A study on the orientated growth, microstructure and thermal conductivity of RF reactively sputtered AlN films

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**A STUDY ON THE ORIENTATED GROWTH, MICRO-
STRUCTURE AND THERMAL CONDUCTIVITY OF
RF REACTIVELY SPUTTERED AlN FILMS**

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**SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

2005

**A Study On The Orientated Growth, Microstructure and
Thermal Conductivity of RF Reactively
Sputtered AlN Films**

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A thesis Submitted to the Nanyang Technological University
in fulfillment of the Requirement for the degree of
Doctor of Philosophy

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Abstract

With many novel properties aluminum nitride has received considerable attention in recent years. Many techniques have been used to deposit AlN films. Among them reactive sputtering is promising for low temperature deposition and its relative low cost.

Preferred orientation (orientated growth/fiber texture) is commonly observed in AlN films deposited by various techniques. The orientated growth has been found to result in a wide range of optical, mechanical, and electronic properties of AlN films in the previous works. However, the basic physical process that controls the orientated growth is still not well understood and systematical studies on this topic are even rare.

The microstructural properties contain essential information on understanding the growth habit of the deposited AlN films. For examples, the morphology, stress and observable phonon modes of the deposited films are strongly related to the orientated growth; the microstrain may even control the orientated growth. The microstructure characterization has not been well carried out in the previous works. This calls for further efforts in order to provide detailed microstructural information of the deposited AlN films.

Currently the study on thermal transport properties of thin film materials is very useful and also challenging topics. AlN is a suitable candidate for such studies both for its high intrinsic thermal conductivity and its applications in future high temperature, high-energy devices with reduced feature size.

In this study AlN films have been deposited by reactive sputtering in argon and nitrogen gas mixture. The orientated growth in the sputtered AlN films has been systematically studied. Various techniques have been used to characterize the deposited films and study the growth habit of these films. The effect of various deposition parameters (e.g. sputtering gas pressure, gas composition, substrate temperature, RF power, gas flow rate, substrate temperature) on the orientated growth has been investigated. A novel

photothermal reflection technique has also been used to study the thermal conductivity of the sputtered AlN films. The experimental efforts lead to the following observations:

- A coincidence between the preferred orientation and the surface morphology of AlN films has been established with the experiment results. The (002) orientated films have pebble-like grain structure. The (101) orientated films show facet (or pyramid-cone) morphology. The (100) orientated films have elongated grain structure.
- Conditions with high nitrogen concentration in sputtering gases, low sputtering gas pressure and small RF power have been found to lead to c-axis / (002) orientated growth in sputtered AlN films. The formation of (002) preferred orientation has been attributed to the features of low sputtering yield/ deposition rate and more effective kinetic energy transfer of incident species to the film surface under these conditions. With the presence of these features close-packed (002) surface plane containing strong Al-N bondings can be formed. Under low nitrogen condition it is found that the backscattered neutral argon particles influences the growth behavior of AlN films by bombarding the film surface. The minimum energy models for orientated growth have also been evaluated. An anisotropy in microstrain ε and elastic strain energy U of different planes has been found in the (002) orientated films with $\varepsilon_{101} < \varepsilon_{002}$ and $U_{101} < U_{002}$. This indicates that the minimum strain energy model is not valid here. The surface energy of individual planes has dominated the orientated growth.
- The AlN films deposited by both pure Al target and AlN targets have shown similar evolution in the preferred orientation with the change in gas composition. The crystalline properties of AlN films deposited with pure Al target are better than those deposited with AlN target. Three phonon modes have been observed in the deposited films and attributed to E_1 (TO), A_1 (TO), and E_2^2 phonon modes of AlN.
- An oxygen-rich amorphous interface layer is commonly found in the deposited AlN films followed by a V-shaped columnar grain growth. A large amount of sub-grains with a 3-D honeycomb-like grain/sub-grain boundary network have also been found.

Abstract

The film grows with the continuous formation of the secondary nuclei and grows vertically rather than across the surface.

- The results of electron beam diffraction have revealed detailed information on the evolution of the orientated growth and the alignment of individual columnar grains. The formation mechanism of the diffraction patterns has been explained in detail.
- Very low thermal conductivities (1-4.5 W/mK) have been found in the deposited AlN films and attributed to the strong phonon scattering by oxygen impurity and grain boundaries.

Chapter 1 Introduction

1.1 Background and motivation

With excellent thermal conductivity (320W/mK), thermal expansion matching to substrate materials (as shown in Table1.1), chemical stability, high hardness, high acoustic velocity, large electromechanical coupling coefficient and a wide band gap (6.2 ev), aluminum nitride has received great interest as a promising candidate material for the substrate/packaging materials (e.g. heat sink, heat spreader, filler materials) for the microelectronic industry, ignition modules, wear-resistant coating, dielectric and passivation layers, surface acoustic wave devices, thin film resonators, and buffer layer for GaN based photoelectric devices [1-5].

Table. 1.1. Physical properties of the materials commonly used
in electronic industry [6-10]

Property	Diamond	Aluminum Nitride	Silicon carbide	Silicon	Gallium Arsenide
Density (g cm ⁻³)	3.515	3.26	3.2	2.33	5.3164
Thermal Conductivity at 300K (W/m k)	2000 (type Ia)	150-320	50-490	150	29.4-58.8
Thermal Exp Coef $\times 10^{-6}$ (1/k)	1.02	4.0	3.4	2.618	6.478
Resistivity (ohm cm)	10^{12} - 10^{16}	10^{14}	10^{-2} - 10^1	3.16×10^5	3.3×10^8
Hardness (brinell)	$6 \cdot 10 \times 10^3$	1200	~	1050	~

The crystallographic texture, the morphology, the microstructure and the stress of thin film materials may have considerable influence on their performance. Examination of these micro-structural properties may give an insight to the reason why some films show better performance over the others [11-12].

The crystallographic texture plays an important role in determining a wide range of optical, mechanical, and electronic properties of thin film materials. Therefore, the control of texture is key to optimize the performance of polycrystalline films. For examples: AlN

films with different preferred orientation have been reported to show better performance in surface acoustic wave (SAW) devices and thin film resonators [13-14]; c-axis orientated AlN films and epilayer can help to grow GaN epilayer for device usage [15-16]. The control of the microstructure of thin film materials, including faceted surface morphologies, is a critical factor in determining coating performance of polycrystalline wear-resistant coatings and diffusion barriers [12]. The chemical composition may influence the optical properties and device performance of the deposited films [17]. Other micro-structural factors such as grain size, boundary phase, and impurity concentration can contribute to the phonon scattering process in these films and influence their heat transport properties [18-19], which will be important in future high temperature, high energy devices and packaging with reduced feature size [20].

With the strong interest in AlN, many techniques, such as sputtering [21-22], chemical vapor deposition [23], laser chemical vapor deposition [24], pulsed laser ablation [25-26], molecular beam epitaxy [27], ion beam assisted deposition [28] and N_2^+ implantation [29], have been used to fabricate AlN thin film / layer on various substrates. In most cases mentioned above, the fabrication temperatures are quite high. High temperature deposition has the disadvantages of the degradation of the substrate and thin film during deposition due to thermal damage. Hence deposition of AlN thin films at low temperature has become increasingly important and valuable [30]. Sputtering technique is promising under circumstances where low temperature deposition and conformal coatings are needed [30-31].

Like other plasma-based deposition techniques, sputtering is a dynamic and non-equilibrium process. Where the growth of the thin film materials is highly dependent on the deposition parameters that affect the reactive/ growth kinetics, for examples: gas pressure, power and gas composition [32]. Hence a variety of microstructure and properties can be expected in the films deposited under different conditions and in the sputtering systems with different set-ups. Then the effort on establishing optimum parameters for the desired properties is always necessary. And an understanding of the basic controlling physical process and the growth mechanism is even more important, as

such an understanding will help on maintaining reproducibility and allowing the transfer of a process from one system to another [33].

In the earlier research works on the sputtered AlN films the researchers have tried to establish the relationship between the deposition parameters and the materials properties (e.g. physical and electrical properties [34-38]). Various efforts including the statistic approach (design of experiment) [39] were made on establishing the optimum parameters for the desired properties. The orientated growth (preferred orientation, texture) was widely observed and found to result in the different properties of the deposited films (which helps to understand why (002) orientated films are generally favored now). However, the formation mechanism of the texture and the basic controlling physical processes were rarely discussed. More recently efforts are made on the study of the formation mechanism of texture in the sputtered films (e.g. AlN, TiN). Various formation mechanisms for the texture in sputtered films, taking into account of the effect of energetic particle, strength of the chemical bonding, minimum surface energy model, and the minimum strain energy model, etc. [40-42] have been proposed. As the results are still not conclusive and sometimes are even conflicting [43] the subject is therefore still open for studies. Systematical studies with detailed discussions on the formation mechanism of preferred orientation and the effect of various deposition parameters on the orientated growth will be useful.

Among the existing research works on the orientated growth of sputtered films the microstructure of the deposited films was always not well studied and discussed. While the microstructure properties, such as surface morphology, cross-sectional structure, interface, impurities, strain/ stress etc. may contain important information of the growth habit of these films. Detailed microstructure characterization helps to correlate the orientated growth and the microstructure properties of the deposited films and get a better understanding of the growth mechanism of these films.

In the open literatures the results on the phonon modes of the deposited AlN films are also not satisfying. The theoretical and experiment results are not well consistent to each other

[44-46]. Hence more efforts are necessary on the measurement of vibrational spectrum of AlN. Moreover, the result of vibrational spectrum measurement can help to estimate the residual stress in the textured films, which is difficult to measure by the conventional x-ray diffraction stress measurement technique [47-48].

The thermal transport property of thin film materials receives more and more interest today as the micro-scale thermal dissipation properties will be important in the future optoelectronic devices, layered structure and thermal barrier layer materials [49-52]. This new and challenging research area calls for both theoretical and experimental efforts to get a better understanding of the microscale heat transfer phenomena in the low-dimensional thin films/ layered structures. Among these tasks the attempt to establish the relation between the thermal transport property and the microstructure of the deposited films are of great importance and urgency [53]. While in the past days very few materials scientist had joined in the research in this area and the microstructure characterization in the existing studies are far from satisfying.

1.2 Objectives

In this work the basic controlling physical process for the orientated growth of reactively sputtered AlN films will be systematically studied with the consideration on various factors that may influence the orientated growth of the deposited films. For example: the energetic particle effect and the minimum energy model for the orientated growth. The effect of various deposition parameters, such as sputtering gas pressure, gas composition, substrate temperature, power, etc., on the orientated growth of reactively sputtered AlN films will be evaluated and discussed.

Various advanced characterization techniques such as x-ray diffraction (XRD), transmission electron microscopy (TEM), field emission gun scanning electron microscopy (FEGSEM), Fourier transformation infrared spectroscopy (FTIR), atomic force microscopy (AFM), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS), etc., will be used to study the microstructure of the deposited films. The microstructure

properties such as morphology, stress, vibrational modes will be correlated to the orientated growth of the deposited films. And the growth mechanism will be discussed in detail based on the knowledge of the fine structure of the deposited AlN films.

The thermal transport properties of the selected AlN films will be studied and correlated to their microstructures.

1.3 Outline of this dissertation

This thesis is divided into ten chapters and presented as follows:

In Chapter 2, the fundamentals of sputtering deposition and thin film mechanism are briefly reviewed. The major experimental techniques used in this study are introduced in Chapter 3. The effect of gas composition on the orientated growth and the microstructure of AlN films is studied in Chapter 4. The effect of sputtering power is investigated in Chapter 5. In Chapter 6, the effect of substrate temperature and gas flow rate is discussed. The effect of sputtering pressure is studied in Chapter 7. TEM results of the fine structure of the films deposited at various gas pressure were presented in Chapter 8, where the microstructure and growth habit of the deposited films were discussed in details. The results and discussions on the thermal transport properties of the deposited AlN films are included in Chapter 9. Chapter 10 contains the suggestions for future works.

Chapter 2 Fundamentals

The contents of this chapter are very important for the understanding of the sputtering deposition and the growth mechanism of sputtered films. And they are the foundations of the explanations and statements made in the experimental part of this work.

2.1 Sputtering deposition

Sputtering is the deposition of particles vaporized from a surface (sputter target) by the physical sputtering process. It is a non-thermal vaporization process where surface atoms are physically ejected by momentum transfer from an energetic bombarding particle that is usually a gaseous ion accelerated by a plasma or an "ion gun"[54].

2.1.1 History of sputtering deposition

Sputtering was first observed in a dc glow discharge tube by Grove in 1842 and used as a method for depositing a film in 1877 [55]. But the invention of much faster process, "vacuum evaporation", some 50 years later caused sputtering to be largely discarded. For a few decades, studies of sputtering process were confined to investigations of the physics of the ion bombardment. This slow development in understanding the phenomena was largely caused by many difficulties associated with making meaningful measurements during sputtering and the poor vacuum obtained by the crude pumping system at that time. It was in the 1920s that the pioneering work of Langmuir laid the foundation for modern plasma physics and led to a much better understanding of the gas discharge environment in which sputtering operates [56]. The increasing interest in refractory-metal and alloy films for microelectronics and cryogenic applications has resulted in a "rebirth" of sputtering as the conventional evaporation technique encounter difficulties under these circumstances [57]. With the development of radio frequency (RF) sputtering and other variants of sputtering systems, it has become one of the major PVD deposition techniques and plays important roles in today's industrial manufacturing and scientific research. More details can be found elsewhere [58].

2.1.2 Principles of sputtering

2.1.2.1 Glow discharge and plasma

There is a fourth phase of matter - the plasma phase - which consists of separated nuclei and electrons... The plasma phase is by far and away the most common - stars are plasma - but it is also by far and away the most difficult to discuss quantitatively.

—Walton [59]

It is necessary to introduce the concepts of plasma and glow discharge before we can start talking about sputtering deposition, as the energetic bombarding particles (gaseous ions) in sputtering are usually generated in a glow discharge and accelerated by a plasma. A glow (emitting a colourful halo of light) discharge is a current flowing through a low-pressure gas. A plasma is a partially ionized gas. There are at least three distinct particle populations: singly charged positive ions, electrons, and neutral gas particles.

A. The components of a dc glow discharge

DC glow discharge is better understood than others. When a direct current (dc) voltage (>breakdown voltage) is applied between the two electrodes spaced some distance apart in a low-pressure working gas (usually it is an inert gas) the gas molecules located between the two electrodes will be ionized and a glow discharge initiated. The process is discussed below.

The applied electrical field will accelerate the electrons emitted from the cathode. When the electrons travel towards the anode they make ionizing impact with the gas molecules. With effective energy transfer by collision a gas molecule will be ionized with the generation of an ion and the emission of a new electron. Consequently the ions will be accelerated by the applied electrical field and move towards the cathode. If the applied voltage is high enough, the ions will, on striking the cathode, eject secondary electrons from the cathode surface. The current in the glow discharge will be determined by the procedures of ionization (by electron impact) and secondary electron emission (by ion

bombardment). Once equilibrium between these two procedures is set up the glow discharge will be a self-sustained. Several luminous and dark regions can be identified in a dc glow discharge, as depicted in Fig. 2.1..

Fig.2.1 The classical luminous and dark regions of a dc glow discharge [60]

In the Aston dark space, the electrons emitted from the cathode have very low energy, and probably cannot either excite or ionize any gas particles. Ions in this region are moving very rapidly towards the cathode.

There are two possible causes for the cathode glow. One is that the low energy electrons emitted from cathode surface are experiencing excitation collisions with gas atoms near cathode surface. The other is that the neutralized ions may initially acquire the orbital electron in an excited state and emit photons to decay to ground state [61].

In the Crookes dark space there is effectively no excitation of neutrals by both the high velocity electrons accelerated across the cathode fall and the low velocity electrons liberated by impact ionization of neutral atoms.

In the negative glow the electrons slowed by the collisions in the dark space have much

larger collision cross-section for the excitation of neutrals. The excitation results in enhanced visible emission.

Most electrons in Faraday dark space have already lost most of their energy by the collisions with the gas molecules. As they have passed through a small retarding field their energy was further reduced. Hence the Faraday dark space is less luminous.

There is a small electric field in the positive column, which can accelerate electrons up to energies sufficient to cause excitation and even ionization, so the luminosity is higher.

The positive column and Faraday dark space are less important in a glow discharge. Sputtering can be operated with the anode placed in negative glow region [57].

B. Plasma chemistry

The result of real time light emission spectroscopy has confirmed the existence of complex chemical reactions and gas species in the plasmas. For example (note that ° and * in the following part denote the neutral and metastable species) [57, 62]:

1. Ionization. The most important process in sustaining the glow discharge is the electron impact ionization. A typical reaction is

The two electrons now can ionize more Ar° . By this multiplication mechanism the glow discharge is sustained. The reverse reaction also occurs and is known as recombination.

2. Excitation. In this case the energy of the electron excites quantized transitions between vibrational, rotational, and electronic states, leaving the molecule in an excited state (denoted by an asterisk). An example is

3. Dissociation. The molecule is broken into smaller atomic or molecular fragments. The products are generally much more chemically active than the parent gas molecule and serve to accelerate reactions.

4. Dissociative ionization. During dissociation one of the excited species may become ionized. For example

5. Electron attachment. Here neutral molecules become negative ions after capturing an electron. For example

6. Dissociative attachment.

7. Symmetrical charge transfer

8. Asymmetric charge transfer

9. Metastable-neutral.

10. Metastable-metastable ionization.

2.1.2.2 Ion-surface interactions

In history two theoretical models have been proposed for sputtering [63], namely:

1. Thermal vaporization theory: in which it is argued that the surface of the target is heated enough to be vaporized due to the bombardment of energetic ions.
2. Momentum transfer theory: in which it is stated that the surface atoms of the target are emitted with the transfer of kinetic moments from the incident particles to the surface atoms of the target.

Today momentum transfer theory is widely accepted and sputtering is believed to result from a collision cascade in the surface layers of the target. The procedure of collision cascade can be simply described as: the incident ions knocks atoms off their equilibrium

sites in the target, thus causing these atoms to move through the materials, to undergo further collisions, and eventually to cause the ejection of atoms through the target surface, as depicted in Fig. 2.2.

Fig.2.2 Synopsis of the interaction events occurring at and near the target surface during sputtering process [60]

Except for the collision cascade a great variety of interactions also occur on the target surface, as illustrated in Fig. 2.2. These interactions include liberation of neutral atoms, ionized atoms, backscattering, x-ray emission, photo generation, secondary electron emission, and the desorption of gas atoms from the target surface [54, 62].

In the target itself, several other processes can occur, including the creation of point defects, local heating, amorphization, implantation, and compound formation.

In sputtering with metallic and compound cathode, cluster emission and negative ion emission were also experimentally observed. For examples, AlN^{-1} , $(\text{AlN})_2^{-1}$, AlN_2^{-1} , AlN_3^{-1} have been found in dc AlN deposition with a metallic Al target. And the negative ion emission was found to result in significant change in composition in the high T_c superconductive oxide films [57, 64].

All the interactions mentioned above depend on the type of ion (mass, charge), the nature of surface atoms involved, and importantly, on the ion energy (sputtering voltage / power). In a real sputtering system, these factors will influence the sputtering yields and the consequent growth of the deposited films.

2.1.2.3 Sputtering yield

The most fundamental parameter characterizing sputtering is sputtering yield S , which is the removal rate of surface atoms due to ion bombardment. And is defined as the mean number of atoms removed from the surface of a solid per incident ion and is given by

$$S = \text{atoms removed} / \text{incident ions}$$

In many textbooks the yield data are given by the sputtering rate $S/(1+\gamma_s)$ [63], where γ_s is the secondary electron coefficient of the target materials. The sputtering rate of compound target is much lower than that of a metallic target because of a reduction in the sputtering yield and an increase in the secondary electron emission [54].

The sputtering yield will be influenced by the following factors:

1. Energy of incident particles E_i .

In a low energy region, a threshold energy (E_0) exists for sputtering. See in Fig.2.3. Larger than this threshold, in a range up to several keV, the sputtering yield increases monotonically with the incident ion energy until a plateau is observed around 10-100 keV. Further increase the ion energy results a decrease in sputtering yield, as the high energy incident ion will more likely pass through the surface layers of the target without undergoing a nuclear collision. The ion gradually loses energy to the viscous damping of the electrons in the target until the cross-section for nuclear stopping grows large enough to make a nuclear collision likely. The displacements that result at the end of the ion track may be too far below the surface to result in sputtering. And there is no advantage to be gained by increasing the ion energy further.

Fig.2.3. Variations of sputtering yield with the incident ion energy [63]

2. The atomic masses of target materials and gas ions

The sputtering yield depends on the atomic mass of the target material. The experimentally observed yield and threshold energy vary periodically with the element's atomic number of the target materials. Comparing various materials, the yields increase consistently as the d shells are filled for the elements located in the same row of the periodic table.

The sputtering yield depends also on the atomic masses of the incident ion, as depicted in Fig. 2.4. There is a general increase in yield as the mass of the ions is increased, but there is a periodic undulation superposed on this trend which coincides with the grouping of the periodic table. It is interesting to find that the maxima occur for the point representing the rare gas. As yet, there is no valid explanation for this periodicity. While by this fact we can understand why rare gases are commonly used in sputtering deposition.

Fig.2.4 Sputtering yield as a function of bombarding ion at 45 keV [55]

3. Target surface binding energy (E_b) and effectiveness of energy transfer

An atom must possess at least a minimum kinetic energy to escape from the target. The height of the potential-energy barrier that is must overcome is the surface binding energy. In fact the heat of sublimation is often used as the effective surface binding energy, as no significant difference is found between the two values. Sputtering yield S is related to E_b by the following equation [62]

$$S \propto \frac{\ln[(E_2 + E_t)/2E_b]}{\ln 2}$$

Where E with suffix 2, t and b denote the energy of sputtered atom, threshold energy and surface binding energy respectively.

The efficiency of the energy transfer by collision will also determine the sputtering yield, as the sputtering yield S is proportional to the energy transfer mass factor γ_m . γ_m is a function of the atomic mass of the incident ion and sputtered atom. S is related to γ_m by the following equation [62]

$$S \propto \gamma_m \equiv \frac{4M_1M_2}{(M_1 + M_2)^2}$$

where M with suffix 1 and 2 denotes the atomic mass of the incident ion and the sputtered atom. Accordingly the transfer of energy is effective when the two masses of M_1 and M_2 are equal or close. For example: the sputtering yield of Al under He^+ is very low as the discrepancy between the masses of these two elements is large.

4. The collision cross section

Sputtering yield S is proportional to the collision cross section $\sigma_0 = \pi a^2$, where a is related to the Bohr radius of the atom a_b , and the atomic numbers Z_1, Z_2 of the incident ion and sputtered atom respectively [62]; i.e.,

$$a = \frac{a_b}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}}$$

5. Other factors.

Other factors such as projectile angle of the incident ions can also influence the sputtering yield. As the energy transferred by collision (E_t) is also proportional to $\cos(\theta)$, where θ is the angle between the moving direction of the incident ion and sputtered atom [11, 65].

In summarization of the above factors, the currently accepted theory for the sputtering yield from collision cascades is due to Sigmund and predicts as [62]:

$$S = \frac{3\alpha}{4\pi^2} \frac{4M_1M_2}{(M_1 + M_2)^2} \frac{E_i}{E_b} \quad (E_i < 1 \text{ keV})$$

and

$$S = 3.56\alpha \frac{Z_1Z_2}{Z_1^{2/3} + Z_2^{2/3}} \left(\frac{M_1}{M_1 + M_2} \right) \frac{S_n(E)}{E_b} \quad (E_i > 1 \text{ keV})$$

where the parameter α , a measure of the efficiency of momentum transfer in collisions, increases monotonically from 0.17 to 1.4 as M_1 / M_2 ranges from 0.1 to 10. The reduced stopping power, $S_n(E)$ is a measure of the energy as well as masses and atomic numbers of the atoms involved. At high energy, S is relatively constant because $S_n(E)$ tends to be independent of energy.

2.1.3 Various sputtering systems

The sputtering processes can be divided into four categories: (1) dc, (2) RF, (3) magnetron, (4) reactive. We recognize, however, that there are important variants within each category (e.g., dc diode, dc triode) and even hybrids between categories (e.g. reactive RF).

2.1.3.1. DC Diode / Cathodic sputtering

When a sputtering target is used as the cathode in a DC glow discharge (Fig.2.1), a DC diode sputtering will take place. Typically, sputtering takes place when the flux of ions generated in the glow discharge incident on the target surface. Through momentum transfer process, surface atoms of target materials, and occasionally clusters of atoms will be knocked free from the target surface and deposited on any solid surface (eg. substrate, chamber wall) [54].

DC diode sputtering has some constitutional problems. For examples: most of the input power is used to accelerate the ions through the sheath, and appears as heat when the ions strike the cathode [57]; at very low pressure, a glow discharge cannot be self-sustained in a common dc diode sputtering system as the mean electron free paths are so long that not enough ionizing impact and secondary electron emission can take place. Different techniques have been used to solve such a problem. When an external electron source (eg. electron gun) is used to make the plasma to be self-sustained at low pressure, it forms a triode system. An alternative method is to use magnetron to enhance gas ionization at low pressure.

2.1.3.2 Magnetron sputtering

In order to enhance the probability of collisions of electrons with sputtering gas atoms at a given pressure in the chamber, the path of the electrons has to be made longer. This can be achieved by the addition of a magnetic field, which is not influencing the motion of the heavy charged ions markedly but, by the Lorenz-force, initiates a circular motion of the electrons. That combined with the effect of the perpendicular electric field will force the electrons to follow a cycloid track rather than being immediately extracted from the

plasma by the electric field. The increased collision probability results in current of 10–100 mA/cm² densities on the target, compared to 1 mA/cm² obtained in non-magnetron configurations. Fig.2.5 is a schematic drawing of a planar magnetron target arrangement. In these configurations even the secondary electrons enhance the ionization by hopping movement close to the target surface.

Fig.2.5 Magnetron sputtering principle (right top) and more efficient target utilisation (left and bottom) [55, 62]

Magnetron sputtering system is always a hybrid system. When a dc power supply is used the system is referred as a dc magnetron system. When a radio frequency (RF) power supply is used the system is called a RF magnetron system.

The physical phenomena that take place in a planar magnetron sputtering system are summarized in Fig.2.6. With this figure the reader can get a sketch view of the concepts of glow discharge, plasma and sputtering.

2.1.3.3. RF sputtering

One drawback of a dc glow discharge is that only electrically conducting targets can be used [57]. Insulators cannot be used because of the immediate build-up of a surface charge of positive ions on the front side of the insulator. Hence a glow discharge cannot

be self-sustained. The use of a radio frequency (usually 13.56 MHz is taken to avoid communication interference) ac power source can alleviate such problems.

Fig.2.6. The physical phenomena that take place in a planar magnetron sputtering system [67]

In RF sputtering the target behaves like a capacitor that is charged in alternate directions by the plasma. Since the charging time is much longer than the ac period, current will flow in the plasma for the entire ac cycle. RF sputtering essentially works because the target self-biases to a negative potential. The negative target bias is a consequence of the fact that electrons are considerably more mobile than ions (at any frequency above 50 kHz, the ions have too much inertia to follow the field without a phase lag; electrons, on the other hand, can easily follow the field), which would enable a net current averaged over a complete cycle to be different from zero, see Fig.2.7 (a). But this cannot happen in a normal capacitor coupled RF sputtering system as no charge can be transferred through the blocking capacitor. Hence the target voltage shifts to a negative value to ensure that there is no net current flow. The formation of the negative target bias is schematically shown in Fig. 2.7 (b). Once this happens, the sputtering procedure behaves like a dc sputtering where positive ion bombardment sputters away target atoms for subsequent deposition [57, 62].

Fig. 2.7. Formation of pulsating negative sheath on capacitively coupled cathode in an rf discharge. (a) Net current / zero self-bias (b) Zero current / non-zero self bias voltage [62]

RF sputtering has some advantage over dc sputtering. For instances: the RF system can be operated at low gas pressures; both metallic target and compound target can be used. While deposition with compound target can cause uncontrollable heating of the target (it has also been argued that in RF sputtering only 50% power resulted in the sputtering of target, hence the sputtering is energy inefficient). Poor conductivity and insufficient target cooling generate thermal stresses, and eventual cracking of the target. Moreover, for alloy and compound targets sputtering, the difference in sputtering yields of individual elements can cause non-stoichiometry of the deposited films. And the sputtering rates of compound targets (e.g., oxides and nitrides) are generally much lower than the sputtering rates of elemental metal targets. To deposit a metal nitride or metal oxide film then, it makes sense to use an elemental metal target in a reactive process gas ambient, typically Ar mixed with N_2 or O_2 (N_2 / O_2 dissociates to atomic nitrogen / oxygen in the plasma)[54]. Reactions in the target surface (not in gas phase), or on the surface of the growing film can lead to the formation of the desired compound, while retaining the high sputtering rate of an elemental metal. While it is also found that with the increase in the frequency the deposition rate of RF sputtering system may be much lower than that of DC sputtering system. This was found in magnetron sputtering with both Al and AlN targets

[57]. RF reactive sputtering, however, is better than dc reactive sputtering as it is more suitable for process control.

2.1.3.4. Reactive sputtering

Reactive sputtering takes place in the presence of the reactive gases, either mixed with an inert working gas (argon is commonly used) or not. The sputtered material chemically reacts with the reactive gas. Compounds such as oxides, nitrides, and carbides can be deposited in this fashion.

The question of where compounds are synthesized (at the target; in the gas; or at the substrate) is central to an understanding of the reactive sputtering. Reactions in the gas phase can be considered unlikely since ions cannot be neutralized in the gas phase. The heat liberated in the chemical reaction cannot be dissipated in a two-body collision. Simultaneous conservation of energy and momentum requires the reaction occur at the surface of the target or the substrate [63, 65].

Most vacuum systems are dynamic systems. For a system with constant pumping speed S and whose pressure is controlled by the inlet gas flow rate Q , $S = Q/p$, where p denotes the inlet/chamber gas pressure, the partial pressure of individual gases can thus be controlled by changing the gas flow rate. If a throttle valve is used the pressure can be also controlled by varying the valve position. In the later case the gas conduction (defined as the gas flow rate per unit pressure differential) between the pump and the vacuum chamber will be changed [55].

An increase in the injection of reactive gas causes an increase in the density of reactive species that are present on the cathode surface and incorporated within the deposited coatings. At a critical injection rate, a transition in operating conditions is generally observed which, for many metal-reactant combinations, is abrupt and involves a significant decrease in deposition rate. If this occurs, the target is referred as being poisoned (compound is formed on the target surface with the reduction in sputtering rate and increase in secondary electron emission). A hysteresis loop then will be observed in the flow rate- deposition rate / pressure curves. The poisoning can cause surface charge

buildup and arcing (flashover) in a DC reactive system. To avoid these problems the hybrid reactive RF sputtering technique is usually used, where the target has a positive polarity during a portion of the wave cycle to allow electrons from the plasma to neutralize positive charge buildup on the poisoned surface [58].

There are many different set-ups for a real sputtering system, such as unbalanced magnetron sputtering, pulsed dc sputtering, hollow cathode sputtering, etc. More information on these can be found elsewhere [57, 63, 65-66].

2.2 Thin film deposition mechanisms

Many methods have been developed for preparing thin films [55, 65]. According to the formation mechanism they can be classified into: 1) chemical/electrochemical methods (e.g. electrolytic, anode oxidation, electroless deposition, sol-gel, etc.) and physical methods [68] (e.g. evaporation, sputtering, laser ablation, etc.); 2) vapour deposition (physical and chemical vapour deposition) and non-vapour deposition. Sputtering falls into the category of physical vapour deposition (PVD). Hence in this section the author will briefly review the mechanism of thin films deposited by physical vapour deposition. Note that the condensation and nucleation theories discussed here may not only be applied for PVD films but also for CVD films [69].

PVD is the production of a condensable vapor by physical means and subsequent deposition of a thin film from the vapor [60]. The thin film deposition process involves three main steps: 1) vaporization of the materials to be deposited (production of the appropriate atomic, molecular, or ionic species; 2) transport of these species to the substrate through a medium; 3) condensation, nucleation and growth on the substrate to form a solid deposit [32]. In sputtering the vapour species (atomic, molecular, ionic species) of materials to be deposited are produced by the collision cascade procedure and transported by the plasma, as introduced in section 2.1. In this section the processes of the condensation, nucleation and growth will be introduced in some detail.

2.2.1 Theories on the nucleation of thin film

2.2.1.1 The kinetic concepts of gases

The kinetic concepts of gases are very important in physical vapour deposition. They provide an estimation of the impingement rate, molecular density, mean free path, and the parameters have influence on the deposition kinetics and purity of a thin film. The kinetic theory enters into models of nearly all aspects of deposition and growth of thin film [60, 70]. Moreover, due to the non-equilibrium nature of sputtering, kinetic related deposition parameters are very useful in process control.

a) Impinging flux of atoms at a surface

This impinging flux $N_{\downarrow}$, or arrival rate, is related to the molecular density n , the mean speed of the incident particles (v) and the pressure p , via the standard kinetic theory formulae [68]

$$N_{\downarrow} = \frac{nv}{4} = \frac{Cp}{(2\pi mkT_{inc})^{1/2}} \text{ per unit area}$$

where $n = p/kT_{inc}$. $v = (8kT_{inc}/\pi m)^{1/2}$. k is Boltzmann constant. C is a constant. m is the molecular weight of gas and T_{inc} is the temperature of incident particles (i.e. the evaporation source temperature). In sputtering deposition the impinging flux of the activated species depend strongly on the sputtering yield, and indirectly, on those parameters influence the sputtering yield.

b) The molecular density, n

At low pressures $n = (100)/(kT_{inc} \times 10^6) p$. This gives $n = 7.2464 \times 10^{18} (p/T_{inc})$. There are still lots of molecules around, even in the best vacuum.

c) The mean free path λ

The mean free path between molecular collisions in the gas phase is inversely related to the density n and the molecular cross section proportional to σ^2 and can be expressed as [68]

$$\lambda = \frac{1}{n\sigma^2} = \frac{1}{\pi(r_1 + r_2)^2 n_2}$$

The collision cross section σ depends on the radius of the sputtered atoms r_1 , radius of the gas molecular r_2 and the density of gas molecules n_2 [63]. As n_2 depends much on the pressure p , λ depends also strongly on the gas pressure and gas species in the deposition system.

2.2.1.2 Impingement, adsorption, thermal accommodation and surface diffusion

The initial step in the formation of thin film is the impingement of vapor species on the substrate [56]. Atoms that impinge on a surface in a vacuum environment are either reflected immediately, re-evaporate after a residence time, or condense on the surface [32]. The incident adatoms / particles will generally lose part of their energy on impingement. These adatoms are attracted to the surface by forces due to dipole or quadrupole on the surface and so they become, at least for a certain time, adsorbed on the surface. The energy loss of a particle that has impinged on the surface and then left it is characterized by the thermal accommodation coefficient α [68, 70]

$$\alpha = \frac{E_{inc} - E_{des}}{E_{inc} - E} = \frac{T_{inc} - T_{des}}{T_{inc} - T}$$

E_{inc} , T_{inc} = energy, temperature of impinging vapor particles.

E_{des} , T_{des} = energy, temperature of the desorbed atoms before equilibration with the substrate;

E , T = energy, temperature of the desorbed atoms after it has equilibrated with the substrate.

$\alpha = 1$ denotes a complete thermal accommodation, $\alpha = 0$ denotes a total elastic reflection. When the particle loses all its “excessive” energy its energy state is then fully determined by the substrate temperature.

The sticking coefficient C_s is defined as

$$C_s = \frac{\text{the number of particles physically adsorbed}}{\text{the number of impinging particles}}$$

It has been found that the coefficient C_s is equal to unity if the energy of the incident particles is less than or equal to about 25 times the desorption energy Q_{des} on the substrate. Since Q_{des} is usually about 1-4 eV and the sputtering particle energy is around 2-5 eV [71-72], it is therefore highly probable that most incident particles will be physically adsorbed.

The adsorption particles stay on the surface for a certain time τ_s given as [68]

$$\tau_s = \frac{1}{\nu} \exp \frac{Q_{\text{des}}}{kT}$$

where ν is the surface-vibrational frequency of the adatoms, k is the Boltzmann constant, Q_{des} the desorption energy of the particles on a given substrate, and T the temperature of the particle, which is generally between the incident particle temperature and the substrate temperature.

The particle that has not been fully accommodated has retained a certain “excess” energy. Due to this energy and the thermal energy from the substrate the particle moves over the surface. The movement is called migration or surface-diffusion. It may happen that the particle will meet another one in the course of its surface-diffusion and form a pair which has a much lower re-evaporation possibility than a single particle and thus the conditions for condensation will be set up. As the binding energy is not the same over the whole surface the adsorbed particles always tend to occupy those positions of steps, kinks, and defects. The adsorbed particle must overcome a certain potential barrier (the activation energy for surface-diffusion jump) on the way of travelling to the nucleation sites. The mean surface-diffusion distance $\bar{X}$ of an adatom is then given by [70]

$$\bar{X} = \sqrt{2}a \exp\left(-\frac{Q_{\text{des}} - Q_{\text{dif}}}{2kT}\right)$$

where ν is the surface-vibrational frequency of the adatom, Q_{des} and Q_{dif} are the desorption and surface-diffusion energy of the particle on a given substrate, and a is the

width of the potential barrier of surface-diffusion.

From the above relation the mobility of an atom on a surface will depend on the energy of the atom, atom-surface interactions, the surface temperature, and the surface energy of substrate (the different crystallography planes of a surface have different surface free energies hence the mobility of an atom will also be different [32]). The dependence of mobility on energy has been quantitatively shown in a recent review on energetic condensation [72]. In Ref. [72] the author also argued that the surface temperature plays more important role on surface mobility than the energy of incident particle.

Another important parameter for thin film condensation is supersaturation. It is defined as the ratio of the impinging flow to the re-evaporation flow $N_{\downarrow}/N_{\uparrow}$. The impinging flow $N_{\downarrow}$ is given by [68]

$$N_{\downarrow} = \frac{Cp}{(2\pi mkT_{inc})^{1/2}} = \frac{n_1}{\tau_s} = n_1 v \exp\left(-\frac{Q_{des}}{kT}\right)$$

Where n_1 is the concentration of individual particles at the substrate surface, and the denotations of other symbols can be found in the paragraphs above.

The condensation is controlled by two quantities: desorption energy Q_{des} and sublimation energy Q_s . When $Q_{des} \gg Q_s$, the condensation occurs without supersaturation and surface coverage is high and vice versa.

With these facts we can see that deposition parameters such as RF power, pressure and temperature in sputtering play important roles in the condensation of gas species.

2.2.1.3 Classical nucleation theories

With the formation of small clusters of adatoms through the combination of several adsorbed atoms (by surface-diffusion of adatoms), the condensation is finally initiated. These clusters are called nuclei, and the process of cluster formation is called nucleation. In classical nucleation theories a supersaturation ratio larger than unity is required for nucleation to occur. The critical nuclei can grow either by direct impingement and

incorporation of atoms from the gas phase (dominant when the activation energy for surface diffusion is very large and temperature is low) or by collisions with adsorbed monomers diffusing over the substrate surface. The processes that take place at the substrate surface are schematically shown in Fig.2.8 [73].

Fig.2.8 The condensation related processes at substrate surface [73]

There are two classical nucleation models, namely, capillary (thermodynamic) model and statistical (atomic) model that deal with the formation mechanism of the stable nuclei.

Capillary (thermodynamic) model: In this theory nucleation involves surface adsorption from a supersaturated vapour and surface diffusion, leading to a critical-size cap-shaped cluster of atoms (the nucleus) in the case where the cohesive forces between the atoms in the nucleus are greater than the adhesive forces between the adatoms and the substrate. The cluster nucleus increases and decreases by adding or losing single atoms. If the nucleus is greater than the critical size (a supercritical nucleus), its further increase becomes energetically favourable. Conversely, if the nucleus is smaller than the critical size (a subcritical nucleus), its further decrease becomes energetically favourable.

Statistical (atomic) model: For high supersaturation, the radius of the critical nuclei is very small (may contain only one atom), i.e. the nucleus consists of a small number of atoms, the thermodynamic approach being no longer adequate. This difficulty can be avoided by using the statistical mechanics to calculate the nucleation rate.

Partial condensation of atoms (with the sticking coefficient less than unity) has been found to be highly dependent on the total impingement time and the substrate temperature. The re-evaporation of aggregates from the substrate has been used to explain the phenomenon of incomplete condensation. The elevating temperature, in one hand, will increase the surface mobility of adatoms and promote the collision nucleation. On the other hand, it will make a high probability for the re-evaporation of the condensations.

In summary, we can see that the condensation and nucleation depend on factors such as the substrate temperature, impingement flux, nature of substrate, and energy of the incident particles. The deposition parameters, such as substrate temperature, type, sputtering pressure, power, can be used to control the growth of sputtered thin films.

2.2.2 Growth and microstructure of thin films

2.2.2.1 The growth of thin films

1). Condensation mechanism of thin films

The process of enlargement of the nuclei to finally form a coherent film is termed growth [74]. After formation the stable nuclei can grow in three different modes [32, 68], i.e. Frank-van der Merwe, Volmer-Weber, and Stranski-Krastanov modes (see Fig.2.9.), depending on the strength of interaction between the atoms of the growing film and the substrate, i.e. the interface energies.

a). Island type (Volmer-Weber / V-W mode), occurs when the smallest stable nucleus grows in three dimensions. The islands formed on the surface by the impinging atoms grow vertically rather than across the surface. And island growth occurs when the energy of cohesion between the atoms being deposited is greater than the energy of adhesion between the deposited atoms and the substrate, i.e., ($s_s < s_o + s_i$).

b). Layer type (Frank-van der Merwe mode), this process occurs when the smallest stable nucleus grows in two dimensions, resulting in complete monolayer coverage of the surface. The second layer may begin to grow before the first is complete. In terms of the

theory of wetting, this type of growth occurs when the film / ambient interfacial energy, s_o , and the film/substrate interfacial energy, s_i , is less than the substrate / ambient interfacial energy, s_s ; i.e., ($s_s > s_o + s_i$).

c). Mixed type (Stranski-Krastonov / S-K mode), is a combination of the previous two modes. Initially the film nucleates and grows two dimensionally for the first few monolayers, but the mode changes to a three dimensional growth as a result of the accumulation of strain energy, s_{st} , from the mismatch in the atom-atom distances between the film and the substrate.

(1) Volmer-Weber: (island growth):

(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):

(3) Stranski-Krastonov: (layers + islands):

Fig.2.9 Three modes of condensation of thin film [68]

2). The growth stages of thin films

In most cases island mechanism takes place, especially in low-temperature sputtering deposition when the adatoms have low surface mobility. Few stages were identified in the island growth mode, based on the observation of evaporated films by electron microscopy. These are as follows:

a). Nucleation, during which small nuclei are formed that are statistically distributed over the substrate surface.

b). Growth of the nuclei and the formation of larger islands, which often have the shape of small crystals. It is also predicted by the classical nucleation theories that after a certain concentration of nuclei is reached additional impinging particles do not form further nuclei but adhere to the existing ones or to the islands formed already.

c). Coalescence of the islands and formation of a more or less connected network containing empty channels/holes. Three coalescence mechanisms have been proposed, namely, Ostwald ripening, cluster mobility, and coalescence by growth. The main idea is that two neighbouring islands are coalesced by a liquid-like behaviour (analogous to the sintering behaviour of two spherical particles). The mass transfer mechanism in this procedure can be both volume and surface diffusion. The coalescence leads to the enlargements of the uncovered areas of substrate, which will result in the formation of secondary nuclei between the islands. The channels/holes will be filled by secondary nuclei and nuclei growth to give a continuous film. The driving force for all the liquid-like behaviour (the coalescing nuclei and the rapid elimination of channels/holes) is the resultant reduction in surface energy by the elimination of high surface curvature [56].

2.2.2.2 Structure zone model

Typically the growth of the film near the interface is influenced by the substrate and/or interface materials, and it takes an appreciable thickness before the film establishes a particular growth mode. Then the structure of a PVD thin film can be described by the structure zone model (SZM), as shown in Fig.2.10. The SZM was first applied to evaporated coatings and later was extended to sputter-deposited films. It was first applied almost exclusively to the large scale microstructure and later extended to include the nanostructure [33].

In Fig.2.10 T denotes the substrate temperature in Kelvin. T_m is the melting point of the coating material. The two axes (P and eV) at the bottom left denote the pressure and particle energy respectively. This model indicates that the deposition parameters, such as substrate temperature, sputtering pressure and incident particle energy, will influence the

final structure of PVD thin films.

Fig.2.10. Structure zone model for sputter-deposited films [75]

Three zones with distinct structural and physical properties were identified in the SZM. At low temperature the structure of thin films in zone 1 consists of tapered columnar grains separated by pores, or voids; and the structure was termed “porous columnar”. In this zone atomic mobility is low, incident atoms adhere where they impinge, and atomic shadowing is the dominant mechanism for growth. At higher homologous temperatures atomic mobility is higher and the “dense columnar” zone 2 structure can form. In this case, the structure still has a distinct columnar appearance, but there are no voids between the columns. In zone 3, at still higher homologous temperatures, re-crystallization and grain growth can occur, and the coatings have “fully dense” equiaxed grain structures. For metallic coatings the zone 1/zone 2 and the zone 2/zone 3 transitions take place at homologous temperatures of 0.3 and 0.5, respectively. The dominant growth mechanisms in zones 2 and 3 have been attributed to surface and bulk diffusion processes, respectively. A zone T was introduced for sputter-deposited materials, where the coatings has a fibrous morphology and is considered to be a transition from zone 1 to zone 2. The formation of the zone T materials is due to the bombardment effect of energetic particles.

With the appearance of new deposition techniques (e.g. non-balanced magnetron sputtering) utilizing high-energy particles (up to 100eV) the SZM is further revised [33, 76]. In conventional planar magnetron sputtering the energy of incident particles is quite

low (2-5eV), thus in the latter discussions the author will simply follow the SZM depicted in Fig.2.10.

2.2.2.3 The orientated growth and morphology of thin films

1). The formation of preferred orientation

The alteration of the preferred orientation of thin films during ion assisted deposition, filtered arc deposition and also reactive magnetron sputtering is a frequently reported phenomenon. Different arrangements of grain/crystal orientation are schematically shown in Fig. 2.11.

Fig.2.11. The different orientations: (a) random orientation; (b) single fiber orientation; (c) double texture; (d) single-crystal orientation. The curved double arrows indicate deviations from the preferred orientations [68]

The single fiber orientation (can also be called a fiber texture) mode is the one most commonly observed in thin films deposited by vapor deposition and is characterized by the alignment of a particular crystallographic axis to be parallel to the substrate normal. Double texture is also observed experimentally [77]. The random orientation and single-crystal orientation modes can be found in equiaxed /randomly oriented and epitaxial films. Many mechanisms have been proposed for the formation of preferred orientation.

A. Model of the surface energy minimization

In island growth mode the crystallographic orientation of the grains is determined by the preferential growth of certain crystal planes over others [32]. As mentioned above the driving force for the coalescence of island is the resultant reduction in surface energy. An additional reduction in surface energy occurs by the formation of preferred boundary planes, leading to well-defined crystallographically shaped islands.

Accordingly orientated growth can be enhanced by “seeding” of the substrate surface with orientated nuclei [78]. Such “seeds” can grow to form orientated films. For example, some researchers [79] suggested that nucleation took place on the lowest surface energy plane of AlN (002), and its growth continued parallel to the substrate surface.

When the nuclei are randomly orientated an orientated film can still be formed with a competition growth over different crystallographic planes. This process is well explained by the evolutionary selection model by Van der Drift [80]. In this model, crystal grains orientated with their slower growing direction normal to the surface are terminated while faster growing directions are preserved as they intersect the grain boundary. Note that this mechanism leads to a preferential deposition of atoms at low-energy surfaces in order to minimize the surface energy. With their experimental results some researchers thought the argument on lowest surface energy is plausible [81]. While the author of this thesis noticed that those researchers lost sight of the fact that a condition with a low atom and ion concentration is necessary for the formation of crystal plane with the lowest surface energy [82-83].

B. Model of the elastic deformation energy minimization

In this model, the preferred orientation is determined by a competition between two thermodynamical parameters, the surface free energy and the strain energy. They argued that at small thicknesses, the film shows an orientation corresponding to that with the lowest surface energy. At larger film thicknesses the strain energy will become larger and the surface energy does not vary. Accordingly, preferred orientation with lowest strain

energy will be favored, as found in TiN films [84-85]. While this model was doubted by other researchers as their results did not support the minimum surface energy model [43].

C. Effect of energetic particle bombardment

Unfortunately, the influence of energetic ions is not considered in the two models above. Other researcher suggested that the energetic ion bombardment can also affect the evolution of preferred orientation, as it was found that at large thickness the plane with the lowest free surface energy is more damaged than loosely packed ones [86]. For more examples, it was argued that the change in preferred orientation during the ion beam assisted deposition is controlled by the growth phenomenon rather than selective nucleation of specific orientations, as the authors found that the misaligned seeds are etched away faster than they could be formed [87]. The intensive ion bombardment at high bias voltage condition resulted in the loss of preferred orientation together with an increasing dissolution of the columnar boundaries due to continuous re-nucleation during the growth [88]. Models of channeling and preferential sputtering have been proposed with the consideration on the effect of energetic particles bombardment on the formation of preferred orientation [89-90].

D. The influence of deposition parameters

It was also experimentally observed that the orientated growth of thin films depend strongly on the parameters such as gas pressure [13, 35, 37-38, 91], gas composition and species [86, 92], target-substrate distance [41, 93], voltage, current [94], substrate temperature [95], film thickness [96], substrate orientation [97]. The experiment results were explained by the theories introduced above.

2). The morphology of thin films

The study on the morphology of thin film materials is of great importance in many circumstances. For examples: in a non-equilibrium growth system the surface morphology contains important kinetic and dynamic information related to the growth

process [98-99]; micro-structural characterization of thin films is very important for the design and improvement of electronic devices [100]; control of film microstructure, including faceted surface morphologies, is a critical factor in determining coating performance of polycrystalline wear-resistant coatings and diffusion barriers [12].

Systematical work to study the morphology of thin films (especially in nano-scale), deposited at various conditions is still rare. The formation mechanisms of the morphology of thin films were not well understood and directly related to the other micro-structural properties such as the orientated growth. Among the existing literatures the morphologies of thin films were found to depend on the factors such as: the orientation and off-axis angle of the substrate materials (which were found to influence the morphology of epitaxial films [101-102]), the effects of temperature [103], impurity concentration [1042], the arriving ratio of III-V elements [105].

Now some researchers start to simulate the morphology of thin films. Unfortunately the current achievements in simulation are far from satisfying, as almost all these computer programs can only be applied for cubic materials and used for the simulation of two-dimensional (2-D) morphology of thin films. To help the readers get an idea of the influence of the orientated growth on the morphology of thin films an example was shown in Figure 2.12. Where the 2-D morphology of a cubic thin film with various preferred orientation was simulated by Kinetic Lattice Monte Carlo (KLMC) method [106]. At the nucleation stage the nuclei may either randomly orientated or preferential orientated, as depicted in Fig 2.12 (a) and (b). With orientated/competitive growth the final morphology of the films with various preferred orientation will be different. Figure 2.12 (c) and (d) show the final structures of randomly and (111) orientated films. The randomly orientated film in Fig. 2.12 (c) shows more facet character, while the (111) orientated film is smoother.

The dependence of 3-D morphology of thin films on the orientated growth has been found experimentally, as shown in Figure.2.13 (a).

Fig.2.12. The simulated 2-D morphology of a cubic thin film. (a) the randomly orientated nuclei; (b) (111) orientated nuclei; (c) the randomly orientated columnar grains; (d) (111) orientated columnar grains.

Figure.2.13. The dependence of 3-D morphology of thin films on the orientated growth. (a) Schematic drawing of a cubic crystal with point-group symmetry $m\bar{3}m$. [107]. (b) the form of a wurtzite AlN crystal [108].

Where the 3-D morphology of a cubic crystal with point-group symmetry $m\bar{3}m$ is [108] shown. Etch figures correspond to the morphologies of the (100)- cube, (111)- octahedron and (110)- rhombododecahedron orientated grains. In Fig.2.13. (b) the form of a hexagonal crystal is also presented. However, the relationship between the morphology and the preferred orientation of hexagonal thin films still needs to be experimentally established.

2.3 The crystallographic structure of AlN

AlN can take many forms of microstructure. The wurtzite structure is the most commonly observed one in thin AlN films (sometimes metastable cubic AlN were also reported [26, 109]). The lattice parameters of wurtzite AlN are found to be $a = 0.31114$ nm, $c = 0.49798$ nm (JCPD card No. 25-1133). Fig.2.14. (a) shows the crystal structure of wurtzite AlN. The white and black balls denote N and Al atoms respectively.

Fig.2.14. The structure of AlN [41]

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-N₍₀₎ bond in the direction of the c -axis, named B₂. The ionic character of the B₂ bond is greater. The bond energy of B₂ is relatively smaller than that of the three equivalent B₁ bonds and is easy to break, so that the energy

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required for energetic particles to be deposited in the direction of the c -axis is great. From Fig. 2.13, it can be seen that the plane (100) is composed of bond B_1 , while planes (002) and (101) consist of the bonds B_1 and B_2 together. Hence high energy is needed for the growth of (002) and (101) orientated planes.

Note here the Miller (three number) indices instead of Miller-Bravais (four number) notation is used in describing the structure of hexagonal AlN. The reason is that the former is a more convenient tool in describing the sheet / fibre textures [107]. Hence in the following chapters the Miller indices will still be followed.

Chapter 3 Experimental Techniques

3.1 The deposition of AlN films

A planar magnetron sputtering system supplied by Coaxial Company in UK was used for the deposition of AlN films in this work. Aluminum target and RF reactive sputtering were mainly used in this work for the reasons mentioned in Chapter 2. These reasons include improved process control (reduced arcing effect, reduced target poisoning) in RF sputtering and higher deposition rate with metallic target.

The sputtering system is composed of a typical bell jar vacuum system with a 500 mm cylinder chamber and two 3-inch water-cooled target holders tilted at about 30 ° with respect to the normal of the horizontal substrate holder, as depicted in Fig.3.1.

Si (100) wafers were used as substrates as silicon is one of the most attractive substrates for the future implementation of GaN and/or AlN-based devices. It allows integration of silicon based circuits on the same substrate [109]. Most AlN films on silicon substrates have been deposited on Si (111) wafers [110-112]. To date AlN films deposited on Si (100) substrates are still highly defecting [5] and requires further studies. In this study Si (100) substrates were mainly used with typical dimension of $2 \times 2 \text{ cm}^2$. Before the deposition the substrates were cleaned with 5% HF solution for 3 minutes, followed by rinsing in acetone and distilled water in an ultrasonic bath.

After loading the substrates to the chamber the system was pumped down to a pressure below 5×10^{-6} Torr with the aid of a turbo molecular pump (TMP). Sometimes liquid nitrogen was used to condense the residual gas molecules and reduce the pumping time.

Fig.3.1 A schematic picture of the Coaxial sputtering system [56]

High-purity argon gas (99.9995%) was introduced into the chamber after the 5×10^{-6} Torr base pressure was reached. Then the 99.99% purity Al target was pre-sputtered for 10

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minutes with the target shutter closed. During pre-sputtering the RF power and pressure of argon were kept at 300 W and 20 mTorr respectively. After heating the substrate to the required deposition temperature nitrogen gas was then introduced into the chamber and the reactive sputtering was initiated. The RF power input was controlled by a power unit, which consists of a RF generator, a blocking capacitor and an impedance-matching network. A two-channel (for argon and nitrogen) mass flow controller (MFC) was used to control the gas composition. The typical deposition conditions are listed in Table.3.1. During each the depositions, only the particular parameter being examined was changed with all the others kept constant.

Table.3. 1 Deposition conditions

Substrate	$2 \times 2 \text{ cm}^2$ (100) Si
Substrate temperature	100 - 500 °C
Substrate-to-target distance	10-14cm
Targets	Al 99.99% purity
Gas	Ar + N ₂ mixtures with 0-100% N ₂
Residual pressure	$< 5 \times 10^{-6}$ Torr
RF power	100-500W
Sputtering pressure	1.4-20 mTorr
Gas flow rate	6-24sccm
Deposition time	1-6 hrs

3.2 The characterization of AlN films

Multiple ex-situ characterization/analysis techniques were used to study the microstructure and properties of the deposited AlN films. In this section the techniques employed will be briefly described.

3.2.1 Thickness Measurement

Numerous methods (e.g. x-ray reflectance, four-point probe method, interference methods) can be used for the measurement of film thickness and each has its own limitations

[113-114]. In this work a JSM-6340F field emission scanning electron microscopy (FESEM) was used to obtain micrographs of the cross-section the AlN films and measure the film thickness. The deposition rates of the sputtered AlN films were determined by dividing their thickness with the deposition time.

3.2.2 X-ray diffraction

A Shimadzu LabX-XRD-6000 and a Rigaku Dmax-2200 X-ray diffraction instruments with Cu K α radiation were used for X-ray diffraction (XRD) measurement. Grazing incidence (GIXRD) scan was used for phase identification and conventional θ -2 θ scan was used to study the preferred orientation. The α angle in grazing incidence XRD measurement was fixed at 0.5° throughout this work.

To enhance the ratio of peak-background/signal-noise intensity parallel beam optics was used in this study, i.e. the incident beam was collimated by a horizontal soller slit and two vertical slits on the front and the backsides of the soller slit. The diffracted beam passed through a vertical or horizontal slit before entering a scintillation detector. The parallel beam geometry will also eliminate the instrument error functions that contribute to asymmetric peak shape broadening: flat specimen, axial divergence, sample displacement, and sample transparency.

Fig.3.2 is a schematic figure illustrating the diffraction geometries of the grazing incidence (note that there is another diffraction geometry for grazing incidence measurement, where the x-ray detector make in-plane 2 θ scan [28, 115]), conventional θ -2 θ methods, and rocking curve measurement. The diffraction planes in θ - 2 θ method are all parallel to the sample surface, as depicted in Fig.3.2 (a). Accordingly this method is very useful in studying preferred orientation in thin film materials. Note that in Si (100) wafers except for the Cu K α (400) peak (69°) sometimes the (100) peak (33°) and Cu K β (400) peak (61°) will also appear in the measured θ -2 θ patterns, although they cannot be found in the standard JCPD card.

(c) Rocking curve measurement of randomly orientated and textured films

Fig.3.2 Several XRD diffraction geometries [116]

The Si (100) peak may overlap with the AlN (100) peak (33.2°) and change the peak intensity. Whether the overlap occurs or not depends on both the deviation of diffraction geometry and the microstructure of the film. But to the author's knowledge this phenomenon was seldomly mentioned in most literatures about AlN films. Care has been taken in this dissertation when analyze the $\theta - 2\theta$ XRD patterns.

With a small incidence angle α in grazing incidence method, the X-ray path length in the thin film layer is greatly increased which results in enhanced peak intensity from the thin

film layer. From Fig. 3.2 (b), it can be seen that diffraction takes place on those planes tilted at a $(\theta - \alpha)$ angle with respect to the substrate normal. Compared to the $\theta - 2\theta$ method, the different diffraction planes in the grazing incidence method are more randomly orientated. As more peaks can be detected this method is extremely useful for phase identification in randomly oriented polycrystalline films with preferred orientation. While in well-oriented films with c-axis (002) parallel to the substrate normal, diffraction can also take place on planes with theta angles equal to the inter-plane angle between (002) plane and themselves, such as on the (103) ($\theta = 33.0^\circ$) plane with a $(\theta - \alpha)$ angle of 32.5° , which is very close to the 31.63° inter-plane angle between (103) and (002). With slight misorientation in lattice plane or deviation in goniometer geometry, diffraction can take place in such scans.

Fig. 3.2 (c) shows the diffraction geometry of rocking curve measurement (omega scan). In this method only the sample is rotated. For the un-textured film (figure on the left) there is no intensity variation with omega. If the film shows a fiber texture (figure on the right) and the fiber axis has some mis-orientation around the substrate normal the angle distribution (FWHM) in omega scan can be used to measure the alignment of the individual grains.

3.2.3 Morphology and surface roughness measurement

A JSM-6340F field emission scanning electron microscope (FESEM) operated at 3-5kV and 4-12 μA was used to study the surface morphology of the deposited AlN films. When the problems of charging and thermal damage are serious (e.g. films with large thickness or on highly-insulative substrate, such as glass), the samples were coated with gold films to minimize charging. The coating time was limited to 10s to avoid observing the morphology of gold instead of that of AlN films.

A Dimension TM 3100 scanning probe microscopy working as an atomic force microscope (AFM) was used to study the surface roughness of AlN films. Figure.3.3 is a schematic figure showing the components of a typical AFM. The main parts are laser generator,

piezoelectric motor (piezo) and detector. The instrument was used in tapping mode, wherein the cantilever is set into oscillation at its resonant frequency, then it is brought close to the sample until the etched single crystal silicon tip briefly contacts the sample surface at the bottom of the oscillation cycle. The contact reduces the amplitude of the cantilever oscillation. During scanning, a feedback loop consists of a NanoScope IIIa controller is used to adjust the position of the piezo that moves the cantilever to keep the cantilever amplitude constant. A topographic map of the sample is created by recording the motion of the piezo required to keep the amplitude constant. In this work, the tip was scanned laterally across a $2 \times 2 \mu\text{m}$ area at room temperature under air ambient.

Fig.3.3 A profile graph of an AFM [117]

3.2.4 Phonon modes and stress measurement

A. Phonon modes measurement

Raman and Fourier transformation infrared spectroscopy (FTIR) were used for phonon modes measurement.

When light is scattered from a molecule, most photons are elastically scattered and have the same energy (frequency) and wavelength as the incident photons. However, a small fraction of light is scattered at optical frequencies different from, and usually lower than, the frequency of the incident photons. The process which leads to this inelastic scattering is termed the Raman effect. The difference in energy between the incident photon and the Raman-scattered photon is equal to the energy of a vibration of the scattering molecule (phonon energy). A plot of intensity of scattered light versus energy difference, then, is a Raman spectrum.

Fig.3.4 Raman scattering effects [118]

An IR spectrum can be obtained when beam of radiation from the infrared region of the electromagnetic spectrum is passed through the material. As the infrared light source changes in wavenumber this gives rise to certain molecular movements such as bending and stretching, and these movements absorb energy at definite values of wavenumber giving rise to peaks/valleys on the infrared spectrum. It is the position and pattern of these peaks that produces the characteristic infrared spectrum for a material. At the heart of an FTIR spectrometer is a Michelson interferometer, as depicted in Fig.3.5. A parallel beam of collimated light from a broadband source is directed at a semitransparent beam splitter. One of the two beams reflects off a movable mirror while the other beam reflects off a fixed mirror. The two beams recombine at the beam splitter, travel through the sample, and finally impinge upon a detector. The detector signal is proportional to the intensity of the interfered beam and the plot of intensity versus optical path (time) difference in real space is the interferogram. When the interferogram is Fourier transformed, the resulting function is a plot of the spectrum in frequency space.

Not all the phonon modes of a molecule are active, but only those that satisfy the selection rule [119-120]. For IR technique, only those modes with change in dipole momentum are IR active. While only those modes with change in polarizability rates are Raman active. The mutual selection rule indicates also that for a molecule with symmetrical center, the IR active modes are Raman inactive and vice versa.

Fig.3.5. Schematic diagram of FTIR spectrometer [121]

A Perkin Elmer S2000 FTIR and a Renishaw micro-Raman 1000 spectrometer were used to study the phonon modes in the deposited films. Both spectrometers were used at an energy resolution of 2 cm^{-1} and at a backscattering geometry (incident laser perpendicular to the substrate surface) without any beam polarization. The FTIR spectra were measured in a range from 4000 to 370 cm^{-1} and signals from the silicon substrate were subtracted from the raw data. With a 514.5 nm Ar ion laser source, the incident laser power at the sample surface was fixed at 1 mW in the Raman measurements. The laser beam was focused on an area of $1 \times 1\text{ }\mu\text{m}^2$.

B. Macro-scale residual stress measurement

The macro-scale residual stress is usually measured by the shift in the XRD peak (strain $\varepsilon_{hkl} = -\cot\theta_{hkl} \times \Delta\theta_{hkl}$), with the assumption that the measured strain of plane (hkl) coincides with the macrostrain predicted by the elastic theory. However there are some limitations on using XRD method to measure the macro-scale residual stress in AlN films. For examples: high 2θ angle should be used in the normal stress measurement methods ($\sin^2\psi$ and $\sin^2\psi_0$ methods) to minimize the measurement error, while at high 2θ angle the diffraction peaks are always absent; even when low angles are used the texture/preferred

orientation (crystallographic plane parallel to the substrate normal) will make the normal stress measurement methods inapplicable. The William-Hall plot method has been shown to be inapplicable for textured films as either not enough XRD peaks can be detected or in most cases nonlinear curve will be obtained, which make the result of linear fitting of the experiment data unreliable [77]. Rietveld and Warren-Averbach (Fourier) line profile analysis involve very complicated mathematic, which requires very high quality data. In practice the XRD data quality is usually too poor for such approaches.

The author finally used the peak shift in FTIR spectra to estimate the stress in the deposited film. This method is useful as it is simple and all the problems existing in XRD methods can be avoided. The peak shift in vibrational spectra was first observed in single crystal materials under high pressure conditions. A simple linear relationship was found between the applied pressure and the peak shift. A peak shift towards high wavenumber indicates a compressive stress and a peak shift towards low wavenumber indicates a tensile stress. Later thin film researchers start to use the peak shift in vibrational spectra to estimate the stress of thin film materials. With a stress coefficient of $8 \text{ cm}^{-1} \text{ GPa}^{-1}$ [5], the value of the stress in the deposited AlN films can be estimated.

3.2.5 Interface and fine structure study

A 200 kV JEM-2010 transmission electron microscopy was used in this work for image and electron diffraction study. The cross-sectional TEM (XTEM) sample was prepared by a conventional technique described elsewhere [122]. The technique involves gluing two samples face-to-face, cutting, mechanical polishing, and dimpling followed by thinning in Ar^+ ion milling. The plan-view sample was made by cutting, mechanical polishing, dimpling and thinning in Ar^+ ion milling from the substrate side.

The author would like to refrain from a too general introduction on the TEM technology here. The necessary information on TEM techniques used in this work will be presented later in the discussions on the experimental results. The readers can refer to two very good textbooks for the fundamentals [123-124].

3.2.6 Element composition measurement

X-ray energy dispersion spectroscopy (EDX), electron energy loss spectroscopy (EELS), and x-ray photoelectron spectroscopy (XPS) were tried in this work. The former two were finally discarded as they give averaged element composition, which always over-estimate the oxygen concentration in the deposited film with the existence of surface contamination.

Fig.3.6 shows the set-up of a typical XPS instrument. The x-ray photon is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron, which will be detected by an electron energy analyzer. For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

Fig.3.6 Schematic diagram of a XPS instrument [125]

An AXIS Ultra x-ray photoelectron spectroscopy (XPS) with an aluminum $K\alpha$ radiation source was used to study the oxygen concentration. An argon ion gun with a 4.0 keV energy was used to remove the surface oxide layer.

Chapter 4 The Effect of Gas Composition on the Orientated Growth and the Microstructure of AlN Films

The deposition and characterization of AlN films are of great interest in the past decade. So far, most results and explanations for the preferred orientation observed have been based on the external process parameters. Since films can be prepared by various deposition techniques using different process parameters, the variations in results and explanation for the preferred orientation of AlN films are considerable and sometimes even conflicting. There is a need for more systematical research efforts in order to understand the basic controlling physical process and the growth mechanism of the deposited AlN films.

4.1 Introduction

Almost all the sputtered AlN films were reactively deposited in an argon and nitrogen gas mixture and by using metallic aluminum target, with only a few exceptions where either an argon and ammonia gas mixture [25, 92] or a compound AlN target was used [91, 126]. For the AlN films deposited in an argon and nitrogen gas mixture, the effect of nitrogen concentrations on the microstructure and properties of the deposited films are not well studied compared to the effect of other deposition parameters. Moreover, the existing studies on the effect of gas composition are not conclusive. For example: it was reported that nitrogen concentration plays less important role in the orientated growth of AlN films [39]; another group found that c-axis orientated growth is favored at high nitrogen concentrations. In their work the formation mechanism of the orientated growth was not discussed [127-128]; other researchers argued that highly c-axis fiber textured AlN films can be obtained at much lower nitrogen concentrations (20%) [129]. In this chapter the results on the influence of nitrogen concentration will be presented and discussed in detail.

4.2 The deposition of AlN films

AlN films were deposited with a 3-inch 99.99% pure Al target and in a gas mixture of 99.9995% purity nitrogen and argon. The detailed information on the pumping down sequence, pre-sputtering, and substrate pre-treatment can be found in Chapter 3. The effect of gas composition was studied by varying the nitrogen concentration from 25, 50, 75, to 100% in the individual depositions. However, other parameters were kept constant at a sputtering pressure of 5 mTorr, substrate temperature of 350°C, RF power of 300 W and gas flow rate of 12 sccm. For comparison AlN films were also deposited at the same conditions by using a commercially available AlN target of 99% purity.

4.3 Results and discussions

4.3.1 Orientated growth

4.3.1.1 AlN films deposited by using an aluminum target

Table 4.1 tabulates the film thickness. Fig.4.1 shows the measured XRD patterns of the deposited films.

Table 4.1 the thickness of the AlN films deposited under various nitrogen concentration

N ₂ %	25	50	75	100
Thickness (nm)	279	429	435	342

All the films were found to have wurtzite (2H-AlN) structure by the grazing incidence XRD scans, as depicted in Fig.4.1 (a). No other crystalline phase was found. For the reader's convenience to testify the XRD result the JCPD file 25-1133 for wurtzite AlN and JCPD file 34-0679 for cubic AlN were included in Appendix 1& 2. From the θ - 2 θ XRD results, as shown in Fig.4.1 (b), it was found that under low nitrogen concentration (25%N₂) the film showed mixed preferred orientation with a strong (101) and weak (100) peaks. At 50% nitrogen concentration, the (101) orientated growth is more obvious.

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(a) Grazing incidence (thin film) method

(b) θ -2 θ method

Fig.4.1 XRD patterns of AlN films deposited under various nitrogen concentrations

Increasing the nitrogen concentration up to 75%, resulted in films with (100), (101) and (002) mixed preferred orientation. With the appearance of a (002) peak and the stronger peak intensity of (002) planes, the result seems to indicate a c-axis orientated growth began to dominate the film growth. This trend was confirmed by further increasing the nitrogen concentration to 100%, where a highly c - axis orientated AlN film was deposited.

The grazing incidence XRD patterns in Fig.4.1 (a) also indicates that all the films except for the ones which were deposited under pure nitrogen conditions have more oriented polycrystalline structures. The films deposited under pure nitrogen conditions were much more orientated, as only two peaks were found. It is no surprise to find the (103) peak in the pattern as it has similar ($\theta - \alpha$) angle to the inter-plane angle between (002) and (103) planes, as mentioned in Chapter 3. While the appearance of (002) peak in this spectrum indicates that, instead of being perfectly perpendicular to the substrate surface, the surface normals of the (002) planes have a large mis-orientation from the substrate normal. Such a result is similar to the case where a rocking curve has a large full width at half maximum (FWHM). In Fig.4.2 the measured rocking curve confirms the large mis-orientation of the (002) axis, as a full width at half maximum (FWHM) of about 16° was observed.

Fig.4.2 The (002) rocking curve of the film deposited in pure nitrogen

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With a heavier atomic mass and sputtering yield than nitrogen ions [55], argon ions will transfer more energy to the target during the bombardment of positive ions in sputtering deposition and thus will generate more aluminum atoms and clusters with higher kinetic energies. Hence a high argon concentration corresponds to a high energy configuration condition.

As is well known, two kinds of Al-N bonds exist in wurtzite AlN, named B_1 and B_2 . The energy required for the formation of B_2 bond is larger than that of B_1 . $\{100\}$ planes consist of only B_1 bonds, while $\{002\}$ and $\{101\}$ planes consist of B_1 and B_2 bonds together [41]. Accordingly, adatoms with higher energy are energetically favorable for the formation of $\{002\}$ and $\{101\}$ surface planes.

Another factor which strongly influences the formation of preferred surface planes is the packing habit of such planes. For the development of close-packed surface planes the adatoms need a longer time to accommodate themselves into the low - energy configured lattice sites before the arrival of the next layer of reactive species. A low deposition rate is necessary in such cases. In view of this it was initially predicted that a high argon concentration is favorable for the formation of $\{101\}$ surface planes because they are both loose-packed and energetically favored under conditions with high arrival rate and incident energy of the adatoms. However the XRD results do not fully support this prediction. For instance at 25% argon concentration, the deposited film does not show a strong (101) preferred orientation. Instead an increase in the peak intensity ratio of (100) to (101) is observed. To understand such a contradiction, the author referred to the deposition rates for more information as they are strongly related to the growth habit of thin films. Fig.4.3 shows the evolution of deposition rate under various nitrogen concentrations.

Above 75 % nitrogen concentration, the deposition rate decreases with increasing nitrogen concentration, which agrees with the low sputtering yield predicted under high nitrogen concentrations. As the observed deposition rate is determined by the competition between deposition and re-sputtering processes, the author attributed the low deposition

Fig.4.3 The deposition rate-nitrogen concentration curve

rate at 25% nitrogen concentration to the re-sputtering effect of adatoms by backscattered neutral argon particles from the target surface (the incidence positive argon ions will be neutralized immediately on contact with the electron cloud of the target surface atoms). As no bias voltage is used in this work the bombardment effect of positive particles on the substrate surface is not considered. The reasons for such a consideration are summarized in the following paragraph.

It has been found that in a typical planar magnetron sputtering system, at energies less than 1000 eV, reflection fractions can be as high as 0.4 and the particles can retain a substantial amount of their original energy [66, 130]. Furthermore, with a strong self-biased electrical field near the cathode the escape of positive ions from the target surface will be limited. The ion beam experiment showed that even without a strong field at the target surface the amount of sputtered ions is on the order of 1% of the sputtered atoms [63]. Moreover, the energies of the sputtered atoms are much lower than the back-scattered gas species and will be less important in the bombardment procedure.

Further evidence of re-sputtering effect can be found in an earlier published work where similar evolution in preferred orientation was observed. The researcher also deposited

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AlN films in gas mixtures of nitrogen and other inert gases with a 20% nitrogen concentration. With increase in atomic number of the inert gases (neon, argon, krypton, xenon) the preferred orientation of AlN films changed from (002) to (101) and then to polycrystalline and finally became amorphous [122]. These results indicate that the bombardment effect of inert gas particles plays an important role in the growth habit of sputtered thin films.

Now with the introduction of a neutral particle bombardment effect the observed evolution of preferred orientation can be more easily understood and can be summarized as follows. {101} planes are favorable under low nitrogen concentration conditions. The bombardment by backscattered argon neutral particles caused the re-sputtering of deposited adatoms, damaged the {101} planes. Which in turn resulted in the low XRD peak intensity and decreased deposition rate. However the deposition rate is still too high for the formation of {002} close - packed surface planes. Instead a loose - packed (100) surface planes were more obvious at 25% nitrogen concentration conditions. It is of interest to note that the densely packed {002} planes have been found to be more damaged under the bombardment of energetic particles [86]. Hence the {002} planes will not be formed under such a condition. Kinetic energy is lost during the collision between incident and re-sputtered particles, which may favor the formation of (100) preferred orientation.

With reduced bombardment by neutral argon particles the deposition rate increases in films deposited at 50% nitrogen concentration. And the (101) preferred orientation is more obvious, which may indicate less damage of the {101} planes by the energetic neutral particles. Further increase of the nitrogen concentration up to 75%, produces no significant change in deposition rate. While the (002) preferred orientation began to be obvious in the deposited film, which indicates that the bombardment effect of neutral argon particles is less obvious above 50% nitrogen concentration. Under pure nitrogen conditions, the low deposition rate condition induced by the low sputtering yield and low kinetic energy of the adatoms is favorable for the growth of {002} close-packed planes.

4.3.1.2 AlN films deposited by compound target

For comparison purposes, the AlN films were also deposited by using a commercially available compound target with 99% purity and at the same deposition conditions. Fig.4.4 shows the measured XRD patterns of the films deposited by using an AlN target.

The results show that the deposited films tend to be amorphous compared to those deposited by using metallic aluminum target. As shown by both the weak peak intensity and the large peak-noise ratio in the grazing incidence and the θ -2 θ XRD patterns. The trend in the evolution of the preferred orientation agrees well with that observed in the films deposited by the pure Al target. So the mechanism of the orientated growth seems to be similar to that discussed for the films deposited by Al target. Accordingly it is possible that, in the films deposited by Al target, a stable AlN layer was formed at the target surface and this AlN layer was sputtered to form the AlN films on the substrates.

(a) Grazing incidence (thin film) method

(b) θ -2 θ method

Fig.4.4 XRD patterns of AlN films deposited by using a compound target

The result that the films are more amorphous-like (show inferior crystalline property compared to those deposited by pure Al target) keeps the author from further using AlN target for the deposition. This may also be the reason why the compound target was seldomly used to deposit AlN film in the open literatures.

4.3.2 Surface morphology

4.3.2.1 AlN films deposited by using an aluminum target

The morphology of the AlN films deposited by using Aluminum target is shown in Fig.4.5.

The films deposited at 25-75% nitrogen concentrations have similar facet structure, which indicates a difference in growth rate of various crystallographic planes [106] and is

Fig.4.5 Surface morphology of AlN films deposited at various nitrogen concentrations
 (a) 25% N₂ (b) 50% N₂ (c) 75% N₂ (d) 100% N₂ (e) Cross sectional micrograph (75% N₂)

commonly observed in the vapor deposition films with preferred orientation. From the XRD patterns shown in Fig.4.1 (b) it seems that the (101) preferred orientation are obvious in all the three films. While the morphology of highly (002) oriented film deposited in pure nitrogen changes to a pebble-like structure. A similar morphology was also observed for the (002) orientated AlN films [81]. Hence it seems that the (002) orientated films are likely to have pebble-like surface morphology. When (101) preferred orientation is strong or dominant, the films are likely to show faceted (or pyramid -cone [127]) structure.

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A typical cross-sectional micrograph of the deposited films is shown in Fig.4.5 (e). The film shows columnar grain structure, which indicates a low surface mobility of adatoms during the growth and this agrees well with that by the structure zone model (SZM) for low temperature deposited films [32].

4.3.2.2 AlN films deposited by using a compound target

Due to the very smooth surface (lacking of features to focus) clear surface morphology of the deposited films cannot be obtained by using the field emission gun SEM (FEGSEM). Hence AFM was used to observe the surface morphology of the films deposited with AlN target. Fig.4.6. shows the AFM images.

(a) Pure argon

(b) 75% N₂ concentration

(c) 50% N₂ concentration

(d) 75% N₂ concentration

(e) Pure nitrogen

Fig.4.6. The 3-D AFM topology of AlN films deposited by using a compound target

The films deposited at 0-75% show similar morphology, as shown in Fig.6 (a)-(c). The Fig.4.6 (e) clearly shows that the fine grain structure in the film deposited in pure nitrogen. This is attributed to the much lower surface mobility of the adatoms at high nitrogen concentration. The lower mass and kinetic energy of N^+ than that of Ar^+ will result in sputtered species with low kinetic energy. As the temperature of substrate was kept constant during the deposition, the variation of surface mobility of the adatoms will be determined only by the kinetic energy of the sputtered species. Hence the observed fine grain structure of AlN film deposited in pure nitrogen can be well explained. The measured surface roughness is shown in Fig.4.7, where R_q and R_a are the root-mean-square and arithmetic mean surface roughness.

The result shows that all these films are very smooth and the effect of grain size on surface roughness is not significant. While this effect cannot be ignored in deposition system with high deposition rate (a few to several tens micrometer per hour). For examples, CVD and high-energy sputtering system. In such systems the effect of competitive and facet growth on the grain structure are more obvious, which in turn results in films with quite different surface roughness. A fine grain film (usually involves an orientated growth of planes with slow growth rate) is usually preferred in such case as lower surface roughness can be expected. The reader is also referred to the next chapter

for more evidence. Such consideration is of practical importance under the circumstance where surface roughness of the deposited films should be well controlled. For example, in the fabrication of AlN SAW devices [41], where a surface roughness below 30 nm is generally required.

Fig.4.7 Surface roughness of the AlN films deposited with a compound target

4.3.3 Vibrational spectra and stress of the films deposited by Al target

As is well known, Raman and FTIR spectroscopy are valuable tools to study materials structural characteristics and physical properties as the characteristic phonon frequency, corresponding to the zone center optical phonon energy, can be altered by factors such as stress, interfaces, structural defects, and impurities [131]. Wurtzite AlN belongs to the $P6_3mc$ (C_{6v}^4) spatial group [132]. Group theory predicts that there are nine optical phonon modes in wurtzite AlN. The zone center optical phonons are reducible into the following representation:

$$\Gamma = A_1 + E_1 + 2E_2 + 2B_1 \quad (1)$$

Where A_1 and E_1 modes are each split into a longitudinal (LO) and a transverse (TO) component due to the long-range macroscopic electric field. The A_1 and E_1 modes are both Raman and Infrared active, the two E_2 modes are Raman active only, and the B_1 modes are absent [131-132]. Due to the polarized vibrational characteristic, the detectable

Raman phonon modes are restricted by the polarization configuration of the incident beam and the detector according to selection rules.

During the past decade many efforts on theoretical calculation and Raman measurements have been made to study the phonon modes in AlN [133]. However, the published results did not agree with each other and are still open to debate, which necessitates further studies. Similar FTIR results have been reported. In FTIR studies most authors did not study the phonon modes but just simply attributed the observed absorption / transmittance peak to Al-N bonding [34, 134]. The measured FTIR spectra were shown in Fig.4.8.

Fig.4.8 FTIR transmittance spectra of the deposited AlN films

A strong FTIR transmittance peak around 686 cm^{-1} can be seen in the film deposited under pure nitrogen conditions. With decrease in nitrogen concentration split peak profiles occur. Two overlapping peaks have been decoupled from the measured transmittance spectra. The two peaks, around 678 cm^{-1} and 622 cm^{-1} , can be attributed to $E_1(\text{TO})$ and $A_1(\text{TO})$ phonon modes in films deposited at 50% nitrogen concentration. A peak shift towards high wave number has also been found with increasing nitrogen concentration. With nitrogen concentrations of 25%, 50%, 75%, 100%, $E_1(\text{TO})$ peaks shift from 676 cm^{-1} to 678 cm^{-1} to 684 cm^{-1} and finally to 686 cm^{-1} , as shown in Fig.4.9.

The result indicates that with the film structure changed from a randomly orientated one to a well c-axis aligned one, increased compressive stress was developed in the deposited films. With the stress free $E_1(\text{TO})$ peak position reported at 673 cm^{-1} and a coefficient of $8 \text{ cm}^{-1} \text{ GPa}^{-1}$ [5], the residual stresses in the deposited films were estimated as - 0.4, - 0.6, -1.4, -1.6 GPa respectively. The FTIR peak shift of the films deposited by AlN target is also shown in the Fig.4.9. No significant deviation in the peak positions was observed in these films. Compared to the films deposited by Al target the FTIR peaks of the films deposited by compound target shift slightly towards low wave numbers at about $668\text{-}671 \text{ cm}^{-1}$. Which correspond to tensile stress about $0.25\text{-}0.75 \text{ GPa}$. One possible reason for the formation of tensile stress is that the more amorphous-like nature of these films, where less crystallographic mismatch and collision of grain boundaries may exist in the films and relieve the stress. The result may also indicate that the film growth is nucleation limited and the coalescence of the nuclei is restricted, resulting in void formation and hence tensile stress.

Fig.4.9 FTIR peak shift in the deposited AlN films

As shown in Fig.4.10, three peaks were found centered around 619 cm^{-1} , 656 cm^{-1} and 821 cm^{-1} in the Raman spectra. Raw data are presented, as the attempted subtraction of silicon background signals from these spectra was not successful. The peak at 821 cm^{-1} is attributed to a phonon mode of the silicon substrate according to a recent published work

[45]. The authors also argued that the silicon substrate contributed to the observed phonon mode around 619 cm^{-1} , which was evident from the Raman spectrum of bare silicon as shown in Fig. 4.10.

With reference to the FTIR results obtained in this study, where signals from silicon have been subtracted, it is believed that an Al-N phonon also contributes to the observed peak around 619 cm^{-1} . The existence of such peaks has been confirmed by polarized Raman measurements on both single crystal and c - axis orientated AlN films [131, 135]. The observed peak positions support the published results for E_2^2 (660 cm^{-1}) and $A_1(\text{TO})$ (614 cm^{-1}) phonon modes [136-137]. Again the Raman results can be related to the microstructures of the deposited film. In backscattering geometry with c-axis perpendicular to the substrate surface, E_2^2 is one of the two phonon modes allowed by Raman selection rules [131-132]. This fact helps to understand the stronger E_2^2 peak

Fig.4.10 Raman spectra of the AlN films deposited by Al target

observed in the (002) orientated films. The observed peak broadening can be attributed to the enhanced phonon scattering effect at grain boundaries and defects in these films [132, 138] since large mis-orientation in (002) planes and grains in the sub-micro meter range have been observed in this work.

As oxygen was found to be the main impurity in the bulk of the deposited film and AlN is easily oxidized when exposed to air, Al-O bonding may exist in the deposited films. As no crystalline aluminum oxide was found by XRD results the oxygen must exist in an amorphous state. However, the typical phonon modes of aluminum oxide at 460 and 640 cm^{-1} (mostly reported in FTIR spectra [139-140]) are not obvious in the measured vibrational spectra. The effort of multiple-peak -fitting including the Al-O mode around 640 cm^{-1} in raman spectra always results in flat curve centered around 640 cm^{-1} , which suggests that even with the existence of the Al-O modes these peaks are very weak. In the open literature no Al-O phonon modes were reported in AlN films deposited under similar or even lower base pressures [24, 34, 134, 141]. Even in an Al_2O_3 thin film the Al-O phonon modes at 460 and 640 cm^{-1} were not obvious / dominant [142]. So it is possible that the low intensity that result in the fact that no Al-O phonon modes were obvious in these films.

To study the existing chemical bondings of Al and N elements the surface chemical composition is qualitatively studied by XPS. Similar element compositions were found in all the AlN films. A typical XPS spectrum (survey scan) of the deposited AlN films was shown in Fig.4.11. Except for Al and N elements O, C were identified as the two impurities that exist at the surface of the deposited film. Typical peak profiles analysis results of N, O, C and Al were shown in Fig.4.12. The observed surface chemical bonding can be mainly attributed to the organic contaminations. There is no strong Al-O bonding found by the XPS measurement as the Al peak was found centered at 76 eV, which correspond to Al-H bonding. The oxygen bondings were found mainly as C-O and COOH.

Fig.4.11 A typical survey scan XPS spectrum at the surface of the deposited film

Fig.4.12 Results of XPS peak profiles analysis

The XPS result indicates no strong evidence of the existence of Al-O bonding at the surface of the deposited film even with the existence of oxygen contamination at the film surface. This agrees with the fact the no obvious Al-O phonon modes are found in the vibrational spectra. As XPS is only sensitive to the outmost few atom layer of the films it should be noted that the results shown above contain mainly the information of surface contamination of the deposited films. Depth-profile analysis is further needed to shown the information of contamination beneath the surface layer. The detailed information on XPS spectra analysis can be found elsewhere [143].

4.3.4 Target damage under high argon concentration

Target damage under 25% nitrogen concentration has been observed when the deposition time was doubled to deposit thicker films. Fig.4.13 shows the surface morphology of the Al target after the deposition. The result shows that under continuous bombardment by high-energy argon ion the target is damaged. In the very rough surface aluminum grains can be identified.

Fig.4.13 Surface damage of Al target after the deposition at high argon concentration and longer deposition time

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The corresponding microstructure of the deposited films is shown in Fig.4.14 and Fig.4.15. As shown in Fig.4.14 (a) and (b) the deposited film shows graphite-like appearance with porous microstructure. XRD result in Fig.4.15 shows that the film contains mixed AlN and Al phase.

Fig.4.14 The morphology of the deposited film (a) The appearance of the samples (about $2 \times 2 \text{ cm}^2$ and $30 \times 5 \text{ cm}^2$), (b) FESEM surface micrograph, (c) Cross-sectional micrograph

The porous microstructure can be attributed to the rough target surface. Where the sputtered target materials were multiple scattered inside the target surface and left the target in randomly direction. The formation of AlN layer at the target surface seems to be difficult under such condition. With the high arriving rate of the sputtered Al species the adatoms have no time to accommodate themselves to the equilibrium position and stick to wherever they impinged. The low temperature condition may further restrict the surface diffusion of the adatoms. Hence a porous microstructure with Al phase was developed. The bombardment by the randomly impinged backscattered argon species may further promote to the formation of the porous microstructure. Hence the deposition of AlN film

at low nitrogen concentration and with long time is not recommend for our sputtering system.

Fig.4.15 Grazing incidence XRD pattern of the deposited film

4.4 Conclusions

The orientated growth and micro-structural property of AlN films deposited under various nitrogen concentrations were studied. The XRD, morphology, XPS and vibrational spectra results have been analysed and the growth mechanism of AlN films has been presented and discussed in detail.

It is found that high nitrogen concentration are favorable for the formation of the c-axis orientated AlN films. The low sputtering yield and low kinetic energy of the adatoms are believe to be responsible for the formation of the close-packed (002) surface plane. The bombardment of neutral argon particles on to the substrate surface plays an important role in the growth habit of AlN films grown under low nitrogen concentration. The bombardment induced resputtering may either reduce the energy or restrain the proper stacking procedure of adatoms. Hence prevent the formation of the surface planes containing high-energy Al-N bondings. Long time bombardment by high-energy particles under low nitrogen concentration is found to damage the target and result in porous films with mixed AlN and Al phases. The AlN films deposited by both Al and AlN targets

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showed similar evolution in the preferred orientation with the change in gas composition. Pure Al target is better than AlN target for the reactive deposition of crystalline AlN films.

The morphology of the deposited films has been studied by FESEM. It is found that the (002) orientated films have pebble-like surface morphology. When (101) preferred orientation is obvious the films are found to have facet or pyramid -cone structure.

Three observed phonon modes have been attributed to $E_1(\text{TO})$, $A_1(\text{TO})$, and E_2^2 phonon modes in AlN. The residual stress in the deposited films have been estimated from the observed $E_1(\text{TO})$ peak shift in the FTIR spectra. The estimated stresses of - 0.4 to -1.6 GPa are observed in films deposited with by pure Al target and 0.25-0.75 GPa for the films deposited by AlN target. The tensile stress state in the films deposited by AlN target are attributed to the more amorphous-like nature of these films.

Chapter 5 The Effect of RF Power on the Orientated Growth and the Microstructure of AlN Films

5.1 Introduction

As introduced in Chapter 2, sputtering yield depends strongly on the energy of incident particles. The fact that the incident ion energy and current density at the target increase with input power also means that the number and average energy of the sputtered target atoms are expected to increase significantly with increasing input power [144]. This was also experimentally observed [145] in reactively sputtered AlN film using aluminum target. Thus the sputtering power is expected to have profound effect on the condensation and growth behavior of thin film materials. For example, the orientated growth and surface morphology of a vapor deposited film are determined by the mechanisms and kinetics processes of the atomic assembly during vapor condensation. Both the mechanisms and the kinetics are sensitive to the energy of impact of the vapor atoms and any other species that bombard the growth surface [144].

Among the open literature that report the effect of deposition parameters on the microstructure of AlN films the effect of sputtering power was paid less attention. Moreover, more emphasis was given to the effect of dc power [41, 146-147] while the effect of RF power is rarely reported. Thus the reported results are far from conclusive. For example, it has been reported that increasing the power resulted in randomly orientated films [35]; other researchers have suggested that high power favors the formation of (002) texture [148]; another group found that orientated growth took place in medium power range, but high or low power led to randomly orientated films. Further increasing the power the aluminum phase appeared in the deposited films [41]. Clearly the effect of sputtering power is still not well understood and further studies are worthy and necessary.

5.2 The deposition of AlN films

AlN films were deposited with a 3-inches 99.99% pure Al target and in a gas mixture of 99.9995% purity nitrogen and argon. For detailed information on the pumping down sequence, pre-sputtering, and substrate pre-treatment please refer back to Chapter 3. The effect of RF power has been studied by varying the power from 100 to 500 W. All the other parameters have been kept constant at a sputtering pressure of 5 mTorr, substrate temperature of 350°C, nitrogen concentration of 75% and a flow rate of 12 sccm. A 75% Nitrogen concentration was chosen because that high nitrogen concentration has been found to favor (002) oriented growth of AlN films. Moreover, under 75 % Nitrogen concentration the low deposition rate found under pure nitrogen condition is avoidable.

5.3 Results and discussions

5.3.1 Orientated growth

Fig.5.1 shows the measured XRD patterns of the films deposited at various powers. The grazing incidence x-ray diffraction (GIXRD) result indicates that all the deposited AlN films have a wurtzite structure and no metastable cubic phase was found, as shown in Fig.5.1 (a). At 100 W, the very weak peak intensity indicates inferior crystalline property of this film to other films.

A very weak (002) peak was found in the θ -2 θ XRD pattern for the film deposited at 100 W, as shown in Fig.5.1 (b). Increasing the power to 200 W the (002) texture is more obvious. A small (101) peak was also found in the θ -2 θ XRD pattern. Increasing the power up to 300 W leads to an increase in the ratio of the peak intensity of (101) and (002) planes. This trend is shown again by the θ -2 θ XRD pattern of the film deposited at 450 W, where the (101) fiber texture dominates in the deposited film. Finally increasing the power to 500 W (the maximum obtainable value under such deposition condition in the sputtering system) the pattern shows a dominating (101) peak and also a small (002) peak. The peak intensity of (101) peak is much higher than that observed in the films deposited at 450 W.

(a) Grazing incidence (thin film) method

(b) θ - 2θ method

Fig.5.1 XRD patterns of AlN films deposited at different power

The evolution of the θ - 2θ XRD pattern shows that $\{101\}$ surface planes are favored at high sputtering powers and $\{002\}$ surface planes are favored at low powers. This indicates that the energy of the incident species plays an important role in the orientated growth of AlN films in reactive sputtering. The experimental result can be explained with the knowledge of the bonding energy of Al-N bonds in different planes and the change in kinetic energy of the sputtering species under various powers. As introduced in the former chapter two kinds of Al-N bond exist in the wurtzite AlN, named as B_1 and B_2 . $\{100\}$ planes consist of only B_1 bond, while $\{002\}$ and $\{101\}$ planes consist of B_1 and B_2 bonds together. The formation energy of B_2 bond is larger than that of B_1 . Thus adatoms with higher energies are energetically favorable for the formation of (002) and (101) surface planes [41]. With an increase in RF power both the sputtering yield and the average kinetic energy of the incident particles near the substrate surface will be increased [144]. Hence high RF power is energetically favorable for the formation of surface planes with higher formation energy.

The fact that (101) instead of (002) preferred orientation was formed at high RF powers can be further related to the packing habit of these two crystallographic planes. $\{002\}$ planes are close-packed planes and were found to grow at a slow rate [149]. As is shown later in the deposition rate - RF power curve (Fig.5.6), the films with (101) preferred orientation deposited at high powers grow much faster. According to the Van der Drift model, in the formation of columnar structure, crystal grains oriented with their slower growing direction normal to the surface are terminated while faster growing directions are preserved as they intersect the grain boundaries [87].

5.3.2 Surface morphology

Low sputtering yields and low kinetic energy of sputtered species introduced by low RF powers result in low deposition rate and surface mobility of the adatoms. Hence a small grain size and a smooth surface were observed in the AlN film deposited at 100 W, as shown in Fig.5.2 (a). With increasing RF power, a continuous growth in grain size is found, as shown in Fig.5.2 (b)-(e). This indicates that better surface mobility of the adatoms in addition to the high growth rate of the film occurs at high sputtering powers.

Fig.5.2 Surface morphology of AlN films deposited at various RF powers

(a) 100 W; (b) 200 W; (c) 300 W; (d) 450 W; (e) 500W; (f) Cross sectional micrograph (500W)

A coincidence in preferred orientation and surface morphology was also observed. Under low power conditions where the (002) preferred orientation dominate, pebble-like grain structure was developed, as shown in Fig. 5.2 (a)-(b). Increasing the power to be greater than 300 W encourages pyramid cone structure, where (101) preferred orientation is distinct, as shown in Fig.5.2 (c)-(e). This result agrees well with that found in the AlN films deposited at various gas composition, as discussed in the former chapter.

To qualitatively understand the coincidence in preferred orientation and surface morphology a SHAPE software with the Donnay-Harker approach [150-151] has been used to simulate the morphology of single crystal AlN. The results and the simulating parameters are shown in Fig.5.3 and Fig.5.4. The basic idea employed in this method is that the morphology of single crystal materials depends only on the growth rates of individual planes. In the simulation the growth rates of individual planes are assumed to be proportional to $\exp(-kd)$, where k is a constant characterizing the growth rate and d is the d -spacing of the individual planes. Only k is changed in the simulation and the simulated morphology is projected along the particular crystallographic orientation. The results agree well with the experimental result with the (002) oriented grains having smooth and rounded morphology; the (100) oriented grains are likely to take elongated shape, and the (101) oriented grains showing facet structure.

Fig.5.3 The simulated plan-view morphology of grains with different planes to be parallel to the substrate surface

Fig.5.4 The major parameters used in the morphology simulation

The pebble-like morphology in (002) orientated films is more straightforwardly shown by the simulated result. The simulation result also confirms that the real morphology of grains with various preferred orientation depends strongly on the growth rate of the individual planes. For (100) orientated film at low deposition rate (high k value) the morphology is more likely to take worm-like (elongated bar) shape. Increasing the deposition rate morphology with facet character will be more obvious. So does the (101) orientated film.

With the low deposition rate, the morphology of the deposited films will show less variability. Only three major types of morphology were observed in this work. It is believed that the morphology of the film can be described with those shown at the right side in Fig.5.3 and characterized by the low growth rate. More variable morphology has

been found in thick (several-tens μm) CVD AlN films with much higher growth rate [152]. Note that the simulated morphology based on the single crystal AlN is very crude. The real morphology of deposited AlN films may be more complex. For examples, the film with combined preferred orientation or large mis-orientation in the preferred orientation may show even complex morphology; and the large amount of sub-grains inside each grain with relative tilting to each other may further complicate the observed morphology.

Further increasing the RF power to 500 W results in also a rough surface of the film, as the facet character of grains became less obvious, as shown in Fig.5.2 (e). This can be attributed to the improved surface mobility of adatoms at larger RF powers, where adatoms are able to diffuse from grain boundaries to lower energy positions with the introduction of vacancies and voids at the grain interfaces [103]. A typical cross-sectional micrograph is also shown in Fig.5.2 (f), where the formation of columnar grains is clearly shown.

Fig.5.5 shows the AFM micrographs of AlN films deposited at various RF powers. A continuous increase in grain size and surface roughness were again observed.

The measured deposition rates and surface roughness values are summarized in Fig.5.6, where R_q and R_a are root-mean-square and arithmetic mean surface roughness respectively. As shown in this figure, an increase in RF power resulted in not only higher deposition rate and larger grain size but also a greatly roughened surface.

The rapid increase in surface roughness above 200 W can be related to the surface morphology of the deposited film. In addition to the roughening effect introduced by large film thickness (or along film growth) the facet (pyramid-cone) structure is believed to be responsible for such rapid increase in surface roughness, as more cavities are formed at the columnar grain boundaries of the facet grains than that of the pebble-like grains with (002) preferred orientation. Hence compared to those (002) preferred orientation the films with (101) preferred orientation should be avoided in the application such as

Chapter 5 The Effect of RF Power...

a) RF power =100 W

b) RF power =200 W

c) RF power =300 W

d) RF power =450 W

e) RF power =500 W

Fig.5.5. AFM micrographs of the AlN films deposited at various powers

Fig.5.6. The evolution of surface roughness and deposition rate with the change in RF power

wear-resistance coatings. Although the larger grains obtained at high power may reduce the phonon scattering at grain boundaries the rough surfaces will introduce additional phonon scattering boundaries at the film surface and degrade the thermal transport properties of the deposited films. Moreover, the large surface roughness found in the films deposited at high power may also make these films unsuitable for device level integration [148]. Thus RF power should be properly controlled to deposit film with desired properties.

5.3.3 Stress measurement

The measured FTIR spectra of the deposited films are similar to those films deposited under various nitrogen concentrations. The two peaks, around 678 cm^{-1} and 622 cm^{-1} , were attributed to $E_1(\text{TO})$ and $A_1(\text{TO})$ phonon modes, as shown in Fig 5.7.

The stress in the deposited films was estimated from the FTIR peak shift. The results are shown in Fig.5.8. The largest peak shift of $E_1(\text{TO})$ phonon and the peak values of stress were found in the films deposited at 200-300 W, where (002) preferred orientation is

obvious. As wurtzite AlN film with (002) fiber texture is more ordered than other AlN films, the alignment / ordering processes of the individual (002) orientated columnar grains is believed to be responsible for the high stress in these films. The large mis-orientation existing in the individual columnar grains may introduce high strain and defect density in these films, which in turn result in high stress.

Fig.5.7 FTIR spectra of the AlN films deposited at various powers

Fig.5.8 Peak shifts in FTIR spectra and the estimated stresses

When we refer to the morphology of the films deposited at 450 and 500 W it can be seen that there is an increase in the grain size. This indicates the improved surface mobility of the adatoms at high power and the coalescence of individual columnar grains with the

film growth. Thus it may help to relieve the stress by reducing defect at grain boundaries. Hence may be a possible reason for the stress reduction in the films deposited at 450 and 500 W.

The film deposited at 100 W shows quite different stress state with respect to the films deposited at other RF powers. The FTIR peak shifts to a low wave-number, which indicate tensile-stress inside the film. When one refers to the XRD patterns, it is found that the film is more amorphous than the other films. Hence the films contains large amount of amorphous domain inside. And these amorphous phases may surround the growing crystalities and act as a “stress damper” [153]. The more obvious nucleation limited growth (due to low kinetic energy and surface mobility of adatoms at low power) may restrict the coalescence of the individual grains and introduce more cavities at the grain boundaries [154]. Hence a tensile stress was developed.

5.4 Conclusions

The evolution of preferred orientation and surface morphology with the change in RF power was studied in this chapter. It was found that that the energy of incident reactive species and the sputtering yield play important role in the formation of the preferred orientation. (002) preferred orientation is favored at low power and (101) preferred orientation is favored under high power condition. The RF power dependence of the orientated growth was related to the stacking habit and the strength of chemical bondings of the individual planes.

A correlation between preferred orientation and morphology of the deposited films is also observed as pyramid cone structure is found in films with (101) preferred orientation and pebble-like grains were found in the film with (002) preferred orientation. The evolution of surface roughness and the stress in the deposited films has also been discussed and related to the observed microstructures.

Chapter 6 The Effect of Total Flow Rate, Temperature on the Orientated Growth and the Microstructure of AlN Films

6.1 Introduction

In most of the reported works the effect of gas flow rate was directly related to the effect of gas composition. With a constant pumping speed S the total pressure and partial pressure of individual gases is controlled solely by the inlet gas flow rate Q ($S=Q/p$, where p denote the inlet/chamber gas pressure). When a throttle valve is used the working pressure can also be controlled by varying the valve position. In this case the gas conduction (defined as the gas flow rate per unit pressure differential) between the pump and the vacuum chamber will be changed. When the system works in a constant pressure with varying gas flow rate, the exhausting rate of the gas species will be different. In this chapter the effect of total gas flow rate has been studied at a constant working pressure with changing valve position.

The substrate temperature is one of the key parameters that influences the microstructure of PVD films [76]. It has been found to be the most important factor that influences the surface mobility of adatoms, even when the high-energy (of hundreds of eV) particles are used in the deposition [72] (the sputtered species normally have energy of a few eV). For epitaxial film growth a critical temperature was usually found where the film growth changes from 3-D to 2-D mode. This results in a significant change in the morphology of the deposited film [103]. Elevating the temperature can also increase the re-evaporation rate of the adatoms. Hence it influences the growth behavior of the deposited thin film. It is experimentally found that the substrate temperature affects the orientated growth in both reactively sputtered ZnO and AlN films [39, 86].

In this chapter the results on the effect of total gas flow rate and the substrate temperature on the orientated growth and the microstructure of AlN films will be presented and discussed.

6.2 The deposition of AlN films

AlN films were deposited with a 3-inches 99.99% pure Al target and in a gas mixture of 99.9995% purity nitrogen and argon. To study the effect of total gas flow rate the total flow rate was changed from 6, 12 to 24 sccm. However, the flow rate ratio of N₂/Ar was kept at a constant value of 75%. The other deposition parameters were kept at constant at a sputtering pressure of 7.5 mTorr, RF power of 300 W and substrate temperature of 350°C. A power of 300 W was chosen to maintain both “c-axis” dominated orientated growth of AlN films and a relative higher deposition rate.

The effect of substrate temperature was studied by varying the substrate temperature from 150, 250, 350, to 500°C in individual depositions. All the other parameters have been kept constant at, a sputtering pressure of 5 mTorr, gas composition of 75% N₂, RF power of 300 W, flow rate of 12 sccm and deposition time of 3 hours.

6.3 Results and discussions

6.3.1 The effect of total gas flow rate

6.3.1.1 XRD results

Fig.6.1 shows the measured XRD patterns of the films deposited at various total gas flow rates. The grazing incidence x-ray diffraction (GIXRD) result indicates that all the deposited AlN films have a randomly orientated polycrystalline wurtzite grain structure and no metastable cubic phase was found, as shown in Fig.6.1 (a). All the three films show similar θ -2 θ XRD patterns, as depicted in Fig.6.1 (b). This indicates that the total gas flow rate has no significant effect on the formation of the preferred orientation in AlN films.

6.3.1.2 Surface morphology of the deposited AlN films

Fig.6.2 shows the surface morphology of the AlN films deposited at various total flow rates. All the films show similar worm-like (elongated bar) grain structure, which are randomly orientated in the in-plane direction. The result indicates that when the (100) and

(101) mixed orientated growth exists in the film, the grains still exhibit worm-like (elongated bar) surface morphology. The observed morphology agrees well with the simulated morphology of AlN films characterized by the low growth rate, as shown in Fig.5.3, Chapter 5. No significant difference in deposition rate was found in the three films, as shown in Fig.6.3.

(a) Grazing incidence (thin film) method

(b) θ -2 θ method

Fig.6.1 XRD patterns of AlN films deposited at various total gas flow rates

Fig.6.2 Surface morphology of AlN films deposited at various flow rates
(a) Flow rate = 6 sccm (b) Flow rate = 12 sccm (c) Flow rate = 24 sccm

Fig.6.3 The measured deposition rates of AlN films deposited at various flow rates

6.3.2 The effect of substrate temperature

6.3.2.1 XRD results

Fig.6.4 shows the XRD patterns of the films deposited at various substrate temperatures. All the films are found to have a polycrystalline wurtzite microstructure, as shown in Fig.6.4 (a). The θ -2 θ method XRD pattern confirms that the substrate temperature has a profound effect on the formation of preferred orientation. With increasing temperature the preferred orientation changed from (101) at 150 °

(a) Grazing incidence (thin film) method

(b) θ - 2θ method

Fig.6.4 XRD patterns of AlN films deposited at various temperatures

Fig.6.5 Surface morphology of AlN films deposited at various substrate temperatures

(a) T=150°C. (b) T=250°C. (c) T=350°C. (d) T=500°C

The measured deposition rates of these films were shown in Fig.6.6. The reduced deposition rate at 500 °C seems to indicate that at high temperature the re-evaporation effect is more obvious.

Fig.6.6 The measured deposition rates of AlN films deposited at various substrate temperatures

6.4 Conclusions

The evolution of preferred orientation and surface morphology with the change in total flow rate and the substrate temperature have been studied. It is found that the total gas flow rate has no significant effect on the formation of the preferred orientation in AlN films. The substrate temperature, however, has a profound effect on the evolution of preferred orientation. While the formation mechanism is not well understood as no obvious trend is seen in the evolution of preferred orientation. The observed morphology was found to be dominated by the orientated growth, as the coincidence in the morphology and preferred orientation are again observed in these films. The enhanced surface mobility of adatoms and re-evaporation are also found in the films deposited at high temperature.

Chapter 7 The Effect of Gas Pressure on the Orientated Growth and the Microstructure of AlN Films

7.1 Introduction

The gas pressure is an important factor that influences the growth behaviour and microstructure of the PVD thin films. For examples, it was reported that in PLD (pulsed laser deposition) deposited AlN films that low pressure resulted in amorphous films. With increasing pressure cubic-phase AlN can be deposited [155]. In sputter deposition the gas pressure is inter-linked to the sputtering power. For low sputtering power, a high chamber pressure reduces the energy of the sputtered atoms and gas species. If the power is kept constant, with an initial increase in the chamber pressure, the ion density increases. The sputtering rate increases with increasing chamber pressure. If the chamber pressure is further increased, the sputtering rate decreases owing to the enhanced scattering effect due to the reduced mean free path of gas species [146]. Low pressure sputtering ($p < 0.75$ mTorr) is now receiving great interest with its many advantages over the conventional sputtering, particularly with new physical processes such as (i) collisionless deposition process; (ii) assistance of fast neutrals in the film growth; and (iii) formation of films from ionized coating material and in the absence of an inert gas. Under such conditions novel materials with new physical properties can be formed [156].

Several groups have reported the effect of sputtering gas pressure on the orientated growth of AlN films. With only one exception [91] it is commonly found that the low sputtering gas pressure is favourable for the c-axis (002) orientated growth [35, 38, 41, 119, 157]. The c-axis orientated growth is attributed mainly to the increased adatom mobility on the growing surface due to the enhanced kinetic energy transfer and longer mean free path of gas species at low pressure [40].

Despite all these efforts, the microstructure of the deposited films is either not well characterized or not systematically studied. Microstructure characterization is very necessary to understand fully the growth mechanisms of the deposited films. The microstructural factors such as the nucleation and growth modes, the interface, the evolution of chemical composition, all can influence the growth behaviour of the deposited films. Only with detailed microstructure characterization can we obtain a deeper insight on the growth behaviour of the AlN films. Moreover, other factors such as the surface energy minimization and the elastic deformation energy minimization model for orientated growth that influence the orientated growth were not discussed in the earlier chapters. These models have been successfully used to explain the orientated growth of TiN films [158]. For the reactively sputtered AlN films less attention has been given to such models.

In this chapter the result on the effect of gas pressure on the orientated growth of reactively sputtered AlN films will be presented. Various advanced characterization techniques have been used to reveal the detailed micro-structural information of the deposited film. The corresponding growth mechanisms of these films are discussed based on the experimental results.

7.2 Experimental

AlN films were deposited with a 3-inches 99.99% pure Al target and in a gas mixture of 99.9995% purity nitrogen and argon. To study the effect of total sputtering gas pressure several gas pressure (2, 3, 5, 7.5, 15, 20 mTorr) were chosen for the deposition of AlN film. The other deposition parameters have been kept constant at a base pressure of 5×10^{-6} Torr, a nitrogen concentration of 75%, a flow rate of 12 sccm, a RF power of 300 W and a substrate temperature of 350°C.

The phase composition and preferred orientation of the deposited films have been studied by the grazing incidence and θ -2 θ XRD scan. XPS is used to measure the chemical composition and FESEM was employed to study the morphology of the deposited films.

The macro-scale stress of the deposited film was measured by FTIR peak shift. The micro-scale strain has been estimated by the XRD line profile analysis.

7.3 Results and discussions

7.3.1 The evolution of preferred orientation

Fig.7.1 shows the measured XRD patterns of the films deposited at various sputtering gas pressure of 2-20 mTorr, at a constant RF power of 300 W, a substrate temperature of 350°C, a N₂ concentration of 75% and a flow rate of 12 sccm.

The grazing incidence x-ray diffraction (GIXRD) result indicates that all the deposited AlN films have a polycrystalline wurtzite grain structure. No other phases were found, as shown in Fig.7.1 (a).

The evolution of the preferred orientation of AlN films with the change in sputtering gas pressure was shown by θ -2 θ XRD patterns in Fig.7.1 (b). Strong c-axis/ (002) textured AlN film was formed at low pressure (2 mTorr). Increasing the pressure to 5 mTorr resulted in AlN films with (002) and (101) mixed preferred orientation. The film deposited at 7.5 mTorr shows mixed (100) and (101) preferred orientation. Further increasing the sputtering gas pressure to 15 mTorr gives two peaks corresponding to the (100) and (101) crystallographic planes, as shown in the θ -2 θ XRD pattern. Similar result is found in the film deposited at 20 mTorr. In conclusion, with increasing gas pressure the preferred orientation of the deposited films tend to change from (002), (101) and (002) mixed preferred orientation, to (100) and (110) mixed preferred orientation. Hence the sputtering pressure has profound effect on the formation of the preferred orientation of the deposited AlN films.

The GIXRD θ -2 θ XRD patterns indicate that all the films except that deposited at 2mTorr are more randomly orientated. The film deposited at 2mTorr instead is better aligned with the (002) axis of individual grains parallel to the substrate surface. The measured rocking

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(a) Grazing incidence (thin film) method

(b) θ - 2θ method

Fig.7.1 XRD patterns of AlN films deposited at various sputtering gas pressure

curve of the film deposited at 2mTorr shows a full width at half maximum (FWHM) of about 16° , as shown in Fig.7.2. This indicates a large mis-orientation of the c-axis orientated grains.

Fig.7.2 Rocking curve of the AlN film deposited at 2 mTorr

7.3.2 Surface morphology

Fig.7.3 shows the surface morphology of the films deposited at various sputtering gas pressure. A coincidence in the morphology and the preferred orientation of the deposited films was observed again. The films deposited at high pressure (≥ 7.5 mTorr) showed elongated grains that were randomly oriented in plane. This agrees well with the simulated morphology of the films showing (101)/(100) or (100) and (101) mixed preferred orientation. With the decrease in the sputtering pressure, pyramid cone/facet structure was found in the film deposited at 5 mTorr, with (002) and (101) mixed preferred orientation was found. At 2 mTorr the morphology of the deposited film changed to pebble-like/sphere-like grain structure, which agrees with the simulated films with strong (002)/c-axis preferred orientation. The cross-sectional micrographs show that all the films have columnar grain structure. A typical cross-sectional micrograph was shown in Fig.7.3 (f).

It was also found that, in the films deposited at high pressures (≥ 7.5 mTorr), there is a continuous increase in the grain size with the decrease in the sputtering gas pressure, as

Fig.7.3. Surface morphology of AlN films deposited at various sputtering pressures

(a) $P = 20$ mTorr (b) $P = 15$ mTorr (c) $P = 7.5$ mTorr (d) $P = 5$ mTorr (e) $P = 2$ mTorr
(f) Cross sectional micrograph ($P = 7.5$ mTorr)

shown in Fig.7.3 (a)-(c). This indicates a low surface mobility of the adatoms under high gas pressure condition, as the coalescence process depends on the surface mobility of adatoms. The coalescence growth mode is valid when the film shows high nucleation density (e.g. nano grains). Fig.7.4 shows a linear reduction in the deposition rate with the increase in gas pressure. Hence the low deposition rate may further contribute to the formation of the AlN film with small grains under high sputtering gas pressure condition. Let us suppose a 3-D grain growth mode (e.g. columnar mode) of these grains and the

grain growth is dominated by the grain coalescence, the film with small thickness would have smaller grains. The two films with larger grains were found at 7.5 and 5 mTorr. The deposition rates for these films are higher than the other film. The change of the morphology from elongated grain structure to pyramid-cone structure of these two films can be attributed to the different preferred orientation formed in the AlN films, as

Fig.7.4 The deposition rate-gas pressure curve

discussed above. A reduction in deposition rate was also found in the film deposited at 2 mTorr, where a c-axis orientated growth was found. This result is not surprising from the view of adatom packing habit, as the formation of close-packed (002) plane needs longer time for the adatoms to accommodate themselves to the lattice site before the arrival of the next incident flux of the reactive species.

7.3.3 The energetic particle and scattering effects

The effect of gas pressure on the sputtering deposition is not straightforward. First, if the power is kept constant, with an initial increase in the chamber pressure, the ion density increases. Thus the sputtering rate increases with the increasing chamber pressure. Second, if the chamber pressure is further increased, the sputtering rate decreases owing to back diffusion (the collision of gas species in the gas phase). The higher the pressure the higher

is the collision frequency, as the mean free path (MFP) λ of the gas species is highly dependent on the pressure. The mean free path of the sputtered species is defined by the following equation [159]:

$$\lambda = \frac{W_2}{n_2 \sigma^2} = \frac{W_2}{2\pi(r_1 + r_2)^2 n_2} \quad [7.1]$$

where n_2 is the density of the gas species, W_2 the weight of the gas molecule, n_2 the gas molecules density, and σ the collision cross section of the gas molecule, which depends on the radius of the sputtered atoms r_1 and of the gas molecule r_2 [63]. n_2 is determined by the gas pressure p and gas temperature. Hence λ is inversely proportional to the gas pressure p in the deposition system. Thus, as the pressure is decreased, the mean free path of the sputtered atoms becomes comparable with the target-to-substrate distance. Hence the sputtered atoms experience less gas phase collisions. The result is that the sputtered Al atoms arrive on the surface of the growing film with most of their original energy retained, which is of the order of several electron volts, giving automatically a substantial energy deposition at the surface of the growing film.

Note the λ (MFP) is also dependent on the gas species. For example, some researcher calculated the mean free path (MFP) of the sputtered aluminum atoms at a pressure of 3.75 mTorr. In pure argon, the mean free path of is about 11.8 mm. In the case of pure nitrogen the MFP is about 21.3 mm [159]. At high nitrogen concentration the MFP will be longer.

In the following section the experiment results will be discussed with the consideration on energetic particle and scattering effects.

It can be seen that an initial increase in the chamber pressure from 2 to 5 mTorr resulted in the high deposition rate. This can be attributed to the high sputtering yield with the increased ion density at these pressures. Consequently the high arriving rate of the sputtered species resulted in the high deposition rate. Further increasing the chamber

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pressure the back diffusion effect became dominant. The back diffusion effect resulted in a linear reduction in sputtering rate with the increase in chamber pressure.

The high chamber pressure will also result in more gas phase collisions of the energetic particles and an increase in the kinetic energy loss of the sputtered species. The sputtered species with low kinetic energy, when adsorbed on the substrate surface, will have a lower surface mobility. Hence a continuous reduction of the grain size was found in the films deposited at 7.5-20 mTorr.

To understand the formation mechanism of the preferred orientation we need to refer back to the bonding strength information of AlN introduced in the earlier chapters. Two kinds of Al-N bond exist in the wurtzite AlN, named as B_1 and B_2 . {100} planes consist of only B_1 bond, while {002} and {101} planes consist of B_1 and B_2 bonds together. The formation energy of B_2 bond is larger than that of B_1 . Thus adatoms with higher energies are energetically favorable for the formation of (002) and (101) surface planes [147]. The evolution of preferred orientation with the change in pressure agrees well with this prediction. At high pressure the adatoms have lower kinetic energy owing to the strong scattering effect. Hence (100) surface plane containing low strength Al-N bond was formed. At low pressure, with less kinetic loss energy by collision, (002) and (101) surface planes containing high strength Al-N bond were formed. For the formation of (002) and (101) preferred orientation the packing habit of adatoms should also be considered. To form the close-packed (002) plane the adatoms need longer time to accommodate themselves the lattice site. Hence a low arrival rate of the reactive species is necessary. Such a pre-requirement is satisfied at lowest pressure, where the sputtering yield is low owing to the low ion density. The scattering effect at high pressure will also disturb the packing of adatoms to the proper lattice site. Hence influence the crystalline property of the deposited film, as shown by the weak peak intensity in the θ -2 θ XRD patterns of the films deposited at high pressure.

The result shows that low pressure is favorable for the formation of (002) orientated film, which is necessary in many circumstances. Note that the lowest pressure is not always

recommended as the practical working pressure varies according to the different instrument set-up. Without effective ionization the plasma will not be self-sustained at low pressure. Under this circumstance a possible way to deposit c-axis orientated film is to reduce the target-substrate distance at the lowest workable pressure. Reducing the target-substrate distance has been found to effectively enhance the transfer of kinetic energy of the incident species to the substrate [14, 41], possibly due to the scattering of the reactive species was reduced with a shorter traveling path.

7.3.4 The chemical composition of the deposited films

The chemical composition in the bulk of the deposited films was studied by XPS. Before the data collection the surface oxide layer was removed using a 4 KeV Ar^+ gun. The ion etching was continued until relative stable data of the element concentration were collected. The result is shown in Fig.7.5.

Fig.7.5 Element concentration of the deposited AlN films

Except for the film deposited at 5 mTorr, where carbon contamination was obvious, oxygen is found to be the major impurity in the film. High oxygen concentration (13-19%) was found in the deposited films, which the author believes is not surprising, as similar high concentration of oxygen impurity has been widely reported in reactively sputtered

AlN film deposited at low temperature [35, 134]. The high concentration of oxygen can be attributed to the vacuum (residual pressure) used in the deposition (5×10^{-6} Torr), as more residual gas species will remain in a high residual chamber pressure. The continuous degassing from the chamber wall during the deposition is another main source of the oxygen impurity in the deposition chamber, as high oxygen concentration was still observed in the reactively sputtered AlN films deposited with a much lower base pressure (3.75×10^{-7} Torr) [134]. The degassing/ baking-out at low temperature (for low temperature sputtering system) may take days for the system to reach a high vacuum, as the degassing rate decays exponentially with the decrease in temperature and degassing time. Hence it is not very practical in this work.

A reduction in the oxygen concentration with the decrease in sputtering gas pressure can be seen in Fig.7.5. As a dynamic pumping procedure is involved in the real deposition system, with the gas flow fixed at constant, the gas conductance will be much higher at low chamber pressure, i.e. the gas species in the chamber are refreshed faster. Hence at low pressure the residual oxygen species inside the chamber are more effectively removed from the sputtering chamber. Similar reduction of oxygen concentration with the decrease in sputtering pressure was also reported by other researchers [40].

With high oxygen concentration and the fact that only AlN phase is crystalline in the deposited films, there must be a lot of amorphous oxygen-rich domains in the these AlN films. At high pressure with the higher oxygen concentration the deposited film tend to be more amorphous. Which can be used to explain why very low XRD peak intensity was found in the films deposited at high pressure, as shown in Fig.7.1 (b).

7.3.5 The macro-scale residual stress in the deposited films

The macro-scale residual stress in the deposited film was estimated from the peak shift in FTIR spectra. The major phonon mode found in the measured FTIR spectra is the $E_1(\text{TO})$ mode, as shown in Fig.7.6.

Fig.7.6 FTIR transmission spectra of the deposited AlN films

The FTIR peak shift and the estimated stress are shown in Fig.7.7. A general trend of the reduction in the stress with the decrease in sputtering gas pressure is found. This agrees with the trend reported by other researchers [40]. As we know the residual stress consists of two part: the thermal mismatch stress and the intrinsic stress. If we assume that gas pressure does not change the substrate temperature the thermal stress does not change. Hence the evolution of the measured residual stress reveals mainly the change of intrinsic

Fig.7.7 The peak shift in FTIR spectra and the estimated stress

stress in these films.

The peak values of the stress are found at 2-5 mTorr. This corresponds to the films where (002) preferred orientation is dominant / obvious. In reference [40] the authors attributed the high stress at low pressure to enhanced peening effect of incident species, which is due to the long mean free path of gas species at low pressure. While the author believe the microstructure effect should be also considered. The alignment process of the columnar grains to place their (002) planes to be parallel to the substrate surface may result in the high stress in these films, as mentioned in Chapter 5. As more oxygen-rich amorphous domains exist in the films deposited at high pressure, these amorphous phases may serve as “stress damper” and result in the stress relaxation [153].

7.3.6 Consideration on the minimum energy models

7.3.6.1 Theory and method

Except for energetic particle effect the minimum surface energy and minimum strain energy models have also been used to explain the formation mechanism of the preferred orientation of thin film materials. With so many factors involved in a film growth process, it is no wonder that a variety of results has been reported and alternative interpretations have been proposed. While in the minimum energy models the discussion on the formation mechanism is more straightforward, as only the Gibbs energy of the deposited film needs to be considered. In this section the orientated growth of the sputtered AlN films will be discussed with the consideration on the minimum surface energy and minimum strain energy models.

Thermodynamically stable system should have lowest Gibbs energy. In thin film materials the overall energy is the summation of surface energy, the strain energy and the stopping energy [158]. The stopping energy describes the density of the deposited energy of ions along a certain crystalline direction and is related to the “channeling effect” of energetic particles. In conventional planar magnetron sputtering (involves mainly low energy particles) the stopping energy can be ignored. However, the stopping energy

should be considered in the deposition techniques utilizing high-energy particles, such as ion beam aid deposition and filtered cathode arc deposition. Thus in conventional planar magnetron sputtering only the surface energy and the strain energy of different lattice plane need to be considered in the formation of the preferred orientation. With a spontaneous effort to reduce the overall energy in the deposited film, the crystallographic plane with minimum surface / strain energy will be favored when the overall energy of the system is dominated by the surface / strain energy. It is generally believed that, at small thicknesses, the film shows an orientation corresponding to that with the lowest surface energy (the impurity can also affect the evolution of preferred orientation by varying the surface energy of the different crystal faces [104]). At large film thickness the strain energy will increase while the surface energy does not vary. Hence the plane with the lowest strain energy will be formed.

A. The surface energy of wurtzite AlN

The surface energy data of AlN is not available in the open literatures. It is a function of the number of broken bonds, bond strength and sublimation energy. As there is not enough data the surface energy of different planes was not calculated in this work. Since (002) basal plane has the lowest surface energy in hexagonal materials [81], the evaluation of the minimum energy model is still practical if we focus our discussion on the films deposited at low pressure, where the (002) plane exists.

B. Anisotropic strain and strain energy of wurtzite AlN

The internal stress will induce a considerable amount of strain energy in the deposited films. It is of interest to note that the stress which can be coupled with the formation of the preferred orientation during deposition is not the thermal stress but the intrinsic stress because the thermal stress is generated in the process of cooling after deposition. The anisotropic strain in different crystallographic planes will result in the difference in the strain energy in these planes.

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There is no available data of strain energy for AlN in the literatures. However, the strain energies U_{hkl} of plane hkl can be estimated by the Eq.7.2 [160].

$$U_{hkl} = \varepsilon_{hkl}^2 E_{hkl} / (1 - \nu) \quad [7.2]$$

where ε_{hkl} is the strain in the hkl lattice plane, E_{hkl} is the Young's modulus of the hkl plane and ν is Poisson's ratio.

The elastic moduli were calculated by using the elastic modulus equation for hexagonal materials [161]:

$$E_{hkl} = \frac{1}{(1 - l_3^2)^2 s_{11} + l_3^4 s_{33} + l_3^2 (1 - l_3^2) (2s_{13} + s_{44})} \quad [7.3]$$

Where l_3 is the cosine of the angle between the unit vector and the hexagonal c axis. S_{ij} is the single crystal elastic stiffness. The value of s_{ij} was calculated from the elastic compliance c_{ij} data taken from the reference [162] and by using the Eq.7.4 [163].

$$\begin{aligned} c_{11} + c_{12} &= s_{33}/s, \quad c_{11} - c_{12} = 1/(s_{11} - s_{12}), \quad c_{13} = -s_{13}/s, \\ c_{33} &= (s_{11} + s_{12})/s, \quad c_{44} = 1/s_{44}, \quad s = s_{33}(s_{11} + s_{12}) - 2s_{13}^2 \end{aligned} \quad [7.4]$$

The inputted and calculated data of c_{ij} , s_{ij} , and E_{hkl} are listed in Table. 7.1. It was found that $E_{101} (308 \text{ GPa}^{-1}) < E_{002} (329) < E_{100} (333)$. Note that the calculated s_{ij} values are

Table. 7.1. The values of c_{ij} , s_{ij} , and E_{hkl} (Gpa)

c_{11}	c_{12}	c_{13}	c_{33}	c_{44}
396	137	108	373	116
s_{11}	s_{12}	s_{13}	s_{33}	s_{44}
3E-3	-0.86E-3	-6.15E-4	3.04E-3	8.62E-3
s_{11}^*	s_{12}^*	s_{13}^*		
3.5E-3	-1.0E-3	-8E-4		
E_{100}	E_{002}	E_{101}		
333	329	308		

* The data found in reference [47]

comparable with those found in reference [47], hence the calculated result is believed to be reasonable.

Note that there are two kinds of stress/ strain, namely microstress / microstrain and macrostress / macrostrain, usually mentioned in the literature. The microstress / microstrain is nonuniform and varies from one grain to another on a microscopic scale. The microstrain produces XRD peak broadening. The macrostress / macrostrain is uniform over large distances and produces peak shift. Hence the macro-scale residual stress is usually measured as the production of the macrostrain ε_{hkl} and the elastic modulus E_{hkl} , with the assumption that the measured strain of plane (hkl) coincides with the macrostrain predicted by the elastic theory. The macrostrain ε_{hkl} is measured by Eq. 7.5, where θ is the peak position, $\Delta\theta$ is the XRD peak shift.

$$\varepsilon_{hkl} = -\cot\theta_{hkl} \times \Delta\theta_{hkl} \quad [7.5]$$

The microstrain in the grain size scale is likely to be responsible for the formation of the preferred orientation. Hence the strain ε_{hkl} of the surface planes is usually estimated by the line broadening of the XRD peaks in θ - 2θ scan.

The measured peak profile is found to be best fitted by a Voigt function [160, 164]. In Voigt function the peak profile is believed to be the convolution of a Gaussian and a Cauchy (Lorentz) component. In XRD peak profile analysis the Gaussian component is believed to contains the information (peak broadening) of micro-strain and Lorentz component contains the information of crystal size. For multiple peaks fitting a pseudo-voigt function can be used, as shown in Eq. 7.6.

$$I_p(\theta) = I_p \{ \eta \cdot L(\theta) + (1 - \eta) \cdot G(\theta) \} \quad [7.6]$$

where $I_p(\theta)$ denotes the experimental curve. $G(\theta)$ and $L(\theta)$ are the Gaussian and Lorentz component of the curve. $L(\theta) = (1 + \theta^2)^{-1}$ and $G(\theta) = \exp[-(\ln 2) \theta^2]$. η is the content of the Lorentz component ($0.328 < \eta < 1$) [155].

The pseudo-Voigt function is used in this work. It should be noted that the method is chosen for both its simplicity and, most important, for there is no strict requirement for very high quality XRD data (which is a must in Rietveld method). The apparent strain of individual planes can be estimated by the full width at half maximum (FWHM) w^G (in radians) of the Gaussian component of the peak profile by using the Eq.7.7.

$$w_{hkl}^G = 4\varepsilon_{hkl}^G \tan\theta_{hkl}^G \quad [7.7]$$

The XRD equipment broadening was measured from the commercial AlN powder of 10 μm size and subtracted from the measured profile of the AlN film with the Eq.7.8 [164].

$$w_{real}^2 = w_{measured}^2 - w_{equipment}^2 \quad [7.8]$$

An Origin 6.1 software is used for the curve fitting. The fitting result is obtained by a 200-time iteration procedure and evaluated by R^2 (the R-factor, i.e. the figure of merit of the fitting). The content of the Lorentz component η is fixed at 0.4 to make the iteration result convergent.

7.3.6.2 Experiment design

The anisotropy of the microstrain in different planes was studied the XRD line profile using the pseudo-Voigt function. As XRD peaks with high intensity were found only in the (002) and (101) planes, the XRD line profile analysis of microstrain will be focused on these two planes. Before the line analysis, the background is subtracted from the raw XRD data. The curve is smoothed and the $\text{Cu K}\alpha_2$ x-ray component is removed.

The films deposited at 2 and 5 mTorr were studied. Another film was deposited at 3 mTorr and about 6 hours with all the other parameters fixed at constant (the same as those shown in section 7.2), aimed to find any changes in the preferred orientation with the increase in film thickness.

7.3.6.3 Results and discussions

The XRD pattern and the morphology of the films deposited at 2 and 5 mTorr can be found in the Fig. 7.1 and Fig.7.2. Fig. 7.8 and Fig.7.9 show the XRD pattern and the morphology of the films deposited at 3 mTorr. A strong (002) preferred orientation with weak (100) and (101) peaks are found in the XRD pattern. The FESEM micrograph shows pebble-like grain structure, which agrees with the strong (002) preferred orientation found by XRD result. A larger grain size, compared to those of the films deposited at 3 hours, is also observed. This may indicate an in-plane grain growth by coalescence process.

Fig.7.8 θ -2 θ XRD pattern of the AlN film deposited at 3 mTorr, 6 hours

Fig.7.9 Surface morphology of the AlN film deposited at 3 mTorr, 6 hours

Cross-sectional TEM (XTEM) electron diffraction is used to reveal the growth behavior of the film. At the lower part (near the interface) of the cross-sectional sample ring pattern is found, which indicates randomly orientated grains. At the upper part the electron diffraction pattern is more ordered and can be attribute a (002) texture. The evolution of the electron diffraction patterns indicates a competing growth takes place in the film deposited at 3 mTorr, with (002) planes survived. This means (002) preferred orientation is favored in the film, even with a larger film thickness. Details of the TEM results can be found in the following chapter.

The results of the XRD line profile analysis for the films deposited at 2, 3 and 5 mTorr is shown in Table.7.2. The FWHM of Gaussian component w_{hkl}^G , the XRD peak position θ_{hkl} , the microstrain ε_{hkl} , and the strain energy U_{hkl} of different planes are included. The film thickness t and the R-factor are also included.

Table.7.2 The result of the XRD line profile analysis

		w_{hkl}^G	θ_{hkl} (degree)	R^2	ε_{hkl} ($\times 10^3$)
AlN powder	(100)	0.252 $\pm$ 0.0046	33.36 $\pm$ 0.0004	0.999	
	(002)	0.266 $\pm$ 0.0048	36.18 $\pm$ 0.0006		
	(101)	0.248 $\pm$ 0.0072	38.08 $\pm$ 0.0006		
2m Torr $t=272$ nm	(002)	0.952 $\pm$ 0.010	35.57 $\pm$ 0.0013	0.993	5.58
3 mTorr $t=836$ nm	(100)	0.287 $\pm$ 0.1344	32.75 $\pm$ 0.0067	0.997	0.93
	(002)	0.885 $\pm$ 0.0072	35.92 $\pm$ 0.0008		5.08
	(101)	0.685 $\pm$ 0.0639	37.85 $\pm$ 0.0079		3.58
5 mTorr $t=435$ nm	(002)	0.694 $\pm$ 0.0018	35.63 $\pm$ 0.0018	0.991	3.90
	(101)	0.629 $\pm$ 0.0240	37.53 $\pm$ 0.0033		3.29

An anisotropy of the microstrain in different planes is found. It is found that $\varepsilon_{101} < \varepsilon_{002}$. With the fact that $E_{101} (308\text{GPa}^{-1}) < E_{002} (329)$ and $\varepsilon_{101} < \varepsilon_{002}$, according to the Eq.7.2, it was found that the strain energy $U_{101} < U_{002}$.

To summarize, the analysis above shows that at low pressure the (002) preferred orientation is favored, even with a larger strain energy. Hence the minimum surface energy model should be used to explain the orientated growth, as (002) plane has the lowest surface energy.

Note that this conclusion should be restricted to the current growth stage with relative small film thickness ($< 1\mu\text{m}$). As anisotropy of the microstrain is found with $\varepsilon_{101} < \varepsilon_{002}$ and $U_{101} < U_{002}$, it is still possible to form (101) preferred orientation at even larger film thickness, since the strain energy is believed to dominate the growth of the films at large film thickness (unfortunately now there is not a critical value to define the film thickness to be large or small). Hence the validity of minimum strain energy model needs to be further evaluated. Moreover, when study the films deposited under different conditions, other factors such as sputtering and deposition rates should also be considered, as they will influence the packing habit of the film. This, in turn, will affect the formation of the preferred orientation.

Then why low sputtering pressure is favorable for the formation of surface plane with lowest surface energy? It was found that a condition with a low atom and ion concentration is necessary for the formation of crystal plane with the lowest surface energy in vapor deposition [82]. At low pressure, with less gas ions generated, a low sputtering yield and low concentration of reactive species is expected. Hence the condition of low atom and ion concentration is satisfied and (002) fiber texture developed.

7.4 Conclusions

In this chapter the effect of sputtering gas pressure on the orientated growth of AlN films has been studied. Several well-known models for the formation of preferred orientation,

named as the energetic particle effect, scattering effect and the minimum energy models have been used to discuss the formation mechanism of the preferred orientation of these films. Low pressure is found to be favorable for the formation of (002) preferred orientation. With the consideration on energetic particle and scattering effects it is attributed to the enhanced energy transfer of incidence species at low pressure. With less scattering and longer mean free path the energy is effectively transferred. Such condition is favorable for the formation of (002) plane with stronger Al-N bond. With the consideration on stacking habit of the adatoms the low sputtering yield at low pressure is believed to be favorable for the stacking of (002) close packed surface planes. Despite the anisotropy in microstrain/ strain energy found in the (101) and (002) AlN planes, with $\epsilon_{101} < \epsilon_{002}$ and $U_{101} < U_{002}$, the experiment result shows the surface energy dominated the formation of the preferred orientation in these films. The evolution of the morphology, the chemical composition and the macrostress with the change in sputtering gas pressure has also been studied and discussed in detail.

Chapter 8 TEM Study on the Growth Habit of AlN Films

8.1 Introduction

TEM has many advantages over other microstructure characterization techniques. For example, high resolution TEM can be used to study the fine structures of the materials such as sub-grain and defects. Such fine structure cannot be revealed in the conventional SEM. Cross-sectional TEM is a valuable method to study the film-substrate interface and the evolution of the microstructure with the film growth, which may contain important information on the growth mechanism of thin film materials. Electron diffraction is a powerful tool to study the crystalline property at microscale. The phase composition and the relative orientation of the neighbouring grains can be revealed by the electron diffraction. TEM has also its own shortcomings. For example, the phase contrast, which is sensitive to the inclination of sample / electron beam, will result in quite different appearance of the surface morphology of the thin films, compared to those in FESEM micrographs.

According to the results in the earlier chapters there are several parameters that strongly influence the orientated growth of the sputtered AlN films, such as power, nitrogen concentration, temperature and gas pressure. The gas pressure is believed to be a representative factor as its effect on the orientated growth and the microstructure is obvious and well understood. Different preferred orientation and morphology discussed before all can be found in the films deposited at various gas pressures. Hence in this work the effort on TEM study is mainly focused on those films deposited at various gas pressures.

8.2 Experimental techniques

8.2.1 Instruments and sample preparation

A 200 kV JEM-2010 transmission electron microscopy is used in the TEM study. A 300 kV JEM-2010F field emission gun transmission electron microscopy is also used in the

study of element mapping and high-resolution image. The interface, fine structure and the growth habit of the deposited films were studied either by the cross-sectional TEM (XTEM), the plan-view image or by the electron diffraction techniques.

The cross-sectional TEM (XTEM) sample was prepared by a conventional technique, which involves gluing two samples face-to-face, cutting, mechanical polishing, and dimpling followed by thinning in Ar^+ ion milling. The plan-view samples were made by cutting, mechanical polishing, dimpling and thinning in Ar^+ ion milling from the substrate side.

An AXIS Ultra x-ray photoelectron spectroscopy (XPS) was used for the depth profile element concentration measurement. An argon ion gun with a 4.0 keV energy was used to remove the top layer during the measurement.

8.2.2 Various focus conditions

De-focus (parallel beam) technique [123, 165] is widely used in the image study in this work. The defocus and overfocus conditions can be realized by over-focusing the condenser lens to ensure a parallel beam and also defocusing or over-focusing the objective lens. Then a Fresnel fringe will be visible at the thin edge of the specimen. With the beam underfocused a bright fringe is visible and with the beam overfocused a dark fringe is visible. The formation of the Fresnel fringe is due to the difference in inner potentials at the different parts of the sample [123]. Two examples showing the image difference under various focusing conditions are presented in Fig.8.1 and Fig.8.2.

Fig.8.1 shows the cross-sectional micrographs of a film deposited at 20 mTorr. Under the de-focus condition more features (e.g. the columnar grain boundaries) can be found in the micrograph, with the help of the Fresnel fringe at the grain boundaries. The difference in the inner potentials at the grain boundaries and in the grains may be due to the difference in phase composition or the difference in the mass and defect density at the two areas.

Fig.8.1 The cross-sectional micrographs of an AlN film deposited at a base pressure of 5×10^{-6} Torr, a sputtering gas pressure of 20 mTorr, a nitrogen concentration of 75%, a flow rate of 12 sccm, a RF power of 300 W and a substrate temperature of 350°C.

(a) Focus condition. (b) Defocus condition

Fig.8.2 The plan-view micrographs of an AlN film deposited at a base pressure of 5×10^{-6} Torr, a sputtering gas pressure of 5 mTorr, a nitrogen concentration of 75%, a flow rate of 12 sccm, a RF power of 450 W and a substrate temperature of 350°C. (a) De-focus condition. (b) Over-focus condition

The micrograph taken under focus condition is featureless. When there is no significant difference in thickness at the dark and bright areas the observed contrast can be mainly attributed to the diffraction contrast, i.e. the difference in the inclination of planes inside the grain to the electron beam.

Fig.8.2 shows the plan-view micrographs of an AlN films deposited at 450W, with a pyramid-cone surface grain structure in the FESEM micrograph. The TEM surface morphology is quite different from that observed by the FESEM. Instead of showing the pyramid-cone structure the TEM surface morphology shows only a contrast difference in the black and white areas, which can be partially attributed to the mass-density contrast originated by the difference in thickness at the different part of the pyramid-cone grains. The image under focus condition is featureless. Under de-focus and over-focus conditions the appearance of the grain boundaries is also different, as shown by the white arrows in the Fig.8.2 (b). The dashed white arrow 1 indicates the same position in the plan-view sample. Accordingly, by the above observation, defocus technique was mainly used in this study.

8.3 Results and discussions

8.3.1 The evolution of the cross-sectional microstructure with the change in the sputtering gas pressure

Fig.8.3 shows the defocused cross-sectional microstructure of the AlN films deposited at 20, 5, 3, and 2 mTorr, with other parameters kept constant at a base pressure of 5×10^{-6} Torr, a nitrogen concentration of 75%, a flow rate of 12 sccm, a RF power of 300 W and a substrate temperature of 350°C. A similar amorphous-like interface layer, which looks different from the upper part of the films, is commonly observed in all the deposited films.

Fig.8.3 The cross-sectional micrographs of the films deposited at various sputtering gas pressures. (a) 20 mTorr. (b) 5 mTorr. (c) 3 mTorr. (d) 2 mTorr.

Above this amorphous-like interface layer the columnar grain structure is found in all the deposited films. V-shaped columnar grains are commonly observed, which indicates a continuous increase in the grain size with the growth of the AlN film. The formation of the columnar grain structure can be attributed to the low mobility of the adatoms during the growth of these films, which is usually found in the films deposited at low temperature. The low mobility of the adatoms will restrict the coalescence procedure of the individual nuclei and grains and prevent a 2-D growth mode of the deposited films. Hence a 3-D nucleation and growth took place and the columnar grain structure is formed. As similar Fresnel fringes are visible inside each columnar grain, as shown in Fig.8.3 (a)

and (b), it seems that sub-grains also exist in the films. The fine structure of the columnar grains will be discussed later.

As the cross-sectional bright field images show less information of the difference in the microstructure of these films selected area diffraction (SAD) technique is used to further study the microstructure of these films. Fig.8.4 shows the SAD patterns of the films deposited at various gas pressures.

Fig.8.4 The SAD patterns of the films deposited at various sputtering gas pressures.

(a) 20 mTorr. (b) 5 mTorr. (c) 3 mTorr. (d) 2 mTorr.

The diameter of the SAD aperture used is about 550 nm, which means the selected area covers almost all the columnar part of the AlN films. The bright-field images corresponding to the SAD pattern in Fig.8.4 can be found in Fig.8.3.

The SAD results agree well with the XRD patterns shown in Fig.7.1. In Fig.8.4 (a) the film deposited at 20 mTorr shows no obvious texture. In Figure 8.4 (b) the film deposited at 5 mTorr shows a mixture of (002) and (101) texture. Note that the character of un-continuous ring (or the bar character) with non-uniform intensity distribution in rings is typical in textured films. The brighter part contains the information of the type (preferred orientation) and angle distribution of the texture. Decreasing the sputtering gas pressure to 3 mTorr results in AlN film with obvious (002) texture, as shown in Fig.8.4 (c). A large angle distribution (about 50 degrees) of the (002)/c -axis of individual columnar grains is also found in Fig.8.4 (c). Further decreasing the sputtering gas pressure to 2 mTorr results in a better alignment of the (002) axis, as shown by the smaller angle distribution (about 30 degree) of the (002) diffraction bar in Fig.8.4 (d). The zone axis of the diffraction pattern shown in Fig.8.4 (d) is identified to be (010), which is perpendicular to the (002) fiber axis. While extra diffraction spots ((120) and (-120)) that do not belong to the [010] zone axis were also found, as marked by the white arrows.

Regardless of the elongation of the diffraction spots the observed pattern in Fig.8.4 (d) looks close to that of an epitaxial AlN film with a two-domain structure [166], where one AlN domain was found to rotate 30 ° around the c-axis with respect to the other domain. The real diffraction pattern can be split into two simple diffraction patterns with two different zone axes, i.e. [010] and [-2-10] zone axes, as shown in Fig.8.5 (a)-(b). A CaRine crystallography 3.1 software was used to calculate the diffraction patterns shown in Fig.8.5.

Although the experimental pattern in Fig.8.4 (d) looks like that of a two-domain epitaxial AlN film, their formation mechanism is quite different. In our case the mechanism can be attributed to the fiber texture of the deposited films. It is briefly introduced in the following paragraphs.

(c) Diffraction pattern of a two-domain structure

Fig.8.5 The calculated diffraction pattern of single crystal AlN with (a) Zone axis=[010].

(b) Zone axis=[-2-10]. (c) A two-domain structure.

Fig.8.6 (a) shows the sections of the reciprocal lattice of a hexagonal structure and of a fiber texture around the c-axis (normal of the (002) basal plane). In hexagonal material with a perfect (002) fiber texture the reciprocal point in the N-order Laue zone ($N = 0, \pm 1, \pm 2$, et al) change to a series of circles, as shown in Fig.8.6 (a). The number N can be calculated by $N = hu_f + kv_f + lw_f$, where $u_f v_f w_f$ are the indices of the fiber texture axis and hkl are the indices of the reciprocal points. As c-axis is the fiber axis we have $[u_f v_f w_f] = [001]$. Using the equation $N = hu_f + kv_f + lw_f$ it was found that $N = 1$. Which means the reciprocal points with a c-axis index l will locate in the l-order Laue zone. These circles in the N-order Laue zone, when projected along the direction perpendicular to the c-axis (e.g. [010] direction) will appear to be a series parallel lines, as shown in Fig.8.6 (b).

According to diffraction theory the reciprocal lattice points with a [010] zone axis has another common feature, i.e. $hu_z + kv_z + lw_z = 0$, where $u_z v_z w_z$ are the indices of the zone axis and $[u_z v_z w_z] = [010]$, hkl are the indices of the reciprocal lattice points. By using the equation $hu_z + kv_z + lw_z = 0$ it was found that $k = 0$. Accordingly in the diffraction pattern of hexagonal materials with a [010] zone axis, the k index of all the spots should be zero.

In the diffraction pattern of a hexagonal materials with a perfect c-axis texture and a [010] zone axis the above two requirements, i.e. $l = N$ and $k = 0$ should be both satisfied. The simulated pattern of a perfect c-axis fiber textured AlN film with a [010] zone axis is shown in Fig.8.6 (b), where the circles denote the planes with the same general direction $\{hkl\}$ (the same length in the reciprocal vectors). The interception of these circles with the N-order Laue zone marks the positions of the observable diffraction points.

Note that those diffraction points with indices of $(-1-2N)$ and $(1-2N)$ (those marked by the white arrows in Fig.8.4 (c)) are also included in this figure, although in these points the condition of $k = 0$ is not hold. Instead the condition of $k = 0$ changed to $k = 2h$. With $l = N$ and $k = 2h$ these points satisfy the diffraction condition of a perfect c-axis textured AlN with a $[-2-10]$ zone axis. Hence the pattern in Fig.8.6 (b) contains the diffraction points with two different zone axes. Now we can see that the simulated pattern agrees well with that of the films deposited at 1.4-2 mTorr. The formation of such pattern can be mainly

(a) Sections of the reciprocal lattice of a hexagonal structure and of a fiber texture around the c-axis / normal of the (002) basal plane.

(b) The calculated SAD pattern of a perfect c-axis/(002) fiber textured AlN film

Fig.8.6 The formation mechanism of the SAD pattern of an AlN film with a perfect (002) fiber texture

attributed to the strong (002) fiber texture in these films.

The arc shape (with an angle of about 30°) of the (002) diffraction spots in Fig.8.4 (d) indicates the existence of a large mis-orientation (about 30°) of the (002) axis in the individual columnar grains. This agrees well with the measured FWHM (16°) of the XRD rocking curve (see Chapter 7), where a large angle distribution was found in the (002) axis.

8.3.2 The microstructure of the interface layer

The microstructure of the interface layer of the films deposited at various gas pressure has been studied by the high resolution TEM (HRTEM) image. A typical image was shown in Fig.8.7. Where the film has been deposited at 3 mTorr, with other parameters kept constant at a base pressure of 5×10^{-6} Torr, a nitrogen concentration of 75%, a flow rate of 12 sccm, a RF power of 300 W and a substrate temperature of 350°C .

Fig.8.7 The HRTEM image at the film-substrate interface of an AlN films deposited at 3 mTorr.

The HRTEM image in Fig.8.7 shows that the interfacial layer is amorphous. This is true

in most of the observed films. For rare case small areas of lattice fringe (with d-spacing around 4 Å) were also found inside the interface layer. But such information is not sufficient to identify the crystalline phase in these areas.

A depth profile element concentration measured by XPS, as shown in Fig.8.8, can give us more information about the interface layer. The film used in this measurement is deposited at 20 mTorr and with a thickness of about 270nm.

Fig.8.8 The depth profile element concentration of an AlN film deposited at 20 mTorr

High oxygen concentration is observed in this film. A continuous decrease in the oxygen concentration is also found with the growth of the film. The highest oxygen concentration is found at the film-substrate interface (about 42% O, 38% Al, 16% N, 4% Si), as shown in Fig.8.8. The result indicates that the interface layer is an oxygen rich layer. Similar oxygen-rich amorphous interface layer is also reported by other researchers [81], where they found also small α - Al_2O_3 crystals inside the interface layer.

The high oxygen concentration in the film can be attributed to the high concentration of

residual impurities in the chamber under the high gas pressure condition. The possible reason for the formation of the oxygen-rich interface layer is that the Al metal has a higher gettering efficiency for oxygen than for nitrogen [167]. Hence oxygen is preferably reacted at the initial growth stage of the film. The amorphous microstructure indicates extremely low surface mobility of the adatoms. This can be attributed to the high impurity concentration near the interface area. When the effective surface diffusion of the adatoms is blocked by the impurity phases the amorphous interface phases are then formed. The nitrogen and oxygen adatoms can both be treated as impurities in the formation of the aluminum oxide and aluminum nitride.

8.3.3 The columnar grain structure of the films deposited at low pressure

With the strong interest in the (002) orientated films the fine structure of the films deposited at low pressure is studied in more detail.

8.3.3.1. The plan-view TEM study

Fig.8.9 shows the plan-view TEM micrographs of the film deposited at 2 mTorr. By varying the focus condition the columnar grains and their grain boundaries are clearly shown in Fig.8.9 (a). Due to the deviation in the focus condition in the different part of this image, the grain boundaries appear bulgy at the upper part and concave at the lower part, as marked by the white arrows. The different appearance of the grain boundaries from the grains indicates different inner potentials in these areas. The possible reasons for the difference in inner potentials are the existence of the cavities, different phases, low density at the grain boundaries.

The contrast (the difference in the brightness in the black and the white grains) in this image has several origins, such as the mass-thickness contrast (due to the difference in mass density and thickness in these grains) and the diffraction contrast (due to the nature of crystalline or amorphous, the various rotation and inclination of these grains with respect to the incident electron beam). The contribution of the mass-thickness contrast is

Fig.8.9 Plan-view TEM micrographs of the film deposited at 2 mTorr. (a) Grain boundaries in different focuses. (b) The surface morphology at a low magnification. (c) Sub-grain boundaries and cavities. (d) Sub-grains

shown in Fig.8.9 (b), where the thickness difference is found. The hill-like structure (in Fig.8.9 (b)) appears dark and the smooth part appears bright in Fig.8.9 (a).

Cavities were found at the intersections of the individual grains, as marked by the dot arrows in Fig.8.9 (c). Some sub-grain boundaries are also found in this image, as marked by the white arrows. It seems that there are sub-grains inside each columnar grains. This prediction was confirmed by the image shown in Fig.8.9 (d), where the image is in focus.

Interestingly it is found that a large amount of AlN sub-grains exist in each columnar grain, as marked by the arrows. With a larger film thickness and columnar grain size the sub-grains and sub-grain boundaries are better shown in the film deposited at 3 mTorr, as shown in Fig.8.10.

Fig.8.10 Plan-view TEM micrographs of the film deposited at 3 mTorr. (a) Image in focus. (b) The columnar grain boundaries (c) Sub-grain boundaries

The image in focus is featureless, as shown in Fig.8.10 (a). By varying the focus condition the columnar grain boundaries and sub-grain boundaries were more clearly shown in Fig.8.10 (b) and (c).

According to the results shown in Fig.8.3, Fig.8.9 and Fig.8.10 the columnar grain structure can be described as the V-shaped columnar grain containing a large amount of sub-grains. Such structure agrees with the Zone 1 structure in the structure zone model (SZT) [32] for PVD thin films. Where the structure of the film is characterized as: tapered columnar grains separated by pores or voids. The existence of a large amount of sub-grains indicates a nucleation limited growth [154], where the incident atoms with low atomic mobility adhere where they impinge and small islands are formed by the impinging atoms grow vertically rather than across the surface. With the continuous formation of the secondary nuclei the channels/holes between the small islands will be filled by secondary nuclei and nuclei growth to give a continuous film.

As high oxygen concentration is commonly found in the bulk of these films and there are no other crystalline phase found by the XRD result, there must be many oxygen rich amorphous domains in these films. It will be very useful in understanding the growth behaviour of the sputtered AlN films if one can find out the distribution of these domains and the distribution of oxygen. In one literature report [81], where a c-axis orientated AlN film deposited at similar condition was reported, the authors claimed the microstructure of the AlN film to be small AlN crystals (the darker grains in the image) dispersed in a matrix of glassy (amorphous) boundary phase (brighter in the image). The claim is mainly based on the difference in image contrast. This leads the author to assume that the grain boundary/sub-grain boundary phases are amorphous and oxygen rich. There should also be deviation in crystalline properties in the grains appearing bright and dark as the former are assumed to contain more amorphous boundary phases (see Fig.8.9 (d)).

With a strong interest in the internal structural difference in the columnar grains nano beam electron diffraction (NBD) study was performed by using an electron beam of 15 nm in diameter. Two grains, bright and dark and marked as 1 and 2 in Fig.8.9 (c), have been studied. No big difference was found in the two grains as the two NBD patterns all indicate the existence of (002) orientated crystalline AlN inside each grain.

Hence the observed difference in image contrast in these two grains cannot be simply attributed to the difference in crystalline properties. Instead it contains also the contribution from in-plane rotation and out plane titling of AlN crystallites. This prevents the image contrast and diffraction technique from giving conclusive result on the crystalline/amorphous nature of the grain/sub-grain boundary phases and the distribution of amorphous phase.

The in-plane rotation of each grains can be reviewed by the SAD pattern of plan- view samples, as shown in Fig 8.11.

Fig.8.11 The plan-view SAD patterns of the film deposited at 2 and 3 mTorr.

(a) P=2mTorr. (b) P=3mTorr.

These patterns clearly shows the (002) fiber texture in the two films. First only diffraction from the planes with [002] zone axis (with plane index $l = 0$) appear in the pattern. This makes these pattern looks different from the ring pattern of a randomly orientated AlN film, where diffraction ring from planes with $l \neq 0$ will also appear). Such patterns indicate that (002) axis of individual columnar grains are aligned along the out-plane direction. Second the ring character indicates that these c-axis aligned columnar grains are randomly orientated in the in-plane direction (see also Fig.8.11 (a)-(b)). The formation mechanism of such a pattern can be understood with the help of Fig.8.6 (a), where in a c-axis fiber textured hexagonal material with a [001] zone axis the reciprocal point in the

N-order Laue zone (here $N=0$) change to a series of circles.

8.3.3.2. The oxygen distribution and its effect on the columnar grain structure

As the NBD is not effective showing the distribution of the amorphous oxygen-rich phases, element mapping is further tried to reveal the distribution of the oxygen. A 300 kV JEM-2010F field emission gun transmission electron microscopy was used for element mapping and the image was taken at a scanning transmission electron microscopy (STEM) mode. Additional ion milling was used before this experiment to avoid any fake result due to surface oxidation. Fig.8.12 shows the result of the element mapping. The AlN film deposited at 3 mTorr is used in this experiment.

Fig.8.12 (b) shows the element Al is uniformly distributed in the films. In Fig.8.12 (c) and (d) the signal intensities of the element N and O are much weaker due to the low atomic weight of these two elements. In Fig.8.12 (d) we do find oxygen at the grain boundaries (as marked by the white arrows) and sub-grain boundaries (as indicated by the dot arrows). While element O is also observed inside the grains. This result does not fully or exclusively support the prediction that oxygen is rich at the grain and sub-grain boundaries. Three facts have lead to this prediction. First, oxygen impurities exist in amorphous state. Second, there is possibility that the grain boundary phases are amorphous in sputtered AlN films with high oxygen contamination [81]. Third, it is experimentally observed that oxygen enrichment at the grain and sub-grain boundaries in evaporated Al films with elevating oxygen concentration [104]. Unfortunately the current mapping results prevent us from drawing decisive conclusions on the oxygen distribution in the AlN films been studied.

However, the author of this work believes that the possibility of oxygen enrichment at the grain and sub-grain boundaries need to be further investigated. There are a few reasons for such a consideration. For examples, the 3-D distributed boundaries network may prevent a clear view of the oxygen distribution at the grain / sub-grain boundaries and inside the grains with overlapping of the grains and boundaries along the thickness direction; the focus condition for mapping experiment is not proper to reveal the grain /

Fig.8.12 Element mapping result of the AlN film deposited at 3 mTorr. (a) Image. (b) The distribution of element Al. (c) The distribution of element N. (d) The distribution of element O

sub-grain boundaries (where de-focus condition is necessary and preferred) and prevent a clear view of oxygen distribution inside the grains. These technical problems must be settled before we can make a sound conclusion on the oxygen distribution.

The oxygen impurities at grain boundaries will promote the formation of three-dimensional (3D) impurity phases and further (in addition to the low temperature condition) block the migration of the grain/sub-grain boundaries. The 3D impurity phases will cover the growing crystal faces and lead to repeated nucleation. Then the film grows in a nucleation-limited mode. The V-shaped columnar grain structure is another evidence

of the blocking effect of three-dimensional boundary network and the nucleation-limited growth mode, which has been found in evaporated Al films [104]. Where with the increase in the oxygen concentration in the sputtering gas the grain structure changed from the columnar grains with parallel boundaries to the V-shaped columns.

8.3.3.3. Other features in the columnar grains

Fig.8.13 (a) shows magnified cross-sectional micrographs of the film deposited at 2 mTorr, where thickness fringes and moiré fringes are found and the later can be attributed to the overlapping of the crystalline columnar AlN grains. A tilting of the columnar grains, as marked by the dot arrows 1 and 2, was also clearly shown in the micrograph. This gives a straightforward view of the large mis-orientation in c-axis orientated columnar grains, which has formerly been shown by the SAD results. Fig.8.13 (b) shows an example of the edge dislocation found in the films deposited at 3 mTorr. Note the dislocation is revealed by moiré fringes instead of lattice fringes. It is a magnified image of dislocation [123]. As the film is polycrystalline and contains large amount of defects (amorphous domains, impurities, boundaries) the overall crystalline properties are poor. Hence no further effort is made to systematically study the dislocations in these films.

Fig.8.13 The tilting of the columnar grains and the dislocation. (a) The tilting of the columnar grains observed in the film deposited at 2 mTorr. (b) The dislocation found in the film deposited at 3 mTorr.

8.3.4 A simple model for the columnar grain structure

Fig. 8.14 (a) shows the cross-sectional micrograph of the film deposited at 3 mTorr. A V-shaped columnar grain structure was observed. Note this film is selected for study for its relative large thickness, which makes the study (by SAD) of the time-related growth behavior of (002) orientated films more practicable. For very thin films the available size of SAD aperture and the selected area are greatly limited.

Fig. 8.14 The growth mode of the film deposited at 3 mTorr. (a) The cross-sectional micrograph. (b) Diffraction pattern of area A. (c) Diffraction pattern of area B. (d) A simple growth model.

Fig. 8.14 (b)-(c) shows the SAD patterns taken at the lower and upper part of the film. The selected areas have been marked by the white circles A and B in Fig.8.14 (a). Taking into consideration of the difference in grain size at the lower and upper part of the V-shaped columnar grain, the size of the selected area aperture used was also different.

The ring character in Fig. 8.14 (b) indicates that near the amorphous interface layer the AlN grains are randomly orientated. Hence a randomly nucleation must have taken place at the initial growth stage of the columnar grains. With the continuous growth of the film the SAD pattern changes from rings to bars (or that of a typical texture materials). This indicate that a competitive growth of different crystallographic planes must took place during the growth of the film, where the (002) surface planes are likely to survive. Such growth behavior support that depicted by the Van der Drift model, where a concept of evolutionary selection was used to describe the competitive growth of individual planes [80].

The growth behavior of the film can be summarized by a simple model, as shown in Fig.8.14 (d), where the arrows indicate the (002) axis at the local area. At the initial growth stage, small randomly orientated AlN crystals were nucleated. As the surface diffusion is very low at low temperature the coalescence of these small grains were restricted. The grain boundary migration is further blocked by the impurity phases at grain boundaries. Hence incident atoms with low atomic mobility adhere where they impinge and small islands are formed by the impinging atoms growing vertically rather than across the surface. The film then grows into a V-shaped columnar structure instead of a parallel columnar structure. Continuous nucleation of secondary nuclei contribute to the vertical growth of the film.

With a competitive growth in different crystallographic planes those columnar grains, composed of mainly other surface planes rather than (002) planes, were terminated inside the film. Those with (002) plane to be parallel to the surface survives. As discussed in the earlier chapters, the low growth rate, the low scattering effect of sputter species, and also the minimum energy model can be used to explain why the (002) preferred orientation is

avored at low pressure condition.

8.4 Conclusions

In this chapter the fine structure of the AlN films deposited at various sputtering gas pressure has been studied in details. An oxygen-rich amorphous interface layer is commonly observed in these films. Its formation can be attributed to the high concentration of the residual oxygen impurity in the chamber and a higher gettering efficiency of Al metal for oxygen than for nitrogen. V-shaped columnar grains and sub-grains with a honeycomb-like grain/sub-grain boundary network are formed on top of the amorphous interface layer. The formation of such kind of columnar grain structure is attributed to the low mobility of surface adatoms at low temperature and the blocking effect of the honeycomb like grain boundary network, which prevents the migration of grain boundaries and the coalescence of the grains. Thus the film grows with the continuous formation of the secondary nuclei and grows vertically rather than across the surface. The prediction of oxygen enrichment at the grain/sub-grain boundaries is not fully supported by the current experimental results and need to be further investigated.

The growth behavior of the film deposited at low pressure was summarized by a simple growth model, i.e. the growth of the film starts with a randomly nucleation stage and followed by a competitive growth of the individual crystallographic planes. The survival of (002) surface planes can be attributed to the factors such as low growth rate, low scattering effect of sputter species under low pressure condition, and also to the minimum energy model for the orientated growth of thin film materials.

Chapter 9 Measurement of Through Plane Thermal Conductivity of the Sputtered AlN Films

In this chapter photothermal deflection technique will be used to measure the through plane thermal conductivity of AlN films. The microstructural effect on the thermal transport properties of AlN films will be evaluated. First a brief review will be given to cover the background information on the thermal transport properties of thin film materials.

9.1 Background

9.1.1 Heat transfer in solids

Heat transfer in solids is controlled by the propagation and scattering processes of heat carriers. There are two major heat carriers in solids - electrons and phonons (the quanta of lattice vibration energy).

9.1.1.1 Metals

In metals thermal conductivity is almost entirely due to the electrons [168]. Good electrical conductors tend to be good thermal conductors. Thermal conductivity and electrical conductivity has been related to each other by Wiedemann-Franz law [169]:

$$\kappa = L_e \sigma T \quad [9.1]$$

Where κ is thermal conductivity, σ is electrical conductivity, L_e denotes lorenz number, and T is temperature.

9.1.1.2 Dielectrics

In dielectric materials heat is conducted mainly by means of the thermal vibrations of atoms. The vibrations act as the conduit for heat transfer by the propagation of waves (phonon) superimposed on these vibrations, as schematically show in Fig. 9.1.

Fig. 9.1. Schematic of phonon motion superimposed on atomic vibrations in a solid [168]

The vibration of an atom in a crystal is like that of a weight suspended by a set of elastic cords. A small weight or stiffer cords give faster vibrations. The factors such as: low atomic mass, strong bonds, simple crystal structure and low anharmonicity (less scattering of phonons), thus will promote high thermal conductivity [170-172] in dielectric materials. For examples: diamond and III-V nitrides.

Kinetic approach and relaxation time approach [168, 173-174] predict that

$$\kappa = \frac{1}{3} C v l \quad [9.2]$$

Where κ is thermal conductivity, C is specific heat per unit volume (In Debye model, at low temperature C decays with T^3 , at high temperature C tend to be constant), v is the average speed of phonons, and l is the mean free path of phonons (l is determined by various scattering procedures).

In dielectric crystals internal / multiple-phonon scattering processes (e.g. Normal scattering (N) and Umklapp (U) scattering) are prominent at high temperature ($T > \text{Debye}$).

temperature Θ_D) and external / boundary and interface scattering processes dominate at low temperature ($T \ll \Theta_D$). With $\Theta_D^{\text{AlN}} \approx 800\text{-}1150\text{K}$ [171, 175], at room temperature the thermal transport properties of AlN will be dominated by external phonon scattering processes. In imperfect crystals and polycrystalline dielectrics defects such as point defect, stacking fault, dislocation and grain boundary, can also scatter phonons and restrict the mean free path of phonons at low temperature. More information on various phonon scattering processes can be found elsewhere [138, 168].

9.1.2 Thermal transport properties of thin film materials

9.1.2.1 The importance of the study on thermal transport properties of thin films

There are many recent and strong interests in the thermal transport properties of low-dimensional materials such as thin film, nano tube/line and superlattice [176-177]. Such interests have both practical and scientific origins.

The practical reason of such studies is the need for effective thermal management in the microscale / device level [173]. The wide use of layered structures in many electronic, optical, and optoelectronic devices have inevitably placed many of these layered structures in situations that require them to remove the heat dissipated quickly and effectively [49]. The continued quest for miniaturization of microelectronics and the increasing heat dissipation in devices make the microscale thermal management more important and necessary than ever before [173, 178-179]. Moreover, the thin films and layered structures may have quite different thermal transport properties with respect to the bulk materials. As a result, accurate thermal characterization of the constituent materials can provide important data for the thermal design of the devices.

From the scientific view it is also necessary to understand the new physical phenomenon and heat transfer mechanism in thin film materials. For example, size effect (the thickness dependence of thermal transport properties) [178-184] has been widely reported in thin films. One or two order decrease in the magnitude of thermal conductivity has been generally observed in various thin films [179, 185]. Table 9.1 summarizes the through

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plane thermal conductivity of various thin films [49]. Note that lateral (along the direction parallel to the substrate surface) thermal conductivity of some films are also included for comparison purpose.

Table 9.1 Measured thermal conductivity of various thin films [49]

Film material	Microstructure	Thickness (μm)	k_{film} (W/mK)	k_{bulk} (W/mK)
SiO_2	Amorphous	0.5-2.0	0.4-1.1	1.2-10.7
TiO_2	-	0.5-2.0	0.5-0.6	7.4-10.4
Al_2O_3	-	0.17-0.46	0.72	20-46
MgF_2	-	0.21-0.58	0.58	15-30
AlN	Dense,	<0.15	0.5	70-180
	Polycrystalline	0.25-1.0	16	
Tb-Fe compound	Dense, amorphous	0.25-1.0	5.3 (parallel)	30-40
			7.0	
Tb-Fe compound	Columnar, amorphous	0.25-1.0	0.3 (parallel) 4.3	30-40

According to the direction of heat flow two kinds of thermal transport properties of thin film materials are of interest: the through (perpendicular to) plane and the lateral thermal transport properties. In microelectronic industry the through plane thermal transport properties are more important as heat is generally generated within the active layers of devices and flows perpendicularly through the layers to substrates (heat spreaders). Materials with high thermal conductivity are need in this case. While in photothermal record layers (CD, DVD), to obtain a high density of memory the lateral thermal transport properties are more important and should be as low as possible [186]. Low thermal conductivity is also necessary in thermoelectric materials [51-52]. With low thermal conductivity thermoelectric thin films can thus better fulfill such a requirement than bulk thermoelectric materials. Hence the low thermal conductivity of thin film materials is not always bad and sometimes can even be utilized for better device performance.

Note that an anisotropy in the through (perpendicular to) plane and lateral (parallel) thermal conductivity of thin film materials is also shown in Table 9.1. An obvious deviation in thermal conductivity was found along the perpendicular and parallel directions of Tb-Fe compound thin films, especially in the Tb-Fe films with columnar structure. Moreover, the columnar structured Tb-Fe films generally have lower thermal conductivity than the dense Tb-Fe films.

Similar anisotropy was also reported in CVD diamond films and attributed to the columnar grain structure [187-188]. The reduced phonon transmittance across the columnar grain boundaries is believed to result in the much lower thermal conductivity along parallel direction. While the through plane thermal conductivity is not deeply affected by the boundaries of columnar grain as phonon reflection at grain boundary is dominant at this case, which seems do not significantly reduce the mean free path of phonons. A graded thermal conductivity (higher at upper part) was also found in these diamond films and related to the cone-shaped columnar structure [188].

9.1.2.2 The status of current research

The current research efforts on the thermal transport properties of thin film materials can be classified into two approaches: macroscopic and microscopic.

The macroscopic approach uses phenomenological models that require no knowledge of the mechanism of energy transport or the microstructure of solids. It focuses on the overall large-scale effects and requires only a constitutive relation or a simple transport law [173]. Intensive efforts have been made on the development of new measuring techniques with improved resolution and accuracy. A large numbers of measuring techniques have been developed. For examples, the various photothermal techniques [189] (e.g. photothermal refraction, photothermal mirage, photothermal deflection etc.), modified ac calorimetric (thermal wave) method [190], 3ω method [191] and Bridge method [192].

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The microscopic approach has become increasingly indispensable for developing novel materials and high performance devices as it provides a fundamental understanding of energy transport phenomena and mechanism in low-dimensional materials. For examples: various scattering mechanisms for heat carriers, i.e. Umklapp process, defect (dislocation, impurity, mass difference) scattering, boundary scattering, have been included in the discussion of the thermal transport properties of thin film materials [19, 193-195]. Continuum model considering the porosity and columnar structure in thermal transport properties of thin film materials has also been proposed [49], where the thin films are treated as composite materials. The validness of the classical energy transport equations in thin film materials is even challenged [196-197] when the dimension of the structure is comparable to the mean free path of phonons [198-199]. Instead phonon confinement at the external boundary, phonon transmittance through the grain/ external boundaries have been proposed to explain the heat transfer phenomena in low dimension structures [200-201]. A decrease in sound speed has also been found to lower the thermal transport properties of thin films [202]. The anisotropy in lateral and through plane thermal conductivity has also been reported in the low-dimensional superlattice structures [203-204].

Although many efforts have been made in the studies of the thermal transport properties of thin films the achievements are far from satisfying and conclusive. There are still many challenging areas which need to be further investigated. For example, among the existing efforts the microstructural information of the measured films is very rare [53], perhaps due to the lack of material scientists joining in this research area. It is an urgent task to establish the relationship between microstructure and thermal transport properties of thin film materials. Research efforts providing both the thermal transport properties and detailed microstructure information are necessary and favorable. This also leads to the research effort made in this chapter.

9.2 Experimental

9.2.1 The deposition and characterization of AlN films

Conditions with low gas pressure and reduced target-substrate distance were used in the deposition of AlN film to avoid high concentration of oxygen contamination. A series of AlN films with different thickness were deposited with conditions summarized in Table.9.2.

Table.9. 2 Deposition conditions

Substrate	D263 glass, $2 \times 2 \text{ cm}^2$ (100) Si
Substrate temperature	350 °C
Substrate-to-target distance	10 cm
Targets	Al 99.99% purity
Gas	Ar + N ₂ mixtures with 75% N ₂
Residual pressure	$< 5 \times 10^{-6}$ Torr
RF power	350 W
Sputtering pressure	2-3, 7.5 mTorr
Gas flow rate	12 sccm
Deposition time	1-6 hrs

Grazing incidence XRD scan and FESEM were used to study the crystalline property and the morphology of the deposited AlN films. XPS was used to estimate the chemical composition of these films.

9.2.2 Measurement of through plane thermal conductivity

Pulsed photothermal reflectance technique (the instrument is home made and in the School of EEE; it has been successfully used for thermal conductivity measurement of many thin films such as diamond, ZnO₂, gold, SiO₂, etc.; the results are comparable or in good agreement with that reported by other researchers) was used to measure the through plane thermal conductivity of the sputtered AlN films. This technique has many advantages such as non-contact, real time signal measurement, little sample preparation

needed, and convection heat losses can be neglected [173, 189]. On the other hand, a complex theoretical / mathematical model is needed to analyze the heat transport issues in the layered structures. Fig. 9.1 shows the schematic diagram of the experiment geometry of photothermal reflectance technique [205].

Fig.9.1. Experiment geometry of photothermal reflectance technique [205]

In this technique, the sample is first struck by the Nd : YAG layer pulse with a full width at half maximum (FWHM) of 8 ns, spot size of 3mm, and a pulse energy of 5 mJ. The sample surface temperature rises sharply and then relaxes with time. This gives rise to a temperature excursion profile that depends on the intrinsic thermal properties of the underlying film and the thermal resistance between layers. The surface temperature change of the sample induces a change in the reflective index of the surface. A continuous HeNe laser (1mW) beam is used to monitor the change in light reflection at the sample surface. As the temperature and reflectivity of gold are inversely related by equation [9.3], the temperature excursion profile can be obtained.

$$\frac{\Delta R}{R_0} = \frac{1}{R_0} \frac{dR}{dT} \Delta T \quad [9.3]$$

where R_0 is the sample reflectivity at temperature T_0 .

A typical experiment curve is shown in Fig.9.2. To extract the thermal properties of the thin film to be measured a precise theoretical model is needed to fit the experimental data. With the analogy between thermal conduction and electrical conduction the transmission-line technique for electrical engineering is used to solve the one-dimensional through-plane heat conduction, where a two layer-model and a three-layer model have been developed [206], see Fig.9.3.

Fig.9.2 Transient surface temperature excursion profile of a 1 μm AlN film

In the two-layer model the film between the heat absorption layer (Au film) and the substrate (silicon) is treated as a thermal resistance R_{th} , which is assumed to consist of a volume resistance internal to the film d/κ_{int} (d is the film thickness and κ_{int} is the internal thermal conductivity of the film), and boundary resistances R_B between layers. Thus

$$R_{th} = d/\kappa_{int} + R_B \quad [9.4]$$

R_B is obtained by extrapolating to zero thickness and κ_{int} can be determined from the slope of the $R_{th} - d$ curve.

Fig.9.3 Three-layer model with a thermal resistance at the layer interface (left) and its equivalent transmission-line representation (right)

Note that the two-layer model is only applicable when κ_{int} has no thickness dependence or the internal resistance of the film d/κ_{int} is considerably large than the boundary resistances R_B . It cannot be directly used for AlN films with thickness dependence on thermal conductivity [207].

The three-layer model is good for multiple parameters fitting. However, in the existing model the interface thermal resistances R_1 (between the Au film and the film to be measured) and R_2 (between the the film to be measured and the silicon) are not considered [207]. When the thermal resistance at the layer interface is considered the extra parameters make the multiple parameters fitting time consuming and sometimes the results are even unreliable.

To solve this problem two steps were used to extract the thermal conductivity of AlN films. First SiO_2 films with different thickness were grown by CVD technique on silicon. Then these samples and AlN samples were coated with gold films in the same batch by electric beam evaporation technique. The two-layer model was used to extract the thermal properties of Au films as that no significant thickness dependence on thermal conductivity

of SiO₂ films was found [205].

In the two layer model the Laplace transformed surface temperature excursion, $\overline{T(s)}$ can be described by [208]:

$$\overline{T(s)} = \frac{1}{e_1 \sqrt{s}} \left(\frac{\cosh \eta_1 \sqrt{s} + e_{21} \sinh \eta_1 \sqrt{s} + R_{th} e_2 \sqrt{s} \cosh \eta_1 \sqrt{s}}{\sinh \eta_1 \sqrt{s} + e_{21} \cosh \eta_1 \sqrt{s} + R_{th} e_2 \sqrt{s} \sinh \eta_1 \sqrt{s}} \right) \quad [9.5]$$

where $e_i = \sqrt{\rho_i c_i k_i}$, $e_{ij} = e_i / e_j$, $\eta_i = d_i / \sqrt{\alpha_i}$, $i = 1, 2$. Subscripts 1, and 2 stand for the gold film, and Si substrate respectively. ρ , c , k , e , α and d are the bulk density, specific heat, thermal conductivity, thermal effusivity and thermal diffusivity, and the thickness of each layer respectively. R_{th} is the thermal resistance between gold and silicon substrate. $Q(s)$ is the Laplace transform of the Nd:YAG laser pulse, which can be described by [208]:

$$Q(s) = \frac{1}{2} \left[1 + \operatorname{Erf} \left(\frac{b}{c} - \frac{cs}{2} \right) \right] \exp \left[-bs + \frac{1}{4} c^2 s^2 \right] \quad [9.6]$$

where $b = 2.02 \times 10^{-8}$, $c = 3.69 \times 10^{-9}$ s are the fitted values to the Nd:YAG pulse.

The bulk density of 1.93×10^4 kg/m³, the specific heat of 129 J/kg K for Au, and the bulk density of 2.33×10^3 kg/m³, specific heat of 712 J/kg K, thermal conductivity of 148 W/mK for Silicon are used in the fitting [209-210]. The fitting parameters are thermal conductivity of gold and R_{th} .

Then a three-layer model was used to extract the thermal conductivity of AlN film in a Au-AlN-Silicon layered structure. The Laplace transformed surface temperature excursion, $T(s)$ can be described by [208]:

$$T(s) = \frac{Q(s)}{e_1 \sqrt{s}} \left[\frac{(\cosh \eta_2 \sqrt{s} + e_{32} \sinh \eta_2 \sqrt{s}) \cosh \eta_1 \sqrt{s} + (e_{31} \cosh \eta_2 \sqrt{s} + e_{21} \sinh \eta_2 \sqrt{s}) \sinh \eta_1 \sqrt{s} + R_1 \cosh \eta_1 \sqrt{s} (e_3 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} \cosh \eta_1 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} \sinh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_1 R_2 e_3 \sqrt{s} e_2 \sqrt{s} \cosh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}}{(e_{21} \sinh \eta_2 \sqrt{s} + e_{31} \cosh \eta_2 \sqrt{s}) \cosh \eta_1 \sqrt{s} + (\cosh \eta_2 \sqrt{s} + e_{32} \sinh \eta_2 \sqrt{s}) \sinh \eta_1 \sqrt{s} + R_1 \sinh \eta_1 \sqrt{s} (e_3 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_2 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_2 (e_3 \sqrt{s} \sinh \eta_1 \sqrt{s} \cosh \eta_2 \sqrt{s} + e_{31} e_2 \sqrt{s} \cosh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}) + R_1 R_2 e_3 \sqrt{s} e_2 \sqrt{s} \sinh \eta_1 \sqrt{s} \sinh \eta_2 \sqrt{s}} \right] \quad [9.7]$$

where $e_i = \sqrt{\rho_i C_i K_i}$, $e_{ij} = e_i / e_j$, $\eta_i = d_i / \sqrt{\alpha_i}$, $i = 1, 2, 3$. Subscripts 1, 2 and 3 stand for the gold film, the AlN and Si substrate respectively. ρ , c , k , e , α and d are the bulk density, specific heat, thermal conductivity, thermal effusivity and thermal diffusivity, and the thickness of each layer respectively. R_1 is the thermal resistance between gold and AlN, R_2 is the thermal resistance between AlN and Si. $Q(s)$ is the Laplace transform of the Nd:YAG laser pulse, which can be described by equation [9.6].

The bulk density of $2.33 \times 10^3 \text{ kg/m}^3$, specific heat of 712 J/kg K, thermal conductivity of 148 W/mK for Silicon and the bulk density of $3.3 \times 10^3 \text{ kg/m}^3$, specific heat of 819.7 J/kgK for bulk AlN [209-210], and the average thermal conductivity for the gold layer of 200 W/mK (obtained in the measurement of Au-SiO₂-Si layered structure) are used in the fitting. The fitting parameters are thermal conductivity of AlN, R_1 , and R_2 .

9.3 Results and discussions

9.3.1 Microstructure of the deposited AlN films

Fig. 9.6 shows the grazing incidence XRD pattern of the AlN films with different thickness. Fig.9.7 shows the surface morphology of these films.

It is noticed that the orientated growth in these films are not the same. In the two thickest films c-axis orientated growth is obvious. While in the other films the grains are either randomly orientated or a-axis oriented. The XRD patterns and the surface morphology of these films agree well with each other. Please refer to the earlier chapters for detailed discussion. The observed difference in textured structure is attributed to variation in

Fig.9.6 Grazing incidence XRD patterns of the AlN films
with different thicknesses

deposition conditions, magnetron configuration, and thickness dependent growth behavior of AlN films.

Slack et al. [175] has estimated in their work that the anisotropy in thermal conductivity of AlN should be less than 5% between values parallel and perpendicular to the c-axis at room temperature and above. Hence the effect of crystalline anisotropy (orientated growth) on the thermal transport properties of the AlN films is ignored in this work. The difference in thermal transport properties of the films with various preferred orientation will only be related to the difference in grain structure and chemical compositions in these films.

The XRD result shows that 100nm AlN film has a poor crystalline property and is

amorphous like. Fig.9.7 (a) shows that the film has a very smooth surface, which indicates either amorphous or very fine grain structure. Such structure can be related to the growth behavior of the sputtered AlN films. As found in the earlier chapters at the initial growth stage an amorphous oxygen-rich layer with a thickness of 20-40 nm was preferably formed and followed by columnar growth of AlN grains. With a higher gettering efficiency than nitrogen to aluminum the residual oxygen impurity in the chamber will be

Fig.9.7. Surface morphology of the deposited AlN films

(a) $t = 100$ nm (b) $t = 240$ nm (c) $t = 397$ nm (d) $t = 756$ nm (e) $t = 1050$ nm
(f) a typical cross-sectional micrograph ($t = 1050$ nm)

preferably consumed at the initial growth stage. Hence the fine columnar AlN grains contain large amount of amorphous domains and the film tend to be amorphous like.

With increase in thickness a continuous improvement in the crystalline properties of the deposited AlN films is also found by the dramatically increase in the XRD peak intensity. At the same time a continuous increase in grain size is also observed in these films, as shown in Fig. 9.7 (a)-(e). The thickness dependence of the columnar grain size can be related to the V-shaped columnar grain growth in AlN films.

The chemical compositions of these AlN films are estimated from the previous XPS results on AlN films deposited at close conditions. Fig. 9.8 shows a XPS depth element profile of a 1 μm AlN film deposited at 5 mTorr, a target-substrate distance of 10 cm, with other parameters kept at constant, see Table 9.2.

Fig.9.8 XPS depth element profile of a 1 μm AlN film deposited at 5 mTorr, a target-substrate distance of 10 cm

An average oxygen concentration of 8.6-11.7% is found in the film deposited at different batches. As commonly a lower (2-3 mTorr) gas pressure is used for the deposition of AlN films in this chapter the oxygen concentration in these films should be lower (see chapter

7 the evolution of oxygen concentration with change in gas pressure) than 8.6-11.7%. The oxygen concentration in the 375 nm film maybe higher than that those in the other films as a 7.5 mTorr gas pressure is used for the deposition of this film.

9.3.2 Through plane thermal conductivity of AlN films

Fig.9.9 shows the fitting results of the Au-SiO₂-Si layered structures by a two-layer model. A linear relationship between thermal resistance R_{th} and thickness d is clearly shown in this figure. This indicates that equation [9.2] is held and the two-layer model is valid for the Au- SiO₂-Si layered structures. Hence the thermal properties of gold layer extracted by the two-layer model are reliable and can be used in the fitting for Au-AlN-Silicon layered structure with a three-layer model. The average thermal conductivity of the gold layer 200 W/mK was used for data fitting in the three-layer model. The measured thermal conductivities of AlN films are shown in Table 9.2 and Fig.9.10.

Fig.9.9 Thermal resistance data for the Au- SiO₂-Si layered structure

Table.9.3 Fitting results of thermal conductivity and thermal boundary resistances of AlN films

Thickness (nm)	Thermal conductivity (W/mK)	$R_1 (\times 10^{-8})$ ($\text{m}^2\text{K/W}$)	$R_2 (\times 10^{-8})$ ($\text{m}^2\text{K/W}$)
100	1.7 ± 0.5	8.3 ± 0.2	8.5 ± 0.3
240	1.4 ± 0.4	7.8 ± 0.5	7.0 ± 0.6
397	1.5 ± 0.3	7.5 ± 1.0	7.5 ± 1.0
756	3.5 ± 0.2	8.0 ± 0.6	5.5 ± 0.8
1050	4.5 ± 0.4	7.0 ± 0.9	6.5 ± 0.8

Fig.9.10 Thermal conductivity of AlN films with different thickness

Refer to the value of bulk AlN (320 W/mK) [211] a two-order decrease in thermal conductivity is found in the sputtered AlN films (1.4-4.5 W/mK). An decrease in thermal conductivity with the decrease in film thickness is also found in Fig.9.10. These results confirms the widely reported size effect and the one / two-order decrease in thermal conductivity in various thin films.

While further study shows that the measured thermal conductivity in this work is much lower than that found by other researchers in AlN films with similar thickness. One

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example is already shown in Table 9.1, where a thermal conductivity of 16 W/mK was found in dense and polycrystalline AlN film (0.25-1 μ m). Another example is that the measured thermal conductivity is even lower than the lateral thermal conductivity of pure AlN films with similar thickness [186], as shown in Fig.9.10 (according to earlier experimental observation, see introduction in section 9.1.2.1, a higher value is expected for the through plane thermal conductivity than the lateral thermal conductivity in thin films with columnar structure). With the knowledge of the fine structure of the deposited AlN films (see earlier Chapters) the author believes that the observed low thermal conductivity in these films is not surprise and can be well explained by the unique microstructure developed in these films.

According to equation 9.2, the C , the average speed of phonons v and the mean free path of phonon l are the factors that determine the thermal conductivity of materials at certain temperature. Due to the difficulty in measurement currently we have very limited knowledge on the specific heat C and average speed of phonons v of thin film materials. Thus the following discussion on the effect of microstructural factors on thermal conductivity will be focused on the microstructural effect on the mean free path of phonon l . At room temperature the mean free path of phonon l in AlN is dominated by phonon scattering at boundary and impurity site. Hence grain boundary structure and impurity concentration/ distribution in the deposited films should be responsible for the reduced thermal conductivity.

Watari [212] estimated that the mean free path of phonons is around 20 nm in bulk AlN ceramics with thermal conductivities around 160 W/mK and grain size ranges from 4 to 40 μ m. As the mean free path of phonon (20 nm) is much lower than the grain size (4-40 μ m) of AlN ceramic Watari concluded that grain boundary scattering is not significant in the bulk AlN ceramics. But this is not true in the sputtered AlN films. As shown in Fig.9.7, columnar grain size (at the film surface) range from a few nanometers to 100 nanometers have been found in AlN films with thickness of 100 to 1050 nm. Moreover, the TEM results in Fig.8.10 clearly shows the existence of a 3-D network of grain/sub-grain boundaries with a size in nano scale. These experimental results indicate

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that the real mean free path of phonon in the sputtered AlN films is much lower than that (20nm) in the bulk AlN due to the fine grain/ sub-grain structure (in nano scale). Regarding the oxygen-rich amorphous phase and interface layer in these films the mean free path of phonon maybe even smaller than the size of subgrains. Note that in the photothermal reflectance technique a 65 μm probe laser beam was used. Hence the measured area covers hundreds or thousands AlN grains/sub-grains and the boundary scattering effect is obviously included in the measured thermal conductivity. With the existence of a nano-sized 3-D network of subgrain boundaries the real mean free path of phonon along the through plane direction is dominated by the size of sub-grains instead of the size of columnar grains. This helps to understand why a slower increase in thermal conductivity with the increase in film thickness has been recorded in the sputtered films even with an obvious columnar grain growth. Similarly we can explain why the measured through plane thermal conductivity are even lower than the lateral thermal conductivity of AlN reported by other researchers [186].

Oxygen is the commonly observed impurity in AlN. Now it is well known that oxygen impurity can significantly deteriorate the thermal transport properties of AlN ceramic and should be avoided in developing AlN with high thermal conductivity [213-214]. To schematically show the effect of oxygen on the thermal conductivity of bulk AlN the results in literature report [214] is listed in Table 9.3.

Table 9.3 Oxygen concentration and thermal conductivity of sintered AlN ceramic

Sintered AlN samples	Oxygen (wt %)	Thermal conductivity(W /mK)
A	2.0	40
B	0.94	51
C	0.73	80
D	0.55	95
E	1.29	71
F	0.82	123
G	0.34	155

In Table 9.3 a significant decrease (from 155 to 40) in the thermal conductivity has been found with an increase in oxygen concentration from 0.34 to 2%. Thus the effect of oxygen impurity on the thermal conductivity of AlN is clearly shown. Virkar [215] predicted that with an increase of oxygen concentration by a factor of n the thermal conductivity of AlN can be decreased down to a minimum by a factor of $\sqrt{n}$. According to this prediction and by using the data of sample A (2% O) in Table 9.3 the lowest thermal conductivity of bulk AlN with 12 % oxygen is calculated to be 16.3 W/mK. With the above discussion now the attribution of the poor thermal conductivity in the sputtered AlN films to the high oxygen concentration is more straightforward, as an oxygen concentration around 8.6-11.7 % has been found in these films (see Fig.9.10).

In the discussion above the effect of grain boundary structure and oxygen concentration on the thermal conductivity of AlN films has been addressed separately. While the author like to point out that in the real case these two factors may interplay with each other. Their influence on the thermal conductivity is more complex and cannot be separated. For example, it is the high oxygen concentration that has led to the formation of cone-shaped columnar grain structure and the 3-D network of sub-grain boundaries; the oxygen distribution may not be homogeneous (it may be preferably distributed in the oxygen-rich interface layer or at the grain/ sub-grain boundaries) and determined by the growth behavior of the sputtered films. Taking into account of these facts the low thermal (and the extremely low thermal conductivity for thinner films) conductivity in the sputtered AlN films can then be better understood.

9.4 Conclusions

Photothermal reflection technique has been used to measure the thermal conductivity of the sputtered AlN films. Very low (1-4.5 W/mK) and a thickness dependence of thermal conductivities have been found in the deposited films and been attributed to the strong phonon scattering by oxygen impurity and grain boundaries in these films.

Chapter 10 Conclusions and Suggestions for Future Works

10.1 Conclusions

The major findings in this work are listed below:

- A coincidence between the preferred orientation and the surface morphology of AlN films has been established with the experiment results. It is found that the (002) orientated films have a pebble-like grain structure. The (101) orientated films show facet (or pyramid-cone) morphology and the (100) orientated films have elongated grain structure. This experimental observation is confirmed by the simulated morphology of single-crystal AlN with particular plane parallel to the substrate surface and can be related to the deviation in growth rate in different crystallographic planes.
- Condition with high nitrogen concentration has been found to result in c-axis orientated film growth. The low sputtering yield and low kinetic energy of the adatoms under high nitrogen condition have been attributed to the formation of close-packed (002) surface plane. Under low nitrogen condition, it is found that the backscattered neutral argon particles influences the growth behavior of AlN films by bombarding the film surface. The bombardment induced re-sputtering prevents the formation of close-packed (002) surface planes either by reducing the energy of atoms or affecting the packing process of the adatoms. This prevents the formation of the surface planes containing high-energy Al-N bondings.
- The AlN films deposited by both pure Al target and AlN targets have showed similar evolution in the preferred orientation with the change in gas composition. While the crystalline properties of AlN films deposited with pure Al target are better than those deposited with AlN target. Three phonon modes have been observed in the deposited films and attributed to E_1 (TO), A_1 (TO), and E_2^2 phonon modes of AlN. The residual stress in the deposited films was estimated by the observed E_1 (TO) peak shift in the FTIR spectra. Compressive stresses of - 0.4, to -1.6 GPa have been found in films

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deposited with pure Al target and tensile stresses of 0.25-0.75 GPa have been found the films deposited with AlN target. The tensile stress state in the films deposited by AlN target is attributed to the more amorphous-like nature of these films.

- By varying RF power it has been found that the incident energy of reactive species and sputtering yield play important role in the formation of the preferred orientation. (002) preferred orientation is favored at low power and (101) preferred orientation under high power condition. The power dependence of the orientated growth has been related to the energy of incident particles, the packing habit of adatoms and the strength of chemical bondings in the individual crystallographic planes.
- The total gas flow rate has little effect on the orientated growth of AlN films. The substrate temperature shows obvious influence on the evolution of preferred orientation. While no obvious trend has been found in this evolution and the effect of substrate temperature is not well understood.
- Condition with low sputtering gas pressure has been found to lead to the formation of (002) preferred orientation. With the consideration on the effect of energetic particles this results has been related to the low sputtering yield of target, the less scattering in gas phase and more effective kinetic energy transfer of reactive species under low pressure conditions. These features satisfy the packing habit of close-packed (002) surface planes with strong Al-N bondings. The minimum energy models for orientated growth have also been evaluated. An anisotropy in microstrain ϵ / strain energy U has been commonly observed in the (101) and (002) crystallographic planes in different AlN films, where it has $\epsilon_{101} < \epsilon_{002}$ and $U_{101} < U_{002}$. While this strain anisotropy has not resulted in the (101) preferred orientation in the films deposited at low pressure. Hence it is believed that the surface energy has dominated the growth of the films deposited at low pressures.
- High oxygen contamination is commonly observed in the bulk of deposited AlN films. XPS depth element profile indicates an even higher oxygen concentration at the

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interface. A decrease in oxygen concentration has also been found with the decrease in sputtering pressure. These results can be explained by the high residual oxygen impurity in the sputtering chamber and a higher gettering efficiency of oxygen than nitrogen to metal Al.

- An oxygen-rich amorphous interface layer is commonly found in the deposited AlN films following by a V-shaped columnar grain growth. A large amount of sub-grains with a 3-D honeycomb-like grain/sub-grain boundary network have also been found in the columnar grains. The formation of such structure can be attributed to the low mobility of adatoms at low temperature and the blocking effect of the 3-D honeycomb-like grain/sub-grain boundary network. Oxygen impurities have also found at the grain /sub-grain boundaries and may further limit the migration of grain boundaries and the coalescence of the neighboring grains. Then the film grows with the continuous formation of the secondary nuclei and grows vertically rather than across the surface. While the real oxygen distribution is not well revealed by the results of nano beam electron diffraction and element mapping studies.
- The results of electron beam diffraction have revealed detailed information on the evolution of the orientated growth and the alignment of individual columnar grains. The formation mechanism of the diffraction patterns has been explained in detail. The evolution in diffraction pattern in different AlN films has been related to the change in microstructure in these films. A simple model is proposed to describe the structure and evolution of the growth of the (002) orientated columnar grains.
- Photothermal reflection technique has been used to measure the thermal conductivity of the sputtered AlN films. Very low (1-4.5 W/mK) and a thickness dependence of thermal conductivities have been found in the deposited films and been attributed to the strong phonon scattering by oxygen impurity and grain boundaries in these films.

10.2 Suggestions for future works

Aluminum nitride is a very interesting and promising candidate material for various optical, mechanical, and electronic applications. In this work research efforts have been focused on the study of orientated growth, microstructure and thermal conductivity of the reactively sputtered AlN films. The results provide some insight into the growth behavior of the sputtered AlN films, the basic physical processes controlling the film growth and the microstructure effect on the thermal transport properties of AlN films. However more efforts are still needed or worth to be carried out in the following area:

- High oxygen contamination is commonly observed in the AlN films deposited in this work, which is a serious problem and makes these AlN films cannot be used in microelectronic applications. Hence to deposit high quality AlN films with minimized oxygen concentration should be the principal target for future researches. An improved pumping capacity and proper baking and gettering system / process may help to realize such a purpose.
- In this work the favorable conditions for c-axis orientated growth of AlN films has been established. However, a large mis-alignment in the c-axis of individual columnar grains still exists. It has been reported that the smaller the mis-alignment is the better is the performance of the AlN-based thin films resonators and SAW devices. Hence further efforts are needed to minimize such mis-alignment in c-axis of individual columnar grains.
- Novel techniques need to be tried to further investigate the distribution of oxygen impurities and oxygen-rich phases in AlN films. The current result is not good enough to draw a decisive conclusion on this topic.
- The oxygen contamination in this work has resulted in a commonly observed oxygen rich interface layer and also a cone-shaped columnar grain structure. Under very high

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vacuum condition such structure may not present. Instead an AlN-Si interface will be formed. Then the effect of other factors (such as substrate surface preparation, substrate orientation, pre-nucleation layers) on the crystallographic nature of the resulted films can be addressed. With the knowledge of the effect of all the factors mentioned above and studied in this work the growth behavior of sputtered AlN films can then be better understood.

- According to the open literature epitaxial AlN film has already been developed by sputtering technique [216], although in a very limited case. Generally a clean and optimized deposition condition, a high substrate temperature (to eliminate columnar grain growth and promote 2-D growth), plus an lattice-matched substrate (e.g off-axis Si (111) [217]) are necessary for the deposition of epitaxial AlN films. Further effort on preparing epitaxial AlN film will be nice and interesting.
- After obtaining AlN films of high purity more effort are worthy for the study of the through plane thermal conductivity of AlN films. For examples, research efforts with the aim to compare the thermal conductivities of AlN films with different impurity concentrations will be very helpful; the effect of post-deposition heat treatment on thermal transport properties of AlN films is worth to be investigated. Note in this part of work systematical and detailed information on the chemical compositions of AlN films are very necessary. Intensive XPS/AES/RBS analysis are needed.
- The lateral thermal conductivity of AlN films need to be studied and compared with that along the through plane direction. Actually the author has made enormous trials to measure the lateral thermal conductivity of AlN films by an ac-calorimetric technique. The very low thermal conductivity in these AlN films has resulted in a very low sensitivity of measurement and a large uncertainty in experimental results. Moreover, there are many technical difficulties need to be solved before the true thermal transport properties can be extracted. For examples, the non-uniformity of heat absorb layer (bismuth layer) has resulted in nonlinear experimental curve; The measurement process is time consuming. The time dependent thermal damage need to be considered.

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In summary, the experimental trials are unsuccessful. While this technique is still worthy to be tried for AlN films with high quality and thermal conductivity. Future works should also be focused on thick films, where deposition techniques with high growth rate may help to ease the difficulties in thermal diffusivity measurement.

References:

1. W.G. Miao, Y. Wu, H.P. Zhou, J. Mater. Sci. Lett. 16 (1997) 1245-1246
2. S.C. Park, H. Kang, S.B. Lee, Surface Science 450 (2000) 117-125
3. A. Giardini, A. Mele, T.M. DiPalma, C. Flamini, S. Orlando, R. Teghil, Thin Solid Films. 295 (1997) 77-82
4. N. Tanaka, H. Okano, T. Usuki and K. Shibata, Jpn. J. Appl. Phys. 33 (1994) 5249-5254
5. J.H. Edgar, C.A. Carosella, C.R. Eddy, Jr, D.T. Smith, J. Mater. Sci-Materials in Electronics. 7 (1996) 247-253
6. J. E. Field, The Properties of Diamond, Academic Press, London, 1979.
7. V. Mitchell, "Aluminium nitride", Mitchell Market Reports, Oxford, UK: Elsevier Advanced Technology, 1994
8. P.T.B. Shaffer, "Materials index", New York: Plenum Pr., 1964
9. P.J. Gielisse, "Wide Bandgap Materials in Future Electronic Applications", IMAPS Poland Conference 2000, <http://www.cyf-kr.edu.pl/academic/OBRMHiR/imaps/data/txt/txt11.htm>
10. J.A. Dean, "Lange's handbook of chemistry", New York: McGraw-Hill, 1973
11. Metallurgical Coatings, Proceedings of the international conference, San Diego California USA, April 18-22 1983 Vol. 1 & 2
12. B.W. Karr, I. Petrov, D. Cahill, and J.E. Greene, Appl. Phys. Lett. 70 (1997) 1703-1705
13. R.S. Naik, R. Reif, J.J. Lutsky, and C.G. Sodini, J. Electrochem. Soc. 146 (1999) 691-696
14. M. Ishihara, S.J. Li, H. Yumoto, K. Akashi, Y. Ide, Thin Solid Films 316 (1998) 152-157
15. P. Kung, A. Saxler, X. Zhang, D. Walker, T.C. Wang, I. Ferguson, And M. Razeghi, Appl. Phys. Lett. 66 (1999) 2958-2960
16. S. Strite and H. Morkoç, J. Vac. Sci. Technol. B. 10 (2000) 1237-1266
17. D.J. Jones, R.H. French, H. Müllejans, S. Loughin, A.D. Dorneich, P.F. Carcia, J. Mater. Res. 14 (1999) 4337-4344

References

18. M. Asheghi, Y.K. Leung, S.S. Wong, and K.E. Goodson, Appl. Phys. Lett. 71 (1997) 1798-800
19. A.D. McConnell, S. Uma, K.E. Goodson, in G. P. Celata et al., (Eds.), Proc. of the Int. Conference on Heat Transfer and Transport Phenomena in Microscale, Begell House, New York, 2000, pp. 413-419
20. P. J. Gielisse, IMAPS POLAND Conference 2000 <http://www.cyf-kr.edu.pl/academic/OBRMHiR/imaps/data/txt/txt11.htm>
21. S. Muhl, J.A. Zapien, J.M. Mendez and E. Andrade, J. Phys. D: Appl. Phys. 30 (1997) 2147-2155
22. G. Carlotti, G. Gbbiotti, F. S. Hickernell, H. M. Liaw, G. Socino, Thin Solid Films. 310 (1997) 34-38
23. A.V. Dobrynin, J. Appy. Phys. 85 (1999) 1876-1882
24. G. Radhakrishnan, J. Appl. Phys. 78 (1995) 6000-6005
25. A.G. Guidoni, A. Mele, T.M.D Palma, C. Flamini, S. Orlando, R. Teghil, Thin solid Films. 295 (1997) 77-82
26. L.D. Wang, H.S. Kwok, Appl. Surf. Sci. 154-155 (2000) 439-443
27. S. Tanaka, R.S. Kern, J. Bentley and R.F. Davis, Jpn. J. Appl. Phys. 35 (1996) 1641-1647
28. I.H. Kim, SH. Kim, Thin Solid Films. 253 (1994) 47-52
29. T. Reier, J.W. Schultze, W. Osterle, C. Buchal, Surf. Coat. Technol. 103-104 (1998) 415-420
30. M. Ishihara, K. Yamamoto, F. Kokai and Y. Koga, Jpn. J. Appl. Phys. 40 (2001) 2413-2416
31. R. Bathe, R.D. Vispute, Dan Habersat , R.P. Sharma , T. Venkatesan , C.J. Scozzie, M. Ervin, B.R. Geil, A.J. Lelis, S.J. Dikshit, R. Bhattacharya , Thin Solid Films. 398-399 (2001) 575-580
32. D.M. Mattox, in "ASM Handbook Vol. 5: Surface engineering", ASM International Handbook Committee, Materials Park, Ohio: ASM International, 1994, p.538-555
33. R. Messier, A.P. Giri, R.A. Roy, J. Vac. Sci. Technol. A, 2 (1984) 500-503
34. V. Dimitrova, D. Manova, T. Paskova, T. Uzunov, N. Ivanov, D. Dechv, Vacuum. 51, (1998) 161-164

References

35. B. Wang, Y.N. Zhao and Z. He, *Vacuum*. 48 (1997) 427-429
36. Y. Nakamura, Y. Watanabe, S. Hirayama, N. Yuusaku, *Surf. Coat. Technol.* 76-77 (1995) 337-340
37. K. Sugiyama, K. Taniguchi, K. Kuwabara, *J. Mater. Sci, Lett.* 9 (1990) 489-492
38. K. Kusaka, T. Hanabusa and K. Tominaga, *Thin Solid Films*, 281-282 (1996) 340-343
39. M. Akiyama, T. Harada, C. Xu, K. Nonaka and T. Watanabe, *Thin Solid Films*. 350 (1999) 85-90
40. H.C. Lee, G.H. Kim, S.K. Hong, K.Y. Lee, Y.J. Yong, C. H. Chun, J.Y. Lee, *Thin Solid Films* 261 (1995) 148-153
41. X.H. Xu, H.S. Wu, C.J. Zhang, Z.H. Jin, *Thin Solid Films*. 388 (2001) 62-67
42. M. Ishihara, S.J. Li, H. Yumoto, K. Akashi, Y. Ide, *Thin Solid Films* 316 (1998) 152-157
43. T.Q. Li, S. Noda, Y. Tsuji, T. Ohsawa, and H. Komiyama, *J. Vac. Sci. Technol. A* 20 (2002) 583-588
44. K. Shimada, T. Sota, and K. Suzuki, *J. Appl. Phys.* 84 (1998) 4951-4958
45. C. T. M. Ribeiro and F. Alvarez, A. R. Zanatta, *Appl. Phys. Lett.* 81 (2002) 1005-1007
46. M. Ishihara, K. Yamamoto, F. Kokai and Y. Koga, *Jpn. J. Appl. Phys.* 40 (2001) 2413-2416
47. K. Kusaka, D. Taniguchi, T. Hanabusa and K. Tominaga, *Vacuum*. 59 (2000) 806-813
48. M. Ferrari and L. Lutterotti, *J. Appl. Phys.* 76 (1994) 7246-55
49. J.C. Lambropoulos, S.D. Jacobs, S.J. Burns, L. Shaw-Klein, S.S. Hwang, *ASM, HTD.* 184 (1991) 21-32
50. D.G. Cahill and S.M. Lee, *J. Appl. Phys.* 83 (1998) 5783-5786
51. D.W. Song, W.L. Liu, T. Zeng, T.B. Tasciuc, G. Chen, J.C. Caylor and T. D. Sands, *Appl. Phys. Lett.* 77 (2000) 3854-3856
52. A. Balandin and K.L. Wang, *J. Appl. Phys.* 84 (1998) 6149-6153
53. C.L. Tien, *J. Heat Transfer*, 116 (1994) 799-807
54. S.L. Rohde, in "ASM handbook Vol. 5: surface engineering", Materials Park, OH:

References

- ASM International, 1994, pp. 573-581
55. R.W. Berry, P. M. Hall and M. T. Harris, "Thin film technology", Princeton, N.J.: Van Nostrand, 1968
56. L.I. Maissel and R. Glang (Eds), "Handbook of thin film technology", New York: McGraw-Hill, 1970
57. S.M. Rossnagel, J.J. Cuomo, W.D. Westwood, "Handbook of plasma processing technology: fundamentals, etching, deposition, and surface interactions", Park Ridge, N.J.: Noyes Publications, 1990
58. D.M. Mattox, "The foundations of vacuum coating technology", Norwich, New York: Noyes Publications, 2003
59. A.J. Walton, "Three phases of matter", Oxford Univ. Press, 1989
60. J.E. Mahan, "Physical vapor deposition of thin films", New York: Wiley, 2000
61. R.V. Stuart, "Vacuum technology, thin films, and sputtering: an introduction", New York: Academic Press, 1983
62. M. Ohring, "The materials science of thin films", Boston: Academic Press, 1992
63. K. Wasa and S. Hayakawa, "Handbook of sputter deposition technology: principles, technology, and applications", Park Ridge, N.J.: Noyes Publications, 1992
64. C. Staudt, R. Heinrich and A. Wucher, in "Atomic collisions in solids", O. Ellegaard, S.P. Møller, J. Schou, and P. Sigmund (Eds), Elsevier Science, 2000, pp. 677-687
65. D.M. Mattox, "Handbook of physical vapor deposition (PVD) processing: film formation, adhesion, surface preparation and contamination control", Westwood, N.J.: Noyes Publications, 1998
66. J.L. Vossen, W. Kern, "Thin film processes", New York: Academic Press, 1978
67. <http://www.angstromsciences.com/technology/sputtering.htm>
68. L. Eckertová, "Physics of thin films", 2nd revised edition, New York: Academic Press, 1986
69. C.E. Morosanu, "Thin films by chemical vapor deposition", Amsterdam; New York; Elsevier; Bucharest, Romania: Editura Tehnica, 1990
70. J.A. Venables, "Introduction to surface and thin film Processes", Cambridge University Press, 2000
71. Y. Taga, R&D Review of Toyota CRDL 28 (1993) 1-8

References

72. O.R. Monteiro, "Thin Film Synthesis by Energetic Condensation", Annual Review of Materials Research. Volume 31, August 2001
73. Akira Shibuya, "Ferroelectric Niobate Thin Films Prepared by Pulsed Laser Deposition and Magnetron Sputtering", Master thesis, Osaka University, 2001
74. O.S. Heavens, "Thin film physics", London, Methuen, 1970
75. J. A. Thornton, J. Vac. Sci. Technol. 11 (1974) 666-670
76. P.J. Kelly, R.D. Arnell, J. Vac. Sci. Technol.A, 16 (1998) 2858-2869
77. E. Zoestbergen, "X-ray analysis of protective coatings", PHD thesis, University of Groningen, Netherlands, 2000.
78. D. Walton, Phil. Mag. (1962) 1671-1679
79. N. Fujimura, T. Nishihara, S. Goto, J. Xu, T. Ito, J. Cryst. Growth. 130 (1993) 269-279
80. A. Van Der Drift, Philips Res. Rep. 22 (1967) 267
81. B.H. Hwang, C. Chen, H. Lu, T.C. Hsu, Mat. Sci. Eng. A-Struct. 325 (2002) 380-388
82. D.N. Lee, J. Mater. Sci. 24 (1989) 4375-4378
83. D.N. Lee, J. Matter. Sci. 34 (1999) 2575-2582
84. J. Pelleg, L.Z. Zervin, S. Lungo, and N. Croitoru, Thin Solid Films 197 (1991) 117-128
85. Z. Zhang and M.G. Lagally, Science 276 (1997) 377-383
86. Y.E. Lee, J.B. Lee, Y.J. Kim, H.K. Yang, J.C. Park, H.J. Kim, J. Vac. Sci. Technol. A 14 (1996) 1943-1948
87. B. Rauschenbach, J.W. Gerlach, Cryst. Res. Technol. 35 (2000) 675-688
88. I. Petrov, L. Hultman, U. Helmersson And J.E. Sundgren, J.E. Greene, Thin Solid Films, 169 (1989) 299-314
89. D. Dobrev, Thin Solid Films 92 (1982) 41-53
90. F. Ying, R.W. Smith, and D.J. Srolovitz, Appl. Phys. Lett. 69 (1996) 3007-3009
91. M. Penza, M.F. De Riccardis, L. Mirengi, M.A. Tagliente and E. Verona, Thin solid films, 259 (1995) 154-162
92. T. Takahashi, F. Takeda and M. Naoe, in "Advanced electronic packaging materials: Symposium on Advanced Electronic Packaging Materials", Andrew T. Barfknecht et

References

- al. (Eds.), Proceedings of the Symposium on Advanced Electronic Packaging Materials, November 27-29, 1989, Boston, Massachusetts, U.S.A. p.277-282
93. M. Ishihara, T. Manabe, T. Kumagai, T. Nakamura, S. Fujiwara, Y. Ebata, S. Shikata, H. Nakahata, A. Hachigo and Y. Koga, *Jpn. J. Appl. Phys.* 40 (2001) 5065-5068
94. S.R. Kirkpatricka, S.L. Rohdea, D.M. Mihuta, M.L. Kurruppu, J.R. Swanson, D.Thomson, J..A. Woollam, *Thin Solid Films* 332 (1998) 16-20
95. N.A. Preschilla, N.M. Elkashef, R.S. Srinivasa, S. Major, *Surf. Coat. Technol.* 108-109 (1998) 328-331
96. R.M. Guerrero and J.R.V. García, *Superficies y Vacío* 9 (1999) 82-84
97. A.A. Yamaguchi, T. Manako, A. Sakai, H. Sunakawa, A. Kimura, M. Nido and A. Usui, *Jpn. J. Appl. Phys. B* 35 (1996) L873-L875
98. B. Krause and K. T.Bröhl, *J. Phys.: Condens. Matter* 12 (2000) 4675–4686
99. M.H. Xie, S.M. Seutter, L.X. Zheng, S.H. Cheung, Y.F. Ng, Huasheng Wu, S.Y. Tong, *Internet. J. Nitride. Semicond. Res.* 5S1, W3.29 (2000)
100. P. Š utta1 and Q. Jackuliak, *Mater.Struct.* 5 (1998) 10-14
101. G.H. Gilmer, H.C. Huang, C. Roland, *Comp. Mater. Sci.* 12 (1998) 354-380
102. M.E. Ware and RJ. Nemanich, *Mat. Res. Soc. Symp. Proc.* 648 (2002) 10.8.1-10.8.5
103. J. Yun, D.S. Dandy, *Diam. Relat. Mater.* 9 (2000) 439-445
104. M. Adamik, P.B. Barna, I. Tomov, *Thin Solid Films.* 317 (1998) 64–68
105. G. Ferro, H. Okumura, S. Yoshida, *J. Cryst. Growth.* 209 (2000) 415-418
106. J. Zhang, J.B. Adams, in L.P. Kubin, J.L. Bassani, K. Cho, H. Gao, R.L.B. Selinger (Eds.) *MRS Proceedings 653: 2000 fall meeting proceedings symposium Z Multiscale Modeling of Materials*, 2000, z10.1
107. P. Fejdi, A. Holocsy, *Mater. Struct.* 8 (2001) 22-24
108. E. Bauer in: *Single-Crystal Films, Proceedings of Intern. Conf., Pennsylvania, 1963*, Maurice H. Francombe and H. Sato (Eds). Pergamon Press, Oxford 1964, p. 43-67
109. A. Barski, U. rossner, J.L. Rouviere, M. Arlery, *MRS Internet. J. Nitride. Semicond. Res.* 1 (1996) No. 21
110. J. Ohta, H. Fujioka, M. Sumiya, M. Furusawa, M. Yoshimoto, H. Koinuma, M. Oshima, *Proceedings of International Workshop on Nitride Semiconductors November 30, IPAP Conference Series 1* (2000) 359-362

References

111. R.D. Vispute, J. Narayan, H. Wu, and K. Jagannadham, J. Appl. Phys. 77 (1995) 4724-4728
112. M. Rehder, Z.L. Zhang, N.R. Perkins, S.E. Babcock, and T.F. Kuech,, MRS Internet J. Nitride Semicond. Res. 4S1, G3.56 (1999)
113. H.G. Tompkins, in: AMS Handbook, Vol. 5: Surface engineering, Materials Park, OH: ASM International, 1994, pp. 630-634
114. L.H. Liu, B. Liu, Y. Shi and J.H. Edgar, MRS Internet J. Nitride Semicond. Res. 6-7 (2001) 1-5
115. S. Matsuno, M. Kuba, T. Nayuki, S. Soga and P.W.T. Yuen, The Rigaku Journal. 17 (2000) 36-44
116. <http://www.msm.cam.ac.uk/dmg/teaching/c21e/sld057.htm>
117. <http://www.personal.psu.edu/users/x/x/xxl128/Works/Introducing%20the%20Application%20of%20AFM%20in%20the%20Field%20of%20Microbiology.doc>
118. <http://www.ece.arizona.edu/~barton/RamanTutorial.doc>
119. A. Garton, "Infrared spectroscopy of polymer blends, composites and surfaces", Oxford University Press, 1992
120. L.J. Radziemski, Richard W. Solarz, Jeffrey A. Paisner, "Laser spectroscopy and its applications", New York: M. Dekker, 1987
121. <http://www.physics.wsu.edu/Courses/515/spring2001/Lab6.pdf>
122. S. Ohuchi, P.E. Russel, J. Vac. Sci. Technol. Sect A 5 (1987) 1630-1634
123. D.B. Williams and C.B. Carter, "Transmission Electron Microscopy: A Textbook for Materials Science", New York: Plenum Press, 1996
124. P.B. Hirsch, A. Howie, R.B. Nigholson, D.W Pashley, "Electron microscopy of thin film crystals", London: Butterworth, 1965
125. http://www.chem.qmw.ac.uk/surfaces/scc/scat5_3.htm
126. M. Akiyama, C. Xu, K. Nonaka, T. Hagio, S. Nishimura, K. Shobu, T.Watanabe, J. Mater. Sci. 33 (1998) 2463-2467
127. C.C. Cheng, Y.C. Chen, .J. Wang and W. R. Chen, Jpn. J. Appl. Phys. 35 (1996) 1880-1885
128. C.C Cheng. K.S. Kao, Y.C. Chen, Alan R. Wilson, in Proceedings of SPIE - The International Society for Optical Engineering, Hiroshi Asanuma (Eds), 4234 (2001)

References

- 328-337
129. H. Okano, Y. Takahashi, T. Tanaka, K. Shibata and S. Nakano, *Jpn. J. Appl. Phys.* 31 (1992) 3446-3451
 130. J.L. Vossen, *J. Vac. Sci. Technol.* 8 (1972) S12
 131. M.S. Liu, K.W. Nugent, S. Praver, L. Abursill, J.L. Peng, Y.Z. Tong and P. Jewsbury, *Int. J. Mod. Phys B.* 12 (1998) 1963-1973
 132. W.J. Meng, J.A. Sell, T.A. Perry, L.E. Rehn, and P.M. Baldo, *J. Appl. Phys.* 75 (1994) 3446-3455
 133. I. Gorczyca, N.E. Christensen, E. L. Peltzer y Blancá, and C. O. Rodriguez, *Phys. Rev. B* 51 (1995) 11936-11939
 134. S. Kumar and T.L. Tansley, *Jpn. J. Appl. Phys.* 34 (1995) 4154-4158
 135. P. Perlin, A. Polian, T. Suski, *Phys. Rev. B.* 47 (1993) 2874-2877
 136. L.E. McNeil, Grimsditch and R. H. French, *J. Am. Ceram. Soc.* 76 (1993) 1132-1136
 137. K. Kim, W.R.L. Lambrecht, and B. Segall, *Phys. Rev. B.* 53 (1996) 16310-16326
 138. J.M. Ziman, "Electrons and phonons: The theory of transport phenomena in solids", Clarendon Press. Oxford, 1960
 139. F. Ansart, H. Ganda, R. Saporte, J.P. Traverse, *Thin Solid Films.* 260 (1995) 38-46
 140. A. Takase, S. Umebayashi and K. Kishi, *Jpn. J. Appl. Phys.* 21 (1982) 1447-1450
 141. A. Kumar, H.L. Chan, J.J. Weimer, L. Sanderson, *Thin solid films.* 308-309 (1997) 406-409
 142. T.W. Kim, S.S. Yom, W.N. Kang, Y.S. Yoon, Chayeon Kim, Sungtae Kim, I.S. Yang and Y.J. Wee, *Appl. Surf. Sci.*, 65/66 (1993) 854-857
 143. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, "Handbook of x-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data", Jill Chastain, Roger C. King, Jr. (Eds). Eden Prairie, Minn.: Physical Electronics, 1995
 144. W. Zou, "Synthesis of Giant Magnetoresistive Multilayers", PHD thesis, University of Virginia, 2001
 145. R. Roth, J. Schubert, M. Martin, E. Fromm, *Thin Solid Films.* 270 (1995) 320-324
 146. M. Farooq, Z. H. Leey, *J. Kor. Phys. Soc.* 40 (2002) 511-515

References

147. T. Terai, T. Kobayashi, T. Mitsuyama, T. Yoneoka, S. Tanaka, *Surf. Coat. Tech.* 106 (1998) 18-22
148. H. Cheng, T. Lin, W. Chen, *Thin Solid Films.* 425 (2003) 85-89
149. G.Y. Meng, S. Xie, D.K. Peng, *Thin Solid Films.* 334 (1998) 145-150
150. E. Dowtv. SI IAPE program, SI IAPE Inc. 196 Beech-wood Avenue. Bogota, NJ 07603. USA.
151. <http://www.shapesoftware.com/>
152. B. Aspar, R. Rodriguez-Clemente, A. Figueras, B. Armas and C. Combescure, *J. Cryst. Growth.* 129 (1993) 56-66
153. Y. Yong, J. Lee, H.S. Kim, and J.Y. Lee, *Appl. Phys. Lett.* 71 (1997) 1489-1491
154. G.F. Iriarte, F. Engelmark, M. Ottosson, and I.V. Katardjiev, *J. Mater. Res.* 18 (2003) 423-432
155. P. Dasgupta, *FIZIKA. A (Zagreb)* 9 (2000) 61-66
156. J. Musil, *Vacumm.* 50 (1998) 363-372
157. H. Lee, J. Lee, *J. Mater. Sci-Mater. E* 15 (1994) 221-225
158. J.P. Zhao, X.Wang, Z.Y. Chen, S.Q. Yang, T.S. Shi, and X.H. Liu, *J. Phys. D: Appl. Phys.* 30 (1997) 5-12
159. K. Kusaka, D. Taniguchi, T. Hanabusa and K. Tominaga *Vacuum.* 66 (2002) 441-446
160. J.I. Langford, *J. Appl. Cryst.* 11 (1978) 10-14
161. M.R. Daymond, M. A. M. Bourke, and R. B. Von Dreele *J. Appl. Phys.* 85 (1999) 739-747
162. A.F. Wright, *J. Appl. Phys.* 82 (1997) 2833-2839
163. J.F. Nye, "Physical properties of crystals: their representation by tensors and matrices", Oxford: Clarendon Press, 1985, p.145
164. Th.H. de Keijser, J.I. Langford, E.J. Mittemeijer and A.B.P. Vogels, *J. Appl. Cryst.* 15 (1982) 308-314
165. D.R. Clarke, *J. Am. Ceram. Soc.* 63 (1980) 104-106
166. U. Kaiser, P.D. Brown, I. Khodos, C.J. Humphreys, H.P.D. Schenk and W. Richter, *J. Mater. Res.* 14 (1999) 2036-2042
167. S. Dushman, *Scientific Foundations of Vacuum Technique*, New York: John Wiley,

References

1966. p. 637
- 168.** R. Berman, "Thermal Conduction in Solids", Oxford: Clarendon Press, 1976
- 169.** Grimvall, Göran, "Thermophysical Properties of Materials", Elsevier Science Pub. Co., 1986
- 170.** M. Tajika, H. Matsubara and W. Rafaniello, J. Am. Ceram. Soc., 82 (1999) 1573-1575
- 171.** A. Witek, Diam. Relat. Mater. 7 (1998) 962-964
- 172.** D.I. Florescu, V.M. Asnin, F.H. Pollak, A.M. Jones, J.C. Ramer, M.J. Schurman, and I. Ferguson, Appl. Phys. Lett. 77 (2000) 1464-1466
- 173.** C.L. Tien, A Majumdar, F.M. Gerner (eds), "Microscale energy transport", Taylor & Francis, Washington D.C, 1998
- 174.** J.C. Russ, "Fundamentals of energy dispersive x-ray analysis", London; Boston: Butterworths, 1984
- 175.** G.A. Slack, R.A. Tanzilli, R.O. Pohl and J.W. Vandersande, J. Phys. Chem. Solids. 48 (1987) 641-647
- 176.** J. Zou and A. Balandin, MRS Spring Meeting, San Francisco, USA. 2001
- 177.** G. Chen, J. Heat Transfer, 119 (1997) 220-229
- 178.** S.M. Lee and D.G. Cahill, J. Appl. Phys. 81 (1997) 2590-2595
- 179.** Y.S. Ju, Kenneth E. Goodson, "Microscale Heat Conduction in Integrated Circuits and Their Constituent Films", Boston: Kluwer Academic, 1999
- 180.** D.L. Decker, L.G. Koshigoe, E.J. Ashley, NBS Special Publication 727, Laser induced damage in optical materials: 1984, pp. 291
- 181.** R. Kato, A. Maesono, and R. P. Tye, TPPM99: 17-19 November 1999, Singapore, Peter Hing (eds), 1999, pp.27-33
- 182.** P. Nath, K.L. Chopra, Thin Solid films. 20 (1974) 53-62
- 183.** S. Orain, Y. Scudeller, and T. Brousse, Eurotherm Seminar No57, "Microscale Heat Transfer", Poitiers, France, 1998
- 184.** G. Chen and P. Hui, TPPM99: 17-19 November 1999, Singapore, Peter Hing (eds), 1999, pp.27-33
- 185.** A. Redondo and J.G. Beery, J. Appl. Phys. 60 (1986) 3882-3885
- 186.** R. Kato, A. Maesono, R. P.Tye, Inter. J. Thermophys, 22 (2001) 617-629

References

187. J.E. Graebner, S. Jin, G.W. Kammlott, J.A. Herb, C.F. Gardinier, Appl. Phys. Lett. 60 (1992) 1576-1578
188. J.E. Graebner, S. Jin, G.W. Kammlott, J.A. Herb, C.F. Gardinier, Nature. 359 (1992) 401-403
189. D. Almond and P. Patel, "Photothermal science and techniques", London: Chapman & Hall, 1996
190. I. Hatta, K. Fujii, A. Sakibara, F. Takahashi, Y. Hamada and Y. Kaneda, Jpn. J. Appl. Phys. 38 (1999) 2988-2992
191. L.J. Sheu and J.D. Lin, Jpn. J. Appl. Phys. 39 (2000) L690-L693
192. K.E. Goodson, O.W. Käding, M. Rösner, and R. Zachai, Appl. Phys. Lett. 66 (1995) 3134-3136
193. J. Zou and A. Balandin, J. Appl. Phys. 89 (2001) 2932-2938
194. D.I. Florescu, V.M. Asnin, and F.H. Pollak, R.J. Molnar, C.E.C. Wood, J. Appl. Phys., 89 (2000) 3295-3300
195. C.Y. Luo, H. Marchand, D.R. Clarke, and S.P. DenBaars, Appl. Phys. Lett. 75 (1999) 4151-4153
196. P.G. Sverdrup, S. Sinha, M. Asheghi, S. Uma, and K.E. Goodson, Appl. Phys. Lett. 78 (2001) 3331-3333
197. P.G. Sverdrup, O. Tornblad, K. Banerjee, D. Yergeau, Z. Yu, R.W. Dutton, and K.E. Goodson, TECHCON2000
198. C.C. Chiu, Y. Liou, Y.D. Juang, Thin Solid Films 260 (1995) 118-123
199. M.V. Simkin and G.D. Mahan, 84 (2000) 927-930
200. G. Chen, Phys. Rev. B. 57 (1998) 14958-14973
201. D.G. Cahill, A. Bullen, and S. M. Lee, High Temperatures-High Pressures 32, 134-142
202. A. Pike, M. Sickmiller, L. Vo, "Thermal Simulation of a Unique Ultra-Thin Semiconductor Packaging Architecture for Improved Power Dissipation", LO Technologies, Inc
203. G. Chen, C.L. Tien, X. Wu, J.S. Smith, J. Heat Transfer, 116 (1994) 325-331
204. M.I. Flik, C.L. Tien, J. Heat. Transfer. 112 (1990) 872-881
205. O.W. Käding, H. Skurk, and K.E. Goodson, Appl. Phys. Lett. 65 (1994) 1629-1631

References

- 206.** G. Chen, P. Hui, Thin Solid Films 339 (1999) 58-67
- 207.** G.C.K. Chen. “Thermal conductivity measurements and modeling of thin films”, PhD Thesis, Nanyang Technological University, 2000
- 208.** Zhao Yimin, First year report (PhD confirmation), School of EEE, Nanyang Technological University, 2003
- 209.** CRC handbook of chemistry and physics, 64th ed. Cleveland, Ohio: CRC Press, 1983/1984
- 210.** J.F Shackelford, “CRC Materials Science and Engineering Handbook”, Boca Raton: CRC Press, 1992
- 211.** G.A. Slack. J. Phys. Chm. Solids. 34 (1973) 321-335
- 212.** K. Watari, K. Ishizaki and T. Fujikawa, J. Mat. Sci. 27 (1992) 2627-2630
- 213.** A. Geith, M. Kulig, T. Hofmann, C. Russell, J. Mater. Sci. 28 (1993) 865-869
- 214.** R. Zahneisen, C. Russel, J. Mater. Sci. 28 (1993) 870-874
- 215.** A.V. Virkar, T.B. Jackson and R.A. Culter, J. Am. Ceram. Soc. 72 (1989) 2031-2042
- 216.** W. J. Meng, J. Heremans, and Y. T. Cheng, Appl. Phys. Lett. 59 (1991) 2097-2099
- 217.** Kanji Yasui, Suguru Hoshino, Tadashi Akahane, Appl. Surf. Sci. 159-160 (2000) 462-467

Publications List

1. H. Cheng and P. Hing, "The evolution of preferred orientation and morphology of AlN films under various RF sputtering powers", *Surf. Coat. Tech.* 167 (2003) 297-301
2. H. Cheng, Y. Sun, P. Hing, "Microstructure evolution of AlN films deposited under various pressures by RF reactive sputtering", *Surf. Coat. Tech.* 166 (2003) 231-236
3. H. Cheng, Y. Sun, P. Hing, "The influence of deposition conditions on structure and morphology of AlN films deposited by RF reactive sputtering", *Thin Solid Films*, 434 (2003) 112-120.
4. H. Cheng, Y. Sun, J.X. Zhang, Y.B. Zhang, S. Yuan and P. Hing, "AlN Films Deposited under Various Nitrogen Concentrations by RF Reactive Sputtering", *J. Cryst. Growth.* 254 (2003) 46-54
5. H. Cheng and P. Hing, "A study on the growth mechanism and microstructure of a C-axis Orientated AlN film deposited by RF reactive sputtering", *ICMAT&IUMRS-ICA*, Dec. 7th-12nd, 2003, Singapore
6. J.X. Zhang, H. Cheng, S. Yuan, P. Hing, et al. "Optimization of the sputtering deposition parameters of highly orientated AlN thin films on Si (100) by reactive RF magnetron sputtering", *ICMAT&IUMRS-ICA*, Dec. 7th-12nd, 2003, Singapore
7. J.X. Zhang, Y.Z. Chen, H. Cheng, A. Uddin, S. Yuan, K. Pita, T.G. Andersson, "Interface study of AlN grown on Si substrates by radio frequency magnetron reactive sputtering", *Thin Solid Films.* 471 (2005) 336-341
8. Yimin Zhao, et al, H, Cheng, P. Hing, "Pulsed photothermal reflectance measurement of the thermal conductivity of sputtered aluminum nitride thin films", *J. Appl. Phys.* 96 (2004) 4563-4568
9. H. Cheng, X.J. Xu, J.X. Zhang, Y. Sun, S. Yuan and P. Hing, "A TEM Study on the Morphology and Microstructure of a C-axis Orientated AlN Film Deposited by RF Reactive Sputtering", under revision

25-1133	Quality: *
CAS Number:	24304-00-5
Molecular Weight:	40.99
Volume[CD]:	41.74
Dx: 3.261	Dm:
S.G.: P6 ₃ mc (186)	
Cell Parameters:	
a 3.111	b c 4.979
α	β γ
SS/FOM: F26=80(.0117, 28)	
I/cor: 1.60	
Rad: CuK α 1	
Lambda: 1.540598	
Filter:	
d-sp:	

AlN
Aluminum Nitride
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 12, 5 (1975)

2 θ	int	h	k	l	2 θ	int	h	k	l	2 θ	int	h	k	l
33.216	100	1	0	0	76.445	1	0	0	4	114.83	<1	2	0	4
36.041	60	0	0	2	81.089	4	2	0	2	118.09	4	3	0	0
37.917	80	1	0	1	85.941	1	1	0	4	125.10	10	2	1	3
49.816	25	1	0	2	94.843	9	2	0	3	131.51	5	3	0	2
59.350	40	1	1	0	98.293	3	2	1	0	136.34	1	0	0	6
66.054	30	1	0	3	101.06	7	2	1	1	148.27	5	2	0	5
69.731	5	2	0	0	104.83	2	1	1	4	152.45	1	1	0	6
71.440	25	1	1	2	109.63	3	2	1	2	155.53	<1	2	1	4
72.629	10	2	0	1	111.12	6	1	0	5					

Appendix 2: The JCPD file NO. 34-0679 for Cubic AlN

<div>34-0679</div> <div>CAS Number:</div> <div>Molecular Weight: 40.99</div> <div>Volume[CD]: 495.48</div> <div>Dx: 3.434 Dm:</div> <div>S.G.: F</div> <div>Cell Parameters:</div> <div>a 7.913 b c</div> <div>α β γ</div> <div>SS/FOM: F 8=16(0.047, 11)</div> <div>I/Icor:</div> <div>Rad: CuKα</div> <div>Lambda: 1.54178</div> <div>Filter: Ni</div> <div>d-sp:</div>	<div>AlN</div> <div>Aluminum Nitride</div> <div>Ref: Kieffer, R. et al., Rev. Int. Hautes Temp. Refract., 13, 97 (1976)</div>
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