CHAPTER 1 INTRODUCTION AND REVIEW

1.1 Motivation

In the present day, Iron industrials are importance parts of industrials in Thailand. It is found that the cost of machining is always very high due to the damage of machining tools, such as wear, fatigue or crack. In order to overcome this problem, surface engineering technologies mainly by using surface treatments and surface coatings on machining materials have been introduced to improve the lifetime and performance of tooling [1, 2]. For example, most cutting tools, such as drills, hobs, mills and machining are widely coated with titanium nitride (TiN) to improve the wear resistance and durability of machining tools because of high hardness and low friction [3-5]. However, the limited of TiN are that they are not stable by occurring oxidation resistance at high temperatures beyond 500^{O}C that can be reached during machining processes [1, 6, 7, 10].

Among these, the addition of aluminum in TiN to form nanostructure titanium aluminium nitride (TiAlN) films in order to overcome the instability at high temperature have been widely developed in many application fields such as cutting tools, biocompatible barrier and satellite temperature control [6-10] because of perform outstanding physical, mechanical, and tribological properties, including high value of hardness (approximately 30-35 GPa), high melting point, chemical inertness, low thermal expansion, low friction coefficient, good wear resistance and corrosion resistance by compared to the TiN films [2, 11-14]. Furthermore, excellent oxidation resistance at high temperature (approximately 750-800 ^{o}C) and low thermal conductivity which performs higher cutting speeds [11]. In addition, at high temperatures, aluminium forms a stable aluminium oxide (Al_2O_3) upon exposure to oxidizing conditions, thus protecting the diffusion of oxygen into the TiAlN layers [6, 8, 9, 15, 16].

The TiAlN films were prepared by different techniques, for example chemical vapor deposition [17], cathodic arc vapor deposition [18], dc and rf reactive magnetron sputtering [1, 2, 6-28]. Comparing to these techniques for preparation the TiAlN thin films, the magnetron sputtering are advantages due to easy handling, low temperature processing, extremely low hydrogen concentration, use of non-toxic gases, simple deposition process high reproducibility and high flexibility of large - scale as well as complex geometry shape production [6, 16]. It have been reports that the preparation of TiAlN thin films have focused on the influence of the deposition parameters, such as target to substrate distance, substrate temperature, substrate biasing, N_2 partial pressure, N_2 flow rate, sputtering current, magnetron discharge power, deposition time and sputtering power, on the crystallization and properties of TiAlN thin films [1, 2, 13-19]. However, the crystal structure and properties of TiAlN thin film prepared by sputtering under different deposition conditions have been widely studied, most of them were prepared at short target to substrate distance [10, 18], applied bias voltage [1, 2 19, 21, 29, 30], high sputtering of targets [23] and substrate heating [29] to form nanostructure. Therefore, the deposition of nanostructure TiAlN thin films which exhibited the good crystal structure and superior mechanical properties have been attractive in the thin film coating for cutting tool manufacturing because of not only eliminate cost of machining such as wear, fatigue or crack but also, for the advantage of low temperature sputtering process with no additional heating process to substrates and no bias substrate can shorten the production time and consequently reduce production costs.

The aim of this study was to deposit nanostructured TiAlN thin films on unheated substrates without substrate biasing at different sputtering currents and deposition times by a DC reactive unbalanced magnetron co-sputtering system. An outstanding feature of the study is also the deposition with a long target-substrate distance of 130 mm with low sputtering current on three different substrates, i.e. glass slides, silicon (100) wafers and carbon coated copper transmission electron microscopy (TEM) grids.

1.2 Research Objectives

It was known that the deposition parameters, for example, substrate heating, target-substrate distance, operating pressure, gas flow, film thickness, deposition time affect to structure and properties of TiAlN thin films such as crystal structure, surface morphology, microstructure, mechanical and tribology properties. Therefore, the thin films depositions by magnetron sputtering method with various parameters were closely relate each other i.e., the short target-substrate distance to made the substrate close to the sputtering plasma so that self heat substrate. In addition, the influence of the thermal effect by heat substrate will increases a high surface temperature, enabling the enhancement of the diffusion and chemical reactions such that the TiAlN thin films become crystals. Moreover, the substrate bias are also enhance the ion bombardment resulting high crystallinity structure but these parameter made complicate for deposited configuration and difficulty in preparation thin films

Therefore, the primary objectives of this work were to study the structure of TiAlN thin films deposited at the long target-substrate distance, unheated substrate, without biasing and low sputtering current in this study, research objectives are categorized as follow:

1. To understand the thin films deposition process of TiAlN by reactive dc unbalance magnetron co-sputtering method subject to the long target-substrate distance on unheated substrate.
2. To determine the optimize parameters for deposition in order to prepare appropriate TiAlN films. Gas flow rate of Ar sputtering gas and N_2 reactive gas are to be considered.
3. To study the influence of the sputtering currents and deposition times on the crystallization of TiAlN thin films.

1.3 Research Boundaries

1. Films deposition will be conducted on the glass slides, silicon wafer and carbon coated copper transmission electron microscopy (TEM) grids by reactive dc unbalance magnetron co-sputtering.
2. Several deposition parameters will be pre-determined. Selected parameters, i.e., Ar sputter gas and reactive gas flow rates, sputtering current and deposition time, will be conditionally manipulated in the study. In these boundaries, a long target-substrate distance is fixed with substrates are unheated, no bias substrate and low sputtering current.

3. Various physical measurements for crystalline structures, surface morphology, film thickness, chemical composition and microstructure of the TiAlN thin films will be investigated and analyzed.
4. Upon analysis and conclusion, the results from the measurements will be evaluated.

1.4 Advantages and Applications

The titanium aluminium nitride are attractive materials because of their several properties such as extreme hardness, high melting point, chemical stability, chemical inertness, good thermodynamically stability, superior oxidation resistance at high temperature, and low wear. From these outstanding properties, titanium aluminium nitride thin film are suitable to be used in many application field for examples, forming tools, dry and high speed cutting tool, the physical masking in dental alloy protective coating, semiconductor devices and optical instruments. In addition, the color of the $Ti_{1-x}Al_xN$ film can be modified by varying the composition. The color possessed by one of the compositions of $Ti_{1-x}Al_xN$ is similar to that of the gum tissue in the oral cavity. Thus, it has a potential for use in dental prostheses. Besides the applications of TiAlN coatings mentioned above, another prospective application is on the temperature controlling for the satellite. In this study, TiAlN thin films can be able have several outstanding and application purposes as follow:

1. Simplicity for applying to mass production due to the process is uncomplicated, i.e. unheated, long target substrate distance, no bias and low sputtering current.
2. Various for adjust the deposition parameters and configurations that effect resulting easy to control structure and properties of the thin film by using the individual sputtering titanium and aluminium targets which to is called "Co-sputtering" target
3. Resourcefulness of the results such as effects of parameters on film property obtained from each phase of study can be applied to suit each applicative purpose of industries.
4. Novel research development in the field of hard coating, biocompatible thin films and temperature controlling can be advantaged to manufacturing industries, dental clinic and satellite application.

1.5 Literatures review

This section will report the literatures review of the effect of sputtering parameters on structure and properties of TiAlN thin film deposited by magnetron sputtering method using the co-sputtering and compound/alloy target.

1.5.1 Effect of Substrate Bias on Structure and Properties of TiAlN Thin Films

The nanocrystalline TiAlN thin films on different kind of substrates deposited by DC or RF magnetron sputtering method also depend on substrate bias. The (Ti, Al)N thin films were deposited onto Si(100) wafers and AISI M42 tool steels at room temperature by DC reactive close-field unbalanced magnetron sputtering in an Ar–N_2 gas mixture using co-sputtering target to study the effect of different substrate bias voltages on mechanical and tribological properties of (Ti, Al)N films. It was found that the hardness and residual stress of the films were increased, whereas the surface roughness and the fraction of aluminium concentration [Al/(Ti+Al)] were decreased respectively, by increasing substrate bias voltages. For the tribological measurements, it was observed that the wear rates decreased with increasing substrate bias voltages. The friction coefficients of the films were highest at ~1.1. Moreover, the film prepared at substrate bias voltages of −80 V performed the best impact resistance [1]. Barshilia et al. [2] also use a four-cathode with individual target of reactive DC unbalanced magnetron sputtering system. Asymmetric bipolar-pulsed DC generators have been used to deposit TiAlN coatings at substrate bias in the range of -30 to 150 V with substrate temperature about 350 °C. The formation of a single phase TiAlN with B1 NaCl structure and the bonding structure was confirmed using XPS. The coatings also indicated improved wear and corrosion resistance. The x-ray peaks were shift to lower 2θ value whereas the hardness increase with increase the substrate bias. The nanoindentation data indicated that these coatings exhibited a hardness of approximately 3700 kg/mm^2

In addition, some researcher focus on the effect of substrate bias voltages on the microstructure and property development of DC magnetron cosputtered ternary TiAlN coating with separated titanium and aluminium targets at a 30° magnetron configuration. It was revealed that an increase in substrate bias imposed no major effect on the composition and phase formation of the (Ti,Al)N coatings, but had significant influence on the development of their microstructure and surface morphology. As the substrate bias increased, the coating structure was densified with development of fine grain size and reduced surface roughness, resulting in a substantial increase of the coating hardness. However as the substrate bias increased over 200 volts, excessive residual stress was built up, causing a fracture of the coatings. It is believed that the microstructure and property enhancement is attributed to an increased translational kinetic energy of the depositing atoms and a greater thermal energy provided to the substrate and the coating material with increasing substrate bias. A densified zone T structure with low porosity and improved properties is produced [30].

Moreover, the composition, structure and microhardness of (Ti,Al)N thin films deposited by DC reactive magnetron co-sputtering technique have been studied. Ramana et al. [21] indicated that the formation of fcc (Ti,Al)N phases from XRD analysis. The atomic composition of films, determined by backscattering techniques, varied with deposition conditions.The microhardness of the films estimated by J-H model is closely related to the atomic composition of the films, particularly to their nitrogen content. The thickness decrease from 1.26 to 1.12 μm however, microhardness decrease from 1941 kg.mm^{-2} to 1847 kg-mm^{-2} as a substrate bias increase to -50 V and then increased to 2906 kg.mm^{-2} with further substrate bias to -100 V

1.5.2 Effect of N_2 Partial Pressure on Structure and Properties of TiAlN Thin Films

In case of TiAlN thin films deposited by reactive sputtering method, there are many researchers study the influence of N_2 partial pressures (P_{N2}/P_t) on structure and properties of the film. Åstrand et al. [31] deposited $Ti_{1-x}Al_xN$ film with a multilayered structure deposited using bipolar pulsed dc dual magnetron sputtering (BPDMS) with co-sputtering target. The result show that the chemical composition and properties of the coatings by just changing the sputtering pulse times and the N_2 partial pressure raging from 0.03 – 0.12 Pa. The chemical composition could be varied between $Ti_{0.84}Al_{0.16}N$ and $Ti_{0.16}Al_{0.84}N$. The coatings with low Al content are columnar, whereas the coatings with high Al content are more glassy. The cell parameter is smaller for the coatings with high Al content and the texture changes from (111) for coatings with low Al content to (200) for coatings with high Al content. The coatings with a high Al content (x>0.58) are XRD amorphous and possessed a lower hardness and elastic modulus.

Furthermore, Musil and Hrubý [25] study is to understand the relationship between the film microhardness and its structure and to prepare hard nanocomposite coatings of the type nc-TiAlN/AlN. $Ti_{1-x}Al_xN$ films were sputtered from DC magnetron sputtering system an alloyed TiAl (60/40 at.%) target in Ar and Ar + N_2 mixture at a constant total pressure of 0.5 Pa. Films were sputtered at different partial pressures of nitrogen ranging from 0 to 0.375 Pa, different substrate temperatures ranging from room temperature RT to 400°C and two substrate biases. The results show that the film structure and microhardness changed with partial pressures of nitrogen. The superhard films are nc-TiAlN/AlN nanocomposite films composed of relatively large (30 nm) TiAlN grains, oriented in one direction and surrounded by an amorphous and/or nc-AlN phase. These films exhibit a high elastic recovery up to 74% and contain about 20 at.% Ti, 25 at.% Al and 55 at.% N.

Beside, Kim et al. [32] focused the characteristics, such as deposition rate, microstructure, surface morphology and mechanical properties, of TiAlN films synthesized by unbalanced magnetron sputtering (UBMS) compare with closed-field unbalanced magnetron sputtering (CFUBMS). TiAlN films were deposited from an alloyed TiAl (50/50 at.%) target at various N_2 partial pressures by two types of magnetron sputtering. The deposition rate of TiAlN films produced by CFUBMS with four magnetron sources was increased up to approximately 1.35 times in comparison with that obtained in the single UBMS. The TiAlN films deposited by two types of magnetron sputtering have similar chemical composition and crystal structure as a function of the N_2 partial pressure. However, TEM analysis showed that TiAlN film synthesized by CFUBMS with four magnetron sources has a denser columnar structure and its column width and grain size were increased up to approximately two times compared with film by the single UBMS. In addition, the hardness and elastic modulus of films by CFUBMS have higher values than those of films by the single UBMS.

Recently, Zhou et al. [33] investigate influence of the nitrogen partial pressure on the mechanical properties of (Ti,Al)N films deposited by DC reactive magnetron sputtering using a Ti–Al mosaic target at a substrate bias of -100 V is investigated. The fcc structure and the diffraction peaks belong to (111), (200), (220) and (311) were observed. With increasing N_2 partial pressure, the intensity of the (111) peak decreases but the intensity of the (220) peak increase. Nanoindentation tests reveal that with increasing N_2 partial pressure, the film hardness and elastic modulus increase initially and then decrease afterwards. Both the hardness and the elastic modulus of the film increase from 33.0 GPa to 43.4 GPa and from 325.1 GPa to 430.8 GPa, respectively when the N_2 partial pressure increases from 3.4 x 10^{-3} Pa to 33.3 x 10^{-3} Pa. Further increasing the N_2 partial pressure to 40.0 x 10^{-3} Pa reduces the hardness and elastic modulus to 41.7 GPa and 408.6 GPa, respectively. The maximum hardness and elastic modulus are 43.4 GPa and 430.8 GPa, respectively.

1.5.3 Effect of Substrate Temperature on Structure and Properties of TiAlN Thin Films

It has been khown that apply thermal into substrate during deposition press will affect to the crystallization, surface morphology and microstructure. Subramanian et al. [29] deposited thin films of about 1μm of TiAlN onto mild steel substrates by reactive DC magnetron sputtering using a target consisting of equal segments of titanium and aluminum. The TiAlN phase had preferred orientations along 111 and 200 with the face-centered cubic structure. Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) analyses indicated that the films were uniform and compact. Photoluminescence (PL) spectra reveal that TiAlN thin films are of good optical quality. Laser Raman studies revealed the presence of characteristic peaks of TiAlN at 312.5, 675, and 1187.5 cm^{-1}. The grain size increased with the annealing temperature up to 700°C and decreased above 700°C. The lattice constant increases with the annealing temperature and then start to decrease at 700°C. TiAlN films deposited at 400°C exhibited a compressive stress. During annealing the residual stress reached a minimum at 600°C and turned tensile stress at 700°C.

Beside, the effect of substrate heating on thermal controlling and optical properties of the temperature controlling of the satellite was observed. Chen et al. [11] deposited TiAlN ternary coating to apply on satellite for thermal controlling. In order to investigate thermal controlling property, TiAlN coatings were deposited on Si wafers by metallic Ti and Al targets. The Ti and the Al targets were powered by DC and RF magnetron sputtering, respectively. For investigating the influence of the heat treatment, the sample with N_2 to Ar ratio of 100% was annealed for 1.5 h in air at the temperatures of 250, 470, 700 and 900 °C, repeatedly. The result indicate that the temperature controlling of the satellite depends on the solar absorptance □α□ and the average thermal emittance (ε) with is in the range of 0.772 – 0.863 and 0.65- 0.67, respectively.

Moreover, Wurher and Yeung [30] focus on the influence of substrate temperature at 120°C, 240°C and 360°C, respectively on the crystal structure, surface morphology, microstructure and microhardness of DC magnetron cosputtered ternary TiAlN coating at a 30° magnetron configuration. As the substrate temperature increased from 120°C to 240 °C, the 2θ values for the (111) reflection of the TiN/TiAlN structure shifted from 37.420° to 37.459°. However, a further increase in temperature from 240 °C to 360 °C resulted in the shift back of the peak positions from 37.459 ° to 37.352 °, It was found that an increase in substrate temperature imposed no major effect on the composition and phase formation of the (Ti,Al)N coatings, but had significant influence on the development of their microstructure and surface morphology. As the substrate temperature increased, the coating structure was densified with development of fine grain size and reduced surface roughness, resulting in a substantial increase of the coating hardness. It is believed that the microstructure and property enhancement with increasing substrate temperature. The adatom mobility and the surface diffusion of atoms are enhanced, producing a densified zone T structure with low porosity.

1.5.4 Effect of Sputtering Current on Structure and Properties of TiAlN Thin Films

The crystal structure, microstructure, surface morphology, chemical composition and mechanical properties of TiAlN thin films depend on the sputtering power. Shum et al. [6] reported that the ($Ti_{1-x}Al_xN$) thin film, with $0 \leq x \leq 1.0$, were deposited onto Si(100) and hardened M42 tool steel substrates at room temperature by DC reactive close-field unbalanced magnetron sputtering at a bias voltage of −50V in an Ar–N_2 gas mixture by varying the sputtering current of Al from 0-7 A with fixed ti current at 5 A. These films were characterized and analyzed using X-ray photoelectron spectroscopy, optical interference method, nanoindentation measurements, scanning electron spectroscopy, scratch tester, cyclic impact tester, reciprocating wear tester, and Raman spectroscopy. It was found that the films deposited under aluminium-free conditions (TiN) had a high compressive stress of ~3.0 GPa. The compressive stress in $Ti_{1-x}Al_xN$ films decreased significantly with an increase in the Al content (x). The films at x = 0.41 exhibited the best adhesion and cohesive strength. The films with high Al contents ($x > 0.09$) showed the presence of interfacial layer in the wear track. Raman scattering results showed that the wear debris in TiN films composed of a mixture of nanocrystalline anatase and rutile TiO_2.

Shum et al. [16] were also studied the influence of Al sputtering current from 0-5 A with fixed Ti sputtering current at 5 A on structural and mechanical properties of Titanium–aluminium–nitride ($Ti_{1-x}Al_xN$) films deposited onto unheated silicon (100) substrates by reactive close-field unbalanced magnetron co-sputtering at a pulsed-bias voltage of 50 V in an Ar–N_2 gas mixture. The effects of aluminium content (x) on structural and mechanical properties of these films have been studied. The stoichiometric composition of TiN and AlN was found as forming a ternary phase of Ti–Al–N. The XRD results exhibited the structural changes in $Ti_{1-x}Al_xN$ films with different Al sputtering current. The films were essentially cubic B1-NaCl TiN with (111) oriented grains in the range of x = 0 to 0.48. The film thickness increased with Al current whereas lattice parameter and grain size decrease. The hardness and young's modulus increase and then decrease with highest value as Al sputtering current of 5 A. In addition, revealed that the improved mechanical properties of $Ti_{1-x}Al_xN$ films with the addition of Al into TiN compound were attributed to their densified microstructure with development of fine grains and reduced surface roughness

Furthermore, Liu et al. [34] produced nanocrystalline $Ti_{1-x}Al_xN$ ($0 \leq x \leq 0.41$) solid solution deposited films by reactive unbalanced close-field magnetron sputtering. The Ti target current was typically 5 A with the Al target current ranging from 0 to 5 A to obtain $Ti_{1-x}Al_xN$ films with different Al concentrations. The observation show that the

XRD 2θ peaks shift toward higher Bragg angles as the Al content increases. The average grain size substantially decreases with increasing Al content in the range of x = 0 – 0.41. The average grain size ranges from about 15–30 nm. The hardness and elastic modulus of the films increase with increasing Al content and reach a maximum for a film at x = 0.41 (hardness = 31.4 GPa and elastic modulus = 312.2 GPa). Nanoindentation measurements showed that the hardness of $Ti_{1-x}Al_xN$ films increased monotonously with the content of Al. A calculation based on a semiempirical method revealed that the effect of intrinsic hardening, which arises from the change of the nature of atomic bonding due to the incorporation of Al atoms into TiN lattice, played a negligible role in the observed hardening phenomena. Further analysis revealed that the grain boundary hardening was also very weak and the improvement of hardness of $Ti_{1-x}Al_xN$ films with relatively low content of Al ($x \leq 0.33$) could be well explained by the Fleischer model of solid solution hardening. However, for $Ti_{1-x}Al_xN$ films with $x > 0.33$, an obvious deviation from the solid solution hardening was observed, probably due to the grain boundary segregation of solutes that might lead to an enhanced effect of grain boundary hardening when the amount of Al is high.

1.5.5 Effect of Target to Substrate Distance on Structure and Properties of TiAlN Thin Films

Wuhrer and Yeung [35] prepared Nanostructure titanium aluminium nitride coatings were by DC magnetron co-sputtering technique to study the effect of target–substrate working distance (WD) on the microstructure and property of the films. The films were deposited to a thickness of 1.5–2.0 μm at nitrogen pressures of 0.4, 0.65 and 2.4 mTorr, respectively. The results show that the closer WD of 65 mm, XRD intensity ratios of major peak reflections and lattice parameters of the TiN/TiAlN structure and the deposition rate were higher. The roughness values were increased with nitrogen pressure for all films and a densified nanograin structure observed. Significantly higher hardness was achieved. The effect of WD became more significant to the nanostructural evolution as the nitrogen pressure was increased. With a close WD, production of nanostructured coatings can be maintained viably over a wider range of nitrogen deposition pressures.

1.5.6 Effect of N_2 Pressure on Structure and Properties of TiAlN Thin Films

A series of (Ti,Al)N coatings were deposited by RF magnetron sputtering using Ti–Al mosaic target in the mixture gas of Ar and N_2 with different N_2 pressures. The results reveal that N_2 partial pressure has an important effect on the (Ti,Al)N coatings. (Ti,Al)N coatings with stoichiometric ratio can be easily synthesized at a suitable range of N_2 partial pressure and the coatings present fcc structure single phase with (111) texture preferential orientation. The coatings are strengthened and reach maximum hardness of 34.4 GPa and elastic modulus of 392 GPa, respectively. (Ti,Al)N coating prepared at lower N_2 partial pressure shows low N and thus has low hardness. On the other hand, at over high N_2 partial pressure, the deposition rate of the coatings decreases greatly because N_2 reacts with Ti–Al target and forms a nitride layer on its surface, while the composition of the coatings has almost no change and the coatings show a nanocrystalline or amorphous structure and lower hardness [24].

1.5.7 Effect of Sputtering Power on Structure and Properties of TiAlN Thin Films

The phase transition and properties of TiAlN thin film were investigated by varying the sputtering power. Zhou et al. [36] were synthesized Pseudobinary ($Ti_{1-x}Al_x$)N films by a new inductively combined rf-plasma assisted planar magnetron sputtering method at different sputtering power (0-150 W) applied to Al target with fixed Ti sputtering power at 150 W. It was found that the Al content of the films depended on sputtering power. The lattice parameters decreased as a function of the Al concentration in the ($Ti_{1-x}Al_x$)N films. The deposited ($Ti_{1-x}Al_x$)N films were identified as having the B1 structure up to 50 mol% having the B1 structure up to 50 mol% Al ($x = 0.5$). In the range from $x = 0.6$ to $x = 0.7$, two phases with the B1 and B4 structures were observed. Oxidation resistance increases with increasing the Al content in the ($Ti_{1-x}Al_x$)N films up to 70 mol% Al, irrespective of coexistence of the B1 and B4 phases in the ($Ti_{1-x}Al_x$)N films with $x = 0.6$ and $x = 0.7$, while both the hardness and Young's modulus show a maximum value, respectively. Beside, electric resistivity increase while residual stress decrease and increase with Al content.

In case of Titanium aluminum nitride films deposited on special dental alloys by reactive RF sputtering at various sputtering power from 45 to 145 W to modify the characteristics of nickel-based and chromium-based dental material, Liu et al. [13] reported that the by varying the power on the Al target, the stoichiometric value of for x the $Ti_{1-x}Al_xN$ coatings can be controlled accordingly. The film exhibited $Ti_{1-x}Al_x$ structure with different Al concentration. A well-controlled composition by adjusting the target input power was achieved. TiAlN films exhibited smooth surface compared with uncoated dental alloys. The mechanical properties of dental alloys were enhanced due to the hard $Ti_{0.75}Al_{0.25}N$ film. The hardness and Young's modulus of $Ti_{0.75}Al_{0.25}N$ film were 32 and 386 GPa, respectively. The wear resistance of the dental alloys was improved with the presence of $Ti_{0.75}Al_{0.25}N$ film.