Synthesis and characterization of Titanium Silicon Nitride (TiSiN) thin film: A review

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Abstract: In-depth studies on transition metal are required to understand about different properties of materials. Different deposition techniques like rf magnetron sputtering, hot pressing, ion beam assisted deposition, ion arc plating and chemical vapour deposition were employed to deposit TiSiN. The morphology, mechanical and structural properties of TiSiN thin film coating has been characterized by different processes (e.g. AFM, SEM, TEM, XRD, Nanoindentation etc.). Many researchers also studied mechanical properties to investigate different parameters like hardness, fracture toughness, Young's modulus etc. This review paper is aimed to summarize all the properties studied by the different researchers on titanium silicon nitride.

1. Introduction
In past decades transition metals are increasingly used for various industrial, scientific and technological applications because of their promising mechanical properties, oxidation resistant and wear resistant characteristics. Among a wide variety of transition metal nitride available in industries, titanium nitride (TiN) is one of the common and important candidates as titanium and nitrogen-based metal nitride possesses very good commercial interest because of their extreme hardness, wear resistant, corrosion resistant, thermal and electrical properties which fit well with most of the industrial requirements. Besides those advantages, binary metal also shows some of the disadvantages like poor oxidation at elevated temperature, intrinsic brittleness etc. Those disadvantages restrict binary metal from specific technological applications [1]. This problem has been sorted out by mixing silicon or aluminium into the TiN network to form a new family of ternary nitride (e.g. TiSiN, TiAlN), in which during the last few years new developments have shown a significant improvement in the quality of such films. Titanium silicon nitride considered being one of the most prominent materials among the all transition metals [2-4]. Titanium and silicon alloys with nitrogen make an outstanding team for hard material coatings. Silicon guarantees excellent resistance to oxidation while the presence of titanium ensures particularly hard coatings. When combined, two elements are wear resistant even at elevated temperature [5-7].
1.1 Titanium Nitride
Titanium nitride mainly uses as a coating material to protect the edge of the different machine tools (e.g. drill bits, milling cutters etc.) and also make it corrosion resistant. It can improve the lifetime of a tool to three times of a factor because of its properties like wear resistant, inert etc. [8]. Because of its extreme hardness, it can improve the substrate’s surface property. It’s chemically stable at normal temperature but can be affected by concentrated acid solution in elevated temperature [9]. TiN has coefficient of friction within the range of 0.4 – 0.9 with another layer of TiN and it forms crystal structure as NaCl type [10]. Vicker’s hardness, modulus of elasticity and coefficient of thermal expansion of TiN is 2400, 251 GPa and 9.35×10^{-6} K^{-1} respectively [9-11].

| Table1. General Properties of Titanium Nitride |
|-----------------------------------------------|
| Chemical formula | TiN |
| Molar mass | 61.84 g/mol |
| Density | 5.22 g/cm³ |
| Melting point | 2930 °C |
| Thermal conductivity | 19.2 W/m°C |
| Vicker’s Hardness | 2400 |
| Modulus of elasticity | 251 GPa |
| Co-efficient of thermal expansion | 9.35×10^{-6} K^{-1} |
| Young’s Modulus | 450-590 GPa |

Different physical vapor deposition (PVD) methods (e.g. sputter deposition, cathodic arc deposition, electron beam heating) and chemical vapor deposition (CVD) used to develop TiN thin film. In both, the process pure titanium is reacted with nitrogen at high energy and vacuum environment to form TiN. Annealing is the other process which is used to develop TiN films on Ti workpieces by reactive growth in nitrogen atmosphere [12]. PVD is the preferable method to deposit TiN on steel as the temperature exceeds the austenizing temperature of steel. TiN can also sputter on the various materials having a high melting point temperature like stainless steel, titanium etc. [13]. Because of its golden colour, it is used to coat costume jewellery and automotive trim for decorative purpose. TiN is also used as a conductive barrier between the active device and contact metals of microelectronics devices. Now it is also used as a metallic material to improve the performance of a transistor. It is also used in fusion power experiment because it tightly bonding nature with oxygen molecules [14].

1.2 Silicon Nitride
Silicon nitride (Si₃N₄) is normally a chemically inert chemical compound made of silicon and nitrogen. It is very hard, high strength in the wide temperature range, high fracture toughness and thermally stable nitride metals. It also has outstanding wear resistance (both impingement and frictional mode), good thermal shock resistance and considerable chemical resistance properties. Its colour varied from dark grey to black and can be polished to a very smooth reflective surface. Generally, silicon nitride is prepared by heating of silicon powders in presence of nitrogen gas [15]. Silicon nitride is difficult to produce as it is bulk material and it cannot be heated over 1900°C as their chances of dissociation of Silicon and Nitrogen. Apart from the conventional way silicon nitride can also be produced by different methods e.g. divide route, carbo thermal reduction of silicon dioxide in nitrogen atmosphere, low-pressure chemical pressure deposition, plasma enhanced chemical vapor deposition etc [16-18].

| Table2. General Properties of Silicon Nitride |
|-----------------------------------------------|
| Chemical formula | Si₃N₄ |
| Molar mass | 140.28 g/mol |
| Density | 3.2 g/cm³ |
| Melting point | 1900 °C |
| Thermal conductivity | 30 W/m°C |
| Hardness | 1580 kg/mm² |
| Modulus of elasticity | 310 GPa |
| Co-efficient of thermal expansion | 3.3×10^{-6} K^{-1} |
Silicon nitride never considered a single material as its material properties strongly depend on fabrication method. Three main types of silicon nitride are Reaction bonded silicon nitride (RBSN), hot pressed silicon nitride (HPSN) and sintered silicon nitride (SSN). The density of reaction bonded silicon nitride is less as compared to other two as it is made by direct nitridation of compacted silicon nitride powder. The choice of material selection depends on its specific application and properties of the components required. RBSN is the lowest cost material among the silicon nitride family where as RBSN provide best mechanical properties. Silicon nitride is rather expensive material, but its performance to cost ratio is excellent in the applications where it can outperform other materials with long life and low maintenance coast. It has several applications in the Automobile industry, high-temperature material preparation, medical science, electronic devices etc. [17, 19-22].

1.3 Titanium Silicon Nitride
The demand for ternary films nitride has been increased from last decade because of their growing demand in different applications (e.g. coatings, aerospace industry, tool hardening electronics devices etc.). Ternary metal nitride (e.g. TiSiN, TiAlN etc.) possesses some improved properties like corrosion protection, high hardness, good wear resistant, low coefficient of friction, and high melting point etc. compared to binary metal nitride metals. Most of the cutting tools are coated with TiN to improve its performance but there is a chance that TiN became oxidized at elevated temperature. Even, sputtered TiN has also two major drawbacks as it subjected to poor step coverage the microelectronics device started to shrink and it also has columnar polycrystalline microstructure. These drawbacks can be eliminated by deposition of silicon into it. Addition of Silicon improves its hardness and possesses excellent abrasion resistance. Thermal, mechanical and chemical properties of Silicon nitride makes it one of the best metal nitride material but because of lack of toughness and reliability still, it cannot be used in some specific applications (e.g. Aerospace industries, surgical tools etc.). Properties of silicon nitride can be improved with the addition of TiN into it. All over Ti-Si-N as a ternary nitride film provided better performance compared to binary metal nitride [23-28].

2. Synthesis of TiSiN
2.1 Physical Vapor Deposition (PVD)
The simplest thermal evaporation method is PVD, in which source material is evaporated at the one end of the chamber and deposited on the substrate at other colder end of the chamber. The basic process of PVD is the production of vapour and then transported to the substrate to deposit on it. Different PVD procedures are classified as per the difference in the method of vapor production, its dependence properties and the level of control available over the deposition. In general, production and transportation of vapor take place under vacuum hence such deposition requires technology and equipment to produce and maintain the low pressure [29-30].

2.1.1 Magnetron Sputtering
This is the most common and popular among all PVD processes available today. From a small lab scale system to big industrial system this technique can adapt easily. Semiconductor's structure, nano wires, simple metal layer and complex structure can be grown by this technique. In this process after energetic ion hit the source material, called target. vapour of the depositing species is produced and atoms are ejected from the target due to energetic collision cascade and this ejection due to collision is known as sputtering. The deposition chamber is evacuated to very low pressure (typically 1mPa or better) to provide sputtering of ions and then it is filled with different process gas (e.g. N₂, Ar etc.). A high electric field is developed in between the target and chamber wall to ignite the plasma. Electrons are then started to accelerate and impacts on the gas atom, ionize it by knocking off electrons. In actual condition this will trigger a cascade of collision and electron emission then it reaches a steady state where gas in the chamber is ionized to form the plasma. Then the positive ions are attracted towards the negatively biased target to induce sputtering. Plasma is normally magnetically placed in the region in front of the target by the strong magnetic fixture. This fixture known as the magnetron, enhance the efficiency of the process [31-36]. Diseren et al. [28] used PVD technique to deposit thin films of Ti-Si-N to enhance the wear resistance properties of TiN. They used various contents of silicon during deposition by reactive unbalanced magnetron sputtering technique. Cylindrical PVD reactor equipped with silicon and titanium targets considered as a deposition system. Their main
purpose of using separate silicon and titanium targets is to adjust Ti: Si ratio in the gas phase. Vaz et al. [37] coated polished high-speed steel and silicon substrate with (Ti, Si)N by reactive rf magnetron sputtering. They used Ti and Si as target materials and deposition carried out in Ar/N₂ gas atmosphere. They maintained 200 W r.f powers to etch substrate in Ar gas atmosphere for the period of 15 minutes. Base pressure was in between 10⁻⁴ Pa to 4×10⁻¹ Pa during deposition. Substrates were heated up to 300°C and d.c. bias ranging +25 V to -75 V was applied. Both the targets were coupled to r.f. source with power in the range of 1.9-3.2 E + 4 Wm⁻² for Ti and 1.8-2.3 E + 4 Wm⁻² for Si. Shen et al. [38] produced thin films of Ti₁₋ₓ₋ₓSiₓNy on a silicon substrate by reactive unbalanced d.c- magnetron sputtering of titanium and silicon in the Ar-N₂ gas atmosphere. Magnetron sputter was direct current biased and operated under the condition of intense Ar-ion plating.

2.1.2 Ion Beam Assisted Deposition
It is a special type of physical vapor deposition technique as it can create a gradual transition in between substrate material and deposited the film with less built-in strain compared to other techniques. Ion beam assisted deposition is a type of deposition technique which is able performs sputtering and ion implantation simultaneously. It also can control the parameters (e.g. ion energy, temperature, the arrival rate of atomic species etc.) independently. This technique can provide a much more durable bond with the substrate compared to other techniques [39-40]. Yokota et al. [41] deposited TiN films onto silicon wafers by Ion beam assisted deposition (IBAD) method. Ion beam assisted deposition system constructed by an electron beam evaporator and electro cyclotron resonance (ECR) to evaporate Ti metal and ionization of N₂ gas respectively. The IBAD system was baked for 24 hours at 250°C to prevent incorporation of oxygen into TiN films. Silicon wafers were heated up to 800°C under N₂ gas atmosphere. N₂ flows into the ECR ion source at the rate of 10-40 sccm. A power of 160 W was supplied to ECR ionizer.

2.2 Chemical Vapor Deposition (CVD)
A chemical vapor deposition is an engineering tool, used to prepare high quality, high-performance solid materials. Application of this process is mainly for the semiconductor industry to develop thin films. In general in CVD substrate is exposed to one or more volatile precursor, which is decomposing on the substrate surface to produce desired product. The volatile product is also produced later which is removed by the gas flow through the reaction chamber. CVD is used by various micro fabrication processes to deposit materials in various forms e.g. polycrystalline, amorphous, monocrystalline etc. CVD perform exceptionally on conformal films and augment substrate surfaces where traditional surface modification techniques are not capable. This process is extremely useful in atomic layer deposition to deposit thin layers of material. Polymerization of CVD is the most versatile process which possesses some very desirable qualities e.g. lubricity, hydrophobicity and weather resistant to super thin coating [42-43].

2.2.1 Plasma Assist CVD
This is a type of synthesis process where a substrate is exposed to more than one volatile precursor in presence of plasma. The role of plasma is to enhance the rate of reaction on the substrate surface. PACVD combines good adhesion property of CVD and low temperature of PVD. So it can avoid the drawbacks like high temperature with deformation and poor adhesion respectively. In PACVD process first electric field is developed to create the plasma and then due to the collisions between plasma ions and electrons energy is generated which is used to start chemical reactions. Temperature is normally varying in between 200-300°C but it is raised to achieve good adhesion [44].

3. Morphology of TiSiN
3.1 Atomic Force Microscopy (AFM)
It's a type of scanning probe microscope (SPM) which designed to measure local properties (e.g. roughness, height, friction, magnetism etc) with a probe. To get an image, the SPM raster-probe scans over a small area of the sample to measure the local properties. The measuring force between the probe and the sample mainly operates AFM. Tip of the probe is 3-6 µm tall pyramids with 15-40 nm end radius. Because of convolution lateral evolution is low compared to its vertical resolution. To acquire the image resolution, AFM can generally measure the vertical and lateral deflections of the
cantilever by using the optical lever. The optical lever operates by reflecting a laser beam off the cantilever. The reflected laser beam strikes a position-sensitive photo-detector consisting of four-segment photo-detector. The differences between the segments of photo-detector of signals indicate the position of the laser spot on the detector and thus the angular deflections of the cantilever. Piezoceramics position the tip with high resolution. Piezoelectric ceramics are a class of materials that expand or contract when in the presence of a voltage gradient. Piezo-ceramics make it possible to create three-dimensional positioning devices of arbitrarily high precision. In contact mode, AFMs use feedback to regulate the force on the sample. The AFM not only measures the force on the sample but also regulates it, allowing acquisition of images at very low forces. The feedback loop consists of the tube scanner that controls the height of the tip; the cantilever and optical lever, which measures the local height of the sample; and a feedback circuit that attempts to keep the cantilever deflection constant by adjusting the voltage applied to the scanner. A well-constructed feedback loop is essential to microscope performance [45-49].

Yokota et al. [41] used ion-beam assisted deposition technique to deposit TiN on silicon wafers. They observed surface roughness of 4 nm was in AFM micrograph of TiN sample. Even, surface roughness inversely proportionate to N-ion beam current and becomes slightly rounder with increasing substrate temperature.

![AFM image on the surface of the TN-10-rTiN films](image)

Fig.1. AFM image on the surface of the TN-10-rTiN films [41]

Lemus and Drew [34] found from their AFM analysis that the roughness (Ra) of polished Si3N4 and Ti surfaces are far less than unpolished Si3N4 and Ti surfaces. Eventually, Shen et al. [38] managed to reduce the roughness of their samples by addition of Si into TiN. This is because of reduction of grain size after addition of Si into it. Yokota et al. [50] developed TiN thin films on Si wafers under 800˚C in presence of nitrogen gas flow rate and nitrogen ion current density by using ion beam assisted deposition technique. As they bombarded the surface of TiN film by energetic nitrogen ion particles so, AFM analysis suggests that bond between Ti and N ions are broken because of bombardment.

### 3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscope is an instrument where entire primary electron beams emitted from an electron source are scanned on the sample and a scanning image is obtained from a detection signal produced by secondary particles generated from the sample. Scanning electron microscope is capable of obtaining a scanned image with high spatial resolution within a low acceleration voltage region. It is mainly used for observation and length measurement sub-micron (1 micron or less) particles such as contact hole and line pattern in semiconductor device samples. Scanning electron microscope is used to find out the topography and condition of the surface [51-54]. To study the microstructural development of Si3N4-TiN composites Bellosi et al. [55] used different sintering processes to develop it. Microstructure of the film analyzes by scanning electron microscopy and it suggests that addition of Silicon powder reduced the grain size of Si3N4-TiN composites. Yasutomi et al. [56] in their experimental work developed Si3N4-TiN film by varying Si/TiN powder ratio under N2 flow rate at 1350˚C temperature. They found from SEM analysis that as dilution of more TiN powder content makes nitride body more porous. Grigorov et al. [57] used different PVD techniques (e.g. reactive evaporation, rf and dc magnetron sputtering and ion assistant deposition technique etc.) to deposit
titanium nitride films on crystalline (100) silicon substrate. They maintained a crystallization temperature (850-900°C) during the deposition technique under N₂ gas atmosphere. The microstructure of the film suggested that film developed under Ar ion-assisted bombardment to create fine grain structure. Herrmann et al. [58] confirmed from SEM analysis that TiN contributes significantly in their densification under the influence of carbon content. In their study, Gogotsoi et al. [59] tried to find the effect of TiN addition on creep behaviour of silicon nitride. As a sample, they used hot pressed silicon nitride with different amount of TiN. The creep of the samples was found at 1100°C-1340°C and they hardly found any crack in the specimen's surface those are tested under 1250°C by SEM analysis. Huang et al. [24] studied the chemical stability of TiN and they also scrutinize the effect of TiN on mechanical properties and microstructure of silicon nitride. They prepared their sample by mixing it with yttria and alumina powder even they also mixed high purity silicon nitride films and ethanol with this powder mixture. They couldn't find any interfacial reaction between TiN and Si₃N₄ from SEM analysis and the interfacial regions between TiN and Si₃N₄ remain intact up to 1800°C. Similarly, Huang et al. [25] used high purity alumina balls instead of silicon nitride ball in their other experiment where they tried to found microstructural, mechanical and morphological properties hot pressed silicon nitride containing two different sizes of TiN particles.

Fig. 2 SEM photograph of microstructure [24]

They found the strong bond in between interfaces of TiN and Si₃N₄ even at very high temperature. Smith and Custer [26] used metal-organic chemical vapor deposition technique to grown titanium silicon nitride films on thermally oxidized bared wafers of Si at a temperature of 300°C to 450°C. They found the sharp reduction of the density of deposited film compared to bulk TiN. Choi et al. [60] compared the R-curve behaviour in between Si₃N₄-TiN and monolithic Si₃N₄. For monolithic Si₃N₄ and for Si₃N₄-TiN they mixed 97 wt% Si₃N₄, 2 wt% Y₂O₃, 1 wt% Al₂O₃ and 57 wt% Si₃N₄, 40 wt% TiN, 2 wt% Al₂O₃ respectively and then they used chemical routing process for the final preparation of the sample. They found some cracks and deflection around the TiN grains. Diserens et al. [28] investigated the cross-sectional morphology of the sample prepared by reactive unbalanced magnetron sputtering technique by SEM analysis. They manage to transform the columnar structure into a finely grained structure with the addition of Si into Ti atoms. Min et al. [61] developed titanium silicon nitride films by metal organic atomic layer deposition technique. During silane supply into the chamber, Si content maintained at 18% and its deposition thickness at 0.22 nm/cycles. Pressure range of silane was maintained within 0.27-13.3Pa. SEM micrograph reveals the presence of negative slope along with step coverage on the Ti-Si-N films. Park et al. [33] deposited Ti-Si-N films on high-speed steel substrate in presence of SiCl₄, TiCl₄, H₂, N₂ and Ar gas mixture to find the effect of silicon addition on microstructure and mechanical properties of TiN. Pressure, temperature and rf power during two hours of deposition they maintained at 1 torr, 500°C, 60 W. Successfully they manage to develop fine micro structured Ti-S-N thin films with a destruction of the columnar grain structure. Lemus and Drew [34] on their observation over diffusion bonding in between in between Ti foil interlayer and Si₃N₄ couldn't found any bonding up to 1400°C from SEM analysis. Blugan et al. [62] also tried to find the influence of Ti addition over Si₃N₄. The average grain size of β-Si₃N₄ was
increased with TiN content up to 20 wt% and Si₃N₄ can retain their sub micrometre grain size with the addition of TiN they came to know from their experimental study. J.S. Lee and H.B. Lim [63] deposited TiN films on Ar ion sputtered silicon wafer at 450°C by using ion arc plating technique in presence of N₂ and Ar gas flow. Base pressure, working pressure and deposition time, arc current, sputtered current maintained at 1×10⁻⁵ torr, 3×10⁻³ torr, 20 minutes, 50 A and 1 A respectively during deposition. After investigating surface morphology and craters by FESEM and TEM they found a size of the particles decreasing with higher number of laser shot. In their experiment Blab et al. [64] sintered TiN powders and amorphous silicon nitride (a-Si₃N₄) powder together at 6.5 GPa in order to prepare dense nano composite at 1300°C. Then the sintered powder also processed under N₂ gas to reduce oxygen affinity. SEM images of the samples revealed the presence of several clusters of pores inside of dense matrix at 1300°C and it decreases with increasing content of silicon nitride.

4. Structure of TiSiN

4.1 X-Ray diffraction (XRD)

The atomic planes of a crystal cause an incident beam of X-rays to interfere with one another as they leave the crystal. This phenomenon is known as X-ray diffraction. Periodic ordered structure of a crystal and scattering of X-ray waves against the atom in a crystal causes interference reflexes in a certain direction, which are tied to the certain crystal structure as well as the specific orientation of incident waves. This effect is used to investigate crystal structure of the sample and structural properties (e.g. grain size, texture and thickness etc.) in various techniques of X-ray diffractometry. The basic XRD method is θ-2θ scan by varying incidence and exit angle symmetrically. Different wave vectors for an incident and scattered beams are in a limit for this. Lattice parameters normally measured from the reflection position after assigning the observed peaks in a scan to the crystal structure. Care always been taken as the lattice parameters may be shifted sometime because of the presence of strain in the sample. The average size of coherently scattered region influenced the wave of peaks mostly [65-66].

Bellosi et al. [55] used three different grades of Si₃N₄ powder to prepare sintered Si₃N₄–TiN composites. Even for sintering three different densification techniques also they used. Their XRD analysis confirms them that the reason behind the dense structure is hot press and gas press sintering whereas; pressure less sintering produces the porous structure. Yasutomi et al. [56] produce net shaped reaction bonded Si₃N₄–TiN by mixing TiN and Si₃N₄ powder. The reason behind the formation of TiN, α and β-Si₃N₄ in nitride bodies is the reaction between metallic Si and nitrogen they came to know from XRD analysis. Grigorov et al. [57] deposited the titanium nitride films on the silicon substrate in order to prevent the diffusion of silicon in different types (e.g. columnar, fine-grained) of titanium nitride films. They found the presence of δ-TiN, α-TiN, δ-TiN, Ti-N layers and their crystalline size by XRD analysis. Huang et al. [24] found from their experimental analysis a complete conversion of α phase of Si₃N₄ into β phase at 1800°C but when temperature reduces up to 1750°C some amount of α-Si₃N₄ returns back. But in their other experiment Huang et al. [25] hardly fond any phases except Si₃N₄ and TiN from XRD study of monolithic Si₃N₄ and TiN-containing Si₃N₄ composites to a 1900°C temperature. Diserens et al. [28] also found the conversion of columnar structure (111) into the finely dense grained structure with the addition of Si into TiN of their PVD deposited Ti-Si-N films. They added Si into TiN film to improve the wear resistance properties of the film. The strong orientation of undoped TiN film at (200) and mixed orientation of Ti-Si-N at (111), (220) and (311) observed by Park et al. [33] found from XRD analysis of their film. Vaz et al. [37] used r.f. reactive magnetron sputtering technique to deposit their film on sputter etched silicon and high-speed steel substrate in presence of Ar and N₂ gas mixture. Initially, the base pressure maintained at 10⁻⁴ Pa and then raised up to 4×10⁻¹ Pa at the time of deposition. They found two different cubic indexed crystallographic structures in the film from XRD analysis. Yokota et al. [41] were rinsed their silicon wafers with alcohol, acetone and solvent naphtha and then deposit TiN films by ion beam assisted deposition technique on it. The deposition was carried out under the pressure of 10⁻² Pa and the ratio of N ion beam current to N₂ flow maintained at 16.5 mA/20 sccm during deposition. They found the strong peak at (200) lattice plane and weak peaks at (111), (220) lattice planes from XRD analysis. In the hotly pressed specimen of Si₃N₄/Ti and foil/Si₃N₄, Lemus and Drew [34] found the presence of Ti₃Si₅, TiSi and TiN from XRD analysis. Even they also found that interface of their polished samples has grown parabolically in compared to ground-based sample. In
presence of Ar and N₂ gas mixture, Shen et al. [38] developed Ti₁₋ₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓₓ.xticks

**4.2 Transmission Electron Microscopy (TEM)**

Transmission electron microscopy considered to be one of the most versatile techniques to analyse the thin film sample. Different characteristics e.g. crystal structure, microstructure, local chemical composition, interfacial relations, defects can be analysed by using different configurations of TEM. Extensive sample preparation is one of the main drawbacks of TEM, potentially introduces artefacts and small volume probe. TEM is based on the principle that a beam of electrons and scattered electrons are shone through a thin foil and focused by an electromagnetic lens into an image respectively. Then the image is collected as intensities on a view screen or camera. In case of bright field mode of TEM contrast in the image formed either through mass thickness contrast or diffraction thickness contrast phenomena. For denser or thicker regions mass thickness contrast is used for scattering or absorb respectively. To block the diffracted beams from projecting back onto the image of their origin, diffraction contrast is used. Sometime strain in the foil causes to appear local diffraction contrast. The dark field mode is also related to close field mode. As in BF mode, here also a diffracted beam is selected and transmitted beam eliminated to form an image with crystallographic information from the selected reciprocal lattice point [67].

**5. Compositional and Electronic structure**

**5.1 Raman spectroscopy**

Raman spectroscopy is a technique used to determine rotational, vibrational and low frequency mode of the system. It’s also used to identify structural figure print of a material in the field of chemistry. It depends on Raman scattering of monochromatic light source of a laser and this light usually interact with molecular vibrations, phonons or other excitation of the systems resulting the energy of the photons may shifted up or down. The information about the vibrational mode of the system is provided by shift of energy. So many research people have used Raman spectroscopy in order to analyze vibrational, rotational and chemical network of their work. As Balasubramanian et al. [68] deposited composite of Ti-Si-N thin film on stainless steel substrate by using reactive dc magnetron sputtering technique in presence of N₂ and Ar gas mixture. To study the behavior of optical and acoustic phonon modes of Ti-Si-N nano composites they have used Raman spectroscopy analysis. They found the acoustic range of Ti-Si-N thin film by the vibration of heavy Ti ions around 150-300 cm⁻¹ and optical range by the vibration of the lighter N ions typically around 400-650 cm⁻¹. Barshilia et al. [69] deposited nanolayered TiN/CrN, TiAlN/CrN multilayer coatings on silicon substrate by using reactive dc magnetron sputtering process to find thermal stability by Raman spectroscopy technique. They couldn’t find any phase transformation and intensity of optical phonon mode increased and shifted towards lower frequency from Raman analysis. In their other experiment Barshilia et al. [70] found better thermal stability of TiSiN film prepared by reactive direct current unbalanced magnetron sputtering technique in presence of Ar+N₂ gas mixture from micro Raman spectroscopy analysis. Zhang et al. [71] prepared Ti-Si-N thin film by using high density plasma assisted vapor deposition technique. They found significant amount of Ti ion dissolution within a-Si:N matrix from Raman spectra analysis. Even they also found that Ti–Si–N coatings consist of nano columnar TiN grains inter dispersed within an a-Si:N matrix. Pilloud et al. [72] used sputtering technique in order to produce 3µm thick, hard Ti-Si-N nano composite materials in presence of Ar+N₂ gas mixture. They found the presence of rutile TiO₂ around the whole film thickness from Raman analysis which indicates oxidation of the film and this can be reduced with the incorporation of Si into the film. Raman analysis also helped them to found the presence of anatase phase within the film and
this will increased with Si concentration within the film. Meng et al. [73] successfully investigated the influence of residual stress of Ti-Si-N thin film on Raman peaks. They manage to establish a linear dependency of residual stress on Raman peaks.

5.2 X-ray photoelectron spectroscopy (XPS)
X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect. Each atom in the surface has core electron with the characteristic binding energy that is conceptual, not strictly, equal to the ionization energy of that electron. When an X-ray beam directs to the sample surface, the energy of the X-ray photon is absorbed completely by the core electron of an atom. If the photon energy, \( h\nu \), is large enough, the core electron will then escape from the atom and emit out of the surface. The emitted electron with the kinetic energy of \( E_k \) is referred to as the photoelectron. The binding energy of the core electron is given by the Ernest relationship: \( h\nu = E_b + E_k + \phi \), \( E_b = h\nu - E_k - \phi \) Where \( h\nu \) is the X-ray photon energy (for Al Ka, \( h\nu =1486.6\text{eV} \)); \( E_k \) is the kinetic energy of photoelectron, which can be measured by the energy analyzer; and \( \phi \) is the work function induced by the analyzer, about 4–5eV. Since the work function, \( \phi \), can be compensated artificially, it is eliminated, giving the binding energy as follows: \( E_b = h\nu - E_k \) [74-78].

Diserens et al. [28] found the presence of titanium, silicon and nitrogen in the film from X-ray photoelectron spectroscopy analysis and also they came to know that nitridation of silicon is because of the partial pressure of nitrogen. Park et al. [33] were performed XPS operation to verify the behaviour of Si on Ti-Si-N films consist of 7 % Si. They found peak binding energy of Si 2p and Ti 2p at 455.6 eV and 101.8 eV respectively. Shen et al. [38] used reactive unbalanced dc magnetron sputtering technique to produced Ti$_{1-x-y}$Si$_x$N$_y$ thin films on Si (100) substrate in presence of Ar and N$_2$ gas mixture. The electron bonding at core level was characterized by XPS technique. The concentration growth of Si and Ti are opposite in nature compare with the current. The concentration of Si increased with increasing current up to 2A whereas Ti concentration decreased. Kwang et al. [79] prepared hard coating layer of Ti-Si-N thin film on SKD11 steel substrate. They used AIP method to prepare TiN film, while Si incorporated into it by sputtering technique. They manage to prepare an uniform film with free Si into it and they hardly find any impurities in their film from XPS analysis. Kim et al. [80] used dc magnetron sputtering technique to develop Ti-Si-N thin film on SKD11 steel substrate with separate Si and Ti targets. XPS analysis of their film confirmed the presence of nano size TiN crystallites surrounded by amorphous Si$_3$N$_4$ and amorphous Si$_3$N$_4$ become thicker with more Si content into it. In presence of TiCl$_4$, N$_2$, H$_2$ and SiCl$_4$ gas mixture Shizi et al. [81] prepared the Ti-Si-N thin film by using plasma enhanced chemical vapor deposition process (PECVD). They have controlled the composition of the film by adjusting the mixing ratio of the chloride within the feed gases. The Si content varied within the range of 0-40 % and higher amount of Si addition helps to develop dense, glass like structure of the film.

6. Mechanical Properties
6.1 Nano-Indentation
Indentation is most commonly used the process to measure mechanical properties of the material. Nanoindentation is capable to measure the hardness of the materials having the small volume. A sharp and hard tip (indenter) normally made of diamond is pushed into the sample as per the depth and load required are recorded. This recorded data forms indentation curve. Nanoindentation can perform two different types of indentation, one is as in traditional macro indentation tests where one attains a single hardness value per experiment; the other is based on the hardness as the material is being indented resulting in hardness as a function of depth. Some nano indenters use an area function based on the geometry of the tip, compensating for elastic load during the test. Use of this area function provides a method of gaining real-time nano-hardness values from a load-displacement graph. Because of the methods dependency on geometry of the indenting tip, any changes from the ideal shape is recorded to correct the projected areas. Macro and micro-indentation test improves by nanoindentation process as it indents on the nano scale with a very precise tip shape. It also can provide real-time load-displacement data when indentation is in progress. In Nanoindentation small loads and tip sizes are used, so the indentation area may only be a few square micrometres or even nanometers. During the course of the instrumented indentation process, a record of the depth of
penetration is made, and then the area of the indent is determined using the known geometry of the indentation tip. Load and depth of penetration, measured during indentation test plotted on the graph to create the load-displacement curve. These curves are used to extract mechanical properties of the material [82-85].

Shen et al. [38] used nanoindentation to measure the hardness of their samples. They observed significant growth in hardness for TiN films with Si addition. The initial hardness of TiN found 18.8 GPa and it increases up to 32.8 GPa with increasing Si concentration. As Nose et al. [86] investigated the influence of Si addition on mechanical properties of Ti-Si-N thin film by nanoindentation process. In presence of Ar+N2 gas mixture they prepared their film by r.f. magnetron sputtering technique. With the addition of very small amount Si content (3-8 %) the hardness of the film increased from 30 to 37 GPa they observed from nanoindentation analysis. Jiang et al. [87] also found similar kind of results from their Ti-Si-N thin film deposited by reactive unbalanced sputtering process in room temperature. They also found with addition of Si the hardness and elastic modulus of Ti-Si-N enhances significantly and it reached its maximum value of 35 and 383.2 GPa respectively with 9% of Si content in the film. Rebouta et al. [88] also managed to enhance the hardness of Ti-Si-N upto 45 GPa with 4-10 % of Si addition during the deposition by dc reactive magnetron sputtering technique. Meng et al [89] prepared series of Ti-Si-N coatings by varying Si content within the range of 0-20 % by plasma assisted vapor deposition technique. They observe the hardness of their film always remain less than 32 GPa and it varies linearly with Si content. Shtansky et al. [90] made a comparative analysis in between Ti-Si-N thin film prepared by using Ti5Si3+Ti and Ti5Si3+TiN targets in magnetron sputtering technique. The nanoindentation analysis of both the films reveals that the hardness remain less than 35 GPa and Young’s modulus varying within the range of 220-250 GPa. Choi et al. [91] used WC–Co substrate to deposit Ti-Si-N thin film by hybrid coating system of ion arc plating and sputtering. They found that hardness of the film increased linearly with temperature enhancement upto 300˚C and after 350˚C hardness started to reduce due to formation of grain growth. Flink et al [92] prepared Ti1-xSixN thin film on cemented carbide substrate by arc evaporation process. During deposition the Si content varying within the range of 0-14 % and it affect significantly on the hardness of the film. They found without any Si content hardness of the film is around 32 GPa whereas when Si content increases up to 14% then hardness becomes 45 GPa. Mei et al. [93] prepared series of Ti-Si-N samples with different Si content by reactive sputtering process in presence Ar+N2+SiH4 gas mixture. After the analysis of mechanical properties of the film by nanoindentation process they found that with 4-9% of Si content, the film becomes harder with hardness of 34.2 GPa and elastic modulus of 398 GPa and further enhancement of Si addition into it causes reduction of hardness and elastic modulus of the film. With the addition of Si content Zhang et al. [94] also found significant enhancement of hardness of Ti-Si-N thin film deposited by ion beam assisted deposition technique. During deposition they varied the Si content within the range of 0-23.7 %. The hardness of the film reached its maximum value of 42 GPa with 11.32 % of Si content from nanoindentation analysis. Guha et al. [95-96] prepared their TiSiN in presence of N2 and H2 gas by using CVD process. They vary the flow rate of H2 and N2 gas during deposition. They found that higher H2, N2 affect significantly to improve different mechanical properties of TiSiN thin film from nanoindentation study.

7. Conclusion

Ternary based metal nitride (e.g.TiSiN, TiAlN, TiMoN) has expanded to cover the vast range of materials and it makes ternary based material of the most demanding in industrial application. It provides some significant properties like low coefficient of friction, high hardness, corrosion protection, good wear resistant and high melting point etc. compared to other coating materials. TiSiN film can provide intrinsic hardness up to 50-60 GPa [97] or 35-50 GPa [98] along with considerable thermal stability at elevated temperature. The surface roughness of TiSiN film is also very low (e.g. 4 nm) found from AFM analysis [50]. Young's modulus, yield strength [95-96] of TiSiN thin film is also higher compared to binary metal nitride.
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