CHARACTERIZATION OF TANTALUM NITRIDE THIN FILMS

SYNTHESIZED BY MAGNETRON SPUTTERING

by

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Abstract

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Tantalum Nitride is chemically inert, oxidation resistant and hard. TaN finds applications as a protective coating due to its excellent wear properties. It has become a very promising diffusion barrier material in Cu interconnect technology in microelectronics. TaN has not been analyzed as much as other transition metal nitrides like the TiN system because TaN exhibits various stable and metastable phases. The emergence of these phases and the different physical, chemical and mechanical properties depend on the growth technique and deposition conditions.

TaN thin films were deposited using magnetron PVD sputtering in the SaNEL lab. The aim of this study was to identify the effect of processing parameters like N_2/Ar ratio, substrate bias and temperature on the emergence of the different phases present in TaN thin films and the effect of deposition conditions on the mechanical properties of these films. The phases present in the

films, deposited at various conditions were explored via low angle X-Ray Diffraction (XRD), hardness response by using Nanoindentation and tribological testing out to assess their frictional and wear behavior. It was observed that at high percentage of Nitrogen in the gas mixture (10% - 25%) the main phase present was FCC TaN and as the Nitrogen content was decreased a mixture of phases was present in these films. The hardness of the films increases as we decrease the Nitrogen content, yielding a film with a hardness of 37.1 GPa at 3% N_2 in the gas mixture with a substrate bias voltage of -100 V.

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Chapter 1

Introduction

1.1 Introduction and Motivation

Due to the increasing demand for industrial applications and because of the current technological advances in surface engineering, hard and temperature resistant coatings have gained much attention. Due to the excessive wear of mechanical tools caused by corrosive environments and high temperatures, their protection is of immense concern. The transition metal nitride coatings like CrN, TiN films have been more frequently studied as protective coatings due to their excellent hardness, wear and corrosion resistance. [1, 2, 3]

Tantalum Nitride is chemically inert, corrosion resistant and hard. [7] TaN thin films are thus gaining increasing attention for thin film resistors and diffusion barriers in the micro-electronics industry. [1] These films are known for their high temperature stability and their ability to resist oxidation up to 800°C. TaSiN coatings can resist oxidation up to 1300°C. [44, 45] There have been investigations carried out on the mechanical properties of TaN films, which clearly indicate their potential of being used as high hardness coatings. [1, 4-6] Some compounds present in TaN at high N_2 flow and higher substrate temperature, such as orthorhombic Ta_4N and FCC TaN have theoretical hardness

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of 61 and 50 GPa respectively, although other researchers have reported the FCC phase to have hardness around 20 GPa [18,19]

Variations in stoichiometry are common in TaN thin films because of their structure. [8] TaN films have been formed by different CVD [8, 9] and PVD methods. [11-17] TaN exhibits different stable and metastable phases such as BCC-$TaN_{0.05}$, hcp-Ta_2N, FCC-TaN, hexagonal-TaN, hexagonal-Ta_5N_6, tetragonal-Ta_4N_5, orthorhombic Ta_4N and orthorhombic-Ta_3N_5 [20], with differing physical, chemical and mechanical properties depending on the growth conditions.

This work focuses on how the changing deposition parameters effect the phases present and mechanical properties like hardness, residual stress of these films.

1.2 Objective

The production of Tantalum Nitride by reactive sputter deposition is a well-established method. [18] Limited work has been experimentally conducted in discovering the various TaN structures.

The aim of this study is:

1. To identify the effect of processing parameters like N_2/Ar ratio, substrate bias and temperature on the emergence of the different phases present in the TaN thin films grown by the dc magnetron sputtering technique.

2. To determine the effect of deposition parameters on the mechanical properties of the films.

Chapter 2

Literature Review

The present day industry demands coatings which are extremely hard, wear resistant, corrosion and oxidation resistant with high lubricity. The current surface engineering technology makes it possible to engineer coatings having excellent mechanical properties, which can be used at high temperatures. Hardness in general, implies a resistance to deformation and for metals this property is a measure of their resistance to permanent or plastic deformation. Superhard coatings with hardness of 40 GPa have attracted large attention because of the scientific curiosity of preparing materials with hardness in the range of diamond (70–90 GPa).

2.1 Transition Metal Nitrides

Transition-metal nitrides, commonly referred to as refractory hard metals, possess unusual combination of physical and chemical properties which makes them attractive from both fundamental and technological points of view. [1] They usually have high melting points, extremely high hardness, good electrical and thermal conductivity, and good corrosion resistance. This unique combination of properties has led to experimental investigations and also made possible a large variety of applications for example, diffusion barriers in microelectronics, hard wear resistant coatings on cutting tools, and a corrosion and abrasion resistant

layers on optical and mechanical components. [29] Unlike TiN system, which is relatively simple with just two compounds present, tetragonal Ti_2N and cubic TiN, the TaN system has variety of compounds and has not been extensively investigated. [47]

2.1.1 Mechanism of Hardness in Transition Metal Nitride Thin Films

According to Veprek, there are three different approaches towards the preparation of superhard materials: intrinsically superhard materials, thin coatings and nanostructured superhard coatings. The hardness enhancement in thin coatings during their deposition by chemical or physical vapor deposition is due to a complex, synergistic effect which involves manipulation of crystallite size, grain boundary densification, formation of point defects, and built-in biaxial compressive stress. [37]

The mechanical behavior of thin films is quite different from that of the bulk material for e.g. for bulk TiN the reported hardness is about 19 GPa. However, for TiN thin films, the hardness value varies from 3.4 GPa to 40 GPa. [30] The large differences arise primarily from differences in thin film microstructures, such as grain size, columnar structure, void density, film purity and so on. It is observed that as the grain size decreases, the hardness of the films increases [50]. This observation can be explained by the Hall-Petch equation which states that yield stress is inversely proportional to the square root of the

grain diameter, and hence hardness increases with decreasing grain size for single phase materials until the grain size reaches a diameter of about 10 nm. With further decrease in grain size, a drop off in hardness is observed. This relationship can be seen in Figure 2-1. This equation is based on the concept that grain boundaries act as barriers to dislocation motion [50]. Crystallographic orientation has been shown to significantly affect the hardness of thin films [4].

Intergrain processes.
Local sliding along grain
and phase boundaries

Intragrain processes.
Dislocation nucleation
and motion

Hardness

Amorphous
phase

Nanocrystalline
phase

Microcrystalline
phase

d_c = 10 nm
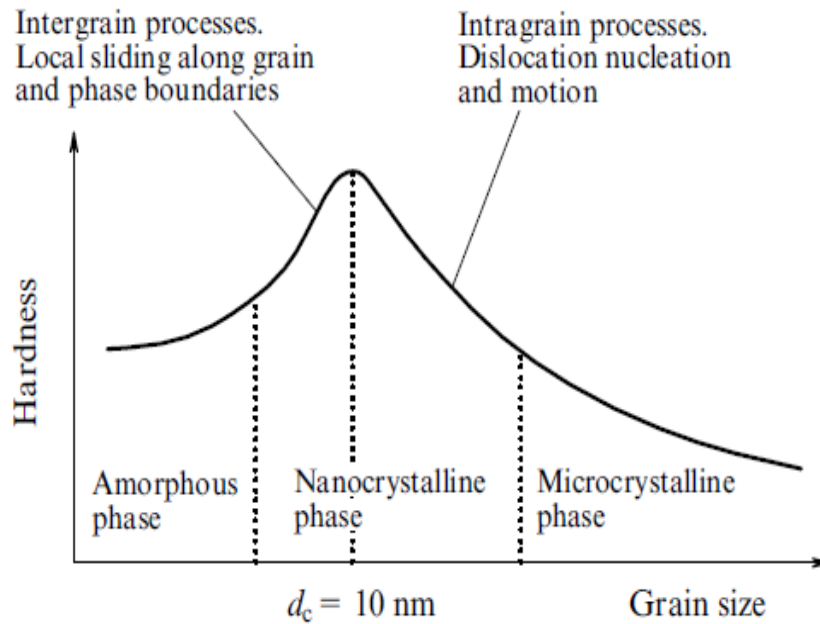
Grain size

Figure 2-1 Hall-Petch Relationship between Hardness and Grain size

2.2 Tantalum Nitride Thin Films

Tantalum and Tantalum Nitride thin films are known for their high temperature stability and chemical inertness. They are used as diffusion barriers in electronics industry. [24, 25] However, it has been observed that Tantalum Nitride has also become important as hard, wear and oxidation resistant coatings.

Pure Tantalum exists in two different phases: the thermodynamically stable body centered cubic (BCC) phase and the metastable tetragonal phase. The phase transformation from tetragonal to BCC phase occurs between $300^{o}C$ – $400^{o}C$. [26] The hardness of BCC-Ta has been reported to be 7 GPa -11 GPa and for tetragonal-TaN to be around 14 GPa. [27, 28] Addition of Nitrogen (pN_2 = 0.026, 0.052, and 0.100 mTorr) increases the hardness of the Ta films with maximum hardness (32 GPa) obtained for the films with pN_2 = 0.100 mTorr. In the case of TaN films with low Nitrogen (pN_2 = 0.026 mTorr), the hardness exhibits a clear microstructural dependence. A decrease in the grain size causes the hardness to increase from 16 to 24 GPa. [50] Investigations carried out on Tantalum Nitride thin films, clearly indicate their potential of being used as very hard coatings. [1] One of the papers reports a theoretical hardness of 61 GPa for one of the orthorhombic phases of TaN. [19] Their properties depend on the deposition technique used and the processing parameters.

2.2.1 Crystal Structure and Phase Transition

TaN thin films are complex, since TaN has different stable phases and metastable phases. [31, 32] TaN hexagonal is the stable phase which usually can be obtained by high temperature sintering at $1300^{o}C$ to $1400^{o}C$. In microelectronics, the cubic metastable phase TaN is preferred as diffusion barrier for Cu interconnections due to its structure integrity with Si and its lower resistivity.

The following phases have been discovered experimentally when TaN thin films are deposited by reactive sputter deposition. On heating the substrate to 300°C and a N_2/Ar flow ratio of 4% − 30% leads to an orthorhombic Ta_4N phase. [19] Tetragonal β-Ta (330) and hexagonal stoichiometric TaN were observed at lower (10% − 20%) flow ratios, whereas orthorhombic TaN and orthorhombic Ta_3N_5 were present at higher (40%) flow ratios. [5] Other researchers report a change in structure upon increasing the N_2/Ar flow ratio from α- or β-Ta to Ta_2N, and finally to TaN. [7, 18] Amorphous Tantalum rich TaN has been observed at flow ratio of 10% N_2, followed by FCC TaN for flow ratios of 20% to 45%. Above a flow ratio of 45% textured FCC-TaN (100) is formed. An increase in hardness for flow ratios between 20% and 45% has been reported. [18]

2.2.2 Phases and Hardness

Hardness of 11.6 GPa in nanocrystalline BCC-Ta thin film grown on a glass substrate by radio frequency (RF) magnetron sputtering has been achieved. [28] The hardness of the film is about one order of magnitude higher than that of bulk coarse-grained Ta (1.17 GPa). [11] Different phases of TaN have been prepared by varying N_2 to Ar ratio. Hardness has been evaluated by rule of mixtures for various phases of TaN. The reported values of theoretical hardness according to rule of mixtures for hexagonal TaN (100), FCC TaN (200), orthorhombic $Ta_6N_{2.5}$, orthorhombic Ta_4N are 15.54 GPa, 49 GPa, 30.8 GPa and 61.8 GPa respectively. [19]

A hardness increase from 25 GPa - 35 GPa to around 70 GPa has been reported in TaN thin films deposited by inductively coupled plasma assisted sputtering. [47] The hardest phase reported by Lee et al was hexagonal TaN. Hardness varying from 22 GPa to 32 GPa has been reported by Westergard, et al., when TaN thin films are deposited by DC magnetron sputtering, by changing N_2 flow rate from 24 sccm to 40 sccm. The phases changed from a mixture of BCC Ta and hexagonal Ta_2N (at 24 sccm) to single phase Ta_2N (at 40 sccm). [46]

According to D. Bernoulli, et al., the hardness of FCC-TaN increases up to N_2/Ar flow ratio of 45% to its maximum value of 21 GPa, followed by decrease in

hardness upon further increasing the ratio. In Figure 2-2, hardness is shown as a function of N_2/Ar ratio. [18]
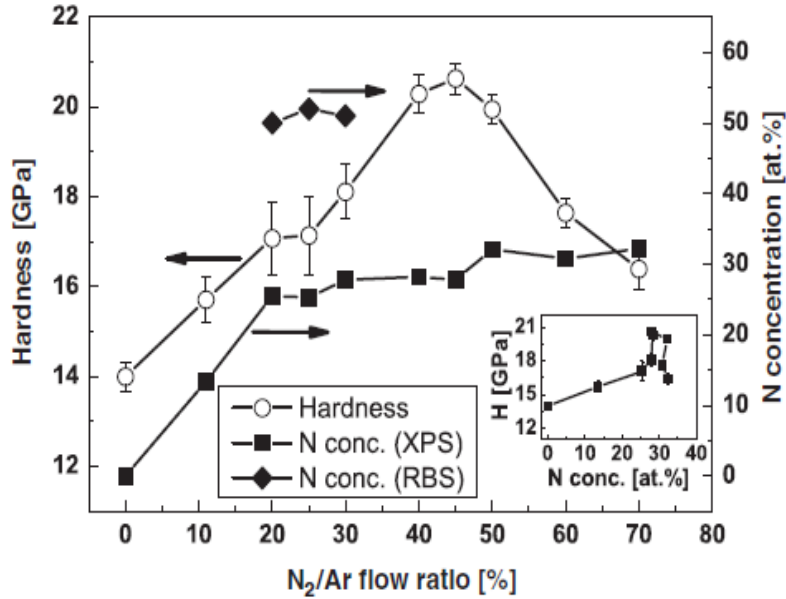
Figure 2-2 Variation in hardness of TaN films with changing N_2/Ar ratio. [18]

TaN phases vary greatly with varying deposition techniques like metal-organic chemical vapor deposition, radio- frequency and DC sputtering and ionized metal plasma and deposition conditions like substrate bias, temperature, N_2 / Ar ratio. [33-35] The change in phases by varying substrate bias has not been studied yet, which we will include in this body of work.

2.2.3 Mechanical and Tribological Properties

As far as the tribological characterization of TaN thin films is concerned, not much work has been done till now. Such analysis is important in order to develop a hard, wear resistant coating. [46] In the work done by Westergard, N_2 flow rate was increased from 24 sccm to 40 sccm. The phases changed from a mixture of BCC Ta and hexagonal Ta_2N (at 24 sccm) to single phase Ta_2N (at 40 sccm). [46] In all these specimens, the surface roughness varied from 60-65 nm. Residual stress of the coatings was found to vary between -2.4 GPa and -5.9 GPa (thickness of coatings ranging between 3.0 and 7.2 μm) and seems to rapidly increase with N_2 flow. The coating abrasive rate was small ranging between 14 and 62 mm^3N mm^{-1} compared with the wear rate of TiN coating being 220 mm^3 N mm−1. Wear rate was found to decrease with increasing N_2 flow. [46]

2.2.4 Applications

TaN has many attractive characteristics such as good wear resistance, high hardness, chemical inertness, and temperature stable electric resistivity. For this reason, TaN has been widely used in the mechanical and microelectronics industries. Ta and TaN thin films have primarily been investigated for their electrical properties. TaN has become a very promising diffusion barrier material in Cu interconnect technology in microelectronics. Various techniques have been explored in qualitative and quantitative characterization of Cu diffusion in TaN.

For example, sheet resistance study of Cu/TaN/Si was done after various temperature annealing. The results show that TaN can stand up to 800°C annealing without Cu breaking through. [36]

Tantalum nitride has superior corrosion and wear resistance and its hardness is higher than that of TiN. The biomedical properties of tantalum nitride thin films synthesized by reactive magnetron sputtering have been investigated and it has been shown that tantalum nitride is an excellent material for the fabrication of commercial artificial heart valves as compared to TiN, based on blood compatibility of the tantalum nitride films, as evaluated by clotting time measurement and platelet adhesion tests. [6]

The Ta–Si–N films with a high (>20 at.%) Si content prepared by reactive magnetron sputtering exhibit an excellent high-temperature oxidation resistance in a flowing air up to 1300°C compared to hard coatings like TiSiN. A very small mass gain after the annealing between 800°C and 1080°C is due to the formation of a thin smooth oxide layer. [44]

TaN are used as protective coatings on steel due to their excellent wear properties. [18] Most of the work on TaN has been done on their application in thin film resistors and diffusion barriers. Very little work has been done on their application in hard wear resistant coatings.

2.3 Tantalum Nitride Thin Film Deposition Techniques

Polycrystalline TaN films have been deposited by a variety of techniques: metal-organic chemical vapor deposition, radio-frequency and DC sputtering, and ionized metal plasma. [30] Most of these deposition methods need to satisfy requirements like good film quality, stability and desired properties, suitable for practical application, low cost and environmental-friendly.

As previously mentioned, TaN exists in various stable and metastable phases, the structural and electrical properties of polycrystalline TaN films vary a lot with different deposition techniques. These films are generally grown by physical and chemical vapor deposition techniques. [4, 19, 21–23]

2.3.1 Physical Vapor Deposition

PVD methods are commonly used in the manufacture of thin film coatings. PVD methods include evaporation, sputter deposition, cathodic arc deposition and pulsed laser deposition. In all methods of PVD, the constituent species, atoms or molecules are produced by either evaporation of a solid source or by using energetic gaseous ions in plasma to knock off, or sputter the atoms from a source target. These atoms travel through a vacuum of very low pressure gas phase, impinge on the substrate and finally condense on the surface to form the film. In reactive sputtering, species is sputtered in presence of a reactive gas (like N_2) and a compound is formed and deposited. [49]

2.3.1.1 Sputter Deposition

In a sputtering process, an inert gas such as Argon is fed into the chamber at low pressure. A bias voltage is applied across the two electrodes and plasma is created. The plasma contains neutral Ar atoms, Ar ions and free electrons and is a conducting medium. Free electrons present in the chamber are accelerated away from the negatively charged cathode (target). Some of these electrons collide with the sputtering gas like Ar, resulting in an Ar^+ ion and an electron. The positive ions are then accelerated to the negatively biased target and dislodge or sputter the target atoms. These atoms are then free to travel through the plasma as a vapor and strike the surface of the wafers and form the deposited film. If the target is conductive, we use DC mode of sputter deposition and to deposit nonconductors like lightly doped silicon, we use RF method. During this process, number of free electrons will collide with Ar^+ ions to form neutral Ar atoms. When the energized electron returns to the ground state, a photon is released in the reaction, resulting in the plasma glow. [49]

In sputter deposition, the target or source sputtering rate is important. Sputtering occurs when the incoming ion transfers enough energy to the target surface to break bonds holding the target atom in place. This depends on the energy and mass of the ions and the target material. The yield, which is the number of atoms from the target per incident ion, depends on energy of ion,

voltage across the sheath and the direction of incidence of the ions. Multiple targets may also be used in these systems for cosputtering.

2.3.1.1.1 Reactive Sputter Deposition In this method, a reactive gas is introduced in the chamber along with the sputtering gas. In case of TaN, the plasma can furnish energy to the N_2 to allow it to dissociate into atomic nitrogen, which can then easily react with the Ta. The reaction usually occurs either on the wafer surface or near the target itself and not in the plasma. Controlling the stoichiometry of reactively sputtered films is sometimes difficult.

2.3.1.1.2 Bias Sputtering Sputtering of the wafer is usually desirable. One application would be for pre-cleaning the wafer before actual deposition. Another application is bias sputter deposition, where deposition and sputtering of the wafer are done simultaneously. A negative bias relative to the plasma is applied to the substrate, which is electrically isolated from the chamber walls. Positive Ar atoms from the plasma will now be accelerated to the wafers to the substrate and sputter off atoms. The energy of the ions can be controlled by controlling the substrate bias.

In sputter cleaning, no deposition is allowed to occur on the wafer surface by usually using a shutter to block sputtered material from the target. A controlled thickness of the material is sputtered off the wafer, removing any contaminants and oxides. In bias sputtering, conditions are chosen so that more deposition

occurs than sputtering. A more planarized film is obtained because of bias sputtering. Also, properties of the film being deposited can be changed by changing the substrate bias. These properties include residual stress, density, resistivity and mechanical properties. The drawback of this method is that the net deposition rate is slow. [49]

2.3.1.1.3 Magnetron Sputter Deposition In both conventional DC and RF sputtering, the efficiency of ionization from energetic collisions between electrons and atoms is rather low. Most electrons lose their energy in non-ionizing collisions and as a result, only a small percentage of them take part in the ionization process with Ar atoms. In RF plasmas electrons gain energy directly from oscillating RF fields, increasing the ionization efficiency to some level. However, the overall deposition rate is still low. In this technique, magnets are used to increase the percentage of electrons that take part in ionization. A magnetic field is applied which traps the electrons near the target surface and causes them to move in a spiral motion until they collide with an Ar atom. The advantages of this technique are several like unintentional wafer heating is reduced, since dense plasma is confined near the target. In addition, lower Ar pressure can be utilized as ionization efficiency is high and film quality would be better, due to less Ar incorporated in them. [49]

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Chapter 3

Synthesis and Characterization

TaN films were synthesized using a home built hybrid Plasma Enhanced Chemical Vapor Deposition (magnetron sputtering) system, followed by detailed characterization. The Tantalum target was of 99.9% purity. The thin films were deposited on (001) Silicon wafers. The details of the deposition conditions for each film are mentioned in this chapter. The thin films were characterized using X-ray diffraction (XRD), which gave us understanding of changing phases with varying deposition conditions. Mechanical and tribological properties of the film were studied using nanoindentation, wear testing and optical profilometry.

3.1 Reactive Magnetron Sputtering System

Magnetron sputtering has been one of the most effective film deposition techniques during the past few years and has been widely for thin film research and applications. The TaN films have been synthesized in the SaNEL lab on the home build PECVD system. Figure 3-1 and 3-2 shows the photographs of the PVD system in the SaNEL lab and the substrate holder respectively. The stainless steel chamber has a cylindrical shape with 47 cm diameter wide and 50 cm height. The system has three 2-inch diameter magnetron guns mounted at the bottom of the chamber. The magnetron guns can support targets with thickness of 0.125", 0.185" or 0.250". Magnetrons aid to direct ions coming from the target after its

bombardment towards the substrate. The targets can be shielded using a pneumatic shutter above the magnetron gun.

Figure 3-1 PVD reactive magnetron sputtering system in Surface and Nano

Engineering Laboratory

The substrate holder as shown in Figure 3-2 is a 10 cm diameter plate where the samples can be mounted and has rotation capability and its temperature can be controlled by a thermal couple.

Figure 3-2 Silicon wafer loaded on the substrate holder

DC or RF power can be applied from any of the available power supplies to any of the three guns or substrate interchangeably. Cooling of the magnetrons and substrate rotation electronic device is done with a water chilling system in order to prevent damage to the magnets. Figure 3-3 shows the magnetron guns of the PVD system.
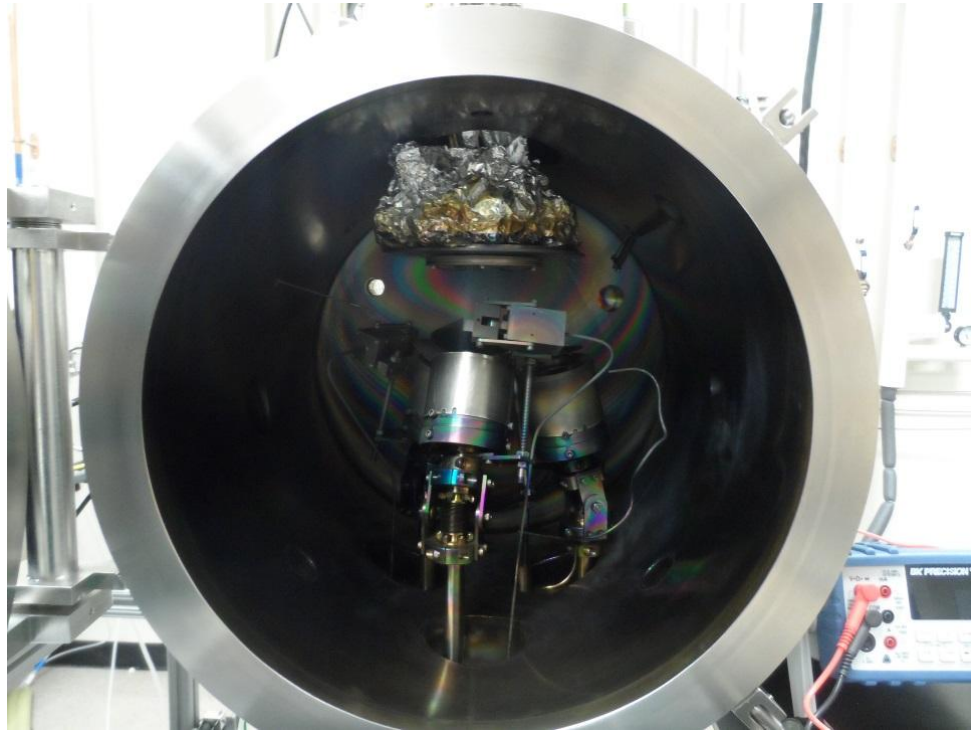
Figure 3-3 Magnetron guns inside the Sputtering Chamber

Roughing is achieved by a mechanical rotary valve pump. It depressurizes the lines, the cryo pump, and the deposition chamber to 20 mtorr. After pumping down the system with the rough pump, a cryo pump and cryo compressor (cooled by a chilled water supply) are used to achieve a base vacuum level in the range of 10^{-7} Torr . A cryo compressor helps to cool the arrays within the cryo pump to 11 K. Three different pressure gages are installed, first gauge is thermocouple gauge and it measures the roughing line pressure. Second one is a Baratron gauge, it measures chamber pressure during deposition and provides input to the cryopump

gate valve for maintaining a set point pressure during deposition. Last is the ion gauge, which measures the pressure when the chamber is exposed to the high vacuum cryo pump. After obtaining an appropriate base pressure, the sputtering gas and the reactive gases can be flown into the chamber. Their flow rate is adjustable and can be controlled precisely by mass flow controllers. Figure 3-4 shows the schematic diagram of the system.
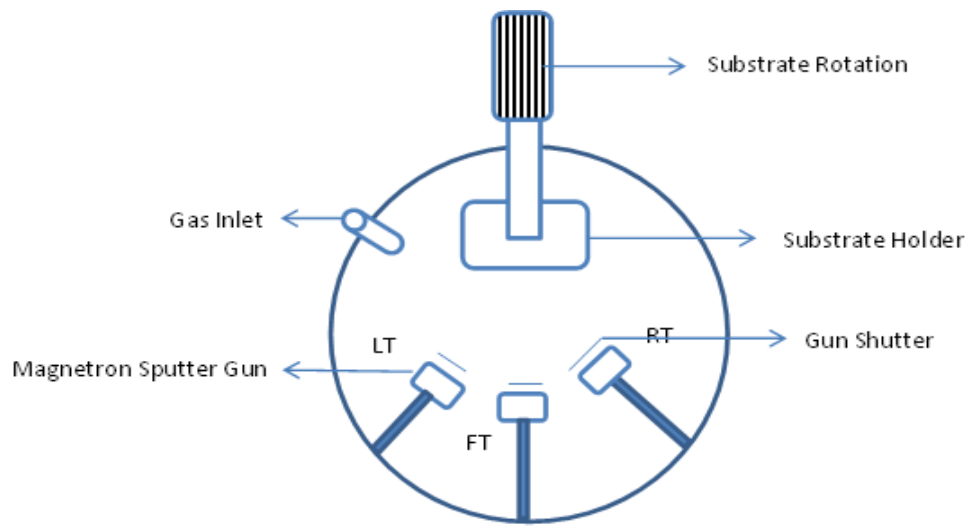
Figure 3-4 Schematic representation of hybrid PVD/CVD system.

3.1.2 Deposition Procedure for TaN Thin Films

Experimental sputtering conditions were specifically selected based on literature review and the initial experiments carried on TiSiN thin films in the SaNEL lab. The TaN films were deposited on Si (100) p-type wafers. The wafers were cleaned with acetone prior to loading in the chamber. The chamber was roughed down to 20 mtorr using mechanical pump and then exposed to the cryo pump by opening the gate valve. A low base pressure in the range of 10^{-7} Torr was achieved before film deposition, and a low working pressure of 5 mTorr was used, to limit the degradation of the films with presence of any trace amounts of oxygen impurities. The target to substrate distance is typically between 6-10 cm, and a negative bias is applied at the substrate to generate plasma and to limit the incorporation of oxygen atoms within the coatings. [51] Each of the targets, as well as the substrate was cleaned for 1 minute with Argon plasma before beginning the film deposition. Sputter cleaning allows good adhesion of the deposited film by eliminating any surface contamination. Rotation was applied to ensure uniform deposition from the magnetron gun involved in the depositions. The substrate heater was carefully calibrated and most of the experiments were carried out at 550˚C. At this temperature the set point programmed to the substrate holder device was 650˚C. Some depositions were also done at 350˚C, to determine the effect of temperature on the mechanical properties of the films.

Bias ranging from -50 V to -300 V was applied at the substrate to determine the effect of bias voltage on crystal structure and film hardness. The Ta target was loaded into the front magnetron, and 50 W DC power was applied. The N_2/Ar ratio was adjusted by controlling their flow rates. The N_2 percentage was varied from 2.5 % to 25 %. Deposition time was 1 hour for all films. A series of TaN thin films were deposited with varying N_2 content, varying bias and varying temperature.

3.2 Characterization of TaN Thin Films

Characterization techniques like XRD was used to study the phases present in the deposited films. The various properties of the films was determined by nanoindentation, optical profilometry, tribological wear testing, SEM-EDX.

3.2.1 XRD

X-Ray Diffraction was conducted to study the crystalline phases present in the films deposited at varying conditions. It was carried out on a Bruker D-8 Advance X-Ray Diffractometer with a Cu Kα radiation source and a wavelength of 1.54 Å. All scans were low angle detector scans. The acceleration voltage and filament current were set at 40 kV and 40 mA, respectively. A small step size of 0.03° and a dwell time of 2 seconds, with auto repeat were used to obtain high resolution scans.

3.2.2 Nanoindentation

Hardness tests were carried out on a Hysitron Ubi 1 Nanoindenter with a cube corner tip. The hardness and elastic modulus were recorded for 9 indentations (3x3 matrix). The average of the values was calculated. Depth controlled indentations were performed at less than 10% of the coating thickness, so that the hardness effect of the underlying substrate is avoided. The films were mounted onto magnetic disks using crystal bond.

3.2.3 Optical Profilometry

The thickness and surface roughness of the film were measured by a Veeco NT-9100 Optical Surface Profilometer. The thickness was measured by calculating the step height between the film and the non-deposited substrate using a 5X objective. Surface roughness, R_a uses the arithmetic average of the absolute values of the height of the sample to estimate the roughness of a surface. Due to presence of residual stresses TaN films have some curvature. The radius of curvature is measured by the profilometer. This value is then plugged in the Stoney's equation, to calculate the residual stress present in the films.

The equation below is the Stoney's Equation

$$\sigma_f = \frac{E_s d_s^2}{6(1-v_s)} * \frac{1}{d_f} * \frac{1}{R}$$

where E_s, d_s, and v_s are the Young's modulus, thickness, and Poisson's Ratio of the Si (100) substrate, respectively, d_f is the thickness of the film, and R is the delta radius of curvature between the Si wafer before and after film deposition.

3.2.4 Tribological Testing

Pin on disc experiments were performed on TaN films to determine their tribological behavior. A 6 mm alumina ball was used as a counter material and a force of 1N was applied. The test run was 100 m. Coefficient of friction and overall wear rate were determined. Wear rates of the films were determined by taking a number of 2-D profiles of the wear track using the optical profilometer. The area under each of the profiles was calculated, and the average value of three profiles was taken. The calculated area was multiplied by the circumference of the wear track to find the wear volume. The wear rate is further obtained by dividing the wear volume with the load applied and the sliding distance (mm^3/Nm).

3.2.5 SEM and EDX

The surface morphology and compositional analysis of the films were characterized by Hitachi S-3000N Variable pressure SEM with an attached EDS. A working distance of 15 mm with high vacuum setting and electron voltage of 20-25 keV was used to obtain images of the coatings.

Chapter 4

Results and Discussion

4.1 Introduction

TaN coatings are of significant interest because of their high hardness, high corrosion and oxidation resistance. However, they have not being explored as much as the well-known hard coating material TiN, because the TaN system unlike the TiN system forms a variety of compounds. Due to the complexity of the TaN system, the chemical and phase compositions of the TaN coatings, has been found to be critically dependent on deposition conditions for all techniques. [47, 48]

The TaN films were deposited and studied in order to determine, how phases of TaN change with varying deposition conditions and consequently its effect on hardness of films and other mechanical properties. The initial deposition conditions for TaN were similar to the conditions of TiSiN, which was then an ongoing project in the SaNEL lab. However, those particular deposition conditions resulted in shattering of the TaN films possibly due to high residual stress. The atomic percentage of Ta in TaSiN films was measured by XPS, which showed an increase of Ta atom percent with increase in power to the Ta target, as expected. The sputtering rate of Tantalum was nearly three times that of Titanium and the residual stress was as high as 5 GPa. Based on these results and literature

review, the power to the Ta target was decreased from 150 W to 50 W. The working pressure was kept low at 5 mTorr to discourage the presence of impurities in the chamber. The substrate bias was kept negative to avoid any oxygen impurities getting incorporated in the film. [39 - 42]

Effect of N_2 content on the phases present, mechanical properties like hardness and wear rate was explored. To determine the effect of the content of N_2 in the films, the percentage of nitrogen was decreased from 25% to 3%, at -100 V substrate bias, keeping other parameters constant. Effect of substrate bias on film properties like hardness was also studied, as this had not been previously explored before by many. Effect of varying temperature on films was analyzed. Rotation was set at 15 rpm for all films to ensure uniform deposition. Deposition conditions for TaN films are given in Table 4-1 and basic results are given in Table 4-2, which will be further discussed.

Table 4-1 Deposition Conditions for TaN films

Film	Substrate		Ta Target			Volumetric Flow Rate (sccm)		% N$_2$	T, ^{o}C
	Bias (V)	Current (mA)	Power (W)	Volts (V)	Current (mA)	Ar	N$_2$		
S100N25	-100	13	50	-320	183	18.75	6.25	25%	550
S100N15	-100	13	50	-294	200	21.2	3.75	15%	550
S100N10	-100	13	50	-289	206	22.5	2.5	10%	550
S100N7	-100	14	50	-290	200	23.25	1.75	7%	550
S100N5	-100	14	50	-286	205	23.75	1.25	5%	550
S100N3	-100	17	50	-266	50	43.5	1.3	3%	550

Table 4-1- continued

Film	Substrate		Ta Target			Volumetric Flow Rate (sccm)		% N$_2$	T, ºC
	Volt. (V)	Current (mA)	Power (W)	Volts (V)	Current (mA)	Ar	N$_2$		
S50N5	-50	13	50	-284	209	23.75	1.25	5%	550
S200N2.5	-200	19	50	-259	230	48.7	1.3	2.5%	550
S200N5	-200	16	50	-277	215	23.75	1.25	5%	550
S200N7	-200	15	50	-281	212	23.25	1.75	7%	550
S300N5	-300	17	50	-276	211	23.75	1.25	5%	550
S100N5 TEMP 350	-100	14	50	-274	214	23.75	1.25	5%	350
S200N5 TEMP 350	-200	16	50	-268	211	23.75	1.25	5%	350

Table 4-2 Basic Results of TaN films

Film	% N$_2$	Substrate Bias (-V)	Deposition Rate (nm/h)	Hardness (GPa)	Residual Stress (GPa)	Deposition Temperature (^{o}C)
S100N25	25%	100	490	22.36	1.95	550
S100N15	15%	100	493	25.88	2.72	550
S100N10	10%	100	523	26.133	1.84	550
S100N7	7%	100	613	34.45	1.03	550
S100N5	5%	100	590	35.5	0.27	550
S100N3	3%	100	516	37.19	1.51	550
S50N5	5%	50	635	31.27	0.137	550
S200N2.5	2.5%	200	556	34.4	4.33	550
S200N5	5%	200	500	37.83	4.52	550
S200N7	7%	200	562	33.23	3.38	550
S300N5	5%	300	435	38.23	3.94	550
S100N5 TEMP. 350	5%	100	663	24.24	0.25	350
S200N5 TEMP. 350	5%	100	550	33.79	3.70	350

4.2 Effect of Varying Nitrogen Content on Film Properties

The TaN films were deposited at 550°C, at 50 W power to Ta target and keeping the substrate bias constant at -100V. The parameter which was changed was the percentage of N_2. Effect of N_2/Ar ratio on crystal structure, hardness, residual stress, wear rate was studied.

4.2.1 Effect of Varying Nitrogen Content on Phases

The N_2/Ar ratio was decreased from 0.33 (25% N_2) to 0.029 (3% N_2) keeping other deposition conditions like substrate bias, pressure and temperature constant at -100 V, 5 mtorr, 550°C respectively. XRD was used to determine the crystalline phases present in the deposited TaN films. All the scans were taken at a low incidence angle of 5 degrees. Refer to figure 4-1. The formation of FCC TaN has been observed for flow ratios 25% N_2 to 7% N_2, with a textured film obtained at 7%, with FCC TaN(111) orientation. At 7% N_2, we can see other phases emerging at 2-theta equal to 38.3^{o}. The emergence of phases shows a transition from a dominant soft FCC phase to a mixture of phases. The emergence of phases other than the FCC phase explains the higher hardness of this film (7% N_2) as compared to those deposited at 15% N_2 and 10% N_2.
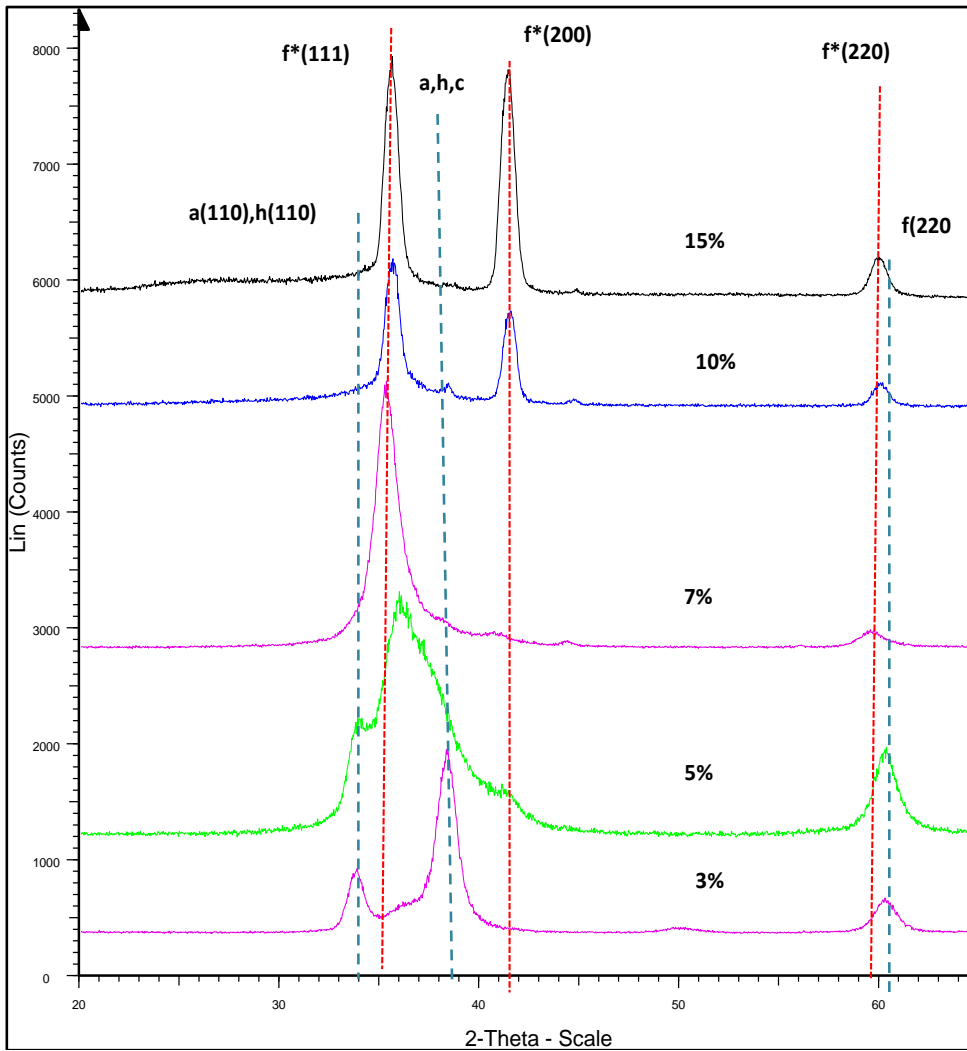
Notation used: a. Ta_4N orthorhombic base centre, f. $TaN_{1.13}$ FCC, c. $Ta_6N_{2.5}$ hexagonal, h. Ta_2N hexagonal, f* TaN FCC

Figure 4-1 Low Angle XRD Scans for TaN films deposited at a substrate bias voltage of -100 V and percentage of N_2 varying from 15% to 3%

With a decrease in the percentage of N_2 upto 5%, a broad peak is observed, which clearly depicts a mixture of phases, as shown in figure 4-2. Broadness of the peak might be due to change in grain size as well. The major phases at 5% N_2 are FCC $TaN_{1.13}$, with orthorhombic Ta_4N, hexagonal Ta_2N and hexagonal $Ta_6N_{2.5}$ still emerging. These phases explain the high hardness of this films as compared to other films which has only FCC phase present. At 3% N_2, the hard orthorhombic Ta_4N and hexagonal Ta_2N completely dominate, which further explains highest hardness of 3% N_2 film as compared to rest of the films. We cannot clearly say which amongst the two phases is present, because of the near 2-theta values for orthorhombic and hexagonal phases. These results depict that as we decrease the percentage of N_2, the hard orthorhombic and the hexagonal phase become dominant and at higher percentage of N_2, the soft FCC phase is the dominant phase.
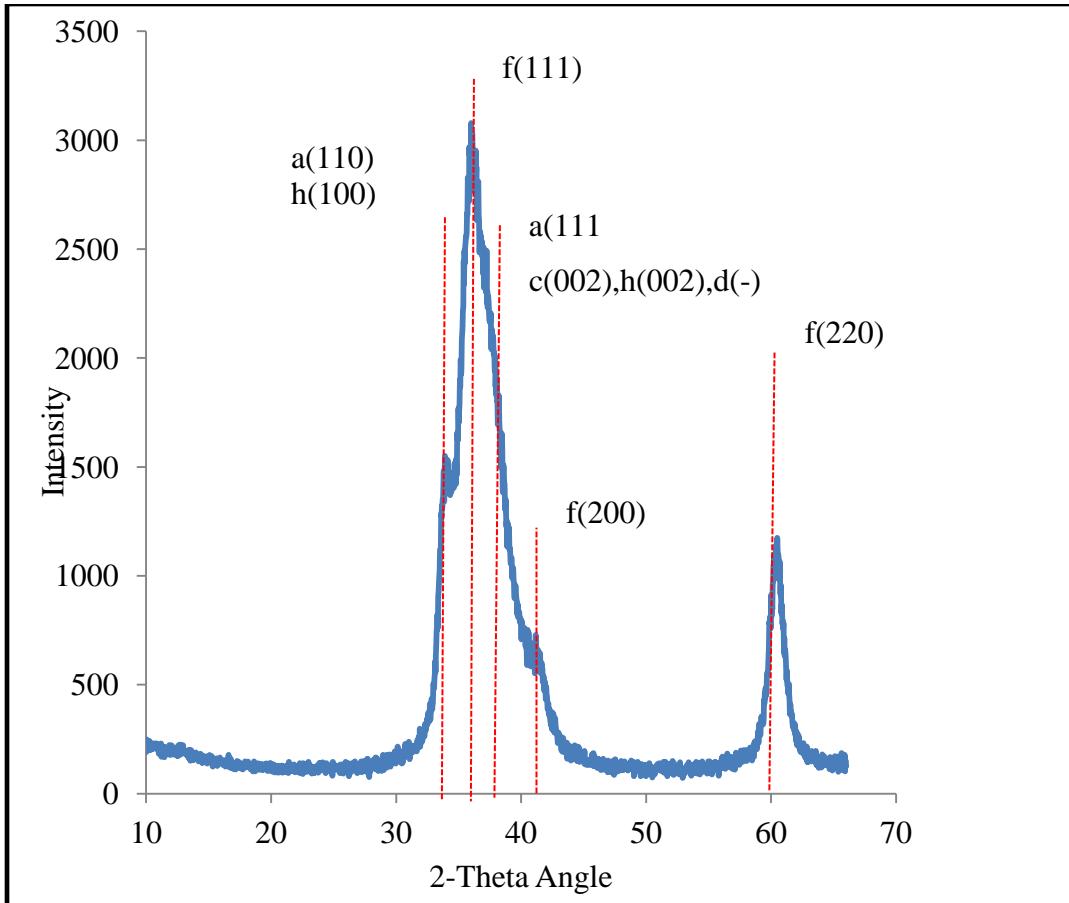
Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ FCC, c. Ta$_6$N$_{2.5}$ hexagonal, d.Ta$_3$N$_5$ orthorhombic, h. Ta$_2$N hexagonal

Figure 4-2 Low Angle XRD scan of TaN film deposited at a substrate bias of -100 V and 5% N$_2$.
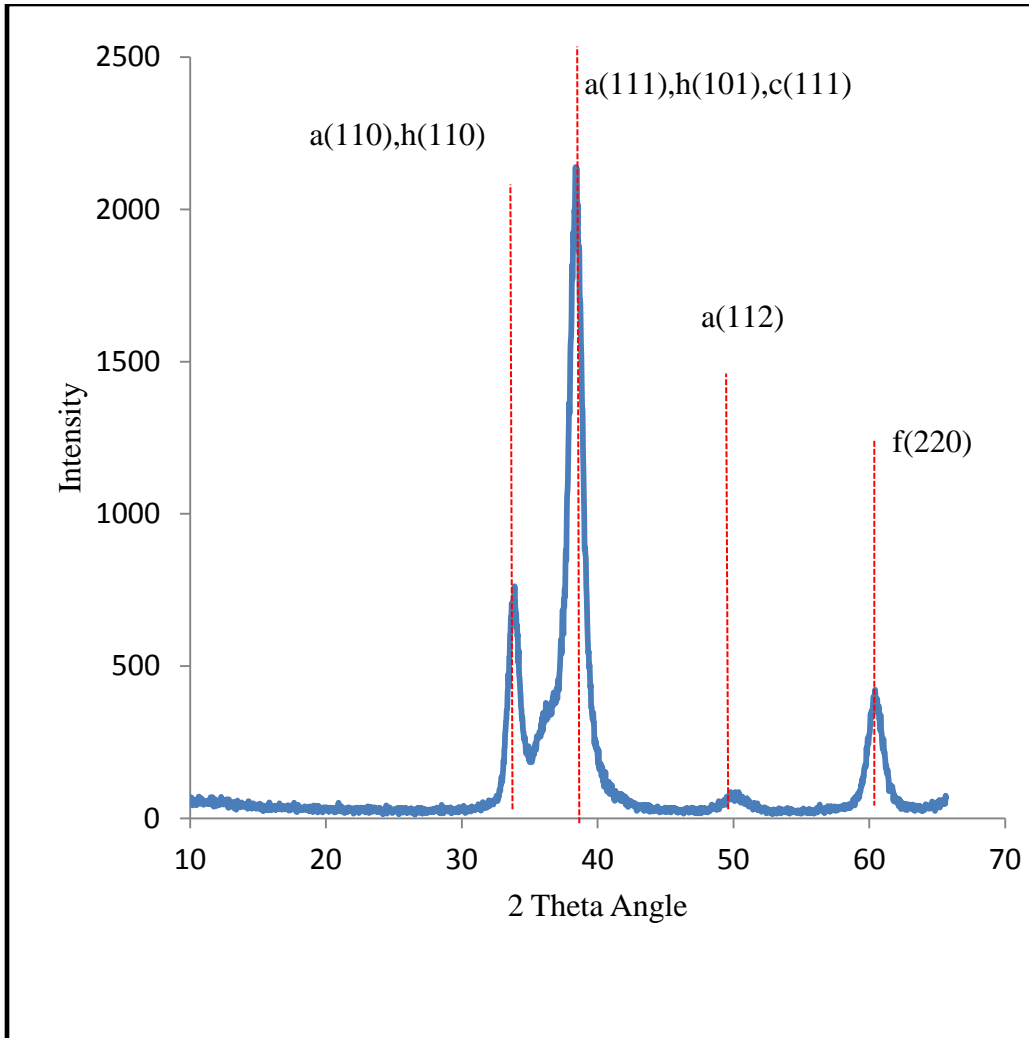
Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ fcc, c. Ta$_6$N$_{2.5}$ hexagonal, d.Ta$_3$N$_5$ orthorhombic, h. Ta$_2$N hexagonal
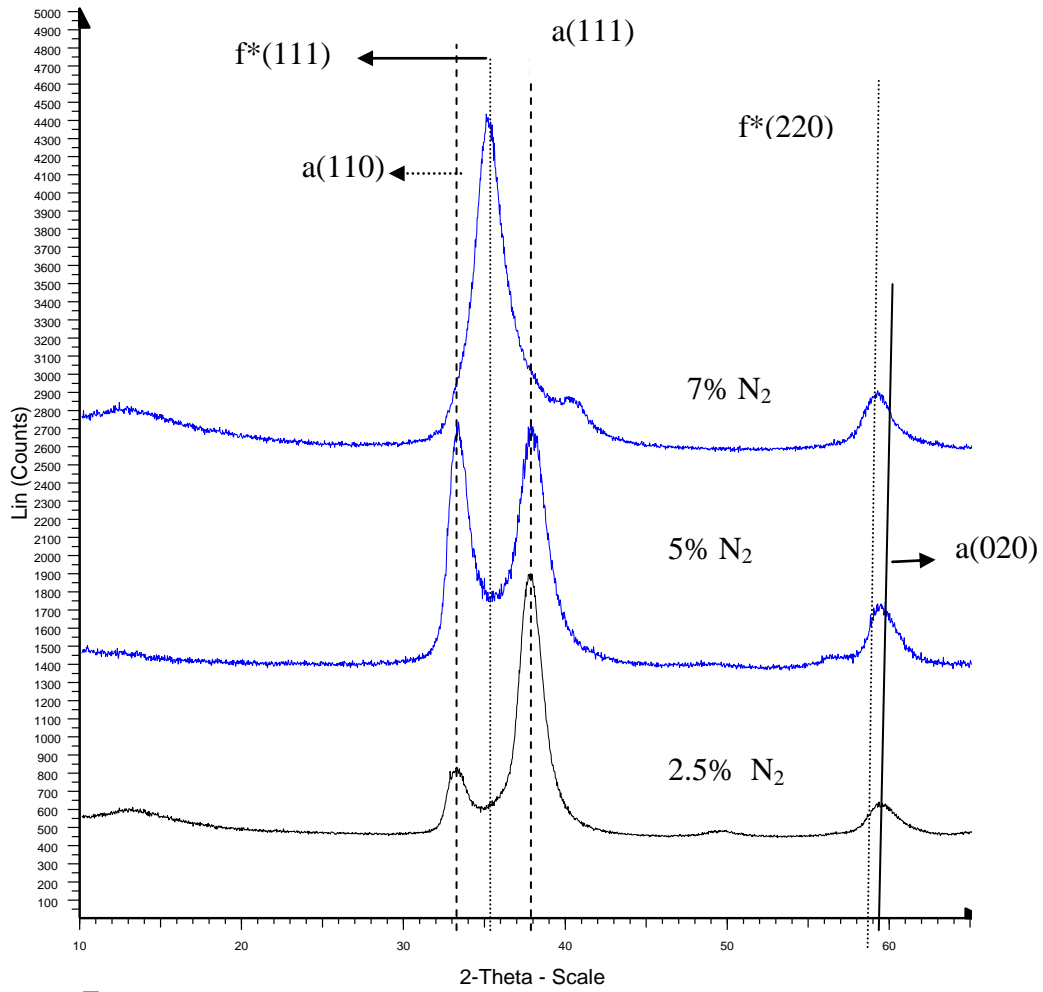
Figure 4-3 Low Angle XRD scan of TaN film deposited at a substrate bias of -100 V and 3% N$_2$

The same trend is observed at -200V substrate bias. As we decrease the N_2 percentage from 7% to 2.5%, the dominant phases change from FCC TaN to orthorhombic Ta_4N, as shown in figure 4-4. At 7% N_2, the main phase is FCC(111) TaN. Other phases which are still emerging are hard orthorhombic Ta_4N, hexagonal Ta_2N. This is also explained by the higher hardness of this film as compared to other FCC TaN films. At 5% N_2, the hard orthorhombic Ta_4N phase is the dominant phase. As we go on decreasing the percentage of N_2 to 2.5%, a textured film is obtained with Ta_4N orthorhombic (111) orientation. The hardness of the film with 2.5% N_2 and -200V substrate bias is 34.42 GPa. This film is less hard than the one deposited with 5% N_2 and -200V substrate bias, which had a hardness of 37.83 GPa. Although the crystal structure for both the films is same, a textured film obtained with 2.5% N_2 might be the reason for the decreased hardness. Residual stress for film with 2.5% N_2 and 5% N_2 is 4.33 and 4.52 GPa respectively.

Notation used: a Ta$_4$N orthorhombic base centre, f* TaN FCC

Figure 4-4 Low Angle XRD scans of TaN films deposited at a substrate bias of -

200 V and varying percentage of N$_2$

4.2.2 Effect of Varying Nitrogen Content on Film Hardness

As we can see in figure 4-5 the hardness of the films is increasing with decreasing N_2. While decreasing the percentage of N_2 from 25% to 10% at a substrate bias of -100 V, the dominant phase is still FCC TaN and the hardness is in the range of 20-26 GPa, which matches the results by Bernoulli, et al. [18]
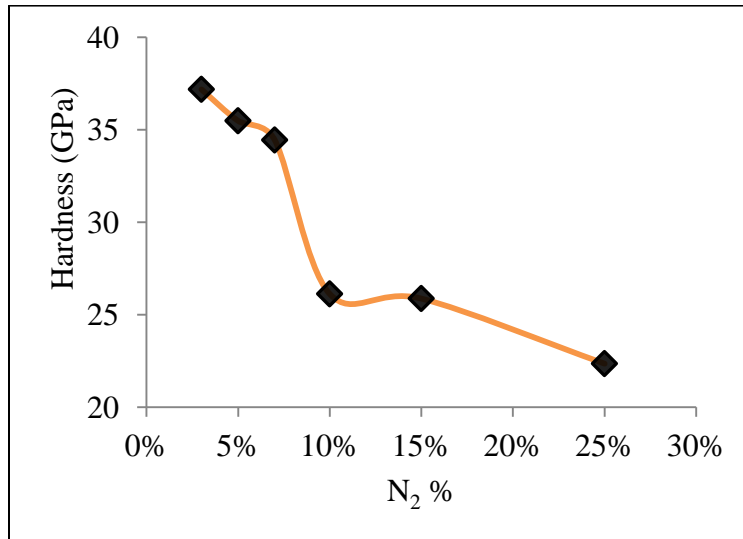
Figure 4-5 Variation in hardness of TaN films with changing percentage of N_2

At 7% N_2, hardness slightly increases, due to presence of other phases around 2-theta equal to 38.3°, which are reportedly the hard phases of TaN. [19] At 5% N_2, the broad peak is clearly visible, which has FCC, orthorhombic, hexagonal phases in it. Further decreasing the N_2 percentage, results in making these hard phases dominant and completely overtakes the less hard FCC phase. It seems that

orthorhombic Ta_4N phase should be contributing to the hardness of this film, along with other phases, as the orthorhombic phase is reportedly one of the hard phases of TaN with a theoretical hardness of 60 GPa.

4.2.3 Effect of Varying Nitrogen Content on Residual Stress

As explained in Chapter 3, we calculated the residual stress for all the films using the Stoney's Equation, after getting the value for the radius of curvature, using the optical profilometer. After deposition of TaN thin films, on the silicon wafers, there is some curvature induced, due to residual stress. Figure 4-6 shows the variation in the residual stresses for the TaN films with changing N_2/Ar ratio.
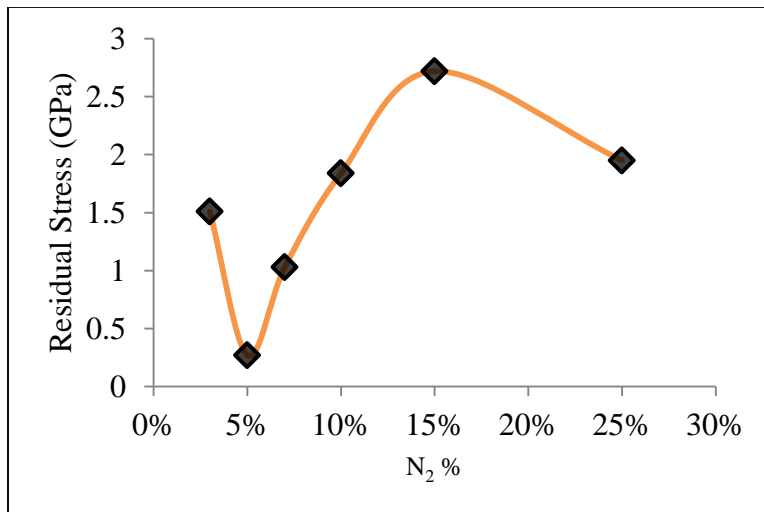

Figure 4-6 Variation in residual stress of TaN films with changing percentage of

N_2

It appears that there is a slight initial decrease in the experimentally calculated residual stress values starting from 3% N_2 to 5% N_2. This might be due to the mixture of phases present in the film at 5% N_2, which relieved the residual stresses present, as compared to the film with 3% N_2, in which only the hard phases were present. However, the trend after 5% N_2 shows that, as we increase the N_2 percentage the residual stress is increasing, till 15%. The increase in residual stress with increase in N_2 could be explained by the fact that, lesser amount of Nitrogen, would mean less nitrogen in interstitial spaces and thus less compressive residual stress.

4.2.4 Effect of Varying Nitrogen Content on Tribological Properties

Pin on disc experiment was performed on TaN films which were deposited at a substrate bias of -100V, temperature 550^oC, 50 W power to Ta target and 5% N_2. Another experiment was performed on a film deposited at -100V substrate bias, 550^oC, 50 W power to Ta and 3% N_2. As mentioned in chapter 3, Al_2O_3 balls were used for the wear tests. The hardness of alumina is approximately 20.5 GPa. Wear tracks were imaged in 2 dimensions. In both the cases i.e films with 5% and 3% N_2, the depth of the wear track was similar, around 0.2 μm and the wear track was irregular towards the bottom. However, in the film deposited with 5% N_2, the wear track was much wider than the wear track of the film deposited with 3% N_2. Refer to figure 4-7 (a), (b). In Figure 4-7 (b), a large peak can be seen towards the

edge of the wear track in the 2-D representation. This peak is actually a piece of debris present in the track. The film with 3% N_2 was harder than the one with 5% N_2. As we can see, the wear rate is much less for the film with 3% N_2. The values of the wear test are shown in table 4-3. Thus, we conclude that decreasing N_2 content increases the hardness of the films and it also makes them more wear resistant. Figure 4-8 (a), (b) shows the friction coefficient of the films deposited with 3% N_2 and 5% N_2, both at a substrate bias of -100V. The coefficient of friction for both the films was high between 0.8 - 0.9. We can conclude that due to the high hardness of the films, excessive wear occurred on the alumina ball, which resulted in the debris seen on the wear tracks and high coefficient of friction.

Table 4-3 Experimentally measured tribological properties as a function of N_2 content in the films

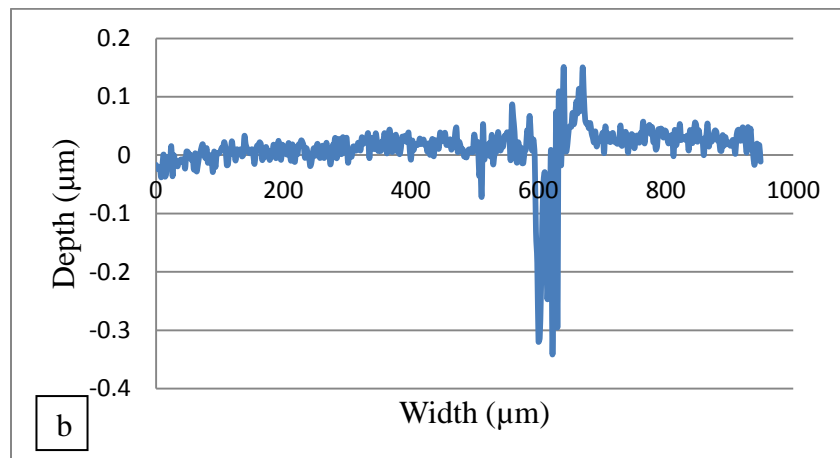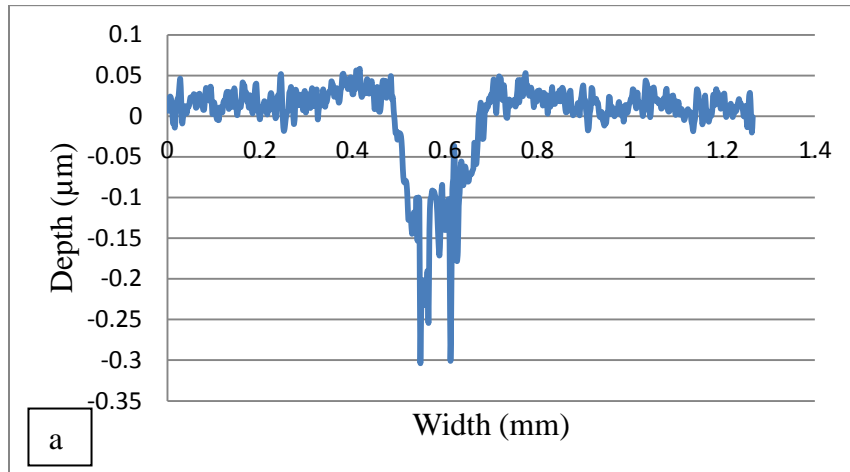| % N_2	Wear Track Radius (mm)	Wear Track Depth (μm)	Wear Track Width (mm)	Distance (m)	Wear Rate (mm^3/Nm)	Coefficient of Friction (μ)
5%	12	0.2	0.182	96	2.8E-05	0.9
3%	6	0.2	0.041	99	3.1E-06	0.9

Figure 4-7 2-D representations of wear track of TaN film deposited with (a) 5% N_2 and substrate bias -100 V, (b) 3% N_2 and substrate bias -100 V
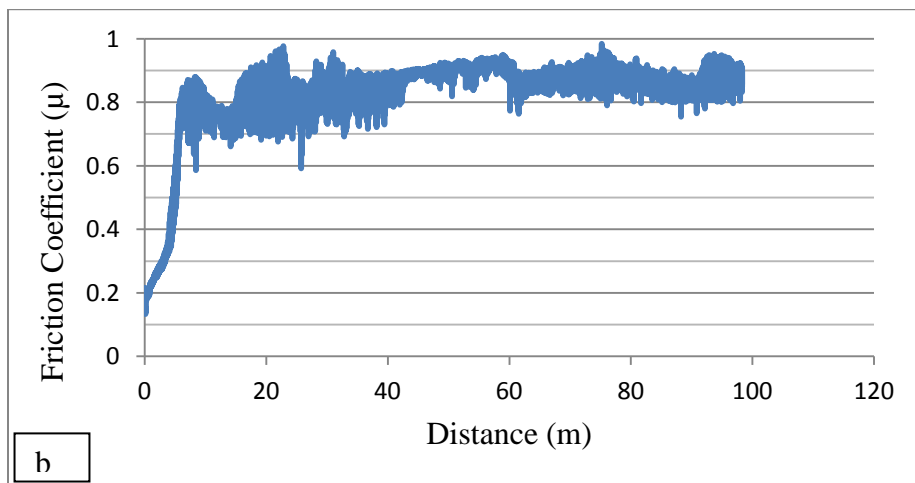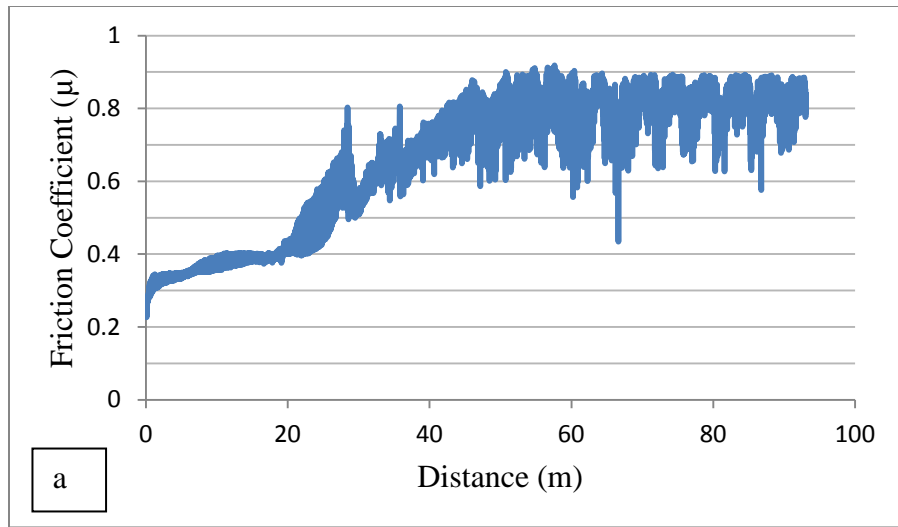
Figure 4-8 Friction Coefficient of TaN film deposited with (a) 3% N_2 and

substrate bias -100 V, (b) 5% N_2 and substrate bias -100 V

4.3 Effect of Varying Substrate Bias Voltage on Films Properties

During bias sputter deposition, energetic ions are bombarding the film surface, which result in altering the film properties. To determine the effect of changing substrate bias on TaN film properties, all the films were deposited at a temperature of $550^{o}C$, with 50 W power to Ta target, at 5% N_2 and the substrate bias was increased from -50 V to -300 V. The film properties which were investigated included crystal structure, deposition rate, hardness and residual stress.

4.3.1 Effect of Varying Substrate Bias Voltage on Deposition Rate

Energetic ions bombard the film during bias sputtering. As a result, the films are re-sputtered throughout the deposition process, making the films more planarized, which results in significantly decreasing the deposition rate. In addition to that, bias sputtering refines the microstructure and decreases the surface roughness of the films deposited using PVD. [43] Figure 4-9 shows the decrease in deposition rate with increase in bias. The surface roughness of the films was calculated using the optical profilometer and was around 10 nm for almost all our films.
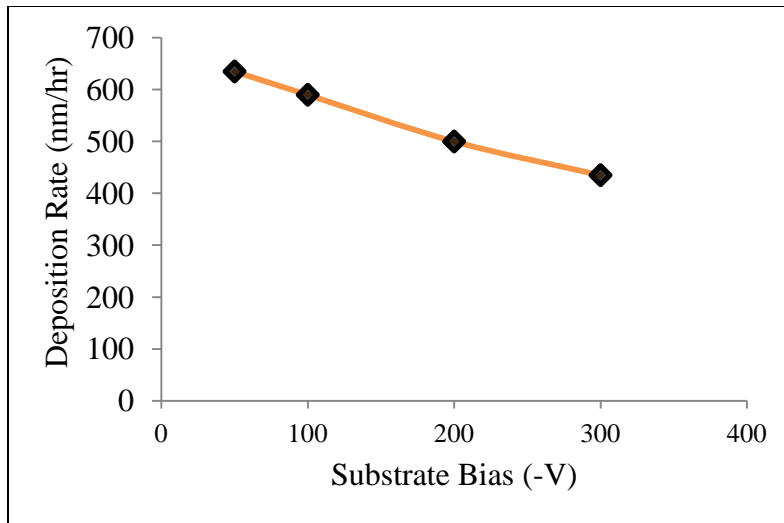
Figure 4-9 Variation in deposition rate (nm/hr) of TaN films with changing

substrate bias (-V)

4.3.2 Effect of Varying Substrate Bias Voltage on Crystal Structure

XRD was used to determine the crystalline phases present in the deposited TaN films. All the scans were detector scans at a low incidence angle of 5 degrees. The effect of substrate bias on the various TaN phases had not been analyzed till now. At 5% N_2 and at a substrate bias of -100 V, high hardness of 35.5 GPa was observed. As shown in figure 4-10, for this particular film, there is a formation of a broad, multi-phase peak. The result suggests that at these deposition conditions, a mixture of phases is present. The dominant phase at these deposition conditions is FCC $TaN_{1.13}$ which has its high intensity peaks at 2-theta 36.02, 41.8, 60.06. The high hardness of this sample, unlike other FCC TaN

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(where hardness is in the range of 20-24 GPa) samples is explained by the presence of other phases like orthorhombic Ta_4N, hexagonal Ta_2N, hexagonal $Ta_6N_{2.5}$, orthorhombic Ta_3N_5. The literature suggests that the orthorhombic Ta_4N phase is the hardest phase with a theoretical hardness of 60 GPa, [19] therefore it seems that orthorhombic Ta_4N phase should be contributing to the hardness of this film, along with other phases. Figure 4-11 shows the low angle XRD of the same film at high resolution.
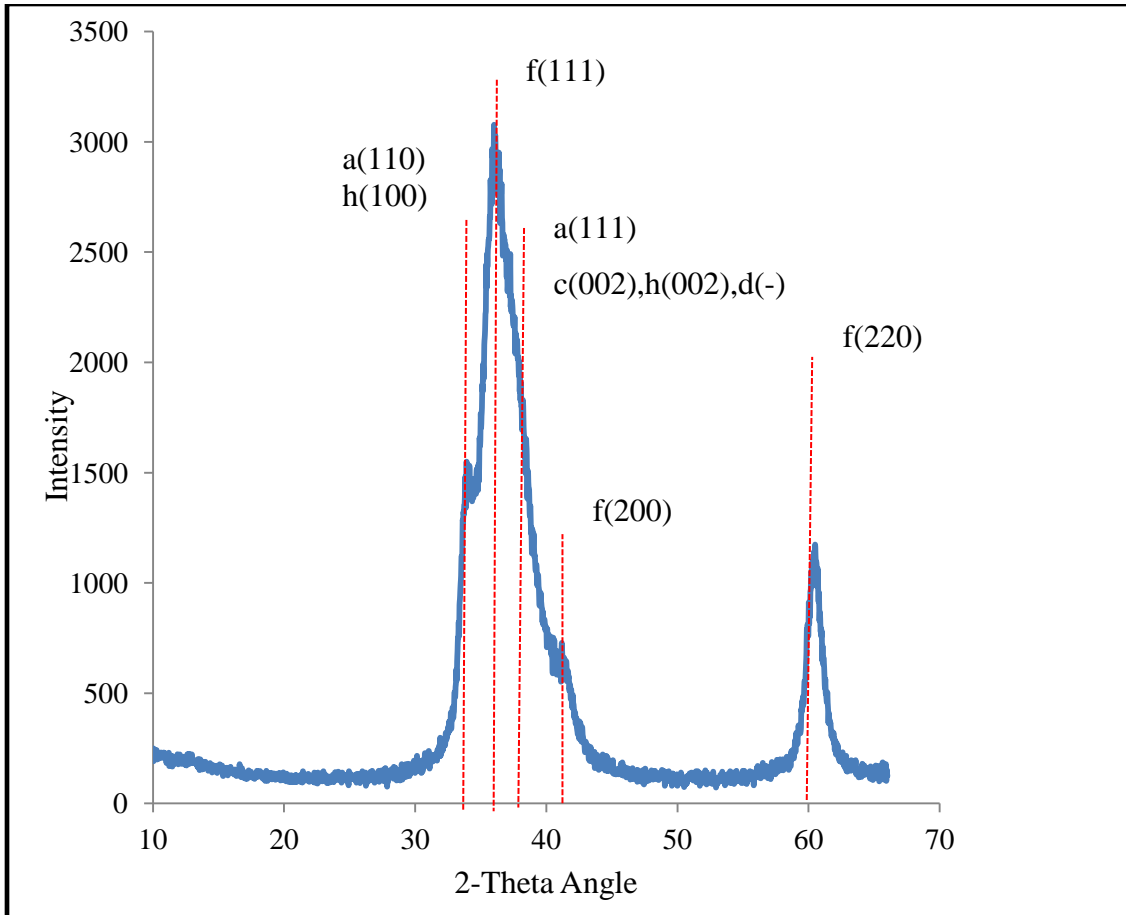
Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ FCC, c.Ta$_6$N$_{2.5}$

hexagonal, d.Ta$_3$N$_5$ orthorhombic, h. Ta$_2$N hexagonal

Figure 4-10 Low angle XRD scan of TaN film deposited with 5% N$_2$, temperature

550°C and substrate bias of -100 V.
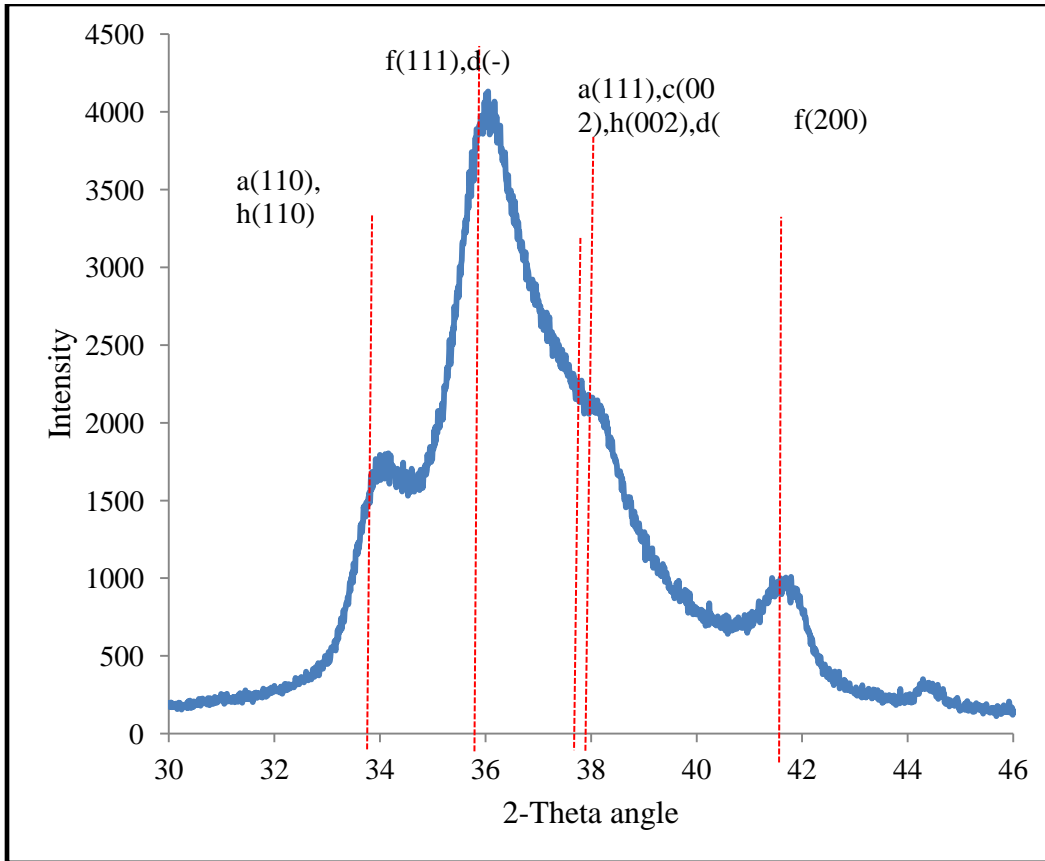
Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ FCC, c. Ta$_6$N$_{2.5}$ hexagonal, d.Ta$_3$N$_5$ orthorhombic, h. Ta$_2$N hexagonal

Figure 4-11 Low Angle XRD scan at high resolution of TaN film deposited with 5% N$_2$, temperature 550°C, substrate bias of -100 V

With increase in substrate bias from -100 V to -200 V, it is clearly seen that the FCC phase is no longer the dominant phase and the orthorhombic Ta$_4$N phase and the hexagonal Ta$_2$N phase are appearing and are the dominant phases.

As we go on increasing the substrate bias up to -300 V, the orthorhombic Ta_4N phase and the hexagonal Ta_2N are still the main phases present. It is noted that low Nitrogen content and high substrate bias are favorable for the formation of the orthorhombic phase.

Notation used: a. Ta_4N orthorhombic base centre, f. $TaN_{1.13}$ fcc, h. Ta_2N HEX

Figure 4-12 Low Angle XRD scan of TaN film deposited with 5% N_2, temperature 550^oC, substrate bias of -200 V.

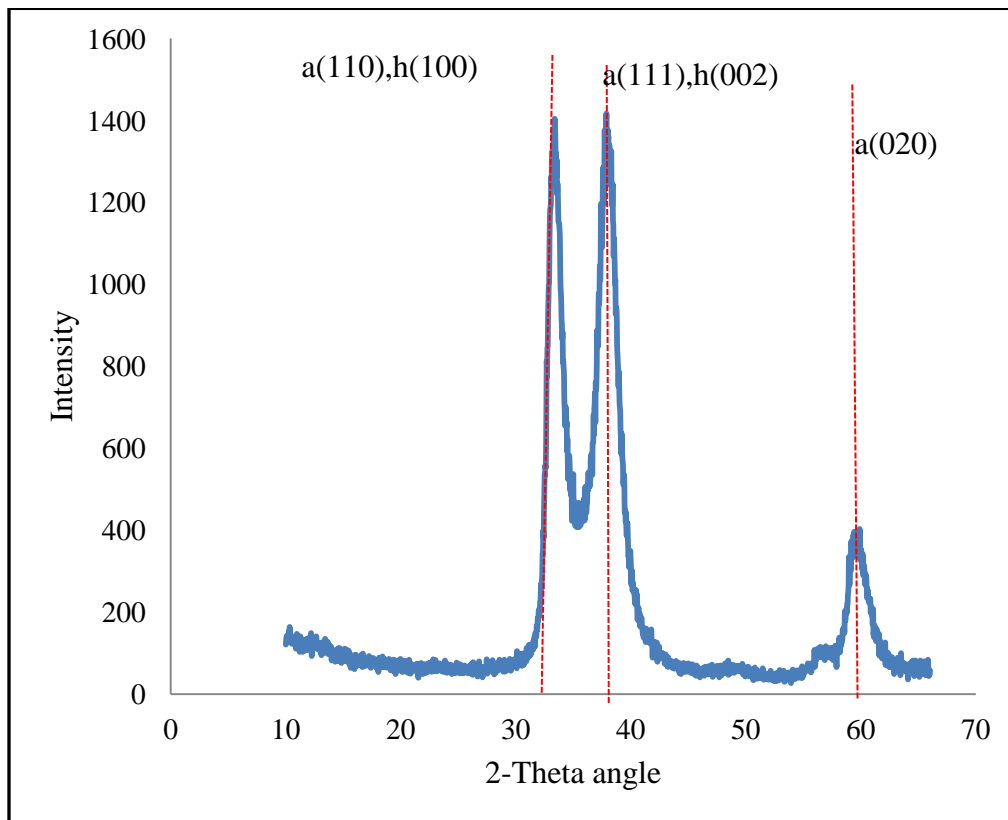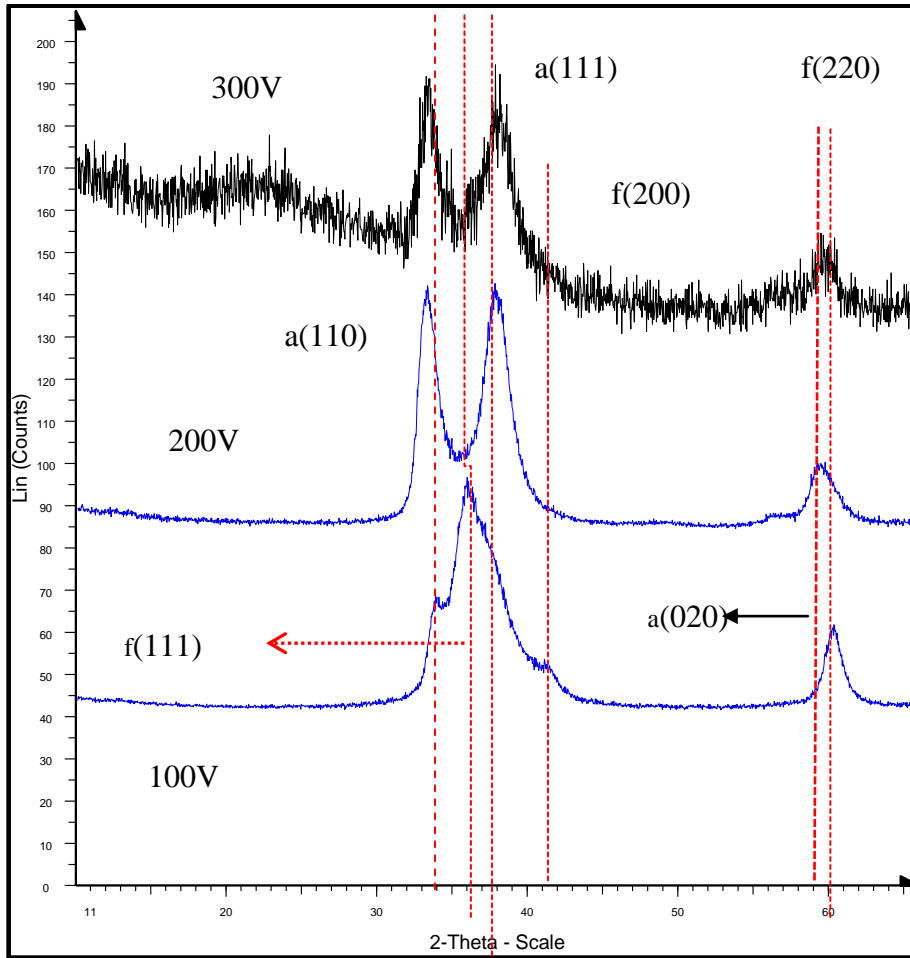Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ FCC

Figure 4-13 Low Angle XRD scans of TaN film deposited at temperature 550°C,

50 W power to Ta target, 5% N$_2$ and varying substrate bias of -100 V, -200 V and

-300 V

4.3.3 Effect of Varying Substrate Bias Voltage on Film Hardness

The bias sputtering refines the microstructure due to re-sputtering during deposition. Nanoindentation was performed on these coatings and the average hardness was obtained from 9 indentation points. As previously mentioned, upon increasing the substrate bias, the phases present changed from dominant FCC $TaN_{1.13}$ to orthorhombic Ta_4N and hexagonal Ta_2N. The presence of these hard phases was also confirmed by the fact that as the substrate bias was increased, the hardness of the film also increased with a value of 37.83 GPa in the film deposited at a substrate bias of -200 V and 38.23 GPa in the film deposited at a substrate bias of -300 V. Figure 4-14 shows the variation in hardness of the films with change in substrate bias.
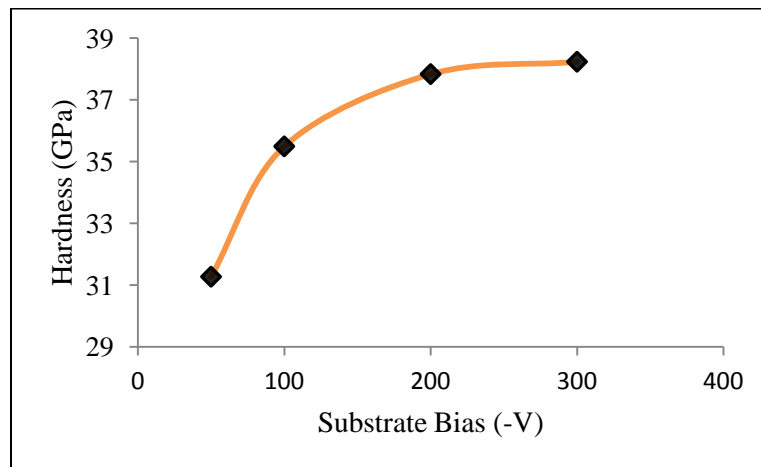
Figure 4-14 Variation in hardness (GPa) of TaN films with changing substrate bias.

The increase in hardness of the film deposited at -200V from the film deposited at -100 V is mainly due to change in phases, with the harder phases present at higher substrate bias. However, the reason for the increase in hardness from -200V to -300 V may be due to increase in residual stresses which temporarily increase the hardness of the film.

4.3.4 Effect of Varying Substrate Bias Voltage on Residual Stress

The residual stress was calculated from the Stoney's equation, after obtaining value of the radius of curvature of the deposited films, using the optical profilometer. Figure 4-15, shows the change in residual stress with varying substrate bias.

Figure 4-15 Variation in residual stress of TaN films with changing substrate bias

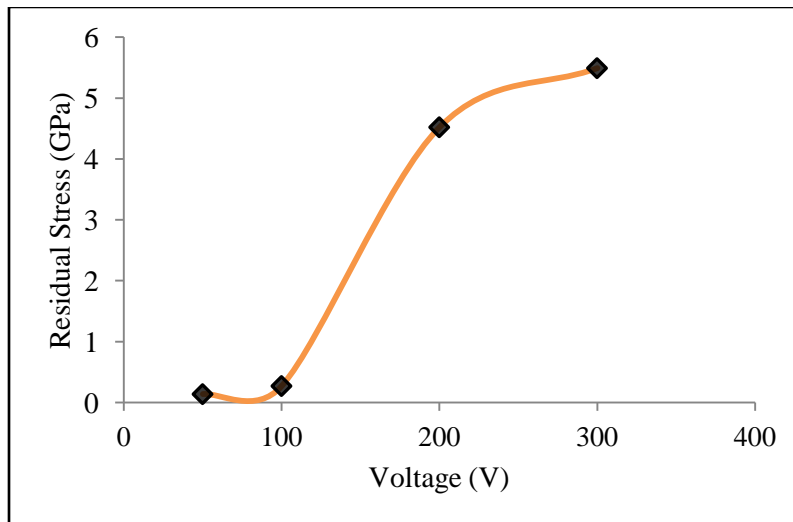The residual stress is very similar for substrate bias -50 V and -100 V, and then increases with increase in substrate bias. Residual stress is effected by stoichiometry, phase, film thickness and deposition conditions. [18] The increase in residual stress with bias can be explained by the fact that with increase in substrate bias, the film deposition rate decreased. The decrease in thickness with increase in substrate bias could be a reason for increased residual stress. The additional energy due to high bias, favors a particular orientation of atoms that would not be normally possible. This translates into residual stress and curvature is induced in the films after deposition.

4.4 Effect of Temperature on Film Properties

TaN films were deposited first at a substrate bias of -100V and -200V, both with 5% N_2 and at temperature 550^oC. To determine the effect of temperature on film properties, films were deposited, keeping other deposition conditions like substrate bias, power to Ta target, percentage of N_2 same, while the temperature was decreased from 550^oC to 350^oC for both -100V and -200V substrate bias.

4.4.1 Effect of Temperature on Deposition rate

Figure 4-16 shows the effect of temperature on the deposition rate of the films. As depicted, with decrease in temperature, the deposition rate increases, which suggests that at low temperature bombardment of ions is less. Decreased

temperature plays the same role as decreased bias as far as film thickness is concerned. With increase in temperature, ions are more energetic and bombard the surface of the substrate, resulting in re-sputtering of films throughout the deposition process, making the films more planarized, which results in significantly decreasing the deposition rate.
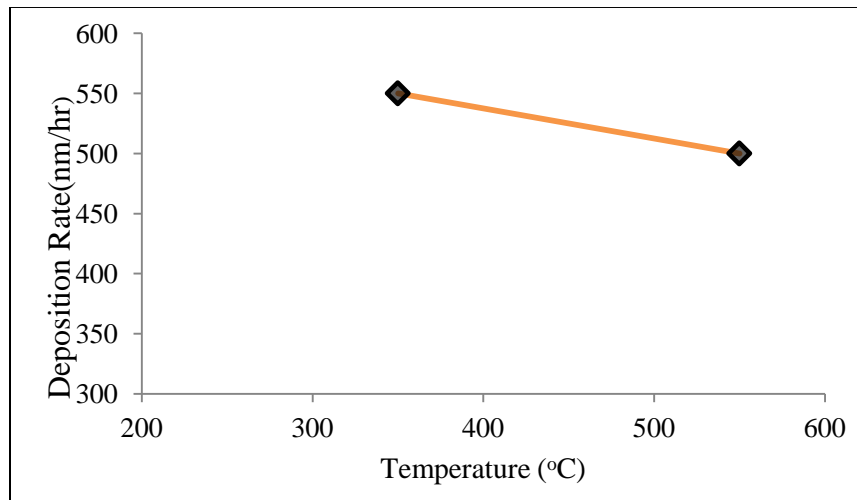
Figure 4-16 Variation in deposition rate (nm/hr) of TaN films with changing

deposition temperature

4.4.2 Effect of Temperature on Crystal Structure

Figure 4-17, shows low angle XRD of films S100N5 at $550^{o}C$ and $350^{o}C$. These films were deposited with 5% N_2 and a substrate bias of -100V. In the case of film deposited at a substrate bias of -100V and temperature $350^{o}C$, it seems that some but not enough reaction between Ta and N_2 has occurred. The high

intensity peak is of tetragonal Ta (330). However, the hardness of this film was higher than that of pure Tantalum, which suggests that there is a transition and TaN is also present. The FCC phase of TaN is present along with tetragonal Ta(330). The film deposited at a substrate bias of -100V and a temperature of $550^{o}C$ shows a broad peak suggesting a mixture of phases, with major phase being FCC $TaN_{1.13}$ and other phases being orthorhombic Ta_4N, hexagonal Ta_2N, thus indicating that the bonding between Tantalum and Nitrogen becomes more active at higher temperature. It can be proposed that enthalpy of formation for orthorhombic Ta_4N, hexagonal Ta_2N phases is higher than the FCC phase.
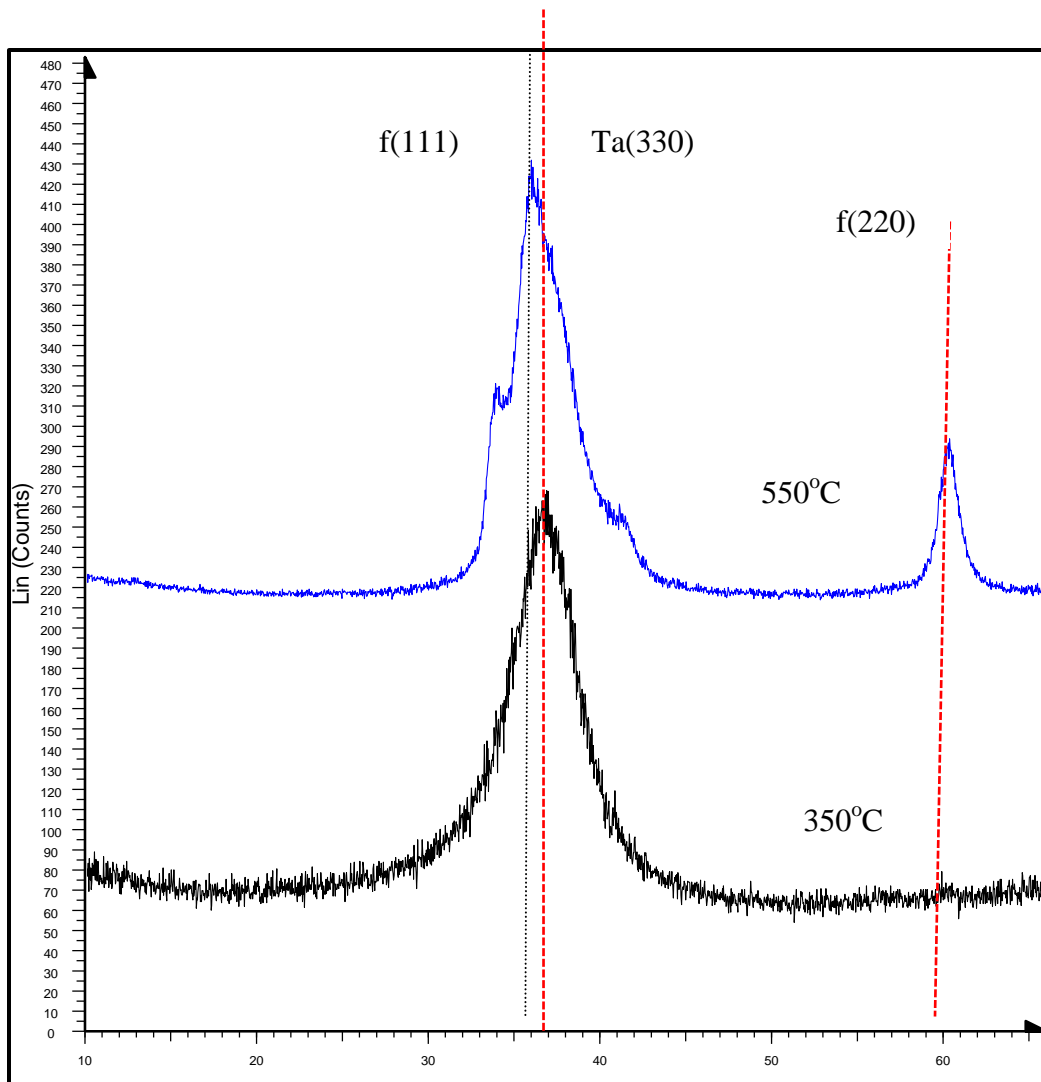
Notation used: Ta tetragonal, f. $TaN_{1.13}$ FCC

Figure 4-17 Low Angle XRD scans of TaN films deposited at a substrate bias of

-100 V and deposition temperatures $350^{o}C$ and $550^{o}C$

The same trend was observed at a substrate bias of -200V. Figure 4-18 shows low angle XRD of films S200N5, which were deposited with 5% N_2 and a substrate bias of -200 V, with temperature 350^oC and 550^oC. Major phase present at -200 V substrate bias and temperature 350^oC is FCC $TaN_{1.13}$, but the broad peak suggests presence of other phases as well. The peaks present in the film deposited at 350^oC around 2-theta equal to 33.35^o and 37.99^o have clearly emerged and are distinct in the film deposited at 550^oC, which also explains the higher hardness of the film deposited at high temperature.

However, hardness of the film deposited at 350^oC and -200 V substrate bias is higher than the film deposited at a temperature of 350^oC and a substrate bias of -100 V. The low angle XRD reveals a slightly broader peak at -200 V substrate bias and temperature 350^oC as compared to the one deposited at -100 V substrate bias and temperature 350^oC. We can conclude that if we apply a higher bias, it supplies the additional energy which is favorable for reaction to take place between Nitrogen and Tantalum.
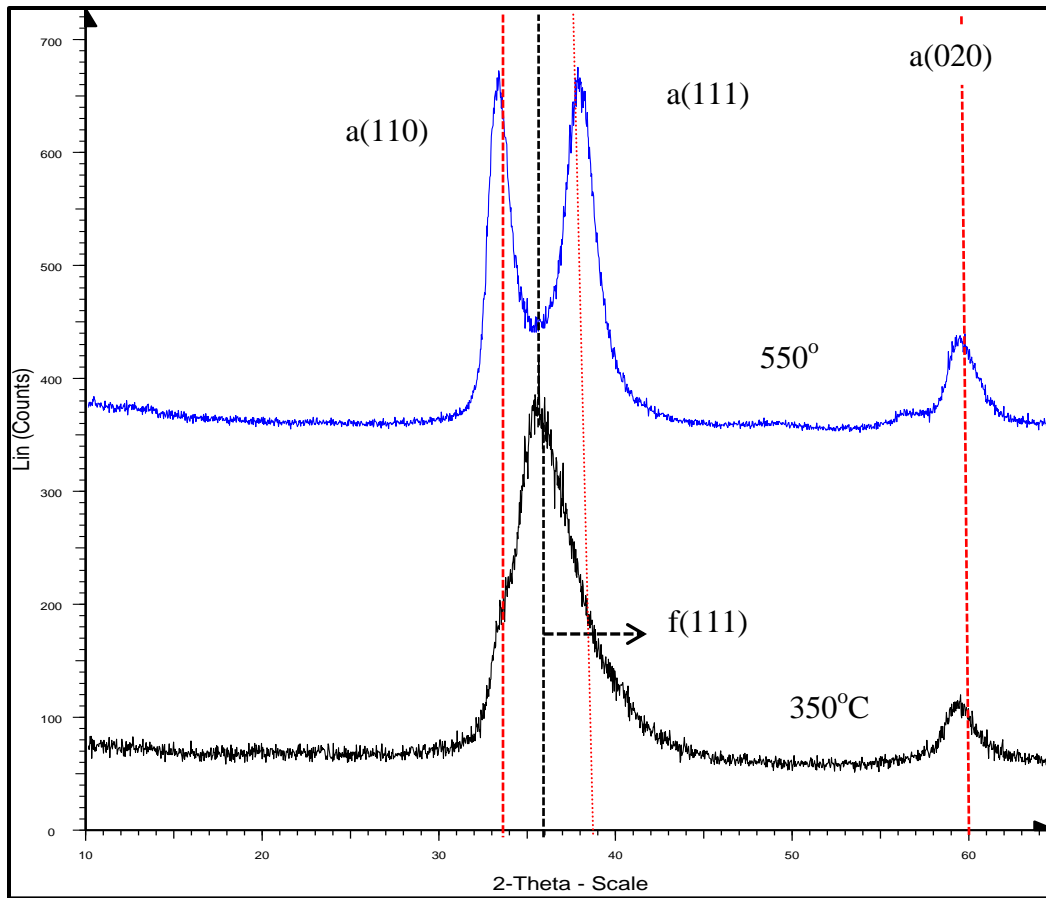
Notation used: a. Ta$_4$N orthorhombic base centre, f. TaN$_{1.13}$ fcc, h. Ta$_2$N hexagonal

Figure 4-18 Low Angle XRD scans of TaN films deposited at a substrate bias of -200 V and deposition temperatures 350°C and 550°C

4.4.3 SEM/EDX of Films Deposited at Varying Temperature

A Hitachi S-3000N Variable pressure SEM attached with EDX was used to obtain images of the surface morphology of the films and also assess the chemical content of the films. The films deposited at lower temperatures showed decreased atomic percentage of Nitrogen, as compared to those deposited at same conditions but higher temperature. This trend was observed both at a substrate bias of -100 V and -200 V. We can say with increase in temperature, additional energy is provided which is favorable for reaction to take place between Tantalum and Nitrogen.
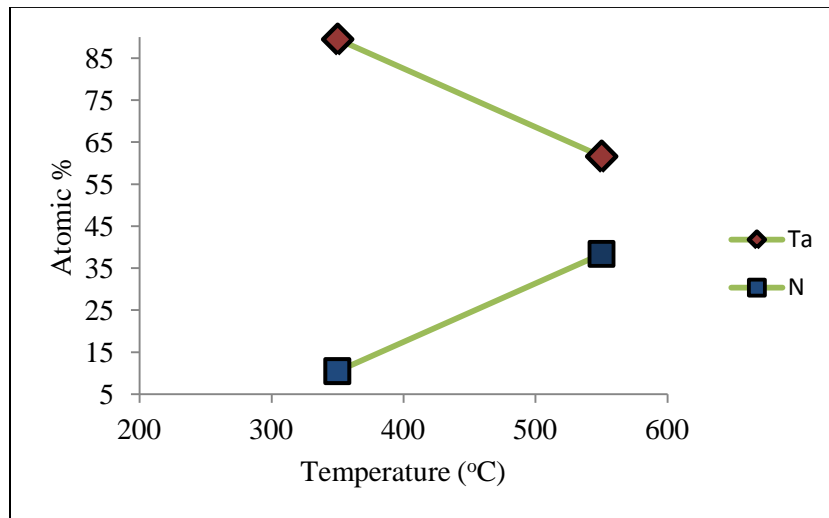
Figure 4-19 Variation in atomic % of Ta and N in TaN films at a substrate bias of

-100 V with changing deposition temperature
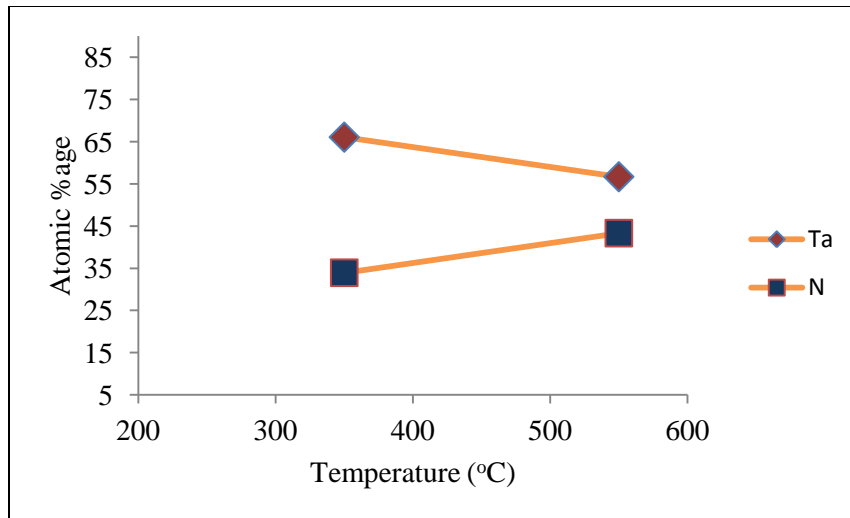
Figure 4-20 Variation in atomic % of Ta and N in TaN films at a substrate bias of

-200 V with changing deposition temperature

4.4.4 Effect of Temperature on Hardness

As mentioned in the previous section, low temperature (around 350°C) decreases the bonding between Ta and Nitrogen, and does not favor the formation of various hard TaN phases, thus hardness of TaN films decreases with decrease in temperature. However, increasing the substrate bias provides extra favorable energy to the atoms, making reaction between Ta and Nitrogen possible. Figure 4-21, 4-22 shows the variation in hardness with temperature.
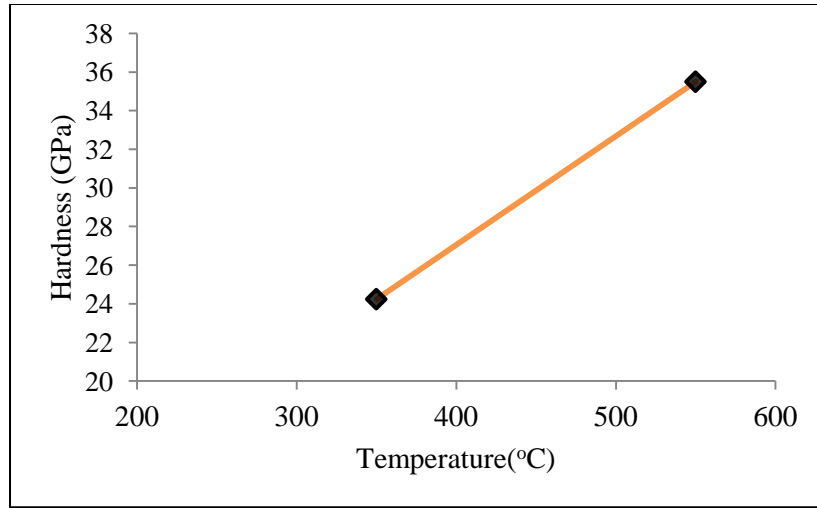
Figure 4-21 Variation in hardness of TaN films deposited at -100 V substrate bias

with varying deposition temperature
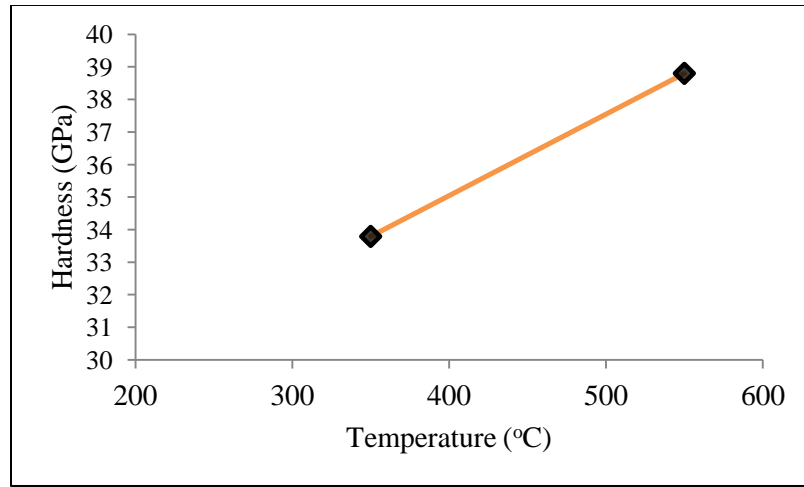
Figure 4-22 Variation in hardness of TaN films deposited at -200 V substrate bias

with varying deposition temperature.

The surface morphology of the films was analyzed by Hitachi S-3000N Variable pressure SEM. Figures 4-23 and 4-24 shows the surface micrographs of the films deposited at a substrate bias of -100 V and temperature 350°C and 550°C respectively. Figures 4-25 and 4-26 shows the surface micrographs of the films deposited at a substrate bias of -200 V and temperature and 350°C and 550°C. Figure 4-27 shows the surface morphology of film deposited at a substrate bias of -300V and temperature 550°C. As shown in the micrographs, all the films are smooth. We also had calculated the surface roughness of the films using the optical profilometer, which was around 10 nm for all films.
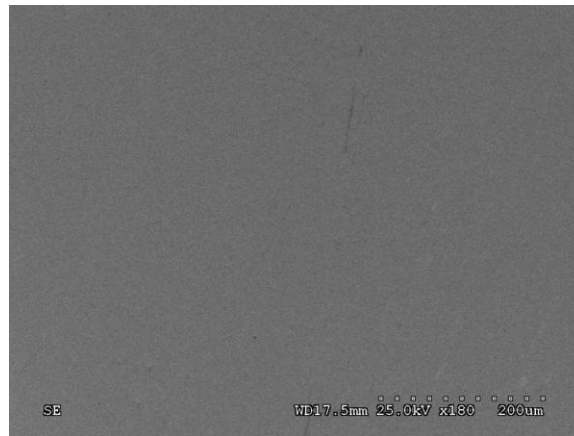
Figure 4-23 SEM of TaN film deposited at a substrate bias of -100 V, 5% N_2 and deposition temperature 350°C
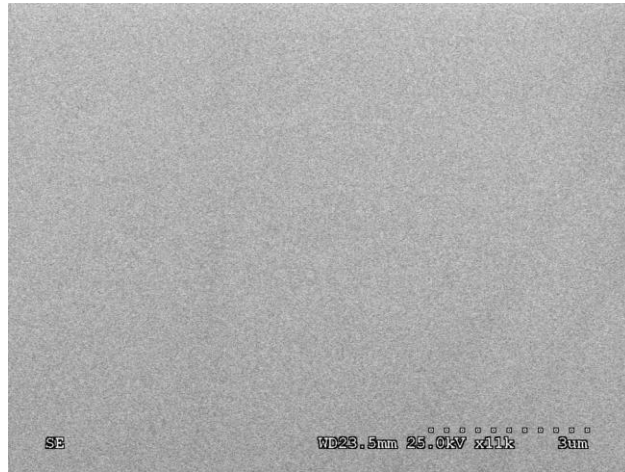
Figure 4-24 SEM of TaN film deposited at a substrate bias of -100 V, 5% N_2 and

deposition temperature 550°C

Figure 4-25 SEM of TaN film deposited at a substrate bias of -200 V, 5% N_2 and

deposition temperature 350°C
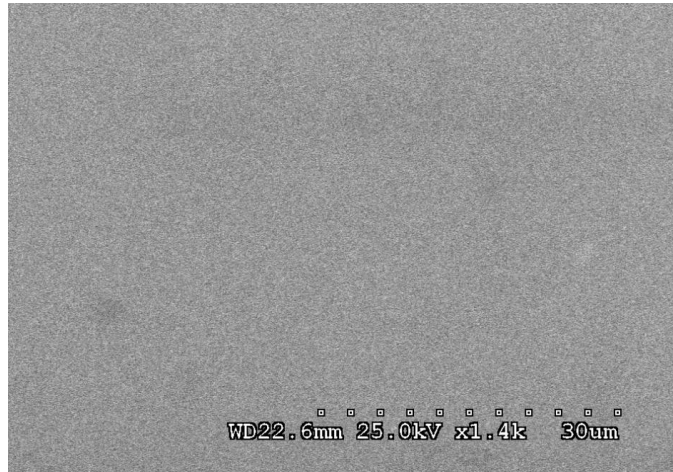
Figure 4-26 SEM of TaN film deposited at a substrate bias of -200 V, 5% N_2 and

deposition temperature 550$^{\text{o}}$C
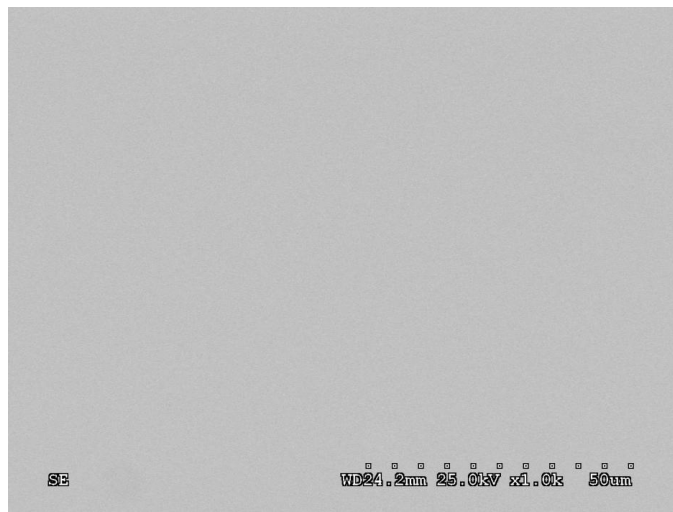
Figure 4-27 SEM of TaN film deposited at a substrate bias of -300 V, 5% N_2 and

deposition temperature 550$^{\text{o}}$C

Figure 4-28 and 4-29 shows the cross section of TaN film analyzed by Hitachi S-3000N Variable pressure SEM, deposited with 5% N_2 at a substrate bias of -200 V at lower and higher magnification respectively. The thickness of the film was around 500 nm. The cross section shows that the film is pretty uniform throughout.

TaN film

Silicon wafer

SE

WD13.3mm 20.0kV x5.5k   5um
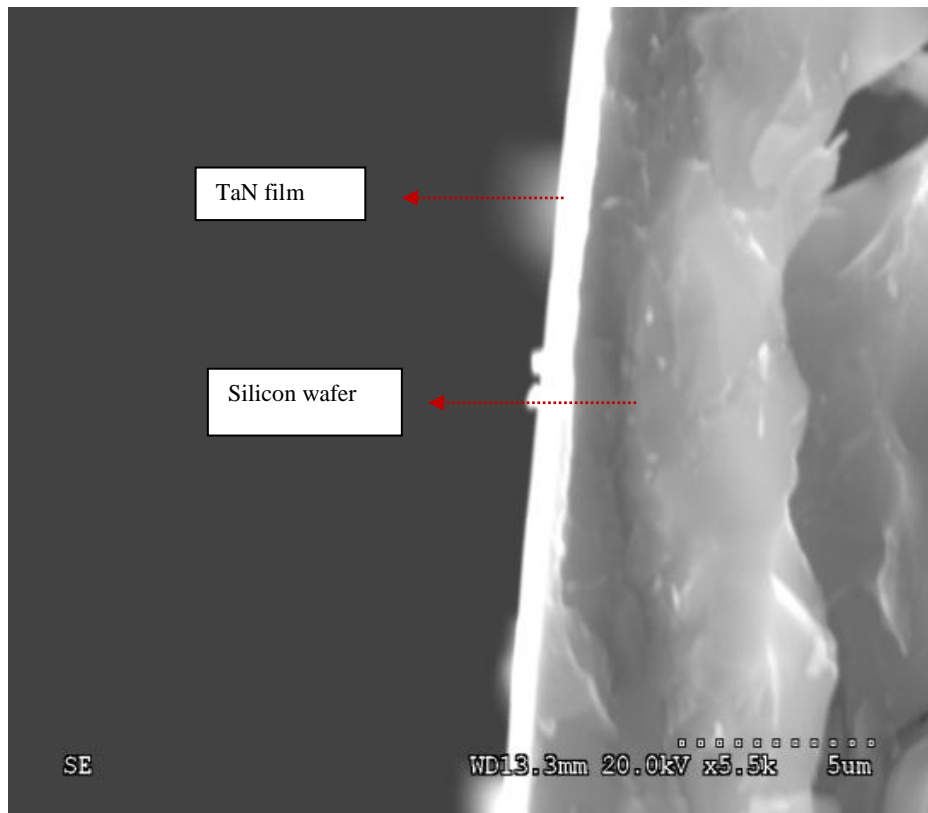
Figure 4-28 Cross section of TaN film at lower magnification
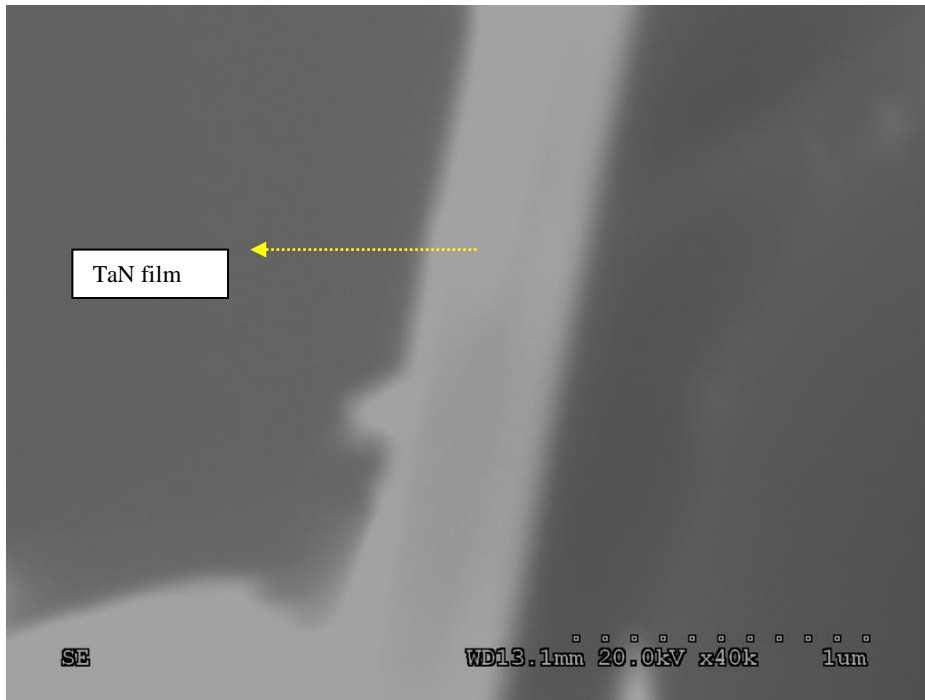
Figure 4-29 Cross section of TaN film at higher magnification

Chapter 5

Conclusions

TaN being a complex system, forms variety of phases depending on the deposition technique and growth conditions. TaN films were deposited using the PVD system in the SaNEL lab. In this research, the effect of deposition conditions like N_2/Ar ratio (percentage of Nitrogen), substrate bias and temperature on the phases and mechanical properties of the films was determined.

Films were deposited by varying the nitrogen percentage from 25% to 3%, keeping substrate bias constant at -100 V, power to the Ta target was 50 W, working pressure of 5 mTorr and temperature was maintained at 550°C. Another set of films were deposited at -200 V substrate bias, 50 W power to Tantalum target, working pressure of 5 mTorr, temperature 550°C and varying the percentage of N_2 from 7% to 2.5%. We found out that at a substrate bias of -100V, decrease in percentage of Nitrogen resulted in an increase in the hardness of the films with the highest value of 37.19 GPa obtained at 3% N_2. The films which had 25% - 10% N_2, had FCC TaN as the dominant phase. The hardness of all these films was in the range of 22-26 GPa, increasing with decrease in N_2. With further decrease in N_2 to 5%, a broad peak was observed, which indicated a mixture of phases. Upon further decreasing N_2 to 3%, the known harder crystalline phases had clearly emerged. The dominant crystal phases which were

present in our hard coatings were orthorhombic Ta_4N, hexagonal Ta_2N. The orthorhombic Ta_4N, hexagonal TaN has been reported as the known hard phases of TaN.

At a substrate bias of -200 V, the hardest phase was achieved at 5% N_2. The hardness of the film further decreased as we decreased the percentage of N_2 to 2.5%. At 5% N_2 and substrate bias of -200 V, the dominant peak is orthorhombic Ta_4N. On decreasing the percentage of N_2 to 2.5%, the dominant phase is still orthorhombic Ta_4N. However this film is textured, which could possibly be the reason for decreased hardness. The residual stress seemed to increase with increase in percentage of Nitrogen, possibly due to incorporation of nitrogen in interstitial sites which lead to larger compressive stresses.

The effect of substrate bias was studied. As we increased the substrate bias, from -50 V to -300 V, the hardness increased. Again, the dominant phases in our hardest coatings seemed to be orthorhombic Ta_4N. The orthorhombic phase was the most dominant at -200 V bias and -300 V bias, which also explains the high hardness of these films as compared to other films deposited at same conditions but with lower substrate bias. The slight increase in hardness of films deposited at a substrate bias of -300 V from the films deposited at substrate bias of -200 V is due to the increase in residual stress, which temporarily increases the

hardness of the films, because the phases present at both these substrate bias values are same.

With increase in substrate bias deposition rate decreases and residual stress increases. The residual stress was very less in the films deposited at -100 V substrate bias. Hardness of the films increases significantly as we increase the substrate bias, however residual stress also increases, which is not very desirable. The highest hardness which we achieved in the films deposited at -100 V substrate bias was 37.23 GPa with 3% N_2, with very less residual stress. Thus, in our case, hard phases of TaN are formed, with less nitrogen content and higher bias. However, higher bias also results in increasing residual stresses in the films.

The effect of temperature was also studied. Films were deposited at 350°C and 550°C keeping other deposition conditions constant at 5% N_2, 5 mTorr working pressure, 50 W power to Ta and substrate bias of -100 V. Same set of experiments was carried out at a substrate bias of -200 V. In both the cases, increase in temperature resulted in increase in bonding and significant reaction between Tantalum and Nitrogen. The increase in temperature resulted in decrease in film thickness, however no significant increase in residual stress was observed. Thus, we can expect significant increase in film hardness upon further increasing the temperature, with no large residual stresses getting induced in the films.

TaSiN has much better oxidation resistance as compared to TaN. Further work would involve incorporating Silicon in these films at different deposition conditions, focus being on improving the mechanical properties of the films especially increasing the hardness. Few experiments have been carried out in this regard. Although initial TaSiN films were lower in hardness as compared to TaN, the deposition conditions can be further manipulated to get much better hardness.

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