CHAPTER-I
INTRODUCTION TO BINARY AND TERNARY METAL NITRIDE SYSTEM
1.1 INTRODUCTION

Now thin films have become to play inevitable role in the development of various decorative coatings, corrosion resistance coatings, optoelectronic devices like microelectronics, optical coating and integrated optics, informatics quantum engineering, metallurgy coatings, surface engineering and solar energy conversion devices. The reasons for the rising importance of thin films are many, like, tailoring the properties according to their thickness and the small mass of the material involved. The most essential parameter that determines various properties is the structure of films. Undoubtedly, modification of the most of the physical characteristics of thin films such as structural, morphological, mechanical and optical properties play a key role in an over widening sphere of industrial, scientific and technical applications. The development of any new material or probing the already known material will have good application potential if they can be deposited in thin film form with the same or improved properties of the bulk material.

Surface engineering, or more general interfacial engineering, has become one of the most important technologies to affect a demonstrable improvement in lifetime and performance of many components. This embraces all interfaces in materials such as grain or phase boundaries and the conjunction of the material to the environment, the surface. Thus, interfacial engineering gives rise to enhanced material properties of both the bulk material with e.g. increased toughness and strength as well as the surface coating with e.g. high hardness, corrosion and wear resistance by applying such important discoveries like the size effects in materials [1]. Due to surface modification techniques, the lifetime of components or tools could be increased by a factor of more than 10 for certain applications. The most commonly used techniques in industry to deposit coatings on tools are chemical vapour deposition (CVD) and physical vapour deposition (PVD) where the coating is synthesized from a vapour phase on a substrate [2].

Nowadays, metal nitride coatings are widely used to improve lifetime and performance of tools. Due to their bond structure, a mixture of covalent, metallic and ionic components, this type of coatings show high hardness, chemical inertness, good electrical conductivity and excellent wear resistance. One of the first materials used in industry to coat tools, and hence, one of the best-known and investigated ones is
titanium nitride (TiN). TiN with its face-centered cubic structure was, and still is, the base for further development of advanced coatings such as Aluminium nitride (AlN), Titanium Aluminium nitride (Ti,Al)N [3]. Another possibility to improve coating properties apart from alloying is the combination of different materials in the coating using several ways such as multilayer arrangements [4] or nanocomposites [5]. In both cases, different goals like very high hardness and toughness or the combination of high wear resistance and low friction can be achieved.

The requirements on coated tools and components in industry are permanently increasing. A general trend for cutting tools goes towards higher cutting speeds and consequently higher temperatures. Also the working temperature of components is steadily increasing since it allows better performance, less pollution and energy losses. The performance of a coated surface is determined, among others, by its structure and residual stresses, particularly when it comes to thermal loads. Stresses and strains in the coating and the substrate due to mechanical and thermal loads are thus of interest to prevent failure. Residual stresses are composed of an intrinsic part resulting from growth defects and a thermal part caused by the mismatch of the thermal expansion coefficients of the coating and the substrate [6]. For a further increase of lifetime, it is of major importance to understand how the structure of a coating, coating architecture and residual stresses might be influenced by thermal processes [7].

Almost universally in high technology applications, a composite material is used where the properties of the surface are intentionally different from those of the core. Thus, materials with surface coatings are used in the entire cross-section of applications ranging from microelectronics, display devices, chemical corrosion, tribology including cutting tools, high temperature oxidation/corrosion, solar cells, thermal insulation and decorative coatings (including toys, automobile components, watch cases, etc.)

A large variety of materials is used to produce these coatings. They are metals, alloys, refractory compounds (e.g. oxides, nitrides, and carbides), intermetallic compounds (e.g. TiAl) and polymers in single or multiple layers. The thickness of the coatings ranges from a few atom layers to million of atom layers. The microstructure and hence the properties of the coatings can be varied widely and at will, thus permitting one to design new material systems with unique properties. (A material system is defined as the combination of the structure and coating.)
Most materials used in high technology applications are composites, i.e., they have a near-surface region with properties differing from those of the bulk materials. This is caused by the requirement that the material exhibit a combination of various, and sometimes conflicting, properties. For example, a particular engineering component may be required to have high hardness and toughness (i.e., resistance to brittle crack propagation). This combination of properties can be obtained by having a composite material with high surface hardness and a tough core. Alternately, the need may be for a high temperature, corrosion resistant material with high elevated temperature strength as is the case with the hot stage blades and vanes in a gas turbine. The solution again is to provide the strength requirement from the bulk and the corrosion requirement from the surface [8-10].

1.1.1 Importance of Hard coatings

Hard coatings based on transition metal nitrides and carbides are widely used today to protect materials against wear. The tools are the key of every industrial production. The tool price usually presents a sizeable share in the product end-price, therefore it is important to enhance the tool lifetime and productivity. The first way is the proper tool material choice. Generally this includes various tool steels and hard metals, whereas in the last decade the ceramic and composite materials (e.g. cermets) have been implemented. Surface coatings find use in drills, reamers, bore cutters, shank cutters, taps, milling tools.

Together with the development of the tool materials, the protective coatings have been developed as well. Their common feature is the protection of the tool by their high hardness and chemical inertness; however, they are relatively brittle and expensive so they are not appropriate for bulk tool material. The combination of bulk material and the coating ensures optimal tool properties. The ecologically questionable galvanic processes (e.g. hard chrome) have been used for over a century to protect the tools, and many other techniques are known today, such as electroless plating, gas and plasma nitriding, etc.

The development of the hard protective coatings in the narrower sense started in the sixties with the chemical (CVD) and physical (PVD) vapor deposition techniques. There are many PVD variants in use today (magnetron sputtering, evaporation by laser, cathode arc, electron beam etc.). Their common feature is the vacuum environment, the substrate temperature is from room temperature up to about 800 °C, and the coating thickness does not exceed a few micrometers.
The most common hard coatings are based on transition metal nitrides (TiN, CrN), but in the last decade there has been a vast increase in multicomponent coatings (TiAlN), multilayer coatings (TiN/TiAlN).

The most important feature of the hard protective coatings is to reduce wear and in this way to increase the tool lifetime. So it is important to know which mechanism has the highest contribution to the wear (abrasion, adhesion, corrosion, high temperature, material sticking etc.) in order to find the most suitable coating for the desired process. A combination of certain coating properties opens possibilities for new technological procedures, e.g. low coefficient of friction and resistance against high temperatures enables dry machining without use of cooling-lubricating liquids. Aside from the price reduction such a procedure is superior from the ecological standpoint.

1.1.2 Transition-metal-nitride

Transition-metal nitrides, commonly referred to as refractory hard metals, possess unusual combination of physical and chemical properties [11], which make them attractive from both fundamental and technological points of view. They usually have high melting points, extremely high hardness, good electrical and thermal conductivity, and good corrosion resistance. This unique combination of properties has challenged both theoretical and experimental investigations [12-15] of the nature of the chemical bond in these materials and also made possible a large variety of applications [11,16] 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. With the increasingly sophisticated micro structural and compositional design of state-of-the-art nitride films, their performance relies on a corresponding stability. Examples of micro structurally engineered materials include meta stable alloy nitrides such as cubic phase TiN films, in a state of compressive residual stress, and compositionally modulated nitride films (e.g. nanolaminates; multilayers; superlattices). Generally, transition metal nitrides include TiN, ZrN, VN, NbN, TaN, and WN and so on.

Even for the data of thin films, the different deposition techniques and various microstructures may cause variation in these characteristics. We find that most of the transition metal nitrides are yellow, brown or gray color, with a face centered cubic structure (sodium chloride structure NaCl). From thermodynamic properties of transition metal nitrides, one can conclude that most of transition metal nitrides listed
above have very high melting point and are very stable at room temperature. Especially TiN, ZrN, HfN and TaN, their melting points are around 2000°C -3000°C, so they are widely used as high temperature coating and diffusion barrier materials for copper interconnect in IC technology. But due to their high hardness and inherent ceramic properties, the mechanical property measurements such as compressive strength and tensile strength measurements have to be performed at elevated temperatures. But generally speaking, they all have very high micro hardness and high Young’s Modulus and has been widely used as super hard coating materials. TiN (Transition metal nitride) was chosen as a binary metal nitride candidate in this work for the characterization.

1.1.3 Group – III nitride

The growth of III-Nitride films and device structures by physical vapor deposition (PVD) matured sufficiently to allow commercialization of light emitting diodes (LED’s), lasers diodes (LDs), and high mobility transistors (FET’s). These devices have utilized the short-wavelength, high-power, and high-temperature characteristics of these semiconductors. However, to improve the microstructural characteristics and lifetime of the present devices and to develop the next generation of devices, an in-depth understanding of the factors that effect growth must be realized. The main limiting factor in the growth of III-nitrides continues to be the lack of sufficiently large and inexpensive substrates for homoepitaxial growth [17, 18].

The group-III nitride-based semiconductors offer great potential for applications to high-temperature electronic devices, including light emitters, diode laser structures, and detectors operating in the visible and near ultraviolet spectrum. The phonon spectrum is one of the most fundamental characteristic of these crystals. It determines their thermal and optical properties including phonon assisted optical transitions. Therefore, a study of lattice dynamics of nitrides is not only of fundamental interest but results in a better understanding of structural parameters responsible for the efficiency of optical devices. It is suggested that the electronic and thermal properties of zincblende (cubic) nitrides will be superior to those of the wurtzite materials due to reduced phonon scattering in the high-symmetry crystals. The cubic nitrides are also believed to be better suited for doping than the wurtzites. However, in the bulk, group-III nitrides grow as crystals of wurtzite structure. Group III nitrides are BN, AlN, GaN, InN & TlN. Among these materials AlN was chosen as a binary nitride for DC sputtering and for material property studies.
1.1.4 Ternary Solid Solutions

Ternary transition metal nitrides are considered to exhibit better properties than binary nitrides since the addition of a third element into a transition metal matrix disrupts the crystal lattice. By adding aluminium into the TiN matrix, the properties were hence suspected to be improved. In addition, Ti (Al) N films have been reported to have higher thermal stability than TiN which further improves the diffusion barrier behavior.

A solid solution can be defined as follows...“A solid solution is a solid-state solution of one or more solutes in a solvent. Such a mixture is considered a solution rather than a compound when the crystal structure of the solvent remains unchanged by addition of the solutes, and when the mixture remains in a single homogeneous phase. The solute may incorporate into the solvent crystal lattice substitutionally, by replacing a solvent particle in the lattice, or interstitially, by fitting into the space between solvent particles. Both of these types of solid solution affect the properties of the material by distorting the crystal lattice and disrupting the physical and electrical homogeneity of the solvent material [19].”

We are expecting to have the spinodal decomposition in TiAlN. The process of the homogeneous nucleation is widespread far and wide; the creation of a nucleus implies the formation of an interface at the boundaries of the new phase. Surface energy is expanded to form this interface. If hypothetical nucleus is too small, the energy that would be released by forming its volume is not enough to create its surface, and nucleation proceeds. As the phase transformation becomes more and more favorable, the formation of a given volume of nucleus frees enough energy to form an increasingly large surface, allowing progressively smaller nuclei to become viable. Eventually, thermal activation will provide enough energy to form stable nuclei. These can then grow until thermodynamic equilibrium is restored [20]. There are also certain transformations where there is no barrier to nucleation. One of these is the spinodal mode of transformation, where phase separation is delayed until the system enters the unstable region where a small perturbation in composition leads to a decrease in energy and thus spontaneous growth of the perturbation. This region of a phase diagram is known as the spinodal region and the phase separation process is known as spinodal decomposition. In the other words the molar free energy of mixing has regions of negative curvature. The mechanism by which the system decomposes into its equilibrium phases is different than the mechanism when the curvature is
positive (case of the nucleation). The process of spinodal decomposition takes place and it occurs spontaneously when the second derivative of the Gibbs energy is negative:

$$\frac{\partial^2 \Delta G^m}{\partial X^2} < 0 \quad (1.1)$$

On the Fig. 1.1 the common case for the spinodal decomposition is presented. On the image (a) the typical binary phase diagram with a miscibility gap in which the spinodal decomposition happens is shown (b) represent the changes of the Gibbs energy according to the composition. The alloy will be unstable because small fluctuations in composition will cause the total free energy to decrease. The area where the second derivative is negative and the spinodal takes place is indicated by red colour. The curve on the Fig. 1.1 demonstrate how the function of the composition changes versus the time, the ‘Up-hill’ diffusion takes place until the equilibrium composition are reached [21].

The pseudo-binary phase diagram was calculated in the following way. Gibbs free energy, G, of a system is defined by

$$G = H - TS \quad (1.2)$$

Where H, T, and S are the system’s enthalpy, temperature, and entropy, respectively [22].

In our case the spinodal decomposition can be schematically represented by the following flow chart:
The result of the process is the formation of nm-sized domains of c-AlN which are coherent with the c-TiAlN matrix. And the c-AlN domains are beneficial in terms of retaining the coating’s hardness during annealing. This phenomenon can prove to be a key factor for explaining the good machining performance of TiAlN coatings [23]. The mechanism of the precipitation hardening which provides one of the most widely used mechanisms for the strengthening of non-ferrous alloys should be mentioned. Precipitation hardening is also called dispersion hardening, is a heat treatment technique used to strengthen malleable materials, including most structural alloys of aluminium and titanium. Changes in solid solubility with temperature produce fine particles of an impurity phase, which impede the movement of dislocations in a crystal’s lattice. Dislocations are often the dominant carriers of plasticity; therefore this serves to harden the material.

1.1.4.1. Density Functional Theory

Today the density functional theory (DFT) formalism is the most used *ab initio* method in computational material science and solid-state physics. The reason for this is the high computational efficiency combined with high accuracy. *Ab initio* is a Latin term that means first principles. This implies that the calculation relies on basic and established laws of nature without additional assumptions or special models. In the 1960s Hohenberg and Kohn [24] presented and proved two theorems, which became the fundament for DFT. The first theorem states that the external potential in which the electrons move, is a unique functional of the ground state electron density. This means that the systems are fully determined by the electron density. Hence, the total energy of the system can be expressed as a functional of the density. The second theorem states that the ground state electron density minimizes the total electronic energy of the system.

The theory was then further developed by Kohn and Sham [25] who used these theorems to derive the Kohn-Sham equations:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + e^2 \int \frac{nl(r')}{|r-r'|} dl + v_{xc}(r) + v_{xc}(r) \right] \psi_n(r) = E_n \psi_n(r)
\] (1.3)

Where the external potential, \(v_{\text{ext}}(n(r))\), is determined from the electronic density, \(n(r)\), instead of from the electron wave functions as for the general Schrödinger equation. \(\psi(r)\) is the time-independent wave function.
1.2 MICROSTRUCTURE–MECHANICAL PROPERTY RELATIONS

Traditionally, the term *hard coating* refers to the property of high hardness in the mechanical sense with good tribological properties. With the development of modern technology in the areas of optical, optoelectronic, and related defense applications, the definition of the term hard coatings can be extended. Thus, a system which operates satisfactorily, in a given environment can be said to be hard with respect to that environment [3]. Thus hard materials can be classified as:

1. Tribologically hard—wear resistant, and low friction.
2. Optically hard—laser, and photonically inert.
3. Radiation hard—high threshold energies for energetic particles such as gamma rays, neutrons, and beta particles.
4. Electrically hard—high band gap, and large electron velocities.

Most hard coatings are ceramic compounds such as oxides, carbides, nitrides, ceramic alloys, cermets, metastable materials such as diamond, and cubic boron nitride. Their properties and environmental resistance depend on the composition, stoichiometry, impurities, microstructure, imperfections, and in the case of coatings, the preferred orientation (texture).

The mechanical properties of materials depend fundamentally on the nature of bonding among their constituent atoms and upon their microstructures on a variety of length scales. During plastic deformation of materials, atoms have to be displaced with respect to one another. The easier this process is established, the more ductile is the material. At ambient temperature dislocations move by a glide process. Plastic deformation can also be obtained by creep processes, which include dislocation climb, atomic diffusion, and mechanisms like grain boundary sliding. Creep rates in polycrystals strongly depend upon the grain size, d, and vary from $d^{-2}$ behavior, in cases where the mechanism is volume diffusion controlled (Nabarro–Herring creep), to $d^{-3}$ behavior, in cases where the mechanism is controlled by interface or grain boundary diffusion (Coble creep) [26]. Thus, the mechanical properties can change dramatically as the grain size is reduced [27].

In conventional metallic materials, strengthening during plastic deformation (work hardening) occurs by an increase of the dislocation density. Hence the hardness increases as the interaction between dislocations increases. This can also be obtained by increasing the grain boundary fraction (grain size reduction), which increases the barrier to dislocation motion. Since the minimum stress required to activate common
dislocation sources (such as a Frank–Read source) is inversely proportional to the distance between dislocation pinning points, these stresses will increase with decreasing grain sizes into the nanophase regime owing to the limitation of the maximum distance between such pinning points [28]. Therefore, grain refinement in the nanoscale regime reduces the density of dislocations, which are necessary for plastic deformation. Hence, small-grained crystalline materials (nanocrystalline materials) show improved strengthening and the theoretical yield stress of a dislocation-free metal may be reached [24]. For ductile materials, the yield strength can be estimated using the Tabor-relation [29] which states that hardness H (obtained from a Vickers indentation) is about three times the yield strength. For hard materials, the hardness is better described by the Marsh-relation [30], which takes into account the elastic modulus (E), the Poisson ratio (ν), and the yield strength. Considering that the theoretical strength of a solid is solely a function of the strength of the interatomic bonds between atoms, the theoretical maximum yield strength would be E/10 [31]. Thus, the theoretical hardness (obtained via a Vickers indentation and using the Marsh-relation) e.g., for TiN (E = 300–400 GPa, m = 0.25) would be 40–53 GPa. In practice, however, the strength of inherently strong solids never meets these theoretical expectations because of the presence of crystal imperfections, microscopic defects and cracks. This is also valid for materials composed of 1–2 nm sized crystals, which are considered to be dislocation-free [32]. Two main types of atoms can be distinguished in nanocrystalline materials; crystal atoms with nearest neighbour configuration corresponding to the lattice and boundary atoms with a variety of interatomic spacings, different from boundary to boundary. A nanocrystalline material typically contains a high number of interfaces with random orientation relationships, and consequently, a substantial fraction of atoms belongs to the interfaces. The interfacial component has a lower atomic density than the crystal [33].

PVD single-phase layers usually show a nanostructure in one or two dimensions. Depending on the ion bombardment used during deposition and the thermodynamic driving force for segregation also a nanostructure in three dimensions can be formed. This can also be obtained by the simultaneous growth of a second phase or by doping with additional atoms during deposition. The amount and type of additional phases and elements can be used to control the orientation and the size of grains in the films [34]. The nanocrystalline materials may contain crystalline, quasi-
crystalline, or amorphous phases of metals, ceramics or their composites. Nanocrystalline materials are of increasing interest because they exhibit mechanical, physical, and chemical properties different from their coarse-grained counterparts. For example, the hardness and yield stress may increase 5–10 times when the grain size is reduced from the macroscopic to the nanometer range [26].

The effect of an increased strengthening with decreasing grain size \( d \) is described by the well known Hall–Petch relation (HPR) [35, 36]:

\[
\sigma_y = \sigma_o + k \frac{1}{\sqrt{d}} \tag{1.4}
\]

where \( \sigma_y \) is the yield stress, \( \sigma_o \) the ‘friction stress’ and \( k \) is the Hall–Petch factor which depends on the material and measures the relative hardening contribution of grain boundaries/ interfaces. However, grain size reduction has a negative effect on creep strength, especially for metallic materials. For brittle materials, such as intermetallic compounds and ceramics, the ductility increases by grain refinement as a result of increased grain boundary volume fraction and, therefore, grain boundary sliding. Nanocrystalline pure metals are much stronger and apparently less ductile than conventional ones. Intermetallics are also strengthened by a grain refinement, but they are also affected by the large percentage of atoms in grain boundaries and other microstructural features. The strengthening effect by grain refinement is limited by the critical grain size, \( d_c \), where the Hall–Petch effect ceases or even reverses. Reasons for this behavior can be an increased porosity at small grain sizes, suppression of dislocation pile-ups, dislocation motion through multiple grains, grain boundary sliding, enhanced grain boundary diffusion or the fact that no dislocations can form in such small grains, thus the concept of mirror forces into the next grain becomes irrelevant [37,38]. The reverse Hall–Petch effect is classified by negative \( k \) values in the HPR. The critical grain size \( d_c \) depends strongly on the nature of a material. While the premises for the Hall–Petch effect are no longer fulfilled below \( d_c \), the nanoscale phenomena are not yet fully understood.

Residual stresses can be defined as the stresses embedded inside a machined or welded component even after the forces causing the stresses are removed. The internal state of the stresses can be either compressive or tensile depending upon the nature of the operation performed on the component. Both the magnitude and distribution of the residual stresses are critical for performance, and should be considered while designing a component. In any free standing body, stress
equilibrium should be maintained, which means that the presence of a tensile residual stress in a component will be balanced by a compressive stress elsewhere in the component. Tensile residual stresses on the surface of a component are generally undesirable since they can aggravate the failure of a component, and often may cause fatigue failure, quench cracking and stress-corrosion cracking. Residual stresses can however be reduced or eliminated by inducing compressive stresses generated by short-peening operation.

WEAR, like corrosion, does not fit handily within the confines of a traditional discipline. Physics, chemistry, metallurgy and mechanical engineering all contribute to this topic. A particular feature of substrate deposition temperature that is attractive for wear applications is its low temperature processing and ability to be applied to distortion prone substrates without increasing stress in the composite. Mechanisms of wear are discussed as are some of the more important tests used for evaluating wear characteristics. Coatings that are used for various wear applications include TiN, AlN and TiAlN. Recent advances include ternary transition metal nitride with Al to provide improved wear resistance. Microlayered metallic coatings also known as composition modulated coatings also offer promise.

CORROSION is affected by a variety of factors including metallurgical, electrochemical, physical chemistry and thermodynamic. Since all of these encompass the field of materials science, the topic of corrosion is essentially covered in many places in this book other than this particular chapter. When selecting a coating it is important to know its position with respect to its substrate in the galvanic series for the intended application. Besides galvanic effects, the substrate and the interfacial zone between it and the coating can noticeably affect the growth and corrosion resistance of the subsequent coating since corrosion is affected by structure, grain size, porosity, metallic impurity content, interactions involving metallic underplates and cleanliness or freedom from processing contaminants [39]. Decorative nitride coatings developed for automotive industry applications are a good example of use of materials science and electrochemistry to improve corrosion resistance properties.
1.3 MATERIAL PROPERTIES OF TITANIUM NITRIDE (TiN)

Over last two decades, TiN has been extensively studied due to its successful use in a variety of thin film applications. For example, the high hardness of TiN makes it a particularly useful material for increasing the wear resistance of high speed steel cutting tools, punches, and metal forming tools. In addition the good corrosion and erosion resistance of TiN, its relative inertness, high sublimation temperature and optical and electronic properties have resulted in TiN coatings being considered for use as diffusion barriers in microelectronic devices, cosmetic gold-colored surfaces, and wavelength selective transparent optical films. Its high hardness and corrosion resistance has made it particularly useful for increasing the wear resistance of high speed steel cutting tools [40], while its high conductivity and diffusion barrier properties have led to its employment in semiconductor metallization schemes [41]. In addition, TiN films have been used for cosmetic faux gold surfaces [42] (such as watch bezels, watch bands, and pen barrels [43]), wavelength selective transparent optical films [44], thin film resistors, tool bit coatings, and, due to its strong infrared reaction, energy-saving coatings for windows.

The interesting properties are related to its structure and bonding characteristics. TiN (Fig.1.2) has a cubic NaCl-type crystal structure with a lattice constant (for stoichiometric materials) of 0.4240nm and a vacancy defect structure that is stable over a wide composition range (0.6<N/Ti<1.16).

1.3.1 Mechanical properties of TiN

The microhardness value is about 19.9GPa (1990 kg/mm$^2$). For TiN thin films, the hardness value varies from 3.4 GPa to 40GPa (340-4000 kg/mm$^2$). The large differences arise primarily from differences in thin film microstructures, such as grain size, columnar vs. equiaxed structure, void density and so on, and film purity. The first microhardness of single crystal TiN thin film is 23±2 GPa (2300±200 kg/mm$^2$). The reason for lower hardness observed in polycrystalline TiN was explained in the paper to be intergrain boundary failure. They interpret that the dislocation mobility is quite low in most of the transition metal nitrides at temperature below 1000$^\circ$C.

Nanoindentation results show that hardness of single crystal TiN thin films is 29GPa which is relatively smaller than polycrystalline TiN 32 GPa. (The average grain size is around 100nm.) We envisage this drop to be related to the decrease in overall dislocation density in these single crystal films. If the grain size of TiN thin
film continues to decrease in nanocrystalline regime, the hardness is starting to
decrease, which is known as negative Hall-Petch relationship.

1.3.2. 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>Metallic Gold</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>61.87</td>
</tr>
<tr>
<td>Density</td>
<td>5.22 g/cm^3</td>
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<tr>
<td>Melting point</td>
<td>2930 °C</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Face Centered Cubic</td>
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<tr>
<td>Space Group</td>
<td>Fm3m</td>
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<tr>
<td>Lattice constant</td>
<td>4.24 Å</td>
</tr>
<tr>
<td>Extreme Hardness</td>
<td>2300HV</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>600 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
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<tr>
<td>Coefficient of Friction</td>
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<tr>
<td>Low Electrical Resistivity</td>
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<tr>
<td>Hall constant</td>
<td>-6.7x10^{11}m^3/C</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient</td>
<td>9.4 x 10^{-6} °C</td>
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<tr>
<td>Thermal Conductivity</td>
<td>0.046 Cal/sec.-cm-°C</td>
</tr>
<tr>
<td>Specific heat</td>
<td>37 J/mol.K</td>
</tr>
</tbody>
</table>

1.3.3. Phase diagram and band structure of TiN

TiN exhibit electrical and thermal conductivity properties which is near to that of pure metals, which can be considered as refractory metals. The phase diagram and band structure are shown in Fig.1.3 and 1.4 respectively. Nevertheless, one should notice that these researches are mainly devoted to stoichiometric or near stoichiometric materials despite the fact that they can also exist far from the stoichiometry. One reason is that the synthesis methods mainly allow easy preparation of only compounds near stoichiometry. Another reason is that the properties of these materials are believed to be most interesting near stoichiometry. As a consequence, one knows the properties of stoichiometric materials much better than those of materials far from stoichiometry. The Ti-N system is rather complex compared to the Ti-C system due to the high solubility limit of nitrogen in both of the usual hexagonal α-Ti and cubic β-Ti phases. It results that the α-Ti solid solution has a large range of existence going up to 25 at.% N. At high N_2 concentration, one obtains an NaCl-type
structure called $\delta$-TiN$_x$, where $x$ can lie between 0.5 and 1.0. It is the most usual Ti-N phase. Another phase with tetragonal structure called $\varepsilon$-Ti$_2$N exists in the vicinity of 31.5 at.% N. Finally, at high temperature above 1153K, another tetragonal phase called $\delta'$-TiN$_x$ exists with $x$ varying between 0.50 and 0.61.

**1.3.4. Applications of TiN**

TiN has been widely used as hard-coating material due to several important characteristics:

1. **High thin film uniformity**: TiN coating conforms uniformly to the substrate. No buildup occurs on corners (unlike plating operations) and coating "throws" well into features.

2. **High hardness**: Hardness is larger than 2000 kg/mm$^2$ in Knoop or Vickers Microhardness measurements. Values of 2500-3000 are typical for TiN thin film and it is higher than hard chrome or carbide material.

3. **Good adhesion**: The coating forms a metallurgical bond to the substrate that will not flake, blister, chip or peel.

4. **Low coefficient of friction**: TiN generally provides relatively low friction against steels, carbides, TiN, ceramics, platings, etc. The coefficient of friction is a system property, not a material property. It depends on many factors such as material, countermaterial, lubrication, environment temperature, speed, loading force, surface finish, surface finish of the countermaterial, and type of motion (reciprocating, rotating). The published values have a large variation from 0.50 to 0.90. A typical value is 0.65 for TiN against steel.

5. **Non-stick TiN**: TiN is an excellent non-stick surface against most other materials. From above discussions, it is obvious to see the reasons that why the titanium nitride (TiN), has served as the most practical and economical protective coating. TiN exhibits a metallic character with golden color and high hardness, high temperature stability, and abrasion resistance. However, the TiN gets oxidized above 500°C to form a rutile-structure which limits its applications in high speed cutting tools.
1.4. MATERIAL PROPERTIES OF ALUMINIUM NITRIDE (AlN)

Aluminium nitride (AlN) thin films are widespread applied because they had some excellent properties such as chemical stability, high thermal conductivity, electrical isolation, a wide band gap (6.2 eV), a thermal expansion coefficient similar to that of GaAs, and a higher acoustic velocity. Therefore, AlN thin films were applied not only to surface passivation of semiconductors and insulators, but also to optical devices in the ultraviolet spectral region, acousto-optic (AO) devices, and surface acoustic wave (SAW) devices. Its wurtizte phase is an extremely wide bandgap (6.2 eV) semiconductor material which has potential application for deep UV optoelectronics. The material is stable at very high temperatures in inert atmospheres. In air, surface oxidation occurs above 700°C, and even at room temperature, surface oxide layers of 5-10 nm have been detected. This oxide layer protects the material up to 1370°C. Above this temperature bulk oxidation occurs. AlN is stable in H₂ and CO₂ atmospheres up to 980°C. For the absence of thermal dynamical data for cubic AlN, we cannot give the relationship between equilibrium partial pressure of gases and cubic AlN in the reaction system at various reaction temperatures.

It is capable in spintronics because of its high Curie temperature if doped with transition metaIs. AlN can also be used as a buffer layer for growth of device-grade GaN as well as for application in sensors, surface acoustic wave devices, and high-temperature electronics. AlN shows excellent field-emission performance in vacuum microelectronic devices due to its small electron affinity value, which is from negative to 0.6 eV. In this sense, nanostructured AlN, such as AlN nanowires and nanorods, is important for extending our knowledge on the potential of nanodevice applications. For growth of bulk AlN the sublimation-recondensation (a kind of physical vapor transport growth) method is the most successful and promising crystal growth technique. With progress of the nitrogen gas flow reaction, a metastable cubic AlN is easily transformed into hexagonal AlN, which might interpret why the cubic AlN is not easy to be found in sputtering thin films. The nitrogen distribution in cubic AlN is cubic and closely packed. Hexagonal AlN phase is obtained via crystalline transition of metastable cubic AlN. It has the advantages of easier doping, easier cleaving for laser facets, and easier contacting. It also has higher electron and hole mobilities than H-AlN.
1.4.1. Lattice positions

The III-Nitride semiconductors may occur as two different crystal structures, namely either wurtzite or zincblende. It is well known that AlN has a hexagonal wurtzite structure and two kinds of cubic structure (a_0=4.12 Å and a_0=7.913 Å). AlN is a covalently bonded material, and has a hexagonal crystal structure called the wurtzite crystal structure. The space group for this structure is P6_3mc. The zincblende structure is a cubic unit cell with F4_3m symmetry that generally grows on cubic substrates such as silicon and GaAs. The stacking sequence along the c-axis is denoted as ...ABCABC... The structure may be seen as two interpenetrating face center cubic unit cells offset ¼ ¼ ¼ along the <111> direction. Figure 1.5 shows the wurtzite structure for AlN, which consists of a hexagonal unit cell with 6 atoms of group III and 6 atoms of group V elements. This structure may be described as two interpenetrating hexagonal close packed sublattices off set from one another by 5/8 of the cell height. The unit cell is described by two lattice constants, a and c, where the former is the distance along one side of the hexagon and the latter is the unit cell height. The structure is described as 2H consisting of an...ABAB... stacking sequence. The hexagonal structure is generally used in opto-electronic applications due to its direct bandgap.

The group III atoms form compounds with N that have four covalent bonds for each atom. AlN can crystallize in two crystal structures; Wurtzite (Fig.1.6) and Zinc blende with the stable one being the wurtzite structure. The wurtzite structure has a hexagonal unit cell with two lattice parameters a and c with an ideal ratio of c/a = \sqrt{8}/3 = 1.633. Four nitrogen atoms surround every group III atom, and four group III atoms, which are arranged at the edges of a tetrahedron, surround every nitrogen atom. For an actual nitride, the structure is distorted from the ideal hexagonal packing of the basic molecule oriented along the stacking direction (c-axis). Because of this small distortion, there are two slightly different bond lengths in the wurtzite structure given by:

\[ B_\parallel = u.c \]  \hspace{1cm} (1.5)

\[ B_{\perp} = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \]  \hspace{1cm} (1.6)
Where \( u \) represents the cell-internal structural parameter (ideal value of 3/8), \( a \) and \( c \) denote the length of the lattice vectors of the structure. \( B_\parallel \) represents the length of bonds parallel to the \( c \)-axis and \( B_\perp \) represents the length of bonds pointing in any other direction. The wurtzite structure with greater \( c/a \) value than the ideal value of 1.633 is unstable, while less than 1.633 is stable. The phase diagram is shown in Fig.1.7.

**1.4.2. Properties of Aluminium Nitride (AlN)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>AlN</td>
</tr>
<tr>
<td>Density</td>
<td>3.3 g/cm³</td>
</tr>
<tr>
<td>Color</td>
<td>Black</td>
</tr>
<tr>
<td>Structure</td>
<td>Cubic/ Hexagonal</td>
</tr>
<tr>
<td>Melting Point</td>
<td>&gt;2200°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>2517°C</td>
</tr>
<tr>
<td>Hardness</td>
<td>1200 HV</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>310 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.22</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>160 GPa</td>
</tr>
<tr>
<td>Compressive strength</td>
<td>1000 MPa</td>
</tr>
<tr>
<td>Modulus of rupture</td>
<td>300-350 MPa</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>140-177 Wm⁻¹k⁻¹</td>
</tr>
<tr>
<td>Coefficient of Expansion</td>
<td>( 4.6 \times 10^6 ) (20 - 400°C)</td>
</tr>
<tr>
<td>Specific heat capacity</td>
<td>740 J Kg⁻¹K⁻¹</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>8.8 at 1MHz</td>
</tr>
<tr>
<td>Resistivity</td>
<td>( &gt;10^{10} ) ohm-cm</td>
</tr>
<tr>
<td>Optical transmission</td>
<td>0.2-12.5 μm</td>
</tr>
<tr>
<td>Band gap</td>
<td>6 eV</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.11</td>
</tr>
</tbody>
</table>

**1.4.3. Applications of AlN:**

AlN thin layers have remarkable hardness, thermal and chemical stability and high electrical resistivity. The most remarkable property exhibited by AlN is its high thermal conductivity – in ceramics materials second only to beryllia. At moderate temperatures (~200°C) its thermal conductivity exceeds that of copper. This high conductivity coupled with high volume resistivity and dielectric strength leads to its application as substrates and packaging for high power or high density assemblies of
microelectronic components. One of the controlling factors which limits the density of packing of electronic components is the need to dissipate heat arising from ohmic losses and maintain the components within their operating temperature range. Substrates made from AlN provide more efficient cooling than conventional and other ceramic substrates, hence their use as chip carriers and heat sinks. The bandgap of single crystal AlN has been measured (using Vacuum UV reflectivity) at 6.2eV. This allows a wavelength of around 200nm to be achieved, in principle. However, there are many difficulties to be overcome if such emitters are to become a commercial reality. The applications of AlN are in the field of

- Optoelectronics,
- Dielectric layers in optical storage media,
- Electronic substrates,
- Chip carriers where high thermal conductivity is essential and military applications.

Epitaxially grown AlN is also used for surface acoustic wave sensors (SAW’s) deposited on silicon wafers because of the AlN piezoelectric properties. Very few places can reliably fabricate these thin films. Because of the cost of AlN its applications have been developed mainly for military aeronautics and transport fields. Other applications of AlN lie in refractory composites for handling of aggressive molten metals, and high efficiency heat exchange systems.

1.5 MATERIAL PROPERTIES OF TITANIUM ALUMINIUM NITRITE

Titanium Aluminum Nitride (TiAlN) coatings, also called Aluminum Titanium nitride consist of a multi layer ceramic coating applied by PVD coating technology, which exhibits high toughness and oxidation stability. These properties make it deal for higher speeds and feeds whilst at the same time improving tool life. TiAlN is suitable for drilling and tapping. It is recommended to use TiAlN when machinery dries.

However TiAlN films exhibit superior oxidation resistance and better cutting performance in the use of higher cutting performance in the use of higher cutting speeds compared with TiN because the Al added to TiN to form a ternary solid solution enhances antioxidation behaviours at high temperature (up to 800 °C). Initially, the addition of Al in TiN had the purpose of improving its high temperature oxidation resistance and hardness. However, for higher Al concentration, the formation of hexagonal AlN, which is believed to be softer than fcc-TiAlN, results in
a significant reduction of film hardness. When coated tools are thermally loaded, the thermal expansion mismatch between the substrate and the film generates thermal stress, even if some amount of relaxation takes place. The thermal expansion mismatch of the supporting substrate and film depends on the Ti/Al ratio. However, Al rich films the thermal expansion mismatch is lower, and weaker thermal stresses favour them for applications in cutting tools even if their hardness remains low. The resistance to fracture and spallation is also strongly related to the film composition and microstructure. TiN-AlN binary-component coatings can integrate their functionalities and show much higher oxidation resistance, lower internal stresses and better adhesion. TiN-AlN binary-components can be formed in two types of structures. One is uniform alloy which AlN concentration is lower than 60%. If AlN concentration is higher than 60%, phase separation results which may lead to precipitation hardening. The other type is multilayer structure where there is no reaction between TiN and AlN. Especially, nanometer-scale multilayer structures attract a lot of interest due to their special interfacial structure which may lead to novel structural and mechanical properties. A novel method to grow highly aligned TiN/AlN superlattice by using pulsed excimer laser. In this method TiN and AlN targets are arranged in a special configuration that they can be ablated in a sequence, giving alternate layer by layer growth of TiN(1 nm)/AlN(4nm). The structure of AlN is determined to be cubic which is metastable and stabilized by the thin layers of TiN.

1.5.1 Properties of TiAlN

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>TiAlN</td>
</tr>
<tr>
<td>Density</td>
<td>4.3 g/cm³</td>
</tr>
<tr>
<td>Colour</td>
<td>Purple</td>
</tr>
<tr>
<td>Structure</td>
<td>Cubic</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>4.194 Å</td>
</tr>
<tr>
<td>Melting Point</td>
<td>&gt;2200°C</td>
</tr>
<tr>
<td>Hardness</td>
<td>2700 HV</td>
</tr>
<tr>
<td>Modulus of Elasticity</td>
<td>632 GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.177</td>
</tr>
<tr>
<td>Co-efficient of friction</td>
<td>0.6</td>
</tr>
<tr>
<td>Coefficient of Expansion</td>
<td>9.4x10⁻⁶</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>1500°F</td>
</tr>
<tr>
<td>Resistivity</td>
<td>0.02-0.4 ohm-cm</td>
</tr>
</tbody>
</table>
1.5.2. Phase diagram of TiAlN

Ternary phase diagrams of transition-metal nitrides and carbides have been extensively measured, primarily by Rudy and co-workers and by Brauer and co-workers. These diagrams are very complex functions of temperature and composition. Figure 1.7 illustrates some of the complexities involved in just one of these diagrams. The number of possible ternary diagrams involving the fourth, fifth, and sixth group transition metals and C and N is very large; description of even the small fraction of those that have been measured is beyond the scope of this text. Generally, these diagrams are only partially investigated over a limited composition and temperature range. Since the pseudobinary systems involving monocarbides and mononitrides have particular interest because of their high melting points and great hardness, they have been extensively investigated. Nearly all monocarbides and mononitrides form complete solid solutions with one another. Solid-solution formation is governed by the same principles established by Hume-Rothery for the simple metals: atomic size differences of the atoms and crystal structure similarities. The degree of solid solution formation depends upon temperature and stability of certain crystal structures. Bonding in transition-metal nitrides and carbides involves simultaneous contributions of metallic, covalent, and ionic bonding to the cohesive energy. The extensive mutual solubility of the monocarbides and the mono- nitrides indicates that the atomic bonding in both the carbides and the nitrides is similar.

1.5.3. Applications of TiAlN

Transition-metal nitrides display a wide spectrum of interesting physical properties that make them useful materials for a variety of different purposes. Hard materials suitable for thin film ceramic coatings are usually carbides, nitrides, borides and silicides of the IVth, Vth and VIth groups in the periodic table. The ceramic compound is thought to form at the surface of the substrate as this is the most energetically favorable. During the 1970’s replaceable cutting inserts together with hard coatings were introduced. One of the first wear-resistant coating materials in the modern cutting tool industry used was TiN [45]. It exhibits high hardness and stiffness which makes it suitable as a cutting tool coating. The main shortcoming is, however, limited stability due to oxidation at temperatures above 500 °C [46]. Today the work temperatures of tools are typically between 800-1200 °C. Therefore, there is a growing interest concerning coating materials with improved thermal stability. The present design concept has been to employ ternary compounds, e.g. (Ti,Al)N [47,48].
(Ti,Al)N offers improved oxidation resistance, better thermal stability, defect (compressive residual stress) hardening, as well as newly discovered age hardening [49]. Together, these factors improve the life time of the tool, and provide the possibility to work at higher cutting speed. (Ti,Al)N has been used as a protective coating for cutting tools since the early 1990’s and is still a work horse for hard coatings [50]. Today, (Ti,Al)N used in metal cutting industry are examples of metastable hard coatings that can be synthesized by arc evaporation at low temperature. Recent years, TiAlN have been developed for various applications such as electronic devices, diffusion barriers, and hard coatings. It exhibits superior mechanical, electrical and oxidation properties at higher temperatures (up to 800°C). (Ti,Al)N film can be used as an intervening layer to improve the biocompatibility of metal substrate in dental application. Ti₆Al₄V is most common titanium alloys used in orthopedic implant because of superior toughness, favorable mechanical properties and excellent biocompatibility.

1.6 AIM OF THE PRESENT WORK

Despite the literature available on several properties of TiN, AlN and TiAlN thin films prepared by DC magnetron sputtering technique, there is lack of complete information concerning the microstructure and tribology. The aim of this thesis is to prepare TiN, AlN and TiAlN nitride films by the DC magnetron sputtering technique and characterize their structural, morphological, tribological and thermal stability properties. Therefore, the present investigation has been carried out on TiN, AlN and TiAlN thin films deposited at different substrate temperatures with the following aims.

(I) To prepare and study the microstructure, optical and tribology properties of TiN thin films.

(II) To prepare AlN films with improved structural properties by optimizing the deposition conditions and its material properties were studied.

(III) To prepare and characterize TiAlN films by sputtering technique for structural, mechanical, mechanical, and corrosion applications.

This thesis is organized into 7 chapters which describes about the preparation of different metal nitride and ternary metal nitride thin films. Chapter 1 gives the introduction about the importance of hard coatings and the physical properties of metal nitrides. Chapter 2 discusses about literature reviews on TiN, AlN, TiAlN films and it gives the theoretical and experimental details of Magnetron sputtering
technique. Chapter 3 discuss about the different characterization tool used to characterize and optimize the thin film samples prepared in this course of research work.

Chapter 4, 5 & 6 gives the details about the structural, morphological, optical, and tribological (Mechanical & Corrosion) properties of TiN, AlN & TiAlN films respectively. Chapter 7 sums up the results of these studies, the conclusions of material property results and its optimized condition were reported and the suggestions for future work are also given.
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