Filtered cathodic vacuum arc deposition of metal nitrides

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Filtered Cathodic Vacuum Arc Deposition of Metal Nitrides

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To my beloved father, **JI Changqing**.

If he were still alive, he would be very proud of me!

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SUMMARY

The numerous applications of group-III nitride semiconductors have attracted significant research interest over the last decade. A novel ion-beam assisted filtered cathodic vacuum arc (I-FCVA) technique has been developed to fabricate III-nitrides using pure metallic target as metal source. For the first time, FCVA technique is capable of handling low melting point metal target such as Ga and In. Binary III-nitrides (AlN, GaN, InN) on Si substrates have been fabricated, characterized and analyzed.

Highly (0002) oriented InN films were prepared. The preferred growth direction was attributed to the minimization of the overall surface and strain energy of the film during the growth. The typical photoluminescence (PL) peak of the InN films was located at 1.15 eV. It was proposed that the observed emission could be attributed to oxygen incorporated at grain boundaries in the form of amorphous oxide or oxynitride.

Self-aligned InN nanofingers have also been successfully fabricated by tuning the growth parameters. The growth mechanism of the InN nanofingers follows the Volmer-Weber mode, which is due to the combined effect of the large lattice mismatch between InN and the substrate, and the energetic species of N ions and In plasma. Excellent field emission characteristics were observed from the InN nanofingers with turn on field of 9.7 V/ μm at a current density of 10 $\mu\text{A}/\text{cm}^2$. The Field enhancement factor was found to be ~ 156 , assuming work function of 1 eV.

GaN thin films were prepared on Si. It was found that the quality of the GaN films was improved by inserting a ZnO buffer layer. Room temperature PL peaked at

369 nm (3.36 eV), corresponding to GaN band edge emission, was observed from the GaN on ZnO buffered Si.

Secondary electron emission (SEE) yields were evaluated from III-nitride film surfaces. The overall SEE yields of the III-nitride thin films on Si were comparable to those of MgO thin films, which is a commonly used high SEE yield material. One-dimensional (1D) nanostructures have shown efficient electron field emission properties. The SEE on AlN coated carbon nanotubes (CNTs) was evaluated. The dependence of SEE yield on the incidence angle revealed that AlN thin films coated on CNTs did not follow the power law as those coated on a Si substrate. The results indicated that the SEE yield was dependent on the nanostructuring of the surface topography.

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ABBREVIATIONS

AFM	Atomic Force Microscopy
FCVA	Filtered cathodic vacuum arc
FE-SEM	Field emission scanning electron microscopy
FWHM	Full width at half maximum
HEMT	High electron mobility transistor
HVPE	Hydride vapor phase epitaxy
HRTEM	High resolution transmission electron microscopy
LED	Light-emitting diode
MBE	Molecular beam epitaxy
MOCVD	Metal organic chemical vapor deposition
PEE	Primary electron energy
PL	Photoluminescence
PMT	Photomultiplier tube
RF	Radio frequency
RMS	Root mean square
RT	Room temperature
SEE	Secondary electron emission
SEELY	Secondary electron emission yield
T _s	Substrate temperature
XPS	X-ray photoelectron diffraction
XRD	X-ray diffraction
TEM	Transmission electron microscopy

CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

1.1.1 Growth of binary compound

The group-III nitride compounds (GaN, InN and AlN) have attracted a great deal of attention both in fundamental research and optical device fabrication over the past few decades. The major reason is that III-nitride semiconductors show excellent optical properties which cover continuously the lasing wavelength from UV-visible (VIS) to near-infrared (NIR) by proper alloying ^[1-3]. Also, the extensive solid solubility among III-nitride compounds have allowed the development and commercialization of green and blue LEDs with efficiencies, brightness and longevity sufficient for, e.g., outdoor displays, traffic lights, and indicator lights in automobiles, as shown in Figure 1-1. The use of nitride-based lasers will allow the storage density

Figure 1-1 Illustration of the many applications of III-V compound semiconductors.

of a digital versatile disk (DVD) to stepwise increase from ~ 1 to ~ 40 Gb. In the context of role reversal, III-nitrides alloys are also the primary candidate materials for UV photodetectors and solar blind detectors for application in monitoring combustion processes, vision through fog, smoke and solar astronomy. Published works on the fabrication, characterization and applications of III-nitrides have been reviewed [4-11].

Group-III nitrides have two possible structures: the hexagonal wurtzite and cubic zinc blend, as shown in Figure 1-2. Most studies of III-nitrides concentrate on the hexagonal structure because the wurtzite structure is the stable phase while the zinc blend structure is metastable. Because of the different cations and ionic radii (Al^{3+} : $0.39 \text{ \AA}$, Ga^{3+} : $0.47 \text{ \AA}$, In^{3+} : $0.79 \text{ \AA}$), AlN, GaN and InN have different lattice constants, band gaps and binding energies [6], as shown in Figure 1-3 and Table 1-1 [8-10]. Despite the applications of GaN-based group III nitrides, individual binary compounds have their merits for the specific applications, such as surface acoustic wave (SAW) devices (AlN [12-14]), blue LEDs and LDs (GaN [15-17]), solar cells (InN [18,19]), and so on.

Figure 1-2 Structures of (a) wurtzite MN and (b) zinc blende MN (M: Al, In, Ga) [7].

Figure 1-3 Plot of the bandgap energy vs. lattice parameter, a , for III-nitrides. Dashed line is corresponding to the old report for InN, and solid line is the new report for InN.

Table 1-1 Basic properties of wurtzite AlN, InN and GaN. ^[8-10]

Properties	AlN	GaN	InN
Lattice constant (nm)	$a = 0.31106$ $c = 0.49795$	$a = 0.3186$ $c = 0.5178$	$a = 0.3540$ $c = 0.5705$
Melting point (°C)	2800	>2573(at 60kba)	1373
Thermal expansion coefficients ($\times 10^{-6} \text{K}^{-1}$)	a : 2.9 c : 3.4	a : 5.59 c : 3.17	a : 3.8 c : 2.9
Thermal conductivity (W/cm K)	2.85/2.0	2.1/1.3	0.45
Young's modulus (GPa)	~344	~210	-
Hardness (GPa)	~20	~15.5	-
Dielectric constants	$\epsilon_0 = 8.5 \pm 0.2$ $\epsilon_\infty = 4.68, 4.86$	$\epsilon_0 = 9.5$ $\epsilon_\infty = 5.35$	$\epsilon_0 = 8.4$ $\epsilon_\infty = 15.3$
Refractive index	1.9~2.15	2.5	2.9
Energy gap (eV)	6.2	3.39	0.7~1.9
Deformation potential (eV)	9.5	8.3	7.1

The melting point and vapor pressure of AlN, GaN and InN are far exceeded those of the typical semiconductor materials. Thus the corresponding equilibrium pressure at melting of GaN, AlN and InN are very high, III-nitride cannot be grown from their stoichiometric method [20-22]. Figure 1-4 shows experimental results and theoretical calculations of the equilibrium pressures of N₂ over III-nitrides system, including the melting temperatures [6]. The growth of III-nitrides (AlN and GaN) was started in 1930, but good quality epilayers could not be obtained until high vacuum technology, such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), was invented in late 1980s (reference for an example, review paper [11]).

Figure 1-4 Equilibrium N₂ pressure over the MN(s) + M(l) systems (M = In, Ga or Al), and melting points (T^M) from high-pressure experiments and theoretical calculations.^[6]

However, the growth of high quality films is still a big challenge for nitride researchers due to the fact that III-nitride-based materials and devices are usually grown on foreign substrates. Commonly used techniques for thin film fabrication include MOCVD, MBE, pulsed laser deposition (PLD), sputtering and so on. MOCVD and MBE are the most popular techniques for the growth of III-nitrides. However, they generally require complex processes, high vacuum, and a relatively high deposition temperature. High temperature deposition has the disadvantage of degrading the substrate and the III-nitrides thin films during deposition due to the thermal damage, like Si, GaAs and GaP substrates ^[6, 23]. Growing of III-nitride directly on Si substrate at high temperature could lead to the unintentional nitridation of the substrate surface ^[24, 25] and poor nucleation of nitrides on the Si substrate, result in a migration of Si to the surface of the nitride layer ^[26, 27]. Thus, deposition of III-nitrides thin films at low temperature has become increasingly important and valuable. Furthermore, plasma/ion beam assisted reactive deposition is becoming more attractive because it enables more precise and more flexible control the parameter, such as ion energy, ion flux and incidence angle ^[28]. Ion-beam assisted filtered cathodic vacuum arc (I-FCVA) is one such a promising technique employing low temperature and low pressure process.

FCVA has the features of not only effectively eliminating macro-particles of cathode material, but also provides an intense source of fully ionized deposited species with energies greater than counterparts produced in thermal evaporation or magnetron sputtering. FCVA has proven its merits in the fabrication of diamond-like carbon (DLC) films ^[29, 30], oxides (Al_2O_3 ^[31], ZnO ^[32], etc.) and nitrides (cBN ^[33, 34], TiN ^[35, 36], Zr_3N_4 ^[37, 38], etc.). Therefore, the investigation of the low temperature deposition process on III-nitrides using I-FCVA will be of significant interest.

1.1.2 Hetero growth of group-III nitrides on Si substrate

It is well known that one of the major obstacles to improve material quality is the lack of a substrate that is well lattice and thermal matched to nitrides. The quality of the III-nitrides films strongly depends on the properties of the substrates, both inherent properties such as lattice constants, thermal expansion coefficients and process induced properties such as surface roughness, step height, and wetting behavior. The lack of lattice-matched substrates result in the high density of defects presented in the films; the different thermal expansion coefficients may also cause the cracking and/or stress of the films. The aforementioned problems will significantly affect the device processing and performance.

The most commonly employed substrates for III-nitrides are presented in Table 1-2. Comparing sapphire and SiC with regards to device fabrication, SiC has advantages in terms of lattice constants and coefficients of thermal expansion matched to III-nitrides (especially AlN and GaN) and higher thermal conductivity. However, SiC substrates are more costly and have a more complex microstructure that is manifest in the subsequently grown films. Among these substrates, Si has lots of attractive advantages, such as low cost, excellent crystal quality, good doping properties, availability of large size wafers, and mature processing techniques. If high quality III-nitrides can be grown on Si substrate, the production of optoelectronic integrated circuits will be possible using the Si-based microelectronics technology. In this aspect, the study of heteroepitaxial growth of III-nitrides on Si is very important.

Table 1-2 Basic properties of Si, Sapphire and 6-H SiC.

Properties	Si	Sapphire	SiC
Structure	Diamond	Corundum	6-H
Lattice constant (nm)	0.54310	a = 0.4765 c = 1.2982	a = 0.30806 c = 1.51173
Melting point (°C)	1414	2030	~2830
Thermal expansion coefficients ($\times 10^{-6} \text{K}^{-1}$)	2.616	6.66 //c 20-50°C 9.03 //c (20~1000°C) 5.0 $\perp$ c	4.46// a-axis 4.16// c-axis
Thermal conductivity (W/cm K)	1.56	0.23 // c-axis 0.25 // a-axis	4.9
Heat capacity (J/K mol)	0.70	77.9	0.71
Young's modulus (GPa)	165.6	452-460 // (0001) 352-484 // (11 $\bar{2}$ 0)	-
Poisson's ratio	0.218		0.183 ~ 0.19
Hardness (GPa)	-	23.9 $\pm$ 2.0	9.2-9.3
Dielectric constants	11.8	8.6 // c-axis 10.55// a-axis	9.6 // c-axis 10.3// a-axis
Refractive index	3.42	1.77 @ 577nm 1.73 @ 2.33 μ m	2.6894 @498nm
Energy gap (eV)	1.124	8.1-8.6	3.02
Resistivity (K Ω cm)	Up to 50	>10 ⁸	-

1.1.3 Evaluation of secondary electron emission of III-nitrides

If energetic electrons strike a target surface in a vacuum, their energy is lost during collisions in a region near the surface, and most of them are transferred to other electrons in the solid. Some of these electrons are liberated from the surface and form a secondary emission (SE) current. The ratio of SEs to incidence electrons is known as SEE coefficient/yield. In general, SEE yield as a function of the primary incident

electron energy first increases with energy, reaches a maximum at a few hundred electron volts and then slowly decreases towards high energies. High SEE materials are valuable for electron multiplication in devices such as cross-field amplifiers^[39].

The SEE phenomena are strongly affected by the surface potential^[40-42]. The electron affinity (EA) (χ) is defined as the energy difference between the vacuum level and the conduction band minimum at the surface, and it represents the energy barrier that conduction-band electrons encounter at the semiconductor/vacuum interface. When $\chi < 0$, all electrons that reach the negative electron affinity (NEA) surface can be emitted into vacuum. NEA results from the combination of a relatively low natural EA, is more likely to occur in a semiconductor exhibiting polar nature and with wide energy bandgap^[2]. Figure 1-5 shows a schematic energy band diagram for a surface exhibiting NEA^[41]. As a result, wide bandgap materials that possess NEA surfaces are attracting attention as potential cold electron emitter materials^[42]. Therefore, it is of research interest to investigate the SEE properties of III-nitride films on Si and nanostructured template (ie., carbon nanotubes (CNTs)).

Figure 1-5 Schematic energy diagram for a surface exhibiting NEA.

1.2 Objectives

The purpose of this thesis is to grow binary III-nitrides (AlN, GaN and InN) (i) at lower temperatures and (ii) on Si substrates. A promising technique to achieve the target is to use I-FCVA method. The main objective is to optimize the deposition parameters for the nitrides growth.

1.2.1 Development of FCVA technique for AlN, InN and GaN growth

There are several challenges for III-nitrides growth using FCVA. First of all, how to generate effective N_2 species? The molecular N_2 is inert and difficult to chemisorb on nitride surface at low temperature, due to the strong N-N bond of the nitrogen molecule. Besides, this molecular nitrogen interacts poorly with the surface of nitrides; the dissociative chemisorption of N_2 is very ineffective. As a result, an activation of nitrogen by plasma or ionization assistance or the use of NH_3 is necessary for effective growth of nitrides. In this work, an ion source was employed to activate the nitrogen ions. The energetic N_2 species overcome the requirements for high equilibrium N_2 pressure over the nitride solids.

The melting points of group III metals are low especially for In (184 K) and Ga (57 K). In general, solid conductive disk targets are employed directly as the cathode in FCVA with direct water cooling. However, it is a challenging task to use low melting point metals as cathode in FCVA. As such a metallic cup is used to hold the low melting point metal which acts as cathode.

1.2.2 Growth and characterization of III-nitrides films

Like many other plasma deposition techniques, FCVA is non-equilibrium process. The properties of the deposited films were strongly dependent on the deposition parameters, such as ion energies, substrate temperature, and substrate bias, *etc.*. Considerable effort on establishing the optimum deposition parameters is often necessary. The preferred orientation (in either (0002) or (10 $\bar{1}$ 0) direction) was always observed in the deposited AlN films prepared by sputtering (see references for examples ^[43, 44]). Many studies were focused on the study of mechanism of texture in sputtered films in terms of the effect of energetic particles, minimum surface and strain energy, the strength of the chemical bonding, *etc.*^[43]. However, only a few reported arc deposition ^[13, 45-46] of AlN films. These systematic studies of the deposition process become significant and help to obtain better insight of the correlated properties of the deposited films.

InN is the least studied material among group-III nitrides ^[47]. Recent reports on InN films with narrow band gaps of 0.65 ~ 1.4 eV ^[48-51] in comparison with previously well-accepted value of 1.9 eV show that the results are still non conclusive and even conflicting. InN/Si system as a solar cell material has the advantages of being non-toxic and possessing high efficiency, as proposed by Yamamoto *et al.* ^[18]. Therefore, the investigation of InN/Si on structural and optical properties with various effects of deposition parameters will be useful.

It was considered that the growth of high quality GaN films on Si substrate has serious problems because of the cracks and high dislocation density of epilayers due to the large mismatches in lattice constants and thermal expansion coefficient between GaN and Si. To overcome these difficulties, attempts are made by introducing several

intermediate layer(s) on Si substrate before the growth of GaN layer. The ZnO buffer layer has potential advantages for GaN hetero-growth, because ZnO is an isomorphic material with wurtzite GaN, which has only 1.8% lattice mismatch with respect to GaN. For the growth of either GaN or ZnO thin films, they have already been used as buffer layers for each other ^[52-55]. Attempts have been made to grow high quality GaN films on different substrates with ZnO buffer layers by PLD ^[53], CVD ^[54] and MBE ^[56]. However, no attempt was carried out using the FCVA technique. To the best of our knowledge, there was no intense RT photoluminescence reported from GaN on ZnO buffered Si. Therefore, the studies of GaN on Si with ZnO buffers constitute a part of the thesis.

1.3 Major contributions

As mentioned above, III-nitride can not be grown from their stoichiometric method due to high equilibrium vapor pressure of nitrogen over the nitrides ^[22-24]. This thesis is the first to research the deposition of group III-nitrides films using the FCVA technique, a non-equilibrium process. Ion beam source was used to generate the reactive nitrogen ions. The growth and characterization of binary III-nitrides thin films have been systematically studied. SEE yield of III-nitride thin films revealed the potential applications of the films in vacuum devices. Moreover, nano-structured InN exhibited good field emission properties. The work opens up avenues for further study of nitride films and nanostructures on Si substrate based on the FCVA technique.

The Major contributions are summarized as followings:

- It is the first time that FCVA has been used for group-III nitride growth. FCVA has been modified by equipping an ion beam source to provide the energetic N ions and using a metallic container for In and Ga target. A boron nitride shield was placed on the metallic cup to eliminate the cup material contaminations. AlN, GaN and InN were successfully fabricated.
- With the assistance of nitrogen ion beam source, InN films with highly preferred (0001) orientation were obtained. Furthermore, InN nanofingers were fabricated, which exhibited field enhancement factor of 157 when assuming a work function of 1 eV. The formation of the InN nanostructures was attributed to Volmer-Weber island growth.
- Hetero-growth of [0001] GaN on Si with ZnO buffers was also demonstrated. The observed RT PL from the ZnO-buffered GaN indicated that the quality of GaN film has been significantly improved as compared to those without ZnO buffer layers.
- SEE properties of III-nitrides were evaluated. The maximum SEE values of 2.5-3 were comparable to that of MgO thin films. SEE was also examined from AlN coated CNTs sample. The inclined-incidence effect is related with the nanostructured topographic configuration. Therefore, SEE yield is also dependent on the nanostructuring of the surface topography.

1.4 Organization

Chapter 1 provides a background of III-nitrides and describes the motivation and the objectives of the research with a brief overview of the studies of group-III nitrides deposition by FCVA.

Chapter 2 describes the experimental details including FCVA technique and growth processes, followed by characterization methods.

Major research results are given in chapter 3, 4, 5 and 6. In chapter 3, the study of AlN is the groundwork, which will pave the way for the GaN and InN work laid on AlN. Properties of InN thin films and nanostructures are given in chapter 4. Chapter 5 covers the results of GaN on Si with and without ZnO buffers. Secondary electron emission properties of FCVA III-nitrides are described in chapter 6.

The thesis ends in chapter 7 with a summary of the main conclusions and recommendations for further research.

CHAPTER 2 EXPERIMENT AND METHODOLOGY

In this chapter, the film growth technique and characterization methods are described. A brief introduction of the ion-beam-assisted filtered cathodic vacuum arc system is given. A description of the characterization techniques is also presented.

2.1 *Experimental technique*

2.1.1 Filtered Cathodic Vacuum Arc (FCVA) system

The cathodic arc is a low-voltage, high-current plasma discharge that takes place between two electrodes in vacuum. It is also called a metal vapor vacuum arc or vacuum arc. The current is concentrated at small “cathode spots” sites at the cathode of the vacuum arc. The current density in the spots is of the order of 10^6 - 10^8 A/cm² [29]. The basic feature of the vacuum arc discharge is the relationship between the metal ion fluxes that is generated at the cathode spots and the current which drives the arc. The plasma ion current is a constant fraction of the arc current, $I_{ion} = \epsilon I_{arc}$, where ϵ is a constant ranging from 0.06 to 0.12 [58]. Ion energy measurement for various metals has been carried out by researchers [59-60]. Previously, the major obstacle for the cathodic vacuum arc deposition was the presence of micro- and nano-particles in the plasma, so-called “droplets” or “macro-particles”. A number of particle filters were used to separate and remove particles from the cathodic arc plasma [61]. The idea was to use curved magnetic ducts to separate macroparticles from cathodic plasma based on the indirect trajectories between cathodes and substrates. However, this approach still did not completely address the problem of macroparticle inclusion in the deposited film because the solid macroparticles were easily multiply reflected from the filter wall,

leading to incomplete filtering. The FCVA system, with a double bend filter, has been developed and demonstrated to be suitable for the industrial applications by Shi, *et al.*^[62]. Films of metal and alloys, including non-equilibrium alloys, high quality diamond-like carbon, ceramics of many different kinds, semiconductors, high-temperature superconductors, and other materials have been fabricated, both as single layer films and multilayer structures by vacuum arc technique^[29].

Figure 2-1 provides a schematic illustration of the off-plane double bend (OPDB) I-FCVA. The system mainly consists of four parts: a cathodic arc source, a plasma-filtering duct, an ion beam source and a deposition chamber. A rotary-cryogenic pump system is connected to the chamber for pumping down to the desired pressure during the deposition. The cathodic vacuum arc source has five main parts: the anode wall, the power supply, the arc trigger, the target and the target cooling system. Before deposition, the chamber is pumped down to a pressure of less than 10^{-6} torr. The power supply is an electrical welding machine with a maximum current of 250 A. The anode is grounded (deposition chamber) and the cathode is connected to the target. A radial electric field is formed via the toroidal duct, coupled with a curvilinear axial magnetic field on the curved toroidal duct that forms a crossed electric-magnetic field filtering assembly. The plasma, which is steered by the field, passes through the duct to the substrate and results in the deposition of films free from any unwanted macroparticles and neutral atoms. The ions are highly energetic, with kinetic energies typically of 50-150 eV^[63], which is considerably higher than those of the evaporated or sputtered atoms, even though the discharge voltage is only around 20 V. The higher the cohesive energy of the solid cathode, the greater the arc burning voltage, power density, average ion charge state, electron temperature and ion kinetic

Figure 2-1 Schematic illustration of the I-FCVA system.

energy (cohesive energy rule^[60]). The high ionization facilitates controlling the energy of the depositing ions by biasing the substrate which has a strong influence on the microstructure of the coating, while the high energy results in self-cleaning of the substrates of contaminants by ion sputtering.

Figure 2-2 shows a schematic drawing of the FCVA chamber in top view. The metal plasma and nitrogen ion fluxes were incidence at an angle of about 45° in respect of the substrate surface. Due to the low melting point of In and Ga, a metallic cup was used to hold the target material. The cup was covered by a boron nitride (BN) plate, which acts as a shield to prevent the arc being generated from the cup and stop the arc from being extinguished. The design is shown in Figure 2-3 (The cup is highlighted in blue and boron nitride in light turquoise.). Furthermore, the BN plate possesses very low surface energy that facilitates the removal of the residual after deposition.

Figure 2-2 Schematic drawing of the FCVA chamber in top view.

Figure 2-3 Schematic diagram of the anode and cathode assembly.

The main features of I-FCVA are as follows: Through a special electromagnetic filter, most of the unwanted macroparticles and neutral atoms could be

removed. Ions within a defined energy range could reach the substrate, thus producing films with good controllability and reproducibility. The high deposition energy of the condensing species during film growth could enhance adhesion. The radio frequency (RF) or linear ion beam source could compensate the possible loss of nitrogen species in the ablating plasma and effectively assist the deposition by providing energetic N ions. Therefore, the technique has the advantage of low temperature synthesis owing to the reaction of energetic N ions and metal plasma. The plasma was observed visually through the viewpoint during the deposition. The pink emission of nitrogen plasma was quite stable. Metal containing plasmas appeared in different colors. Aluminum plasma was in red, indium bright blue-violet, and gallium bright blue. After the plasmas were ignited, a region of bright red/blue-violet/light-blue appeared in front of the substrates.

- ❖ The use of activated nitrogen derived from ion beam source avoids the extremely high pressure required when molecular nitrogen is used as the nitrogen source. Ionic species of nitrogen, e.g. N^+ and N_2^+ , are sufficiently energetic to form the solid nitrides.
- ❖ Metals (Al, In, Ga) cathode is transferred to the plasma state at microscopic, non-stationary cathode spots. The plasma expanding from cathode spots contains ions that are usually multiply charged and have a kinetic energy in the range of 18- 150 eV, depending on the cathode material. The higher the cohesive energy of the solid cathode, the greater the arc burning voltage, power density, average ion charge state, electron temperature, and ion kinetic energy.

For metal plasma generated from the cathodic arc, the actual ion energy reaching the substrate will possess their original ion energy if it is an electrically floating substrate, because the substrate will have the same potential as the plasma beam. However, if the substrate is biased, the actual ion energy reaching the substrate can be calculated by

$$E_i = e(V_p - V_b) + E_0 \tag{2.1}$$

where E_i is the ion energy reaching the substrate, e is the electron charge, V_p is the plasma potential, V_b is the substrate bias, and E_o is the original ion energy in the plasma. Table 2-1 gives the energy for metals Al, Ga, and In cathodic arc plasma. The burning voltage is used to refer to the potential difference between anode and cathode. It is different with the charging or supply voltage that is supplied to the arc electrode by the electrical power supply.

Table 2-1 Cohesive energy, temperature of plasma electrons (T_e) in the charge-state freezing zone, burning voltage at 300A (V), kinetic energies for M (Al, Ga, In) cathodic arc plasmas (Ref. 59,60,64).

Element	Atomic number N	T_e (eV)	V(V) @300A (eV)	Cohesive energy (eV/atom)	Kinetic ion energy (eV)
Al	13	3.1	23.6	3.39	33
Ga	31	2.0	-	2.81	-
In	49	2.1	17.5	2.52	17.5

2.1.2 Ion beam source

An ion beam source is equipped in the deposition chamber. A photo of the system is shown in Figure 2-4. The ion source generates a flux of positive ions, so a neutralizer who supplies electrons to eliminate the space charge is needed. An optimum source operation relates to beam and accelerator current, to beam composition, and mean beam energy. When the RF power is increased, the plasma density gets larger, and hence a large ion current is injected into the plasma sheath resulting in an increased beam current. The beam energy is determined by the ion charge and beam voltage. During the experiment, nitrogen gas was used as source gas, the RF power was set constant 250 W and the beam voltage was varied from 50 to 650 V by beam DC power supply.

Figure 2-4 A Photo of the experimental setup of the I-FCVA.

2.2 Methodology

2.2.1 Surface profiler

The Surface Profile Measuring System (TENCOR P-10) was used to measure the thickness and curvatures of the films before and after deposition.

The internal stress was determined by the radius of curvature technique, which compares the curvatures of the bare substrate and the substrate coated with a film. The stress is given by Stoney's equation:

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_c} \left(\frac{1}{R} - \frac{1}{R_0} \right) \quad (2.2)$$

where E_s , ν_s , t_s and t_c are the Young's modulus, Poisson's ratio, thickness of the substrate and thickness of the films, respectively. R and R_0 are the radii of curvature of the film substrate composite and bare substrate, respectively [65]. For each film, the radius of curvature at different locations was measured and averaged. The substrates were measured prior to deposition to yield R_0 .

2.2.2 X-ray diffractometer

X-ray diffraction exploits the Bragg equation:

$$\lambda = 2d \sin \theta \quad (2.3)$$

where λ is the wavelength of the incident x-ray, d is the spacing of the planes, and 2θ is the diffraction angle. By considering all possible crystal orientations, d can be determined from the equation corresponding to spectrum, and the crystal structure and lattice constant can thus be determined. For cubic structure, the lattice parameter (a) for each diffraction plane can be calculated through the spacing of the (hkl) lattice plane, and taken into Bragg's equation:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \Rightarrow a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta} \quad (2.4)$$

Similarly, the lattice parameters of the hexagonal structure, a and c , can be calculated from the equation:

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + hk + k^2) + \frac{\lambda^2}{4c^2} l^2 \quad (2.5)$$

The grain size (D) was estimated from the full width at half maximum (FWHM) of the peak (radians) using Scherrer's equation,

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (2.6)$$

where λ is wavelength of the x-ray, B is the FWHM of the peak (radians) corrected for instrumental broadening, θ is the Bragg angle.

The x-ray diffraction pattern were obtained using the Siemens D5005 X-Ray diffractometer (XRD) with either glancing incident mode (2θ) or load-coupled mode ($\theta/2\theta$) by using $\text{CuK}\alpha$ ($\lambda = 0.154$ nm) radiation (40 kV, 40 mA). The incident angle was fixed at 1° for glance scanning, the 2θ scanning step was set at 0.05° and the counting time at each step was 2 seconds.

2.2.3 Microscopy

Atomic force microscopy (AFM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Raman spectroscopy were used for the film characterizations.

- ❖ AFM was used to analyze the surface morphology of the films in tapping mode (Digital Instruments NanoScope IIIa). The resolution of root mean square (RMS) roughness is 0.1 nm.
- ❖ Scanning electron microscopy (SEM) was employed to investigate the film surface and cross-sectional view. SEM images were obtained with SEM (JEOL JSM-6340F and JEOL JSM-5910 LV).
- ❖ Transmission electron microscopy (TEM) was performed on some of the samples to characterize the microstructure. The TEM samples with nanostructure were scratched from the substrate and then dispersing the specimens onto carbon-coated copper grids. Plane-view and cross-section samples were thinned to electron transparency by Ar ion milling. Detailed studies of the microstructure were carried out using TEM (JEOL JEM-2010) operating at 200 kV.
- ❖ Raman spectroscopy yields information about crystal lattices and their stresses, impurities and free carriers. The Raman effect is an inelastic scattering process, where an incident photon exchanges energy with the crystal lattice in the form of an optical phonon and emerges with a shifted energy. Room temperature Raman spectra were taken with Renishaw micro-Raman spectrometers, equipped with 514nm / 244 nm laser line as the excitation source. The incident laser was focused on the sample through an optical microscope, and the resolution is 1 cm^{-1} .

2.2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) analysis was performed on the surface of the samples using a Kratos-Axis spectrometer with Dual-Anode Al K_{α} (1486.6 eV) X-ray radiation (150 W, 15 kV and 10 mA) and hemispherical electron energy analyzer. The base vacuum of the chamber is 2×10^{-9} Torr. The survey spectra in the range of 0-1100 eV were recorded in 1 eV step followed by high-resolution spectra over different element peaks in 0.1 eV step, from which the detailed composition was calculated. Curve fitting was performed after a Shirley background subtraction by non-linear least square fitting using a mixed Gauss/Lorentz function. To remove surface contamination layer, Ar ion bombardment was carried out for 480 seconds using a differential pumping ion gun (Kratos Macro Beam) with an accelerating voltage of 4 keV and a gas pressure of 1×10^{-7} Torr.

2.2.5 Photoluminescence (PL) spectroscopy

Photoluminescence spectroscopy is one of the most direct and widely used experimental probes for the electronic band structure of semiconductors. A photon energy greater than the bandgap is absorbed, creating an electron-hole pair that subsequently recombines and emits another photon.

Two different laser excitation sources were used for InN experiments. One is a TRIAX 320 spectrofluorimeter (Jobin-Yvon Co.) with 1 W laser diode (Coherent Co.) at a wavelength of 808 nm as an excitation source (as shown in Figure 2-5). Emitted light was focused on the monochromator, monitored at the exit slit by a photon-counting R5108 photomultiplier tube.

Figure 2-5 Schematic graph of PL set up.

Another is a continuous wavelength Ar^+ laser ($\lambda=488 \text{ nm}$) (Omnichrone Model 170-B) at room temperature and under a liquid nitrogen environment. The fluorescence was analyzed with an OREL Model 77200 monochromator, and the signal was detected by an OREL SP7 1905 InGaAs detector (600-2000 nm) and finally amplified by a Stanford SR830SP lock-in amplifier.

2.2.6 Spectrophotometer

Transmittance was measured by UV-Vis spectrophotometer (HP 8453, 190nm ~ 1100nm) and UV-Vis-NIR spectrophotometer (PerkinElmer Lambda 900, 200 ~ 3500 nm). The transmittance was automatically calibrated against a bare quartz substrate as a reference sample, and the absorption coefficient was obtained from the transmittance. Absorption coefficient α was calculated from the relation:

$$T = A \exp(-\alpha d) \quad (2.7)$$

where T is the transmittance of thin film, A is a constant and d is the film thickness.

2.2.7 Electron emission

❖ Field emission

When an electric field is directed towards a solid at room temperature, electrons that are emitted from the solid are called field emission. Energy diagram of field emission is shown in Figure 2-6. An electron at an energy of E_i is free to move inside the solid. When it reaches the surface, it tries to move away and out of the surface. The solid then lacks a negative charge and the resulting Coulomb force attracts the electron back into the solid. The potential energy is Φ_s . If an electric field directed towards the emitting surface, the electron potential is bent as additional potential energy Φ_e . The total potential energy is Φ_t . The solid and vacuum is now separated by a triangle barrier. The tail of the electron wave function is able to penetrate to the vacuum and hence tunneling occurs.

Figure 2-6 Energy diagram of field emission.

In this work, the field emission studies were carried out in a chamber having a vacuum of $\sim 8.0 \times 10^{-7}$ torr at room temperature. Sapphire substrate with InN nanofingers was clamped on a Teflon plate using silver paste to act as cathode and ITO

glass as anode. The thicknesses of the spacer were 50 and 100 μm , and the sample area was 12.5 mm². A voltage was applied between the anode and the cathode to supply an electric field sweeping from 300-1600V. The emission current was monitored by a Keithley 6517A electrometer. A CCD camera was used to record the spatial distribution of the emission sites.

❖ Secondary electron emission (SEE)

The measurement of SEE yield was carried out in a SEM (JEOL-JSM-5910LV) by measuring the specimen current after biasing the specimen in two separate experiments, as shown in Figure 2-7. The sample to ground current was measured by a low noise current preamplifier (Stanford Research Systems, SR570). The electron beam was generated by the electron gun in the SEM system. The beam current was measured by a Faraday cup attached in the SEM system and fixed to 100 pA by adjusting the spot size for different electron beam energies. In the first measurement, the sample was positively biased (+ 45V) and the sample to ground current (I_+) was measured for a selected primary beam energy. The positive bias is adequate to ensure complete electron collection so that I_+ is the total incident electron current. Subsequently, the sample to ground current (I_-) was measured with the sample biased at negative voltage (- 45V) in order to repel the SEs from the sample's surface. The difference in sample to ground current measured under the different biasing is taken as the SEE. The expression is given by equation 2.8.

$$\gamma = (I_+ - I_-) / I_+ \quad (2.8)$$

Figure 2-7 Schematic set up diagram for measuring secondary electron emission yield.

CHAPTER 3 ALUMINUM NITRIDE

In this chapter, the influences of nitrogen ion energy, substrate temperature and substrate bias on the structural and mechanical properties of the AlN films were presented. The tutorial nature of the chapter will provide the framework necessary to discuss the results on InN and GaN to follow. Parts of the work have been published [66-67].

3.1 Introduction

AlN, as a III-V compound material, exhibits the widest band gap of all III-V semiconductors. It was first synthesized in 1877, but it was not until the middle of the 1980s that its potential for application in microelectronics was realized. It is widely used in many applications, including high temperature refractory ceramics, and is an excellent alternative protection material against wear and corrosion [68], and is a promising material for use in surface acoustic wave (SAW) devices [69-70]. The advanced features of AlN are into direct and wide band gap (6.2 eV), high thermal conductivity (~260 W/mK at 300 K), high mechanical properties (hardness of ~20 GPa), high electrical resistivity ($10^9 \sim 10^{11} \Omega\text{m}$), fast sound propagation (~9 km/s) and relatively high piezoelectric constants [4,11,71-74]. Currently there is much research into developing LED to operate in the ultraviolet using the GaN based semiconductors and the AlGaIn alloy. An inefficient LED emission at 210 nm has been reported recently [75].

As a result of these extensive applications, the composition, crystal quality, and orientation of AlN thin films have been investigated by ion-beam assisted sputtering

[76-80], PLD [81-83], arc deposition [46, 84], MOCVD/MOVPE [75, 85, 86] and MBE [87-88]. However, the system of FCVA is simpler and more economic, and the growth temperature by FCVA is much lower than that by MOCVD. The high thermal stability of NH_3 necessitates the use of high substrate temperatures, typically more than 550 °C for InN and above 900 °C for GaN and AlN, during the growth by MOCVD [89].

It has been concluded that substrate bias, incidence ion energy as well as angle and the ratio of argon/nitrogen play an important role in the evolution of preferential orientation of *c*- or *a*- axis [13, 85, 90, 91]. The intrinsic and thermal stresses of AlN deposited on Si were also affected significantly by the deposition parameters [92]. The surface roughness is one of the important parameters, especially when the AlN films are employed for SAW applications. The smoothest AlN thin film, to the best of our knowledge, is *c*-axis-preferred prepared by reactive sputtering method [93], the RMS of which is 0.29 nm.

3.2 Experimental details

The aluminum plasma was produced from the arc spots on the aluminum cathode. A radial electric field is introduced in the system via the torus duct, coupled with a curvilinear axial magnetic field on the curved toroidal duct that forms a crossed electric-magnetic field filtering assembly. Nitrogen ions were generated by a direct current linear ion source (2.5×20 cm) equipped in the deposition chamber. Three series of samples were prepared to study the effects of (1) N ion energy, (2) substrate temperature (T_s), and (3) bias (B_s) on the film quality. The nitrogen gas flow rate was optimized to be 55 sccm during films deposition process. The discharge voltage,

filament current and ion current were 30 V, 7 A and 45-55 mA, respectively. Substrates were cleaned in ultrasonic baths of acetone and deionized water, and then blown dry with N₂. Substrate temperature was measured with a thermocouple placed between the substrate and the substrate heater. Si (100) wafer and quartz substrates were fixed mechanically on a substrate electrode. The deposition chamber was pre-evacuated to 1.1×10^{-5} Torr by a rotary and cryo-pump system and backfilled with the required gases (argon) during film growth. Argon gas was introduced into the target region to assist the generation and the stability of arc. The samples were placed in the center of the chamber.

3.3 Results and discussion

3.3.1 Structure characterization

XRD and AFM were used to characterize the structural properties of the AlN films. Figure 3-1 (a), (b) and (c) are the XRD patterns of AlN films on Si (100) as a function of N ion energy, T_s and substrate bias, respectively. The diffraction patterns showed an absence of AlN peaks for the films deposited at the N ion energy below 300 eV at RT and without bias. This indicated that the AlN films were either amorphous in nature or had nano-crystalline phases, which were too small to yield a diffraction pattern. Our previous work ^[94] disclosed that AlN films deposited by the FCVA without ion-assisted deposition was amorphous. However, for the films deposited at high N ion energy of 400 eV and above, a weak peak located at 36.5° appeared, which was identified as AlN (0002), suggesting the presence of nanocrystallite AlN. Hence, nitrogen ion energy plays an important role in the crystallization of AlN films due to the energy-induced chemical incorporation between Al and N atoms.

Figure 3-1 XRD of AlN films as a function of (a) N ion energy: 200, 300, 400, and 650 eV, T_s : RT, B_s : without bias; (b) T_s : 150, 250 and 350 °C, N ion energy: 400 eV, B_s : without bias; and (c) B_s : 50, 100, and 200 V, N ion energy: 400 eV, T_s : RT.

In order to further improve the crystal quality of the AlN films, substrate temperature and bias were employed individually for investigation. When the T_s was in the range of 150 ~ 350 °C (the nitrogen ion energy was kept 400 eV and without bias), AlN films showed ($10\bar{1}0$) preferential orientation. A weak XRD peak centered at 33.2 °, corresponding to ($10\bar{1}0$) plane of AlN, was observed for films deposited at 150 °C. When T_s was raised from RT to 350 °C, the ($10\bar{1}0$) peak was enhanced. The increase of T_s resulted in the increase in the intensity of the AlN ($10\bar{1}0$) peak, and a decrease in the full width at half maximum intensity (FWHM) of the peak, indicating a continuous

increase in the crystalline quality. Similarly, the films showed high a -axis orientation which corresponded to AlN (10 $\bar{1}$ 0) plane when negative bias of 50-100 V was applied to the substrate. The N ion energy and the T_s were 400 eV and RT, respectively. The films prepared at -50 V exhibited the strongest AlN (10 $\bar{1}$ 0) peak. A marked decrease of the XRD peak intensity of AlN (10 $\bar{1}$ 0) plane was observed with any further increase of negative bias beyond 50 V. When the negative bias was employed, positively charged ion species were attracted to the negative potential substrate. At lower bias voltages, the adatom mobility was enhanced owing to the increase in momentum transfer from the bombarding positive ions. However, with further increase of the negative bias voltage, the effects of re-sputtering, defect formation, and ion entrapments were pronounced, which resulted in the reduced crystalline quality. By using Scherrer's equation (see equation 2.6), the average crystallite size calculated from (10 $\bar{1}$ 0) reflection was ranging from 24 to 44 nm.

Figure 3-2 gives a typical AFM image of the AlN film, showing the smooth surface composed of regular granular grains. It should be mentioned that all the films exhibited very smooth surface at various deposition conditions. The analyzed RMS roughness was in the range of 0.1 to 1.6 nm. In this aspect, I-FCVA deposited a -axis preferred AlN films with smooth surface may be suitable for SAW application, especially for transverse mode SAW. This is because, for SAW applications, the surface acoustic wave is propagating on the surface and the energy is concentrated almost within the wavelength from the surface to the inside. Thus, the surface roughness of the film is required to be less than 30 nm in general [35, 95].

Figure 3-2 Typical AFM image of AlN thin films.

3.3.2 Optical characterization

All the deposited AlN films are transparent and uniform as illustrated in Figure 3-3 and 3-4. The average transmission of the films is higher than 85% in the Vis-NIR range. It was found that the transmittance cutoff of the AlN films had slightly red shifted with an increase of the N energy from 200 to 650 eV. Figure 3-4 shows the transmittance spectra of AlN films deposited at various T_s . For the direct-transition semiconductors, the optical absorption coefficient α of AlN is expected to obey the dependence on photon energy $h\nu$ and bandgap energy E_g , $\alpha^2 = h\nu - E_g$. The bandgap E can be determined from the interception with the energy axis by extrapolating the linear portion to the energy axis. The absorption coefficient α was calculated from the relation, $T = A \exp(-\alpha d)$, where T is the transmittance of thin film, A is a constant, and d is the film thickness. The constant A is approximately unity, as the reflectivity is negligible and insignificant near the absorption edge. The determined band gap value of the AlN films was about ~6.0 eV.

Figure 3-3 Transmittance spectra of the AlN films deposited at room temperature and without bias, the N ion energies were 200, 300, 400 and 650 eV respectively.

Figure 3-4 Transmittance spectra of the AlN films deposited at various T_s . (Nitrogen ion energy is 400 eV, without bias.)

3.3.3 Raman characterization

It is well known that the Raman effects in solids originate from inelastic scattering of light by crystal lattice vibrations. A change in Raman peak characteristics can be induced by many internal and external parameters such as stress, grain size, temperature and crystallinity. AlN usually crystallizes in wurtzite structure. The factor group analysis at the Γ point^[96] shows that there are six Raman-active phonons modes in hexagonal structure crystals: $\Gamma_{vib}^{opt} = A_1 + 2B_1 + E_1 + 2E_2$. All modes are Raman active except for the silent B_1 mode. Therefore, the Raman active modes are $A_1(\text{LO})$, $A_1(\text{TO})$, $E_1(\text{LO})$, $E_1(\text{TO})$, $E_2(\text{high})$ and $E_2(\text{low})$. Many theoretical and experimental works on AlN have been reported during the past decades^[97-100]. However, the results were inconsistent and are open for debate. The Raman signal of AlN overlaps with that of Si when the sample is excited by visible laser. However, the Raman signal of Si is suppressed under the UV laser due to the absorption. UV Raman was therefore used for the study.

Figure 3-5 (a), (b), and (c) are the UV Raman spectra of the AlN thin films deposited at various parameters. A strong and broad peak at $\sim 885 \text{ cm}^{-1}$ assigned to AlN $A_1(\text{LO})$ was observed from all the films. The intensity of the $A_1(\text{LO})$ peak increases significantly with increasing N ion energy, indicating the enhanced crystallinity, and this is in agreement with the XRD result. As the T_s increases, not only is the intensity of $A_1(\text{LO})$ enhanced, but also the $E_2(\text{high})$ mode ($\sim 680 \text{ cm}^{-1}$) as shown in Figure 3-6 (b). However, the $E_2(\text{high})$ mode was not detected in the films deposited under negative bias as shown in Figure 3-6 (c). According to the selection rule, $A_1(\text{LO})$ and E_2 can be observed in back scattering $z(x,-)z$ configuration, which is widely employed. In fact the selection rule is for ideal crystals. However, the deposited films are not ideal

Figure 3-5 UV Raman spectra of the AlN thin films on Si(100): (a) N ion energy: 200, 300, 400 and 650 eV, T_s : RT and without bias; (b) T_s : RT, 150, 250 and 350 °C, at 400 eV and without bias; and (c) B_s : -50, -100, and -200V, at RT and 400 eV.

crystals, so the selection rule will relax which will result in the absence of Raman active modes.

Due to the short wavelength of the UV source, the excited phonons are from shallow surface. Therefore, the surface signals, such as oxygen (1550 cm^{-1}) from the atmosphere were more pronounced. In addition, the sharp peak at 2330 cm^{-1} corresponds to the non-bonded trapped molecular N_2 and/or N_2 species adsorbed on the surface of the film. Oxygen and nitrogen related peaks were detected from all the samples. However, for the films deposited at higher T_s , the nitrogen related peak increased. Furthermore, a peak at $\sim 1260\text{ cm}^{-1}$ was observed from the spectra of the film deposited at $350\text{ }^\circ\text{C}$ and with negative substrate bias. It was associated with $-\text{N}=\text{N}-$ groups and/or Al bonded to non-intentional superficial contaminations ^[101]. Additional 1430 cm^{-1} signal could be identified from the films deposited with bias, which was also $-\text{N}=\text{N}-$ related. Therefore, the detected nitrogen could also be related to the deposition conditions, which may lead to the high content of nitrogen present in the films.

3.3.4 Mechanical characterization

The mechanical property of the AlN films was studied in terms of stress (strain). Stresses in thin films consist of two major components, namely thermal and intrinsic. Thermal stress results from the different thermal expansion coefficients of films and substrate, and is normally induced by difference in deposition and operation temperatures. Intrinsic stress sometimes referred to as intrinsic, residual or structural stress, arises from incomplete structural-ordering processes during film growth as well as from film impurities. The stresses of the AlN films were calculated using Stoney's formula, (equation 2.2).

The evaluated stress as a function of T_s and bias is shown in Figure 3-6. With an increase in the film deposition temperature, the mobility of the atoms in the films increases greatly and enhances surface sputtering and diffusion of ion beam-induced point defects towards the film surface. The atoms can easily diffuse from one position to other. Then, the atoms can adjust the position and shift outside to a more equilibrium position, which can release the strain in the films. This results in the decrease of the internal stress at higher deposition temperatures. However, the increase of substrate bias results in higher ion energy, thus resulting in larger atomic peening effect and bigger internal stress. When the substrate bias is increased further, more energy is transferred to the atoms by the bombardment of the energetic ions. The effect of stress relaxation becomes more pronounced and leads to smaller internal stress.

Figure 3-6 Dependence of internal stress in the AlN films at T_s of RT, 150, 250 and 350 °C at 400 eV and without bias; and with B_s of -50, -100 and -200V at RT and 400 eV.

Compressive stress is generated by energetic ion impacts^[102]. The variation in the stress is expected to arise from the stress relief process. The relief process is strongly determined by the ease with which the material flows (i.e. the yield stress). The yield stress, σ_y , is related to the indentation hardness, H , by the formula:

$$H \approx 3\sigma_y \quad (3.1)^{[102]}$$

The films with lower hardness sustain smaller residual compressive stress. The hardness of the films depends on the bonding and chemical structure of the material and was correlated with the stress. The hardness could be as high as 16 GPa^[67] due to the bond contraction and lone pair interaction at nitride surface^[103].

3.3.5 Chemical composition

XPS measurement was employed to examine the composition of the deposited films. The typical XPS spectra of AlN films deposited on Si at N energy of 400 eV, RT/without bias, are shown in Figure 3-7. The as-deposited film exhibited strong peaks related to the presence of atmospheric contaminations C and O. After Ar⁺ etching for 10 minutes, residual carbon was completely removed while some oxygen can still be detected. The N 1s peak became the strongest in the spectra and Al 2p and Al 2s peaks were more intense.

As a result of electrical charging of the samples during analysis, there was some shift in the binding energy of the spectra of the as-deposited films. As a reference, the C 1s line relative to hydrocarbon contamination was set as 285 eV with respect to the Fermi level. The peak of the examined film was centered at 287 eV. Therefore, a correction of 2 eV was needed for the spectra. Figure 3-8 (a) and (b) show the XPS spectra for the corresponding Al 2p and N1s core level of the same sample

Figure 3-7 Typical XPS spectra of AlN film deposited at 400 eV at RT and without bias.

after energy shift correction. The contribution as shown in Figure 3-8(a), centered at about 74 eV, was assigned to Al $2p_{3/2}$ in Al-N bonds. The value is within the wide range of reported values from 73.1 to 74.7 eV ^[104-106]. The contribution of N 1s core level as shown in Figure 3-8 (b) of the same sample, centered at 396.9 eV was assigned to N-Al bonding which is in good agreement with the literature values and was considered to have a spread of 0.4 eV ^[45, 107].

The bonding states are further investigated by fitting analysis from the spectra after 10 minutes sputtering, as they are composed of several components corresponding to different chemical states, as shown in Figure 3-9. The major contribution that resulted from Al 2p peak (Figure 3-9(a)) deconvolution is 74.1 eV, which is consistent with that of Al 2p in Al-N bonds, whereas the small peak at a higher binding energy is assigned to Al in oxide-like bonding ^[108]. In the N s1 spectra (Figure 3-9 (b)), the binding energy at 397.1 eV is attributed to the Al-N bond, which

Figure 3-8 (a) Al 2p and (b) N 1s core-level spectra of film deposited at nitrogen ion energy of 400 eV, RT and without bias.

Figure 3-9 (a) Al 2p, (b) N 1s and (c) O 1s spectra (raw and deconvolution data) from a 10 minutes Ar sputtering surface.

is lower than that of the N-N bond in gas at 399.5 eV ^[109]. Figure 3-9(c) shows the O 1s spectra, the peaks position at 532.4 eV and 531.5 eV can be assigned to O-O and Al-O-N respectively ^[108], indicating the oxygen is partially physically adsorbed or

trapped within the coating except bonding with Al. The data for selected AlN thin films deposited at different conditions are summarized in Table 3-1.

Table 3-1 Composition of AlN prepared at various substrate temperatures as determined by XPS (after 10 min etching).

Substrate temperature (°C)		RT	350	RT
N ₂ ⁺ energy(eV)		400	400	400
Bias (-V)		-	-	-200
Atomic Conc %	O 1s	13.81	19.67	10.44
	N 1s	44.02	46.09	46.89
	Al 2p	42.17	34.24	42.69

In summary, oxygen was contained in all films at around 15 at.%. All the films were nitrogen rich, which was in agreement with the Raman results. Al and N were in major part involved in nitride-like bonds.

3.3.6 Discussion

Most of AlN films prepared by CVD, MBE, PLD, and reactive sputtering are c-axis oriented [43-46, 83-87]. There are only a few reports on a-axis oriented films for transverse SAW device [70-71, 84]. In general, preferred orientation was due to the energy variation during the deposition processes. The AlN film prepared at 350 °C showed highly (10 $\bar{1}$ 0) preferred orientation. Meanwhile, the films prepared with a negative substrate bias also show (10 $\bar{1}$ 0) preferred orientation. Similar phenomenon was observed by Takikawa *et al.* [84] using shielded reactive arc deposition.

Nucleation of AlN is formed along {0001} and {10 $\bar{1}$ 0} planes. The nucleation sites on the substrate are random at the initial stage of film growth. Only the nuclei

with growth direction normal to the substrate surface are able to grow bigger. Other nuclei grow at inclined angle so that their growth is stopped by other planes. This geometrical selection causes preferential orientation. Figure 3-10 shows the crystalline lattice structure of AlN^[44]. In this structure, each Al atom is surrounded by four N atoms, forming a distorted tetrahedron with three Al-N_(i) (*i* = 1, 2, 3) bonds named B₁ and one Al-N₀ bond in the direction of the *c*-axis, named B₂, where the bond energy of B₁ is relatively larger than that of B₂. The plane (10 $\bar{1}$ 0) is composed of bond B₁, while planes (0002) and (11 $\bar{2}$ 0) consist of both B₁ and B₂ bonds. The formation energy required for the film growth along the planes of (0002) and (11 $\bar{2}$ 0) are relatively large. Therefore, (10 $\bar{1}$ 0) plane should be dominant because it is the closest packing and low-energy configuration of the hexagonal structure. The (10 $\bar{1}$ 0) orientation could be enhanced if the distance between the target and the substrate is sufficiently long^[13, 44], which can be understood in the viewpoint of extended periodic bond chain (PBC) theory^[13]. The collisions of Al and N atoms occur in the space between the target and the substrate. The Al-N dimers will be formed and deposited on the substrate when the distance is long. The two kinds of growth units, atoms (Al, N) and dimers (Al-N), result in preferential orientation of (0001) and (10 $\bar{1}$ 0) respectively, as depicted in Figure 3-11. For our I-FCVA system, the distance between the Al target and the substrate is much longer than the mean free path of the Al atom. Therefore, the (10 $\bar{1}$ 0) orientation is enhanced.

Figure 3-10 The crystal structure of AlN [44].

Figure 3-11 Schematized depositions of growth units of atoms N, Al on hard deposition sites in (a) 001 and (b) 100 prism, and a growth unit of dimer Al-N on hard deposition sites in $(\bar{a})$ 001 and $(\bar{b})$ 100 prism [13].

3.4 Summary

The AlN films prepared by the I-FCVA can be in crystalline or amorphous structure with smooth surface. The RMS values of all AlN films were less than 2.0 nm. All films were transparent and uniform and exhibited compressive stress. The internal stress relaxed at high T_s and/or with negative substrate bias. Furthermore, the studied AlN films were in near stoichiometric Al-N bond from XPS. Therefore, I-FCVA is a promising technique for obtaining smooth AlN films with a -axis preferential orientation which should find application in SAW devices and in other areas.

The successful fabrication of AlN thin films using I-FCVA paves the way for the two highly important III-nitride semiconductors, InN and GaN, which will be discussed in the following Chapters.

CHAPTER 4 INDIUM NITRIDE

In this chapter, the fabrication and characterization of InN thin films are presented. Two types of In sources were employed to prepare InN films. The effects of nitrogen ion energy and T_s on the structural and optical properties of InN films have been investigated. Most importantly, we have successfully fabricated InN nanostructures using I-FCVA by tuning the deposition parameters. We have also demonstrated, for the first time, the efficient field emission properties of InN nanostructures.

4.1 Introduction

InN is an important member of the III-nitrides compound semiconductor family. InN has a narrow bandgap and an electron saturation velocity ideally suited for application in telecommunication devices. It is one of the best alternative materials for the new generation of high power, high frequency and high electron mobility transistors. However, it has not received the attention it deserves until the last few years. There are difficulties in the preparation of high quality samples because of its thermal instability at conventional thin film growth temperatures and the equilibrium vapor pressure of nitrogen over the InN, which is of several orders higher than that over AlN and GaN. Recently, significant improvements in the growth techniques greatly accelerated the research interests in fabricating high quality single crystalline InN films and InN nanostructures. However, the quality is still inadequate for device applications. Moreover, all bandgap values were derived from the optical absorption until the observation from photoluminescence from InN films in 2001. Recently, the

band gap of InN was reported experimentally and theoretically to be 0.6-0.65 eV^[110], 0.7-0.8 eV^[48, 51], 0.9 eV^[49] and around 1.1 eV^[50] by both photoluminescence and optical absorption data, which conflicts with the previously well-accepted value of ~1.89 eV, making the exact value of band gap ambiguous. In 1984, Tansley and Foley^[111] found a maximum RT electron mobility of 2700 cm²/Vs with carrier concentration of 5.3×10¹⁶ cm⁻³ in films grown by RF sputtering. This result indicated the potential application of InN for high mobility FET devices. InN is also predicted to be a potential material for low-cost solar cells with high efficiency, optical coatings, various types of sensors^[4] and good plasma filter material in thermophotovoltaic systems. According to theoretical calculations^[112], InN has excellent stable and transient electron transport properties. The cut-off frequency of an InN field effect transistor can be higher than 400 GHz. The possibility of a low bandgap for InN will expand the energy spectrum of III-nitride alloy system, which significantly spanning their applications. Furthermore, InN could be a good field emitter material for vacuum devices.

The reasons of the dramatically reduced bandgap include the incorporation of oxygen and the Burstein-Moss shift^[113-116]. Besides, Shubina *et al.*^[117, 118] has demonstrated that the origin of the deviations in experimental data for the InN bandgap is most likely related to the precipitation of indium in the metallic phase that leads to additional optical losses associated with the Mie resonances in metallic clusters. Furthermore, InN samples grown by different techniques often display different material properties, which complicates the investigation of InN. Up to now, the actual bandgap of InN and the reasons of narrowing are ongoing debate. The progress in the development of InN-based hetero-structures and devices is still in the primary stage.

The progress in improving the InN film quality indicates that InN film itself almost approaches the application for practical devices.

It is well known that the growth of InN is one of the most difficult tasks among the III-nitrides because the equilibrium vapor pressure of nitrogen over the InN is much higher than that of other III-nitrides. On the other hand, the absence of both lattice and thermal coefficient matched substrates makes the growth of high quality InN crystals difficult. Sapphire substrates are commonly used for InN growth, although the lattice constant difference between InN and sapphire is as large as 25%. Consequently, various buffer layers have been used to improve the crystal quality of InN. In addition, among III-nitride nanostructures, InN is attractive to its narrow band gap. As a result, high quality single crystal InN with narrow band gap, fabricated by reactive evaporation, sputtering ^[119-121], MOCVD ^[122-125] MBE ^[117,126,127], and other methods ^[113,128], were reported. However, very few investigations have focused on InN nanostructures and its field emission property. Up to now, the growth of InN nanostructures has been carried out by vapor-solid (VS) ^[129], vapor-liquid-solid (VLS) ^[130] and solvo-thermal ^[131] approaches. There are also some reports on the synthesis of InN nanostructure through conventional film growth route, by molecular beam epitaxy (MBE) ^[132] and metal-organic vapor-phase epitaxy (MOVPE) ^[133]. Therefore, the studies of hetero-growth of InN thin films and nanostructures are very important.

4.2 Experiment

The growth procedure of InN is similar to that of AlN. The difference is the use of a RF ion beam source instead of a dc linear ion beam source. Indium has a low melting point of 157 °C which makes it not suitable as a target in the FCVA as the

entire target will melt during the arcing process. In order to overcome such a problem, In target was contained in a metallic cup. To test the idea, indium pellets were first used as it could be easily filled in a metal cup which acted as cathode. However, we found out later that the InN films were severely contaminated with oxygen as it could be easily trapped in the target during the heating and melting process. Thus, pure indium disk target (50 mm diameter, 99.99%) was then used. The cup was shielded with a boron nitride plate and mounted onto a water-cooled copper plate. Energetic nitrogen ions were generated by the RF ion beam source. RF power was optimized at 250 W. Arc current was set at 70 A. A two-step growth process was employed where a ~40 nm-thick InN buffer layer was first deposited at a low temperature (160 °C) and then followed by InN layer growth at a high temperature. The two-step growth process was expected to ensure the fabrication of high-crystal quality InN films on Si. Two series of samples have been deposited: (1) The N ion energy was adjusted in the range of 50~300 eV with a constant ion current of ~30 mA and (2) T_s was varied from 250 to 475 °C at N ion energy of 300 eV.

4.3 Results and discussion

4.3.1 Indium pellet target

In this series, indium pellets were melted in an Al cup which was used as a target. The samples were prepared under various T_s (250 °C to 350 °C). The N ion energy was kept constant at 300 eV and the working pressure was around 1.4×10^{-4} torr. All the samples exhibited weak crystallinity. Two weak (0002) and (10 $\bar{1}$ 1) planes of α -InN films were observed for the films deposited at T_s of 350 °C.

The T_s -dependent PL emissions of the InN films at 77 K are shown in Figure 4-1 (a). All the samples exhibited a broad luminescence band ranging from 0.95 to 1.85 eV. For the films deposited at 350 °C, PL showed the strongest intensity and the peak was centered at 1.30 eV. The PL intensity significantly decreased when T_s was reduced from 350 to 250 °C. With the increase of growth temperature, the PL peak became more intense and narrower due to the improvement in crystallinity. It should be mentioned that the PL peak position did not change with T_s . As shown in Figure 4-1 (b), the PL peak position remains at 1.3 eV when measured at 77 K. The FWHM of the PL was slightly increased from 240 meV to 270 meV when the temperature was increased from 77 K to 300 K.

It is well known that the bandgap energy of most semiconductors generally decreases with increasing temperature due to the thermal dilation of crystal lattice and the electron-phonon interactions. However, this dependency is smaller in nitride III-V compound semiconductors. The amorphous nature was considered to be the reason for the broad band emission.

Figure 4-1 (a) PL spectra measured at 77K of the InN films prepared at different T_s . (b) PL spectra at 77K and 300K for the sample deposited at 350 °C.

XPS measurement was used to evaluate the composition of the InN films. Figure 4-2 shows the typical XPS spectra of the InN film deposited at 350 °C. The presence of oxygen could be observed from both the spectra before and after 8 minutes Ar^+ etching, indicating that the film was not stoichiometric in In and N. The elemental composition of InN films deposited at various T_s are presented in Table 4-1. The films could be summarized in the form of InO_xN_y . The enrichment of oxygen in the films was suspected to be from the melted target. Therefore, the PL emission of 1.3 eV is not from InN but from InO_xN_y , where x is around 40 %. It was suspected that the high content of oxygen originated from the process of target preparation using In pellets. In order to improve the quality of the InN films, a pure In target was used in the following studies.

Figure 4-2 Typical XPS spectra of InN film deposited 350 °C (a) before etching and (b) after etching.

Table 4-1 Elemental composition of InN films deposited at various T_s .

Substrate temperature (°C)		250	320	350
Atomic Conc %	O 1s	46.65	47.96	44.06
	N 1s	6.55	9.57	7.40
	In 3d	46.80	42.47	48.06

4.3.2 Pure Indium target

The XPS measurement for the InN films prepared using pure In target is shown in Figure 4-3. After etching, about ~10 at.% oxygen could still be detected. The typical atomic density for In, N and O is 52.1%, 31.9% and 16% respectively after sputtering. However, the oxygen component is much lower than that of the In pellets. Therefore, several series of samples using pure In target were prepared and studied.

Figure 4-3 Typical XPS spectrum of the InN film after etching.

4.3.2.1 Effect of substrate

The growth morphology of thin films is strongly affected by the lattice mismatch between the film and the substrate. The substrate nature influences the early stages of film development, which in turn determines the further evolution of morphology and texture. The film growth proceeds to minimize the energy of the system (the growing film and the substrate surface), which is similar to any other physical processes. The energy of the system is usually composed of three terms: the free surface energy of the substrate (E_s), the surface energy of the grown film (E_f) and

the interface energy between the substrate and the deposited film ($E_{f/s}$), which could be evaluated by contact angle. The schematic diagram of interface energy vs contact angle is shown in Figure 4-4.

In general, large mismatches either produce three-dimensional growth (Volmer-Weber (V-W) growth) or start with layer by layer growth and change to three-dimensional (3D) after a critical thickness (Stranski-Krastonov (S-K) growth), as shown in the Figure 4-5. The film growth takes place in different modes depending on the competition between E_s and $E_f + E_{f/s}$. If $E_s \gg E_f + E_{f/s}$, it is energetically

Figure 4-4 Illustration of contact angle vs. interface energy

Figure 4-5 Schematic diagrams of three types of growth mode.

favorable for the deposited material to cover the entire substrate (Frank van der Merwe growth mode) like in the lattice-matched case. Otherwise, the deposited material forms 3D islands on the substrate to minimize the surface energy of the deposited material as in lattice mismatch system. The growth mode of S-K or V-W depends on how much $E_f + E_{f/s}$ is larger than E_s .

Figure 4-6 gives an example of large lattice mismatch case of InN on sapphire. Experiments were done by varying the deposition time from 1 minute to 20 minutes. The deposition was kept at constant nitrogen ion energy of 300 eV, and the substrate temperature was 350 °C with nitrogen flow rate of 30 sccm. Surface morphology of each samples was recorded using SEM. Random nucleation occurs at the very beginning stage of the film growth, where there exists very large lattice mismatch between the substrate and the growing film. During 3D island or V-W growth, small clusters are nucleated directly on the substrate surface. The clusters then grow into islands by ripening /coalescence. Figure 4-6 (a) shows the InN surface deposited for only 1 minute. The surface is covered with small grains. The driving force for coalescence is the reduction in surface energy causing the islands to become taller and rounder. After 5 minutes, the surface was covered with larger grains and rougher surface (Figure 4-6 (b)). However, 5 more minutes later (Figure 4-6 (c)), some of the grains grew significantly due to the nuclei coalescence. This is probably due to the collapse of the previously formed islands upon each other. As islands continue to coalesce, holes and channels are left in an otherwise continuous film. These voids are eventually filled by secondary nucleation and island growth occurs. Hence, a further 5 minutes deposition led to a uniform distribution of grain size. The films grown under this condition were not dense, which would otherwise affect the quality of the film.

Figure 4-6 SEM images of InN on sapphire deposited for (a) 1, (b) 5, (c) 10, and (d) 20 minutes.

From the view point of lattice mismatch, InN on Si(111) should exhibit better crystallinity because the lattice mismatch of InN/Si(111) (8 %) was smaller than that of InN/sapphire (0001) (25 %), whilst there was no lattice coherent between InN and quartz. Figure 4-7 shows the typical SEM images of the InN thin films deposited on quartz, sapphire (0001) and Si (111) respectively. The experimental parameters were as same as those in Figure 4-6. SEM images indicated the surface morphology was strongly dependent on the substrate. All the films showed a rough surface with irregular grains. InN/quartz thin films showed non-uniform granular grains with many voids. InN/sapphire (0001) thin films exhibited rough surfaces with spindly grains. It was considered after the first stage nucleation, the grains grew laterally. InN/Si (111) thin film looked rougher with irregular shapes. The grain boundaries were easily

Figure 4-7 Plane-view SEM images of the InN on (a) quartz, (b) sapphire (0001) and (c) Si (111).

identified from all the samples.

However, it has been suggested that the difference in interface (interfacial layer) of InN/substrates surface and the oxygen incorporation might affect the films crystal quality ^[113]. An intermix layer of AlInN alloy at InN/Al₂O₃ interface (Al was originated from the sapphire) could reduce the lattice mismatch of the film with respect to the substrate, leading to an improvement in the crystallinity ^[134]. On the other hand, the formation of interfacial layer of SiN_x layer at InN/Si interface might degrade the crystal quality of InN.

It is well known that 3D growth could be partly transformed to 2D growth by insertion of an InN layer grown at low temperature (LT). The LT-InN buffer layer provides the high density nucleation centers and promotes the lateral growth of the main layer. Si(111) has the smallest lattice mismatch among Si, sapphire (0001) and quartz substrates. Thus, two-step growth method is employed on Si (111) for all the prepared films.

4.3.2.2 Effect of N ion energy

In this series, samples were prepared at 420 °C after the growth of LT InN layer. XRD spectra of InN thin films deposited by varying the N ion energies from 50 to 200 eV are shown in Figure 4-8. Six intense XRD peaks located at 31.36, 33.15, 43.25, 57.01, 61.62, and 65.4° along with two weak bands peaked at 69.58 and 73.26°, corresponding to (0002), (10 $\bar{1}$ 1), (10 $\bar{1}$ 2), (11 $\bar{2}$ 3), (11 $\bar{2}$ 2), (0004), (20 $\bar{2}$ 2), and (10 $\bar{1}$ 4) of hexagonal InN respectively. Besides the variation in peak intensity, there was no significant change in the peak positions observed for an increase in the N ion energy. In order to study the texture evolution as a function of ion energy, the (0002) and (10 $\bar{1}$ 1) planes were selected for comparison, as depicted in Figure 4-8 (b). As the nitrogen ion energy increased from 50 to 100 eV, the intensity of the (0002) peak increased dramatically by ~6 times so as to peak (10 $\bar{1}$ 1) (see the inset of enlarged peak in figure 4-8(b)) became too small to be identified. However, any further increase in the N ion energy beyond 100 eV led to a drastic decrease in the (0002) peak intensity and an increase in (10 $\bar{1}$ 1) peak intensity. At 200 eV, the (0002) peak became very weak and pronounced InN related (10 $\bar{1}$ 1) peak appeared.

Figure 4-9 shows the full width at half maximum (FWHM) of peaks (0002) and (10 $\bar{1}$ 1) as well as the peak intensity ratio of $I_{(0002)} / I_{(10\bar{1}1)}$ as a function of N ion energy. Both the peak intensity of (0002) plane and the ratio of $I_{(0002)} / I_{(10\bar{1}1)}$ reached maxima at the N energy of 100 eV. The average grain size (D) calculated from the Scherrer formula, was between 13 to 15 nm for nitrogen ion energy below 100 eV, and reduced to 8.5 nm at 150 eV.

Figure 4-8 XRD spectra of the InN thin films deposited at various nitrogen ion energies.

Figure 4-9 FWHM of peaks (0002) and (1011), peak intensity ratio of $I_{(0002)}/I_{(1011)}$ as a function of nitrogen ion energy.

The morphology and microstructure of the thin films are strongly related to the deposition processes. Substrate temperature, working pressure, energy and incidence

angle of the bombarding species are considered to be major deposition parameters. One of the most commonly used models to illustrate the preferred orientation is explained in terms of the surface energy of the film and kinetic factors (for example references ^[135,136]). The surface energy is the difference between the free energy of the surface and that of the bulk ^[137]. For bulk crystals, minimization of the surface energy is the driving force for the evolution of crystalline morphology. Hence, under equilibrium conditions, if there is no influence of epitaxy between the film and the substrate, the film exhibits self-texture and grows with the crystallographic plane of the lowest free energy (i.e., parallel to the surface). However, the properties of the deposited InN films depend strongly on processing parameters due to the non-equilibrium nature.

In the following study, samples were deposited at T_s of 420 °C. The energetic N ion beam was directly aimed at the substrate during deposition. Due to the high energy impingement of the reactive species, equilibrium conditions may not dominate morphological evolution. Since the Si substrate was covered with a layer of native oxide, the nucleation and the early stage growth of LT-InN buffer layer took place in random orientations. Following the early random orientation growth, preferred orientation gradually occurred, and was determined by the minimization of the overall energy of the film as well as the sum of the surface energy and the strain energy. The surface energy is dominant in the early stage of the film growth; but it should not be responsible for film orientation.

It is well known that ionic or atomic bombardment induces intrinsic stress in the films through the “atomic peening” effect, which varies with the bombarding ion’s energy. Therefore, the associated strain energy could also play a role in texture

evolution. Thus, the growing films have a driving force to lower both the surface energy and the strain energy. For films deposited at low-energy, the surface energy fraction of the overall energy was dominant. This might explain the dominance of the (0001) morphology for $V=100$ eV. There was a tendency for hexagonal InN to proceed on the predominant growth of the grains with the (0002) crystallographic plane parallel to the substrate surface under low ion energy deposition environment. This was signified by the rapid increase in the ratio of $I_{(0002)} / I_{(10\bar{1}1)}$ from 2.66 to 59.6 when the nitrogen ion energy increased from 50 to about 100 eV (The ratio of $I_{(0002)} / I_{(10\bar{1}1)}$ is about 2 for random oriented InN powder, PDF: 02-1450.). The surface energy did not change with the increase of bombarding ions energy while the strain energy increased with it ^[138]. The increase of nitrogen ion energy led to the increased atomic peening effect and the enhancement of adatom surface mobility. The bombarding ions knocked surface atoms deeper into the subsurface of the growing films and became trapped in the layer, resulting in microscopic compressive stress. Consequently, surface atoms moved to energetic preferred places resulting in $(10\bar{1}1)$ preferred texture as N ion energy increased to 200 eV. As indicated below, the films grown at 100 eV had the smallest internal stress and those deposited at 200 eV had the largest. This indicated that the surface energy was dominant for the films deposited at low ion energy, and the strain energy was dominant for the films deposited at high ion energy (ie., 200 eV). High (low) surface energy and low (high) strain energy resulted in the (0002) / $(10\bar{1}1)$ preferred orientation growth. Similar texture evolution of AlN deposited by dual ion beam has been reported by Hentzell *et al.* ^[139]. The competition between the surface energy and the strain energy is believed to determine the texturing of InN films with various nitrogen ion energies.

The internal stress was determined by a curvature method. The stress was calculated by Stoney's equation (see equation 2.2). For Si (100) substrate, $E_s = 180$ GPa, $\nu_s = 0.26$. Figure 4-10 is the dependence of the internal stress of InN films on N ion energy. It should be noted that the variation trend of the internal stress was similar to that (10 $\bar{1}1$) peak intensity in comparison with Figure 4-9, indicating the stress had a strong effect on the texture. The intrinsic stress in the film has been proposed to originate from the "atomic peening mechanism" in which reflected atoms bombard the growing film ^[140]. The intrinsic stress in polycrystalline films was depended strongly on the mobility of atoms during film growth ^[141]. For films deposited at low N ion energy, weak ion peening effect resulted in less dense films which release strain by defects, so that the film had smaller stress. The increase of N ion energy led to an increase of the atomic peening effect and enhancement of adatom surface mobility, resulted in the rapid increase of internal stress to ~230 MPa at 200 eV. The measured stress composed of two components: thermal stresses and intrinsic stresses. Because all the films were

Figure 4-10 Dependence of the internal stress of the InN films on nitrogen ion energy.

deposited at the same T_s , the thermal stress should be the same for all films and the influence of the thermal stress could be negligible on the variation of the internal stress. The surface energy did not vary with the energy of bombarding particles while the strain energy increased with it as mentioned above. The particle momentum could be increased and the increase of strain energy with N ion energy in I-FCVA process is similar to that in sputtering process ^[138].

The evolution of surface morphology with N ion energy was examined by AFM. AFM images of InN films prepared at various ion energies are presented in Figure 4-11. Films deposited at 50 eV exhibited regular grains with RMS of 7.5 nm. At 100 eV, the film surface was covered with large grains with RMS of 4.8 nm. The AFM images obtained on the samples deposited at 150 and 200 eV showed the obviously reduced RMS from 8.2 to 2.7 nm (Figure 4-11 (c) and (d)). It is natural to assume that the growth is preceded by the energetically favorable (0002) crystalline planes in the low energy deposition condition. In this case, the surface topology would be rather smooth since the nucleated crystal planes are parallel to the overall growth direction ^[142]. As the N ion energy increases, the impinging of the energetic ions will transfer more momentum energy to the film surface. This increases the mobility of surface adatoms and leads to the increase of the surface roughness. Further increase in the N ion energy results in a deeper penetration of atoms into the film subsurface. Thus the depleted surface area will be partially refilled by the new arriving ions and results in the densification of the film ^[143]. This may contribute to the dense and smooth morphology with smallest RMS for films deposited at 200 eV.

Figure 4-11 AFM images of InN thin films prepared at various ion energies: (a) 50 eV, RMS=7.5 nm; (b) 100 eV, RMS=4.8 nm; (c) 150 eV, RMS=8.2 nm; and (d) 200 eV, RMS=2.7 nm.

Figure 4-12 shows the RT visible Raman spectra of the InN films on silicon substrates. Two intense Raman active optical phonons have been clearly observed and are assigned to $A_1(\text{LO})$ at $\sim 588 \text{ cm}^{-1}$ and $E_2(\text{high})$ at $\sim 490 \text{ cm}^{-1}$ of the hexagonal phase of InN films. At nitrogen ion energies of 50 and 100 eV, a Raman scattering peak at $\sim 449 \text{ cm}^{-1}$ is observed which is attributed to $A_1(\text{TO})$ phonon mode of InN film. The Raman spectra of the InN films grown at lower N ion energy have obvious multi-peak at low-frequency edge of the $A_1(\text{LO})$ phonon. In order to clarify the phonon modes, a mixture of Gaussian and Lorentzian fitting was performed in the range of $400\text{--}700 \text{ cm}^{-1}$ and the results are shown in Figure 4-12 b and Table I. All fitted peaks, $A_1(\text{TO})$ at $\sim 449 \text{ cm}^{-1}$, $A_1(\text{LO})$ at $\sim 588 \text{ cm}^{-1}$ and $E_2(\text{high})$ at $\sim 490 \text{ cm}^{-1}$ are consistent reports of InN films deposited on sapphire and GaAs substrates ^[144,145], except for the feature at

around $564\text{--}570\text{ cm}^{-1}$ (the peak of $\sim 520\text{ cm}^{-1}$ is the signal of Si substrate). According to the selection rule, in Raman geometry configuration of $z(x,-)z$, the $A_1(\text{LO})$ and $E_2(\text{high})$ are active for hexagonal crystalline InN. The presence of $A_1(\text{LO})$ and $E_2(\text{high})$ modes again confirmed the hexagonal structure of our InN films.

For polycrystalline structures, all Raman-active modes might appear. The feature at $564\text{--}470\text{ cm}^{-1}$ could be assigned to $E_1(\text{LO})$ phonon mode, which is similar to the report by Inushima *et al.* [146]. Normally, the broadened peak is due to the reduced phonon coherence caused by the lattice disorder, the formation of nanocrystals or the presence of defects and impurities. The dependence of the structural properties on ion energy is consistent with that afore-mentioned XRD study. Also the existence of microscopic defects, such as metal ion and nitrogen ion vacancies, in the deposited films, will reduce the effective symmetry and certain atomic displacements of

Figure 4-12 Raman spectra of the InN films on silicon substrates prepared at various nitrogen ion energies.

neighboring atoms will result in non-zero first-order polarizability derivatives. The internal stress, induced by the ionic and atomic bombardment, presented in the films may also cause the Raman shift.

Table 4-2 Raman shift of the InN deposited at various nitrogen ion energies.

InN	Raman scattering peaks in cm^{-1}					
	50 eV	100 eV	150 eV	200 eV	Ref.144	Ref.146
A ₁ (LO)	590	589	588	588	586	580
E ₁ (LO)	570	568	565	568	593	570
E ₂ (high)	488	488	489	490	488	488
A ₁ (TO)	449	449	447	-	447	480

In summary, InN films prepared at various N ion energies exhibited polycrystalline wurtzite structure. The preferred orientation was attributed to the minimization of the overall surface and strain energy of the film during growth.

4.3.2.3 Effect of substrate temperature

Substrate temperature (T_s) is one of the parameters which might affect the properties of the deposited films significantly. Various T_s were employed for InN depositions. The nitrogen ion energy was kept at a constant of 300 eV.

The XRD patterns of the InN thin films deposited on Si (111) at different T_s are shown in Figure 4-13 (the signal from the silicon substrate was subtracted). Grazing incidence XRD was employed to identify the phase and texture in the thin film since the X-ray path length in the layer is greatly increased and thus the peak intensity is enhanced. Figure 4-13 (a) shows the grazing scanning profiles. All XRD peaks were

Figure 4-13 (a) 2θ XRD profile of InN films prepared at T_s of 350, 380, 420 and 475 °C. (b) $\theta/2\theta$ XRD of films deposited at 420 and 475 °C.

InN related, as labeled in the figure. For films deposited at various temperatures, planes (0002), (1011), (1120), (1013), (1122), (0004), and (2022) could be detected, indicating obvious polycrystalline structure. $\theta/2\theta$ XRD patterns of films deposited at 420 and 475 °C are shown in Figure 4-13 (b). For films deposited at 475 °C, only [0001] planes could be observed, suggesting (0001) preferred orientation of the InN films. The inset is the corresponding (0002) peak for each spectrum.

By considering all possible crystal orientations, the distance, d , between two planes can be calculated from the XRD spectrum using equation 2.3. Hence, the crystal structure and lattice constant can be determined. The lattice parameters, a and c , of the hexagonal structure, calculated from equation 2.5, are depicted in Figure 4-14. The lattice constant a for all the films studied was 0.3~0.5% larger than that of bulk value. The lattice constant c was in the range of 5.752~5.711 Å, which was in agreement with the reported values of hexagonal InN. The improvement in the crystalline quality of

Figure 4-14 Lattice constant a and c values dependence on T_s .

the films with the increasing of T_s was evident from the reduced FWHM of the diffraction peak from 0.67 to 0.47° . The average grain size, calculated using Scherrer's equation for the (0002) peak, was increased from 12 to 18 nm. Oxygen is viewed as a common contaminant of InN and is present either at the interface of the substrates or trapped between the grain boundaries. However, the lattice constant estimated for the films deposited at 475°C ($c = 5.711\text{\AA}$) was very near to that of high quality InN reported. This suggested that the InN film was not oxidized in the form of indium oxide, which is consistent with the XRD result as indium oxide related peaks could not be detected by the X-ray spectrometer.

The surface morphology of InN thin films deposited on Si (111) at various T_s , taken from SEM are shown in Figure 4-15. The sample grown at low T_s consists of circular grains, which looks smoother than that of the sample grown at high T_s . At 475°C , the clusters size is uniform with diameter $\sim 150\text{-}200$ nm. These clusters in SEM might be the aggregation of small grains, therefore, it might not be able to reveal the

Figure 4-15 Surface SEM images of InN films deposited at substrate temperature of (a) 350, (b) 420, and (c) 475 °C.

exact grain size. In general, large lattice mismatch will lead to three-dimensional island growth. The grains are not continuous (V-W growth mode) and the size and density of islands depend on the growth temperature. Larger grains with low density grow epitaxially up to a few average monolayers but tend to become polycrystalline at an early stage at T_s . However, sparse formation of 3-D islands at initial stage is suppressed at relatively low temperature. Thus LT InN buffer was grown as amorphous or polycrystalline. At higher T_s , the surface adatoms obtained higher momentum which enhances their surface mobility and therefore the grain size increased.

Figure 4-16 gives much clearer TEM plain view of InN film deposited at 475 °C on Si substrate. Irregular grains with various sizes could be observed clearly from the TEM images (a)-(b). This crater textured feature has been observed previously in ZnO films prepared by PLD ^[147]. The morphology was associated with the concurrent growth of separate nucleated islands of InN that grew as hexagonal crystallites in the film thickness direction and impinged laterally by growth in the $[10\bar{1}0]$ directions.

Figure 4-16 (a)- (c), Plain view TEM images of InN, the inset of (b) is the electron diffraction pattern of an individual grain, and the inset of (c) is SAED of grain boundary area; (d)-(e), HR-TEM images; (f) is EDX pattern recorded from the boundary.

Each irregular crater was composed of a few grains such that it had a radial symmetry. The individual grain was of perfect crystalline quality as verified by the selected area electron diffraction pattern (SAED) shown in the inset of figure (b). The grain was

grown along c -axis or c -axis normal to the surface. Images(c) and (d) are the HR-TEM of the grains. The distance between the two adjacent planes of both grains was 0.307 nm and this corresponded to InN $[10\bar{1}0]$ direction. However, the grain boundary did not show any diffraction pattern regardless of any adjustment in the position of the sample. This reveals the amorphous nature of the boundary region. The inset of Fig 4-16(c) is SAED of the boundary area. The lattice spacing is determined to be 0.568 nm in the rectangular region as shown in Fig. 4-16(d). The region was most likely corresponding to InN (0001). Both the SAED pattern and lattice constant suggested that the grains were disoriented. Fig 4-16(e) gives a much clearer lattice diffraction fringes. The distance between two planes confirmed the InN $[10\bar{1}0]$ direction. From the energy dispersive spectrometry (EDS) analysis, the composition of the grain boundary area consisted of In, N and O, which indicated that the amorphous boundary phase is oxygen related. The presence of the oxygen was consistent with the XPS analysis.

The InN films have been further investigated by Raman spectroscopy. Figure 4-17 displays the typical room temperature visible Raman spectrum of the InN films on Si (111) prepared at various T_s . Two phonons have been clearly observed and are assigned to $A_1(\text{LO})$ at $\sim 588 \text{ cm}^{-1}$ and $E_2(\text{high})$ at $\sim 490 \text{ cm}^{-1}$ of the hexagonal phase of InN films. It should be mentioned that $\sim 449 \text{ cm}^{-1}$ Raman scattering peak is due to $A_1(\text{TO})$ phonon mode of InN films. For those films deposited at 420 °C and lower, they have the similar shape. The observed Raman spectra are very similar to those discussed above with N ion energy dependency.

Figure 4-17 Raman spectrum of the InN films on Si (111) prepared at various T_s .

The PL emission spectra of the InN films on Si (111) are shown in Figure 4-18. The InN thin films exhibit band edge luminescence of ~ 1.15 eV with FWHM of 105 meV. This differs from the reported values of 1.81–2.16 eV and 0.6–0.9 eV for InN deposited on Si substrates. However, it was red shifted in comparison with the films fabricated from the indium pellets, which contained more oxygen. It should be noted that the PL peak position did not change, as depicted in Figure 4-18 (a), except that the PL intensity increased with the increase of T_s . The increased PL intensity was due to the increased crystallinity as was evident from XRD. Figure 4-18 (b) shows that the PL position and shape remained while the PL intensity increased with the excitation power. However, the integrated peak intensity increased linearly with the excitation power, as shown in the inset of Figure 4-18 (b). This indicated that the origin of the PL emission was not donor acceptor pair-like or deep-emissions but the direct band edge transition.

Figure 4-18 RT PL spectra of the InN thin films at different T_s . (b) PL emission as a function of excitation power. The inset is RT integrated PL peak intensity as a function of excitation power.

Although the crystalline quality of the InN on quartz was not as good as that on Si, all films were polycrystalline. Therefore, the PL emission and the bandgap derived from the optical absorption should be comparable. Figure 4-19 shows the optical transmittance and the plot of squared absorption coefficient (α^2) vs energy curves of InN films deposited at various T_s of 350 ~ 475 °C. The transmittance of all the films was over 70 % in Vis-NIR range. Absorption coefficient α was calculated from the relation, $T = A \exp(-\alpha d)$. The bandgap (E) can be determined using the equation $\alpha^2 = h\nu - E_g$. However, according to Carrier and Wei^[148], the calculated α^2 was not a linear function of E . The larger the value of absorption coefficient that is used to draw the line, the larger the bandgap value will be. Therefore, the bandgap determined by

Figure 4-19 (a) Transmittance of the InN thin films deposited at different T_s . (b) The absorption coefficient squared vs photon energy at RT.

the linear extrapolation method depends on the position of the straight line drawn. Figure 4-19 (b) shows the estimated bandgap value of 1.2 eV extrapolating as extrapolated from $\alpha^2 = 20 \times 10^8 \text{ cm}^{-2}$. It should be mentioned that this value is very close to the PL emission peak. However, if $\alpha^2 = 50 \times 10^8 \text{ cm}^{-2}$ is used to determine the bandgap, bandgap values will increase by 0.2-0.4 eV, as depicted in the inset of Figure 4-19 (b). This could be one of the reasons why the bandgap value is overestimated by optical absorption measurement method.

In the classical Mie theory ^[149], the extinction losses of a metallic sphere embedded in a matrix depend on the complex dielectric functions of both matrix material and metal. The dispersed small metallic particles result in resonant light scattering and absorption. Therefore, with a little excess of In metal in the samples, the absorption edge energy in the InN/In composite can shift down to the principle absorption ^[117, 118]. If the bandgap value of 1.4 eV, as determined by thermal detected

optical absorption^[118] were the true bandgap; the observed 1.05-1.17 eV PL emissions from our samples may satisfy the Mie resonance effect. However, the linear excitation power dependence of PL intensity supports the band-to-band edge transition, indicating that the Mie theory may not be responsible for the observed band gap value.

Oxygen is viewed as the most likely factor which may attribute to the observed 1.15 eV emission because our InN films contains ~16 at.% of oxygen as determined by XPS. Alexandrov *et al.*^[150] proposed that segregated oxygen species could substitute N sites as InO and form a ternary semiconductor of $\text{InO}_y\text{N}_{1-y}$ with y above 0.1. However, in this work, such high oxygen content was not formed in any crystallized oxide or oxynitride. So how does the oxygen exist in the film? There are two common ways by which oxygen may affect the bandgap of InN. One is oxygen in the form of high density optical active centers or formation of alloy phase, InN_xO_y , with a bandgap different from InN. The other is oxygen bonded with In directly forming oxide phase either in crystalline or amorphous nature. However, the oxygen in InN may not be soluble beyond an upper limit of ~0.3% for film growth by MBE at 500 °C. Oxygen substituting N sites may create a deeper donor state in InN. Electron concentration of about 10^{20} cm^{-3} , corresponding to a donor concentration of 0.3% in MBE grown InN which contained only 1 - 6 at.% of O_2 was reported by Yoshimoto *et al.*^[151]. The concentration of O_N donors in heavily doped InN samples may be significantly less than the oxygen concentration measured by SIMS. The high oxygen content in our InN films is not in the form of any crystallized oxide or oxynitride alloys as deduced from the XRD and TEM results.

HRTEM analysis indicated the segregation of remaining oxygen in our InN thin films in amorphous phases, such as amorphous indium oxide or oxynitride, at

grain boundary since oxygen can easily be trapped in these areas. Butcher *et al.* [152] has demonstrated that large amount of oxygen could be incorporated at the grain boundaries in polycrystalline GaN. Therefore, it is believed that the oxygen incorporated in our InN films may lead to the formation of amorphous In-O/In-O-N phases at the grain boundaries which results in the observed bandgap of ~ 1.15 eV. It is also evident from our previous experiment that when the films are nearly amorphous with oxygen content as high as 40 at.%, strong PL emission peaked at 1.3 eV could be obtained. It suggests that higher oxygen concentration in amorphous phases leads to the blue shift of the band-edge emission. The high oxygen concentration in the form of amorphous In-O/In-O-N phases among the grain boundaries and those amorphous phases coexist in the films results in the observed band gap of ~ 1.15 eV.

4.3.2.4 InN nanostructure

Based on the X-ray photoemission measurement, the location of surface Fermi level of InN has been proven to close to (or above) the conduction band minimum, yielding to a free electron accumulated surface. $\text{In}_x\text{Ga}_{1-x}\text{N}$ ($0.92 \leq x \leq 1$) could be considered as a degenerate semiconductor, of which the surface work function is the only surface barrier through which electrons tunnel from the surface to vacuum [153,154]. Accordingly, the field emission properties of InN are of great interest. InN has been expected to be a good field emitter material for potential nanoscale applications [155]. Up to now, much progress has been made in the synthesis of AlN and GaN nanostructures; especially GaN, AlN and their alloys nanostructures have demonstrated excellent field emission (FE) and other properties in many nanodevice applications. Among these nitrides nanostructures, InN is attractive due to its narrow

bandgap. However, very few investigations focused on InN nanostructures and their optical properties. By adjusting the growth parameters, InN nanostructured films can also be deposited using I-FCVA. The InN nanostructures were studied in such a way to exploit the possible application in nano-devices^[156].

InN is not lattice matched with sapphire substrate although they are of the same crystal structure. Two-step growth was utilized in the above discussed InN films, where the first step consisted of the deposition of a 40-nm InN buffer at low temperature. InN nanostructure films were grown directly on the substrate at nitrogen ion energy of 300 eV and T_s of 420 °C, and the ratio of Ar/N₂ was kept at 1/6.

The typical 2 θ -scanning XRD pattern of the InN nanostructures deposited on sapphire (0001) substrate is shown in Figure 4-20. InN related XRD peaks located at 28.9, 31.4, 33.2, 43.2, 51.5, 57, and 61.6 ° correspond to hexagonal InN(10 $\bar{1}$ 0), (0002), (10 $\bar{1}$ 1), (10 $\bar{1}$ 2), (11 $\bar{2}$ 0), (10 $\bar{1}$ 3) and (11 $\bar{2}$ 2) planes respectively. The lattice parameters were calculated to be $a = 3.556$ Å and $c = 5.693$ Å.

Figure 4-20 2 θ -scanning XRD of the InN thin films.

Figure 4-21 Typical SEM image of the InN nanostructure (a) plain view & (b) cross-sectional view of InN/Sapphire.

Figure 4-21 shows the typical FE-SEM images of the InN nanostructures. It is clear from Figure 4-21 (a) that uniform isolated nano-sized features with average diameter of 20 nm covers the whole surface of the sapphire substrate, and from the cross-sectional view in Figure 4-21 (b), the InN exhibits columnar structure oriented normal to the surface.

TEM characterization provides a much clearer view of nanostructures. Figure 4-22 shows the cross-sectional view of the specimen using TEM. Finger-like nanostructures are clearly shown in Figure 4-22 (a). The contrast differences, resulting from slight variations in structural orientation, locally change the Bragg diffraction condition. This indicates the nanofingers are not perfect single crystals. The gap between individual nanofingers is about 20 nm. The inset of Figure 4-22 (a) is an electron-diffraction pattern recorded from many nanofingers. The observation reveals the polycrystalline structure and the diffraction rings are consistent with InN planes. A single nanofinger, which is about 50 nm in length and 20 nm in diameter, has been selected for HR-TEM analysis (Figure 4-22 (b) and (c)). Figure 4-22 (d) and (e) display magnified HR lattice images recorded from the top and stem part of a single

nanofinger. Both lattice images of nanofinger exhibit perfect hexagonal InN (0002) planes, indicating the growth of individual nanofinger along c-axis. These HRTEM images of the nanofinger show perfect InN hexagonal lattice. The nanofingers have diameters of ~ 20 nm as estimated from FE-SEM and TEM images and the entire length equals to the film thickness which is ~ 250 nm.

Figure 4-22 (a) TEM images of the InN nanofingers on sapphire. The inset shows electron diffraction pattern taken from the InN nanofingers. (b) and (c) HRTEM image of a single InN nanofinger. (d) and (e) HR-TEM lattice images of top and stem of the single InN nanofinger respectively.

III-V 1D nano-materials often show physical and chemical properties due to their peculiar structure. There is no report on field emission property of InN nanostructure up-to-now to the best of our knowledge. The investigation on field emission property of InN nanofingers is considered important and necessary. Figure

4-23 shows the plots of emission current density versus applied voltage, ranging from 300-1600 V for 50 and 100 μm thick spacers. After the first few cycles, the sample became stable. The turn on field, which is defined as the field that produces an emission current density of $10 \mu\text{A}/\text{cm}^2$, is 9.7 and 11.2 $\text{V}/\mu\text{m}$ for two spacers, respectively. The value is dependent on the thickness of the spacer. Similar phenomenon from AlN nanoarchitectures has been reported by Yin *et al.*^[157].

The emission characteristics were analyzed using Fowler-Nordheim (FN) theory. Based on the FN model, FE current from a metal or semiconductor is attributed to the tunneling of electrons from the material into vacuum under the influence of an electric field^[158]. The FN law states that the total current I as a function of the local field at the emitter surface F is approximately given by

$$I \propto \frac{F^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{\beta F}\right) \quad (4.1)$$

where B is $6.83 \times 10^9 [V \text{ eV}^{3/2} / \text{m}]$ and ϕ is the work function. F is local applied field and is usually taken as

$$F = \beta V / d \quad (4.2)$$

where V is the applied voltage, d is the distance between cathode and anode, β is the field enhancement factor and $E = V/d$ is the macroscopic field. When plotting $\ln(I/V^2)$ versus $1/V$, we should obtain a straight line with a slope that depends on ϕ , β and d . The plot of InN nanofingers depicted in Figure 4-23 (b) shows similar characteristic for both spacers. The rough linear dependence indicates that the emission current is caused by tunneling effect. If we assume the work function (ϕ) of InN is 1 eV (the work function of InN is not available in the literature), field enhancement factors corresponding to 50 and 100 μm thick spacer are decided to be 156 and 77 respectively

Figure 4-23 (a) Typical FE current density vs applied field for the InN nanostructures at 50 and 100 μm thick spacers. (b) F-N plots corresponding to 50 and 100 μm thick spacers.

from the straight line in F-N plot. The difference in the field enhancement factor indicates that the local electric field varies with the spacer. Therefore, we consider that the screening effect between the adjacent emitters plays a role in the field-emission process. According to the model proposed by Filip and co-workers ^[159], the local electric field can be expressed as

$$F = s \frac{V}{r} + (1-s) \frac{V}{d} \quad (4.3)$$

where r is the radius of the emitter and s is the parameter describing the degree of the screening effect. By substituting the experimental values of r (i.e. 10 nm) and the field enhancement factor of 156 and 77, respectively for 50 and 100 μm, the screening effect parameters are estimated to be 0.0310 and 0.0076. It has been found that the screening effect is smaller for thicker spacer during the field emission process. If InN has similar work function value as other nitrides, the field enhancement factor of InN

nanofingers will be comparable with AlN nanoneedles^[160] and GaN nanorods^[161,162], thus showing the potential application of InN nanostructures.

The emission stability of the InN nanofingers at macroscopic field of 14 V/ μm (current density of $>10 \mu\text{A}/\text{cm}^2$) has been tested for 1,000 minutes. As shown in Figure 4-24, no obvious emission current degradation was observed, indicating the electron emission from the InN nanofingers is very stable. The inset of Figure 4-24 is an optical image showing uniform spatial distribution of the emission. It should be noted that no emission current was detected even at a macroscopic field as high as 20 V/ μm for the as-grown InN film under lower nitrogen ion energy (ie., without nanostructures). The FE confirmed that the nanofingers do play an important role in field emission property.

The mechanism of the formation of the InN nanofingers should be S-K growth mode due to the large lattice mismatch. However, with the assistance of nitrogen ion beam, the growth of the InN follows V-W mode rather than S-K mode. This is due to the high N_2^+ and indium plasma fluxes as well as the low T_s , of which $E_s \ll E_f + E_{f/s}$. During the process the generated reactive nitrogen ion (N_2^+) beams are mixed with Ar^+ and energetic indium plasma, and their subsequent bombardment, interaction with surfaces, modifying the film structure and composition. Ion bombardment enhances adatom surface mobility and stimulates the early stages of 3D clusters formation. The clusters act as nano-sized seeds, which are grown without catalyst on the substrate. This is followed by the growth of InN nanofingers on the seeds and normal to the surface.

Figure 4-24 The stability of the emission from the InN nanofingers under applied field of 14 V/ μm . The inset is the emission image from the InN nanofingers captured at 25 V/ μm .

4.4 Summary

In summary, InN films have been grown by an I-FCVA technique at low temperature. XRD study reveals that the InN films exhibit polycrystalline wurtzite structure. The preferred orientation is attributed to the minimization of the overall surface and strain energy of the film during growth. Both Raman $A_1(\text{LO})$ and E_2^2 modes are observed from the deposited films, confirming the hexagonal structure of the InN films.

Under the optimized growth conditions of the InN films, highly (0001) preferred orientation with PL emission of 1.15 eV were obtained. XPS and EDX analysis revealed that the band edge emission of 1.15 eV was related to oxygen incorporated at grain boundaries in the form of amorphous oxide or oxynitride.

In addition, InN nanostructures have also been prepared. The growth mechanism of the self-assembling InN nanostructures follows the V-W mode, due to the combined effect of the large lattice mismatch between InN and substrates and the energetic source species of nitrogen ions and indium plasma. The I-FCVA InN nanostructures exhibit good FE properties, which imply potential applications in field emission devices.

I-FCVA provides an alternative method to fabricate InN films. The growth conditions of high ion fluxes and the low T_s of I-FCVA technique provide V-W growth mode, which is undesirable for conventional film growth, because only 3D clusters are formed ^[163]. This regime, however, is favorable for nanostructures formation. Thus I-FCVA technique can also be used for nanostructure fabrication. I-FCVA technique has a significant potential for the development of InN and related thin films as well as nanostructures.

CHAPTER 5 GALLIUM NITRIDE

In above chapters, we have demonstrated that AlN and InN could be successfully fabricated by I-FCVA on Si substrate. In this chapter, GaN on Si prepared by I-FCVA will be discussed.

5.1 Introduction

Gallium nitride is a very interesting semiconductor in the III-V family, having a bandgap ideal for blue emission. This short wavelength light emission cannot be obtained from conventional III-V semiconductors. GaN based nitride semiconductors have several advantages over other wide band gap semiconductors such as SiC and diamond. They can be doped both p and n-type, have direct band-gaps and form hetero-structures for device applications ^[164]. A number of reviews on the progress of GaN were published ^[8-9, 11, 165-166]. Besides the recent rapid development of GaN optoelectronic device technology, many other challenges for the new applications and novel techniques on fields of displays have been attempted. Optical data storage, high power and high frequency electronics and optoelectronic integration circuits are some of the emerging applications. Moreover, the fact that films with comparatively high defect densities still have significant performance excites the interest in the investigation of polycrystalline ^[167,168] and even amorphous GaN ^[169,170]. The most successful among all growth methods are MOCVD and MBE. In spite of the rapid development, many problems remain to be overcome. Understanding of the fundamental mechanisms of impurity incorporation, particularly p-type, and native defect formation is important. The role of Ga and N vacancies in doping, the purported

hydrogen passivation of acceptors and the defects responsible for unintentional n-type doping represent some controversial issues that should be addressed in research for further progress in the device arena. The main technological issue is the lack of substrates to produce high crystalline quality films. Sapphire and SiC are commonly used as substrates because of the lack of large-area GaN bulk crystals. The thermal conductivity of Si is similar to that of GaN and this makes it attractive as substrate for high power GaN applications. Furthermore, Si substrate offers extremely low cost and very large area wafer and the technology is well-established. However, the growth of high quality GaN films on Si substrates has serious problems. The large lattice mismatch results in cracks and high dislocation density of GaN epilayer. To overcome these difficulties, intermediate layers were introduced before GaN growth, such as SiC^[171], AlN^[172,173], Si₃N₄^[174,175], ZnO^[176-179].

The ZnO buffer layer has potential advantages for GaN hetero-growth, as it is an isomorphic material with wurtzite GaN; only 1.8% and 0.4% for a-axis and c-axis, lattice mismatch with respect to GaN, respectively^[180]. For the growth of either GaN or ZnO thin films, they have already been used as buffer layers for each other^[176-180]. Attempts have been made to grow high quality GaN films on different substrates with ZnO buffer layers by PLD^[177], CVD^[176] and MBE^[180]. However, there are some important problems associated with the use of ZnO as a substrate for GaN epitaxy. Use of substrates other than GaN presents not only the disadvantages of lattice and thermal mismatch, but also the possibility of unintentional contamination from the substrate during the growth. In particular, ZnO is degraded at high temperatures^[181]. Up to now, there was no intense RT PL reported from GaN on ZnO buffered Si. FCVA has proven its merit in preparing high-crystal quality ZnO films. Since ZnO and GaN can be

grown sequentially on Si using FCVA technique, high-crystal quality GaN may be prepared at low temperature.

5.2 Experiment

ZnO was first grown on Si as a buffer layer, followed by a GaN layer. For GaN growth, gallium (melting point: $\sim 30^\circ\text{C}$) was put in a Ti cup which acted as cathode. Nitrogen ions were generated by a RF ion source equipped in the deposition chamber. The RF power was optimized to be 250 W. The N ion energy and nitrogen flow rate was varied from 50 to 300 eV and 10 to 30 sccm, respectively. The deposition temperature was in the range of 350 to 475°C . For ZnO films, metallic zinc (purity 99.99%) was used as cathode target, and oxygen was employed as the reactive gas, with its flow rate controlled at 60 sccm during the deposition. The arc was operated in dc mode with current at 60 A. Substrates were then fixed mechanically on substrate electrode with a resistive heater. The deposition chamber was pre-evacuated to 1.1×10^{-5} Torr by a rotary and cryo-pump system. The operating pressure during the film growth was around 3.5×10^{-4} Torr.

5.3 Results and discussion

The first two series of samples were deposited on Si and quartz substrates at T_s of 350°C , as a function of nitrogen flow rate and nitrogen ion energy. XRD diffraction spectra of all films deposited at 350°C showed an absence of GaN peaks, which indicated that the GaN films were either amorphous in nature or exhibited nanocrystalline phases that were too small to yield a diffraction pattern. ZnO has been used as buffer layers for GaN growth. GaN with ZnO buffers also exhibited amorphous

structure. Typical cross-sectional SEM images of GaN films with and without buffer layer are presented in Figure 5-1. From the SEM cross-section images, no obvious structure could be observed from GaN film deposited directly on Si (100) (Figure 5-1 (a)), but the GaN thin film with a ZnO buffer layer composed of columnar structures (Figure 5-1 (b)). However, the columnar grains did not extend through the interface of GaN/ZnO to the free surface although the film was dense. The thickness of the GaN films was estimated to be in the range of 200-250 nm.

Figure 5-1 Cross-sectional SEM images of GaN on Si (a) without and (b) with ZnO buffer layer.

TEM images of GaN/ZnO/Si showing the substrate interface region are presented in Figure 5-2. Abrupt interface of GaN/ZnO can be clearly observed. ZnO layer consists of columnar grains. The crystal quality of ZnO was quite good as revealed by the SAED pattern in the bottom right inset of Figure 5-2. However, GaN was amorphous in nature from the SAED image and this is consistent with the XRD result. The amorphous nature of GaN suggested that T_s was not high enough.

Figure 5-2 Cross-sectional TEM image of GaN/ZnO/Si deposited at 350 °C.

When the T_s was increased to 450 °C, the crystal quality of GaN films was enhanced. Grazing incidence XRD was employed to identify the texture in the thin film. As the X-ray path length in the layer is greatly increased, the peak intensity is enhanced. The grazing scanning (2θ) XRD spectrum of GaN/Si in Figure 5-3 showed the major peaks of (0002) and ($10\bar{1}3$) located at 34.6 ° and 63.6°, respectively. In grazing incidence XRD measurement with incidence angle α , the diffraction takes place with those planes tilted at an angle $(\theta-\alpha)$ with respect to the substrate surface ^[182]. The θ is the half angle between the incidence and diffraction directions. For highly oriented GaN (0002) films, diffraction can also take place on ($hkul$) planes with $(\theta-\alpha)$ angles equal to the inter-plane angle between the (0002) and ($hkul$) planes. For grazing incidence angle 1°, GaN($10\bar{1}3$) plane has a $(\theta-\alpha)$ angle of 30.9 °, which is very close to the 32 ° interplane angle between (0002) and ($10\bar{1}3$) planes. All these peaks belong to ZnO and GaN with hexagonal structure due to the small lattice mismatch. XRD pattern

Figure 5-3 2θ XRD pattern of GaN deposited on Si with/without ZnO buffer at 450 °C, A, B, C, and D are corresponding to the ZnO thickness of 60, 120, 250 and 360 nm.

also indicates that the intensity of (0002) and (10 $\bar{1}3$) became stronger with increasing the ZnO buffer layer thickness. The best crystal quality was obtained from the sample with 250 nm-thick ZnO buffer.

Both GaN films (with and without ZnO (250nm)) showed (0002) peaks in the ω - 2θ XRD patterns as shown in Figure 5-4. Both samples exhibited Si(111) and GaN (0002) peaks. The intensity of (0002) peak of the film with ZnO buffer layer was near two orders of magnitude stronger than that of the film without buffer layers. The FWHM of GaN (0002) peak was 0.32° (0.45°) with (without) ZnO buffer layer. The XRD scans demonstrate the high-crystal quality films. Therefore, c-axis oriented GaN/ZnO films were obtained.

Figure 5-4 ω -2 θ XRD of (a) GaN/Si and (b) GaN/ZnO(250nm)/Si films.

Figure 5-5 (a) and (b) show the AFM topographies of ZnO buffer layers of thickness 120 and 250 nm, respectively. Figure 5-5 (c) and (d) show the AFM images of the respective samples with ~ 150 nm GaN deposited onto the ZnO with various thicknesses. The RMS surface roughness of the ZnO were measured to be about 2.4 and 3.5 nm for the thickness of 120 and 250 nm, respectively. The RMS of the GaN on the corresponding ZnO buffer layers were 5.4 and 7.3 nm, respectively. AFM images reveal that the surface roughness of both GaN and ZnO surfaces increase with increasing the thickness of underlying ZnO buffer layers.

All the ZnO and GaN films look transparent. Figure 5-6 shows the typical transmittance of ZnO/quartz, GaN/quartz and GaN/ZnO/quartz films deposited at 450 °C. The average transmittance was over 80 % for all the films. The transmittance of GaN/ZnO/quartz slightly decreased in comparison with that of ZnO/quartz. It is worthy to note that the transmittance result is much better than the reported values [183,184]. ZnO film has a falloff at 380 nm. GaN deposited directly on quartz has a

Figure 5-5 Typical AFM image of the ZnO and GaN/ZnO films, (a) 120 nm thick ZnO, (b) 250 nm thick ZnO, (c) GaN on 120 nm thick ZnO, and (d) GaN on 250 nm thick ZnO.

broader falloff up to 200 nm. GaN/ZnO has a slightly lower transmission; the band-edge has broader shoulder which does not fall down to zero directly. The bandgaps of GaN and ZnO were estimated to be 3.34 and 3.27 eV respectively, from the plots of absorbance squared vs. energy as shown in the inset of Figure 5-6.

Room temperature PL spectra were acquired in the wavelength range of 350 – 850 nm; the excitation light was the 325 nm line of He-Cd laser. Figure 5-7 shows the PL spectrum of the GaN deposited directly on Si. Two weak peaks of ~420 and ~550 nm could be observed, which were attributed to defects. PL spectra of GaN on ZnO buffered Si and ZnO on Si are shown in Figure 5-8. For the ZnO film (Figure 5-9 (b)), the spectrum consisted of a peak at 378 nm and a shoulder (388 nm) at higher wavelength. It was correlated with the ZnO band-edge emission^[185]. The PL peak of

Figure 5-6 Transmittance of GaN and ZnO films on quartz.

Figure 5-7 Room temperature PL spectrum of GaN/Si deposited at 450 °C.

GaN/ZnO/Si was centered at 369 nm, as shown in Figure 5-9 (a). The PL peak intensity was increased nearly 4 times. Therefore, the ~369 nm emission was attributed to band edge transition of GaN layer. The shoulder at 378 nm was related to the ZnO

Figure 5-8 Room temperature PL spectra of the (a) GaN/ZnO/Si and (b) ZnO/Si.

buffer layer. Furthermore, no yellow band feature could be observed in the visible range for GaN on Si with ZnO buffer layer. To the best of our knowledge, RT PL from GaN (low temperature process of 450 °) on Si substrate with ZnO buffer layer has not been reported yet. The observed PL emission indicated that the quality of GaN was improved due to the lattice matched ZnO buffer. Although from the XRD result, preferred orientation of (0002) ZnO was demonstrated, the broad PL peak of ZnO revealed that the crystal quality of ZnO was not very high. The quality of GaN could be further enhanced by improving the crystal quality of ZnO buffer layer.

X-ray photoelectron spectroscopy (XPS) analysis was performed on the surface of the samples to determine its composition. The typical XPS spectra of the GaN films with and without Ar⁺ cleaning are displayed in Figure 5-9. Before the cleaning procedure all the films exhibited strong peaks related to the presence of atmospheric contaminants, C and O. After Ar⁺ cleaning, residual carbon was completely removed while some oxygen could still be detected. After surface cleaning, the N1s peaks were

Figure 5-9 Typical XPS spectra of the GaN films.

the most pronounced. Ga 3s, Ga 3p, Ga 3d and Ga LMMb Auger transition were observed in both spectra.

Figure 5-10 shows the XPS spectra for the corresponding Ga 3d and N 1s core levels of GaN/ZnO/Si film after Ar^+ cleaning. The major peak in Figure 5-10 (a) centered at 19.8 eV is the typical value for GaN and is 1.2 eV higher than metal Ga (18.6 eV) ^[186]. The shoulder in the higher energy side is attributed to the Ga-O bond ^[187]. For the N1s core level shown in Figure 5-10 (b), the peak centered at 397.3 eV agreed with that for N-Ga bonding. However, the peak at 392.3 eV is not related to N. It could be due to Ga Auger transition ^[188]. The element depth-concentration of the GaN/Si and GaN/ZnO/Si films, which were calculated from the spectra, were shown in Table 5.1. The values of N 1s were obtained after deconvolution of Ga LMMb. The

results of the GaN after etching showed a small amount oxygen contamination of 4.46 % and 5.44% corresponding to GaN/Si and GaN/ZnO/Si, respectively.

Figure 5-10 Ga3d and N1s XPS core level spectra of the GaN/ZnO/Si films after etching.

Table 5-1 XPS element concentration of GaN films

Element	GaN/Si		GaN/ZnO/Si	
	Before etching (Atomic Conc.%)	After etching (Atomic Conc.%)	Before etching (Atomic Conc.%)	After etching (Atomic Conc.%)
O 1s	14.11	4.46	27.53	5.44
N 1s	33.39	51.4	29.15	52.66
C 1s	33.3	0	20.87	0
Ga 3p	19.2	44.14	22.46	41.9

5.4 Summary

GaN films on Si with and without ZnO buffer layer were successfully fabricated. It was found that the quality of the films improved with increasing deposition temperature up to 450 °C. XPS analysis showed that small amount of oxygen contaminant was found in GaN films and the films were slightly nitrogen rich. The transmittance of GaN on quartz with ZnO buffer layer is over 80 % which is much better than the reported values. RT PL at 369 nm (3.36 eV) was observed from the GaN on ZnO buffered Si. The ZnO buffer layer is beneficial to obtain high quality GaN films as verified from the optical transmittance and PL results.

I-FCVA technique can be used to grow GaN from liquid Ga target. The quality of film using Si as substrate at low temperature with ZnO buffer layers can be improved further if lower base pressure and high quality single crystal ZnO can be obtained.

CHAPTER 6 SECONDARY ELECTRON EMISSION OF III-NITRIDES

Semiconductors with negative electron affinity (NEA) are widely used as photo- and cold-cathode emitters^[189]. Surfaces of III-nitrides (such as AlN, GaN) are known to have a low or NEA^[190,191], which allows electrons to escape easily into the vacuum. Thus, they promise to exhibit a high secondary electron emission (SEE) yield which increases with decreasing work function (ϕ) of the material^[192]. This makes them promising in developing efficient radiation detectors or cathode emitters^[193]. In this chapter, the SEE properties of III-nitride films prepared by I-FCVA will be evaluated.

6.1 Introduction

When a solid is irradiated by an electron beam, the bombarded surface emits electrons which are commonly composed of two categories: (1) secondary electrons (SE) having energy between 0 ~ 50 eV and (2) inelastically and elastically backscattered electrons having energies slightly lower than that of the primary electron beam^[194, 195]. The average number of secondary and backscattered electrons produced by a single primary electron is defined as SE yield (σ) and backscattered electron yield (η), respectively, and the sum is referred to the total electron emission yield (γ). If the energy of incident electrons is in the lower keV range, the intensity of the electron emission current can exceed the incident electron beam current. It has been demonstrated that III-nitride coatings are effective in improving the field emission characteristics of Si tips^[196].

The theoretical treatments of SEE processes include (1) generation of internal SE by kinetic impact of the primary electrons, (2) transport of the internal SE through the bulk sample towards the surface and (3) escape of the electrons through the solid-vacuum surface ^[194]. The primary electrons are assumed to travel in a forward path. They slow down due to collisions with electrons and ions and kinetic energy is transferred to the internally generated SE. The rate of the loss of the primary electron energy is given by power law relationship:

$$-\frac{dE}{dx} = \frac{A}{E^n} \quad (6.1)$$

where E is the energy of a primary electron at a depth x , and A is an arbitrary constant. According Salehi *et al.* ^[197], the escape probability, i.e., the probability of escape of a secondary electron generated at a distance x below the surface is,

$$f(x) = f(0)\exp(-x/R_s) \quad (6.2)$$

where R_s is the mean range of a secondary electron. When the primary beam is incident at an angle θ normal to the surface, the probability of escape of the secondaries traveling a distance x within the material will be:

$$f(x) = f(0)\exp(-x \cos \theta / R_s) \quad (6.3)$$

Therefore, plot of $\ln(\gamma_\theta)$ against $(1-\cos\theta)$ for a given primary energy E_p should yield a straight line:

$$\ln \gamma_\theta = k(1 - \cos \theta) + a \quad (6.4)$$

where γ_θ is the value of γ for a primary angle of incidence θ .

6.2 Experiment

The study of SEE was performed by measuring the electron beam current passing through the film and comparing it with the incident beam current. The schematic diagram of the setup is shown in Figure 2-7. The electron beam was generated by a SEM electron gun, whose energy could vary from 0.8 to 25 keV. The sample was first biased by +45 V which forces the emitted electrons to return to the sample. The sample current was measured as the primary electron intensity (I_+). Then the sample was biased by -45 V to repel the secondary electrons from the sample surface. The current measured was the net current (I_-) on the sample. It should be noted that γ includes both the secondary electrons and the inelastically and elastically scattered electrons. Therefore the SEE yield is $\gamma = (I_+ - I_-) / I_+$ (equation 3.8).

6.3 Results and discussion

6.3.1 SEE yield of III-nitrides thin film on Si

AlN thin films deposited on Si substrates with various thicknesses and at different N ion energies were studied. Figure 6-1 shows the SEE yields of AlN deposited at N ion energy between 200 ~ 650 eV. The films exhibited amorphous structure at N ion energy of 200 and 300 eV, and weak polycrystallinity at 400 and 650 eV. The surface roughness was less than 1 nm for all films. No strong dependence of SEE yield on the deposition parameter of N ion energy was observed. The γ was as large as 2.3 at primary electron energy (PEE) of 0.8 keV. The SEE yield reduced to 1 when PEE increased to around 3 keV. Inset of Figure 6-1 shows the time decay of γ peak value profile. The SEE yield decreased quickly in the first few seconds and then down to 1 within 2 minutes.

Figure 6-1 SEE yields of AlN films, the inset is a typical time decay of γ peak value where the primary electron energy is 0.8 keV and the incidence electron current is 100 pA.

Figure 6-2 SEE of AlN films with thickness of 30, 80, and 450 nm.

Figure 6-2 is the SEE yield of AlN film with thickness of 30, 80, and 450 nm. The SEE yield increased slightly for thicker film. The maximum SEE (γ) yield was 2.5 with 450 nm-thick AlN when PEE was 0.7 keV. SEE yield then decreased rapidly as

increasing PEE. The SE generated by the primary electrons in the film move to the surface first with relatively weak electron-electron (e-e) scattering in wide bandgap materials, and then escaping from the surface if they have enough energy to overcome the work function of the materials. The SE generated near the surface can escape from the solid given the true NEA condition of the surface. However, as the primary electron energy increases, the majority of SE are excited deeper into the solid and have more time to thermalize to the bottom of the band. At very low primary energy, the internal SEs escape efficiently, and only a few SEs are created due to the small primary energy. The observed yield rises with primary energy because the number of internal SEs generated increase with primary energy. However, at high primary energies, the exponential nature of the escape process causes the decrease in the number of internal SEs that escape to be more rapid than the increase in generation of internal SEs. As a result, the total yield decreases with increasing PEE.

Figure 6-3 is the typical SEE yields of the AlN, GaN and InN films as a function of primary ion energy at normal incidence. Within the limitation in the primary energy, the peak SEE occurred at PEE of 0.7 keV for the AlN and GaN and the corresponding peak values were 2.5 and 2.2 respectively. For the InN thin film, the peak SEE was around 2.3 at PEE of 1 keV. The SEE yields reduced to 1 when PEE increased to ~5 keV for the AlN and GaN whereas the SEE yield of the InN reduced to 1 more slowly. This can be explained by the difference in conductivity of the samples. In wide bandgap semiconductors, the minimum kinetic energy for SE to escape is the electron affinity χ . The wide band gap prevents SE with kinetic energy less than the band gap value from participating in such e-e collisions. For these electrons, electron-phonon and electron-impurity collisions are mainly responsible for the energy loss.

Figure 6-3 SEE yields as a function of primary electron energy for the AlN, GaN and InN thin films.

The SEE yield exceeds 1 when the number of the emitted SE is larger than the number of arriving primary electrons. Subsequently, the electrons moving from the emitting sample into vacuum requires a certain level of electrical conductivity to replenish the lost electrons. Otherwise, sample charging will reduce the SEE yield to below one. The bandgaps of AlN and GaN are larger than that of InN and the resistance of InN thin films are only in several tens to hundreds ohms. Therefore, the charging effect resulted in a rapid decrease of the SEE to 1 for AlN and GaN.

6.3.2 SEE yield of AlN on aligned CNTs

One dimensional III-nitride semiconductors have stimulated a great deal of research interests for the application in cold cathode emitters due to the combination of the NEA surface and a large field enhancement factor inherited from the nanostructure [198]. However, very few reports investigated 1D nanostructures effect on SEE [199].

CNTs template is a very effective way to form nanostructures. In this section, SEE measurement from AlN coated CNTs was investigated.

Aligned CNTs on Si were synthesized by chemical vapor deposition using 5% Co composite as a catalyst layer. The base pressure of the reactor was evacuated to 10^{-2} Torr using a rotary pump. The substrate was heated up to 600 °C and the ratio of the flowing gas mixture of H₂ and N₂ is 90/30 sccm. Acetylene (C₂H₂) of 10 sccm was then introduced into the chamber when the temperature reached 600 °C. The growth pressure was maintained at 10– 20 Torr during the CVD process and the growth time was set at 5 min. In addition, a negative dc bias could also be applied to the substrate to promote the growth of aligned CNTs.

Figure 6-4 shows the SEM images of CNTs before and after AlN coating. The thickness of AlN was about 80 nm. AlN almost covered the whole surface. SEE yield of the AlN thin films prepared under various deposition conditions exhibited peak value of γ in the range of 1.8 – 2.4 at PEE of 0.7 – 1.0 keV as discussed above. The film with moderate SEE yield was selected for comparison study. Figure 6-5 shows γ of the AlN thin film on Si and on CNTs as a function of PEE. It has been found that the AlN coated CNTs has a higher γ than those film deposited on Si substrate. SEE reached a maximum for electron energies of 1 keV and then decreased rapidly with increasing primary energy. Slight enhancement in SEE had been found for AlN deposited on CNTs as compared with CNTs on Si substrate. The peak value of γ increased from 1.98 to 2.38. Furthermore, the range of PEE values enlarged from 0.8 ~3 keV to 0.8 ~9 keV for $\gamma \geq 1$. This result suggests that the rough topography of AlN/CNT enhances the SEE yield. When electrons are incident on a solid surface, it was experimentally observed that the bound electrons in the solid could gain enough

Figure 6-4 SEM images of the CNTs (a) before and (b) after AlN coating.

Figure 6-5 SEE yield of the AlN thin films on Si and CNT.

energy through collision processes from the incoming electrons, to overcome the binding surface potentials and emerged as free electrons from the solid surface. Therefore, the SEE is greatly affected by the surface condition of the solid.

Angular dependence of SEE yield from the AlN films has been measured to clarify SEE yield mechanism. The SEE yield was measured on samples for tilt

incidence angles (θ) ramping from 0 to 50 °. The increase of SEE yields with increasing θ is due to the small escape depth of the SEs. Therefore, the longer the penetration distances of the PE within the escape depth of the SEs, the higher the yield. The power law was well established to explain the SEE properties. The power theory predicts that the normalized yield γ/γ_0 , where γ_0 is the SEE yield maximum at normal incidence, should vary as $1/\cos\theta$ ^[195]. Figure 6-6 shows that the experimental data for the AlN/Si and AlN/CNT do not match with the theory for the simple case and appears independent of samples at large θ values. The curve fits are $\exp[0.89(1-\cos\theta)]$ and $\exp[0.31(1-\cos\theta)]$ respectively. Similar treatments were found in TiN films ^[200]. However, the fitted curves did not match very well in the case of the AlN/CNTs at the points circled in the figure. The lack of agreement with theory began to occur far from the grazing incidence. Thus, this did not appear to be just a surface-related phenomenon.

Figure 6-6 Normalized peak yield from the AlN/CNTs and AlN/Si vs. primary beam incidence angle, at PEE = 1 keV.

The power law in another expression, ie., the relationship between the SEE yield and primary incidence angle can be described by a straight line plot (see equation 6.4). Figure 6-7 gives the plots of $\ln(\gamma_\theta)$ vs. $(1-\cos\theta)$ for the AlN on Si and CNTs at PEE 0.9 keV and 1 keV. The plots of the film deposited on Si can be fitted with straight lines. However, AlN/CNTs does not follow continuous straight line relationship but a two lines one with different slopes. The discontinuity occurs at the incidence angle between 20° and 30° . The slopes of that AlN on Si increased with an increase in PEE. Below 20° , the AlN/CNTs showed similar behavior as the AlN/Si. However, above 20° , there is less dependency of SEE on incidence angle. This indicates that the SEE yields not only surface morphology dependent but also a nanostructured topography dependent since there exists strong local field of the sharp CNT tips [199].

Figure 6-7 Plots of angular dependence of $\ln(\gamma_\theta)$ against $(1-\cos\theta)$ for the AlN on Si and CNTs. k_i and k_i' are slopes of fitted lines.

In order to investigate the SEE of AlN/CNTs when bombarded by energetic ions, high resolution nuclear microprobe measurement was carried out at the Centre for Ion Beam Applications (CIBA) at the National University of Singapore. A beam of 2 MeV protons was focused to about $\sim 150 \times 200 \text{ nm}^2$ and the scan area was $20 \times 20 \text{ }\mu\text{m}^2$. The SEs have been detected using AMPTEK (MD 502) detector at an glancing angle to the sample. The beam current was below 1 pA. Measurements were done in 3 scans at different points of each sample. Normalization between different scans and samples were made by assuming a constant current. MgO film is one of the most studied insulators with high SEE yield. For comparison, SEE of FCVA-MgO thin film was also measured. Figure 6-8 gives the average SEE efficiency from CNTs, AlN/CNTs and MgO/CNTs. On average the AlN/CNTs sample showed much better SEE yield than other samples, which was consistent with the measurement performed with incident electron beam in SEM. It is interesting to observe that the AlN/CNTs sample exhibited superior SEE yield when bombarded by proton or electron.

Figure 6-8 SEE efficiency from CNT, MgO/CNT and AlN/CNT.

Generally, radiation detectors are only efficient for one type of radiation (e.g. ions or electrons). The AlN/CNTs may be promising for highly-sought universal radiation detectors.

6.4 Summary

In Summary, the SEE yields of I-FCVA III-nitrides (AlN, GaN) thin films were comparable with that of MgO thin films^[40, 201-202]. This shows the potential application of the films in vacuum devices. Furthermore, the SEE yield could be enhanced by using 1D nanostructures as template under both electrons and ions bombardment due to the local field enhancement, which could make it useful in highly efficient radiation detectors.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The I-FCVA technique has been developed to fabricate binary group III nitrides (AlN, GaN, InN) on Si substrates at low temperature (475 °C).

- Highly *a*-axis oriented AlN films have been fabricated at T_s of 350 °C, or by employing 50 V negative bias to the substrate. AlN films exhibited smooth surface morphology. The RMS values of all the AlN films were less than 2.0 nm measured by AFM, which was smaller than that of AlN films grown by MBE, CVD and sputtering. AlN thin films had ~10 at. % oxygen as estimated by XPS. It was found that the films were nearly stiochiometric in Al-N bonding.
- InN films exhibited wurtzite structure, as confirmed by XRD, TEM and Raman spectroscopy. The preferred orientation is attributed to the minimization of the overall surface and strain energy of the film during growth. Under the optimized growth conditions of InN films, highly (0001) preferred orientation exhibited RT PL emission at 1.15 eV. HR-TEM revealed the amorphous structure of the grain boundaries. EDX analysis showed the incorporation of oxygen at the grain boundaries. Therefore, oxygen in the form of amorphous phases (e.g., amorphous oxide or oxynitride) may be attributed to the observed PL emission at 1.15 eV.
- InN nanostructures were fabricated by tuning the deposition parameters. The growth mechanism of the self-assembling InN nanostructures follows the V-W mode, which is due to the combined effect of the large lattice mismatch

between InN and substrates, and the energetic source species of nitrogen ions and indium plasma. The I-FCVA InN nanostructures exhibit good FE properties.

- GaN films on Si with and without ZnO buffer were successfully fabricated. The ZnO buffer layer is beneficial to obtain high quality GaN films. Room temperature PL at 369 nm (3.36 eV) was observed from the GaN on ZnO buffered Si.
- The SEE yields of III-nitrides thin films prepared by I-FCVA was comparable to those of MgO thin films, showing the potential application of the films in vacuum devices. Furthermore, SEE yield is not only surface morphology dependent, but also nanostructured topography dependent as analyzed from the incidence angle dependence.

7.2 Recommendations for future research

- High oxygen contamination is commonly observed from all the deposited films (AlN, InN and GaN). In order to improve the quality of the nitrides, the oxygen concentration in the films should be reduced. An improved pumping capacity and proper baking and gettering system / process may help to realize such an objective.
- Although favorable condition for highly preferred (0001) InN has been established in this work, large disordered grains were still found in the films. The improvement could be done by further optimization the system and the growth process.

- ZnO buffer has been found beneficial for hetero-growth of GaN film on Si, but the quality of GaN does not reach the same level as those prepared by MBE or MOCVD. One of the reasons is that the T_s (450 °C) is not high enough. However, ZnO layer will degrade under high temperature as the diffusion length of Zn and O can be as long as 200 nm at 800 °C. More works on GaN with ZnO buffers can be continued by inserting another thin buffer (such as low temperature GaN), and increasing the T_s to 600 °C.
- SEE properties of III-nitrides are less studied despite their potential application in high efficient radiation detector. The relationship between the SEE yield and the nanostructured topography was not well understood.

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