

CHAPTER-1

INTRODUCTION

Abstract

This chapter presents the various applications and physical properties of stoichiometric and sub-stoichiometric titanium nitride thin films. From the literature study, the formation and stability of various metal-substituted TiN thin films are discussed. Motivation and objectives of the research work and then finally the outline of the thesis is presented, including a brief summary of the contents therein.

1.1 Background

Thin films find application in a diverse range of technologies that includes electronic, optical, photonic, semiconductor, tribology, and medical applications. The advent of nanoscience and technology has further increased the range of applications of thin films. One of the more important applications of thin films are in the areas of tribology, enhanced protection of bulk materials in harsh environments and increasing the life time of mechanical components. Material systems generally employed for such applications are based on metal oxides, metal carbides, metal borides and metal nitrides. A recurring theme in thin film work is the multi-functionality of a given material. The current thesis focuses on the growth of sub-stoichiometric and metal-substituted titanium nitride thin films and demonstrating their use in mechanical, optical, optoelectronic and electronic applications, thus establishing the multifunctional nature of the material.

1.2 Titanium nitride

Binary transition metal nitrides (MeN, Me = Ti, Zr, Hf, V, Nb, Ta, Cretc.) are known as refractory compounds with major interest as functional coatings in surface engineering applications. Thin films of these transition nitrides (TMN) are the subject of intense studies both theoretically and experimentally. TiN is regarded as a prototype transition-metal nitride system that has received by far the most attention [1-2]. TiN thin film exhibits a unique combination of properties like high hardness, high wear resistance, high melting point, good chemical inertness and gold-like color. These properties are a consequence of the

complex chemical bonding which has covalent, ionic and metallic contributions. TiN thin films are widely used in variety of applications such as hard, protective, wear resistance and decorative coatings. TiN shows a metallic luster and have a thermal and electrical conductivity of the order of magnitude of pure metals. It is also used very successfully in semiconductor industry as interconnector and diffusion barriers in ULSI circuits [3-7]. In addition, TiN films have been used for cosmetic gold surface [8] wavelength selective transparent optical films [9-11], thin film resistors [12-14], tool bit coatings, and, due to its strong infrared reflection, energy-saving coating for windows and also used in biomedical applications [15-18].

Recent experimental and theoretical investigations have disclosed interesting and extended application of TiN thin film in microelectronics and biotechnology industries. For example, use of TiN as a potential gate metal in metal-oxide-semiconductors (MOS) devices with high k -gate dielectric [19-21] and corrosion-resistance metal layer in complementary metal-oxide-semiconductors (CMOS) bioelectronics devices is reported [22-23]. In addition, a further application of TiN as a Ohmic contact material in n-type semiconductors such as Si, Ge and CdS [24-27] and charge collector in dye-sensitized solar cells [28-31] has been demonstrated.

TiN has good superconducting properties with a relatively high transition temperature (T_c) about 6 K [32-33], which extended its use to superconducting waveguide microresonators [34-35]. Disorder-driven superconductor-insulator transition (by decreasing the film thickness) was observed in TiN thin films recently [36-38]. Below a certain critical temperature and in the presence of a magnetic field TiN becomes a

superinsulator, *i.e.* it reaches a state of zero electrical conductance. The electrical resistance of superinsulator is become infinity, opposite to the superconductor of zero resistance at low temperature. The superinsulator nature in titanium nitride thin film was first discovered by Vinokur [39-40] *et al.* from Argonne National Laboratory, USA. Titanium nitride thin films are, thus, an ideal example of multi-functionality.

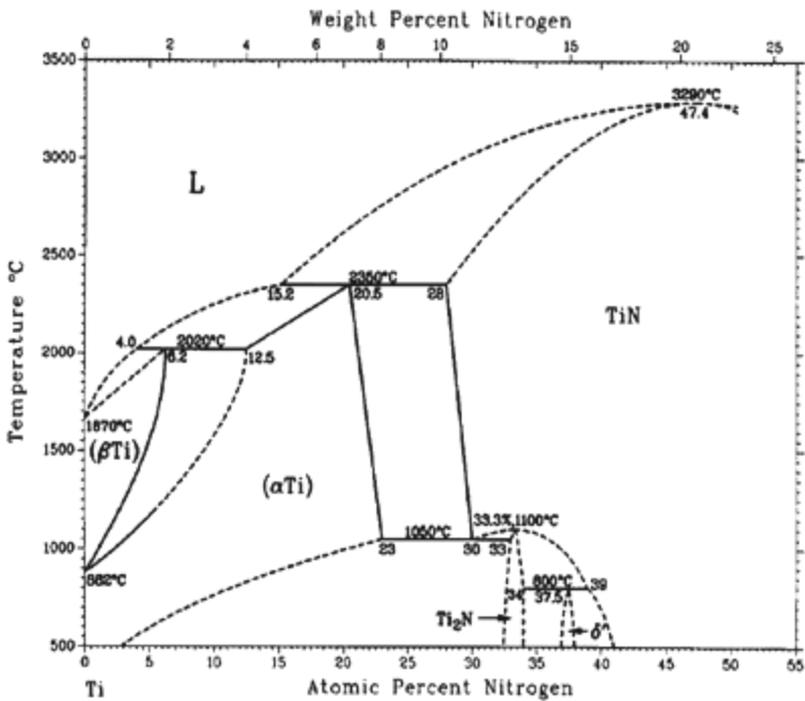


Figure 1.1. Temperature and nitrogen atomic percentage dependent phase diagram of Ti-N system (reference 41)

1.3 Physical and chemical characteristics of titanium nitride (bulk and thin films)

Some important properties of TiN have been summarized in Table 1.1. Several crystallographic phases of TiN exist depending on temperature and nitrogen atomic percentage as shown in the phase diagram of the Ti-N system in figure 1.1 [41]. The primary nitride phase TiN, crystallizes in the rock salt structure (Fm3m) with a lattice parameter of 4.24\AA for the stoichiometric TiN (N/Ti=1). Sub-stoichiometric Ti_2N (N/Ti=0.5), the other major Ti-N compound, has two known phases, $\epsilon\text{-Ti}_2\text{N}$ and $\delta'\text{-Ti}_2\text{N}$. The rocksalt structure of TiN is indicative of an increase in the number of valence electrons from Ti to TiN. Clearly, this suggests that N is responsible for the increase in valence electrons. The unit cell of stoichiometric TiN is shown in the figure 1.2.

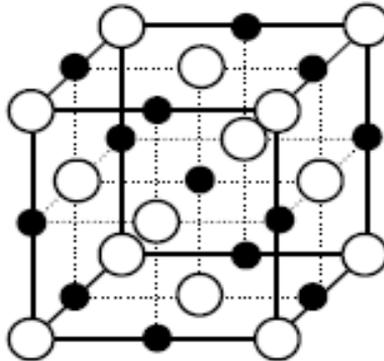


Figure 1.2 Unit cell of TiN (Open circles: Ti atoms, Solid circles: N atoms)

Table 1 .1 Physical properties of stoichiometric TiN thin films

Crystal structure	Face Centered Cubic (FCC)
Appearance	Gold color
Density	5.40 g/cm ³
Melting Point	2930°C
Thermal conductivity	30 Watt/m. K
Thermal Expansion Coefficient	$9.4 \times 10^{-6} /^{\circ}\text{C}$
Electrical resistivity	$20 \pm 6 \mu\Omega\text{-cm}$
Hall-coefficient	$-6.7 \times 10^{11} \text{ m}^3/\text{C}$
Temperature Resistance	Begins to oxidize around 600 °C in air. More resistant in an inert atmospheric
Chemical Resistance	Highly inert to acid, base, solvents, caustic etc
Hardness	Values of 25 – 28 GPa
Young' s modulus	590 GPa
Coefficient of Friction	TiN generally provides low friction against steels, carbides, ceramics and plating. A typical value is 0.65 for TiN against steel
Adhesion	The TiN coating forms a metallurgical bond to the substrate that will not flake, blister, chip or peel. In fact, the coating is actually implanted slightly into the surface layer of the substrate
Non-stick	TiN is an excellent non-stick surface against most of the materials

The ϵ -Ti₂N phase crystallizes in the anti-rutile" (P42/mnm) structure at temperatures below 900°C, which consists of a bcc Ti lattice, with N atoms filling one-half of the available octahedral sites (rather than all of the octahedral sites as in TiN). In general, transition metal nitrides are Hagg compounds in which the crystal structure is either hcp or fcc. However, the ϵ -TiN_x is a non-Hagg type transition metal nitride with an unusual tetragonal structure which is related to both to the bcc β -Ti and to the hcp α -Ti [42]. The unit cell is tetragonal with $a=4.945 \text{ \AA}$ and $c=3.034 \text{ \AA}$. ϵ -Ti₂N can be obtained from the disordered δ -TiN_x only at high temperatures because the transition is kinetically hindered and high activation energy must be provided to initiate it. The δ' -Ti₂N phase is, however, only metastable and transforms by ageing into thermodynamically stable ϵ -Ti₂N which crystallizes in the tetragonal primitive antirutile structure. It is essentially a vacancy-ordered form of the rocksalt structure with a small tetragonal distortion. Thus, as N is added to Ti, Ti transforms from the hcp α -Ti phase to the tetragonal ϵ -Ti₂N phase, and finally to fcc δ' -Ti₂N and δ -TiN phases. Again, this also suggests that as the N fraction increases, the number of valence electrons increases. The color of the Ti₂N phases has been reported as a bright yellow [43], as opposed to the golden yellow for TiN [44]. The units cells of tetragonal δ' -Ti₂N and ϵ -Ti₂N phases have been shown in the figure 1.3. Table 1.2 presents the structural information of Ti-N system of different crystal structures.

Table 1.2. Complete structural information of Ti-N system with various crystallographic phases

phase		$x = \text{N/Ti}$	Crystal structure	Lattice parameters
$\alpha\text{-Ti (N)}$		$0 < x < 0.40$	Hexagonal	$a = 2.956 \text{ \AA}^{\circ}$, $c = 4.765 \text{ \AA}^{\circ}$
Ti_2N	$\varepsilon\text{-Ti}_2\text{N}$	$0.40 < x < 0.52$	Tetragonal	$a = 4.945 \text{ \AA}^{\circ}$, $c = 3.034 \text{ \AA}^{\circ}$
	$\delta'\text{-Ti}_2\text{N}$	$0.52 < x < 0.59$		$a = 4.140 \text{ \AA}^{\circ}$, $c = 8.805 \text{ \AA}^{\circ}$
$\delta\text{-TiN}$		$0.6 < x < 1.2$	Cubic (NaCl)	$a = 4.24 \text{ \AA}^{\circ}$

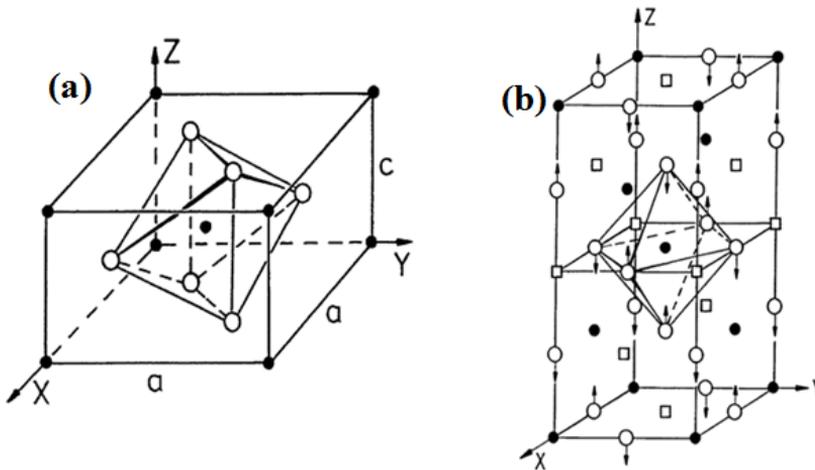


Figure 1.3 (a) Tetragonal unit cell of $\varepsilon\text{-Ti}_2\text{N}$. Full circles: N atoms; empty circles: Ti atoms (b) tetragonal unit cell of $\delta'\text{-Ti}_2\text{N}$. Full circles: N atoms; squares: N vacancies; empty circles: Ti atoms. (reference R. Eibler, *J. Phys: Cond. Matter*, **10** (1998) 10223)

Nanocrystalline TiN thin films possess different microstructural features depending on the method of preparation. The physical properties of the film are in turn dependent on the microstructure. For example, hardness of TiN is inversely proportional to the grain size according to the famous Hall-Petch relation. The hardness of TiN is intimately connected to the chemical bonding and electronic structure is a key to the unusual behavior of hardness in the rock salt structure. Many theoretical studies of their electronic structure have revealed an unusual mixture of covalent, metallic, and ionic contributions to bonding [45-49]. It is reported that the high hardness of TiN is due to a favorable occupancy of the hybridized Ti3d and N2p states leading to the covalent character [50].

TiN thin film exhibits high reflectance in the visible and IR region due to free electron intraband absorption. In contrast, interband transitions are responsible for colors, and other optical properties of these compounds. According to the band structure diagram of TiN [51], four transitions take place at $\Gamma'_{25} \rightarrow \Gamma_{12}$, $\Gamma_{15} \rightarrow \Gamma_{12}$, $X_5 \rightarrow X_2$ and $L_3 \rightarrow L'_3$ critical points in the Brillouin zone which correspond to the interband transitions at 1.0, 2.3, 3.9, and 5.6 eV. The lowest band gap transition ($\Gamma'_{25} \rightarrow \Gamma_{12}$) located at 1.0 eV is very weak and is responsible for the color of TiN film. In stoichiometric TiN this energy transition occurs at the same energy as in gold and thus it exhibits the golden-yellow color [51, 52]. In nanocrystalline TiN films this weak interband transition cannot be experimentally observed and discriminated from the strong dominating contribution of the intraband absorption in the SE spectra at low photon energy [53]. An optical energy transition at 3.5 eV has been assigned to Ti-N2p transition. Figure 1.4 shows the band structure of diagram of a nanocrystalline TiN thin film.

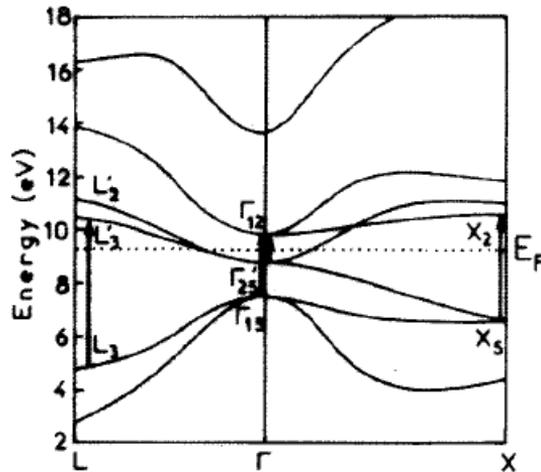


Figure 1.4 Band structure diagram around the centre of the Brillouin zone and the possible assignment of interband transition at Γ and in the vicinity of L and X points (reference 51)

The electrical conductivity of TiN is due to the intersection of the valence band of the Ti 3d electrons' with the Fermi level (E_F) [51]. The electrical resistivity of TiN thin films strongly depends on experimental parameters and film properties such as defects, impurities, microstructure, composition and structure as well. The presence of point defects together with the grain boundaries modifies the electron interactions with the Ti and N atoms and the electronic structure of the pure stoichiometric TiN.

Stoichiometric face centered cubic TiN possesses inversion symmetry, which forbids the first-order Raman scattering. However, TiN with defects or substitutional impurities, breaks the crystal symmetry and defect (impurity)-induced first-order Raman scattering can be observed

[54]. Previous studies of Raman scattering of TiN thin films have reported that low frequency scattering below 370 cm^{-1} is caused by acoustical phonons and the high frequency scattering above 500 cm^{-1} is due to optical phonons [32]. The scattering intensities in the acoustical branch are largely determined by the vibrations of the heavy Ti ions, while the scattering in the optical branch is mainly due to the lighter N ions [55]. Figure 1.5 shows the Raman spectra of TiN thin films.

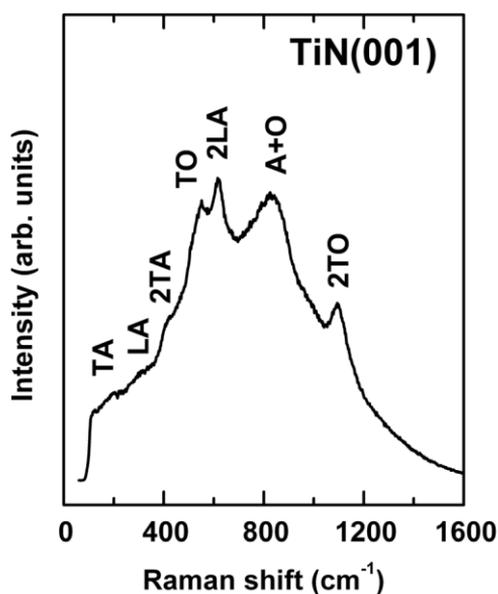


Figure 1.5 Raman spectrum of stoichiometric single-crystal TiN (001) (reference 54)

1.4 Sub-stoichiometric TiN_x

The properties discussed in the previous section, for stoichiometric TiN, vary significantly in non-stoichiometric TiN_x ([N] / [Ti] ≠ 1) phases. Varying nitrogen content of the film causes the

introduction of sub-stoichiometric Ti-N phases leading to a wide range of compositions. The stoichiometry/composition variations in TiN_x thin films lead to change in crystal structure, chemical bonding and free electron concentration. The major source of non-stoichiometry in TiN_x thin film is anion vacancies for $x < 1$ and interstitial N atoms for $x > 1$ [56] where the cation vacancies are present at the Ti sub lattice.

Stoichiometric crystalline TiN is a good conductor of electricity whereas amorphous or nitrogen deficient (sub-stoichiometric) TiN is a very good insulator [57-59]. Both amorphous and sub-stoichiometric TiN film exhibits high electrical resistivity and high transmission of light in the visible region. One of the main factors that cause the deviation of physical properties of TiN thin films from those of the bulk is the presence of sub-stoichiometric impurities. The properties of TiN are extremely sensitive not only to nitrogen fraction, but to impurities as well, especially oxygen. Controlling oxygen content is of extreme importance, since the free energy of formation for titanium oxides is much lower than that for TiN [60-61] and some amount of undesirable titanium oxides may form even with a small amount of oxygen present. Oxygen presence alone has been shown to adversely affect many properties, including conductivity, hardness, adhesion, as well as optical properties. Other impurities, such as water vapor, can cause similar problems. Thus, it is of key importance that some attempt be made to determine what nitride phases and impurities are present.

The rock salt cubic crystalline phase (δ -TiN) is stable for a wide range of x in TiN_x ($0.6 \leq x \leq 1.2$). The lattice parameter varies appropriately with nitrogen composition [56, 62]. Figure 1.6 shows the increase of lattice constant with nitrogen composition. In the

substoichiometric range, high density of nitride vacancies are known to be formed in the crystal lattice, leading to shrinkage of the cubic lattice parameter as x decreases.

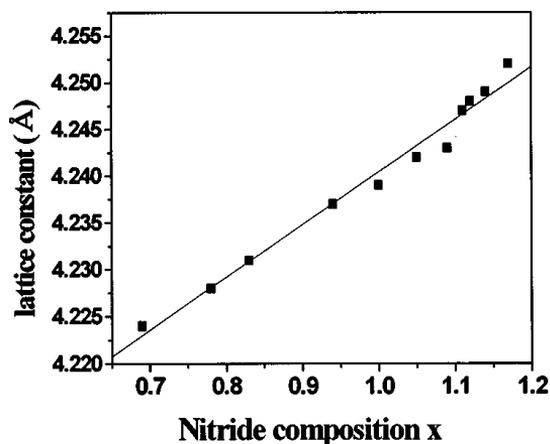


Figure 1.6 Variation of lattice constant with nitride composition x of substoichiometric TiN_x (reference 62)

Information about the electronic or mechanical properties of the ϵ and δ' phases, and even less of the other sub-stoichiometric Ti-N phases is limited. However, due to the large number of N vacancies in both phases of Ti_2N , it is expected that the electronic properties will be quite adversely affected. The hardness of sub-stoichiometric TiN_x is reduced due to the presence of nitrogen vacancies.

The colour of TiN also varies strongly with composition. With increasing nitrogen content the color changes from a titanium grey to light yellow (Ti_2N) to golden (TiN) to brown to bronze, and finally red [43], with the presence of H_2O or O_2 adding a purple hue [63]. Such variations of color and other properties with composition implies that

when composition may not be directly measured, external properties such as lattice parameter and colour may be used to get a rough idea of composition.

Reflectance spectrum of TiN_x film exhibits a minimum in the visible region [64]. The reflectance minimum is strongly dependent on the nitrogen composition. Variation in colour of the films is due to the change in reflectance minimum position which is very sensitive to the defects and impurity levels. There have been several studies [44, 65-66] to explain the color variation from the alteration in reflectance minima. Therefore, reflectance spectrum is a powerful tool to characterize the TiN thin films (estimate the composition and predicting the color) [64]. Typical reflectance spectrum of TiN_x films are shown in figure 1.7.

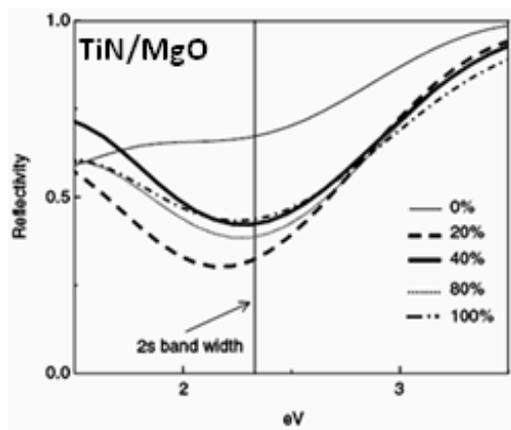


Figure 1.7 Variation of reflectance minima of TiN_x thin films with nitrogen atomic percentage (reference 64)

TiN films exhibit a minimum in resistivity for $\text{N/Ti} = 1$ which increases for sub-stoichiometric and over-stoichiometric phases. This is because of the presence of nitrogen and titanium vacancies in sub-

stoichiometric and over-stoichiometric phases respectively. The resistivity of sub (over)-stoichiometric TiN_x is mainly due to two kinds of carrier scattering, one due to nitrogen (titanium) atoms randomly distributed at vacant interstitials, another attributable to grain boundary scattering [67]. Typical variation of resistivity as a function of nitrogen stoichiometry x , is shown in figure 1.8

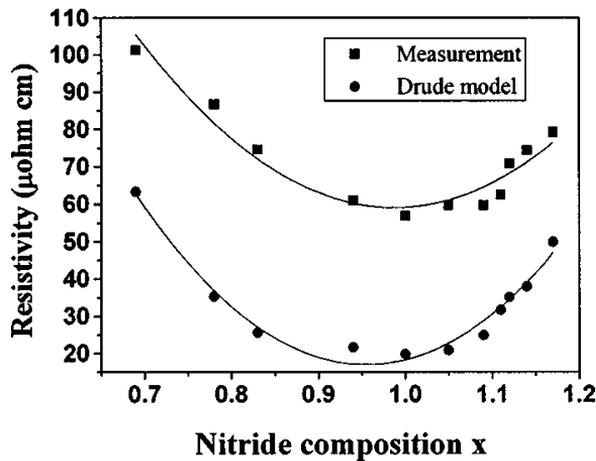


Figure 1.8 Variation dc four probe resistivity of TiN_x film with nitrogen composition. The film has minimum resistivity for $x=1$ (reference 62)

1.5 Metal substituted TiN thin films

The addition of a metal or multilayer stack of TiN and another metal nitride improves the physical and chemical properties. Ternary and multinary transition metal nitrides (TMN) have gained special attention because they provide a broader range of nitride structure types for a fine-tuning of mechanical and electrical properties. These materials may form multiphase (nanocomposite) or single-phase (solid solution) structures,

depending on the properties of the substituting metallic element, process parameters, or post growth treatments. In metal substituted TiN thin films, the Ti atoms are replaced by substituted metal atoms (Me=Zr, V, Cr, Ta, W, Mo and Nb) and stabilizing the ternary $Ti_{1-x}Me_xN$ phase over the entire range. Depending on the mutual solubility between the binary nitrides (TiN-MeN), these solid solutions may be either stable or metastable [68]. Holleck [69] introduced the concept of phase field in PVD deposited films of two components, i.e., a diagram depicting the phase expected to form during PVD deposition with kinetically limited growth conditions as a function of composition and substrate temperature. As an example, by calculating the free energies of formation for solution phases in the TiN-MeN systems and empirical studies the PVD phase field diagram could be constructed. In addition to stoichiometric binary and ternary nitride formation, the phase diagrams also predict the formation of sub-stoichiometric phases, like Ti_2N and Ti_2MeN etc.

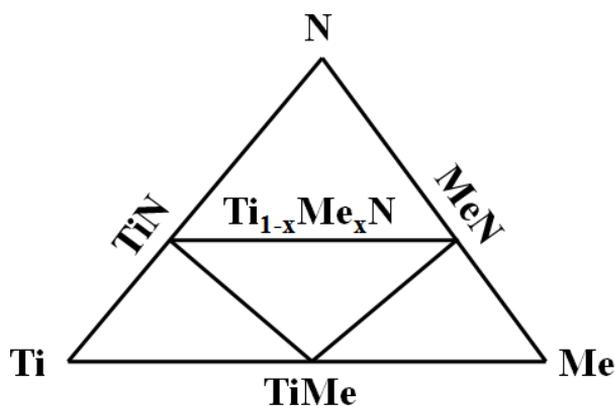


Figure 1.9 General isothermal phase field diagram of ternary Ti-Me-N system.

For example, the Ti-Al-N system exhibits the lines between the binary phases TiN, Ti₂N and AlN, TiAl, Al₂Ti, Al₃Ti and AlTi₂ from Ti-Al alloy and ternary compounds TiAlN, Ti₂AlN and TiAl₂N. For the TiN-ZrN pseudobinary system, recent *ab initio* calculations have shown that below 1000 °C the bulk phase diagram exhibits a large miscibility gap extending over the whole compositional range. However, Ti_{1-x}Zr_xN arc-deposited films retained their as-grown single-phase structure up to 1200 °C [70]. The issue of phase stability in ternary TMN is more critical when Ta, Mo, or W metal is used for substitution, because the ground energy phase of TaN, MoN, or WN binary nitrides is the hexagonal structure [71, 72]. However, metastable ternary solid solutions with rocksalt structure have been produced by different PVD techniques in many systems, such as, Ti-Zr-N [70, 73-77], Ti-Ta-N [78-80], Ti-Nb-N [77, 81-83] Ti-Cr-N [84-86] Ti-V-N [87] , Ti-W-N [88] and Ti-Mo-N [89].

Most of the binary transition metal nitrides (MeN) with NaCl structure are miscible with TiN. However, the difference in the lattice parameters for binary nitrides (MeN) with respect to TiN results in the existence of a miscibility gap. The possibility of forming Ti_{1-x}Me_xN solid solutions with the rock salt structure over the whole compositional range regardless of the valence electron configuration of the constituent metals was recently demonstrated from *ab initio* calculations [90]. However, different bonding types with nitrogen (metallic, ionic, and covalent) and variation of band structure were clearly evidenced depending on the valence electron configuration. The ternary compound Ti_{1-x}Me_xN (Me=Zr, V, Cr, Nb) is crystallized in the rock salt structure in the whole composition range of 0≤x≤1. The validity of Vegard's law, which relates

the composition and lattice parameter, confirms the miscibility between the binary counter parts TiN and MeN.

The main interest in the study of properties of metal-substituted TiN is centered on the improvement of their functional properties and technological applications. Several first principle calculations have shown that the metal substitution modifies the bonding nature, band structure and crystal symmetry [90, 91] which have a marked effect on the optical, electronic, vibrational and mechanical properties. For instance in Al substituted TiN, Ti atoms are replaced by Al atoms and the ternary compound $Ti_{1-x}Al_xN$ is stabilized in the rock salt cubic structure. The compound thus formed, cubic phase $Ti_{1-x}Al_xN$, was found to have superior oxidation resistance [92-94]. Similarly, addition of Si in to TiN improves the mechanical properties. Ternary $Ti_{1-x}Si_xN$ thin films have superior mechanical properties than the binary TiN and SiN [95-98].

The hardness of single layer TiN film is about 25GPa. Superhard coatings (hardness ≥ 40 GPa) have been developed using titanium nitride nanocrystals embedded in amorphous silicon nitride matrix. TiN superlattices with NbN, CrN, TaN and VN are superhard materials. For example, the hardness of TiN/VN superlattices is 56 GPa [99] and TiN/NbN is 51 GPa [100]. On the other hand, sub-stoichiometric TiN is also very interesting since it has unusual physical properties that can be exploited. The electrical resistivity of sub-stoichiometric TiN_x increases and the material behaves like a semiconductor. The electronic structures should, however, be sensitive to the presence of vacancies and changes significantly from those for the stoichiometric phase. The vacancy concentration as well as the alloy composition is shown crucial to the electronic and mechanical properties.

It is thus possible to design multifunctional coatings, which mean one coating that fulfills several demands, but also that there can be one type of coating for each application. Simple binary TiN is not enough and recent research has therefore focused on ternary and multinary coatings. It was found that the properties of TiN thin films can be improved by the addition of the metal or semiconductor. In summary, titanium nitride is an important multifunctional material that continues and needs to be studied.

1.6 Motivation and objectives

It is evident from the literature review presented in the previous section that there are many “open” questions that remain to be addressed.

The growth of titanium nitride thin films in 100 % nitrogen atmosphere during sputtering is an aspect that has not been investigated. The implication of growth in 100% N₂ on physical behavior of TiN based is, therefore, not well understood. Conditions for the stabilization of monophase Ti₂N in thin films form has not been reported extensively. There are almost no reports on the optical constants and nanomechanical behavior of Ti₂N thin films. The conductivity of titanium nitride films is largely attributed to its unique band and electronic structure. However, the microstructural origins of the conductivity are not investigated. The optical constants and microstructural origin of electrical conductivity of metal substituted titanium nitride have also not been reported. The motivation of the current thesis is to address some of these issues.

The objective of the present work is, therefore, to deposit stoichiometric and non-stoichiometric nanostructured titanium nitride thin films on various substrates by RF reactive magnetron sputtering and investigate their physical properties.

From the Ti-N phase system, it is seen Ti_2N phase is a line compound existing for a small window of nitrogen partial pressure and substrate temperature. The first attempt is to stabilize single phase tetragonal Ti_2N thin films at low temperatures and study the structure, composition, microstructure, mechanical, optical and electrical properties.

The second objective is to study the structural, microstructural, mechanical, tribological, optical, electronic and electrical properties of Nb-substitute TiN films. Nb has a valence electron configuration of d^4s^2 , its atomic radius is 146 pm (which is close to Ti 140 pm) and is easily soluble in TiN. Furthermore, it is known that the TiN-NbN system is miscible and the compound $(Ti,Nb)N$ is a stable pseudo-binary alloy [101]. Therefore, the solid solution $Ti_{1-x}Nb_xN$ stabilizes in the rocksalt structure in the entire range of x and is expected to improve the mechanical, tribological and electrical properties compared with their binary counter parts TiN and NbN. Hence, Nb was selected as the metal for substitution in TiN to form $Ti_{1-x}Nb_xN$ films.

The electrical properties of granular TiN_x and TiN based thin films are strongly dependent on the microstructure. In this case, surface roughness and grain boundaries will contribute to the overall resistivity of the film due to electron-surface and electron-grain boundary scattering. It is important to investigate the microstructural origin of the electrical properties of TiN_x thin films. The prime objective of the last

section is; therefore, study the microstructure dependent electrical and electron transport properties of TiN_x and $\text{Ti}_{1-x}\text{Nb}_x\text{N}$ thin films using conductive-atomic force microscopy (C-AFM).

1.7 Thesis outline

In this work Ti, TiN_x and $\text{Ti}_{1-x}\text{Nb}_x\text{N}$ thin films were deposited by RF reactive magnetron sputtering on glass, quartz, silicon (311) and 316 LN nuclear grade stainless steel substrates. Including this introductory chapter, the thesis is organized into seven chapters.

Chapter 1 discusses the basic physical properties and various applications of TiN thin films.

Chapter 2 describes the experimental techniques used to deposit and characterize the films. Comprehensive description of the RF reactive sputter deposition of Ti, TiN_x and $\text{Ti}_{1-x}\text{Nb}_x\text{N}$, and optimized conditions are presented. The details of the characterization techniques used, x-ray diffraction, field emission-scanning electron microscopy, atomic force microscopy, energy dispersive x-ray spectroscopy, UV-VIS-IR spectrophotometer and nanoindentation are presented.

Chapter 3 presents the results of studies on physical properties of pure Ti and stoichiometric TiN thin films.

In chapter 4, the influence of substrate temperature T_s , on the structure, composition of TiN_x films is reported. The successful deposition of single

phase Ti_2N films and their structural, morphological, mechanical, optical, and electrical properties is the main feature of this chapter.

Chapter 5 presents the influence of Nb concentration on the physical properties of TiN thin films. It is observed that the structure, microstructure, mechanical, optical, electrical and vibrational properties of $\text{Ti}_{1-x}\text{Nb}_x\text{N}$ ($0 \leq x \leq 1$) films are strongly affected by Nb concentration. The hardness and Young's modulus increased, whereas electrical resistivity decreased with an increase in the Nb concentration in the films. The complex dielectric function of $\text{Ti}_{1-x}\text{Nb}_x\text{N}$ ($0 \leq x \leq 1$) films in the energy range 1.5 to 5.5 eV is calculated by fitting reflectance spectra based on Drude-Lorentz model.

In chapter 6, results of investigations on the microstructure dependent electrical properties of TiN_x and $\text{Ti}_{1-x}\text{Nb}_x\text{N}$ thin films by conductive-atomic force microscopy (C-AFM). Detailed study of C-AFM results *i.e.* surface conductivity map and local electron transport is presented.

Chapter 7 presents the various conclusions that can be drawn from the present investigations and discusses the scope for future work.