CHAPTER 1

INTRODUCTION TO TRANSITION METAL NITRIDES

During the past few years there have been growing demands for transition metal carbides, nitrides and boron compounds in the form of thin films. Owing to their physical and chemical properties they have been considered for a wide variety of technological applications, decorative coatings, optical coatings, metallurgy coatings, surface engineering coatings, optoelectronic devices including gate electrodes and interconnections in Very-Large-Scale Integration (VLSI), single-layer solar collectors and tribological coatings. Transition metal hard coatings are used to improve the materials surface properties and to increase their wear and corrosion resistance. However in the last decades, single/multi element nitrides have gained special consideration for improving the binary, ternary and quaternary nitride properties. The reason for importance in the form of thin films is the tailoring properties and the minimum thickness with small mass of the material concerned. Moreover, a proper tailoring of the micro and nano-structure of the layers can further enhance the feature, since dislocations and cracks can be neglected by using proper deposition techniques.

Transition metal nitrides/refractory hard metal coatings are getting considerable attentions because of their physical and chemical properties, which make them very attractive for advanced technological applications. They typically have superior mechanical properties, golden color, and used in various applications such as diffusion barriers in the microelectronic industry and protection layer used in the fission reactors. These materials are
traditionally used for the creation of corrosion- and wear-resistant coatings. Along with high melting temperatures (of at least 1500°C), the major criteria of choosing these materials are their thermodynamic stability at high temperatures and numerous individual properties playing an important role under specific operating conditions (hardness, wear resistance, thermal expansion, scale resistance, thermal resistance, corrosion resistance, electric resistance, etc.). These characteristics are responsible for the improvement of the operating parameters of titanium alloys and, in particular, their wear and corrosion resistance as a result of oxidation, nitriding, and carburization (Fedirko et al. 2006).

1.1 TRANSITION METAL NITRIDES

Generally, transition metal nitrides comprise of Titanium Nitride (TiN), Zirconium Nitride (ZrN), Chromium Nitride (CrN), Vanadium Nitride (VN), Niobium Nitride (NbN), Tantalum Nitride (TaN) and Tungsten Nitride (WN) and so on. Each of these in thin film form has different properties and microstructures which depend on the deposition process. Even we find the same material which will have different color with variation in nitrogen content. Normally transition metal nitrides are yellow, brown and gray in color with face centered cubic structure. Most of the metals given above have very high melting point and are stable at room temperature. Especially TiN, ZrN and TaN having the melting point around 2000-3000 °C was widely used as high temperature coating. The mechanical properties like high hardness and Young’s modulus has been widely used as super hard coating material.

1.1.1 Properties of Transition Metal Nitrides

Transition metal Nitrides are ideal for various technologically important applications because of their
High melting points
• durability
• Extreme hardness and brittleness
• Good wear resistance
• Good thermal and electrical conductivity
• high refractive index
• low optical losses
• High density
• High strength
• High fracture toughness
• Excellent corrosion resistance
• Very refractory
• High maximum service temperature – up to 2890°C
• Coefficient of thermal expansion
• Modulus of elasticity similar to steel
• Lowest electrical resistivity
• Low coefficient of friction
• Higher oxidation resistance at elevated temperature
• Chemical inertness
• Ionic electrical conduction etc.,

In transition metal nitrides, like Titanium Nitride (TiN) is the most useful materials, used as protective coatings, high hardness, wear resistance and thermal stability. The optimization of the coating structure can then improve the mechanical features of the coating, for example through the use
of a multilayer structure made of thin layers (100 atomic layers or less) of different materials. In this kind of structures, the atoms near the interfaces between two layers are displaced from their normal lattice positions and their strain energy is proportional to the shear modulus of the material, given by the ratio of shear stress to the shear strain. When a dislocation moves along a material, an energy barrier is encountered at the interface between a layer with a lower shear modulus and a layer with a higher shear modulus. As a consequence, in a multilayer structure the propagation of dislocations and cracks can be strongly reduced, thus increasing the resistance of the structure. Out of these materials Titanium Nitride (TiN) so called binary nitride is chosen in this work for preparation in the form of thin film and characterization.

1.1.2 Material Properties of Titanium Nitride (TiN)

TiN coating has been studied by researchers due to its variety of application in various fields. Titanium Nitride films have attracted considerable attention not only from fundamental scientific interest but also from practical point of view for growing applications in many industries. Due to its high wear resistance and corrosion resistance, it is used as the premier material for thin protective coating in order to improve the surface properties of some metals/materials. It is also used as an antireflective coating and as a diffusion barrier in the microelectronics industry. Titanium Nitride also exhibits a brittle behavior which can be a liability in its use as thin coating materials (Lala et al. 2001). TiN thin films have been serving the industry as anti-wear, anti-corrosion and decorative coatings or as diffusion barriers for more than 20 years. The significant and widespread availabilities of TiN films mainly own to their remarkable physical and chemical properties including high hardness, high melting point, chemical inertness, good thermodynamic stability, enhanced wear and corrosion resistance (Mori et al. 1999).
### 1.1.3 Properties of TiN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>TiN</td>
</tr>
<tr>
<td>Color</td>
<td>yellow-brown crystals</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Face centered cubic, cF8</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Range of Composition</td>
<td>TiN&lt;sub&gt;0.6 - 1.1&lt;/sub&gt;</td>
</tr>
<tr>
<td>Coordination geometry</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>4.24 Å</td>
</tr>
<tr>
<td>Surface Micro-Hardness</td>
<td>2400 HV</td>
</tr>
<tr>
<td>Specific heat</td>
<td>37 J/mol.K</td>
</tr>
<tr>
<td>Electrical Resistivity (bulk)(µohm.cm)</td>
<td>25 µ Ω·cm</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td>9.4 X 10&lt;sup&gt;-6&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Young's modulus (GPa)</td>
<td>590 Giga Pascals</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>612 GPa</td>
</tr>
<tr>
<td>Poisson’s Ratio</td>
<td>0.25</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>0.5 – 0.9</td>
</tr>
<tr>
<td>Hall constant</td>
<td>6.7 x 10&lt;sup&gt;11&lt;/sup&gt; m&lt;sup&gt;3&lt;/sup&gt;/C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>19.2 W/ (m&lt;sup&gt;0&lt;/sup&gt;C)</td>
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### 1.1.4 Physical Constants of TiN

<table>
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<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol.)</td>
<td>61.87</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.22</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>4.506</td>
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</table>
## Crystal Structure, Phase Diagram and Band Structure of TiN

TiN, crystallizes in the rocksalt structure (Fm3m) with a lattice parameter of 4.24 Å for the stoichiometric material. The close packed structure consists of FCC Ti sub-lattice with N filling all octahedral sites. This is due to the relatively small size of the N atoms compared to Ti as shown in Figure 1.1. To accommodate the interstitial nitrogen, Ti must transform from a bcc structure to fcc, and N₂ must decompose to atomic nitrogen 2N. TiN is indicative of an increase in the number of valence electrons from Ti to TiN. N is responsible for the increase in valence electrons. The largely metallic nature of TiN is also clearly shown by the TiN band structure, shown in Figure 1.2. Metallic bonding is a general characteristic of the interstitial nitrides (such as Ti, V, Zr, Nb, Hf and Ta nitrides), which all exhibit high electrical and thermal conductivity. Many researchers have reported that, TiN₁₋ₓ, showing an increase in resistivity with decreasing nitrogen fraction. The interstitial nitrides are stable over wide compositional ranges, generally with extensive vacancy concentrations on non-metal sites, and to a lesser extent on metal sites. Generally, N vacancies are seen predominantly for nitrogen fractions less than 1, while Ti vacancies are seen predominantly for nitrogen fractions greater than 1. The color of TiN also varies strongly with composition; with increasing nitrogen content the color changes from a titanium grey to light yellow (Ti₂N) to golden (TiN) (Patrick R LeClair1998). The phase diagram of TiN is shown in Figure 1.3. The TiN is rather complex due to the high solubility limit of nitrogen in both hexagonal α-Ti and cubic β-Ti phases.

### Melting Point (°C)  2930 °C

### Superconducting transition temperature  5.6 K

### Magnetic susceptibility  38 x 10⁻⁶ emu/mol

### Soluble in water  Insoluble
It results in α-Ti has a large range of existence going up to 25 at% of N. At high concentration, one obtains a NaCl-type structure called δ – TiN$_x$, where $x$ lies in between 0.5 to 1. Another tetragonal structure called ε – Ti$_2$N exists in atomic% of N. At high temperature above 1153 K, tetragonal phase called δ’- TiN$_x$, with $x$ varying between 0.50-0.61 (Ashok et al. 2009).

(Source: https://en.wikipedia.org/wiki/Titanium_nitride)

**Figure 1.1 Crystal Structure of Titanium Nitride**

(Source: Patrick R. LeClair 1998)

**Figure 1.2 Phase diagram of TiN**

(Source: Patrick R. LeClair 1998)
Titanium Nitride (TiN) exhibits the characteristic properties of covalent compounds such as materials with thermodynamic stability and high hardness number, and of metals such as good thermal and electrical conductivities. Due to these unique properties, TiN is an important material in the advanced metallization area for ultra-large-scale integrated circuits and in advanced surface protective coating area for steels (Katsuhiro Yokota et al. 2000). TiN films are used as a diffusion barrier material between Cu conduction lines and Si substrates for ULSI circuits, and as a gate material of MOS-FET devices. TiN films as gate electrodes with lower resistances were deposited on Si wafers at 900–1100°C (Katsuhiro Yokota et al. 2006).

Titanium Nitride (TiN) possesses a unique and interesting array of properties. For example, its high hardness, wear and corrosion resistance has made it useful for coating high speed steel cutting tools, while its high
electrical conductivity and diffusion barrier properties have led to its employment in semiconductor metallization schemes and thin film resistors. Furthermore, TiN films have been used decoratively for cosmetic artificial gold surfaces, and its high infrared reflection has made it useful for selectively transparent films (‘heat mirrors’), solar absorbers for high temperature use, and energy-saving window coatings (LeClaire et al. 2000). Due to their attractive properties, TiN coatings have been extensively used in various fields of application. This nitride of a transition metal has a high melting point, a high hardness value, advantageous optical properties and metallic conductivity. Coating of cutting tools for increasing wear resistance is probably the best known application. More specific examples of TiN utilization include diffusion barriers for semiconductors or filtering by ultra-fine particles. TiN coating on glass is also popular for the production of decorative panels in architecture or solar glass in automotive industry. The reflected colors are silver, blue and gold whereas transmitted ones are brown and grey (Straumalet al. 1999). The mechanical durability of thin films is of much importance for coated products and is well known to be influenced by the mechanical and tribological properties of thin films (adhesion strength, internal stress, hardness, frictional resistance of the surface, etc.). Although there are a lot of studies on the mechanical properties of thin films deposited on glass, investigations have been limited from the viewpoint of geometry of the coating system (Suzuki 1999).

Applied as a thin coating, TiN is used to harden and protect cutting and sliding surfaces and as a non-toxic exterior for implants. The motor racing industry has been a major user of nitride titanium components, with successful applications on valves, and valve gear, connecting rods, bearings, hubs and other sliding and wearing surfaces, high corrosion resistance and good oxidization resistance.
Different versions of this method find application in producing nitride films for solid-state microelectronics and other technological applications: barrier layers in multilayer contact systems of integrated circuits; surface-hardening, anti-wear, and corrosion-resistant coatings; electron emitters and cathodes for thermionic converters; coatings for orthopedic applications; and others.

Titanium Nitride (TiN) is widely used in cemented carbides such as cermet’s and electrodes in electrochemical capacitors because of its high wear resistance and good thermal stability associated with high hardness and high corrosion resistance (LIU Fei et al. 2011). Titanium and its alloys have low density, high strength, high fatigue resistance and high chemical stability. These properties are very useful for many applications in different fields, such as biomedicine and in the aerospace and mechanical industries. Titanium is a light metal. Due to its low density and modulus of elasticity and high corrosion resistance and biocompatibility, it is extensively used in the automotive, aircraft, and chemical industry and in medicine (Fedirko et al. 2006). TiN is a hard, refractory material and an excellent metallic-type conductor (Mark Q Snyder et al. 2007).

1.1.7 Methods of Thin Films Preparation

Reactive sputtering is widely used to grow films of various chemical compounds. Exhaustive reviews devoted to the preparation, composition, structure, and properties of films of interstitial compounds, including Ti, Ta, Mo, W and Si nitrides, can be found in (Ignatenko et al. 2005). Engineered structures such as super-lattices, nano-laminates, nanotubes, nano-composites, smart materials, photonic band gap materials, moleculely doped polymers, and structured materials all have the capacity to expand and increase the functionality of thin films and coatings used in a variety of applications and provide new applications. New advanced
Deposition processes and hybrid processes are being used and developed to deposit advanced thin film materials and structures not possible with conventional techniques a decade ago. For example, until recently it was important to deposit fully dense films for all applications, but now films with engineered porosity are finding a wide range of new applications. Hybrid processes, combining unbalanced magnetron sputtering and filtered cathodic arc deposition for example, are achieving thin film materials with record hardness (Peter M Martin 2010; Antonella Rizzo et al. 2012).

Thin film technology is a well-known process which is widely used to get the novel materials. Scientists have been continuously working to increase the properties of the crystal in form of thin films. Another important reason for the rapid growth of thin film technology is the improved understanding of the physical and chemical properties of films, surfaces and interface properties have been made possible by the significant advances in analytical instrumentation (Werner Kern & Klaus K Schuegraf 2010).

The concept of coating in the form of thin films is well-known and widely used for the design of suitable coating so as to progress their behavior in exact applications. Thus the use of coatings has been proven to be very effective for the development of novel thin film materials with tailored properties. In particular, dealing with protective coatings for mechanical processing (cutting, milling, machining etc.) and aeronautical/aerospace applications (components for turbines to be used in harsh environments, elements exposed to strong frictions needing good anti-fretting properties etc.), the increasingly demanding technological requirements lead to find coatings which must work in very strict operational conditions (machining of very hard materials, high work speeds, high temperatures, harsh atmosphere etc.). Also, the needs for productivity drive the materials research to the realization and optimization of coating films which are capable of strongly
increasing the lifetime of the coated tools. As a consequence, these tribological coatings must satisfy various requirements, like strong mechanical resistance, high hardness, high wear resistance, good thermal stability and strong adhesion to the coated tool. In addition, the current and future strict environmental regulations affect the processes of development and improvement of materials technology, inducing the need to substitute many materials and substances presently used in a lot of technological processes.

In this context, an environmentally sustainable technology is represented by the realization of conversion layers made by thin film coatings and the deposition of primers by Physical Vapor Deposition (PVD) techniques. These techniques are very versatile methods for thin film deposition, thus allowing the tailoring of the film properties and the optimization of coatings according to the desired application. The purpose of coating optimization for mechanical applications, both coating material (e.g., nitride, carbide, oxide etc.) and coating structure (single layer, multilayers, gradient composition layer etc.) have to be considered. The enormous flexibility provided by the thin films growth processes allows the fabrication of desired geometrical, topographical, physical, crystallographic and metallurgical in lesser dimensions.

1.1.8  Aim of the Present Work

Despite the literature available on several properties of TiN thin films mainly depend on the method of preparation and deposition conditions. DC reactive magnetron sputtering technique gives more stable and reproducible properties of TiN thin films. But, there is lack of complete information concerning on the preparation and characterization of TiN thin films with supported discharge (triode) sputtering. In the present investigation an attempt has been made in preparation of TiN thin films using DC
magnetron sputtering technique with supported discharge to enhance the properties. Hence a systematic study has been made in the present investigation on preparation and characterization of TiN thin films with supported discharge.

The main objectives on the investigation include,

1. To study the discharge characteristics of the DC magnetron reactive sputtering with supported discharge

2. To optimize the deposition parameters of DC magnetron sputtering with supported discharge by coating Titanium thin films with and without supported discharge.

3. To prepare TiN coatings under various deposition conditions such as different working pressures, for different partial pressures of Nitrogen, target to substrate distances, and target powers and characterize these thin films for structural, micro-structural, morphological, electrical and optical properties.

1.1.9 Organization of Thesis

The structure of the thesis in the present investigation is as follows:

Chapter 1: Describes the various properties, importance and applications of transition metal nitride and literature survey of supported discharge, Ti and TiN thin films.

Chapter 2: Shows the description of sputtering system with supported discharge.

Chapter 3: Characteristics of the supported discharge system.
Chapter 4: Illustrated the influence of sputtering process parameter optimization for desired film thickness, composition, structural / micro-structural and electrical properties for Ti target system.

Chapter 5: Presents the influence of process parameters on the film structure, micro-structure, optical and electrical properties of TiN thin films.

Chapter 6: Presents the influence of annealing on the film structure, micro-structure, optical and electrical properties of TiN thin films.

Chapter 7: Summary of the work carried out in this thesis and a brief information about the scope for future work.

1.2 REVIEW OF LITERATURE SURVEY

1.2.1 Introduction

The following section provides the overall idea about the work reported on TiN thin films prepared by different deposition methods by various researchers. Various deposition techniques such as vacuum evaporation, ion plating, reactive and non-reactive sputtering, chemical vapor deposition and sputtering have been employed for preparation on TiN thin films. Each deposition technique with its processing parameters yields films with different properties. The DC magnetron reactive sputtering technique is the one of the important techniques to deposit wide variety of Nitride material. The reported results in the literature survey about Ti and TiN thin films using sputtering technique has been summarized in this section.

1.2.2 Literature Survey of Titanium Nitride

Fontana & Muzart (1998) modified the conventional diode magnetron sputtering systems with grid which result in higher ionization rates
and possibility of maintaining the discharge at lower pressures. The introduction of a grounded or positively biased grid in front of the target increases the target current substantially compared with the diode configuration and discharge can be maintained at a lower target voltage, thus increasing the deposition rate. A triode ion plating system with a hot cathode has been described Gunasekhar & Mohan (1991). The system performance is studied, by studying the discharge behavior of the bias voltage and bias current, at the substrate, for different anode currents, filament voltages and pressures. The observed result has been explained on the basis of ionization at the respective electrodes. The studies have revealed the importance of inter-electrode spacing in the enhancement of ionization, in ion plating systems, at lower pressure.

Sagás et al. (2011) studied the influence of electromagnetic confinement on the characteristics of a triode magnetron sputtering system. They studied insertion of a grounded grid between the target and the substrate makes the magnetron sputtering more flexible, due to the possibility of adjusting the “electrostatic confinement” by the modification of the grid-target distance. It is noticed that the magnetron efficiency strongly depends on the inter-electrode distance and magnetic trap configuration.

V-N coating has been produced by high current density triode magnetron sputtering in the reactive mode by Farges et al. (1992). They studied the influence of basic deposition parameters, mainly nitrogen partial pressure, on the composition, crystal structure and hardness of the V-N films were investigated using electron probe microanalysis. Chekoura et al. (2005) deposited CrN films by magnetron and triode sputtering methods. They studied the structure and stress versus thickness using SEM, STM, XRD, stress measurements for both the thin films. Fontana & Muzart (1999) prepared reactive deposited TiN films using a modified magnetron sputtering
system called triode magnetron sputtering. The introduction of grounded grid in front of a conventional magnetron sputtering results in a stable glow discharge, suitable for reactive film deposition. Thus, triode magnetron sputtering is a much more suitable approach for the deposition of films in the reactive mode than conventional magnetron sputtering.

Devia et al. (2011) prepared TiAlN films on AISI O1 tool steel using a triode magnetron sputtering system. The bias voltage effect on the composition, thickness, crystallography, microstructure, hardness and adhesion strength has been investigated. Wouters et al. (1997) deposited TiN coatings by triode ion plating in a mixture of Ar and N₂ with a varying total current through the melt. The current Iₚₘ from the plasma to the Ti-melt in the crucible has been modified from 0 A up to 100 A. As Iₚₘ is increased, a major effect on the plasma and on the film microstructure (preferred orientation, stress-free lattice parameter, residual stress, thickness and micro-hardness) has been observed.

TiN films with a thicknesses varying from 70 to 300 nm has been deposited onto Cu substrates using reactive D.C. triode sputtering by Benhenda et al. (1995). The as-deposited films characterized by AES, TEM and XRD. Sagás et al. (2011) studied Berg's model, employed in the reactive sputter deposition of TiN by a TMS system. The grid acts as the anode, and the glow discharge is formed between the target and grid. In ion plating to enhance ionization is to use a negatively biased hot filament (Salmenoja & Korhonen 1986). The use of an additional electron emitting filament brings an extra variable to be taken into account in process control. Hard, adhesive and dense titanium nitride coatings were prepared in a triode ion-plating system (Rousseau & Guille 1988). This work shows and explains the influence of the discharge current density on the film characteristics. Microstructure,
densification, crystalline composition and hardness are functions of the chosen value for the discharge current density.

Ying-long LIU et al. (2014) investigated nano-mechanical properties of nanostructured Ti metallic material. The pure Ti film has been prepared by magnetron sputtering at the bias voltage of 0 to 140 V. The microstructure of Ti films has been characterized by XRD, SEM and HRTEM. Titanium Nitride thin films has been deposited on Si substrate with DC reactive magnetron sputtering by Kaykhosrow Khojier et al. (2013). The effect of argon flow rate on the structural, morphological, mechanical, and electrical properties has been studied using XRD, AFM, nano indentation test and four-point probe instrument, respectively.

Narges Fani & Hadi Savaloni (2013) has investigated preparation of TiN thin films, using a plasma focus device. Titanium nitride thin films has been coated on 304 type stainless steel substrates by fixing the distance from the anode (source) and at different angles with respect to the anode axis. The nanocrystalline TiN thin films has been prepared using RPLD through ablation of high purity titanium targets in the presence of low-pressure nitrogen gas, with constant temperature and laser power using Nd:YAG laser operating at 1064 nm by (Krishnan et al. 2013). The deposited film has been characterized using GIXRD, PEBS, and AFM for their structure, composition, and morphology, respectively.

Titanium Nitride thin films have been deposited on SS (316L) with 4 kJ plasma focus device by Omrani et al. (2012). The energy flux delivered to SS surface is expected to be 2.69x10^{13} \text{ keV cm}^{-2}\text{ns}^{-1}. X-ray diffraction shows the formation of a nano-crystalline TiN coating on the surface. A stoichiometric and nonstoichiometric Titanium Nitride (TiN\textsubscript{x}) film has been prepared with sputtering method by Varvara Karagkiozaki et al. (2009). The morphological, structural, optical, and wettability properties of the TiN\textsubscript{x} films
have been obtained by AFM, X-ray diffraction, spectroscopic ellipsometry, and contact angle measurements. Kumar et al. (2011) has prepared thin film specimens of TiN/Ti multi-layers, significantly 3-5 mm size using microfabrication techniques on Silicon On-Insulator (SOI) wafers. Marco Annunziata et al. (2011) investigated the surface characteristics of TiN-coated titanium plasma sprayed (TiN-TPS) and uncoated TPS surface and their biological features towards both primary human bone and bacterial cultures.

An energetic TiN cathode has been fabricated for effective electrocatalytic debromination of 2,2-4,4-tetrabromodiphenyl ethers (BDE-47); by placing Ti foils in an aqueous suspension of TiN nanoparticles, then drying the system at 50°C for 12 hours by Jingyang Su et al. (2012). TEM and SEM characterization showed that the TiN nanoparticles average size has been approximately 50 nm and ideal nano-cubic structures have been distributed uniformly on the Ti substrate. Gómez et al. (2010) deposited Titanium Nitride (TiN) films on M2 and D2 steel substrates in a TMS chamber. They kept the temperature; gas flow and pressure as constant and the substrate bias has either decreased or increased in a sequence of steps.

Xiaoli Cui et al. (2009) prepared TiN films with good uniformity and adhesion at room temperature by using an aqueous suspension with nano-crystalline TiN powders and electrophoretic deposition of nano-crystalline TiN powders onto a Ti substrate. TiN films with a wide range of colors from yellow to blue have been obtained by varying the deposition time. A thin film of Titanium Nitride (TiN) has been deposited on stainless steel substrates using DL-SAIP with vicarious circular holes by Yanhui Zhao et al. (2011). The results indicate that TiN film with the distance of 10 mm between the double-layered shield plates had the least droplets. The deposition rate of the films prepared with the new technique has been more uniformity than that of all the other shielded arc ion plating.
Nishat Arshi et al. (2012) deposited Titanium Nitride (TiN) film on silicon (100) substrate using DC magnetron sputtering technique. The effect of argon flow rate (5, 10, 15 and 20 SCCM) on the structural and morphological properties has been studied using XRD and FESEM, respectively. A morphological, structural and electrochemical study of Titanium Nitride (TiN$_x$) thin films has been prepared with DC reactive sputtering on titanium substrates Cunha et al. (2011). They tried at different compositions of TiN$_x$ (0 < x < 1.34) aiming a selection of the good coatings for dry biomedical electrodes.

Thulasi Raman et al. (2014) deposited TiN films using reactive magnetron sputtering on Cu substrate at room temperature. The cycle ability performance at different currents indicate that TiN would be a promising material for long stable life of lithium ion batteries. The growth rate during reactive HIPIMS of titanium nitride has been investigated by Mitschker et al. (2013). They rotated a 200 μm slit in front of the substrate synchronous with the HIPIMS pulses which is used to distribute the incoming flux over the substrate. The dynamics of the growth rate and the composition of the resulting films are dependent on current of an HIPIMS pulse.

Azadeh Jafari et al. (2014) has prepared of Titanium Nitride (TiN) thin films on stainless steel substrates by a DC magnetron sputtering method and annealed at different annealing temperatures of 500, 600, and 700° C for 120 min in nitrogen/argon atmospheres. These results suggest that annealed TiN films can be good applicant for tokamak first wall due to their structural and optical properties. The TiN thin films have been prepared on silicon (p-type 100) substrates by at room temperature by reactive DC magnetron sputtering by Reza Bavadi & Shahoo Valedbagi (2012) by varying substrate temperature. XRD and AFM analysis has been used to evaluate the crystal structure and surface morphology.
Po-Jui Su et al. (2012) investigated the application of TiN thin film as the coating material for Atomic Force Microscope (AFM) probes. They have deposited TiN thin films by IBSD using a Ti target with nitrogen as the reactive gas and argon as the carrier gas. The nitrogen partial pressure has affected the composition, crystallinity, and resistivity of TiN films. Vasu et al. (2011) investigated the local current and topography measurements on the surface of titanium nitride thin films by C-AFM with two compositions, stoichiometric TiN and sub-stoichiometric TiN (0.76). Subramanian et al. (2009) has prepared TiN thin films using reactive DC magnetron sputtering technique on Mild Steel (MS) substrate with brush plated Ni interlayer. With brush plated Ni interlayer in TiN thin films, the micro hardness, wear resistance and corrosion resistance increased compared to TiN without Ni as an interlayer. TiN thin films have grown on Si at different rates in a homemade ultra-high vacuum chamber using dc reactive sputtering at high nitrogen pressures, at room temperature by Lorite et al. (2013). Titanium nitride films on silicon substrates produces, a non-continuous thin film with a distribution of holes that has an optical extinction coefficient comparable to that of gold nanostructures under certain growth condition. The full Raman spectra of TiN thin film show SERS of 40 % compare bare silicon substrates which demonstrate an attractive material with potential application for plasmonic application such as the development of SERS active templates.

Popović et al. (2012) prepared polycrystalline Titanium Nitride (TiN) layers with columnar microstructure at 150°C by DC reactive sputtering on Si (100) wafers. The samples has been implanted at room temperature and under a pressure of 1×10−4 Pa with 80-keV vanadium ions or 200-keV Ar+ions provided by the 500-kV implanter. Shayestehaminzadeh et al. (2013) prepared the ultra-thin TiN films using HiPIMS at 35°C to 600°C on MgO (100) substrates. The HiPIMS process deposited denser and smoother films compared to DC Magnetron Sputtering for all growth temperatures.
Viorel-Aurel Serban et al. (2013) prepared the titanium nitride layers on steel substrate by PJA method (combining reactive plasma spraying method with electric arc thermal spraying), using titanium wire electrode. In this way the advantages of each method in part have been combined for obtaining improved quality coatings and achieved high productivity. Zalnezhad et al. (2013) improved fretting fatigue life of Al7075-T6 alloy by covering it with a TiN thin film hard coating using the magnetron sputtering technique. TiN coated films exhibits with best surface hardness, adhesion strength and roughness. The fretting fatigue lives of coated specimens with high surface hardness and adhesion strength improved of 61% and 16% at high bending stress, 39% and 77% at low bending stress, respectively, when comparing with uncoated substrates. TiN thin film has been deposited using DC reactive sputtering on Si substrate and implanted with argon ions at 200 keV by Popović et al. (2015). The implanted TiN sample has been annealed before or after ion irradiation at 600 °C and 700 °C, respectively.

Naofumi Ohtsu et al. (2014), studied the optimal settings for the fabrication of the nitride layer on Ti using focused low-power pulsed Nd:YAG laser irradiation in a nitrogen atmosphere. They investigated the effects of nitrogen gas pressure, laser power, and number of laser shots on the thickness of the produced nitride layer. The pressure of nitrogen gas is the most important factor for nitride layer thickness control and an atmospheric pressure is required to form a practical nitride layer using focused low-power laser irradiation in a nitrogen atmosphere.

Liqiang Zhang et al. (2013) prepared the TiN thin films by magnetron sputtering and investigated the structure, morphology, hardness, stress and fracture toughness. Van Bui et al. (2013) deposited TiN films via thermal ALD at 350 °C on Si wafers with thickness in the range of 0.65–20 nm. They compared the resistivity of ultra-thin TiN films with the thickness
0.65 to 20 nm using both spectroscopic ellipsometry and electrical characterization techniques.

Titanium Nitride and titanium oxynitride film has been deposited by varying the plasma current density 10 mA/cm$^2$ to 40 mA/cm$^2$ using DC magnetron sputtering at constant gas flow rate and deposition time. Sample has been characterized by GIXRD, XPS, Nano-indentation and colorimetric analysis. Different colored films like golden, blue, pink and green has been obtained at different current densities. The color variation may be due to oxygen atoms replacing the nitrogen positions in TiN lattice.

The TiN film has been formed by reactive sputtering in Ar and N$_2$ ambient by DC magnetron sputtering by Jin-Ping Ao et al. (2013). They evaluated the electrical performance of AlGaN/GaN HFETs with TiN gate and its thermal stability. The device has been thermally treated at 600 °C for 1 h but there has been no degradation found in the Schottky contact.

Ultrathin TiN film has grown by reactive dc magnetron sputtering on thermally oxidized Si (100) substrates Ingason et al. (2009). XPS and XRD measurements show that the TiN grain stoichiometry and grain size increases with increasing growth temperature. Thin TiN film has grown on SiO$_2$ at various growth temperatures with reactive HiPIMS by Magnus et al. (2011). The HiPIMS process produces denser films at lower growth temperature and also a much smoother surface which may be due to intense low energy ion irradiation from Ti$^+$, N$^+$ and Ti$^{2+}$ ions during growth.

TiN films of 50 nm and 500 nm thickness has been deposited on M2 tool steel substrates by reactive closed field unbalanced magnetron sputtering operating in Direct Current (DC) and Pulsed Magnetron Sputtering (PMS) modes by Iordanova et al. (2012). Papken Eh. Hovsepian et al. (2014) deposited TiN films using HIPIMS enabled four cathodes industrial size
coating system equipped with HIPIMS power supplies. OES measurement has been carried out to examine the plasma generated by the various combinations of HIPIMS and UBM cathodes. The Combination of HIPIMS with dc-UBM sputtering is an effective tool for improving the productivity of the deposition process.

Calcium has been added into titanium nitride coatings deposited using a hybrid magnetron sputtering–arc evaporation process by Hodroj & Pierson (2011). The calcium content in the films has been adjusted by the variation of the pulsed DC current applied to the Ca sputtering target. The films were characterized by X-ray diffraction and optical reflectance studies may be suitable for decorative applications.

TiN sample has been deposited using reactive magnetron sputtering by Yuste et al. (2011). They investigated (i) post-deposition annealing treatments up to 500°C, (ii) doping the TiN layers with aluminum and (iii) deposition of antireflective coatings of TiO₂ in multi-layers structures. The crystalline structure and chemical composition of the multilayers has been studied by XRD and RBS respectively. SE, FTIR and direct emissivity measurements has been employed to determine the optical properties transmissivity T and emissivity ε.

Subramanian et al. (2011) prepared Ti/TiN multilayered coatings of 200 layers with the thickness of 1.5 μm by a reactive DC magnetron sputtering technique. The deposited films were characterized by XPS, Raman, mechanical properties (wear resistance) and corrosion properties. Subramanian et al. (2011) presented the performance of three titanium nitride coatings: TiN, TiON, and TiAlN for biomedical applications.

Katariya et al. (2012) deposited nano-crystalline Titanium Nitride (TiN) coatings on Si (100) substrates using reactive pulsed direct current
magnetron sputtering. The nitrogen flow rate has been pulsed during the deposition with time 5, 20, 40, 50 and 60 s. XRD, FESEM, TEM, Raman spectroscopy and PEBS technique have been employed to study the microstructure of the as-deposited coatings. Nano-mechanical characterization of the coatings has been carried out using nano-indentation, nano-scratch and wear testing techniques.

Pedrosa et al. (2013) deposited Silver-added TiN thin films by DC reactive sputtering with Ag contents ranging from 0 to 50 at.% on the silicon substrate for bio-electrode. The coating has been characterized regarding their composition, morphology and structure, and their influence on the variation of the electrical resistivity and thermal properties. The C-TiN film has been deposited using DC magnetron sputtering Sofiane Sedira et al. (2014). The films have been analyzed using XRD, SEM with EDX, FTIR, Raman, UV-Visible and potentiodynamic polarization. Analysis shows that doping with carbon in low concentration led to formation of Titanium Carbide (TiC). The obtained film can be used as protective layers for medical implants.

TiN/TiAlN multilayer of 2 nm thickness have been prepared using reactive DC magnetron sputtering method by Ananthakumar et al. (2012). The films were characterized using XRD, XPS and TEM. The results of electrochemical experiments indicated that a TiN/TiAlN multilayer coating has better corrosion resistance in 3.5% NaCl solution. Ti/TiN multilayer has been deposited by DC reactive magnetron sputtering method using a titanium target and an Ar–N₂ mixture discharge gas Subramanian et al. (2011). XRD and XPS technique has been employed to study the structure of the coatings and bonding between them.

Yibing Xie et al. (2013) prepared the Tin nano-arrays with a short nanotube and long nano-pore structure by an anodization process. The morphology and microstructure characterization has been conducted using
FESEM and X-ray diffraction. The electrochemical properties have been investigated through cyclic voltammetry and electrochemical impedance spectrum measurements. Well-defined TiN nano-arrays contribute a much higher capacitance performance than Titanium Oxide (TiO2) in the super capacitor application due to the extraordinarily improved electrical conductivity.

Titanium Nitride (TiN<sub>x</sub>) has been deposited using magnetron sputtering on Si (100) substrate by varying time of deposition to produce coatings with variable thickness in the range of 20–120 nm by Martinez et al. (2014). A TiNx coating has been characterized by investigating its structure, composition and mechanical properties. NRA combined with RBS analyses indicates that the grown coatings have the stoichiometric of TiN.

Lawand et al. (2012) et al. prepared Ti and TiN thin films by DC magnetron sputtering process silicon substrates. AFM and XRD studies have been carried out to analyze the structural properties of thin films. The nano-structure TiN has been modified on the laboratory self-made pMEA using magnetron sputtering method by JIANG Ting-Jun et al. (2014). The performance of modified pMEA has been investigated. The research on neuro-electrical and neurochemical recording has been studied in vitro.

The TiN has been deposited on AZ91D magnesium alloy using the PVD methods with the final layers by a simple chemical-type treatment Tacikowski et al. (2014). The tightened multilayer obtained by the hybrid treatment is composed of a TiN surface layer and an aluminum sub-layer diffusively bonded with the substrate, separated by a thin transition titanium sub-layer. The tightening of the composite titanium nitride layers plays the crucial role in achieving this significant improvement of the corrosion resistance. Plasmonic stacks composed of Au, TiN<sub>x</sub> and Ti layers and the corresponding single film has been fabricated on Corning glass (Eagle2000).
substrates with conventional RF magnetron sputtering system by Kim et al. (2012). Optical properties, Surface Plasmon Resonance (SPR) response characteristics, and the adhesion properties of the plasmonic stacks with TiNₙ adhesion layers has been analyzed and compared with those of the Au single stack and the plasmonic stacks with conventional titanium adhesion layer. It has been proved that TiNₓ layer could provide good adhesion strength at the glass/TiNₓ and TiNₓ/Au interfaces, which is comparable with that of Ti layer.

White et al. (2014) prepared Titanium Nitride (TiNₓ) thin films using RF magnetron sputter deposition by varying the nitrogen content in the reactive gas mixture. The effect of nitrogen gas flow rate on the surface and interface morphology, chemical composition and optical properties of TiN thin films has been studied using AFM, SEM, XPS and SE. SE analysis indicated that the films deposited at low (0–5 SCCM) nitrogen flow rates have the highest absorption at energies <2 eV. AFM analysis shows that the roughness decreases and plateaus at approximately 1.5 nm with the introduction of a small N₂ flow rate.

The effect of Aluminum (Al) addition to TiN thin films matrix on the structural, mechanical and corrosion resistance properties of titanium aluminum nitride has been studied by Subramanian et al. (2010). Ti₁₋ₓ AlₓN where x = 0, 0.5 and 1 films has been coated onto substrates like Si wafer, AISI 316L stainless steel and low carbon steel by a direct current magnetron sputtering process. XRD, TEM, Raman spectrum and XPS analyses has used to study the structural properties of these films.

Yuan Ji et al. (2014) worked on the TEOLED using the TiN as the anode for the micro-displays based on the CMOS integrated circuit substrate. The luminance reaches beyond 2700 cd/m² when the operating voltage is below 5 V. The power efficiency reaches 13 lm/W at the luminance of 1000 cd/ m². It has been proved that TiN is a good candidate for the anode of the
TEOLED due to its good electrical and optical characteristics. Qiuyu Wang et al. (2013) used TiN as consumable anode to produce metallic titanium in molten salts. The electrochemical dissolution of TiN anode has been investigated in NaCl-KCl molten salt. The nitrogen has been evaluated at the anode during electrolysis. The titanium ion species is changed between Ti $^{2+}$ and Ti $^{3+}$ depending on the electrochemically dissolving potentials of TiN. The product on the cathode has been analyzed using SEM and XRD. The results show that pure titanium powders can be prepared by the TiN electro-refining in a molten salt bath.

Arash Yazdani et al. (2011) have introduced active screen plasma nitriding method as a novel approach for deposition of nano-sized titanium nitride. H11 tool steel samples has been coated by plasma nitriding method at 550 °C for 5, 7.5 and 10 h, using three gas mixtures consisted of H$_2$/N$_2$=3, 1 and 1/3. SEM, XRD and XPS have been employed to investigate the coating properties such as grain size, layer thickness and chemical composition.

Theo Sinkovits et al. (2014) have discussed the use of combining two XRD stress analysis to clarify the effect of interruptions during growth on the residual stress of TiN films. Madaoui et al. (2014) prepared (TiN) and titanium carbonitride on steel substrates XC48 using magnetron sputtering technique. The films were characterized for hardness and corrosion properties. The result indicates that the coated XC48 steel displays a better resistance to uniform and pitting corrosion than the bare material.

Oskouei et al. (2012) have studied de-lamination of a TiN thin film coated on aluminum alloy 7075-T6 substrate under fatigue loading conditions. TiN coating of 3 μm in thickness has been deposited onto the aluminum substrate using a PVD process. SEM and XRD used to analyze the structure of the coating. Mainul et al. (2012) have grown Titanium Nitride (TiN) nanowires in single crystal Magnesium Oxide (MgO) substrates using a
bottom-up pulsed laser deposition method. Ti–N based gaseous reactants in the laser plume supersaturate the catalytic gold (Au) liquid located on the substrate surfaces. This bottom-up approach gives rise to a one-dimensional TiN nanowire structure (length: 200–300 nm and diameter: 20–30 nm) capped with a catalytic Au seed. Fan-Yi Ouyang & Wei-Lun Tai (2013) prepared nano-crystalline TiN and TiN/Ti barriers with the high packing factors of 0.7–0.8, on the metal substrates using unbalanced magnetron sputtering systems. The microstructure and properties of TiN and TiN/Ti barriers has been characterized using SEM, XRD, AFM, SIMS and corrosion properties. TiN barrier can be advantageously used for the application of flexible dye-sensitized solar cells technology. Chunlin He et al. (2013) deposited TiN thin films on AISI304 stainless steel using a DC reactive magnetron sputtering process. They studied the relation between the corrosion initiation and the structural defects using Atomic Force Microscopy (AFM). They conclude that the structural defects strongly associated with the bias voltages.

Chi-Lung Chang et al. (2014) prepared TiN thin films using a unipolar mode HiPIMS process. The deposited TiN films has been investigated by varying the duty cycles from 2 to 10% to have peak power density ranging from 208 to 1064W/cm². DC magnetron sputtered TiN thin film (duty cycle = 100%) has also deposited for comparison. Compare to DC magnetron sputtering, HiPIMS deposited TiN thin film exhibits a denser structure and smoother surface at low duty cycles. A filtered cathodic vacuum arc system has been used to reactively deposit nano-composite HSS-TiN films from a cold-sprayed HSS-Ti cathode by Pagon et al. (2014). The microstructure of the films depends on the energy of the depositing flux (controlled by substrate bias) and the substrate temperature. At room temperature and a low substrate bias of −25 V a fine nano crystalline microstructure has been produced.
Oskouei & Ibrahim (2012) investigated the fatigue behavior of aluminum alloy 7075-T6 coated with 3-µm-thick Titanium Nitride (TiN) coatings using a PVD process. The high operating temperature of the deposition process remarkably reduces the tensile properties of the coating-substrate which has been compared to the uncoated Al 7075-T6. TiN metal layer has been patterned by lithographic techniques on Si substrates. These films have been sputter deposited on p-type Si(100) wafers by DC reactive magnetron sputtering nerve stimulation purposes by Lawand (2102). Henry et al. (2013) prepared protective nanostructured Ti$_{1-x}$Al$_x$N ($0 \leq x \leq 1$) coatings, by RF magnetron reactive sputtering onto steel substrates and Si (100). The Ti$_{1-x}$Al$_x$N thin films have been tested for wear and scratch properties. Ti-rich coatings confirm better tribological properties due to a higher toughness and a higher elastic modulus.

The nano-structure TiN has been prepared by pMEA using magnetron sputtering method by JIANG Ting-Jun (2014). The microelectrode modified with nano-TiN had the ability to response low concentration of neurotransmitters. Jhu-Ling Zeng et al. (2013) prepared cubic BaTiO$_3$ films exhibiting nano-layered structures on TiN-coated substrates. The corrosion resistance remarkably increases for BaTiO$_3$/TiN/Si in alkaline NaOH solutions owing to the thick and dense nano-layered BaTiO$_3$ films. Nan-Hung Chen et al. (2014) prepared the 21.65 atomic % Cu-TiN ceramic coatings in reactive atmospheres by arc ion plating/magnetron sputtering. This coating has been used to protect and decorate the materials on which they have deposited.

Lee et al. (2013) deposited CrN and TiN on of stainless steel 316L using CAIP. The corrosion resistance and electrical conductivity of the CrN- and TiN-coated SS316L has been evaluated to estimate its potential applicability as a PEMFC bipolar plate material. In comparison to uncoated...
SS316L, CrN- and TiN-coated SS316L exhibit lower ICR. Caicedo et al. (2015) characterize the electrochemical behavior of [TiN/TiAlN]$_n$ multilayer coatings under corrosion–erosion condition. The multilayer’s with bilayer numbers (n) of 2, 6, 12, and 24 and/or bilayer period (Λ) of 1500 nm, 500 nm, 250 nm, 150 nm and 125 nm were deposited by magnetron sputtering technique on Si (100) and AISI 1045 steel substrates. The results indicate that TiN/TiAlN multilayer coatings deposited on AISI 1045 steel represent a practical solution for applications in corrosive–erosive environments.

Dinesh Kumar et al. (2015) studied the effects of N$_2$ gas flow rates on the properties of reactive sputtered nano-crystalline thin films deposited on Si substrates. The increased values of friction coefficient and high wear of ball were observed in the film consisting of FCC TiN phase due to hard film/soft ball interaction. Jin Sook Lee & Lim et al. (2015) studied the depth profiling of titanium nitride coated on silicon substrate using Laser Ablation (LA)-ICP-MS. The columnar structure of TiN, with low thermal conductivity and a high melting point, showed clear craters with less thermal degradation compared to Si substrate.

Carbon doped Titanium Nitride thin film has been successfully deposited using DC magnetron sputtering by Sofiane Sedira et al. (2014). Deposited thin film has been investigated by FTIR, XRD, Raman, SEM and EDX. Serkan Oktay et al. (2015) prepared TiN and (Ti, Re)N coatings on HSS substrates by a hybrid coating system composed of cathodic arc PVD and magnetron sputtering techniques. The (Ti, Re) N coating consists of TiN and ReN$_x$ (x > 1.33) phases.