oxide. The deposition methods that can be used to fabricate zinc nitride and related compounds are also discussed in this section.

2.1 Nitride compounds

Within the last decades, the progress made in developing the group-III-nitride semiconductors is remarkable. The entire III-nitrides family was established, well studied and understood. The III-nitrides have been recognized as important materials for optoelectronic as well as for high temperature and high power applications because of their excellent optical and electrical properties. The hexagonal wurtzite phases of the III-nitride compounds have direct optical band gaps in the range from 1.9 eV (α-InN) to 3.4 eV (α-GaN), then further to 6.2 eV (α-AlN) [15]. And the band gaps (also direct) of the cubic modifications of III-nitrides cover from 1.7 eV (β-InN) to 3.2 eV (β-GaN), then further to 4.9 eV (β-AlN) [15]. Moreover, the group-III-nitrides family (AlGaN)
exhibits the excellent capability to form a complete series of ternary or even quaternary compounds, which, theoretically, allows the III-nitrides to achieve any band gap value within whole visible region and the deep ultraviolet region, seen in Figure 2-1. In terms of electrical properties, finely controlled n-type as well as p-type doping of III-nitride semiconductors has been accomplished and high electron mobility was observed. A high electron mobility of 1700 cm$^2$V$^{-1}$s$^{-1}$ has been reported in AlGaN/GaN heterostructures [16].

Figure 2-1 Bandgap and bowing parameters of hexagonal (α-phase) and cubic (β-phase) InN, GaN, AlN and their alloys versus lattice constant $a_0$ [15] (Reprinted with permission from Journal of Physics D: Applied Physics 31, 2653 (1998). Copyright 1998 IOP PUBLISHING, LTD.).

LEDs based on III-nitride compounds provide a choice of wavelength of operation from green/blue region into deep ultraviolet region [1], such as blue LEDs (~430 nm) with a p-GaN/n-InGaN/n-GaN double heterostructure [17], UV-A (340 – 400 nm) LEDs with an Al$_{0.2}$Ga$_{0.8}$N/GaN [18] or Al$_x$Ga$_{1-x}$N/Al$_y$Ga$_{1-y}$N [19] multiple quantum...
well (MQW) structure, UV-B (290 – 340 nm) light emitting diodes (LEDs) with a quaternary AlInGaN MQW active region [20], and UV-C (100 – 290 nm) LEDs used very high-quality AlGaN layers with high Al concentration [21]. The III-nitrides based laser diodes (LDs) also filled the empty space of blue-violet-UV region solid state light source with an excellent performance. The lifetimes of III-nitrides LDs exceeded 10,000 h, and therefore became commercially acceptable [22]. Equally important with light sources, AlGaN based ultraviolet photo-detectors with high quantum efficiency, high speed and low dark currents have been achieved. Photoconductors, photovoltaic detectors, and surface acoustic wave detectors are all developed using III-nitride compounds.

The group-III- nitride semiconductors also have shown great potential in the field of high-speed and high-power electronics because of the strong bond strength, the wide band gap, great thermal stability and thermal conductivity. High power electronic devices with very high speed based on InAlN/(In)GaN [23] or GaN/AlGaN [2] quantum wells have been successfully demonstrated.

2.2 Zinc nitride

Zn$_3$N$_2$ power was first synthesized by Juza and Hahn [3] in the year of 1940 and remains a relatively unstudied material for more than 50 years. In the year of 1993, the zinc nitride thin films were first fabricated by direct reaction between NH$_3$ and zinc films on quartz substrates which were kept at 410$^\circ$C [4]. Randomly orientated polycrystalline cubic zinc nitride films were obtained with the evaluated lattice constant $\alpha$ of 9.78(1) Å. The optical band gap of zinc nitride films was first examined to be 3.2 eV with a direct
transition. Due to the high reaction temperature as well as a reaction environment that usually contains trace amounts of oxygen or water, the films were partially oxidized which explains why the measured band gap was so close to that of ZnO. In the year of 1997, the crystalline structure of Zn$_3$N$_2$ was refined by analyzing neutron time-of-flight powder diffraction data [5]. The cubic anti-bixbyite structure with lattice constant $\alpha$ of 9.7691(1) Å was reported.

In the year of 1998, reactive RF magnetron sputtering was first utilized to prepare zinc nitride thin films [24]. A metallic zinc target and the nitrogen-argon gas mixture were used. Based on the x-ray diffraction (XRD) (see Figure 2-2), pure Zn metal films were formed when the nitrogen concentration in the sputtering gas was 5%, and the Zn$_3$N$_2$–Zn mixed films were observed when the nitrogen concentration increased to 15%. When the nitrogen concentration reached in the range of 20% to 100%, pure Zn$_3$N$_2$ thin films were deposited with the orientation heavily affected by the nitrogen concentration in the sputtering gas. The nearly stoichiometric value between N and Zn was reported in this paper, based on the x-ray photoelectron spectroscopy (XPS) data, in which oxygen and hydrogen related peaks were also observed. The authors also suggested that the N-Zn bond had more iconicity than the N-B, N-Al and N-Si bonds due to relatively large chemical shift in N 1s observed in XPS measurements. The electrical properties of zinc nitride thin films were also studied by room temperature Hall effect measurements. The n-type conductivity was reported with high electron mobility (over 100 cm$^2$V$^{-1}$s$^{-1}$). The carrier concentration was ranged from 1.2x10$^{20}$ to 6x10$^{18}$ depended on nitrogen fraction in the sputtering gas. Moreover, an optical band gap of 1.23 eV was calculated which was dramatically lower than the value reported in ref. 4.
In 2003, zinc nitride thin films were deposited by direct-current (DC) magnetron sputtering of zinc target in nitrogen and argon ambient [25] and plasma-enhanced chemical vapor deposition (PECVD) from a Zn(C₂H₅)₂ and NH₃ gas mixture [26] in order to obtain nitrogen doped zinc oxide through oxidation of zinc nitride thin films. Worth to notice here is that in the PECVD work [26], along with secondary (100) and (110) peaks of ZnO, the main diffraction peak of as-deposited zinc nitride thin film corresponded to (321) ZnN phase, rather than the normally reported (400) ZnN phase. In the year of 2004, potentiostatic electrolysis of zinc electrodes in the molten LiCl·KCl·Li₃N system was employed to produce zinc nitride thin films [27]. The zinc nitride was synthesized, and the formation mechanism and dependence on applied potential were
discussed. The change of the chemical condition at the surface due to the reaction with ambient atmosphere was observed.

In 2005, thermal decomposition behavior of Zn$_3$N$_2$ powder was investigated by F. Zong et al. [28] using thermal gravimetric analysis and differential thermal analysis techniques. It indicated that the *thermal oxidation of zinc nitride powder* in air consists of two steps, namely surface oxidation between 200°C to 500°C and fast thermal oxidation when temperature increases beyond 500°C. The same group was also investigated the zinc nitride nanowires [29,30]. In these two papers, zinc nitride nanowires were prepared by nitridation of zinc powder under a flow of ammonia at atmospheric pressure and temperature of 600°C. Zinc nitride nanowires with a diameter of 30 to 100 nm and a length of 10 to 20 µm were observed by scanning electron microscopy and transmission electron microscopy. The optical band gap of zinc nitride nanowires was measured to be 3.22 eV by room temperature photoluminescence. Also, in the same year, metal-organic chemical vapor deposition was used to grow the zinc nitride thin films by using Zn[N(SiMe$_3$)$_2$]$_2$ and ammonia as precursors [31]. Both the deposition temperature and the mass flow rate of ammonia affected the crystallinity of the zinc nitride thin films. Also, a further study on zinc nitride thin films prepared by molten salt electrochemical process [27] was published by the same group [32]. A surface layer of Zn(OH)$_2$ and ZnO were observed in XPS measurements and an optical band gap of 1.01 eV was obtained from optical reflectance data by using the Kubelka-Munk function.

In 2006, the electron effective mass in polycrystalline Zn$_3$N$_2$ thin films was first investigated and reported to be $(0.29\pm0.05)m_e$ [33]. Both *RF plasma-assisted molecular beam epitaxy (PAMBE)* and *metal organic chemical vapor deposition (MOCVD)* methods
were used to grow zinc nitride thin films. It was concluded that the optical band gap variation as a function of carrier concentration for zinc nitride thin films could be explained by the Burstein-Moss effect (i.e., the variation of the band gap due to the states near the conduction band that are populated [34]). The band-gap was reported to be of direct nature and its value was reported as 1.06 eV. All zinc nitride thin films in this paper were n-type and the carrier concentration and mobility ranged from $1.5 \times 10^{19}$ to $1.6 \times 10^{20}$ cm$^{-3}$ and from 8.6 to 156 cm$^2$V$^{-1}$s$^{-1}$, respectively. PAMBE was used in the same year by another group to fabricate zinc nitride thin films [35]. The main result of this paper was that $\alpha$-plane (1120) sapphire substrates are suitable for heteroepitaxial growth for high-quality zinc nitride thin films.

After investigating zinc nitride nanowires in 2005 [29,30], F. Zong and co-workers studied the structural properties of zinc nitride hollow micro-balls [36] prepared by the nitridation of zinc powder through the exact same procedure mentioned earlier [29,30]. It was found possible that the nitridation of zinc powder produced both zinc nitride nanowires and empty balls. The same group then reported zinc nitride thin films prepared by reactive RF magnetron sputtering of a zinc nitride target in nitrogen with an indirect band gap of 2.12 eV [37]. This was the first time an indirect band gap of zinc nitride thin films was reported. Another very similar paper was also published by the same group in different journal, again reporting an indirect band gap of 2.12 eV [38].

In 2007, due to an increasing interest in zinc nitride, theoretical studies were performed on zinc nitride related materials. A first-principles study of defect equilibria in lithium zinc nitride was performed [39]. The formation energies of native defects and their thermal equilibrium concentrations were evaluated. It was suggested that the
formation of holes of a high concentration occurs even in undoped LiZnN. Although this was not a theoretical study directly on pure zinc nitride, this paper provided some insight into the formation of native defects, like zinc interstitials or nitrogen vacancies.

Later in the same year, another theoretical study on oxygen-containing zinc nitride was performed based on density functional theory (DFT) [40]. In this paper, it was concluded that zinc nitride with nitrogen replaced by oxygen was more stable than that with interstitial oxygen or with zinc replaced by oxygen. The substitution of oxygen for nitrogen in defective zinc nitride was found responsible for the observed n-type conduction character. The authors also pointed out that a possible way to achieve p-type Zn$_3$N$_2$ was to introduce an effective defect, like interstitial O. Also in the year of 2007, pulsed filtered cathodic vacuum arc deposition was employed in zinc nitride thin film fabrication [41]. A new value of energy band gap of zinc nitride thin film of 2.47 eV with a direct transition was reported. ZnN target was used again by the E. Aperathitis group in zinc nitride thin film fabrication by RF magnetron sputtering in either pure Ar or pure N$_2$ [42,43]. It was found that the ZnN thin films deposited in pure Ar were opaque and conductive due to excess of Zn, while the films prepared in pure N$_2$ were transparent and very resistive. After oxidation at 400°C, films of both types converted to p-type ZnO:N with low hole concentration. What needs to mention here is that a wide band gap (above 3 eV) was observed in both the as-deposited films and the oxidized films in these two papers.

In 2008, our group began a project on zinc nitride films and some preliminary work was reported at an IEEE conference [44]. Zinc nitride thin films were prepared by RF reactive magnetron sputtering of Zn target in nitrogen containing atmosphere. The
deposition pressure was varied in the range of several mTorr up to 20 mTorr and was found to have little effect on the film quality in term of crystallinity. A significant fraction of nitride phase and Zn-N bonding configurations in the film material were confirmed by XRD and XPS. In the same year, another theoretical study on native defects in Zn$_3$N$_2$ [45] was conducted by the R. Long group based on their former work [40]. As in their earlier work, this study was based on the density functional theory. Atomic geometry, electronic structure and formation energy of native defects in Zn$_3$N$_2$ have been studied to interpret the different behaviors of defective Zn$_3$N$_2$. N vacancies, as well as substitutional oxygen with nitrogen defects [40], were concluded to be responsible for the n-type conduction character and the optical band gap change was attributed to various defects. A study on the stoichiometry and the thermal stability of zinc nitride powders prepared by ammonolysis reactions was reported [46]. In this paper, zinc nitride powders were found to be stable in argon atmosphere up to their decomposition point at around 700°C. And the calculated bond valence sums (a theoretical method used to estimate the bonding state of atoms [47]) implied that Zn$_3$N$_2$ cannot be described as a 100% ionic compound. The band gap was measured to be approximately 0.9 eV. Another paper [48] was published by E. Aperathitis group with very similar content with to their previous two papers [42,43].

In the year of 2009, T. Yang et al. [49] reported zinc nitride thin films prepared by RF magnetron sputtering of Zn in nitrogen and argon plasma with only one diffraction peak of (400) direction. A direct band gap of 1.01 eV was obtained from the relation between optical band gap and optical absorption coefficient. In the same year, terbium (Tb) doped zinc nitride thin films were prepared by DC magnetron sputtering of Zn in a
mixture of argon and nitrogen gases [50]. Green photoluminescence was observed in Tb doped zinc nitride thin films and an indirect band gap of 2.4 eV was determined. Another research on the effect of heat treatments on the optical properties of zinc nitride prepared by electron beam evaporation deposition was published [51]. A direct band gap of 3.2 eV of films thermal treated at 350°C was found. It was also observed that with increasing annealing temperature, the carrier concentration and conductivity decreased. Optical parameters, such as refractive index and extinction coefficient, were calculated.

Some device related papers were published in this same year. E. Aperathitis group reported successful fabrication of transparent thin film transistors using n-type zinc nitride thin films as channel [6]. As can be seen in Figure 2-3, 200 nm thick indium-tin-oxides (ITO) was used as gate, 170 nm thick HfO₂ was used as dielectric layer, and 70 nm zinc nitride thin film was used as channel layer in this study. This field effect

![TFT structure configuration](image-url)

**Figure 2-3** The TFT structure configuration used and its output characteristics ($I_{DS}$–$V_{DS}$) after annealing at 300 °C and 400 °C [6] (Reprinted with permission from Thin Solid Films 518, 1036 (2009). Copyright 2009 ELSEVIER S.A.).
transistor device was found to operate in enhancement mode, and the turn on voltage
decreased and the saturation current increased with the increase in the thermal oxidation
level of the nitride.

Another successful fabrication of thin film transistors using zinc nitride and oxy-
nitride materials was reported [52]. Amorphous zinc oxy-nitride thin films with high
electron mobility were formed by carefully adjusting the ratio of oxygen to nitrogen in
sputtering gases. Upon annealing, a significant increase of the resistance of the film to the
deterioration caused by absorption of moisture or pollutants was reported in this paper
also. Bottom-gate thin film transistors were made by using Cr as both gate metal and
source/drain contact metal, 330 nm thick Si$_3$N$_4$ layer was used as a gate dielectric layer,
and the high mobility amorphous zinc oxy-nitride thin film served as a channel layer. The
device operated in depletion mode, opposite from what was reported in ref. 6.

In 2010, zinc nitride thin films were attracting even more interest. The structural
stability of zinc nitride powder under high pressure was studied based on the diamond
anvil cell technique by using in situ high pressure energy dispersive x-ray diffraction with
synchrotron radiation [53]. Zinc nitride powder was stable in the pressure range up to
25.2 GPa and the bulk modulus $B_0$ was found to be 228(2) GPa. The zinc nitride hollow
structures were fabricated and characterized by C. Cao group [54]. Spherically shaped
hollow microstructures of zinc nitride were synthesized by nitridation of zinc powder.
The band gap was characterized to be 2.81 eV with indirect transition. RF plasma
assisted reactive pulsed laser ablation deposition again was employed in zinc nitride thin
film fabrication [55]. Spectroscopic ellipsometry (SE) measurement was first utilized in
zinc nitride thin film characterization but in a very superficial way. The zinc nitride thin
films in this study were found to be n-type material with direct band gap of 3.2 eV. 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. The effect of high temperature on crystal structure of zinc nitride thin film was also studied [56]. Zinc nitride thin films were grown by RF sputtering of zinc target in argon and nitrogen ambient and then characterized by high temperature x-ray diffraction measurement under vacuum. The results indicated that the gradual transformation of the zinc nitride phase occurred at temperature greater than 320°C. G. Z. Xing et al. [57] reported zinc nitride thin films with a band gap of 1.01 eV grown by RF magnetron sputtering of zinc target in pure nitrogen atmosphere. The two distinct conduction mechanisms for zinc nitride thin films depended on different temperatures were observed. In low range of temperature up to 275 K, the activation of unintentionally introduced impurities was the main reason of the changing of conductivity, while, in the temperature range from 275 K to 400 K, excitation of intrinsic valence electrons was taking over the changing of conductivity.

In 2011, theoretical calculations of structural, electronic and thermodynamic properties of cubic zinc nitride under high pressure were reported [58]. It was found that zinc nitride has a higher covalent character with the increase in pressure. Zinc nitride nano-needles were prepared in a direct reaction between zinc powders and ammonia and characterized by C. Cao group [59]. The band gap of the zinc nitride nano-needles was determined to be 2.72 with indirect transition, which is slightly lower than the band gap of zinc nitride hollow structure reported in their previous paper [54]. The same group prepared zinc nitride hollow structures again [60] using a different method, the solvo-solid preparation method. The hydrogen absorption capability of zinc nitride hollow
structures at 100°C was then investigated. Formation of zinc nitride thin films by pulsed laser ablation of zinc selenide in nitrogen ambient was studied as well [61]. This work reported large fraction of oxygen incorporated in thin films and the band gap was 3.5 eV. The optical properties of zinc nitride thin films examined by SE measurement were reported by C. Garcia Nunez group [62]. The refractive index and extinction coefficient of zinc nitride thin films deposited at a substrate temperature of 100°C were roughly determined.

In 2012, the group of C. Garcia Nunez studied the unintentional incorporation of oxygen in zinc nitride thin films deposited by RF magnetron sputtering of zinc target in nitrogen and argon ambient [63]. The results showed that the oxygen content depended on the growth rate. The optical energy band gaps of zinc nitride thin films in this study were found to be 1.25 eV to 1.46 eV as substrate temperature decreasing. A maximum mobility of 100 cm²V⁻¹s⁻¹ and a minimum carrier concentration of 3.2x10¹⁸ cm⁻³ were achieved. Later in the same year, the same group reported thin film transistors (TFT) based on zinc nitride as a channel layer for optoelectronic devices [7]. Zinc nitride layers were grown by RF magnetron sputtering in (Ar+N₂) ambient using a Zn target. Bottom- and top-gate thin film transistors were fabricated by photolithography processes. Normally off transistor characteristics with a threshold voltage of 6V were obtained in the bottom-gate configuration without post-growth annealing. In the saturation region, those transistors produced enhanced output characteristics under illumination with infrared/visible light.

Also in 2012, zinc nitride in nano-tower form was reported by C. Cao group [64]. From the characterization results, the influence of different nano structures on electrical
or optical properties is very limited. Pulsed Laser Ablation Deposition (PLD) was again employed on zinc nitride and transistor structure fabrication [65]. Non-linear current-voltage (I-V) transfer characteristics suggested a large density of interface trap states. By co-workers from our group, the photo-response, like photoconductivity, of zinc nitride was investigated [66], which indicates that zinc nitride may be suitable for photodetection applications.

2.3 Zinc oxy-nitrides and nitrogen-doped zinc oxides

In 1998, zinc oxy-nitride thin films were first reported by M. Futsuhara et al. [67] and prepared by reactive RF magnetron sputtering of zinc oxide target in nitrogen-argon mixtures on borosilicate glass substrates. The band gap of these zinc oxy-nitride thin films decreased from 3.26 eV to 2.30 eV with the increasing of nitrogen fraction in the sputtering gas from 0% to 75%. N-type conductivity was seen.

In 2001, nitrogen doped zinc oxide films were grown by plasma-assisted metal-organic chemical vapor deposition on sapphire substrate [68]. Oxygen and nitrogen at a ratio of 1:1 were used as carrier gas in this case. Higher optical absorption and n-type conductivity were observed in these nitrogen doped zinc oxide thin films. P-type nitrogen doped zinc oxide thin films were fabricated by pulsed laser reactive deposition using a pure Zn target in N₂O plasma [69]. The microwave-input power and the deposition pressure were found very important to achieve the p-type conductivity. After optimization, p-type zinc oxide thin films with carrier density of 3x10^{18} to 6x10^{18} cm⁻³, resistivity of 2 to 5 Ωcm and mobility of 0.1 to 0.4 cm²V⁻¹s⁻¹ were reported.
In 2002, nitrogen-related local vibrational modes in ZnO:N were carefully examined [70] by Raman spectroscopy. The nitrogen doped zinc oxide thin films were fabricated by chemical vapor deposition on GaN/sapphire substrates using NO$_2$ as oxygen precursor and NH$_3$ as nitrogen source. Modes located at 275, 510, 582, 643 and 856 cm$^{-1}$ were interpreted as nitrogen related local vibrational modes.

In the year of 2003, p-type nitrogen doped zinc oxide thin films were reported by Z. Ji’s group through oxidation of zinc nitride thin films deposited by DC magnetron sputtering [25]. P-type ZnO thin films were obtained at an oxidation temperature between 350°C to 500°C, while n-type conductivity was observed when oxidation temperature reached 550°C or higher. The highest hole concentration of 5.78x10$^{17}$ cm$^{-3}$ was achieved at 500°C. The same group reported another fabrication method for p-type nitrogen doped zinc oxide [71] in which the p-type films with hole density of 2.5x10$^{17}$ cm$^{-3}$ were synthesized by pyrolysis of zinc-acetate-ammonia solution. Y. C. Liu’s group published their results on preparing p-type nitrogen doped zinc oxide thin films by oxidizing zinc nitride also [26]. The zinc nitride thin films were grown by PECVD from a Zn(C$_2$H$_5$)$_2$ and NH$_3$ gas mixture, as mentioned in section 2.2. A phase transformation from cubic antibixbyite zinc nitride to hexagonal zinc oxide was observed at the annealing temperature of 500°C. And when temperature increased to 700°C, p-type ZnO thin film with a carrier density of 4.16x10$^{17}$ cm$^{-3}$ was obtained.

In 2004, ion implantation was used to achieve nitrogen doped zinc oxide [72]. The zinc oxide thin films were grown by high quality metal organic vapor phase epitaxy method on sapphire substrates using a GaN-nucleation layer. The post-implantation temperature of 800°C was believed to be the healing temperature. However, in this paper,
although the carrier concentration increased after nitrogen implantation, p-type conductivity was still not observed. In the same year, a further study on p-type nitrogen doped zinc oxides [73] was reported by Y. C. Liu’s group (Figure 2-4) based on their previous work [26]. The acceptor bound exciton (A°X) emission from the nitrogen acceptors located at 3.335 eV was observed in photoluminescence spectra, and the acceptor energy level is estimated to be \(\sim 130\) meV above the valence band. Moreover, in this paper, a p-n junction between p-type ZnO:N thin film and n-type Si substrate was formed.

![Figure 2-4 The I-V characteristics of the p-ZnO:N/n-Si annealed at different thermal oxidation temperatures [73] (Reprinted with permission from Journal of Physics: Condensed Matter 16, 4635 (2004). Copyright 2004 IOP PUBLISHING, LTD.)(b)](image)

In 2005, another case of fabricating p-type nitrogen doped zinc oxide by thermal oxidation of sputter-deposited zinc nitride was reported [74]. P-type conductivity with carrier concentration in mid-\(10^{17}\) cm\(^{-3}\) range and mobility of \(\sim 10\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) was achieved. Like reported in ref. 73, neutral acceptor bound excitons related peak at 3.36 eV was
again seen in photoluminescence spectra. A transmittance of ~80% in the whole visible spectrum was also observed. Also, oxidation of zinc oxy-nitrides as a way to prepare p-type ZnO:N thin films was reported [75]. Zinc oxy-nitride thin films were deposited by plasma enhance chemical vapor deposition using diethylzinc, NH\(_3\) and CO\(_2\) as the zinc, nitrogen and oxygen sources respectively. The conduction type transition was observed as the increasing of the temperature of thermal oxidation. The p-type nitrogen doped zinc oxide thin films were obtained after the thermal treatment at 600°C with the carrier concentration of 2.7x10\(^{16}\) cm\(^{-3}\).

In 2006, the effects of nitrogen doping and illumination on conductivity behavior of nitrogen doped zinc oxide thin films were studied [76]. The thin films were prepared by RF magnetron sputtering of a ZnO target in nitrogen ambient. Two types of nitrogen doping were observed by XPS, namely the substitution of \(N\) atom for O sub-lattice and the substitution of \(N\) molecule for O sub-lattice. The former behaved as an acceptor and the latter one behaved as a donor, which may explain the conducting type changing (from n to p then back to n) with time and/or by illumination observed in this paper. Another very similar paper was published one year later by the same group [77]. The electrical transport properties of nitrogen doped zinc oxide thin films were examined by Y. C. Liu’s group [78]. It was suggested that the Hall mobility was affected by all of the three factors, the lattice scattering, the ionized impurities scatterings, and the dislocation scatterings. From the temperature dependence of the hole concentration, it also was obtained that the thermal ionization energy of the nitrogen acceptor is 170 meV.

In 2007, Raman spectroscopy data on nitrogen doped ZnO thin films were again very carefully examined [79]. Low pressure chemical vapor deposition (LPCVD) with
diethylzinc as a zinc precursor and diluted nitric monoxide gas as dopant was used for the fabrication of nitrogen doped zinc oxide thin films. Some new nitrogen-related as well as carbon-related Raman peaks were observed and more importantly, the intensity and the intensity ratio of carbon-related defect complex Raman peaks were found to be sensitive parameters that reflect the conductivity type of ZnO:N. The influence of substrate temperature on nitrogen-doped zinc oxide thin films deposited by RF magnetron sputtering of a ZnO target in argon and nitrogen ambient was reported [80]. Unlike the papers mentioned before, all nitrogen doped zinc oxide films were reported to be n-type with a band gap increasing from 1.99 eV to 3.3 eV with increasing the substrate temperature from room temperature to 250°C, due decreasing nitrogen incorporation into the film. P-type nitrogen doped zinc oxide thin films were again reported by E. Aperathitis’ group [42] and were obtained by thermal oxidation of zinc nitride films deposited by RF magnetron sputtering from a zinc nitride target in either argon or nitrogen ambient. Another very similar paper was published in the same year by the same group [43] in different journal. Later, the successful control of band gap varying of nitrogen doped zinc oxide thin films by varying RF sputtering power during the deposition was reported [81]. The nitrogen doped zinc oxide thin films were prepared by reactive RF magnetron sputtering of a ZnO target in oxygen and nitrogen mixture ambient. And it was found that the band gap of films narrowed from 3.29 eV to 1.75 eV with the RF power of sputtering was increased from 80 W to 200 W. It also indicated that the band gap narrowing was caused by the mixing of shallower N 2p states with the valence band of ZnO based on first-principles density-functional theory.
In 2008, a focused study XPS of nitrogen doped zinc oxide thin films, obtained by implanting of nitrogen in ZnO thin film, prepared by DC magnetron reactive sputtering of Zn target in argon and oxygen mixture, was published [82]. Several different types of bonding configurations for chemisorbed nitrogen were assigned. Pulsed laser deposition was also used for the fabrication of nitrogen doped zinc oxide thin films [83]. ZnO:N thin films in this paper were all of n-type conductivity but from the photoluminescence measurements, acceptor-bound-exciton emission due to oxygen substitution by nitrogen at 3.31 eV were also observed. The relationship between the parameters of reactive RF diode sputtering from a zinc oxide target and the crystalline, electrical and optical properties of n-/p-type ZnO thin films was studied [84]. The presence of nitrogen at oxygen sites forming nitrogen-oxygen acceptor complexes in ZnO was proven by secondary ion mass spectroscopy and Raman spectroscopy in this paper. P-type nitrogen doped zinc oxide thin films with carrier concentration of $3.6 \times 10^{14}$ cm$^{-3}$ and mobility of 22 cm$^2$V$^{-1}$s$^{-1}$ were obtained at optimal deposition condition. The ferromagnetism in (Mn, N)-co-doped ZnO thin films was investigated [85]. Mn doped zinc nitride thin films were first fabricated and then thermally oxidized to Mn doped zinc oxy-nitride thin films. P-type conductivity was observed in Mn doped zinc oxy-nitride thin films.

In 2009, the microstructure and optical properties of N-incorporated polycrystalline zinc oxide films were studied [86]. Nitrogen doped zinc oxide thin films were fabricated by RF magnetron sputtering of ZnO target in a mixture of argon and nitrogen with varied nitrogen ratio. The grain sizes for the films in this paper decreased with the increase of the nitrogen fraction in the sputtering gas from 26.46 nm to 21.26 nm, and the values of optical band gap decreased from 3.18 eV to 2.95 eV. Later, the
effects of air exposure on the chemical and electronic structure of nitrogen doped zinc oxide thin films were investigated [87]. Soft x-ray emission spectroscopy was employed in this investigation. Nitrogen doped zinc oxide thin films were prepared by RF magnetron sputtering of Zn target in nitrogen and oxygen gas mixtures. It was found that while the ZnO:N thin films were stable in vacuum, they degraded in ambient air and finally became zinc oxide. The degree of this degradation was dependent on the initial nitrogen ratio in the ZnO:N thin films. Also in this paper, the authors suggested that the degradation caused the shift of the valence band maximum which was responsible for the changing of reported band gap values for zinc nitride and oxy-nitride thin films. T. Zaidi et al. [88] reported n-type, p-type and semi-insulating as grown nitrogen doped zinc oxide thin films prepared by metal organic chemical vapor deposition using diethyl zinc, oxygen and ammonia as the zinc and oxygen precursors and the dopant source respectively. It was concluded that the best results of nitrogen doping were achieved at growth temperature above 500°C and VI-II ratio between 500 and 550. Careful control of growth parameters, precursor flow rates and post growth annealing in this window gave the desired p, n and semi-insulating characteristics to the films. In the same year, the growth temperature dependence of local structural and electrical properties of nitrogen doped zinc oxide thin film was studied [89]. The films were fabricated using pulsed laser deposition at different substrate temperatures. It was suggested that the surface of the films exhibited both n-type (associated with oxygen vacancies) and p-type (nitrogen acceptors) conductivity, and the distribution of n-type and p-type regions was varying with the substrate temperature. The effects of nitrogen doping in zinc oxide thin films during or after deposition and the successful fabrication of metal-semiconductor-metal
photo-detectors using ZnO:N thin films was reported [90]. Another case for p-type nitrogen doped zinc oxide thin films fabrication be thermal oxidation of zinc nitride thin films was reported [91]. Zinc nitride thin films prepared by RF reactive magnetron sputtering of Zn target in argon and nitrogen were then thermal oxidized in different temperatures. It was found that the annealing temperatures played a key role for the p-type characteristics of ZnO:N thin films because both the doped nitrogen concentration and the activation probability for the doped nitrogen atoms are related to annealing temperature, and a good balance between them is needed.

As far as device related work, in 2010, aluminum and nitrogen co-doped p-type zinc oxide were fabricated using a dual RF co-sputtering growth technique equipped with zinc and aluminum targets in ambient of argon, oxygen and nitrogen [92]. A homo p-n junction was then fabricated using this Al/N co-doped p-type zinc oxide and n-type zinc oxide nanorods (see Figure 2-5).

![Figure 2-5 I–V measurements of a hybrid homo-junction on an FTO substrate with a Pt(100 nm)/Ti(30 nm) top electrode. Inset is the schematic of a hybrid homo-junction fabricated on an FTO substrate [92] (Reprinted with permission from Thin Solid Films 518, 6587 (2010). Copyright 2010 ELSEVIER S.A.).](image-url)
In 2011, rectifying behavior was observed (see Figure 2-6) between n-type zinc nitride and nitrogen-doped p-type zinc oxide [93]. The two layers were prepared by RF sputtering from a zinc nitride target but under different ambient (pure N$_2$ ambient for n-type zinc nitride layer and Ar/O$_2$ mixture ambient for p-type nitrogen-doped zinc oxide).

**Figure 2-6** Current–Voltage characteristics of the fabricated p-ZnO/n-ZnN diode from a single sputtering target. The inset shows cross-section of the p/n diode. [93] (Reprinted with permission from Thin Solid Films 520, 1202 (2011). Copyright 2011 ELSEVIER S.A.).

In 2012, a study of nitrogen-doped ZnO shell was reported [94]. It was found that the degree of transparency and the nature of conductivity were strongly influenced by the levels of N-doping. Higher nitrogen doping led to decline in electrical resistivity and mobility due to an enhancement of free charge carriers. Presence of both (N$_2$)$_O$ donor and (N)$_O$ acceptor peaks in x-ray photoelectron spectroscopy could be responsible for the formation of higher carrier concentration in ZnO films.
2.4 Fabrication Methods

2.4.1 Direct chemical reaction methods

The direct chemical reaction is one of the simplest approaches to fabricate zinc nitride and related oxide thin films. It usually requires two reactants which contain zinc and/or nitrogen, a proper reaction temperature, and a relatively longer fabrication time in order to fully break the original chemical bonds and form new ones. Films that are prepared by direct chemical reaction are usually polycrystalline with no preferred orientations. The surface quality is very poor, i.e., the surface is very rough.

The direct reaction between pure metal zinc powder or zinc thin films and reactive gases, such as NH₃, is one possible approach. It was reported that zinc nitride thin films were fabricated by a 4-hour reaction of 10 µm zinc thin film at 410°C in NH₃ flow [4]. It was also reported that zinc nitride powder [28,46], nanowires [29,30], hollow balls [36,54,60], nanoneedles [59], and nanotowers [64] were synthesized by nitridation of zinc power with ammonia gas at 600°C for 2 hours.

Pyrolysis is another method to obtain zinc nitride and related oxide thin films. It involves a thermo-chemical decomposition of organic material by nebulizing, a bonding re-forming and the change of the chemical composition and the physical phase. In one reported case [71], zinc-acetate (Zn(CH₃COO)₂·2H₂O)-ammonia (NH₃) solution was nebulized and then nucleated to form nitrogen doped ZnO thin film at a heated substrate at a substrate temperature of 518°C.

Electrochemistry-based methods are also possible. This involves electron transfer at the interface of the species in a solution and the electrodes. Zinc nitride thin films were
formed by electrochemical method using zinc electrode and a mixture of LiCl-KCl and Li₃N [27,32].

2.4.2 Evaporation and laser ablation methods

The evaporation deposition process involves a controllable transfer of atoms from a melt to the substrate where the film is nucleated and grown. The main difference between evaporation and sputtering, another physical deposition technique which will be discussed in next section, is that, in sputtering the atoms have higher energies, since they are ejected from source surfaces usually maintained at room temperature, through the impact of ions [95]. High-vacuum ambient and suitable heating sources are required to evaporate high quality thin films. The temperature is the main factor influencing the deposition rates due to the equilibrium vapor pressure is affected heavily by temperature.

Electron beam evaporation

Electron beam evaporation is the technique utilizing electron beam as the heat source for melting the material that is to be deposited. It provides the advantage of eliminating the undesired contamination comparing to the resistively heated evaporation. In a recent work, zinc nitride thin films were deposited by electron beam evaporation [51]. A base vacuum of 3 x 10⁻⁵ Torr was reached and an acceleration voltage of 2.5 kV and electron beam current of 8 to 14 mA were used.

Pulsed laser ablation deposition

Somewhat similar to electron beam evaporation, pulsed laser deposition employs the laser as the energy source. Unlike other evaporation techniques, the energy source, i.e., laser beam/pulse, is usually generated outside of the vacuum chamber, and then
focused on the target inside the chamber. Electronic excitation of target atoms and/or ablation of the surface will be caused by the energy from the laser beam. Gases can be introduced in the deposition chamber for the purpose of enhancing reaction or maintaining film stoichiometry. Several cases on fabricating zinc nitride or nitrogen-doped zinc oxide thin films using pulsed laser deposition were reported. ArF excimer laser operating at 193 nm, KrF excimer laser operating at 248 nm, Q-switched Nd:YAG laser operating at 532 nm, 1064 nm, or 355 nm were utilized in these works. A target of pure metal zinc, zinc oxide, zinc selenide, or mixture of zinc oxide or zinc nitride powders and a ambient gas of N$_2$O, N$_2$ and/or O$_2$ were used [55,61,69,83,89].

2.4.3 Chemical vapor deposition methods

The chemical vapor deposition (CVD), unlike physical vapor deposition which depends on material transfer from target, is based on gas-solid chemical reactions. Usually a volatile solid material and/or reactive gases are the precursors, while nonvolatile solid forms and deposits on a heated substrate as a result of the chemical reactions. A large variety of films including metals, semiconductors, as well as inorganic and organic compounds in either a crystalline or amorphous form can be fabricated by CVD processes [95]. In addition, CVD offers the capability of controllable deposition of films with widely varying stoichiometry [95]. Because of the advantages mentioned above, different versions of CVD processing have been developed, and many of them, namely plasma-enhanced chemical vapor deposition (PECVD), metal-organic chemical vapor deposition (MOCVD) and low pressure chemical vapor deposition (LPCVD) [79], were also used to form zinc nitride or related materials.
**Plasma enhanced chemical vapor deposition**

The major advantage of the PECVD process is the low reaction temperature comparing with the traditional thermal CVD. The reason is that the ion bombardment resulting from the plasma helps decompose gas reactant into desirable species, which allows the reaction to happen at a lower temperature. Zinc nitride thin films were deposited at a low temperature of 140°C by PECVD using diethylzinc (DEZ), NH$_3$ and H$_2$ as zinc source, nitrogen source and carrier gas respectively [26]. The same group fabricated nitrogen-doped zinc oxide thin film by PECVD at a even lower temperature of 100°C using DEZ, NH$_3$, CO$_2$, and Ar as zinc source, nitrogen source, oxygen source and carrier gas respectively [75,78].

**Metal-organic chemical vapor deposition (MOCVD)**

One of the distinguish factors between MOCVD and other CVD methods is the chemical nature of the precursor gases [95]. The metal-organics are generally easier to evaporate at a relatively low temperature. The fact that all reactants are in the gas phase gives the MOCVD the ability to achieve more precise electronic control of gas flow rates and partial pressures [95]. It also shows other advantages like large-area deposition, fine composition control and good film uniformity. The MOCVD is mainly used in epitaxial growth of semiconductor films and oxides or metal films deposition. Nitrogen-doped ZnO films were deposited on (0006) sapphire substrate at 600°C by plasma-assisted MOCVD using DEZ, N$_2$, O$_2$ and Ar as zinc, nitrogen, and oxygen source and carrier gas respectively [68]. The combination of DEZ, NH$_3$ and O$_2$ was used as precursors for ZnO:N preparation [88]. Zn$_3$N$_2$ thin films were fabricated also by plasma-assisted MOCVD at a lower temperature of 260°C [33] or 450°C [73] using dimethylzinc (DMZ)
and NH₃ as zinc and nitrogen sources, respectively. The combination of Zn[N(SiMe₃)₂]₂ and NH₃ was also employed as precursors in MOCVD process for zinc nitride thin films [31]

To complete this sub-section, ZnO:N thin films were also obtained by conventional thermal CVD [70]. Metallic zinc, NO₂ and NH₃ were used as zinc, oxygen and nitrogen precursors respectively. The reaction temperature was 650°C which is slightly higher than that in MOCVD process and much higher than that in PECVD process.

2.4.4 Epitaxial methods

The epitaxial deposition process is used to grow single crystal thin films which match the lattice parameters of a crystalline substrate. Depending on the film–substrate combination, there are two types of epitaxy, homoepitaxy and heteroepitaxy. In homoepitaxy, the material deposited as single crystal thin film is identical with the material of substrate, for example epitaxial layer of Si on Si wafers. There is a perfect match of lattice parameters in homoepitaxy, which introduces no interfacial-bond straining. Oppositely, in the heteroepitaxy, the materials of thin film and substrate are different. Consequently, there is a mismatch of certain level (typically much less than a percent) in terms of the lattice constant and other parameters. Thus, a strained interface between substrate and thin film is introduced, and, depending on the degree of mismatch, the epitaxial growth may be limited in terms of film thickness achievable.

*Molecular beam epitaxy*
Molecular beam epitaxy (MBE) and CVD-based techniques can be used to achieve epitaxial growth. MBE is a highly controlled process that one or more evaporated beams of atoms or molecules interact with substrate for quality single crystal epitaxial layer in an ultrahigh vacuum (~10^{-10} torr) [95]. Zinc nitride thin films were fabricated by plasma-assisted MBE using evaporated zinc and nitrogen plasma [33,35].

2.4.5 Plasma-based deposition methods

These methods are different from the evaporation processes and do not rely on transferring thermal energy to the target for the transport of material. In the plasma-based deposition processes, plasma is used to create energetic ions, which bombard a target and eject, or sputter, atoms from it which are then deposited onto a properly positioned substrate.

Sputtering deposition

Sputtering deposition is one of the physical vapor deposition processes. It utilizes plasma generated between a pair of electrodes to eject atoms out of a target material by bombarding and it, and eventually forming a film on substrate. The two electrodes, the cathode or target and the anode or substrate, are connected to either a DC or a RF power supply. After high vacuum is reached in the chamber, working gases, typically argon, are introduced to serve as the media in which the plasma is initiated and maintained. While plasma is initiated, positive gas ions in the discharge strike the target and physically eject or sputter the atoms out through momentum and energy transfer. The sputtered atoms enter and pass through the discharge region and finally deposit on the growing film surface [95]. Along with atoms of target materials, other particles, such as electrons, ions,
and radiation (x-rays and other photons) are also emitted. And they all affect the growth and the properties of the thin film.

If a DC source is used as the power supply, then the process is called DC sputtering. Zinc nitride and related oxides have been prepared by this method. Pure metallic zinc sputtered under argon and nitrogen mixture or argon, nitrogen and oxygen as working gases are the most common combinations for the deposition of zinc nitride thin films [25,50] or the related oxides [52,82].

The RF sputtering process will be discussed in a more detailed way in next section since it is one of the most used for the deposition of zinc nitride and is the main fabrication method employed in this project.

Arc plasma deposition

Arcs are the gas discharges with high current (tens to hundreds of amps.) and low DC voltage (tens of volts) [96]. In order to initiate vacuum arcs, two metal electrodes with very small areas, typically one is a sharp needle pressing against a flatter surface. Current is passed first with the two electrodes in contact, and then the electrodes are separated and kept a short distance apart to form a pass of extremely high current densities. This current discharge melts and vaporizes particles of the electrodes which become the sources of the material to be deposited. The impact energy of the depositing ions at the growth surface can be controlled by electric field since the electrode material is near 100% ionized. Depending on which electrode is melted, vacuum arc deposition is referred to as either anode-arc plasma deposition or cathode-arc plasma deposition. Zinc nitride thin films were deposited by pulsed filtered cathodic vacuum arc deposition technique with an arc current of 650 A [41].
Chapter 3

Experimental: Fabrication and related characterization techniques

In this section, the thin film deposition method involved in this project, reactive radio frequency magnetron sputtering, and the related characterization techniques are introduced and discussed.

3.1 Reactive radio frequency magnetron sputtering

Reactive radio frequency (RF) magnetron sputtering is a hybrid process of reactive sputtering, magnetron sputtering and RF sputtering. Therefore, there are quite a lot factors which influence the process, such as chemical reactions, the diffusion of particles in the plasma and the changing of surface condition of the target as well as the substrate, caused by plasma bombardment and reactions. As mentioned in previous section, the underlying physics of sputtering is transfer of momentum and energy from energetic particles to the surface atoms of the target [95]. This leads to one of the most fundamental parameters of sputtering, the sputter yield. The sputter yield is used to measure the efficiency of sputtering and its definition is the number of particles ejected from a target surface per incident ion. It varies with different target materials, different types of bombarding ions, as well as the energy of the ions.
Unlike the DC sputtering process where plasma is finely confined to the target, the confinement of RF sputtering plasma is weaker and the plasma tends to fill the whole vacuum chamber, which often affects the substrate and the film growth [95]. In order to minimize the ion bombardment on substrate as well as maximize the efficiency of sputtering of the target, the area of ground electrode is larger than the area of the powered target electrode. This is called electrode-size effect. In practice, the substrate stage and the wall of vacuum chamber are usually connected and grounded together, comprising the opposite electrode [97].

The word “reactive” indicates that objective compound thin film is obtained by a reaction between target material and a reactive gas, which is usually mixed with an inert gas, argon. This reaction process may occur at the surface of the target, within the space between target and substrate, and, to a lesser degree, at the surface of the substrate.

![Generic hysteresis curves for system pressure vs reactive-gas flow rate during reactive sputtering. Dotted line represents behavior with inert gas.][97]

The hysteresis effect is also introduced because of the presence of the reactive gases. The working pressure in the vacuum chamber during the deposition shows step
changes due to the hysteresis effect, seen in Figure 3-1. In state I, the increase of flow rate of reactive gas up to $F_r$(start) will not cause the corresponding increase of total working gas because of the reduction of reactive gas during the reaction. In this state, the atomic ratio of reactive dopant to sputtered material increases with increase of reactive gas. When the reactive gas increases beyond the critical point $F_r$(start), the total system pressure increases sharply and the state II starts. In state II, the working pressure changes correspondingly with the change of reactive gas, acting like noble gases. However, if the reactive gas is reduced beyond the other critical point, $F_r$(critical), the working pressure drops back and the whole system goes back to state I. Moreover, in state II, the excess of reactive gas will lead to the formation of compound at the target surface, which will significantly lower the sputter rate as well as the deposition rate.

The deposition rate and target properties are also key factors in reactive RF sputtering because the target properties, surface condition of the target in particular, influences the deposition rate significantly. When the surface condition of the target changed, for instance, compounds formed on the surface of target, the deposition rate may change dramatically. And the changing of target surface condition is also related to the sputtering gas pressure. One way to prevent this undesirable effect is to sputtering directly from compound targets. However, usually it is much harder to fabricate high-purity compound target than metal target, and as a result of which, the purity of the film sputtered directly from a compound target will not be expected as pure as the reactively sputtered film.

The “magnetron” implies that an electron confining magnetic field, another powerful assistance, is added to regular RF sputtering process. The presence of magnetic
field brings several benefits, increasing the deposition rate by increasing the current flow under the same applied voltage, and directing the sputtered particles by reducing collisions between particles at a relatively low operating pressure are the two main advantages. Also, better uniformity of the deposited thin films is usually achieved by a magnetron sputtering process.

Both zinc nitride thin films and zinc oxy-nitride thin films have been fabricated by RF sputtering. Pure zinc [24,44,49,56,57,62,63,66,74,81,87,91], zinc oxide [67,76,77,80,84,86,90], and zinc nitride [6,37,38,42,43,48] were used as the sputtering target. In some cases, in order to introduce dopants during the deposition, small metal flakes were fixed on top of the target, with the metals being manganese (Mn) [85] or terbium (Tb) [50] for example. Pure argon [6,48,84], pure nitrogen [37,38,48,57,62,76,77], argon-nitrogen mixture [24,42-44,49,56,63,66,67,74,80,84-86,91], argon-oxygen mixture [84], oxygen-nitrogen mixture [81,87], or argon-nitrogen-oxygen mixture [90] were used as sputtering gases.

In this project, the zinc nitride and oxy-nitride films were deposited on silicon, glass and/or transparent conducting oxides (TCO) substrates using a magnetron radio-frequency sputtering system (Torr International, Inc.). A 3-inch diameter Zn (purity 99.995%, Kurt J. Lesker) target was used and the substrates were mounted on a rotating holder at a distance of 10 cm from the target in a sputter-up geometry. The substrate temperature could be controlled from room temperature up to 400°C. The base pressure was in the low 10⁻⁶ Torr range, maintained by a combination of a dry mechanical pump and a turbo-molecular pump. Prior to film deposition, a pre-sputtering step is usually performed for 5 min at RF power of 80 W with Ar gas atmosphere. The thickness of all
films is monitored by a quartz crystal thickness monitor and later some of them are also verified by profilometry.

3.2 Characterization techniques relevant to our work

X-ray diffraction

The X-ray diffraction (XRD) technique is one of the common but very useful material characterization methods. It is widely used in material science to identify components in materials, study crystalline structure, microstructure, and grain size in thin films. The X-ray is a form of electromagnetic radiation with a wavelength in the range of 0.01 to 10 nm, corresponding to photon energies in the range of 120 eV to 120 keV. Due to their penetrating ability, x-rays are divided into hard x-rays and soft x-rays. Usually only the hard x-rays, in the range of 0.01 to 0.1 nm (1 to 120 keV), are used in diffraction applications.

The basic principle of the XRD technique is described by the Bragg’s Law,

\[ n\lambda = 2dsin\theta \]  

(1)

where the variable d is the distance between atomic layers in a crystal, the variable \( \lambda \) is the wavelength of the incident x-ray beam, and the variable n is an integer. From the positions and the intensities of XRD patterns, the crystal structure of unknown material can be identified, the average spacing between layers of atoms can be found, the orientation of single crystal or grain can be determined, and the size, shape and internal stress of small crystalline regions can be measured.
As the main method for crystallographic characterization, XRD has several modifications, of which there are three categories, relevant to our project: powder diffraction, thin film diffraction, and small angle x-ray scattering (SAXS).

In all XRD techniques, powder XRD is perhaps the most widely used. The sample can be in a powdery form, or particles in liquid suspensions or even polycrystalline solids (bulk or thin film materials). The term 'powder' really means that the crystalline domains are randomly oriented in the sample. The x-ray source and detector are scanned in $\theta/2\theta$ configuration. Both the transmission and the reflection geometry can be used.

The thin film diffraction can be used to investigate both the thin film, especially an epitaxial layer, and the substrate below. Because the substrate is involved, the measurement is normally conducted in reflection geometry. Also due to the good crystallinity, high angular resolution is needed. The rocking curve measurement, grazing incidence x-ray diffraction (GIXRD) measurement, and texture measurement are three of the mostly used techniques in thin film diffraction category. In rocking curve measurement, the detector is fixed at 20 position and the sample is scanned around $\theta$. Because the peak will broaden if defects are present in the film, this technique is usually used to examine the quality of the thin film [98]. In GIXRD measurement, while the detector does 20 scan, the incident x-ray is fixed at a very small angle with respect to the sample surface [99]. A parallel x-ray beam is often used, and the signal comes from the thin film only. The texture measurement, also called pole figure, is utilized to determine the orientation distribution in a polycrystalline sample. The detector is fixed at 20 position and the sample is scanned by in-plane rotation around the plane normal at
different azimuthal angles [100]. Therefore, the spectrum is plotted in polar coordinates around a given crystallographic orientation.

SAXS measurement typically is used for large length scale structures, such as high molecular weight polymers, self-assembled superstructures, and biological macromolecules [101]. Based on Bragg’s Law, the scattering angle will be small for the same x-ray wavelength if the d-spacing is large. Therefore, the scattering angle should be smaller than 1°. However, due to this small angular separation of the direct beam and the scattered beam, SAXS measurement requires large specimen-to-detector distances (0.5 to 1 m) and high quality collimating optics [101].

Raman spectroscopy

The Raman spectroscopy technique [102] utilizes the Raman scattering process, which is an inelastic scattering of electromagnetic waves or photons (typically laser radiation in the visible range) off of characteristic molecular or lattice vibrations (phonons). Because of the interaction with the valence electrons participating in chemical bonds, the energy of laser photons is shifted up or down, which gives information about the vibrational and rotational modes as well as bonding configurations in the sample; vibrational information is specific to the chemical bonds and symmetry of molecules. Therefore, it provides a fingerprint by which the molecules, bonds or materials can be identified. Thus Raman spectroscopy measurements can provide structural and chemical information which is complementary to that from XRD measurements and other techniques. Raman scattering, just like XRD, probes the volume of the film, but unlike XRD, it can identify the presence of bonding configurations that are not necessarily part of a crystalline phase.
Scanning electron microscopy and energy dispersive x-ray spectroscopy

Scanning electron microscopy (SEM) images the surface of samples by scanning it with a high-energy beam of electrons. The beam interacts with the atoms at or near the surface of sample to produce signal that contains information about the topography of sample surface and composition. This signal consists of secondary electrons, back-scattered electrons, and characteristic x-rays. The secondary electrons are normally used for imaging the surface of the sample. This can result in a very high resolution, up to nanometers, and a characteristic three-dimensional appearance, which therefore enables the possibility to understand the surface structures and details of the sample. The back-scattered electrons are usually used for imaging the distribution of different elements in the sample due to the intensity of the back-scattered electrons signal is strongly related to the atomic number of the specimen. The characteristic x-rays are often used to identify the composition and measure the abundance of elements in the sample.

Energy dispersive x-ray spectroscopy (EDXS) is an analytical technique for composition analysis by using the characteristic x-ray signal emitted by the sample. The fundamental principle of EDXS is the characteristic x-ray emitted by each element is uniquely identified due to the unique atomic structure each element has. The EDXS can be used both to identify elements and to quantitatively analyze the composition in the sample. The accuracy of EDXS spectrum is important and can be affected by various factors. The overlapping of characteristic x-ray of different elements, the energy of incoming beams, the uniformity of the sample, and the roughness of the surface are all the possible factors to reduce the accuracy of the measurement.
**X-ray photoelectron spectroscopy**

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique, which requires ultra-high-vacuum condition and can be used to study the chemical bonding configurations in materials by examining high-resolution spectra of the lines corresponding to chemical elements of interest. In an XPS measurement, mostly the material from the top several nanometers of the sample, interacts with a monochromatic x-ray beam, resulting in the emission of electrons form the various electronic levels of the atoms contained. The kinetic energy of these photoelectrons is characteristic of their original atoms and the chemical bonding configurations involved.

Due to the inherent surface sensitivity, only the material within several nanometers of the surface can be accessed. This limitation can, in principle, be avoided by employing in-situ ion etching (i.e., depth profiling), but, unfortunately, in the case of zinc nitride and related materials, ion-bombardment (typically with Ar ions) removes predominantly nitrogen and changes the composition of the surface under testing. Therefore, XPS measurements on Zn$_2$N$_2$ and related materials can be employed only as a qualitative tool upon using proper assumptions about the presence and the nature of any surface contamination.

**Optical spectrophotometry**

Optical spectrophotometry is a technique that measures the optical transmittance and reflectance of the sample as a function of the wavelength. A continuous-spectrum light beam, generated by an incandescent source, is passed through a monochromator to select a narrow wavelength range, and is then applied to the sample. Then, the photon flux density of the transmitted or reflected light is measured with a light sensor, for
example a photodiode, as the wavelength is varied (by adjusting the monochromator settings). The transmittance or reflectance value for each wavelength of the sample is then compared with the transmission (or reflectance) values from the reference. Based on the hardware structure inside, the instruments are divided into two major classes, the single beam devices and the double beam devices. In a double beam spectrophotometer, the light intensity between two light paths is compared, one for reference sample and the other one for the test sample. On the other hand, in the single beam spectrophotometer, the relative light intensity of the beam before and after a test sample is inserted is measured. Although comparison measurements from double beam instruments are easier and more stable, single beam instruments can have a larger dynamic range and are optically simpler and more compact.

*Spectroscopic ellipsometry*

Ellipsometry is a sensitive optical technique, used for the investigation of the physical properties of thin films by analyzing the change of the polarization state of the incident light after reflection from a plane surface. Incident light with known polarization state is applied to the sample and the change of the polarization produced by the sample is detected and analyzed, from which fundamental physical parameters, such as the complex refractive index or the dielectric function, and related sample properties, including morphology, optical band gap, electrical conductivity and film thickness, are probed [103,104].

The angles \((\psi, \Delta)\), which are measured in an ellipsometric measurement, can be related to the relative amplitude ratio \((\tan \psi)\) and the phase shift difference between the complex amplitude reflection coefficients by the equation \(\tan \psi \exp(i\Delta) = r_p/r_s\), where \(r_p\)
and \( r \) are the complex amplitude reflection coefficients for incident light with parallel (p) and perpendicular (s) polarizations [104]. These two experimentally measured angles \((\psi, \Delta)\) are functions of the optical properties and the thickness of the thin film. A data analysis is required to extract these characteristics. First of all, an optical model is built based on the nature of the sample. All possible layers, surface roughness, interface mixture and so on need to be considered. After an optical model is built, calculated \((\psi, \Delta)\) spectra are generated from the optical model with the initial values assigned to the unknown parameters. With the goal of minimizing the difference between calculated and experimental spectra of \((\psi, \Delta)\), iterative adjustments of the unknown parameters are conducted. After the successful fit of the experimental spectra of \((\psi, \Delta)\), the index of refraction \(n\), extinction coefficient \(k\), and other important optical parameters, as well as the thickness, of the sample are obtained.

Compared to single-wavelength ellipsometry, spectroscopic ellipsometry (SE), employs broad band light sources, which cover the full near-infrared to near-ultraviolet range, and generates multiple pairs of \(\psi\) and \(\Delta\) values, which makes possible the analysis of complex structures such as multilayers, interface roughness, inhomogeneous layers and anisotropic layers [103,104]. For better accuracy, the spectral range of SE measurement should be wide enough since the light must penetrate through the film, reflect from an underlying interface, return through the film, and proceed to the detector [103].

**Hall effect measurement**

The Hall effect measurement is a very powerful technique to investigate electrical properties of materials, and is applicable to thin films. The underlying theory, the Hall
effect [105,106], refers to potential difference called Hall voltage on opposite sides of an electrically conducting or semi-conducting thin film, created by a magnetic field applied perpendicularly, and transverse to a flowing electric current. The van der Pauw configuration [107] is the most commonly used in Hall effect measurement to measure the resistivity and other electrical properties. The main advantage of the van der Pauw configuration is its ability to accurately measure the properties of the sample in any arbitrary shape. From the measurement, the sheet resistance, doping type, sheet carrier density of the majority carrier, and the mobility of the majority carrier can be calculated. The four point probe measurement [106] is another widely used method to determine resistivity of material. By passing a current through the two outer probes and measuring the voltage between the two inner probes, the resistivity of material can be measured. By using four-probe configuration, the errors caused by the usually unknown contact resistances between each probe and the sample are eliminated, together with the spreading resistance under each probe, and the probe resistance.
Chapter 4

Results and discussions

This section describes results on characterization, defects modeling, and device related work of zinc nitride and zinc oxy-nitride thin films.

4.1 Characterization of zinc nitride and zinc oxy-nitride thin films

Different types of characterization were performed on the zinc nitride and oxy-nitride thin films in order to understand the properties of this material and how the fabrication conditions influence them.

4.1.1 Micro-structure and crystallinity

X-ray diffraction (XRD) measurement and Raman scattering were employed to study the micro-structural properties of zinc nitride and oxy-nitride thin films. XRD patterns were obtained using a PANalytical X’Pert Pro MPD and Scintag XDS-2000 x-ray powder diffractometer with a Cu Kα radiation source. Raman scattering measurements were performed using a JY Horiba LabRam Raman spectrometer with a He-Ne (632.8 nm) laser excitation.
Zinc nitride films deposited in \((N_2+Ar)\) atmosphere: sputtering gas composition dependence

Figure 4-1 XRD patterns of samples deposited at varied \(N_2/(N_2+Ar)\) ratios at a fixed substrate temperature of 200°C.

XRD spectra for films deposited at different \(N_2/(N_2+Ar)\) ratios, 10\%, 20\%, 50\%, 80\%, and 100\% are depicted in Figure 4-1. At the \(N_2/(N_2+Ar)\) ratio of 10\%, no diffraction peak was observed, which indicates the amorphous phase of zinc nitride was formed. At 20\%, only a very weak XRD diffraction peak is seen, located at 36.8°, and associated with the (400) plane of cubic anti-bixbyite structure of zinc nitride [6,43,108,109]. When the \(N_2\) content increases to 50\% of the total sputtering gas mixture, the (400) plane zinc nitride peak becomes much sharper and more dominant. In Table 4.1, we provide the full width at half maximum (FWHM) values of the dominant peak, the (400) plane cubic zinc nitride peak located at 36.8°, for some of samples. The FWHM decreases from 0.96° at 20\% to 0.18° at 50\%, which, again, can be associated with improved crystallinity. Concurrently, at the 50\% \(N_2/(N_2+Ar)\) ratio, peaks located at 43.4° (the (332) plane of zinc nitride), 53.1° (the (440) plane of zinc nitride), and 34.2° (the
(002) plane of zinc oxide), are seen. The peak located at 34.2° indicates the presence of zinc oxide in the film even though deposition occurs in an oxygen-free environment. We attribute the presence of ZnO to water contamination [25], as also discussed below where XPS data are presented. When the N₂ content is further increased to 80% of the total sputtering gas mixture, the (400) plane zinc nitride peak becomes even more dominant. Better orientation and comparable FWHM (0.28°) are observed in this film obtained with N₂/(N₂+Ar) ratio of 80%. Finally, when the nitrogen ratio is increased to 100% (i.e., pure nitrogen ambient), the FWHM of (400) plane zinc nitride peak broadens to 0.39° from 0.18° (50%), indicating that the crystalline quality of films decreases. To summarize the observed dependence, with the increase of N₂ content in the total sputtering gas, the films attain higher crystalline quality, reaching the best value at 50% nitrogen fraction, and then deteriorating somewhat, but acquiring a higher degree of preferential crystallite orientation.

Table 4.1 FWHM values of the (400) XRD peak for some of zinc nitride samples.

<table>
<thead>
<tr>
<th>N₂-to-total gas ratio dependence (for a substrate temperature, fixed at 200°C)</th>
<th>(400) XRD FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂-to-total gas ratio</td>
<td>20%</td>
</tr>
<tr>
<td>(400) XRD FWHM</td>
<td>0.96(6)°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate temperature dependence (for a N₂-to-total gas ratio fixed at 80%)</th>
<th>(400) XRD FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate temperature</td>
<td>RT</td>
</tr>
<tr>
<td>(400) XRD FWHM</td>
<td>1.00(2)°</td>
</tr>
</tbody>
</table>

In the Raman scattering data, shown in Figure 4-2, the dominant band is centered at 572 cm⁻¹ which has been assigned to a nitrogen-related local vibrational mode [70]. This peak is very wide, which can generally be associated with poor crystallinity or the lack of it. It appears likely therefore that the film consists of a mixture of amorphous and crystalline phases with significant disorder. The weak Raman peaks located at 427 cm⁻¹ are close to the characteristic E₂ mode of wurtzite ZnO which is reported at 437 cm⁻¹.
The peak located at 707 cm\(^{-1}\) has never been reported, and we speculate here that it is also related to Zn-N bonding configurations, as it does not appear correlated with the ZnO peak at 427 cm\(^{-1}\).

Figure 4-2 Raman spectra of films deposited on silicon substrate with varied N\(_2\)/(N\(_2\)+Ar) ratios at a fixed substrate temperature of 200\(^\circ\)C.

The lattice constant is calculated to be 9.758 Å, based on the (400) peak by using Bragg’s equation,

\[ n\lambda = 2d\sin\theta \tag{1} \]

and this is in good agreement with our theoretical calculation 9.839 Å [110] as well as values reported by others, 9.6756 Å (experimental work) [6] and 9.769 Å (theoretical work) [36]. By using Scherrer’s formula,

\[ L = (K*\lambda)/(B*\cos\theta) \tag{2} \]

where K is Scherrer constant, \( \lambda \) is the x-ray wavelength, B is the FWHM, and \( \theta \) is the Bragg Angle, the mean grain size (L) is obtained to be 12.9(2) nm for the film prepared at 200\(^\circ\)C and N\(_2\)/(N\(_2\)+Ar) ratio of 80%. These numbers roughly agree with what is observed.
from the SEM image of the film surface, shown later. The value of 0.9 is used for the Scherrer constant, $K$ [86].

Zinc nitride films deposited in (N$_2$+Ar) atmosphere: substrate temperature dependence

*Figure 4-3 XRD patterns of samples deposited at varied substrate temperatures at a fixed nitrogen ratio of 80% in (N$_2$+Ar) ambient.*

Figure 4-3 shows XRD patterns of films deposited at different substrate temperatures, in the range from room temperature to 350°C, in (N$_2$+Ar) atmosphere. For the zinc nitride films, the trend of the FWHM values observed, listed in Table 4.1, is first as a decrease then an increase, suggesting that the highest crystalline quality of films was reached at a substrate temperature of 200°C. From room temperature to 200°C, the crystallinity of the sample improved significantly, as seen from the Figure 4-3, and upon increasing the substrate temperature further to 300°C, the crystallinity of the film slightly decreases.

The Raman scattering data is shown in Figure 4-4. The nitrogen-related local vibrational mode centered at 572 cm$^{-1}$ is still dominant and wide. The crystallinity is
slightly increased with the increase of substrate temperature, which is consisted with XRD data. It is seen that the peak located at 427 cm\(^{-1}\) which is the oxygen-related mode, is suppressed as the substrate temperature increases.

![Raman spectra of films deposited on silicon substrate with varied substrate temperatures at a fixed nitrogen ratio of 80% in (N\(_2\)+Ar) ambient.](image)

**Figure 4-4 Raman spectra of films deposited on silicon substrate with varied substrate temperatures at a fixed nitrogen ratio of 80% in (N\(_2\)+Ar) ambient.**

*Zinc oxy-nitride films deposited in (N\(_2\)+Ar with 1% O\(_2\)) atmosphere: sputtering gas composition dependence*

In Figure 4-5, XRD patterns of zinc oxy-nitride thin films prepared at different N\(_2\)/(N\(_2\)+Ar with 1% O\(_2\)) ratios are shown. It is found that the nitrogen concentration in the sputtering gas mixture is the key factor which affects the crystallinity of thin films. By comparing the XRD spectra with or without oxygen at same nitrogen ratio, it is easy to see that the intentionally introduced oxygen impedes the crystallization of zinc nitride. It also needs to be pointed out that, in these samples, prepared in an oxygen-containing atmosphere, the only observed diffraction peaks come from the zinc nitride phase, and no zinc oxide related reflections are observed.
Figure 4-5 XRD patterns of samples deposited at varied $N_2/(N_2+Ar$ with 1% $O_2$) ratio at a fixed substrate temperature of 200°C.

Figure 4-6 shows the Raman scattering spectra of films deposited at different $N_2/(N_2+Ar$ with 1% $O_2$) ratios with a fixed substrate temperature of 200°C. Comparing with XRD pattern above, the oxygen phase appears in Raman data rather than XRD data, which suggests the formation of amorphous or partially amorphous zinc oxide phase.

Figure 4-6 Raman spectra of films deposited on silicon substrates with varied $N_2/(N_2+Ar$ with 1% $O_2$) ratios at a fixed substrate temperature of 200°C.
Zinc oxy-nitride films deposited in \( (N_2 + Ar \text{ with } 1\% \text{ O}_2) \) atmosphere: substrate temperature dependence

![XRD patterns of samples deposited at varied substrate temperatures at a fixed nitrogen ratio of 80\% in \( (N_2 + Ar \text{ with } 1\% \text{ O}_2) \) ambient.](image)

For zinc oxy-nitride thin films, shown in Figure 4-7, crystalline phase is observed at a substrate temperature of 200\°C or higher. It needs to be noticed that the (400) ZnN peak shifted from 36.8\° to 37.1\°, which indicates the lattice strain, possibly due to oxygen incorporation.

**Zinc oxy-nitride films deposited in \( (N_2 + Ar \text{ with } 1\% \text{ O}_2) \) atmosphere: total sputtering gas pressure dependence**

We also studied the film formation as a function of the sputtering gas pressure in the deposition chamber. In Figure 4-8 (a) and (b), XRD patterns from zinc nitride or oxy-nitride thin films, deposited at either 8 mTorr or 16 mTorr, with different oxygen content in the sputtering gas mixture, are presented. For the zinc nitride thin films (0\% of oxygen...
content in sputtering gas mixture, N\textsubscript{2}/total sputtering gas mixture ratio of 80\%), the XRD peak, located at 36.8\(^\circ\), and associated with the (400) plane of cubic anti-bixbyite structure of zinc nitride, is observed [10,11]. When the sputtering gas pressure is increased from 8 mTorr to 16 mTorr, the FWHM values of the dominant peak, the (400) cubic zinc nitride reflection, decreases, suggesting that the crystallinity (i.e., the crystallite size) of the zinc nitride phase increases with the increase of the working pressure. Also, we attribute the presence of ZnO, indicated by the small ZnO related peak in the XRD pattern of the sample prepared at an oxygen-free ambient with a working pressure of 16 mTorr, to the apparently unavoidable trace amounts of water contamination in the deposition chamber [11,24]. As far as the zinc oxy-nitride thin films, the intensity of the (400) zinc nitride peak significantly decreased, not only when the oxygen concentration increased but also when the working pressure increased from 8 mTorr to 16 mTorr. We note that when the working pressure is kept at 8 mTorr, the presence of oxygen (0.2\% or 0.4\%) in the sputtering gas mixture does not result in the formation of the crystalline zinc oxide phase, since only zinc nitride related peaks were observed. However, when the sputtering pressure increased to 16 mTorr, the peak located at 34.2\(^\circ\), which is associated with the (002) reflection of the ZnO phase, is clearly seen [10,11], which indicates the formation of the crystalline ZnO phase. Upon increasing the oxygen concentration in the sputtering gas mixture from 0\% to 0.4\%, the crystallized zinc oxide phase becomes dominant and coexists with the zinc nitride phase in the film material.
Figure 4-8 XRD pattern for samples deposited at varied $O_2/(N_2+Ar$ with 1% $O_2$) ratios at a fixed substrate temperature of 200°C and a fixed working pressure of (a) 8 mTorr or (b) 16 mTorr.

In the sample group for which the $O_2$-to-total sputtering gas mixture ratio was kept at 0.2%, films fabricated at an even higher working pressure of 20 mTorr were investigated, and their XRD patterns are presented in Figure 4-9. Consistent with what was observed earlier, a well-defined and very narrow (400) zinc nitride peak was observed at a working pressure of 8 mTorr. Upon increasing the working pressure to 12 mTorr and then to 16 mTorr, the intensity of the (400) zinc nitride peak dramatically decreased. Also, (002) ZnO and (101) ZnO peaks appeared, indicating a change from zinc nitride phase to a ZnO phase. We note here that the small peak around 36.5° can be attributed to both the (400)-plane zinc nitride phase and (101)-plane ZnO phase. The competition between formation of zinc nitride phase and ZnO phase appears to lead to a nearly amorphous film, which explains why the intensity of the peaks was very low, and the peaks are generally broader. When the working pressure further increased to 20 mTorr, the dominant XRD reflection changed from the (400)-plane zinc nitride to the (002)-plane ZnO. The narrow and well-defined (002)-plane ZnO peak is clearly observed in the XRD patterns. Comparing this case with the case of oxygen fraction in sputtering
gas mixture of 0.4%, we observe that the pressure level which apparently triggers the formation of the crystalline ZnO phase increases from 16 mTorr to 20 mTorr.

![XRD patterns for samples deposited at varied working pressure at a fixed substrate temperature of 200°C and O2/(N2+Ar with 1% O2) ratio of 0.2%.]

**Figure 4-9 XRD patterns for samples deposited at varied working pressure at a fixed substrate temperature of 200°C and O2/(N2+Ar with 1% O2) ratio of 0.2%.**

**Summary on Microstructure and Crystallinity**

With the increase of the N2 content in the total sputtering gas mixture, the films attain higher crystallinity and acquire a higher degree of preferential crystallite orientation. The substrate temperature influences the crystallinity of zinc nitride thin film significantly. The crystallinity of zinc nitride thin film increases with the increase of substrate temperature. Also, somewhat unexpectedly, based on Raman scattering data, it appears that the higher substrate temperature helps to prevent surface oxidation of zinc nitride thin films to a certain degree.

Similarly to what we observed in zinc nitride thin films, in the formation of zinc oxy-nitride thin films, the nitrogen-to-total sputtering gases ratio and the substrate temperature are still the key factors. The deposition pressure is another important
parameter that can control the oxygen incorporation. Although the role of the intentionally introduced oxygen in the film formation process is not fully understood, several important points can be made here. First, the intentionally introduced oxygen impedes the crystallization of zinc nitride. Second, at lower deposition pressure, very little zinc oxide related XRD peaks are observed after this small amount of oxygen is introduced, which suggests that the incorporation of oxygen into zinc nitride thin film increases film’s resistivity to surface oxidation. Third, with increase of the deposition pressure, oxygen is more easily incorporated in the films. Fourth, the co-existence of both zinc nitride phase and zinc oxide phase was observed, and the relative fraction of these two phase influences the properties, especially the electrical and optical properties, in a significant way.

4.1.2 Surface morphology

Scanning electron microscopy (SEM) was utilized to study the properties of surface morphology of zinc nitride and oxy-nitride thin film samples. SEM images were obtained using a Hitachi S-4800 II field emission scanning electron microscope.

Zinc nitride films deposited in (N₂+Ar) atmosphere: sputtering gas composition dependence

Figure 4-10 shows the surface SEM images of zinc nitride thin films deposited at varied N₂/(N₂+Ar) ratios, from 20% to 80%. It can be seen from the Figure 4-10 that by appearance the films are homogeneous and crack-free. Also the grains pack compactly. For the film deposited on Si substrate at a substrate temperature of 200°C and a
N$_2$/(N$_2$+Ar) ratio of 80%, the grain size (noting that the larger grains shown in figures actually consist of smaller grains), is about 20 nm, which is in reasonable agreement with the mean grain size evaluation, using the Scherrer’s formula and the XRD data above. With the increase of the N$_2$ content in the sputtering gas mixture, a smoother surface, as well as clearer the grain boundaries and bigger grain sizes are observed.

![SEM images](image1)

**Figure 4-10** SEM images of zinc nitride thin films deposited at a substrate temperature of 200°C with varied N$_2$/(N$_2$+Ar) ratios, 20% (left), 50% (middle), and 80% (right). The size of scale bar is 1 µm.

**Zinc nitride films deposited in (N$_2$+Ar) atmosphere: substrate temperature dependence**

![SEM images](image2)

**Figure 4-11** SEM images of zinc nitride thin films deposited at N$_2$/(N$_2$+Ar) ratio of 80% with varied substrate temperature, RT (left), 200°C (middle), and 300°C (right). The size of scale bar is 1 µm.

The surfaces of zinc nitride thin films fabricated at different substrate temperatures, from room temperature (RT) to 300°C, are shown in Figure 4-11. The grain sizes increase significantly with the increase of the substrate temperatures, especially from 200°C to 300°C.
**Zinc oxy-nitride films deposited in \((N_2+Ar)\) atmosphere: total sputtering gas pressure dependence**

In Figure 4-12, the surface SEM images of zinc nitride thin films, deposited at a fixed \(N_2/(N_2+Ar)\) ratio of 80% and substrate temperature of 200°C, but at different working pressure, 8 mTorr and 16 mTorr, are shown. The surface of film prepared in higher pressure is smoother. The grain sizes for both films are about the same. It indicates the effect of working pressure on the surface morphology of zinc nitride thin film is limited, which correlates with the XRD data described above.

*Figure 4-12 SEM images of zinc nitride thin films deposited at the same \(N_2/(N_2+Ar)\) ratio of 80% and substrate temperature of 200°C but with different working pressure, 8 mTorr (left) and 16 mTorr (right). The size of scale bar is 1 µm.*

**Zinc nitride films deposited in \((N_2+Ar)\) atmosphere: film thickness dependence**

The effect of film thickness on surface morphology is shown in Figure 4-13. The grain size, as well as the crystallinity, increases with the increase of the thickness of films.
Figure 4-13 SEM images of zinc nitride thin films deposited at $N_2/(N_2+Ar)$ ratio of 80% and substrate temperature of 200$^\circ$C with varied thickness, 200 nm (left), 400 nm (middle), and 1000 nm (right). The size of scale bar is 1 $\mu$m.

Zinc oxy-nitride films deposited in $(N_2+Ar$ with 1% $O_2$) atmosphere: sputtering gas composition dependence

Figure 4-14 SEM images of zinc oxy-nitride thin films deposited at substrate temperature of 200$^\circ$C with varied $O_2/(N_2+Ar$ with 1% $O_2$) ratio, 0.8% (left), 0.4% (middle), and 0.2% (right). The size of scale bar is 1 $\mu$m.

Figure 4-14 presents the SEM images of zinc oxy-nitride thin films prepared at different $O_2/(N_2+Ar$ with 1% $O_2$) ratios, from 0.2% to 0.8%. At the 0.85 case, many bright little spots are seen in the surface of film, which relates to the oxygen incorporated into film. With the decrease of the oxygen concentration in the sputtering gases, it leads to a better film crystallinity. The surface of zinc nitride thin film at 80% of $N_2$ concentration is almost identical with the surface of zinc oxy-nitride thin film at 0.2% of $O_2$ concentration ($N_2$ concentration is also 80% in this case).
Zinc oxy-nitride films deposited in \((N_2+Ar\text{ with } 1\% \text{ } O_2)\) atmosphere: total sputtering gas pressure dependence

Figure 4-15 SEM images of zinc oxy-nitride thin films deposited at the same \(O_2/(N_2+Ar\text{ with } 1\% \text{ } O_2)\) ratio of 0.2\% and substrate temperature of 200\(^\circ\)C but with different working pressure, 8 mTorr (left), 16 mTorr (middle), and 20 mTorr (right). The size of scale bar is 1 \(\mu\)m.

The SEM images of the surfaces of zinc oxy-nitride thin films are shown in Figure 4-15 and Figure 4-16. As seen in Figure 4-15, the surface of the film deposited at 8 mTorr is almost identical to the surface of zinc nitride film (Figure 4-12). When the working pressure increased to 16 mTorr, the grain size decreases and the grain boundaries are not as clear as in the previous case, which can be interpreted in terms of the presence of a significant fraction of an amorphous phase. When the working pressure reached 20 mTorr, somewhat better defined grains were formed but still of a smaller size.

Based on XRD data presented earlier, the change of grain size appears related to the formation of the oxide phase. Similar changes are also observed in Figure 4-16. With higher oxygen content in the sputtering gas mixture, the change of the dominant phase, from crystalline zinc nitride phase to crystalline ZnO phase, occurred at a lower working pressure, 16 mTorr, instead of 20 mTorr, which also matches the XRD data. It can be seen that under higher working pressure, oxygen in sputtering gas mixture is more efficiently incorporated into films and affects the properties of the films more.
Figure 4-16 SEM images of zinc oxy-nitride thin films deposited at the same O\textsubscript{2}/(N\textsubscript{2}+Ar with 1% O\textsubscript{2}) ratio of 0.4% and substrate temperature of 200\textdegree C but with different working pressure, 8 mTorr (left) and 16 mTorr (right). The size of scale bar is 1 µm.

The stability of zinc nitride and oxy-nitride thin film in ambient atmosphere

The film stability under ambient laboratory conditions was studied and related SEM results are shown in Figure 4-17. The SEM images of zinc nitride film prepared at N\textsubscript{2}/(N\textsubscript{2}+Ar) ratio of 80%, substrate temperature of 200\textdegree C, and the working pressure of 8 mTorr were taken right after deposition (upper left) and after staying in the ambient for one week (lower left). As seen in figure, the surface is much rougher than before and many white bright little spots are observed, which indicates the oxidation of the film. The right row of Figure 4-17 shows the SEM images of the zinc oxy-nitride thin film, as control group, deposited at O\textsubscript{2}/(N\textsubscript{2}+Ar with 1% O\textsubscript{2}) ratio of 0.2% (N\textsubscript{2} is kept 80%), right after deposition (upper right) and after staying a dry-air condition for one week (lower right). The EDXS data for these samples were also listed in Table 4.2. Although the chemical composition results from EDXS here are not exactly quantitatively accurate due to the large fraction of signal came from the substrate (which will be discussed later in next subsection), they still show qualitatively the significant impact of humidity in the air.
on the degree of oxidation of zinc nitride films. It is clear that zinc nitride thin films are very susceptible to humidity in the air ambient.

![SEM images of zinc nitride thin films before (upper left) and after (lower left) the one week exposure to ambient. And the zinc oxy-nitride thin film before (upper right) and after (lower right) the one week exposure to dry-air.](image)

*Figure 4-17 SEM images of zinc nitride thin films before (upper left) and after (lower left) the one week exposure to ambient. And the zinc oxy-nitride thin film before (upper right) and after (lower right) the one week exposure to dry-air.*

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Zn</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitride film originally prepared at oxygen-free environment (corresponding to the images at left column in Figure 4-17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>34.08</td>
<td>23.40</td>
<td>5.72</td>
<td>36.80</td>
</tr>
<tr>
<td>After one-week staying in the ambient</td>
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<td>20.99</td>
<td>38.50</td>
<td>39.44</td>
</tr>
<tr>
<td>Zinc nitride film originally prepared at oxygen-contained environment (corresponding to the images at right column in Figure 4-17)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>34.49</td>
<td>24.46</td>
<td>6.76</td>
<td>33.78</td>
</tr>
<tr>
<td>After one-week staying in the dry-air condition</td>
<td>32.63</td>
<td>20.01</td>
<td>8.20</td>
<td>39.16</td>
</tr>
</tbody>
</table>
Summary on Surface Morphology

With the improvement of crystallinity of zinc nitride or oxy-nitride thin films, (as a result of the increase in the N\textsubscript{2} content in the sputtering gas mixture or the substrate temperature) clearer grain boundaries, bigger grain sizes, and smoother surfaces are observed. The effect of oxidation of zinc nitride films on the surface morphology was also presented via SEM work. The most important factor that facilitates oxidation was determined to be the humidity in the air ambient.

4.1.3 Chemical composition and bonding states

X-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDXS) were employed to study the chemical bonding states and composition of zinc nitride thin films. XPS was performed using a Perkin-Elmer 5500 x-ray photoelectron spectrometer with Al K\alpha radiation with x-ray photon energy of 1486.6 eV. EDXS results were obtained using a Hitachi S-4800 II field emission scanning electron microscope.

Single zinc nitride thin film analysis

XPS was performed on both as-deposited film surfaces and on 10 min Ar-ion-sputtered surfaces (by using an argon-ion gun with ion energy set at 1.5 keV and emission current of 20 mA, with a raster size of 3x3 mm). The binding energies (BE) are referenced with respect to the Zn2p\textsubscript{3/2} line in metallic zinc at 1022.5 eV which is known
to change by only 0.2 eV or less upon oxidation [25,67] and therefore was our only possible (although not perfect) choice of a reference line in this study.

In Figures 4-18, survey spectra of XPS of zinc nitride film, deposited at a substrate temperature of 200°C and a N$_2$/N$_2$+Ar ratio of 80%, for both for the as-deposited surface and for the surface after 10 min sputtering treatment (estimated to remove about 20 nm of the material) are presented. It can be seen that, after 10 min sputtering with Ar, the O 1s peak is reduced and N 1s peak is increased.

![Figure 4-18 Survey spectra of zinc nitride film deposited at a substrate temperature of 200°C and a N$_2$/N$_2$+Ar ratio of 80%.](image)

**Figure 4-18** Survey spectra of zinc nitride film deposited at a substrate temperature of 200 °C and a N$_2$/N$_2$+Ar ratio of 80%.

Figure 4-19 (a)-(d) show the Zn 2p line, O 1s line, Zn Auger L$_3$M$_{4,5}$M$_{4,5}$ line, and N 1s line, respectively, from high-resolution spectra of the same zinc nitride film. And Figures 4-20 (a)-(d) show curve the fitting results of XPS spectra of Zn 2p line, O 1s line, Zn Auger L$_3$M$_{4,5}$M$_{4,5}$ line, and N 1s line, respectively.

In Figure 4-19(a), two well defined Zn peaks are observed. One, located at a binding energy (BE) = 1021.96 eV, is related to the Zn 2p$_{3/2}$ peak, and the other one, located at BE = 1045.02 eV, corresponds to the Zn 2p$_{1/2}$ peak. After 10 min sputtering,
those peaks remain sharp and essentially do not change. Also after sputtering treatment, a weak shoulder appears between the Zn 2p$_{3/2}$ peak and Zn 2p$_{1/2}$ peak, which has been observed previously in spectra but not discussed [25,44,50,111]. This shoulder appears only in the XPS spectra of zinc nitride, but not in the XPS spectra of ZnO or Zn [25,44], and could be plasmon related.

![Figure 4-19](image)

**Figure 4-19** The XPS (a) Zn2p line, (b) O1s line, (c) Zn Auger L$_3$M$_{4,5}$M$_{4,5}$ line, and (d) N1s line from high-resolution spectra of zinc nitride film deposited at a substrate temperature of 200°C and a N$_2$/(N$_2$+Ar) ratio of 80%.

In Figure 4-19(b), O1s spectra are plotted. At the as-deposited surface, the spectrum consists of a H-O related peak at BE = 531.95 eV, which is due to water adsorption [25] and a O-Zn related peak at BE = 530.39 eV [112]. After 10 min
sputtering with Ar, the 531.95 eV peak disappears, which indicates that H-O bonds are only present in the surface region. Also, a significant fraction of the O-Zn bonds is removed as well, which, again, can be interpreted in terms of an oxidized film surface, and an almost oxygen-free film volume.

Figure 4-20 Curve fitting results for XPS (a) Zn2p line, (b) O1s line, (c) Zn Auger L3M4,5M4,5 line, and (d) N1s line from high-resolution spectra of zinc nitride film deposited at a substrate temperature of 200°C and a N2/(N2+Ar) ratio of 80%.

In Figure 4-19(c), the Zn Auger L3M4,5M4,5 region of the spectra is presented. On the as-deposited surface of the film, most Zn is in the form of either O-Zn or N-Zn. This is also observed by Yang et al. [6], but is different from the observation by Toyoura et al. [79], who reported that the outer surface mainly consists of Zn(OH)2 rather than ZnO. It
is clearly seen that after 10 min sputtering the metallic Zn peaks, located at BE = 494 eV and 490.6 eV [25,113], are dominant and the spectrum is shifted. Both changes can be associated with de-nitridation of the material as result of the Ar-ion bombardment, which is a known problem in XPS depth profiling of nitride materials [114,115]. The as-deposited surface spectrum shows contributions from OH-Zn (499.8 eV), O-Zn (498.8 eV) [25,113], and N-Zn bonding (496.6 eV), and no contribution from the metallic Zn phase is observed. After 10 min sputtering the N-Zn phase remains while the OH-Zn and O-Zn phases are significantly reduced.

In Figure 4-19(d), N1s spectra are shown. In the spectrum of the as-deposited surface, two peaks, located at BE = 396.27 eV and 398.57 eV, are observed. They correspond to N-Zn bonds reported at 395.8 eV, and N-H bonds reported at 398.3 eV [25]. The well-defined N-H bonding peak indicates the same water-contamination issue as is observed from the O1s spectra. After sputtering, this N-H bonding peak is removed while the Zn-N bonding peak remains and shifts 0.4 eV to higher energy reaching 396.72 eV, which agrees with the results reported by K. Toyoura et al. [79]. Moreover, a new peak located at BE = 405.03 eV appears. This 405.03 eV peak is believed to be related to molecular nitrogen [50] which implies that N-N bonds exist within the films.

Zinc nitride films deposited in (N$_2$+Ar) atmosphere: sputtering gas composition dependence

Figure 4-21 to Figure 4-24 shows the XPS N1s line, O1s line, Zn2p line, and Zn Auger L$_3$M$_{4.5}$M$_{4.5}$ line of zinc nitride thin films deposited at varied N$_2$/ (N$_2$+Ar) ratios. It is shown, in Figure 4-21, that at the surface, the spectra of N1s line are almost the same.
They all contain two peaks. One at higher binding energy is associated with H-N bonding, and another one at lower binding energy corresponds to Zn-N bonding. After 10 min sputtering, the peak located at 398 eV, related to H-N bonding, is removed, while Zn-N bonding remained. Also the molecular N₂ bonding (404 eV) shows up after sputtering. It needs to be noticed that the peaks shift to lower binding energy with the increase of nitrogen ratio after the sputtering treatment. The same shifts are also observed in the O1s line, Zn2p line, and Zn Auger L₃M₄,5M₅,5 line.

![Figure 4-21 XPS spectra of N1s line for different N₂/(N₂+Ar) ratios before (left) and after (right) sputtering treatment.](image)

In Figure 4-22, it can be seen that at the surface, with the decrease of N₂/(N₂+Ar) ratios in sputtering gas mixture, the O-Zn bonding becomes more pronounced. On the other hand, the O-H bonding is hardly affected by the nitrogen content in total sputtering gas mixture. After the sputtering treatment, the peaks corresponding to O-H bonding were almost removed and the correlation between O-Zn bonding and N₂/(N₂+Ar) ratios in sputtering gas mixture becomes clearer to review. Figure 4-23 presents the XPS spectra of Zn2p line for different N₂/(N₂+Ar) ratios. It can be seen that the peaks are hardly shifted before and after sputtering treatment, which makes a great reference.
In Figure 4-24, it can be seen that at the surface, with the decrease of \( \frac{N_2}{(N_2+Ar)} \) ratios in sputtering gas mixture, the O-Zn bonding becomes more pronounced. This can be seen as either increasing of O-Zn bonding or decreasing of N-Zn bonding. Because the possible oxygen contamination should be identical for all samples, we interpret this dependence in terms of a decreasing of N-Zn bonding. After the sputtering treatment, films surface is de-nitrified (i.e., nitrogen is removed at a disproportionally higher rate) and the peaks corresponding to metallic Zn become dominant.
Figure 4-24 XPS spectra of Zn Auger $L_3M_{4.5}M_{4.5}$ line for different $N_2/(N_2+Ar)$ ratios before (left) and after (right) sputtering treatment.

Table 4.3 EDXS results for both 500 nm and 1µm thick zinc nitride films deposited at a substrate temperature of 200°C and $N_2/(N_2+Ar)$ ratio of 80%. The acceleration voltage was varied between 5 kV and 20kV, and the Si signal observed in the 500 nm thick film case is due to the substrate.

<table>
<thead>
<tr>
<th>500 nm thick film (atomic%)</th>
<th>N</th>
<th>Zn</th>
<th>O</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>5kV</td>
<td>36.51</td>
<td>58.46</td>
<td>5.03</td>
<td></td>
</tr>
<tr>
<td>20kV</td>
<td>34.08</td>
<td>23.40</td>
<td>5.72</td>
<td>36.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1 µm thick film (atomic%)</th>
<th>N</th>
<th>Zn</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>5kV</td>
<td>38.25</td>
<td>57.31</td>
<td>1.63</td>
</tr>
<tr>
<td>20kV</td>
<td>40.76</td>
<td>53.02</td>
<td>4.76</td>
</tr>
</tbody>
</table>

Due to the surface oxidation and de-nitridation caused by Ar-ion sputtering, the XPS results not suitable for quantitative evaluation of the composition of zinc nitride thin films. In order to obtain quantitative information on chemical composition, we performed a series of EDXS measurements on films with different thicknesses deposited on Si substrates. Different accelerating voltages were used in order to eliminate the effect of the substrate. We have found that at a low voltage of 5 kV the signal from the zinc nitride film is maximized at the expense of the substrate signal, and the compositional data are reliable, as illustrated by the data in Table 4.3. Our films exhibit a Zn:N ratio which is
very close to the stoichiometric value of 1.5, and they contain only a small amount of zinc oxide phase (i.e., oxygen).

**Zinc oxy-nitride films deposited in \((N_2+Ar\ with\ 1\%\ O_2)\) atmosphere: total sputtering gas pressure dependence**

The chemical composition of the films was studied by EDXS, as illustrated by the data in Table 4.4. A working distance of 15 mm and a low accelerating voltage of 5 kV, at which the signal from the thin films is maximized at the expense of the substrate signal, were used.

*Table 4.4 EDXS results of zinc nitride and oxy-nitride thin films deposited at different working pressures.*

<table>
<thead>
<tr>
<th>Working pressure: 8 mtorr</th>
<th>O\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>N\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>Zn (atomic%)</th>
<th>N (atomic%)</th>
<th>O (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>80%</td>
<td>58.46</td>
<td>36.51</td>
<td>5.03</td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>58.11</td>
<td>35.60</td>
<td>6.29</td>
<td></td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>57.98</td>
<td>33.02</td>
<td>9.00</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Working pressure: 16 mtorr</th>
<th>O\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>N\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>Zn (atomic%)</th>
<th>N (atomic%)</th>
<th>O (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>80%</td>
<td>60.33</td>
<td>35.42</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>51.32</td>
<td>8.33</td>
<td>40.35</td>
<td></td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>52.66</td>
<td>19.52</td>
<td>27.83</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O\textsubscript{2}/total sputtering gas mixture = 0.2% and N\textsubscript{2}/total sputtering gas mixture = 80%</th>
<th>Working pressure: 20 mtorr</th>
<th>54.49</th>
<th>20.87</th>
<th>24.64</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working pressure: 16 mtorr</td>
<td>51.32</td>
<td>8.33</td>
<td>40.35</td>
<td></td>
</tr>
<tr>
<td>Working pressure: 8 mtorr</td>
<td>58.11</td>
<td>35.60</td>
<td>6.29</td>
<td></td>
</tr>
</tbody>
</table>

As seen in Table 4.4, the two zinc nitride thin films (oxygen ratio of 0%) were almost identical in terms of chemical composition. They also exhibited a Zn:N ratio which was very close to the stoichiometric value of 1.5, and contained only a small amount of oxygen. At a working pressure of 8 mTorr, with the increase of oxygen concentration in the sputtering gas mixture, the oxygen in the films increased only a little which is consistent with what XRD data suggested. When the working pressure increased
to 16 mTorr, the oxygen concentration in the film reached the maximum (40.35%) in the nearly amorphous film, and then decreased to 27.83% for the film in which crystalline zinc nitride and crystalline zinc oxide coexisted. This oxygen concentration of 27.83% is very close to that of the zinc oxy-nitride thin film deposited at a working pressure of 20 mTorr and O$_2$-to-total sputtering gases ratio of 0.2%, in which the two crystalline phases also coexist.

**Summary on Chemical Composition and Bonding States**

The formation of zinc nitride is again confirmed by the observation of N-Zn bonds in the XPS spectra. A nearly stoichiometric value of Zn:N ratio was established in the quantitative analysis of chemical concentration by EDXS. Moreover, it is found from the XPS spectra that the surface of the zinc nitride thin film contains water, as suggested by the presence of H-O and H-N bonds, which also explained the presence of O in the EDXS data for films prepared at oxygen-free environment. After sputtering removal of a very thin surface layer during the XPS measurement, the complete absence of H-O bonds and the significant reduction of O-Zn bonds indicate an oxidized film surface and an almost oxygen-free film volume. Also, molecular N$_2$ bonds appear after the sputtering, which indicates the existence of N-N bonds in the thin film and is, most likely, partially responsible for the n-type conductivity. The intentional incorporation of oxygen into zinc nitride thin films and the way of controlling this process were also confirmed by EDXS.

**4.1.4 Electrical properties**

Room temperature Hall-effect measurements and resistivity measurements were used to characterize the electrical properties of zinc nitride and oxy-nitride thin films. The
measurements were carried out on an H-50 Hall system from MMR Tech. Inc. utilizing a standard four point Van der Pauw contact configuration. Four-probe resistivity measurements were also used to independently verify the resistivity values.

![Figure 4-25 I–V curves for different metal contacts on zinc nitride films](image)

In any electrical measurements (including the Hall-effect measurement and the four-probe resistivity measurement in this work), the quality of the contacts is very important. Good ohmic contacts are always needed both in electrical measurements and in devices structures. Three different metals are employed as metal contacts on our zinc nitride films. In Figure 4-25, there are the current-voltage (I-V) curves for all three of metals: gold, aluminum and copper. It is clear that contacts between our zinc nitride and any of the three metals are ohmic. It needs to be pointed out here that the resistances of these three metal films, which can be calculated from the slope of each line, do not represent properly the resistivity of the metals due to different fabrication methods, distances and film thicknesses.

Therefore, in this research, 200 nm-thick copper film contacts (in a Van der Pauw configuration) were deposited on the zinc nitride samples for room-temperature Hall
effect and resistivity measurements. The magnitude of the magnetic field was set at 2500 G, and the optimal current, being sample dependent (i.e., carrier concentration dependent) is determined automatically by the Hall effect system.

_Zinc nitride films deposited in (N\textsubscript{2}+Ar) atmosphere: sputtering gas composition dependence and substrate temperature dependence._

The electrical properties of zinc nitride thin films deposited under either different N\textsubscript{2}/(N\textsubscript{2}+Ar) ratios or different substrate temperatures were examined first. All films were found to exhibit n-type conductivity. For this set of samples, the carrier concentration is estimated to be in the range of 10\textsuperscript{20} cm\textsuperscript{-3} to 10\textsuperscript{21} cm\textsuperscript{-3}. Mobility values are in the range of 40 to 90 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} and the resistivity is \( \sim 5\times10^{-3} \) Ωcm. These numerical values are in broad agreement with published data by other groups [6].

As can be seen from Figure 4-26, the carrier density is affected both by the substrate temperature and by the nitrogen ratio. In the case of the substrate temperature dependence, the carrier density first decreases and then increases as the substrate temperature is increased. This is likely due to increased nitrogen incorporation in the films at higher temperature. In the case of the nitrogen ratio dependence, the carrier density increases first and then decreases with increasing the fraction of nitrogen in the total sputtering gas mixture. The increase is most likely caused by enhanced reaction between zinc and nitrogen, and the subsequent decrease can be attributed the formation of nitrogen-nitrogen bonds (as confirmed by XPS) in the films due to the high nitrogen content of the plasma. Possibly, this is related to the gain or loss of Zn interstitial defects.
Figure 4.26 Electrical properties, obtained from Hall-effect and resistivity measurements for zinc nitride films deposited under either different \(N_2/(N_2+Ar)\) ratios or different substrate temperatures.

As a consequence of the change of carrier density, resistivity and sheet resistance are changing correspondingly (first increasing then decreasing versus substrate temperature, and first decreasing then increasing versus nitrogen ratio). This agrees in part with reports that increasing the fraction of nitrogen in the plasma produced films with lower carrier density [6,32]. We must point out here that the resistivity and sheet resistance change very little when the substrate temperature increases from 200°C to 300°C, as opposed to the much sharper change which is observed when the substrate temperature increases from room temperature to 200°C. The carrier density, on the other hand, changes by almost the same amount in these two steps. Somewhat similar observations can be made in the nitrogen ratio dependence case.
In polycrystalline semiconductors, the mobility is affected by either impurity scattering or grain boundary scattering. In this work, in the case of the substrate temperature dependence, the crystallinity of films prepared at room temperature and 100°C are almost identical in terms of the FWHM of (400) zinc nitride XRD peak. Mobility increases with decreasing of the carrier density which indicates that the impurity scattering mechanism is dominant in this region. As temperature increases from 100°C to 200°C, the crystallinity improves significantly, and the mobility increases even though the carrier concentration also increases. This means that, at the higher temperatures, grain boundary scattering controls the mobility. Finally, when substrate temperature increases to 300°C, the impurity scattering becomes dominant again since the crystallinity of the 200°C film and 300°C film are about the same. In the case of the nitrogen ratio dependence, the mobility is high even though the crystallinity of film is poor (20% film), and, with the increase of the nitrogen, the mobility decreases, just as the carrier concentration decreases. More studies are needed to understand such behavior fully.

Zinc oxy-nitride films deposited in (N₂+Ar with 1% O₂) atmosphere: sputtering gas composition dependence

Hall Effect measurements and resistivity measurements were performed on zinc oxy-nitride thin films deposited at varied O₂/(N₂+Ar with 1% O₂) ratios to investigate the electrical properties. All samples were n-type. As shown in Figure 4-27, the resistivity of the samples, prepared at O₂/(N₂+Ar with 1% O₂) ratios from 0.2% to 0.7% decreases with the increase of oxygen content in sputtering gases (i.e, with the decrease of nitrogen concentration in sputtering gas mixture). So does the sheet resistance. When oxygen
content reaches 0.8%, the resistivity, as well as the sheet resistance, of the film increases. This behavior is very similar to what was observed in zinc nitride thin film case. The mobility of zinc oxy-nitride thin films first increases with increase of oxygen fraction but then decreases when oxygen fraction reaches 0.8%. The same trends are seen in the carrier concentration of films. First, the concentration is increasing with increase of oxygen amount in sputtering gas mixture, then starting to decrease when oxygen amount reaches 0.8% of total sputtering gas.

Figure 4-27 Electrical properties, obtained from Hall-effect and resistivity measurements for zinc oxy-nitride thin films at varied O₂/(N₂+Ar with 1% O₂) ratios.
Zinc oxy-nitride films deposited in (N$_2$+Ar with 1% O$_2$) atmosphere: total sputtering gas pressure dependence

Electrical properties of zinc oxy-nitride thin films deposited in (N$_2$+Ar with 1% O$_2$) ambient with varied total sputtering gas pressure were investigated and presented in Table 4.5. All films were found to exhibit n-type conductivity. As seen in Table 4.5, at a working pressure of 8 mTorr, the majority carrier concentration in the films decreased significantly from $10^{21}$ cm$^{-3}$ to $10^{19}$ cm$^{-3}$ while oxygen concentration in sputtering gases increased from 0% to 0.2%. This may be related to the loss of Zn interstitial defects. However, upon further increase of the oxygen content in sputtering gas from 0.2% to 0.4%, the majority carrier concentration was affected very little. The mobility was in the range of 50 to 80 cm$^2$V$^{-1}$s$^{-1}$ and the resistivity slightly decreased with increase of the oxygen fraction in sputtering gas mixture. When the working pressure increased to 16 mTorr, compared with films prepared at 8 mTorr at the same concentration of oxygen in sputtering gas mixture, the majority carrier concentration decreased. An exception is the films fabricated at 0.2% of oxygen concentration, which can be attributed to their mostly amorphous nature. This is likely due to stronger oxygen incorporation in the films and, consequently, a more significant loss of Zn interstitial defects. It was also observed that the mobility decreased from $\sim 70$ cm$^2$V$^{-1}$s$^{-1}$ to $\sim 12$ cm$^2$V$^{-1}$s$^{-1}$ while sample’s nature changed from polycrystalline zinc nitride (0% of oxygen content in sputtering gas mixture) to amorphous zinc oxy-nitride (0.2% of oxygen content in sputtering gas mixture), and then slightly increased to $\sim 20$ cm$^2$V$^{-1}$s$^{-1}$ while the zinc oxide phase became dominant and coexisted with zinc nitride phase (0.4% of oxygen content in sputtering gas
mixture). The same trend was also seen in the group of samples prepared at an oxygen fraction in sputtering gases of 0.2% but different working pressures.

Table 4.5 Parameters in Hall effect and resistivity measurements of zinc nitride and oxy-nitride thin films deposited at different working pressures.

<table>
<thead>
<tr>
<th>O₂/total sputtering gas mixture (%)</th>
<th>N₂/total sputtering gas mixture (%)</th>
<th>Resistivity (Ohm·cm) (×10⁻²)</th>
<th>Mobility (cm²/Vs)</th>
<th>Density (cm⁻³) (×10¹⁹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Working pressure: 8 mTorr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>80%</td>
<td>0.78</td>
<td>53.55</td>
<td>149</td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>0.75</td>
<td>68.86</td>
<td>1.20</td>
</tr>
<tr>
<td>0.3%</td>
<td>70%</td>
<td>0.66</td>
<td>78.02</td>
<td>1.22</td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>0.52</td>
<td>66.40</td>
<td>1.82</td>
</tr>
<tr>
<td><strong>Working pressure: 16 mTorr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>80%</td>
<td>0.69</td>
<td>75.65</td>
<td>1.20</td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>2.43</td>
<td>11.67</td>
<td>2.20</td>
</tr>
<tr>
<td>0.3%</td>
<td>70%</td>
<td>0.95</td>
<td>72.78</td>
<td>0.90</td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>8.06</td>
<td>20.39</td>
<td>0.38</td>
</tr>
<tr>
<td><strong>O₂/total sputtering gas mixture = 0.2% and N₂/total sputtering gas mixture = 80%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>working pressure: 20mTorr</td>
<td></td>
<td>2.98</td>
<td>24.31</td>
<td>0.86</td>
</tr>
<tr>
<td>working pressure: 16mTorr</td>
<td></td>
<td>2.43</td>
<td>11.67</td>
<td>2.20</td>
</tr>
<tr>
<td>working pressure: 12mTorr</td>
<td></td>
<td>0.58</td>
<td>13.73</td>
<td>7.82</td>
</tr>
<tr>
<td>working pressure: 8mTorr</td>
<td></td>
<td>0.75</td>
<td>68.86</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 4.6 Parameters in Hall effect and resistivity measurements of zinc oxy-nitride thin films (presented in Table 4.5) after annealing treatment.

<table>
<thead>
<tr>
<th>O₂/total sputtering gas mixture (%)</th>
<th>N₂/total sputtering gas mixture (%)</th>
<th>Resistivity (Ohm·cm) (×10⁻²)</th>
<th>Mobility (cm²/Vs)</th>
<th>Density (cm⁻³) (×10¹⁹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Working pressure: 8 mTorr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>n-type</td>
<td>0.85</td>
<td>6.24</td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>n-type</td>
<td>3.19</td>
<td>12.13</td>
</tr>
<tr>
<td><strong>Working pressure: 16 mTorr</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2%</td>
<td>80%</td>
<td>p-type</td>
<td>159</td>
<td>0.51</td>
</tr>
<tr>
<td>0.4%</td>
<td>60%</td>
<td>too resistive for Hall effect measurement</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>O₂/total sputtering gas mixture = 0.2% and N₂/total sputtering gas mixture = 80%</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>working pressure: 20mTorr</td>
<td>p-type</td>
<td>14300</td>
<td>2.04</td>
<td>0.00214</td>
</tr>
<tr>
<td>working pressure: 16mTorr</td>
<td>p-type</td>
<td>159</td>
<td>0.51</td>
<td>0.76</td>
</tr>
<tr>
<td>working pressure: 12mTorr</td>
<td>n-type</td>
<td>7.88</td>
<td>3.57</td>
<td>2.22</td>
</tr>
<tr>
<td>working pressure: 8mTorr</td>
<td>n-type</td>
<td>0.85</td>
<td>6.24</td>
<td>11.70</td>
</tr>
</tbody>
</table>
After the oxygen was controllably incorporated into zinc nitride thin films, thermal treatment was employed to activate dopants. Zinc oxy-nitride thin films were annealed in air for 4 hours at 400\(^\circ\)C. Hall-effect measurements were then performed on these samples, and the results are provided in Table 4.6. After the annealing treatment, the mobility of samples drastically decreased to less than 10 cm\(^2\)V\(^{-1}\)s\(^{-1}\), the carrier concentration also decreased and the resistivity increased. A comparison with results in published work (on using zinc nitride to obtain p-type doped ZnO) [26,42,71,73,75,91], shows that in our case the resistivity is relatively lower and the carrier concentration is significantly higher. In addition, the conductivity type of these samples in which zinc nitride phase and zinc oxide phase coexist, turned from n-type to p-type. The change of the conductivity type can be attributed to the oxygen incorporations, combined with the effect of the annealing process (which activates dopants), which decreased the source of free electrons, in either Zn interstitial or N vacancy forms. Consequently, the free holes provided by N exceeded the free electrons, becoming to the majority carrier. The thin film could be seen as nitrogen doped zinc oxide film in which N substitutes for O creating holes that become the majority carriers. As mentioned earlier, this is also consistent with the reasons for the change in the electrical properties of the as-deposited samples, even though the conducting type remains n-type for all samples before annealing. Such a process is of significant interest to the fabrication of p-type zinc oxy-nitride [25,26,71,73,75,77,84,91] as it can be used to obtain p-type zinc oxide with some potential advantages. This process can be a first step of introducing oxygen in a nitride film, upon providing better uniformity within the volume of the film as opposed to thermal oxidation of zinc nitride (used in the cited work above), which tends to be
stronger on the surface than in the volume. A post-deposition thermal treatment (under optimized conditions) of these films could then be used to activate most of the remaining nitrogen as a dopant of the ZnO material.

**Summary on Electrical Properties**

The electrical properties of zinc nitride thin film were found to depend on deposition conditions, such as nitrogen to total sputtering gas ratio and substrate temperature, and therefore the crystallinity of the films and the chemical bonding states that comprise the material. By changing the deposition condition, the majority carrier concentration and the resistivity of zinc nitride thin films are controllably modified within a certain range. The electrical properties of the zinc oxy-nitride films are closely related to the chemical composition as well as the bonding states of oxygen with zinc and nitrogen (phase-related) inside the film. By controlling the fraction of ZnO phase and ZnN phase, the electrical properties of zinc oxy-nitride can be controlled. After the post-deposition thermal treatment, some of zinc oxy-nitride thin films show p-type conductivity.

**4.1.5 Optical properties**

Spectrophotometry and spectroscopic ellipsometry were employed to study the optical properties of zinc nitride and oxy-nitride thin films. The optical transmittance and reflectance of the films were measured with a Lambda 1050 UV/VIS/NIR spectrometer over the wavelength range from 350 nm to 2000 nm at room temperature. Spectroscopic ellipsometry (SE) was performed using the instrument models M-2000FI™ (J. A.
Woollam Co., Inc.) and IR-VASE (J. A. Woollam Co., Inc.) over the photon energy range from 0.15 eV to 5.5 eV at angles of incidence of 55°, 65°, and 75°.

**Single zinc nitride thin film analysis**

Spectroscopic ellipsometry was employed to obtain a better understanding of the optical properties of zinc nitride thin films. In this work, ellipsometry angles (\( \psi \), \( \Delta \)) were obtained in both the infrared and the UV-visible ranges (total range: 0.15 eV – 6.5 eV). The structural model for the zinc nitride film is a four medium system consisting of the ambient, a zinc nitride surface roughness layer, a bulk-like zinc nitride layer, and the glass substrate. The optical effect of surface roughness can be simulated using a model consisting of a layer whose thickness is to be determined and whose optical properties are given by an effective medium theory assuming a 0.5/0.5 volume fraction mixture of the underlying bulk-like medium and the overlying ambient medium. For microscopic roughness layers at the nanometer thickness scale on both metals and semiconductors, the Bruggeman effective medium theory has been found to be suitable for extracting the roughness thickness \([88,90]\), an approach which has been also used for modeling the surface roughness in this work.

An isotropic dielectric function for both the surface and bulk layers is assumed in order to analyze the (\( \psi \), \( \Delta \)) measurements. In the UV-visible range, the dielectric function of the bulk zinc nitride layer is modeled using three direct gap critical point (CP) oscillators, based on the assumption of parabolic bands, along with a Drude free electron component. In the infrared region, the bulk zinc nitride layer is modeled using Drude and
Gaussian absorption characteristics along with additional non-absorbing dispersion that influences only $\varepsilon_1$.

Figure 4-28 Experimental and generated ellipsometric $\Delta$ and $\psi$ spectra in (a) UV-visible and (b) infrared ranges.

After the ($\psi$, $\Delta$) data are obtained, analysis based on least-squares regression is applied to the ellipsometric spectra collected at three angles of incidence. The results presented here are for zinc nitride film prepared at nitrogen ratio of $N_2/(N_2+Ar) = 80\%$ and a substrate temperature of 200°C. By fitting the experimental data using the models for the structure and optical properties described above, the dielectric function parameters, listed in Table 4.7, as well as the two thicknesses, are obtained. The data and best fitting results for ($\psi$, $\Delta$) are presented in Figure 4-28, demonstrating the high quality
of the fits. An exact inversion is performed for the central angle of incidence using the fixed thicknesses obtained in the least squares regression. This enables extraction of the index of refraction and extinction coefficient more directly from the \((\psi, \Delta)\) spectra, as well as evaluation of possible errors in the analysis due to the assumption of the four medium structures. These errors appear in the form of spectral artifacts in \(n\) and \(k\). In addition, a comparison of the inverted index of refraction and extinction coefficient and the analytical form calculated from the best fitting parameters in least squares regression provides an assessment of the validity of the analytical form.

Table 4.7 Key parameters of the analytical form of the dielectric function used in the optical model

<table>
<thead>
<tr>
<th></th>
<th>(A_n)</th>
<th>(E_n) (eV)</th>
<th>(\Gamma_n) (eV)</th>
<th>(\phi_n) (deg)</th>
<th>(\nu_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1</td>
<td>12.66±0.38</td>
<td>1.255±0.005</td>
<td>0.347±0.012</td>
<td>-28.74±1.28</td>
<td>0.0669±0.0015</td>
</tr>
<tr>
<td>CP2</td>
<td>7.23±0.63</td>
<td>4.152±0.642</td>
<td>1.664±0.797</td>
<td>64.06±5.32</td>
<td>0.0800±0.0055</td>
</tr>
</tbody>
</table>

\(\rho \ (\Omega cm)\) \((6.61±0.89)×10^{-3}\) \(\tau \ (s)\) \((5.78±0.62)×10^{-13}\)

Figure 4-29 The index of refraction and the extinction coefficient for zinc nitride films obtained from a best fit analytical expression (lines) or from exact inversion (points). Note the abscissa scale transition at 0.5 eV.

The results of this comparison are shown in Figure 4-29. As seen from the figure, the inverted and analytical forms for the dielectric function match well, indicating that the
analytical model is a close approximation. However, weak artifacts do appear most clearly in \( n \) near 1.2 and 1.8 eV. These artifacts cannot be eliminated through adjustment of the surface roughness and bulk thicknesses, and are attributed to the inability to exactly match the interference fringe pattern with a two layer model for the film. It is likely that deviations from the two layer model, e.g. due to ion bombardment modification of the substrate in the initial stages of growth, accounts for the artifacts; however, the deviations do not affect the conclusion of this study.

From the parameters of the first critical point as shown in Table 4.7, we conclude that the film exhibits a direct band gap of 1.26 eV, which is reasonably close but lower than the absorption onset value obtained from optical transmittance data, 1.39 eV (seen later in Table 4.9). The difference is attributed to the inaccuracies of the extrapolation method and the use of absorption coefficient data well above the band gap where the assumptions of parabolic bands and constant matrix element are likely to break down. From the Drude contribution in the infrared range, the resistivity is estimated to be \( 6.6 \times 10^{-3} \ \Omega \text{cm} \) (see Table 4.7), which is in good agreement with the direct dc measurement, \( 7.8 \times 10^{-3} \ \Omega \text{cm} \).

<table>
<thead>
<tr>
<th>Sample (deposition conditions)</th>
<th>Key physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_2 ) partial ratio</td>
<td>Substrate Temp.</td>
</tr>
<tr>
<td>20%</td>
<td>200°C</td>
</tr>
<tr>
<td>50%</td>
<td>200°C</td>
</tr>
<tr>
<td>80%</td>
<td>200°C</td>
</tr>
<tr>
<td>50%</td>
<td>Room Temp.</td>
</tr>
<tr>
<td>50%</td>
<td>300°C</td>
</tr>
</tbody>
</table>

Several other zinc nitride thin film samples prepared under different deposition conditions were also analyzed by spectroscopic ellipsometry. The values of the band gap
and the resistivity are listed in Table 4.8. Comparing with the direct measured optical on-site (Table 4.9) and the resistivity (Figure 4-26) respectively, the results agree with each other fairly well.

Zinc nitride films deposited in \((N_2+Ar)\) atmosphere: sputtering gas composition dependence and substrate temperature dependence

![Figure 4-30 Optical transmittance spectra of films deposited at (a) varied \(N_2/(N_2+Ar)\) ratio with a fixed substrate temperature of 200°C and (b) varied substrate temperatures with a fixed \(N_2/(N_2+Ar)\) ratio of 80%. The similar results were obtained from zinc nitride films prepared in a different sputtering system by collaborating group [116].

Optical transmittance spectra for films deposited at different \(N_2/(N_2+Ar)\) ratios are presented in Figure 4-30(a). The films show much higher transmittance in the near infrared range than in the visible range suggesting the presence of an absorption onset due to a band gap in the near infrared. This behavior is consistent with the results reported by T. Yang et al. [6]. In addition, it can be seen that the films change significantly when the nitrogen concentration increases from 20% to 50%. After 50%, the transmittance of films exhibits the same pattern while shifting to longer wavelength. This may be related to the crystallinity of the films, as discussed in consideration of the XRD data above. The transparency of films was found to correlate to some degree with the
crystallinity of the films, as well as the nitrogen fraction in the sputtering gas mixture. The very poor crystallinity of the 20% case sample may be the reason for the much broader, gradual absorption onset and higher transmittance in the visible range. In the range of 50% to 100% nitrogen ratio, the transmittance in the infrared increases with the increase of nitrogen fraction which may be due to the reduction in free carrier concentration with increasing nitrogen fraction as described in the next subsection.

Figure 4-30(b) shows the optical transmittance spectra of films deposited at different substrate temperatures from room temperature up to 300°C. It can be seen that the substrate temperature has a significant impact on the transmittance of zinc nitride films. For this series however, a correlation is no longer observed between high infrared transmittance and low carrier concentration (results presented in previous subsection). In addition, there is a well-defined shoulder appearing in the spectra of the film deposited at 300°C, which was also apparent in optical transmittance spectra of zinc nitride films prepared by T. Yang et al. [6] using RF sputtering with zinc target in (N₂+Ar) atmosphere. This shoulder appears when the absorption onset is sharp and when the interference features generate increasing transmission with decreasing wavelength at the particular wavelength of the absorption onset. The sharpest absorption onsets occur for the two highest temperature samples, consistent with the enhanced crystallinity. For these two samples, the well-defined absorption onset increases in wavelength with the increase in temperature from 200°C to 300°C.

Analysis of both the transmittance and reflectance can yield the absorption coefficient α which enables an evaluation of the lowest band gap transitions [117]. If the band gap is direct, a plot of (hνα)² versus photon energy should be linear and an
extrapolation to zero ordinate provides the band gap value. This methodology is based on the assumptions of parabolic valence and conduction bands in $k$-space, a constant momentum matrix with photon energy, no excitonic interactions, and a constant index of refraction over the photon energy range of the extrapolation. If the band gap is indirect, a plot of $(h\nu\alpha)^{1/2}$ versus photon energy should be linear as well, but with an analogous set of assumptions. The primary distinguishing factor between lowest direct and indirect band gaps is in the magnitude of the absorption coefficient at a given energy above the absorption onset. In sub-micron thin films, a lowest indirect gap is generally below the sensitivity limits of transmission and reflection measurements due to the orders of magnitude lower transition probability due to the weak electron-phonon coupling.

![Figure 4-31 Optical transmittance data plots used to obtain conventionally-defined absorption onset values for zinc nitride films prepared under either (a) different $N_2/(N_2 + Ar)$ ratios and fixed substrate temperature or (b) different substrate temperatures and a fixed $N_2/(N_2 + Ar)$ ratio. Transmittance and reflectance data were used to obtain the absorption coefficient $\alpha$.](image)

As can be seen from Figure 4-31, the magnitude of the absorption coefficient and its shape for the zinc nitride films is consistent with a direct band gap, a conclusion which is also confirmed by spectroscopic ellipsometry measurement discussed above. The values of the absorption onset are obtained from an extrapolation of the higher energy
range of linearity in Figure 4-31 and are listed in Table 4.9 for comparison purposes, as is commonly done in the literature of zinc nitride thin films \[6,26,30,43,49\]. From Table 4.9, using this method, the values of the absorption onset of zinc nitride films deposited under different conditions are all close to 1.40 eV. The absorption onset decreases in energy with increasing nitrogen fraction in the total sputtering gas mixture. Considering the substrate temperature dependence, the values of the absorption onset of 1.48 eV (100°C) and 1.47 eV (200°C) are about the same. However, there is an observable an increase from 1.43 eV (room temperature) to 1.48 eV and then a decrease from 1.47 eV to 1.38 eV (300°C). So it can be concluded that, by increasing the substrate temperature, the conventionally-defined absorption onset first increases and then decreases. These trends, obtained by extrapolation of the absorption coefficient, are consistent with the results in the raw transmittance data of Figure 4-30.

**Table 4.9 The values of the conventionally defined absorption onset for zinc nitride films fabricated under different deposition conditions.**

<table>
<thead>
<tr>
<th>Nitrogen Ratio Dependence</th>
<th>20%</th>
<th>50%</th>
<th>80%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.68eV</td>
<td>1.47eV</td>
<td>1.39eV</td>
<td>1.35eV</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate Temperature Dependence</th>
<th>Room Temperature</th>
<th>100°C</th>
<th>200°C</th>
<th>300°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.43eV</td>
<td>1.48eV</td>
<td>1.47eV</td>
<td>1.38eV</td>
<td></td>
</tr>
</tbody>
</table>

**Zinc oxy-nitride films deposited in \(N_2+Ar\) with 1% \(O_2\) atmosphere: total sputtering gas pressure dependence**

Figure 4-32 (a) and (b) show the optical transmittance spectra of zinc nitride and oxy-nitride thin films prepared at varied \(O_2\)-to-total sputtering gas ratios, at a fixed substrate temperature of 200°C and a fixed working pressure of either 8 mTorr or 16 mTorr. At a sputtering pressure of 8 mTorr, the increase of oxygen content in the
sputtering gas mixture shifts the onset of the high transmittance only very slightly to lower wavelength, meaning that the optical band gap increases slightly. At a total sputtering pressure of 16 mTorr, the effect of the increase of the oxygen concentration is significant. The onset of the high transmittance shifts from a wavelength of 920 nm (0\% of oxygen concentration) to 400 nm (0.4\% of oxygen concentration).

**Figure 4-32** Optical transmittance spectra for samples deposited at different $O_2/(N_2+Ar$ with 1\% $O_2$) ratios at a fixed substrate temperature of 200°C and a fixed working pressure of either (a) 8 mTorr or (b) 16 mTorr.

**Figure 4-33** Optical transmittance spectra for samples deposited at varied working pressures at a fixed substrate temperature of 200°C and $O_2/(N_2+Ar$ with 1\% $O_2$) ratio of 0.2\%.
In Figure 4-33, the optical transmittance spectra of samples deposited at different working pressures, from 8 mTorr to 20 mTorr, at a fixed substrate temperature of 200°C and O\textsubscript{2}-to-total sputtering gases ratio of 0.2% are shown. By increasing the sputtering pressure in the chamber, the incorporation of oxygen into the thin films is enhanced and the optical band gap of the film material changes accordingly. The shift of the onset, from the wavelength of 920 nm (at sputtering pressure of 8 mTorr) to 760 nm (12 mTorr) to 400 nm (16 mTorr) and then to 480 nm (20 mTorr), suggests the oxygen incorporation in the thin film first increases significantly and then decreases a little, which is consistent with what is observed in the EDXS results (Table 4.4).

By analysis of both the transmittance and reflectance, the optical band gaps for all samples were estimated and listed in Table 4.10. As shown in Table 4.10, the trends of the changes in the band gap agree with the changes in the optical transmittance data. The largest band gap is found to be 2.02 eV, significantly less than the band gap of zinc oxide (3.2 eV), which indicates that the film consists of a mixed oxy-nitride phase, which is in agreement with the XRD data above.

<table>
<thead>
<tr>
<th>Working pressure: 8 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}/total sputtering gas mixture (%)</td>
</tr>
<tr>
<td>1.41 eV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Working pressure: 16 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}/total sputtering gas mixture (%)</td>
</tr>
<tr>
<td>1.43 eV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>O\textsubscript{2}/total sputtering gas mixture = 0.2% and N\textsubscript{2}/total sputtering gas mixture = 80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>working pressure (mTorr)</td>
</tr>
<tr>
<td>1.35 eV</td>
</tr>
</tbody>
</table>
Summary on Optical Properties

The optical transmittance of zinc nitride thin film is mainly influenced by the crystallinity of the films, which is related to both the nitrogen concentration in sputtering gas mixture and substrate temperature. The transparency of films was found to correlate to some degree with the crystallinity of the films. Using the relation between absorption coefficient and the value of optical on-set, the optical band gaps of zinc nitride thin films are determined. A direct optical band gap of around 1.4 eV is found. The band gaps of zinc oxy-nitride thin films range from 1.35 eV to 2.02 eV with the change of the deposition conditions. It suggests that the optical properties of zinc oxy-nitride thin film are closely related to the composition of the thin films as well as the bonding states of oxygen with zinc and nitrogen (phase-related) inside the film.

4.2 Theoretical modeling work of zinc nitride material

In material science, total energies or total energy differences are very important and related to almost all physical properties. With the ability to predict the total energy of the system of electrons and nuclei, quantum-mechanical calculations allow us to get better understanding of material properties. It has provided extremely precise calculation of the total energy of simple one-atom system by the quantum-mechanical rules. And it is also believed that the quantum-mechanical rules will predict the total energies of more complicated systems accurately since the rules for aggregates of atoms are just the simple and straightforward extensions of the rules for one-atom system [118]. Among all quantum-mechanical calculation methods, *ab initio* total energy pseudopotential method
has been developed significantly in recent decades; the modeling capability of which has been grown from few-atom system to thousand-atom system [118].

In order to perform total-energy pseudopotential calculations, a large number of simplifications and approximations are required [118-120]. The main simplification and approximations involved in this study are (i) Born-Oppenheimer approximation [118], which separates the electronic and nuclear coordinates in the many-body wave function, (ii) the density-functional theory (DFT) [121,122], which addresses the electron-electron interactions, (iii) the supercell approximation [123], which deals with the aperiodic configuration of atoms as well as relaxation of the electronic coordinates.

Within the DFT, more simplifications and approximations are made to describe the effects of exchange and correlation in an electron gas [118]. The local density approximation (LDA) is the most widely used approximation, in which the electron density is assumed to be homogeneous when calculating the exchange-correlation energy. On the other hand, the generalized gradient approximation (GGA) takes into account the gradient of the electron density.

All our computations were performed by ab initio total energy calculations within the generalized gradient (GGA) and local density (LDA) approximations to density-functional theory [121,122] using the Vienna ab initio simulation package [124-127] of codes. In this implementation, core electrons are implicitly treated by ultrasoft Vanderbilt type pseudopotentials [128] as supplied by Kresse et al. [129] using the Ceperly and Alder exchange-correlation functional as parameterized by Perdew and Zunger for the LDA [130] and by Perdew and Wang (PW91) for the GGA [131,132]. For each calculation, irreducible $k$-points were generated according to the Monkhorst-Pack scheme
A k-point density equivalent to 4 k-points in the irreducible part of the Brillouin zone resulted from tests for energy convergence in the 40-atom primitive cell. The single-particle wave functions were expanded in a plane-wave basis using a 420 eV energy cutoff for LDA and 460 eV for GGA. These values were determined to be sufficient by performing convergence tests for an accuracy of 1 meV. The absolute minimum in total energy was obtained by varying the lattice constant. Full relaxation of ions was performed to find the minimum energy for each configuration. All atoms were allowed to relax until a force tolerance of 1 meV/Å was reached for each atom. The calculations for the density of states (DOS) and local density of states (LDOS) were performed with Methfessel-Paxton scheme for the energy [134]. Computations for inclusion of defects were performed initially in a supercell with 40 atoms and then in a larger 320-atom supercell of pure Zn$_3$N$_2$ constructed by periodically repeating the 40-atom primitive cell in three dimensions. Based on the type of defects, an atom of a different kind was either added or removed or replaced in these supercells of Zn$_3$N$_2$.

### 4.2.1 Optimization of pure zinc nitride structure

Pure zinc nitride belongs to the space group $Ia\overline{3}$ with space group number 206. It has a cubic anti-bixbyite structure with a Pearson symbol cI80 [5]. The primitive cell of Zn$_3$N$_2$ consists of a Zn$_{24}$N$_{16}$ unit of 40 atoms in a cubic shape. We computed the lattice constant of this cell to be 9.839 Å as shown in Table 4.11. Positions of the forty atom bases in this cell are listed in Table 4.12 and the corresponding atomic structure is shown in Figure 4-34. The Zn$_3$N$_2$ structure can be regarded as a face-centered cubic (FCC) arrangement of N atoms with the larger Zn atoms occupying 3/4 of the tetrahedral sites.
The absence of the Zn atoms in the unoccupied tetrahedral holes produces a slight distortion of the FCC structure, as shown in Figure 4-34. The N atoms forming the face-centered cubic are occupied by two distinct N positions. The first type, N1, occupy the 8b Wyckoff position [135] and the second type, N2, occupy the 24d Wyckoff position. The Zn atoms in the tetrahedral sites occupy the 48e Wyckoff position. As a result of the distortion, the Zn atoms in the tetrahedral sites have three distinct nearest-neighbor Zn-N2 distances. The details about atomic geometry will be talked in next section. The bulk modulus was computed to be 140.19 GPa with GGA and 176.6 GPa with LDA. Comparison with other values in the literature is shown in Table 4.11.

We show the computed band structure of the pure zinc nitride in Figure 4-35, along with the electronic DOS. Figure 4-35 shows that the conduction band (CB) minimum and the valence band (VB) maximum are both located at \( \Gamma \) point. The band structure also shows no band-gap due to the well-known error in the LDA and GGA methods of density functional theory, which leads to the underestimation of approx. \( \approx 50\% \). For small band-
gap materials such as Ge, with an experimental measured gap of \( \sim 0.7 \) eV, these approximations yield a zero band-gap like the present case. We therefore suggest that pure \( \text{Zn}_3\text{N}_2 \) is a small band gap material possibly less than \( 1 \) eV. This is smaller than experimental reports of \( 1.26 \) eV \([11]\), \( 2.25 \) eV \([51]\) and \( 3.2 \) eV \([4]\). This large experimental uncertainty makes comparison with our computation difficult. Differences in fabrication methods are known to cause significant changes in physical properties of this material. A common contaminant in growth of zinc nitride is oxygen of which there is always a small fraction (5\text{-}6\% at least) in the material \([11]\), which increases the value of the band gap. Therefore, we expect the true band gap of pure zinc nitride to be smaller than experimental reports in agreement with our estimate.

Table 4.11. *Calculated and experimental structural data, lattice constant \( a \), bulk modulus \( B \), bond lengths between the Zn atom and nearest N atom of the first or second type \( d_{(Zn-N1)} \) and \( d_{(Zn-N2)} \) respectively, in the \( \text{Zn}_3\text{N}_2 \) structure.*

<table>
<thead>
<tr>
<th>Structure</th>
<th>This work</th>
<th>Other theoretical results</th>
<th>Other experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) (Å)</td>
<td>9.839 (GGA)</td>
<td>9.667(^a), 9.769(^b)</td>
<td>9.7691(1)(^c), 9.758(^d)</td>
</tr>
<tr>
<td>( d_{(Zn-N1)} ) (Å)</td>
<td>2.14 (GGA)</td>
<td>2.095(^a), 2.122(^b)</td>
<td>2.133(^c)</td>
</tr>
<tr>
<td>( d_{(Zn-N2)} ) (Å)</td>
<td>2.01, 2.06, 2.33 (GGA)</td>
<td>(1.990, 2.019, 2.096)(^a)</td>
<td>(1.996, 2.068, 2.262)(^c)</td>
</tr>
<tr>
<td>( B ) (GPa)</td>
<td>140.2 (GGA)</td>
<td>202.2(^a)</td>
<td>228(2)(^c)</td>
</tr>
<tr>
<td></td>
<td>176.6 (LDA)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Ref. 58, theory uses GGA.
\(^b\)Ref. 40 & 45, theory uses LDA.
\(^c\)Ref. 5, experiment.
\(^d\)Ref. 11, experiment.
\(^e\)Ref. 53, experiment.

The DOS in Figure 4-35 indicates that the states near the top of VB arise mainly from N-2p states and Zn-3d states. The peak in the CB at around 2 eV is dominated by N-2p, Zn-4s and Zn-3p states. This observation is consistent with previous theoretical work on zinc nitride \([45,58]\). The appearance of N-2p states, near the Fermi energy, in the VB and CB signifies their importance in the electronic behavior of zinc nitride.
Table 4.12. The list of the forty atom bases vectors for the primitive cell of Zn$_3$N$_2$. The lattice vectors of this anti-bixbyte cubic structure with lattice constant a are given in Cartesian coordinates as: $a_1 = (a/2)(-1, 1, 1)$, $a_2 = (a/2)(1, -1, 1)$, and $a_3 = (a/2)(1, 1, -1)$. There are four internal free parameters in the primitive cell given by “$X_M$”, “$Y_M$”, and “$Z_M$” (where $M = 1, 2$). There is only one internal free parameter, $X_1$ for the N2 atomic site, and the remaining three, $X_2$, $Y_2$ and $Z_2$, are for Zn. $Y_1$ and $Z_1$ do not exist.

<table>
<thead>
<tr>
<th>Atomic type</th>
<th>Basis atom number</th>
<th>Position vector</th>
<th>Wyckoff Letter$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>B$_1$</td>
<td>$\frac{1}{2} a_1 + \frac{1}{2} a_2 + \frac{1}{2} a_3$</td>
<td>8h</td>
</tr>
<tr>
<td>N1</td>
<td>B$_2$</td>
<td>$\frac{3}{2} a_1$</td>
<td>8b</td>
</tr>
<tr>
<td>N1</td>
<td>B$_3$</td>
<td>$\frac{1}{2} a_2$</td>
<td>8b</td>
</tr>
<tr>
<td>N1</td>
<td>B$_4$</td>
<td>$\frac{1}{2} a_3$</td>
<td>8b</td>
</tr>
<tr>
<td>N2</td>
<td>B$_5$</td>
<td>$\frac{1}{2} a_1 + (\frac{1}{4} + X_1) a_2 + X_1 a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_6$</td>
<td>$\frac{1}{2} a_1 + (\frac{1}{4} - X_1) a_2 - (\frac{1}{2} + X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_7$</td>
<td>$X_1 a_1 + \frac{1}{4} a_2 + (\frac{1}{4} + X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_8$</td>
<td>$\frac{1}{2} + X_1) a_1 - \frac{1}{4} a_2 + (\frac{1}{4} - X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_9$</td>
<td>$(\frac{1}{4} + X_1) a_1 + X_1 a_2 + \frac{1}{4} a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{10}$</td>
<td>$(\frac{1}{4} - X_1) a_1 - (\frac{1}{2} + X_1) a_2 - \frac{1}{4} a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{11}$</td>
<td>$-\frac{1}{4} a_1 - (\frac{1}{4} + X_1) a_2 - X_1 a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{12}$</td>
<td>$\frac{1}{4} a_1 - (\frac{1}{4} - X_1) a_2 + (\frac{1}{2} + X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{13}$</td>
<td>$-X_1 a_1 - \frac{1}{4} a_2 - (\frac{1}{4} + X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{14}$</td>
<td>$(\frac{1}{2} + X_1) a_1 + \frac{1}{4} a_2 - (\frac{1}{4} - X_1) a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{15}$</td>
<td>$(-\frac{1}{4} + X_1) a_1 - X_1 a_2 - \frac{1}{4} a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>N2</td>
<td>B$_{16}$</td>
<td>$(-\frac{1}{4} - X_1) a_1 + (\frac{1}{4} + X_1) a_2 + \frac{1}{4} a_3$</td>
<td>24d</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{17}$</td>
<td>$(Y_2 + Z_2) a_1 + (X_2 + Z_2) a_2 + (X_2 + Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{18}$</td>
<td>$(\frac{1}{2} + Y_2 - Z_2) a_1 - (X_2 - Z_2) a_2 + (\frac{1}{2} - X_2 - Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{19}$</td>
<td>$(Y_2 - Z_2) a_1 + (\frac{1}{2} - X_2 - Z_2) a_2 + (\frac{1}{2} - X_2 + Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{20}$</td>
<td>$(\frac{1}{2} - Y_2 - Z_2) a_1 - (\frac{1}{2} - X_2 + Z_2) a_2 + (\frac{1}{2} - X_2 - Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{21}$</td>
<td>$(X_2 + Y_2) a_1 + (Y_2 + Z_2) a_2 + (X_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{22}$</td>
<td>$(\frac{1}{2} - X_2 - Y_2) a_1 - (\frac{1}{2} + Y_2 - Z_2) a_2 - (X_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{23}$</td>
<td>$(\frac{1}{2} + X_2 + Y_2) a_1 + (Y_2 - Z_2) a_2 + (\frac{1}{2} - X_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{24}$</td>
<td>$(X_2 - Y_2) a_1 + (\frac{1}{2} - Y_2 - Z_2) a_2 - (\frac{1}{2} - X_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{25}$</td>
<td>$(X_2 + Z_2) a_1 + (X_2 + Y_2) a_2 + (Y_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{26}$</td>
<td>$-X_1 (X_2 - Z_2) a_1 + (\frac{1}{2} - X_2 - Y_2) a_2 - (\frac{1}{2} + Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{27}$</td>
<td>$-X_1 (\frac{1}{2} - X_2 - Z_2) a_1 + (\frac{1}{2} - X_2 + Y_2) a_2 + (Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{28}$</td>
<td>$-X_1 (\frac{1}{2} - X_2 + Z_2) a_1 + (X_2 - Y_2) a_2 + (\frac{1}{2} - Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{29}$</td>
<td>$-(Y_2 + Z_2) a_1 - (X_2 + Z_2) a_2 - (X_2 + Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{30}$</td>
<td>$(\frac{1}{2} + Y_2 - Z_2) a_1 + (X_2 - Z_2) a_2 - (\frac{1}{2} - X_2 - Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{31}$</td>
<td>$(Y_2 - Z_2) a_1 - (\frac{1}{2} - X_2 - Z_2) a_2 + (\frac{1}{2} - X_2 + Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{32}$</td>
<td>$(\frac{1}{2} - Y_2 - Z_2) a_1 + (\frac{1}{2} - Y_2 + Z_2) a_2 - (X_2 - Y_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{33}$</td>
<td>$(X_2 + Y_2) a_1 - (Y_2 + Z_2) a_2 - (X_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{34}$</td>
<td>$(\frac{1}{2} - X_2 - Y_2) a_1 + (\frac{1}{2} - Y_2 - Z_2) a_2 + (X_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{35}$</td>
<td>$-X_1 (\frac{1}{2} - X_2 + Y_2) a_1 - (\frac{1}{2} - Y_2 - Z_2) a_2 - (\frac{1}{2} - X_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{36}$</td>
<td>$-X_1 (\frac{1}{2} - X_2 + Z_2) a_1 - (\frac{1}{2} - X_2 - Y_2) a_2 + (\frac{1}{2} - X_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{37}$</td>
<td>$(X_2 + Z_2) a_1 - (X_2 + Y_2) a_2 - (Y_2 + Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{38}$</td>
<td>$(X_2 - Z_2) a_1 - (\frac{1}{2} - Y_2 - Z_2) a_2 + (\frac{1}{2} + Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{39}$</td>
<td>$-X_1 (\frac{1}{2} - X_2 - Z_2) a_1 - (\frac{1}{2} - X_2 + Y_2) a_2 - (Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
<tr>
<td>Zn</td>
<td>B$_{40}$</td>
<td>$(\frac{1}{2} - X_2 + Z_2) a_1 - (X_2 - Y_2) a_2 - (\frac{1}{2} - Y_2 - Z_2) a_3$</td>
<td>48e</td>
</tr>
</tbody>
</table>

$^a$Ref. 135
4.2.2 Atomic geometry of pure and defective Zn$_3$N$_2$

The bond lengths in pure Zn$_3$N$_2$, are 2.14 Å for Zn-N1 and 2.01 Å, 2.06 Å, and 2.33 Å for Zn-N2. These values listed in Table 4.11 are in agreement with previous theoretical [40,45,58] and experimental work [5,11,53]. The geometry of atomic positions was influenced by the type of defect introduced. When a vacancy was formed at N1 position, the nearest Zn neighbors, six in total, were pushed farther by ~ 8%. However, in the cases of vacancies at N2 or Zn positions, nearest neighbors, six Zn atoms...
or four N atoms respectively, stayed almost unchanged. Their mutual distances changed by less than 0.5%. It shows that the effect of the relaxation response by introducing a N vacancy is strongly influenced by its location and nearest neighbor environment. For interstitial defect introduced at high symmetry Wyckoff position 8a, (0, 0, 0), there are six Zn and six N nearest neighbor atoms. The average bond lengths from defect to Zn atoms and to N atoms are, respectively, 2.48 Å and 2.38 Å (for Zn as defect), 2.15 Å and 2.65 Å (for N), 2.41 Å and 2.46 Å (for Cu), 2.50 Å and 2.56 Å (for Ag), and 2.52 Å and 2.60 Å (for Au). Similarly when copper family elements substituted N at N1 position, the average bond lengths to nearest Zn atoms were 2.48 Å (for Cu) and 2.59 Å (for Ag and Au), all of which are larger than the one in pure Zn$_3$N$_2$, of 2.14 Å. These changes in the bond lengths suggest that radii of the defect atoms are the main factor determining the atomic geometry for the interstitial position. This contrasts with the case, when copper family elements substituted Zn, the bond lengths to N at N1 position are 2.14 Å (for Cu), 2.46 Å (for Ag) and 2.33 Å (for Au), all of which are closer to the value in pure Zn$_3$N$_2$, 2.14 Å. These lengths cannot be merely explained away by the differing atomic radii. The electronic bonding differences affect these lengths. The same trend is observed in the N2-Zn case.

4.2.3 Study on native defects

We simulated possible native defects, namely N vacancy at two types of nitrogen (V$_{N1}$, V$_{N2}$), Zn vacancy (V$_{Zn}$), and self-interstitial of N (I$_N$) and Zn (I$_{Zn}$) at high symmetry Wyckoff position 8a, (0, 0, 0).

The formation energies $E_{\text{form}}$ for the defective zinc nitride are calculated by
where \( E(X) \) is the total energy derived from supercell calculations with one defect \( X \) in the cell. \( X \) takes the values \( V_{N1}, V_{N2}, V_{Zn}, I_N, I_{Zn} \). \( E(\text{pure}) \) denotes the total energy of the pure \( \text{Zn}_3\text{N}_2 \), supercell of 40 atoms or 320 atoms. In this study; \( n_i \) denotes the number of atoms of type \( i \) (host atoms and/or impurity atoms) that were added to \( (n_i = +1) \) and/or removed from \( (n_i = -1) \) the supercell when the defect was introduced with \( \mu_i \) being the corresponding chemical potential of the species \( i \). For instance, \( \mu_N \) is determined from the \( \text{N}_2 \) molecule as it is computed as half of the total energy of the \( \text{N}_2 \) molecule, and \( \mu_{Zn} \) is the total energy per \( \text{Zn} \) atom in the bulk hexagonal closed pack phase of metal \( \text{Zn} \). Chemical potentials for \( \text{Cu}, \text{Au}, \text{and Ag} \) were computed from their face-centered-cubic bulk phases.

Table 4.13. Formation energies (in eV) of native defects of \( \text{Zn}_3\text{N}_2 \) computed with varying supercell sizes. Values in Ref. 45 were calculated in a 80-atom cell, but the authors indicated the difference in values from their computations in a 40-atom unit cell is within 5% of these.

<table>
<thead>
<tr>
<th>Types of defects</th>
<th>( E_{\text{form}} ) (eV) at 40-atom cell</th>
<th>( E_{\text{form}} ) (eV) at 320-atom cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_{Zn} )</td>
<td>4.40 (14.39(^a))</td>
<td>1.23</td>
</tr>
<tr>
<td>( I_N )</td>
<td>5.94 (4.41(^a))</td>
<td>5.82</td>
</tr>
<tr>
<td>( V_{Zn} )</td>
<td>2.32 (2.99(^a))</td>
<td>1.95</td>
</tr>
<tr>
<td>( V_{N1} )</td>
<td>1.44 (4.71(^a))</td>
<td>0.04</td>
</tr>
<tr>
<td>( V_{N2} )</td>
<td>1.46 (2.58(^a))</td>
<td>0.29</td>
</tr>
</tbody>
</table>

\(^a\) values from Ref. 45.

The formation energies for various defects computed from Eq. (3) are listed in Table 4.13. Two cell sizes are used to calculate the formation energies for ease of comparison with earlier results from the literature. It is found that the formation energies change significantly with the change of the size of the supercell from 40 to 320, which indicates the extent of finite-size effects. For example we observe, from Table 4.13, that the least change with cell size happens for \( I_N \) where the difference is only 2% between
results for the 40 atom vs. 320 atom cell. On the other extreme is the case of $V_{N1}$ where the corresponding change is 97%. It shows the importance of using large cell sizes. Formation energy values from Long et al. [45], have been included in Table 4.13. The disagreement seems to have arisen from smaller cell sizes used in their study.

Based on the results from the 320-atom cell, the smallest formation energy, by one order of magnitude, for N1 vacancy may suggests its propensity in experimental observation [11,33,42,43,48,57]. Upon the existence of such vacancies and exposure to air, replacement of N1 site vacancies by oxygen may be possible. The DOS in Figure 4-35 has already indicated that nitrogen p states influence the electronic behavior of zinc nitride significantly. Thus the N vacancy may be the reason of disagreement in electronic band gap reported in experimental work [4,11,51], which differ in sample preparation and hence material chemical composition.

Next to $V_{N1}$ and $V_{N2}$, $I_{Zn}$ has the third lowest formation energy with a value that is only about half of the value of $V_{Zn}$ and one fifth of the value of $I_N$. Based on the observation in earlier experimental work [11,33,42,43,48,57], there is a gradually emerging consensus that excess of zinc and deficiency of nitrogen are the two main factors responsible for n-type conductivity of zinc nitride. And our results here support this conclusion.

In Figure 4-36, DOS of pure $Zn_3N_2$ and with different types of native defects is shown. With respect to its own Fermi energy, the filled and empty DOS of $V_{N1}$ are shifted to a lower energy level, compared to the case of pure zinc nitride. A similar shift, though lesser in magnitude is seen for the case of $V_{N2}$ and $I_{Zn}$. This correlates well with these three defects exhibiting the lowest formation energies. This case contrasts with the
case of $V_{\text{Zn}}$ and $I_N$ where the filled state DOS shifts to the right in Figure 4-36 and these two defects have the highest formation energies. The shift of the DOS to lower energy level for $V_{N1}$, $V_{N2}$, and $I_{\text{Zn}}$ is accompanied by the first peak in the CB getting closer to the Fermi energy ($E_F$) indicative of n-type character as seen in experiment [11,33,42,43,51,135].

![DOS diagram](image)

Figure 4-36 DOS of Zn$_3$N$_2$ (pure) with no defects and with different types of native defects: a vacancy at the first type of nitrogen site ($V_{N1}$), a vacancy at the second type of nitrogen site ($V_{N2}$), a vacancy at the zinc site ($V_{\text{Zn}}$), a nitrogen interstitial ($I_N$), and a zinc interstitial ($I_{\text{Zn}}$). Both interstitials are positioned at high symmetry Wyckoff position 8a (0, 0, 0). Energy is relative to the Fermi energy ($E_F$) represented by the dashed line.

### 4.2.4 Study on non-native defects: copper family as possible p-type dopants

Oxygen, due to its natural incorporation with zinc nitride, should perhaps be the first choice for a study on non-native defects in zinc nitride material. However, a study on oxygen as point defect in zinc nitride has already been conducted [40] back in 2007 as mentioned in Chapter 2. Moreover, although oxygen incorporation is a promising way to tune the electrical conductivity of material from n-type to p-type, it also results the
increase of the optical band gap, which does not serve the purpose of using this material as p-type absorber layer in photovoltaic application. Therefore, copper family elements are considered here. Copper family elements, Cu, Ag, and Au have one less outer shell electron than zinc. They have also been theoretically investigated earlier, as p-type dopants in zinc oxide [136]. Therefore, we simulated single atom defects of these elements, in a 320 atom cell, as potential p-type dopants of zinc nitride. The formation energies of defective zinc nitride with single atom Cu, as a defect at possible positions, namely substitution defect at Zn (Cu\textsubscript{Zn}) and N (two types, Cu\textsubscript{N1} and Cu\textsubscript{N2}) positions and interstitial (I\textsubscript{Cu}) at high symmetry Wickoff position 8a (0, 0, 0), are listed in Table 4.14. Similar results for Ag and Au are listed as well.

Table 4.14 shows that the formation energy increases with the increase of the atom radii for defects at the interstitial position or Zn substitution position. No such trend is observed at other sites. The formation energies of defects of a given element follow in descending order for the interstitial, Zn substitution, N2 substitution and N1 substitution positions. It is surprising to note that for all three copper family elements, the formation energy of substitution defects at N1 position is the smallest among all four possible positions. This indicates favorability to substitute N at the N1 site even over substitution of Zn. We speculate on two causes for this occurrence; (i) the native defect N1 vacancy is easily formed based on data from Table 4.13, and (ii) the charge separation which is required to form metal-nitrogen bond, i.e. to form the species N\textsuperscript{3-}, is unlikely to be complete, particularly for the corresponding compounds of copper family elements. This latter speculation would be consistent with observations in noble metal nitrides [137-141].
Table 4.14 Computed formation energies (in eV) of single atom Cu, Ag and Au defects as interstitials or substitution defects in Zn$_3$N$_2$.

<table>
<thead>
<tr>
<th>Types of defects</th>
<th>$E_{\text{form}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{Cu}}$</td>
<td>2.19</td>
</tr>
<tr>
<td>$I_{\text{Ag}}$</td>
<td>3.18</td>
</tr>
<tr>
<td>$I_{\text{Au}}$</td>
<td>4.00</td>
</tr>
<tr>
<td>Cu$_{\text{Zn}}$</td>
<td>1.57</td>
</tr>
<tr>
<td>Ag$_{\text{Zn}}$</td>
<td>2.44</td>
</tr>
<tr>
<td>Au$_{\text{Zn}}$</td>
<td>2.98</td>
</tr>
<tr>
<td>Cu$_{\text{N1}}$</td>
<td>0.53</td>
</tr>
<tr>
<td>Ag$_{\text{N1}}$</td>
<td>0.56</td>
</tr>
<tr>
<td>Au$_{\text{N1}}$</td>
<td>-0.34</td>
</tr>
<tr>
<td>Cu$_{\text{N2}}$</td>
<td>1.27</td>
</tr>
<tr>
<td>Ag$_{\text{N2}}$</td>
<td>1.52</td>
</tr>
<tr>
<td>Au$_{\text{N2}}$</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Figure 4-37 LDOS of pure Zn$_3$N$_2$ and with different substitution defects at the N1 position of nitrogen. The LDOS is only the portion of total density of states projected onto the defect and its nearest neighbor atoms. Energy is relative to the Fermi energy ($E_F$) represented by the dashed line.

Figure 4-37 shows the LDOS of pure Zn$_3$N$_2$ and with different substitution defects at the N1 position. The effects, in the LDOS, of substitution defects at the N2 positions are similar to those at N1. Therefore, only the N1 case is shown in Figure 4-37.
The LDOS is only the portion of total density of states projected onto the defect and its nearest neighbor atoms. For a substitution defect at N1 or N2 position, there are six Zn nearest neighbors. Figure 4-37 shows the magnitude of the defect-introduced states in Cu_{N1} is higher than that in Ag_{N1} or Au_{N1}. In addition, the location of these states in Cu_{N1} is different than that in Ag_{N1}, or Au_{N1}. The defect-introduced states for Cu_{N1} are located close to the top of the valence band, while in Ag_{N1} or Au_{N1}, they are located much higher in energy. This suggests that Cu-doped zinc nitride is likely to show p-type character while Ag- or Au-doped zinc nitride may display n-type conducting behavior.

![Figure 4-38 LDOS of pure Zn\(_3\)N\(_2\) and with different substitution defects at the Zn position. The LDOS is only the portion of total density of states projected onto the defect and its nearest neighbor atoms. Energy is relative to the Fermi energy (E\(_F\)) represented by the dashed line.](image)

In Figure 4-38, LDOSs of pure Zn\(_3\)N\(_2\) and with different substitution defects at the Zn position are presented. To differentiate the effect of vacancy formation and then substitution by a dopant atom the LDOS for V\(_{Zn}\) is shown. For substitution defect at Zn
position, there are four N nearest neighbors. The effect of copper family elements as substitution defects at Zn position on the electronic properties at the edges of valence band and conduction band is very similar and all show an increase in the density at $E_F$.

Figure 4-39 gives the LDOS of pure Zn$_3$N$_2$ and with different interstitial defects. To compare with native defects, LDOS for I$_N$ and I$_{Zn}$ are shown. The nearest neighbor atoms of interstitial defect include six Zn atoms and six N atoms. In Figure 4-39, it can be seen that the copper family of elements as interstitial defects all produce a shift in the LDOS to lower energy levels. This is similar to the effect of Zn as an interstitial defect.

![Figure 4-39 LDOS of pure Zn$_3$N$_2$ and with different interstitial defects at the high symmetry Wyckoff position 8a (0, 0, 0). The LDOS is only the portion of total density of states projected onto the defect and its nearest neighbor atoms. Energy is relative to the Fermi energy ($E_F$) represented by the dashed line.](image)

Summary on the Theoretical Modeling results

Structural, electronic and energetic properties of (i) pure Zn$_3$N$_2$ and (ii) point defects of native species Zn and N and copper group elements Cu, Ag and Au were
investigated, with DFT computations. The bulk modulus of pure Zn$_3$N$_2$ was found to be 140.19 GPa with GGA and 176.6 GPa with LDA. The band structure of pure Zn$_3$N$_2$ was calculated. It confirmed the direct bandgap behavior and suggested a value of less than 1 eV for pure Zn$_3$N$_2$. The analysis of the DOS of pure Zn$_3$N$_2$ showed clearly that electronic behavior is closely related to and, therefore, easily affected by nitrogen. The formation energies of native defects indicated that nitrogen vacancies and zinc interstitials are energetically favored over nitrogen interstitials. When doped with copper family elements, point defects are likely to appear at a nitrogen site rather than at zinc or interstitial sites. The LDOS of copper family elements suggests that Cu-doped zinc nitride will tend to show the p-type character while Ag- or Au-doped zinc nitride may display n-type conducting behavior.

4.3 Fabrication of device-related structures

In this section, based the understanding of zinc nitride and oxy-nitride obtained from characterizations discussed above, several multi-layer device-related structures were fabricated and characterized.

4.3.1 Rectifying p-n junctions and photovoltaic effect

The p-n junction is an extremely important and fundamental structure for opto-electronic and electrical applications, such as in diodes, bipolar transistors, photodetectors, LEDs, and photovoltaic devices.
4.3.1.1 Property optimization of p-type and n-type layers

As mentioned in section 4.1.4, a change of the conductivity type of zinc oxy-nitride thin films was observed after post-deposition thermal treatment. Based on these initial results, more studies were performed with the purposes of widening the tuning range of the electrical and optical properties of zinc oxy-nitride thin films and establishing a reliable correlation between the properties of zinc oxy-nitride thin films and the amount of oxygen incorporated in the films. The effects of the oxygen content in the sputtering gas mixture and the annealing time on the oxygen incorporation were investigated over a larger range as well as in a more systematic way than the initial work presented in section 4.1.4.

Figure 4-40 XRD pattern for samples deposited at varied O\textsubscript{2} content in sputtering gas mixture at a fixed working pressure of 20 mTorr and a fixed substrate temperature of 200°C.

A set of samples was prepared at a fixed substrate temperature of 200°C and a fixed total sputtering pressure of 20 mTorr and several oxygen content levels in the sputtering gas mixture, namely, 0%, 0.2% and 2%. The post-deposition thermal treatment
was performed in an air ambient at a fixed temperature of 400°C with varied annealing time, from 3hrs to 20hrs. All characterizations discussed below, if not being described specifically, were carried out under the same conditions which were described in the previous sections.

![XRD pattern of samples deposited at O2 content in sputtering gas mixture of 0% and then annealed in air at 400°C.](image)

*Figure 4-41 XRD pattern of samples deposited at O2 content in sputtering gas mixture of 0% and then annealed in air at 400°C.*

The XRD patterns of these samples before and after annealing are shown in Figure 4-40 (as-deposited samples), Figure 4-41 (effect of annealing on sample deposited at O2 content of 0%) and Figure 4-42 (effect of annealing on sample deposited at O2 content of 0.2%). The XRD patterns of the annealed samples which were originally deposited at O2 content of 2% are not presented because the effect of this annealing step on crystalline structure of this sample was quite limited. As can be clearly seen in Figure 4-40, a dominant phase transformation, from (400)-plane ZnN phase to (002)-plane ZnO phase, occurs, which is also consistent with what was discussed previously. This means that, at the deposition pressure of 20 mTorr and the substrate temperature of 200°C, 2% of oxygen content in the sputtering gas mixture was high enough for oxygen species to
react with the film materials and form ZnO rich material. In Figure 4-41, with the increase of annealing time, although the ZnN-related phase stayed dominant, the ZnO-related phase ((002)-plane ZnO and (101)-plane ZnO) became more and more prominent. After the annealing time reached 5 hours, any further increase of the annealing time (15 hours and 20 hours) affects less and less the structure of the films. This observation was also verified by optical (spectrophotometry) and chemical composition (EDXS) measurements.

![XRD pattern of samples deposited at O<sub>2</sub> content in sputtering gas mixture of 0.2% and then annealed in air at 400°C.](image)

*Figure 4-42 XRD pattern of samples deposited at O<sub>2</sub> content in sputtering gas mixture of 0.2% and then annealed in air at 400°C.*

In Figure 4-42, the (002) ZnO reflection is seen in as-deposited films, whereas the (101) ZnO reflection is seen in films annealed 3 or 4 hours in air at 400°C. When the annealing time reached 5 hours or longer (15 or 20 hours), the (002) ZnO reflection is again seen. Along with the return of the (002) ZnO reflection, the (440)-phase ZnN phase could be identified more clearly. Finally the micro structure of film was found stabilized in a state of co-existence of the ZnO phase and the ZnN phase. The evolution
of these phases observed in zinc oxy-nitride films as a function of the deposition conditions would be of interest for future work.

Table 4.15 below shows the EDXS results of samples before and after annealing. The data for samples annealed for 15 or 20 hours were not included due to the similarity with that of sample annealed for 5 hours. It could be noticed that, in each sample, although the fraction of zinc nitride phase (or zinc oxide phase) is different, the Zn-to-N ratio and the Zn-to-O ratio are very close to the stoichiometric values of Zn$_3$N$_2$ and ZnO respectively.

Table 4.15 EDXS results of samples deposited at varied O$_2$ content in sputtering gas mixture at a fixed working pressure of 20 mTorr before and after thermal treatment

<table>
<thead>
<tr>
<th>O$_2$/total sputtering gas mixture (%)</th>
<th>N$_2$/total sputtering gas mixture (%)</th>
<th>Zn (atomic%)</th>
<th>N (atomic%)</th>
<th>O (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td></td>
<td>60.50</td>
<td>36.28</td>
<td>3.22</td>
</tr>
<tr>
<td>0.0%</td>
<td>80%</td>
<td>54.49</td>
<td>20.87</td>
<td>24.64</td>
</tr>
<tr>
<td>2.0%</td>
<td>80%</td>
<td>50.24</td>
<td>49.76</td>
<td></td>
</tr>
<tr>
<td>After 3hrs annealing in air at 400°C</td>
<td></td>
<td>54.88</td>
<td>14.22</td>
<td>30.89</td>
</tr>
<tr>
<td>0.0%</td>
<td>80%</td>
<td>53.82</td>
<td>12.38</td>
<td>33.80</td>
</tr>
<tr>
<td>2.0%</td>
<td>80%</td>
<td>56.50</td>
<td></td>
<td>43.50</td>
</tr>
<tr>
<td>After 4hrs annealing in air at 400°C</td>
<td></td>
<td>51.62</td>
<td>23.18</td>
<td>25.20</td>
</tr>
<tr>
<td>0.0%</td>
<td>80%</td>
<td>55.23</td>
<td>22.63</td>
<td>22.14</td>
</tr>
<tr>
<td>2.0%</td>
<td>80%</td>
<td>56.34</td>
<td></td>
<td>43.66</td>
</tr>
<tr>
<td>After 5hrs annealing in air at 400°C</td>
<td></td>
<td>50.51</td>
<td>14.33</td>
<td>35.16</td>
</tr>
<tr>
<td>0.0%</td>
<td>80%</td>
<td>50.03</td>
<td>13.47</td>
<td>36.50</td>
</tr>
<tr>
<td>2.0%</td>
<td>80%</td>
<td>55.34</td>
<td></td>
<td>44.66</td>
</tr>
</tbody>
</table>

For the sample prepared at oxygen content in total sputtering gas mixture of 0%, before and after annealing, the oxygen concentration in the film increased from 3.22% (as-deposited) to as high as 35.16%. It is worth noticing that the increase of the oxygen
concentration in the film was not monotonic with the increase of annealing time. This was also observed for the sample deposited at the oxygen content in total sputtering gas mixture of 0.2%. The reason for this is not clear at this time, but it may be related to formation of a surface cap layer and/or the escape of O or N upon annealing.

For the sample prepared at oxygen content in total sputtering gas mixture of 0.2%, before and after annealing, the oxygen concentration inside the films was at the same level as the annealed sample, originally deposited at 0% of O\textsubscript{2} content in total sputtering gas mixture. However, as can be seen below, the optical and the electrical properties of these two sets of samples were quite different. The differences are likely due to the different micro-structures of these two sets of samples (discussion on Figure 4-41 and Figure 4-42). Therefore, not only the concentration of oxygen inside the films but also the bonding states between Zn, O and N affect the properties of zinc oxy-nitride.

\[ \text{Figure 4-43 Optical transmittance spectra for samples deposited at varied oxygen content in sputtering gas mixture at a fixed working pressure of 20 mTorr.} \]

Figure 4-43 shows optical transmittance spectra of three as-deposited samples which were fabricated at different oxygen content in sputtering gas mixture. It is clear
that the incorporated oxygen in the zinc oxy-nitride thin films influenced the optical properties significantly. In Table 4.16, the calculated optical band gaps for samples before and after thermal treatment are listed. The values of the band gap of these films ranges from 1.31 eV to 3.27 eV, depending on the amount of incorporated O in the film as well as the chemical bonding states among Zn, N and O atoms. Again, in order to achieve the band gap tuning with higher accuracy, more studies on the mechanism of O incorporation, and its effect on the chemical bonding states are needed.

Table 4.16 The values of the conventionally defined optical band gaps for samples deposited at varied O\textsubscript{2} content in sputtering gas mixture at a fixed working pressure of 20 mTorr before and after thermal treatment.

<table>
<thead>
<tr>
<th>Annealing Time: 0hrs (as-deposited)</th>
<th>O\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>0%</th>
<th>0.2%</th>
<th>2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap value (eV)</td>
<td>1.31</td>
<td>1.83</td>
<td>3.27</td>
<td></td>
</tr>
<tr>
<td>Annealing Time: 3hrs</td>
<td>O\textsubscript{2}/total sputtering gas mixture (%)</td>
<td>0%</td>
<td>0.2%</td>
<td>2%</td>
</tr>
<tr>
<td>Band gap value (eV)</td>
<td>1.43</td>
<td>1.94</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>Annealing Time: 4hrs</td>
<td>O\textsubscript{2}/total sputtering gas mixture (%)</td>
<td>0%</td>
<td>0.2%</td>
<td>2%</td>
</tr>
<tr>
<td>Band gap value (eV)</td>
<td>1.39</td>
<td>1.82</td>
<td>3.22</td>
<td></td>
</tr>
<tr>
<td>Annealing Time: 5hrs</td>
<td>O\textsubscript{2}/total sputtering gas mixture (%)</td>
<td>0%</td>
<td>0.2%</td>
<td>2%</td>
</tr>
<tr>
<td>Band gap value (eV)</td>
<td>1.47</td>
<td>1.99</td>
<td>3.25</td>
<td></td>
</tr>
</tbody>
</table>

Hall-effect measurements were then performed and the results are provided in Table 4.17. After the annealing treatment, similar to the observation discussed in the last of section 4.1.4, the mobility, as well as the carrier concentration, of samples decreased and the resistivity increased. The electrical properties of the film prepared at the oxygen to total sputtering gas mixture ratio of 0.2% and then annealed for 4 hrs were found to be reproducible; the conductivity type and other Hall-effect parameters were identical to what was observed in initial work (see Table 4.6). However, no conductivity-change was
observed in these additional samples. The sample prepared at the O\textsubscript{2} content in sputtering gas mixture of 2\% was too resistive to be measured by the Hall-effect set-up available to us. Therefore, a doping diffusion of aluminum was performed on this sample. A thin layer of Al (10 nm) was deposited on the substrate prior the deposition of zinc oxy-nitride thin film. The electrical properties were measured after a 20-hour annealing in air at 400\textdegree C and the results was listed in Table 4.17.

Table 4.17 Parameters in Hall effect and resistivity measurements of samples deposited at varied O\textsubscript{2} content in sputtering gas mixture at a fixed working pressure of 20 mTorr before and after thermal treatment.

<table>
<thead>
<tr>
<th>O\textsubscript{2}/total sputtering gas mixture (%)</th>
<th>Conducting Type</th>
<th>Resistivity (Ohm*cm) (×10\textsuperscript{-2})</th>
<th>Mobility (cm\textsuperscript{2}/Vs)</th>
<th>Density (cm\textsuperscript{-3}) (×10\textsuperscript{19})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0%</td>
<td>n-type</td>
<td>0.73</td>
<td>21.60</td>
<td>3.98</td>
</tr>
<tr>
<td>0.2%</td>
<td>n-type</td>
<td>3.03</td>
<td>22.57</td>
<td>0.91</td>
</tr>
<tr>
<td>2.0%</td>
<td></td>
<td>Too resistive to measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 3hrs annealing in air at 400\textdegree C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0%</td>
<td>n-type</td>
<td>0.88</td>
<td>5.95</td>
<td>11.90</td>
</tr>
<tr>
<td>0.2%</td>
<td>n-type</td>
<td>4530</td>
<td>1.64</td>
<td>0.83</td>
</tr>
<tr>
<td>2.0%</td>
<td></td>
<td>Too resistive to measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 4hrs annealing in air at 400\textdegree C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0%</td>
<td>n-type</td>
<td>1.26</td>
<td>7.47</td>
<td>6.62</td>
</tr>
<tr>
<td>0.2%</td>
<td>p-type</td>
<td>13900</td>
<td>1.38</td>
<td>0.00324</td>
</tr>
<tr>
<td>2.0%</td>
<td></td>
<td>Too resistive to measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 5hrs annealing in air at 400\textdegree C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0%</td>
<td>n-type</td>
<td>0.81</td>
<td>10.23</td>
<td>7.35</td>
</tr>
<tr>
<td>0.2%</td>
<td>n-type</td>
<td>628</td>
<td>8.13</td>
<td>0.0122</td>
</tr>
<tr>
<td>2.0%</td>
<td></td>
<td>Too resistive to measure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 20hrs annealing in air at 400\textdegree C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0% (Al-doped)</td>
<td>n-type</td>
<td>135</td>
<td>0.16</td>
<td>2.84</td>
</tr>
</tbody>
</table>
4.3.1.2 Fabrication and characterization of a p-n junction

A p-n junction was then fabricated using the following two layers: (i) a p-type layer of zinc oxy-nitride, which was first prepared at oxygen content in sputtering gas mixture of 0.2% and then annealed in air at 400°C for 4 hours; (ii) an n-type layer of Al doped zinc oxy-nitride first prepared at the oxygen content in sputtering gas mixture of 2%. 200 nm thick sputter-deposited Cu layers were employed as electrical contacts. A schematic of the cross-section of the p-n junction structure is shown in Figure 4-44.

![Schematic of cross-section of p-n junction](image)

Figure 4-44 The schematic of the cross-section of the p-n junction structure made by zinc oxy-nitride thin films.

I-V measurements were taken using a sourcemeter (Keithley 2400), and a typical I-V curve of this p-n junction is shown in Figure 4-45. A clear rectifying behavior is observed. The threshold voltage of this p-n junction is about 0.5 V and an increase in the reverse current (i.e., the onset of a breakdown) is observed beyond 1 V.

By replacing the Cu contact layer at n-type side with a fluorine doped SnO₂ CTO layer (TEC-15, Pilkington), a single p-n junction solar cell configuration was obtained. The back Cu contact was shaped as a dot with diameter of 0.4 cm, so the area of the back
contact was 0.13 cm². I-V measurements were taken again using a sourcemeter (Keithley 2400) under dark conditions and under illumination of AM 1.5 on a solar simulator (Oriel Instruments Newport 450 W), calibrated to 100 mW/cm².

![I-V Characterization of the p-n junction](image)

**Figure 4-45 I-V characterization of the p-n junction.**

Therefore the incident power ($P_{in}$) on each cell was calculated to be

$$P_{in} = P_{total} \times \text{Area of the back contact}$$

$$= 100 \text{ mW/cm}^2 \times 0.13 \text{ cm}^2 = 13 \text{ mW}$$

The I-V characterization under the illumination of room lighting or solar simulator is presented in Figure 4-46. The photovoltaic effect is clearly observed. Figure 4-47 showed the current density curve under illumination of solar simulator and the power curve as a function of the voltage. The short circuit current density ($J_{sc}$) and the open circuit voltage ($V_{oc}$) were determined to be 0.908 mA/cm² and 0.455 V respectively. The maxima power ($P_{max}$), 0.034 mW, was reached when the voltage ($V_{mp}$) equaled to 0.333 V. Based on the definition, the fill factor (FF) and the efficiency of this single junction solar cell configuration were found to be
\[
\text{FF} = \frac{P_{\text{max}}}{(J_{\text{sc}} \times \text{Area of the back contact} \times V_{\text{oc}})} \quad (5)
\]

\[
= 0.034 \text{ mW} / (0.908 \text{ mA/cm}^2 \times 0.13 \text{ cm}^2 \times 0.455 \text{ V}) = 63.3\%
\]

And

\[
\text{Efficiency} = \frac{P_{\text{max}}}{P_{\text{in}}} \quad (6)
\]

\[
= 0.034 \text{ mW} / 13 \text{ mW} = 0.26\%
\]

respectively.

![Figure 4-46 I-V characterization of the single p-n junction solar cell configuration under the illumination of room light as well as solar simulator.](image)

Although the efficiency of this single junction solar cell configuration is low, the open circuit voltage of 0.455 V and the fill factor of 63.3% are quite substantial, compared, for example, to those of CdTe solar cells with highest independently confirmed efficiency, namely an open circuit voltage of 0.845 V and a fill factor of 75.5% [142]. This first result can be considered very promising especially if the problem of low short-circuit current is identified and solved. Based on the electrical properties, major carrier density in particularly, of the p and n layers, the depletion region of this p-n junction is mainly in p-type absorber layer side, from which the capacity of separating the
light-generated electron-hole pair will be benefited. However, on the other hand, the optical band gap of the p-type layer (1.82 eV), as an absorber layer, is a little high, which decreases the theoretical maximum values of both the short-circuit current and the efficiency. In order to improve the overall performance, the following efforts should be made: (i) designing the thickness, the band gap values and micro-structure (like anti-reflection layer) of each layer to guarantee the maximum portion of incident light to reach the absorber layer and to be absorbed; (ii) engineering the band structure of the junction to achieve the highest build-in potential to separate the electron-hole pair; (iii) enhancing the interface conditions between each layer to minimize the recombination of electron-hole pair and increase the short-circuit circuit.

Figure 4-47 Current density of the single p-n junction solar cell configuration under illumination of solar simulator (left axis) and power (right axis) as a function of voltage (J-V).

Summary on Rectifying p-n Junctions and PV Effect

By controlling the fraction of ZnO phase and ZnN phase, the electrical and optical properties of zinc oxy-nitride are the subject of tuning, and therefore a p-n junction are fabricated, which makes the realization of electronic and photovoltaic applications
possible. A single junction solar cell configuration with the efficiency of 0.26% is fabricated using zinc oxy-nitride, the electrical and optical properties of which are carefully designed. The open-circuit voltage of 0.455 V and the fill factor of 63.3% are substantial.

### 4.3.2 Rectifying metal-semiconductor junctions

As a semiconductor material, junctions of zinc nitride with different metals could be either ohmic or rectifying. As mentioned earlier (in section 4.1.4), the ohmic behavior was observed between zinc nitride thin film and several metals, like copper (Cu), silver (Ag), and gold (Au), respectively. The formation of rectifying metal-semiconductor (MS) junctions, functioning like p-n junctions, is of interest to device applications as well.

![Figure 4-48 The optimized Current-voltage (I-V) curve for Ti-ZnN MS junction along with I-V curves under different contact configuration.](image)

MS junction was formed between titanium (Ti) and zinc nitride. A 200 nm Ti thin film was grown on glass substrate first, and then a 400 nm thick zinc nitride thin film was deposited under what we consider to be optimized, oxygen-free conditions. By improving
the quality of the contact on zinc nitride thin film, the better defined rectifying behavior was observed, shown in Figure 4-48.

4.3.3 Metal-insulator-semiconductor junctions

![Diagram of Ti-SiO₂-ZnN MIS junction](image)

Figure 4-49 A schematic of the cross-section of Ti-SiO₂-ZnN MIS junction.

Besides the p-n junction and MS junction discussed above, metal-insulator-semiconductor (MIS) junctions are another fundamental structure for devices, including such as metal-insulator-semiconductor field-effect transistors (MISFETs). The MIS structure has a dielectric layer between metal and semiconductor layers. In Figure 4-49, it is a MIS junction made by titanium, silicon dioxide (SiO₂), and zinc nitride. A 200 nm thick Ti layer was first deposited on glass substrate, followed by the growth of an 80 nm thick SiO₂ layer. On top of SiO₂ layer, the zinc nitride thin film was deposited at the optimized condition with a thickness of 400 ~ 500 nm.

From the SEM images of Ti-SiO₂-ZnN MIS junction, Figure 4-50, it can be seen that the intended sandwich structure has formed and is uniform across the film cross-section studied. The Ti layer, SiO₂ layer and ZnN layer can be easily identified.

The capacitance-voltage (C-V) measurement was performed on this MIS structure. A layer of silver (Ag) was painted on the top of zinc nitride layer as the front contact of this MIS structure. The area of the Ag front contact is about 1.4 cm².
Figure 4-50 SEM images of cross-section of Ti-SiO$_2$-ZnN MIS junction.
The frequency of the alternating-current (AC) voltage used this measurement was $2 \times 10^4$ Hz. The potential at the Ag front contact (semiconductor side of MIS junction) was served as reference potential.

*Figure 4-51 Mott-Schottky plot and J-V curve (inserted) of Ti-SiO$_2$-ZnN MIS junction*

Figure 4-51 shows the Mott-Schottky plot and the current density curve as a function of voltage (J-V) of Ti-SiO$_2$-ZnN MIS junction. A back-to-back rectifying behavior was detected. One of the possible reasons could be that a layer of highly resistive ZnO was formed naturally on top of the zinc nitride layer prior to the painting of Ag layer. This highly resistive ZnO layer served as another “insulator” layer and, along with the zinc nitride layer beneath and Ag layer above, another MIS junction was constructed. The whole structure, therefore, became a metal-insulator-semiconductor-insulator-metal (Ag-ZnO-ZnN-SiO$_2$-Ti) structure instead of the original designed MIS structure.
Chapter 5

Concluding remarks and future work

5.1 Concluding Remarks

The structural, electrical and optical properties as well as chemical bonding states and composition of zinc nitride and oxy-nitride thin films were carefully examined. A better understanding of the relationship between the properties of zinc nitride thin films and deposition conditions has been achieved. The zinc nitride thin films have a Zn:N ratio which is very close to the stoichiometric value of 1.5, and they contain only a small amount of zinc oxide phase. A single junction solar cell configuration with the efficiency of 0.26%, along with several other device-related multi-layer structures was fabricated based on the zinc nitride/zinc oxy-nitride material system. A more detailed summary of the results of this project is given next.

- With the increase of the $N_2$ content in the total sputtering gas mixture, the films attain higher crystallinity and acquire a higher degree of preferential crystallite orientation. The substrate temperature influences the crystallinity of zinc nitride thin film significantly. The crystallinity of zinc nitride thin film increases with the increase of substrate temperature. Also, somewhat unexpectedly, based on Raman...
scattering data, it appears that the higher substrate temperature helps to prevent surface oxidation of zinc nitride thin films to a certain degree.

- Similarly to what we observed in zinc nitride thin films, in the formation of zinc oxy-nitride thin films, the nitrogen-to-total sputtering gases ratio and the substrate temperature are still the key factors. The deposition pressure is another important parameter that can control the oxygen incorporation. Although the role of the intentionally introduced oxygen in the film formation process is not fully understood, several important points can be made here. First, the intentionally introduced oxygen impedes the crystallization of zinc nitride. Second, at lower deposition pressure, very little zinc oxide related XRD peaks are observed after this small amount of oxygen is introduced, which suggests that the incorporation of oxygen into zinc nitride thin film increases film’s resistivity to surface oxidation. Third, with increase of the deposition pressure, oxygen is more easily incorporated in the films. Fourth, the coexistence of both zinc nitride phase and zinc oxide phase was observed, and the relative fraction of these two phases influences the properties, especially the electrical and optical properties, in a significant way.

- With the improvement of crystallinity of zinc nitride or oxy-nitride thin films, (as a result of the increase in the \( N_2 \) content in the sputtering gas mixture or the substrate temperature) clearer grain boundaries, bigger grain sizes, and smoother surfaces are observed. The effect of oxidation of zinc nitride films on the surface morphology was also presented via SEM work. The most important factor that facilitates oxidation was determined to be the humidity in the air ambient.
• The formation of zinc nitride is again confirmed by the observation of N-Zn bonds in the XPS spectra. A nearly stoichiometric value of Zn:N ratio was established in the quantitative analysis of chemical concentration by EDXS. Moreover, it is found from the XPS spectra that the surface of the zinc nitride thin film contains water, as suggested by the presence of H-O and H-N bonds, which also explained the presence of O in the EDXS data for films prepared at oxygen-free environment. After sputtering removal of a very thin surface layer during the XPS measurement, the complete absence of H-O bonds and the significant reduction of O-Zn bonds indicate an oxidized film surface and an almost oxygen-free film volume. Also, molecular N₂ bonds appear after the sputtering, which indicates the existence of N-N bonds in the thin film and is, most likely, partially responsible for the n-type conductivity. The intentional incorporation of oxygen into zinc nitride thin films and the way of controlling this process were also confirmed by EDXS.

• The electrical properties of zinc nitride thin film were found to depend on deposition conditions, such as nitrogen to total sputtering gas ratio and substrate temperature, and therefore the crystallinity of the films and the chemical bonding states that comprise the material. By changing the deposition condition, the majority carrier concentration and the resistivity of zinc nitride thin films are controllably modified within a certain range. The electrical properties of the zinc oxy-nitride films are closely related to the chemical composition as well as the bonding states of oxygen with zinc and nitrogen (phase-related) inside the film. By controlling the fraction of ZnO phase and ZnN phase, the electrical properties
of zinc oxy-nitride can be controlled. After the post-deposition thermal treatment, some of zinc oxy-nitride thin films show p-type conductivity.

- The optical transmittance of zinc nitride thin film is mainly influenced by the crystallinity of the films, which is related to both the nitrogen concentration in sputtering gas mixture and substrate temperature. The transparency of films was found to correlate to some degree with the crystallinity of the films. Using the relation between absorption coefficient and the value of optical on-set, the optical band gaps of zinc nitride thin films are determined. A direct optical band gap of around 1.4 eV is found. The band gaps of zinc oxy-nitride thin films range from 1.35 eV to 2.02 eV with the change of the deposition conditions. It suggests that the optical properties of zinc oxy-nitride thin film are closely related to the composition of the thin films as well as the bonding states of oxygen with zinc and nitrogen (phase-related) inside the film.

- Structural, electronic and energetic properties of (i) pure $\text{Zn}_3\text{N}_2$ and (ii) point defects of native species $\text{Zn}$ and $\text{N}$ and copper group elements $\text{Cu}$, $\text{Ag}$ and $\text{Au}$ were investigated, with DFT computations. The bulk modulus of pure $\text{Zn}_3\text{N}_2$ was found to be 140.19 GPa with GGA and 176.6 GPa with LDA. The band structure of pure $\text{Zn}_3\text{N}_2$ was calculated. It confirmed the direct bandgap behavior and suggested a value of less than 1 eV for pure $\text{Zn}_3\text{N}_2$. The analysis of the DOS of pure $\text{Zn}_3\text{N}_2$ showed clearly that electronic behavior is closely related to and, therefore, easily affected by nitrogen. The formation energies of native defects indicated that nitrogen vacancies and zinc interstitials are energetically favored over nitrogen interstitials. When doped with copper family elements, point defects
are likely to appear at a nitrogen site rather than at zinc or interstitial sites. The LDOS of copper family elements suggests that Cu-doped zinc nitride will tend to show the p-type character while Ag- or Au-doped zinc nitride may display n-type conducting behavior.

- By controlling the fraction of ZnO phase and ZnN phase, the electrical and optical properties of zinc oxy-nitride are the subject of tuning, and therefore a p-n junction are fabricated, which makes the realization of electronic and photovoltaic applications possible. A single junction solar cell configuration with the efficiency of 0.26% is fabricated using zinc oxy-nitride, the electrical and optical properties of which are carefully designed. The open-circuit voltage of $0.455 \, V$ and the fill factor of 63.3% are impressive.

5.2 Future work

This study has shown the potential of zinc nitride and oxy-nitride, for electronic and PV applications. However, further studies are needed in several areas in order to fully examine and overcome the remaining difficulties, such as the mechanism of oxygen incorporation, gaining larger property-tuning range, and optimizing performance of junctions and PV structures.

In the case of pure zinc nitride, more studies are needed to fully understand the connection between electrical properties and deposition conditions, as well as to gain more controllability of electrical properties. Although during this project, the control of electrical properties was achieved to some degree, the connection between electrical properties and deposition conditions is still not well understood. The possibility for
controlling the phase formation and micro-structure of thin film during deposition, the mechanism of native defects formation during deposition, as well as finding ways to avoid undesired oxidation, need to be further explored and overcome. CVD and MBE methods should be studied in more detail as they could potentially provide higher purity and better crystalline quality. In-situ characterization techniques, like spectroscopic ellipsometry and/or angle-resolved photoemission spectroscopy, could be employed to gain more information during the process of growth. Low temperature characterization methods are other options that can provide more insight. Through the change of the temperature, the change of the defects activity will be observed and analyzed for better understanding on the effect of defects.

In the case zinc oxy-nitride, exploring further the phase formation preference between zinc and oxygen, as well as their relationship with zinc nitride phase in the film, would be of interest. Controlling oxygen, as a natural defect in zinc nitride, may provide this material system with many new possibilities. On the other hand, incorporation of oxygen in zinc nitride system makes a complex system more complex. Therefore, the deep understanding on (i) the mechanism of co-existence of zinc nitride and zinc oxide phases and (ii) the chemical bonding states among Zn, O, and N becomes very crucial. The more the understanding is, the better this advantage is taken and utilized. At this time, the role of the intentionally introduced oxygen in the film formation process is not fully understood.

More device-related work is clearly needed. Although the properties of zinc nitride and zinc oxy-nitride are not fully controlled yet, devices based on zinc nitride and related materials have been realized, namely the transistor using zinc nitride as channel
layer and the p-n junction between zinc nitride and other materials (Si for instance). And in this project, a p-n junction between zinc oxy-nitride with different oxygen content was fabricated. More significant, the photovoltaic effect was observed. Although the efficiency is only 0.26%, the fill factor and the open circuit voltage are quite good. The optimization of this single junction solar cell configuration should be performed. By modifying the parameters of the junction (like varying the thickness of each layer), adding micro-structure (anti-reflecting structure for example), and improving the material itself, the efficiency of this single junction solar cell configuration could be increased significantly. Additionally, more electrical measurements are needed after properties of thin films are controlled and the devices are fabricated.

As far as modeling and theoretical work, other candidates for dopants, both n-type and p-type candidates, should be investigated. For any semiconductor material system, controllable doping is needed in device applications. Due to the relatively complex atomic structure, the theoretical investigations on not only the defect formation mechanism but also the diffusion behavior of impurities in the lattice would be preferred. Consequently, the effects of the incorporation and diffusion of these dopants in the original lattice on the electrical and optical properties of material will be revealed. A deeper understanding of this material will be provided and serves as a great guidance for experimental works to achieve full controllability of properties of this material.
5.3. List of Publications Resulting from this Research

Journal Publications:


Peer Reviewed National/International Conference Papers:


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