Master Thesis

Growth and Phase Stability of
Titanium Aluminum Nitride Deposited by
High Power Impulse Magnetron Sputtering

Chung Chuan, Lai
LiTH-IFM-A-Ex--11/2535--SE

Supervisor: Kostas Sarakinos, Linköpings universitet
Examiner: Ulf Helmersson, Linköpings universitet
In this work, we investigate the relation between the diffusion behavior of Ti$_{1-x}$Al$_x$N at elevated temperatures and the microstructure. Thin film samples are synthesized by reactive co-sputtering with two cathodes. One cathode equipped with Ti target is connected to a high power impulse magnetron sputtering (HiPIMS) power supply, and the other cathode equipped with Al target is operated with a direct current power source. The spinodal decomposition of cubic metastable Ti$_{1-x}$Al$_x$N controlled by thermally activated diffusion is observed for diffusion behavior. Various HiPIMS pulsing frequencies are used to achieve different microstructure, while altered power applied to Al target is used to change the Al content in films. In the phase composition analysis achieved by GI-XRD, the right-shift of (111) film peak along with increasing Al-power is observed. A saturation of the right-shift and h-AlN peaks are also observed at certain Al-power. The chemical composition determined by ERDA shows trends of reducing Al solubility limit in metastable phase and O contamination upon decreasing the pulsing frequency. More N deficiency is found in samples deposited with higher frequency. In the 500 Hz and 250 Hz samples deposited into similar composition and thickness, no apparent difference of the microstructure is observed from the SEM cross-sectional images. From HT-XRD, we observe higher intensity of TiO$_2$ and h-AlN peaks in 500 Hz sample at elevated temperature as compared with 250 Hz one. From the reduction of O contamination, denser Ti$_{1-x}$Al$_x$N films are able to be deposited with lower HiPIMS pulsing frequency. In addition, the higher intensity observed in HT-XRD patterns indicates that the 500 Hz sample is more open to diffusion and therefore allows the new formed phases to grow in larger grains.
ABSTRACT

In this work, we investigate the relation between the diffusion behavior of Ti$_{1-x}$Al$_x$N at elevated temperatures and the microstructure. Thin film samples are synthesized by reactive co-sputtering with two cathodes. One cathode equipped with Ti target is connected to a high power impulse magnetron sputtering (HiPIMS) power supply, and the other cathode equipped with Al target is operated with a direct current power source. The spinodal decomposition of cubic metastable Ti$_{1-x}$Al$_x$N controlled by thermally activated diffusion is observed for diffusion behavior. Various HiPIMS pulsing frequencies are used to achieve different microstructure, while altered power applied to Al target is used to change the Al content in films. In the phase composition analysis achieved by GI-XRD, the right-shift of (111) film peak along with increasing Al-power is observed. A saturation of the right-shift and h-AlN peaks are also observed at certain Al-power. The chemical composition determined by ERDA shows trends of reducing Al solubility limit in metastable phase and O contamination upon decreasing the pulsing frequency. More N deficiency is found in samples deposited with higher frequency. In the 500 Hz and 250 Hz samples deposited into similar composition and thickness, no apparent difference of the microstructure is observed from the SEM cross-sectional images. From HT-XRD, we observe higher intensity of TiO$_2$ and h-AlN peaks in 500 Hz sample at elevated temperature as compared with 250 Hz one. From the reduction of O contamination, denser Ti$_{1-x}$Al$_x$N films are able to be deposited with lower HiPIMS pulsing frequency. In addition, the higher intensity observed in HT-XRD patterns indicates that the 500 Hz sample is more open to diffusion and therefore allows the new formed phases to grow in larger grains.
ACKNOWLEDGEMENT

Before starting this article, I would like to show all my appreciation to the people who supported me finishing this work, in every aspect. Without any of you, the work will never be done. I would like to thank

**Ulf Helmersson**, for accepting me as a member in the Plasma and Coating Physics group. Your patient listening and knowledge always make the discussion with you helpful. I am very happy for the time in your group, thank you and your politeness!

**Kostas Sarakinos**, for being an excellent supervisor who always gives me time from your intensive schedule for discussing and giving advices. I am very grateful for your patient guidance helping me work through all the troubles. Your encouragement for trials and the funny talk with you at leisure time gives me a nice experience to work with you, thank you!

**Asim Aijaz**, for being a great teacher and friend who always encourages and help me when I stuck with problems. You taught me all the lab operation at Edward in the beginning of my work in detail and arranged your work-time just for my experiments, thank you!

**Daniel Magnfält**, for your introduction at Ginnungagap and sharing your experience on the work. Especially you saved my samples in the chamber for several times. It is happy and meaningful to discuss with you about the work, thank you and your books!

**Jens Jenson**, for the ERDA measurement. Your evaluations for the data and explanations for the plots are very helpful, thank you!

**Jens Birch** and **Fredrik Eriksson**, for all the XRD lectures and tutorials that you bring. You
are always willing to help me solving the problem of the patterns and giving priceless experiences, thank you!

**Leif Johansson**, for your instructions of the department. Your help is very important, which makes me working smoothly here, thank you!

**Agne Zukauskaite**, for your help of sample polishing and your nice instructions. Talking with you during depositions is always happy, thank you!

**Petter Larsson**, for solving all kinds of technical problems during the experiment. Your advices about the substrate for high temperature experiment really helped my work proceeding to the final stage. Thank you and the Ta substrate you brought to me!

**Mattias Samuelsson**, for the scientific articles that you gave me, no matter they are related to my work or just my interest. I benefited a lot from your guidance of SEM and the discuss with you about SEM images. Thank you and your licorice candy!

**Daniel Lundin**, for the nice discussion about plasma physics. You explained me your doctoral thesis patiently and gave me helpful tips about opposing, thank you!

**Montri Aiempanakit**, for your experience about reactive sputtering in detail. It is also very happy to have a chat with you when you have time. Thank you and your souvenir!

**Group members**, for offering me a nice working space and atmosphere in the Plasma and Coating Physics group.

**Bo Lü**, for being my best friend in Sweden and fighting together for our master degree. I appreciate a lot to all your generous support and treatment as a host. You and your family offered me a nice and unforgettable feast during the Chinese New Year. Thank you and your lovely family members.

**Magnus Karlsson, Viktor Johansson, and Peter Jason**, for giving me a nice office space and relaxing talks. All you support is necessary. Especially for Viktor, who spent many hours rebuilding the deposition system with me for thousand times. Thank you all!

**My whole family**, for always being my best and last backup through all time. Sorry for making you worry and thank you for your understanding during this study. Without you and what you provide for me, I will never stand in this height. Thank you all!
# TABLE OF CONTENTS

1 INTRODUCTION ...........................................................................................................1
   1.1 Background and Motivation ....................................................................................1
   1.2 Aim and Research Strategy ....................................................................................4

2 Ti-Al-N TERNARY SYSTEM .......................................................................................7
   2.1 Ti-Al-N ....................................................................................................................7
   2.2 Spinodal Decomposition .........................................................................................11

3 FUNDAMENTALS OF THIN FILM DEPOSITION .....................................................13
   3.1 The Sputtering Process ..........................................................................................13
      3.1.1 The Magnetron Sputtering Process .................................................................14
      3.1.2 The Reactive Sputtering Process ....................................................................15
      3.1.3 High Power Impulse Magnetron Sputtering ..................................................16
   3.2 Thin Film Nucleation and Growth .........................................................................17

4 THIN FILM ANALYSIS METHODS ...........................................................................21
   4.1 X-Ray Diffractometry ............................................................................................21
      4.1.1 The Symmetrical θ-2θ Configuration ...............................................................23
      4.1.2 The Grazing Incidence Configuration .............................................................23
   4.2 Scanning Electron Microscopy ..............................................................................23
   4.3 Elastic Recoil Detection Analysis ..........................................................................26
5 EXPERIMENT ........................................................................................................29
6 RESULTS AND DISCUSSION ........................................................................35
7 SUMMARY AND FUTURE OUTLOOK ..........................................................45
8 REFERENCES ......................................................................................................47
1 INTRODUCTION

1.1 Background and Motivation
Thin films and coatings\textsuperscript{1} are microstructures with thicknesses ranging from a few nanometers up to several micrometers and they are used to modify the surface properties of a given material (substrate). Already from the ancient time of history, metal or alloy films with preferred colors or metallic reflections were applied on substrates for decorative purposes \cite{1}. The film material that time had to possess a good malleability, in order to reduce its thickness scale and to apply the coating uniformly onto the surface of the underlying substrate. Nowadays films are synthesized with different compositions and structures to expand and to enhance their functionality and they are used in vast range of technologically relevant areas, such as, optics, microelectronics, bio-medicine, data storage, surface protection of cutting tools and machine component. Titanium aluminum nitride (Ti-Al-N), which is the topic of the present thesis, is a typical example of film material for surface protection of cutting tools operating at elevated temperatures \cite{2}.

A large number of films are employed to protect bulk materials from environmental physical or chemical damages. These films may well exhibit higher hardness, higher toughness, smaller friction coefficient, better wear resistance, and better chemical stability as compared to the underlying substrate materials. Ceramics such as metal nitrides, oxides, carbides and silicides were the materials to be used already from the early-mid 1900's for the purpose of

\textsuperscript{1} Though the terms thin film, film and coating are different in some aspects, they will be hereinafter used interchangeably throughout the thesis.
protective coatings [3]. The early stage of research on ceramics focused on the binary compounds (e.g. WC and TiC), due to lesser complexity and easier control of binary systems. TiN is among the best-known and -studied binary systems. It was the first commercialized hard coating for cutting tools in the history, because of its outstanding wear resistance and moderate hardness. It is also versatile due to its excellent electrical conductivity, rather small diffusivity to many aggressive chemicals and gases, and very favorable gold-colored appearance. It has served as an excellent hard coating material for more than 40 years, while it is still frequently used in fields other than surface protection [4].

Although TiN is a well-established hard protective coating solution, its oxidation resistance at elevated temperatures sets a critical limitation to the operation conditions. Especially during the operation of cutting tools coated with TiN, the temperature increase induced by the friction between the tool and its counter surface at the contact is inevitable for most cases. TiN has a thermodynamically favored tendency to replace the bonded nitrogen with gas oxygen molecule, following by the out-gassing of nitrogen. This oxidation process is activated thermally between 500 °C to 700 °C, leaving oxidized titanium with reduced hardness on the substrate. Along with its bad wear resistance and adhesion, the titanium oxide layer is either removed or delaminated soon, exposing fresh TiN coating (to be oxidized repeatedly) or substrate leading to tool failure [5, 6, 7, 8]. In order to improve the oxidation behavior of TiN, in the mid 1980's Al has been added forming the Ti-Al-N ternary system [9, 10, 11, 12]. The Al has higher mobility than Ti moving through the parent phase and the oxides of titanium and aluminum, which makes Al to be oxidized more in amount than Ti. The oxidized Al forms a dense aluminum oxide layer on the surface of the coating, where the layer can effectively retard further penetration of oxygen and extend the life-time as compared to pure TiN [6, 7, 13].

Additional advantages besides the enhanced oxidation resistance by adding Al into TiN were also reported in the late 1980's. One was the improvement of mechanical properties of the coatings with respect to the binary counterparts TiN and AlN. Many groups observed increase of the hardness of Ti-Al-N coatings during heat treatment above 700 °C [6, 7, 14, 15, 16, 17] and around 1990s, mechanisms were proposed to explain this behavior. The mechanisms were based on the age hardening effect triggered by a thermodynamic phenomenon, known as the spinodal decomposition. Spinodal decomposition creates domains with different composition in the coatings retarding the motion of dislocations [18, 19, 20, 21]. Ohnuma et al. [22] further
suggested that during spinodal decomposition Ti- and Al-rich domains (c-TiN and c-AlN rich domains) are formed from the metastable Ti$_{1-x}$Al$_x$N matrix. The spinodally decomposed domains exhibit more favorable behaviors in tribology tests, as opposed to the thermodynamically stable phases, (i.e. c-TiN phase with wurtzite AlN). Mayrhofer et al. [23] presented evidence for the spinodal decomposition of Ti$_{1-x}$Al$_x$N coatings by thermal analyzing the heat flow during the decomposition, along with observations in the changes of phase compositions and microstructures.

It is therefore evident from the previous paragraphs that understanding of the atomistic mechanisms that determine the phase stability of metastable Ti$_{1-x}$Al$_x$N is a prerequisite for developing experimental strategies that would allow for synthesis of Ti$_{1-x}$Al$_x$N films with superior properties [22]. The AlN content within the metastable phase is directly related to the phase stability of the system, where the higher AlN content leads to a greater driving force for decomposition of Ti$_{1-x}$Al$_x$N coatings in terms of thermodynamics. Though better performance with respect to oxidation resistance and mechanical properties of films can be observed with increasing the AlN content, the degradation of above properties will take place when the solubility limit of AlN is exceeded. In order to obtain better control of its phase stability and decomposition behavior related with AlN content, the solubility limit of the Ti$_{1-x}$Al$_x$N solid solution was investigated. The experimental and computational solubility limit of the TiN-AlN system have been reported by many groups [22, 23, 24, 25, 26, 27], where it typically ranges from 50 to 70 % AlN within the solid solution for different growth conditions.

The growth conditions for sputtering based physical vapor deposition (PVD) processes and their resulting microstructure and mechanical properties of the Ti$_{1-x}$Al$_x$N coatings have been examined as well. Wuhrer et al. [28, 29] reported that by increasing the power applied to the cathode, higher micro-hardness of Ti$_{1-x}$Al$_x$N films can be achieved as a result of the grain refinement. Shetty et al. [30] reported that less porous and harder Ti$_{1-x}$Al$_x$N films can be grown by depositing films at relatively high substrate bias voltages and temperatures. On the other hand, the energetic bombardment during growth can increase the mobility of adatoms, changing the microstructure and activating decomposition of the metastable phase even within the solubility limit [31]. Investigating the resulting microstructure of the films is a good approach to trace back the growth kinetics. Adibi et al. [32] observed the incoherency within the microstructures due to the phase separation with electron diffraction patterns and the
phase transformation with x-ray diffraction when increasing the substrate temperature during deposition. They concluded that high AlN-content can only be achieved by thin film growing under kinetically-limited conditions, e.g., moderate substrate heating and ion bombardment. It is also known that the spinodal decomposition is a thermodynamically spontaneous process, and this decomposition is initialized by thermally activated diffusion for atoms in the parent phase. Since diffusion processes are known to be affected by microstructure [33], we seek to explore the feasibility of controlling decomposition kinetics and phase stability of TiAlN at elevated temperatures through control of microstructure of the films. In order to investigate this, a growth process with capability of microstructure modification is needed.

High power impulse magnetron sputtering (HiPIMS), is a thin film deposition technique that exhibits enhanced capability of controlling the film microstructure as compared to sputtering-based state of the art approaches. The HiPIMS process allows for the generation of an ultra dense plasma which leads to ionization degrees of the sputtered material much larger than those achieved in conventional magnetron sputtering techniques, e.g. direct current magnetron sputtering (DCMS). The plasma conditions of HiPIMS process greatly enhance the flux of energetic ionized species towards the growing film during deposition [34]. The energetic flux available at the substrate is a rather important feature in sputtering-based deposition methods, since they transfer momentum to the deposited layers tailoring the adatom mobility. This in turn provide means for affecting the film microstructure, as well as the resulting properties. Many works have shown the effect of the enhanced energetic fluxes during HiPIMS, which includes growth of smooth and dense films [35, 36], improvement of film adhesion and deposition of more uniform films on complex-shaped substrates [36, 37]. In addition, it has been reported that by tuning process conditions in the HiPIMS parameter space, e.g. the frequency, the pulse width and the target current, different microstructures can be achieved [34]. These changes of the microstructure within the film may affect diffusion process during thermal treatment at elevated temperatures.

1.2 Aim and Research Strategy
The goal of this work is to investigate and understand the relation between the microstructure and the phase stability of Ti$_{1-x}$Al$_x$N films at elevated temperatures. HiPIMS deposition process is used due to its capability of controlling the ionization of sputtered material by changing the HiPIMS operation parameters, e.g. the average power density and the pulse shape. The degree
of ionization determines the ion bombarding behavior at substrate, affecting the deposition kinetics and the resulting microstructure of the growing film. A variety of frequencies with the same pulse width are employed. All samples are prepared by reactive co-sputtering with two cathodes under constant flow of sputtering gas Ar and reactive gas N\textsubscript{2}. One cathode equipped with Ti target is connected to a HiPIMS power supply, while the other cathode equipped with Al target is fed by a DCMS power supply. Series of samples with different Al-content are first deposited to obtain desired Al-content while maintaining the cubic metastable phase for TiAlN prior to the thermal analysis. The film chemical compositions is determined by elastic recoil detection analysis (ERDA) and the phases composition are investigated by grazing incident x-ray diffractometry (GI-XRD). Samples grown by different HiPIMS pulsing frequencies with similar Al-content are further investigated with respect to their high temperature phase separation behavior. High temperature x-ray diffractometry (HT-XRD) is performed for this purpose. Scanning electron microscopy (SEM) is employed to study the film microstructure. The results from the various techniques are combined determine the relation between microstructure and high temperature phase stability of the Ti\textsubscript{1-x}Al\textsubscript{x}N films.
Ceramics are an important class of structural materials and surface coatings, which exhibit high strength to weight ratio, high strength at elevated temperatures (non-softening), and are chemically inert to most aggressive environments. Among these ceramic coatings, transition metal nitrides (TM-N) are known for their extremely high hardness and the wear resistance, such as TiAlN, the material investigated in present work.

2.1 Ti-Al-N
Titanium-aluminum-nitrogen is a well-studied ternary system from the 1980's. The first reported phase was the Ti\(_2\)AlN in 1963, which is characterized by the high temperature abrasion resistance and good thermal-electrical conductivity [39]. A simplified phase diagram of Ti-Al-N is shown in figure 2-1. Depending on the chemical composition, the following phases can be synthesized: a Perovskite phase Ti\(_3\)AlN and two MAX phase Ti\(_2\)AlN\(_x\), Ti\(_4\)AlN\(_3\) [40, 41]. The metastable Ti\(_{1-x}\)Al\(_x\)N phase exists as the solid solution phase between its binary counter parts TiN and AlN, where \(x\) varies from zero to unity and stands for the atomic content of AlN. Since the idea of synthesizing the metastable phase was to enhance TiN for surface protection purposes, TiN will be introduced first for the reader's convenience.

In the large group of hard coating materials, titanium nitride (TiN) is one of the late discovered material as compared to other ceramics such as tungsten carbide (WC) and aluminum nitride (AlN). Though titanium was in fact identified in history from 1790s, its reduction method from the titanium oxide (TiO\(_2\)) ores had not been found until early 1900s. Soon as the element could be purified, it became widely used in the form of alloys, oxides and
nitride coatings. Since 1950s, titanium nitride coating has been massively studied in academia and used in industry. The coating was mostly synthesized by chemical vapor deposition (CVD) techniques in the beginning because of better adhesion and wear resistance on carbide tools, while nowadays it can be fabricated by many different methods, chemically and physically, which allow for a large variety in its properties. Various elements and compounds can be added into TiN system to enhance specific properties for different operation conditions, such as TiCN, TiBCN and TiOCN [3, 4, 38]. Titanium nitride is an option for electrical contact as well, since it has good corrosion resistance [42] and wear resistance together with good electrical conductivity. In addition, titanium nitride is used as diffusion barrier in microelectronics industry [43].

Titanium nitride has rock-salt crystal structure, c-TiN (or NaCl crystal structure, Fig. 2-2 (a)), with a mass density of 5.44 mg/cm³. As the result of different growth methods and operation conditions, it does not always exhibit composition [Ti]/[N] equal to unity [38], while the atomic ratio between titanium and nitrogen determines the color of titanium nitride. Stoichiometric titanium nitride has metallic shiny gold color, which is favorable to be applied as decorative coatings. It has been reported that the color of titanium coatings is gray when it suffers from nitrogen deficiency. With increasing the nitrogen content, the color becomes pale and yellowish, and finally reaches the yellow-gold color as the nitrogen content in the film close to the titanium. Overstoichiometric nitrogen turns the appearance into dark yellow and brown [38, 45, 46]. Depending on the [Ti]/[N] ratio, the microhardness of titanium nitride can

Figure 2.1 The simplified ternary phase diagram of Ti-Al-N ternary system. Adapted from [41].

![Figure 2.1](image-url)
varies from few hundreds to more than 2000 kg/mm$^2$ (4 to more than 20 GPa), and a common TiN hard coatings will have the hardness in the range of 1500 to 2200 kg/mm$^2$ (14 to 20 GPa) [38].

The critical drawback of titanium nitride is the coating failure at the operation temperatures higher than 500 °C, due to the replacement of nitrogen by oxygen on the outer most layer. Though the oxygen diffusion rate is rather slow through the nitride and the oxide layer, the large molar volume difference between these two compounds introduces high stress at the interface. As more titanium nitride gets oxidized and reaches the certain critical point in terms of the molar volume difference, the titanium oxide layer spalls from the coating, and the fresh titanium nitride layer remains exposed to the oxidation environment. The oxidation-exposure cycles continue and finally the substrate is exposed without protection, leading to the tool failure. The oxidation of titanium nitride becomes a severe problem since temperature increasing during the operation of tools is usually inevitable, and the oxidized coating is largely softened to less than 200 kg/mm$^2$ (< 2 GPa) [7, 38, 47]. In order to overcome the oxidation problem, Al was added to TiN system forming the Ti$_{1-x}$Al$_x$N metastable phase.

As expected, the addition of aluminum into titanium nitride coatings improves the high temperature oxidation property of the coatings. At elevated temperatures, the oxygen attacks and replaces nitrogen bonds from the surface of the film for Ti and Al atoms as well. The

Figure 2.2 The unit cell of (a) Rock-salt and (b) Hexagonal wurtzite crystal structures. Adapted from [44].
oxidized aluminum has a well-known property to form a very densely packed thin alumina layer on the surface, which is very difficult to be penetrated by oxygen, i.e., has very low diffusivity to oxygen. The out-diffusion of nitrogen and the diffusion of oxygen are retarded by the alumina layer, and further oxidation of the fresh nitrides can therefore be delayed [6, 7]. The Ti$_{1-x}$Al$_x$N coating has lower oxidation rate and hardness reduction up to 700 °C, which is a comparatively higher operation temperature as compared to the TiN coating. Moreover, it has been observed that the mechanical properties of TiAlN coatings improve drastically along with increasing the Al-content in the film [11].

Within the solubility limit of the solid solution, the metastable Ti$_{1-x}$Al$_x$N has the rock-salt crystal structure, denoted as c-Ti$_{1-x}$Al$_x$N (Fig. 2-1), with the metal (cation) sites occupied by Ti or Al atoms. Its solubility limit of Al into the TiN system has been reported by many groups by means of experiments [22, 26] and calculations [24, 25], and is generally regarded as $x$ around 0.55 to 0.65 at. %. It has also been reported by Adibi et al. [32] that the growth condition for sputtering based PVD processes can affect the solubility limit. The energy provided during the growth can increase the surface mobility for the films, and therefore increase the tendency to decompose the metastable phase. When exceeding the solubility limit, the system lowers its free energy by phase separating, or decomposing, into cubic phase c-TiN + c-Ti$_{1-x}$Al$_x$N (fig. 2-2) and finally into c-TiN and hexagonal phase h-AlN (to be more specific, it is wurtzite crystal structure AlN, Fig. 2-2 (b)). The decomposition causes deterioration of the coatings, which lose protection from oxygen and has similar behavior as pure TiN coatings when used at elevated temperatures [22, 48].

An age hardening effect of the c-Ti$_{1-x}$Al$_x$N metastable phase can be observed above 700 °C, which is an important and preferred feature for a hard coating operated at elevated temperature. A thermal activated phase separation, called spinodal decomposition, causes the formation of fine Ti- and Al-rich domains (around few nanometers in diameter) distributed within the matrix. The domains can be considered as c-Ti$_{1-x}$Al$_x$N phase but with low and high $x$ value respectively, and their lattice are usually perfectly coherent through the matrix. The lattice parameter difference between TiN ($a = 4.242$) and AlN ($a = 4.045$) in their rock-salt cubic structure introduces the coherent strains in the lattice, working as obstacles to the movement of dislocations. Further increase of the temperature increases the separation of TiN and AlN, i.e., depletes the Al and Ti from the Ti- and Al-rich domains. Hexagonal phase h-AlN starts to nucleate and grow from Al-rich domains (c-AlN) until all the metastable phase
transforms into c-TiN and h-AlN phases. The hardness and wear resistance in this stage reduces drastically, leading to the coating failure [23, 33].

2.2 Spinodal Decomposition

The so-called spinodal decomposition is one of the diffusion controlled continuous phase transformations which happens without nucleation and growth. It is often called a thermodynamically spontaneous phase transformation process, since the system does not have a barrier of nucleation to overcome. As soon as the diffusion is activated by heat or other forms of energy, the atoms spontaneously diffuse 'up-hill' from lower concentration regions to higher. This up-hill diffusion does not even out the concentration in the matrix, but locally forms high concentrate locally and deplete the region nearby (In different view, the depletion for one species means high concentration for other species), for example high Al and Ti concentrations in the case of metastable Ti$_{1-x}$Al$_x$N. Unlike the high concentration interruption at the boundaries of nuclei, the spinodal domains are continuous in concentration through parent phase. Therefore, it is hard to define 'boundaries' for spinodal domains (and the reason called it domains instead of grains). The domains can randomly appear and disappear at any place through the parent phase, since the concentration and the lattice remain in almost perfect coherency locally. This makes the prediction and the observation of phase transformation through spinodal decomposition much more difficult than others [33].

An A-B binary system is given as an example, where its free energy diagram at certain temperature $T_0$ is shown in figure 2.3 (a) and the corresponding phase diagram is shown in figure 2.3 (b). The binodal points a and f defined by a tangential line cutting through the lowest points of the curve, represent the stable states at the temperature with concentration between $X_1$ and $X_2$. The region between the binodal points is called the miscibility gap of the phase diagram (the solid curve in figure 2.3 (b)). Any concentration within this region is thermodynamically unstable or metastable, and can lower the total energy of the system by decomposing into the stable phases $X_1$ and $X_2$ through diffusion. Within the miscibility gap, a region with negative curvature ($\frac{d^2 G}{d X_B^2} < 0$) in the free energy diagram, as the region between points b and e in figure 2.3 (a), is where the spinodal decomposition takes place. The curvature of the free energy is directly proportional to the inter-diffusion coefficient of the elements (A and B atoms) within the parent phase, according to the solution of Fick's diffusion laws. The negative diffusion coefficient gives the 'up-hill' diffusion fluxes in the
calculation, which is the solution for spinodal decomposition. As indicated in figure 2.3 (a), the metastable state solid solution with total concentration $X_0$ can lower its free energy from $G_0$ to $G_1$ through phase separation to the states at c and d points. The spinodal decomposition will continue until the concentration moved out from the region b-e. The energy release from the spinodal decomposition will help the following decomposition in the regions a-b and e-f. At these regions, phase separation proceeds through normal nucleation and growth processes, which consumes energy to overcome the barrier for nucleation [33].

Figure 2.3 The (a) free energy diagram at temperature $T_0$ and (b) phase diagram of an A-B binary system with miscibility gap. Adapted from [33].
3 FUNDAMENTALS OF THIN FILM DEPOSITION

Thin films can be nowadays synthesized by a variety of physical vapor deposition (PVD) techniques. The principle of PVD is to create vapor from either a solid, or sometimes a liquid, source. The vapor is subsequently transported onto a substrate where a film is formed. The vapor is either created by thermal means or by momentum transfer. The latter is also known as 'sputtering' and is the topic of the next section [1].

3.1 The Sputtering Process

The sputtering is the process that causes ejection of surface atoms by bombarding this surface with energetic species. A simplified schematic illustration of the sputtering process is shown in figure 3.1. In practice, the surface, or the source to eject atoms, is called the target, while the energetic species are commonly inert gas (the sputtering gas) ions, such as $\text{Ar}^+$, to reduce the reactions with any component in the chamber. By applying a negative potential on the cathode, on which the target is mounted, the $\text{Ar}^+$ ions are accelerated towards the cathode and sputter out electrons and target species from the target surface. Electrons emitted from the surface, also known as secondary electrons, are repelled from the cathode and generate more sputtering gas ions through collision events, i.e.,

$$e^- + \text{Ar} \rightarrow \text{Ar}^+ + 2e^- \quad (3.1)$$

which create a plasma maintaining the density of gas ions. The ejected target species are transferred through the gas phase to be deposited on a substrate and eventually form a film. The ratio that describes the number of ejected target species per impinging ion is called sputtering yield and depends on the projectile energy and the surface binding energy of the
target material [1].

In order to reduce the probability for the sputtered particles to be scattered before reaching the substrate, most sputtering depositions are carried out in an evacuated chamber. The fewer the collisions before the emitted target atoms condensate, the higher kinetic energy can be transported to the substrate in the way of energetic bombardment, which allows for modifications of the film properties [1, 2].

3.1.1 The Magnetron Sputtering Process

Due to the high escaping rate of secondary electrons in the sputtering process described in section 3.1, which is referred as the diode sputtering, the cathode needs to be fed constantly with high voltages (in the order of kV) under high sputtering gas pressure to maintain a constant plasma density. This results in high energy consumption by the power supply, low deposition rate due to the high operating pressure, and substrate heating by energetic electrons due to the high potential at cathode. In addition, the constant high voltage keeps the cathode temperature high, which reduces the life-time of cathode and increases the risk of melting a solid target.

By placing a set of well-designed permanent magnets below the target, the Lorentz force
confines the secondary electrons in the spiral trajectories in the vicinity of the target surface, which increases the time before secondary electrons lost to the chamber and the probability to ionize the sputtering gas. In this way, the plasma density can be sustained by higher ionization efficiency and the voltage applied to the cathode can be lowered. This modification of sputtering process is known as magnetron sputtering [1].

In most cases in magnetron sputtering processes, the cathode is supplied with a constant voltage generating a constant target discharge current. This technique is known as direct current magnetron sputtering (dcMS) and has served for more than 30 years the thin film and coating industry [1, 49].

### 3.1.2 The Reactive Sputtering Process

By adding a reactive gas (e.g. O$_2$ and N$_2$) along with sputtering gas during sputtering deposition, compound films can be synthesized, while the process is referred as the reactive sputtering process. In a typical reactive sputtering process, compound molecules formed on the target surface upon the presence of reactive gas are sputtered and transported to the substrate, while the formation of compound molecules at target surface is referred as the target poisoning. Depending on the composition of gas atmosphere, the compound coverage on the target surface, also known as the degree of poisoning, can be different, which is crucial for film composition and other process characteristics, such as deposition rate and target voltage [50].

When the target coverage is low, understoichiometry films, i.e. films without sufficient incorporation of reactive gas atoms, are formed. This operation region is known as metallic mode. Upon increasing the content of reactive gas in the sputtering atmosphere, the target coverage becomes more pronounced. Deposition from a fully covered target, which is referred as compound mode, leads to the growth of stoichiometric films. In addition, lower deposition rates are commonly observed in the compound mode since the compound usually possesses lower sputtering yield as compared to the elemental target. Change of applied voltage needed to maintain the same target power or current is also observed, since the emission probability of secondary electrons is different for the compound and the elemental target. For example, upon the poisoning of an Al target by nitrogen, the voltage applied to the target decreases when increasing the nitrogen partial pressure. The opposite is observed for Ti target. [50].
To achieve the desired stoichiometry and maintain high deposition rate, operation in the intermediate region between metallic and compound modes, or the transition zone, is required. However, in some cases the transition mode is unstable accompanied by a hysteresis in the process parameters. Typically the transition zone is more unstable for highly reactive combinations of targets and reactive gases. For instance in this work, the Al target has a wider transition region as compared to the Ti target. To overcome this problem, a feedback system can be installed to monitor and control the deposition parameters, which helps reaching a dynamically stable operating point in transition mode. Berg et al. [50] also proposed several concepts to stabilize the operating point in reactive sputtering, such as partial pressure of the reactive gas, the pumping speed of the system, the target current and the target size.

3.1.3 High Power Impulse Magnetron Sputtering

In conventional magnetron sputtering such as dcMS the electron density (~$10^{14}$ - $10^{16}$ m$^{-3}$) and thus the degree of ionization of target species (less than 10 %, mostly neutrals) are generally low. Ions of target species generated during deposition are desired due to the capability of controlling their energies and trajectories by electric and magnetic fields, which provides additional means for tailoring film properties. Applying higher power to the target and thus increasing the electron density is one solution for dcMS to achieve higher degrees of ionization. However in practice, this pathway is limited by the maximum thermal load that the target can accommodate [34, 49].

A novel technique, High power impulse magnetron sputtering (HiPIMS), alleviates the limitations of dcMS by providing power in the form of pulses, which is typically operating in the range of 10 Hz to 10 kHz for frequencies with few tens of micro-seconds for the pulse width. The low duty cycle, which means a low pulse-on time to pulse-off time ratio, results in higher power density (~few kWcm$^{-2}$) during pulse-on time with low time-average power as for dcMS (~few tens of Wcm$^{-2}$) that the target and the cooling system can withstand. Higher electron density (~$10^{18}$ m$^{-3}$) and ionization degree (up to 80 % for Ti) was reported as compared to dcMS. Improved thin film properties such as adhesion enhancement, porosity reduction, and deposition of uniform films on complex-shaped substrates have been reported [34, 49]. In addition the grain refinement has also been observed in [51], as the evidence to a more energetic ion bombardment. For reactive HiPIMS processes, the increased power density improves the removal of compounds from target surface, which reduces the hysteresis.
effects and makes operation in transition mode more controllable [34, 49, 52].

### 3.2 Thin Film Nucleation and Growth

In thin films grown by PVD, the film microstructure largely affects the film functionality. It is therefore important to understand the thermodynamics (energy minimization) and kinetics (diffusion processes) during growth in order to be able to tailor film properties. In the following sections, thermodynamic and kinetic aspects controlling thin film formation are briefly discussed [1].

According to thermodynamics, the surface tension for heterogeneous nucleation process in PVD need to be balanced in order to minimized the surface energy. This can be mathematically described by the expression,

\[ \gamma_{SV} = \gamma_{SF} + \gamma_{FV} \cdot \cos \theta_W \]  

(3.2)

which is also known as Young's equation. The \( \gamma_{SV} \), \( \gamma_{SF} \), and \( \gamma_{FV} \) are the surface tension for substrate-vapor, substrate-film and film-vapor interfaces respectively. The \( \theta_W \) is referred as the wetting angle or contact angle for the growing film on the substrate and is shown in figure 3.2. Depending on the relations between the surface tension components in Eq (3.2) the following growth modes are observed [1].

1. When the relation \( \gamma_{SV} < \gamma_{SF} + \gamma_{FV} \) is true, the adatom species has stronger bonds with the same species and the solutions to Eq (3.2) gives a wetting angle \( \theta_W \) deviating away from 0 °. Adatoms grow in clusters with respect to the wetting angle, leading to the growth mode referred to as island (Volmer-Weber) growth.

2. On the other hand, when \( \gamma_{SV} > \gamma_{SF} + \gamma_{FV} \) holds, the adatoms tend to bond with the

![Figure 3.2 Schematic drawing of the surface tensions balanced according to Young's equation. Adapted from [1].](image-url)
substrate surface atoms and the solution of wetting angle to Eq (3.2) becomes close to 0°. The growth in this case spreads layers of adatoms on the surface uniformly and is referred to as layer (Frank-van der Merwe) growth.

(3) Besides previous two modes, a special relation is observed which increases the wetting angle from 0° along with the formation of the first few monolayers. The change in the wetting angles leads to the layer growth only in the beginning and the island growth afterward. [1, 53, 54].

In PVD the island growth is more frequently observed resulting in polycrystalline film structures. However the origin of this growth mode is kinetic (limited diffusion), also known owing to the non-equilibrium characteristic of the growth process. The diffusion behavior is affected by deposition parameters such as, the substrate temperature, deposition rate, energetic bombardment and the presence of impurities. Structure zone models (SZM's) has been proposed to describe the influence of the adatom diffusion on the final structure as a function of the homologous temperature $T = T_s / T_m$, where $T_s$ and $T_m$ are the substrate temperature and the melting temperature in Kelvin [54, 55].

In zone I ($T \leq 0.2$) the energy provided to the film forming species is not sufficient to activate adatom surface diffusion. Incoming atoms sit at the place where they first condense to the surface, which is known as 'hit-and-stick' or 'ballistic' growth and shadows the region behind grown structures. A porous and thin columnar structure with very rough surface is commonly

![Figure 3.3](image.png)

Figure 3.3 The illustration of (a) the island, (b) the layer, and (c) the mixing growth modes. Adapted from [1].
observed in zone I (Fig. 3.4) [54, 55].

When the homologous temperature is increased to the range from 0.2 to 0.4, surface diffusion is activated. The diffusing adatoms on the surface are tend to rest in the plane with lower surface energy and therefore these planes grow faster and dominate other planes, while grains with the fast growing plane oriented to the source of film forming species can grow even faster. Grains without fast growing orientations will be interrupted and overgrown, resulting in the V-shaped features in the film. This microstructure is referred to as zone T. [54, 55].

An even higher homologous temperature ($T > 0.4$) allows for bulk diffusion to occurs. The smaller grains and the V-shaped features are eliminated by the diffusion, and the grain boundaries are also straightened. In addition, voids are filled in and the rough surface due to the facets is flattened. As the result, the wider columnar grains with much less porosity in comparison with zone I and T are observed [54, 55].

The zones I, T, and II are valid for metallic elemental films. However, when impurity species are incorporated, intentionally or non-intentionally, impurity phases may be segregated at the grain boundaries, hindering the crystal growth of the film forming species. This gives rise to a globular microstructure in films, and is referred as an addition zone III, where the size of grains depends on substrate temperature. Similar effect can be observed in films grown under ion irradiation where energetic species interrupt crystal growth. A characteristic example is the work by Alami.et al., which has reported the growth of CrN film with globular microstructure by HiPIMS, a technique which is known to provide high fluxes of energetic ions towards the growing film [34, 51, 55].
4 THIN FILM ANALYSIS METHODS

4.1 X-Ray Diffractometry

Since crystals possess unique ordered structures and lattice parameters for each phase, studying their diffraction behavior is a good way to analyze the microstructure and phase composition of crystalline samples. Diffraction is an elastic scattering interaction between photons and surface electrons upon the impinging of electromagnetic radiation onto a surface, which mostly occurs when the wavelength of incoming wave is in similar length scale with the periodic structure of surface. The x-rays with energies in between 3 keV and 8 keV are the most suitable for the purpose of observing the diffraction of crystalline samples, which have periodicity commonly in the length scale of $10^{-10}$ m. In addition, x-ray diffractometry provides a non-destructive and relatively less preparatory way of phase and structure analysis.

The basic principle of x-ray diffractometry is described by the Bragg's diffraction equation for coherent conditions:

$$\delta_1 + \delta_2 = n \lambda = 2d_{hkl} \cos \left( \frac{T}{2} - \theta_B \right) = 2d_{hkl} \sin \theta_B .$$  \hspace{1cm} (4.1)

As shown in figure 4.1, when the x-ray with wave length $\lambda$ impinges on the surface at an incidence angle $\theta_B$, the difference in the path length $(\delta_1 + \delta_2)$ between the planes with inter-plane spacing $d_{hkl}$ will be an integer number of the wavelength $n\lambda$. The scattering will be coherent as represented by the direction of wavefronts. The coherent scattering has higher intensity as compared to other cases, which is recorded in the intensity-to-receiving angle
pattern as a diffraction peak. By comparing the position of peaks with the reference patterns, the phase composition can be investigated. In addition, the peak width, height, and shift with respect to the reference can also give information about the coherent domain size (can be approximated grain size), the film thickness, the residual stress and the preferred orientation in samples [44].

For most laboratory x-ray diffractometry, copper x-ray sources are used, where the background radiations and characteristic x-rays besides Cu Kα-radiations are absorbed by the Be-window and the Ni-filter. The samples are only irradiated by Cu Kα-radiations which have wavelength around 1.54 Å having two specific emission lines Kα₁ and Kα₂ with slight energy difference.

Figure 4.1 The illustration of the Bragg's diffraction condition. The radiations come from A, be diffracted on crystal surface layers B toward the direction of C. Adapted from [44].

For symmetrical scans: \( \omega = \theta \)

For grazing incident scans: \( \omega = \text{fixed angle} \)

Figure 4.2 The schematic illustration of symmetrical and grazing incident scanning configurations.
4.1.1 The Symmetrical $\theta$-2$\theta$ Configuration
The most commonly used method to study phase composition by x-ray diffractometry is through the symmetrical $\theta$-2$\theta$ configuration. As shown in figure. 4.2, the positioning of the detector is always equal to the incident angle. The diffraction peaks in this configuration are given only by the planes which are parallel to the specimen surface. The presence of the diffraction is largely affected by the preferred orientation in the sample [44, 56].

4.1.2 The Grazing Incidence Configuration
In the grazing incidence configuration, scanning through various 2$\theta$ angles with a fixed grazing incident angle $\omega$ (Fig. 4.2) gives information about grains in different orientations as compared to the symmetric $\theta$-2$\theta$ scan. Furthermore the low incident angle increases the intensity ratio between film and substrate, due to a larger sampling volume as shown in figure 4.3. In this work, some samples were grown on single crystalline Si (100) substrates which gave a strong Si diffraction peak at around 69.13° and therefore made the diffraction from the film difficult to be observed using symmetrical scans. Grazing incidence x-ray diffractometry (GI-XRD) was therefore utilized for phase composition analysis. The GI-XRD usually has a lower intensity as compared to symmetrical scan, since the receiving reflections are away from the primary beam. Therefore a parallel plate collimator with lower angular resolution but higher acceptance angle as compared to slit optics is usually used [44, 56].

4.2 Scanning Electron Microscopy
The *scanning electron microscopy* (SEM) is a tool to analyze the surface topographical,
compositional and diffraction pattern of organic or inorganic samples. In SEM shorter wavelength of accelerated electrons provide higher resolution as compared to the optical microscopy (OM) which is limited to the edge of violet visible light (~300 nm). Its larger depth of focus (up to 1000 nm) is one of the most favorable feature allowing 3-D images to be visualized in the topographic mode. In addition, most SEM measurements are usually easier in operation and sample preparation as compared to the other electron microscopy techniques, such as transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) [57].

A typical SEM instrument can be divided into four units: an electron emitting and accelerating unit (an electron gun), sets of electromagnetic lenses for beam focusing, electron collectors (detectors) and an image processing unit (Fig. 4.4). Upon the impinging of the electron beam onto the sample surface, the electrons penetrate into the material forming a pear-shaped interaction volume, from which electrons and electromagnetic radiations are emitted (Fig. 4.5). The incident electrons scattered through the sample are referred to as back-scattering electrons (BSE). The electrons generated as a result of inelastic scattering interactions of the incident beam are referred to as secondary electrons (SE) and Auger electrons (AE), where SE are always dominating AE. The electron yield of the surface is

![Figure 4.4](image.png)

*Figure 4.4* The illustration of a simplified SEM system. Adapted from [57].
greatly affected by geometrical and elemental features, such as surface inclination and atomic number as depicted in figure 4.6 (a) and (b). Here different amount of collected electrons from different region of the surface gives rise to a contrast in the resulting signals, which are amplified by the image processing unit and give topographical or compositional information about the surface [57].

SEM is a powerful instrument which is widely used for compositional mapping, fractography, [57].

Figure 4.5  Schematic drawing of the SEM sampling volume and emissions from the interactions of incident electrons with target atoms.

Figure 4.6  Schematic drawing of the effects on electron emission from the sample surface when irradiated by accelerated electrons in SEM, which depend on (a) the geometry of the surface and (b) the atomic number of materials.
and cross-sectional microstructure observations. However, SEM operations are limited by the conductivity of the samples, where accumulation of charges in sample by the incident electrons may locally repel the incoming electrons resulting in the loss of surface information [57].

### 4.3 Elastic Recoil Detection Analysis

*Elastic recoil detection analysis* (ERDA) is one of the ion beam surface analysis methods which was first demonstrated in 1978 by L'Ecuyer et al. and in 1979 by Doyle et al. It is very similar in the detection mechanism to another widely used ion beam technique called *Rutherford backscattering spectroscopy* (RBS). Both ERDA and RBS are valuable techniques to obtain compositional depth profile of samples. This is done by drawing out information from the forward and back-scattered particles, which are ejected from the sample surface upon the collision between incident ion beam with a given energy and atoms at the surface. The commonly used energy of the accelerated ions ranges from hundreds of keV to tens of MeV allowing for a penetration depth in the order of few to tens of micrometers, which is usually difficult from an electron beam. ERDA is a more powerful tool as compared with RBS due to its light element sensitivity (e.g. C, N, O) and depth resolution, which is even poor for RBS when a heavier element substrate (e.g. Si, Cu, Fe) is used. ERDA overcomes the drawback by employing heavy ions (e.g., Au$^{13+}$, Au$^{15+}$, I$^{7+}$), which enhances the probability of generating recoil events and thus increases the sensitivity [58].

In an ERDA measurement, the accelerated heavy ions are incident on the surface of sample, where the beam is tilted for a certain angle $\theta_i$ from the surface normal. According to the basic physical principles of energy and momentum conservations, the collision event between a projectile and a resting surface atom of smaller mass will generate the recoil in forward direction with its recoil angle $\Phi$ from the incident direction. Upon the collision, the energy of the recoil $E_r$ is governed by the energy of incident beam $E_p$

$$E_r = kE_p$$  \hspace{1cm} (4.4)

by the kinematic factor $k$

$$k = \frac{4m_p m_r \cos^2(\theta_s)}{m_p + m_r^2}.$$  \hspace{1cm} (4.2)

The $m_p$ and $m_r$ are mass of the incident ion and the recoil, while $\theta_s$ is the scattering angle of
the primary beam, as shown in figure 4.3.1. The scattered ions from the primary beam are prevented to enter the detector by putting the detector away from the scattering angle, and by inserting a stopping foil in front of the detector, which only allows light elements to pass through. The output energy spectra collected from the detector can be converted into the concentration depth profile for the sample by taking different energy loss for recoils coming from different depths $i$ to account [58].

In this work, ERDA was used for extracting the atomic ratio between titanium, aluminum, and nitrogen in the films. Oxygen data was also an rather important indicator for the porosity in the coatings, while the absence of fluctuations in the composition depth profile gave information about the stability of the deposition process.

Figure 4.7 Schematic drawing of the generation of recoil upon the impinging of energetic ion to a resting surface atom. Adapted from [58].
In this work, all samples were prepared in the UHV system, named 'Ginnungagap', in the clean room of physics house, Linköping University, which has a cylindrical upper part, connected to the transportation chamber and the main pump, and a semispherical lower part, equipped with two cathodes, as shown in figure 5.1. The background pressure was in the range of $10^{-8}$ torr achieved by a PFEIFFER BALZERS, TCP 380 turbo-molecular pump in combination with a membrane pump as a clean forepumping source. The pressure in the chamber was measured by a BALZER, TPG300 Penning-Pirani multi-range gauge, which works from $10^{-3}$ torr down to $10^{-10}$ torr, while during depositions the pressure was measured

![Figure 5.1](image-url)  

**Figure 5.1** A schematic drawing of the deposition chamber operated in this work.
by a MKS, TYPE 270B signal conditioner connected with a capacitance gauge, which works in the order of mtorr. Substrates were introduced into the chamber through a load-lock and a transportation chamber, which had their pressure typically in the order of $10^{-7}$ and $10^{-8}$ mtorr. The substrate holder in the main chamber was placed at the confocal point of the two cathodes at a target-to-substrate distance of approximately 13 cm.

Before depositions, all substrates were cleaned in ultrasonic bath of acetone for 5 minutes and then of isopropanol for another 5 minutes. The films were grown by reactive co-sputtering carried out by the cathodes, where the targets were two 2 inch Ti and Al targets (~99.95 % purity). The cathode equipped with Ti target was operated by HiPIMS using a MELEC, SPIK 1000 A pulsing unit fed by an ADVANCED ENERGY, MDX PINNACLE dc-generator. It is known that in HiPIMS, target voltage and current are time-dependent quantities. These quantities were measured by a CHAUVIN ARNOUX, C160 current clamp attached to a homemade voltage divider, which allowed for an output of the same voltage to the cathode. The current clamp and the voltage divider were connected to a TEKTRONIX, TDS 520C oscilloscope which monitored the above quantities during depositions. The Al cathode was operated in dc-mode by an ADVANCED ENERGY, MDX 1K power supply. During depositions, reactive gas N$_2$ and sputtering gas Ar were supplied to the chamber by a MKS, Multi Gas Controller 647 B which allows for maximum flow of 100 SCCM for each gas channel. The substrate table was rotated at constant speed of 120 RPM during growth in order to have better compositional homogeneity through the films.

Various frequencies were used on the HiPIMS cathode to change the degrees of ionization and therefore the energetic bombardment, leading to the alternation in the film properties. Prior to deposition, the change of applied voltage along with increasing nitrogen supply for each

**Table 5.1** Table of samples in set 1 and their corresponding deposition parameters.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ti Target</th>
<th>Al Target</th>
<th>Gas Flow</th>
<th>Deposition Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency (Hz)</td>
<td>Pulse-Width (μs)</td>
<td>Avg. Power (W)</td>
<td>Const. Power (W)</td>
</tr>
<tr>
<td>1-1</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>1-2</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>0</td>
</tr>
<tr>
<td>1-3</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>0</td>
</tr>
<tr>
<td>1-4</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>0</td>
</tr>
<tr>
<td>1-5</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>
working frequency was recorded to determine the working point and the behavior of target poisoning. Operating in metallic mode was avoided within all depositions in order not to have elemental Ti and Al atoms in films.

In sample set 1, the TiN films were deposited to investigate the stoichiometry of each condition and the deposition parameters are shown in table 5.1. Two additional 2000 Hz samples (1-4 and 1-5) were made to study the effect on the stoichiometry with varied nitrogen supply. The stoichiometry of TiN films was determined by visual inspection, as mentioned in section 2.1. Different Ti powers were used in order to make the deposition rate and therefore the film thickness through different conditions more similar, which typically decreases when lowering the HiPIMS frequency.

In sample set 2, the TiAlN films were grown to study the phase composition and crystal structure for varied Al-content in each condition. The films were prepared with constant Ti power and nitrogen flow, while the Al power was varied in coarse steps (≥ 5 SCCM). The

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-2</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>20</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-3</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>40</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-4</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>60</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-5</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>65</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-6</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>75</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-7</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-8</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>25</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-9</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>35</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-10</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>40</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-11</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>50</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-12</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-13</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>25</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-14</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>32</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-15</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>40</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-16</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>50</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
</tbody>
</table>
Deposition parameters are given in Table 5.2. The study of film phase composition and crystal structure were achieved by a PHILLIPS, X'Pert x-ray diffractometer operating in the GI-XRD configuration with the incident angle at 3°. Transitions from solid solution phase to separated phase in the samples were also identified from the diffraction patterns.

Based on the results of set 2, the set 3 of TiAlN samples were deposited to study the chemical composition close to the solubility limit. The Ti power and nitrogen supply were kept fixed and the Al power was varied in finer steps as compared to set 2. The deposition parameters for set 3 are listed in Table 5.3. The solubility limit of each frequency was determined by the presence of identifiable h-AlN diffraction peak. ERDA measurements were employed to identify the Ti-to-Al and nitrogen-to-metal atomic ratio, as well as the oxygen content in films. These detection in ERDA was carried out by isotope ions of iodine ($^{127}$I$^{+}$) which were accelerated to 30 MeV and impinged on the sample surface at the incident angle $\theta_i = 24^\circ$, while the recoil angle was fixed at 45°. The program used to evaluate the final composition data was Conversion of Time-Energy Spectra (CONTES, a program for ERDA data Analysis) programmed by M.S. Janson, Uppsala University, 2004.

In sample set 4, the TiAlN films with approximately 50:50 Ti-to-Al ratio were deposited to observe the microstructure and to investigate the transformation of phases at elevated temperatures. The deposition parameters are given in Table 5.4. The Al powers were varied for different frequencies to have the desired composition, which was obtained by linearly

**Table 5.3** Table of samples in set 3 and their corresponding deposition parameters.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-2</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>70</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-3</td>
<td>2000</td>
<td>50</td>
<td>120</td>
<td>75</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-4</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-5</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>48</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-6</td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>50</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-7</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-8</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>32</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>3-9</td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>35</td>
<td>90</td>
<td>5</td>
<td>30</td>
</tr>
</tbody>
</table>
extrapolating the Al power with respect to the chemical composition data of sample set 3. Different deposition times were used in order to achieve similar film thickness, making the results more comparable. The 2000 Hz condition was excluded from set 4 because of its high oxygen content determined by ERDA, which may change the phase composition in the film. The microstructure of sample set 4 was observed from cross-sectional images taken by a LEO 1550 Gemini SEM with the electron beam accelerated to 5 keV. HT-XRD was used to study the phase composition and decomposition behavior at elevated temperature achieving by a PHILLIPS, X'Pert x-ray diffractometer. During HT-XRD measurements, the samples were inserted in an evacuated chamber (~10^{-5} mbar) and heated up in the step of 150 ° from 700 to 1150 °C by Ta filaments. Scans were made at each temperature after holding for 30 minutes and at ambient temperature, where one extra scan was made for samples at 1150 °C after holding for extra 3 hours.

In this work, 18×18 mm single crystalline silicon substrates with polished (100) surface were used in the depositions of sample sets 1 to 3. In set 4, single crystalline Si and poly crystalline Ta substrates (10×10 mm) were used for different measurements. The single crystalline Si substrate is beneficial to SEM cross-sectional observations since it can be cleaved easily and perfectly, while the Ta substrate is less reactive with the TiAlN film in their interfaces at elevated temperatures used in HT-XRD as compared to Si.

Table 5.4 Table of samples in set 4 and their corresponding deposition parameters.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td></td>
<td>500</td>
<td>50</td>
<td>160</td>
<td>39</td>
<td>90</td>
<td>5</td>
<td></td>
<td>150</td>
</tr>
<tr>
<td>4-2</td>
<td></td>
<td>250</td>
<td>50</td>
<td>220</td>
<td>29</td>
<td>90</td>
<td>5</td>
<td></td>
<td>240</td>
</tr>
</tbody>
</table>

33
6 RESULTS AND DISCUSSION

The XRD patterns recorded from samples within set 2 with pulsing frequencies of 2000 Hz, 500 Hz and 250 Hz are shown in figure 6.1 (a), (b), and (c) respectively. The dotted lines indicate the peak position of bulk unstrained c-TiN, c-AlN, and h-AlN [59]. In the diffraction patterns corresponding to pure TiN films, i.e. films grown at an Al power equal to zero, one peak with strong diffraction intensity and the other with relatively weaker intensity can be observed at approximately 36.5 ° and 42.5 °. These peaks can be attributed to the TiN (111) and (200) peaks. The TiN (111) peaks in figure 6.1 (b) and (c) are found left-shift with respect to the (111) peak position of the reference, which is not the case for the (111) peak in figure 6.1 (a). In general, the peak position in XRD patterns is determined by the size (or inter-plane spacing) of the lattice contributing to the reflection as given in Eq. (3.1), which is therefore affected by residual strain and chemical composition of the lattice. The results obtained here will be discussed later in the present section after presenting the chemical composition data.

It is also observed that the intensity of the TiN (111) peak decreases with reducing the pulsing frequency, while the peak becomes broaden at the same time. The peak height (intensity) and width are in general determined by the coherent domain size (in proportional to the grain size) and the film thickness. Since the thicknesses of the films in set 2 are not the same, the discussion of these differences is postponed for the samples in set 4, where the films of similar thicknesses were deposited.

Upon increasing power applied to the Al target, right-shift of the (111) as well as the (200) peak can be seen. As mentioned above that increase of diffraction angle means the decrease in the lattice size. According to the work by Adibi et al. [60], the decrease of the lattice size
Figure 6.1 The GI-XRD spectra of TiAlN films deposited with (a) 2000 Hz, (b) 500 Hz and (c) 250 Hz HiPIMS frequencies on Ti target and variant DCMS power on the Al target.
Figure 6.1 (d) The (111) peak positions of the metastable phase with respect to GI-XRD spectra in figure 6.1 (a), (b), and (c).
indicates that Al atoms are incorporated into the TiN lattice forming the cubic metastable phase (c-Ti$_{1-x}$Al$_x$N). The reason is that c-AlN has smaller lattice in comparison to c-TiN resulting in the shrinkage of the average lattice size with respect to TiN.

The angular position of the (111) peak as a function of the power applied on the Al target is plotted in figure 6.1 (d). It is observed that the change of the peak position is marginal above a certain power limit. This limit is approximate 40, 37, and 32 W for samples grown at a pulsing frequency of 2000, 500, and 250 Hz, respectively. This behavior indicates the saturation of the metal sublattice with respect to the Al incorporation. In addition for the power above this limit (75, 50, 40 W for 2000, 500, 250 Hz), intensity maxima at ~33 º for 2000 and 500 Hz and at ~35 º for 250 Hz appears, which can be assigned to the h-AlN peaks. At the same time, the intensity of the c-Ti$_{1-x}$Al$_x$N (111) peak decreases significantly. These facts indicate that samples grown at these conditions have been decomposed into the stable h-AlN and c-TiN phases.

The composition results from ERDA are listed in table 6.1. An understoichiometry in terms of N contents can be observed from the films grown at 2000 Hz, which is not the case for the films grown at 500 and 250 Hz. These results are consistent with the color of the corresponding TiN samples in set 1 (Fig 6.2). The sample grown at 500 and 250 Hz exhibit golden-like color while the film deposited at 2000 Hz has a gray-like appearance. It is worth mention that the color of the samples grown at the pulsing frequency of 2000 Hz remained

<table>
<thead>
<tr>
<th>No.</th>
<th>Al Target Power (W)</th>
<th>[Al] / [Ti+Al]</th>
<th>[N] / [Ti+Al]</th>
<th>Oxygen (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>0</td>
<td>0</td>
<td>0.89</td>
<td>21</td>
</tr>
<tr>
<td>3-2</td>
<td>70</td>
<td>0.68</td>
<td>0.85</td>
<td>15</td>
</tr>
<tr>
<td>3-3</td>
<td>75</td>
<td>0.70</td>
<td>0.85</td>
<td>17</td>
</tr>
<tr>
<td>3-4</td>
<td>0</td>
<td>0</td>
<td>0.96</td>
<td>14</td>
</tr>
<tr>
<td>3-5</td>
<td>48</td>
<td>0.62</td>
<td>0.96</td>
<td>12</td>
</tr>
<tr>
<td>3-6</td>
<td>50</td>
<td>0.64</td>
<td>0.96</td>
<td>12</td>
</tr>
<tr>
<td>3-7</td>
<td>0</td>
<td>0</td>
<td>1.13</td>
<td>11</td>
</tr>
<tr>
<td>3-8</td>
<td>32</td>
<td>0.57</td>
<td>1.00</td>
<td>10</td>
</tr>
<tr>
<td>3-9</td>
<td>35</td>
<td>0.61</td>
<td>1.00</td>
<td>10</td>
</tr>
</tbody>
</table>
grey (sample 1-4 and 1-5) even when the nitrogen supply during deposition increased. This is in contrast with the results from Sproul et. al. [61], which have shown an increase of nitrogen incorporation in TiN films from 0.70 to 1.01 ([N]/[Ti] ratio) by increasing nitrogen partial pressure during depositions. This behavior can be explained by the results from Vasu et al. [62] which have reported that the [N]/[Ti] ratio increased from 0.38 to 1.1 as the temperature of substrate heating during depositions changed from ~25 to 500 °C. In our case, the films were deposited at relatively long target-to-substrate distance with small cathode diameters, which led to small thermal load from the plasma. Though we are not in the position to confirm the reason for the stoichiometric TiN films deposited with pulsing frequencies of 500 and 250 Hz, we suggest two explanations for this behavior:

1. The higher plasma density generated upon decreasing HiPIMS frequencies is able to dissociate larger amount of nitrogen molecules (N\(_2\)) into mono-atoms and ions (N or N\(^+\)), which are typically more reactive than molecular form. The increasing of dissociated species can poison the target more completely, and also increase the reaction between the elemental species on the substrate side.

2. The higher potential applied to the cathode during the pulse-on time of lower HiPIMS duty-cycle is able to accelerate the electrons to higher energy towards the substrate. When the energetic electrons impinge on the substrate, the substrate is heated which improves the nitrogen incorporation as described above.

O content of samples in set 3 is also listed in table 6.1. It shows that the O content reduces with decreasing the pulsing frequency. This behavior can be explained by the enhanced energetic bombardment created upon decreasing the HiPIMS pulsing frequency, as described in section 3.1.3. Denser structure in films can therefore be deposited with assisted by this
enhanced bombardment, which prevents post-deposition O incorporation. In addition, the O detected in films is not incorporated during deposition since the same pressure was used through all depositions of samples in set 3. The same pressure in the chamber gives similar formation time of O monolayer during deposition, which means that the number of O atoms incorporated in films is fewer with higher deposition rate. We show later in the section that the deposition rate decreases with the pulsing frequency. Along with the increase of O content with increasing the frequency indicates the incorporation of oxygen should take place at the other time than during deposition.

The left-shift of TiN (111) peak observed in figure 6.1 (b) and (c) as compared to figure 6.1 (a) can partly be explained by the amount of oxygen incorporated into the c-TiN lattice. The c-TiO has shorter lattice constant as compared to c-TiN (4.17 and 4.24 Å for c-TiO and c-TiN), which shrinks the average lattice size in the same way as c-AlN incorporates into c-TiN. This shrinkage of c-TiN lattice can shift the (111) peak position to the right in the angle of ~0.63 °, calculated by inserting the lattice constants above into Eq. (3.1). However since the diffraction peak of c-TiO is not observed in the XRD patterns, there should not be significant amount of O incorporate into c-TiN lattice forming c-TiO. Therefore, the peak position should be less affected by the O content in films.

From the Ti-to-Al atomic ratio, a reduction of the solubility limit upon decreasing the pulsing frequency is observed. According to Adibi et al. [32] the limited surface mobility can stabilize the metastable phase with higher incorporated c-AlN. In our case, this indicates that the lower pulsing frequency, the higher surface mobility is provided to growing films. The higher surface mobility can either be provided by the electron introduced substrate heating as mentioned above, or by the momentum transferred from the energetic bombardment.

The SEM images for set 4 samples are shown in figure 6.3 (a) and (b), which have thicknesses around 930 and 860 nm respectively. In combination with the deposition time listed in table 5.4, deposition rates of 6.20 and 3.58 nm/min can be calculated, which shows a reduction around 42 % when lowering the duty-cycle of HiPIMS. However a possible different deposition rate from Al cathode also needs to be considered, which is introduced by varied Al power used in the samples.

In addition, no apparent difference in the microstructure is observed from the SEM image. A transition to a more granular structure by increasing peak current as reported by Alami et al.
Figure 6.3 The SEM cross-sectional images of TiAlN samples deposited with (a) 500 Hz and (b) 250 Hz HiPIMS frequencies. Both images were taken under magnitude of 150,000 X.
Figure 6.4 The HT-XRD spectra of TiAlN films deposited with (a) 500 Hz, and (b) 250 Hz HiPIMS frequencies. The substrate peak is labeled with 'S' at the bottom of both diagrams.
[51] is not observed in our work as the pulsing frequency changed from 500 to 250 Hz. In combination with the O content listed in table 6.1, we suggest that there is a minor change of the microstructure which is beyond the resolution of the analytic method (SEM) that we used in this work. On the other hand, the change of energetic bombardment by varying the pulsing frequency from 500 to 250 Hz is probably not large enough to make significant change in microstructure that is detectable for the resolution of SEM.

The HT-XRD diffraction patterns of samples in set 4 are shown in figure 6.4 (a) for 500 Hz and (b) for 250 Hz. Reference scan was made for the Ta substrate, which is inserted at the bottom of each figure and labeled with 'Ta sub.'. In addition, the only diffraction peak contributed by the substrate in the scanned region is at 38.47 ° according to the powder diffraction reference of Ta and is labeled with an 'S' below x-axis for both figures [63]. It is observed that the intensity of Ta substrate decreases at elevated temperature and increases afterwards. This change of intensity means that the grain size of Ta substrate varies upon heating. The grain size changes because the Ta was annealed in the temperature we used, which reduces and regains intensity when the Ta recrystallizes and growth again.

Since samples in set 4 were deposited into similar thicknesses and chemical compositions, the comparison of their XRD patterns is more straight forward. In the XRD patterns of the as deposited films (labelled 'as dep.'), the left-shift of the (111) peak is more pronounced for the sample grown with pulsing frequency of 250 Hz. This observation is consistent with the notion that an increase of HiPIMS pulsing frequency generates more intense energetic bombardment on the growing film. It is known that the energetic bombardment introduces particle implantation into the film, which expands the lattice size of the growing species. When the bombardment is enhanced, more ions are implanted into the film leading to a larger expansion of lattice and therefore more pronounced left shift in diffraction peak. In addition, a similar peak shape (height and width) is observed from the XRD patterns of as deposited samples. Since the samples are alike in thickness, the high resemblance in the peak shape means there is no much difference in the grain size as well as the microstructure. This observation is also confirmed by the SEM images without significant difference in the microstructure showed in figure 6.3 earlier in this section.

Upon the heating process of both samples, relaxations of (111) peak are observed at 700 °C as the peak shifted to higher diffraction angle, which releases some of the residual strain induced
by the sputtering process. Meanwhile, the (111) peak broadening at 700 °C indicates the initial stage of spinodal decomposition, which forms the coherent c-AlN domains out from the parent phase. These domains grow in number faster than in their size, which destructively interfere the reflections from the cubic metastable phase and therefore the (111) peak reduce in intensity and diverse in width. At 1000 °C the film peak for both conditions slightly moves back to left, indicating the depletion of AlN in the parent phase. At the same time the depleted metastable phase starts to grow fine TiN grains, which gives rise to a broad TiN peak.

As the temperature elevated to 1150 °C, the (111) film peak for both conditions vanishes completely and the TiN (111) peak continues to grow in intensity, which indicate the exhaustion of the parent phase and the increasing grain size of TiN phase. The h-AlN grains start to grow in size and their reflections arise at 34 ° and 36.5 °. In addition, the reflections from rutile (TiO₂) phase¹ were observed at ~36 ° meaning a detectable amount of titanium had been oxidized during the heat treatment.

After holding at 1150 °C for 3 hours, the 500 Hz sample shows higher intensity for both h-AlN peaks than the 250 Hz sample, while the rutile phase also had higher reflection intensity for the first (~36 °) and the second (~39 °) peaks in the 500 Hz sample. The larger coherent domain size of h-AlN and rutile phases may indicate that the 500 Hz sample is more favorable for grain growth. Since the grain growth is also a diffusion controlled process, the 500 Hz sample shows an open structure in terms of diffusion which is probably more porous as compared to the 250 Hz sample. Though the difference is undetectable from SEM images, the oxygen contents shown in table 6.1 agree with the results from HT-XRD. When the operation frequency of HiPIMS is lower, the films become denser which prevent oxygen incorporation and retard growth processes.

---

¹ There are several polymorphs for titanium dioxide (TiO₂), and three of them can be found in nature: the metastable phase anatase, brookite, and the stable phase rutile. Rutile is one of the most stable phase for TiO₂ within all temperature range, and therefore it was challenging to reduce pure Ti in history [3].
7 SUMMARY AND FUTURE OUTLOOK

In this work, we seek for the feasibility of controlling the phase stability Ti$_{1-x}$Al$_x$N metastable phase at elevated temperatures through modification of microstructure in films. We deposited thin film samples by reactive co-sputtering with two cathodes. The cathode connected to a HiPIMS power supply was equipped with a Ti target, while the other cathode operated by a direct current power supply was equipped with an Al target. Various pulsing frequencies were used to change the microstructure and altered power on Al target was tuned to achieve different Al content in films. Films were first deposited to qualitatively investigate their phase composition achieved by GI-XRD, and then extra films were prepared for analyzing quantitatively chemical composition by ERDA. Based on the results from GI-XRD and ERDA, samples with desired phase and composition were grown. Microstructures of last samples were compared from SEM images, which were related to their phase transition behavior at elevated temperatures studied by HT-XRD.

We observed the start and saturation of (111) peak right-shift in GI-XRD patterns along with increasing the Al cathode power. This is due to the incorporation and saturation of Al atom in TiN lattice. The h-AlN peaks were also observed soon after the decomposition of the metastable phase. In the results of ERDA, the Al solubility limit was found to decrease with reducing the pulsing frequency, indicating that higher energy was provided to growing films at lower frequency. Moreover, a reduction of O content was also observed when decreasing pulsing frequencies, meaning that denser films was deposited when the frequency was lower.

Larger grain size (approximated from the diffraction peak intensity) were determined from the HT-XRD patterns of the sample deposited with higher HiPIMS frequency. The reduction in
grain size indicates the diffusion controlled grain growth was more retarded in 250 Hz sample as compared to 500 Hz. We suggested that a denser film which is more difficult to activate diffusion processes was deposited by lower HiPIMS pulsing frequency. Unfortunately that the relation between the microstructure and the diffusion behavior of Ti$_{1-x}$Al$_x$N films was not fully established. Since the variation in deposition parameters used were not large enough to have apparent transition in the microstructure, we were not able to compare the difference between samples observed by SEM. However the observations from HT-XRD patterns can be an important starting point of studying the feasibility of controlling the diffusion behavior by modifying the microstructure of Ti$_{1-x}$Al$_x$N films.

To continue from this point, expansion of the deposition parameter space, such as higher frequencies or longer pulse-widths, is needed to make more comparable difference in terms of the microstructure. We can also apply the substrate heating or bias voltage to eliminate the O incorporation in samples. On the other hand, thermal analysis (TA) and heat flow analysis can also be employed to determine the direction of heat flow as well as the amount of enthalpy during the decomposition events of TiAlN system at elevated temperatures. The results from TA and calorimetry can be informative to draw out conclusions of the tendency of phase transformation and therefore the diffusion behavior.

In addition, we observed the trend of increasing nitrogen incorporation by lowering HiPIMS frequencies which led to Ti$_{1-x}$Al$_x$N films with desired stoichiometry. However in this work, we are not able to confirm the mechanism of this observation. More detailed studies need to be performed to investigate the reactions on target surface and growing film along with the gas composition during reactive sputtering.
8 REFERENCES


[52] S.M. Rossnagel, J.L. Vossen, W. Kern, Thin Film Processes II, Academic Press,
New York, USA (1984)


[63]  JCPDS – ICDD, 04-0788 for cubic Ta.