Investigation of Titanium Silicon Nitride: A Review

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Abstract Nano-tribological studies are required to develop in-depth understanding on interfacial phenomena of different materials that are used in different industrial (e.g. aerospace industry, coatings, tool hardening electronics devices etc.) applications. In a recent year, tribological studies on transition metals increase because of their promising mechanical properties, hardness, oxidation resistant and wear resistant characteristics. Titanium silicon nitride is considered to be one of the most prominent materials among all the transition metals. Silicon provides excellent resistance to oxidation and titanium guarantees hard coatings. So, combination of two can be developed a useful coating material which can provide wear resistance even at elevated temperature.

Keywords Titanium silicon nitride · CVD · PVD · Microstructure Mechanical properties

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1 Introduction

In past decades, thin films are increasingly used for various industrial, scientific and technological applications. Interests in transition metals have grown considerably because of its resilience, high wear resistant, high strength and high toughness [1–3]. Titanium as a transition metal is considered being one of the hardest, wear resistant and decorative coating materials [1–4]. Among a wide variety of transition metal nitride available in industries, titanium nitride (TiN) is the most common and important material 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 group of materials to form new family of ternary nitride (e.g. TiSiN, TiAlN), in which for past few years much more progress has shown a remarkable development in the quality of such films [1, 5–7].

1.1 Titanium Silicon Nitride

Advances of ternary films nitride have been made in the last decade because of their growing demand in industrial applications. Ternary metal nitride (e.g. TiSiN, TiAlN, etc.) possesses properties like low coefficient of friction, high hardness, moderate wear resistant, corrosion protection and significant melting point, etc., as compared to binary-based coatings. Nowadays most of the cutting tools are coated with TiN binary nitride coating to improve tool's performance. But TiN became oxidized at elevated temperature. Sputtered TiN also associated with two major drawbacks as the microelectronics device size started to shrink it subjected to poor step coverage and columnar polycrystalline microstructure. Deposition of silicon into it indicates clear improvement of mechanical properties in terms of hardness and abrasion resistance as well as it possesses excellent abrasion resistance. Silicon nitride is also considered as one of the best metal nitride material because of its thermal, mechanical and chemical properties but still it cannot be used in some applications because of lack of toughness and reliability. Toughness, density and reliability of silicon nitride can be enhanced by the addition of TiN into it. All over titanium silicon nitride as a ternary nitride films provides better performance compared to binary metal nitride [8–13].

2 Morphology of TiSiN

2.1 Atomic Force Microscopy (AFM)

Yokota et al. [14] used ion beam assisted deposition technique to deposit TiN on silicon wafer. Deposition chamber consisted of electron cyclotron resonance ion source to ionize nitrogen. Irregular surface roughness of 4 nm was observed in the AFM micrograph of a single TiN sample. It was found that surface roughness increases when N-ion beam current decreases and it became round in shape with increasing substrate temperature (Fig. 1).

AFM analysis of the sample prepared by Lemus and Drew [15] suggests that the roughness (R_a) of polished titanium (Ti) surfaces (53.4 nm) is slightly less than silicon nitride (Si_3N_4) (63.4 nm) but for unpolished Si_3N_4 and Ti, the value of roughness is 584 and 1140 nm, respectively.

Shen et al. [16] measured roughness of their samples by atomic force microscopy (AFM). They found that addition of Si into TiN causes grain size development and reduce roughness of surface.

Yokota et al. [17] deposited TiN films on Si wafers by using PVD (ion beam assisted deposition) technique. Electron cyclotron resonance is (ECR) used to ionize nitrogen gas in high neutral ratio of nitrogen ion to titanium. Deposition was carried out in N_2 gas flow rate and temperature was maintained at 800 °C. Nitrogen ion particle also used to bombard the TiN film surface. AFM technique used to investigate surface morphology of the films. The probe of AFM scanned the surface area of 10 × 10 μm^2 at a rate of 5 Hz/line. They found that bombardment causes breakage of chemical bonds between Ti and N and increased ion current causes variation in deposited TiN.

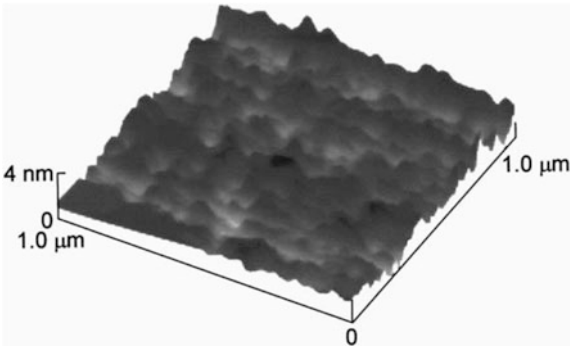

Fig. 1 AFM image on the surface of the TN-10-rTiN films [15]

2.2 Scanning Electron Microscopy (SEM)

Bellosi et al. [3] studied microstructure development of Si_3N_4–TiN composites related with sintering process. They used three different grades of Si_3N_4 and TiN powders for sintering process. In first case, silicon nitride powder with sintering aids (3 wt% Al_2O_3 and 8 wt% Y_2O_3) homogenized for 48 h in water and then dried in other case 20–40 vol% was added and homogenized in isobutyl alcohol. Three different densification methods were used for sintering, e.g. hot pressing (HP) in high temperature and pressure at 1800 °C and 30 MPa, respectively, pressure less sintering (PS) in N_2 atmosphere at 1850 °C for 60 min, gas pressure sintering within 1800–1850 °C for cycle A and B respectively for 60 min. They also found from microstructural analysis by scanning electron microscopy that in first case TiN powder of grain sizes 0.2–7 μm were found where as in second case particle size of TiN reduces up to 0.2–3 μm without having any large particles.

Yasutomi et al. [18] tried to get reaction bonded net shaped electroconductive Si_3N_4–TiN in this experimental work. They used Si and TiN powders with for the production of TiN and Si_3N_4. At first, they suspended powder mixture into methanol (50 vol%) for a period of 24 h with Si_3N_4 balls. They varied composition of Si/TiN ratio to control TiN in nitride body within 20–70 vol%. Then mixture was dried in room temperature followed by kneading with polyethylene-based thermoplastic resin binder. Then mixture was crushed under 0.5 mm. Then it was dewaxed in argon filled furnace. At last, it passed through the N_2 gas atmosphere at 1350 °C. From SEM analysis, they found that nitride body became more porous as the TiN content increases.

Three different PVD techniques (rf and dc magnetron sputtering, reactive evaporation and ion assistant deposition) were used by Grigorov et al. [19] to deposit titanium nitride films on crystalline (100) silicon of 20 Ω cm substrate. They performed this experiment under crystallization temperature (850–900 °C). Two distinct titanium layer of 60 mm thickness was deposited on silicon substrate in N_2 atmosphere. They specified the layer prepared in presence of Ar ion bombardment as B_o and without Ar ion bombardment as B_+. From SEM, they found that a columnar growth of B_o layer occupied 25–30% of layer's volume and fine-grained structure of B_+ layers with a grain size of 150 nm.

Herrmann et al. [20] in order to find out the dependence of densification behaviour on TiN content and its grain size; they prepared samples of Si_3N_4 (LC 12S, HCST), TiN of various grade or Ti powders to investigate the influence of carbon content in densification. They also used Y_2O_3 powders as sintering additives and prepared two series of samples. First group of materials contained Y_2O_3 (5 wt%) and Al_2O_3 (2 wt%) powder as additives. TiN grade C, Ti(C,N)-30/70 or Ti(C,N)-50/50 is also used as dispersoid after preparing it in isopropanolic solution in a attrition mill. Second group of materials is prepared under the constant ratio of Si_3N_4 to sintering additives (Y_2O_3, Al_2O_3:Si_3N_4). In two steps of preparation, first they mixed Si_3N_4 and sintered the additives in attrition mill and in second step they dried it. Ball mill was used to mix TiN powders. Additives were also baked for 8 h at 280 °C in

air and up to 500 °C in Ar gas atmosphere for TiN–Si_3N_4 and TiN–Si(C, N) composites, respectively. They confirmed from SEM analysis that TiN contributes in densification as the grain sizes change during sintering.

Gogotsi et al. [8], in order to find the effect of TiN addition on creep behaviour of hot pressed doped silicon nitride, used mixture of hot pressed silicon nitride and TiN as a sample for study. Uniform distribution of TiN particles was obtained after ball milling of Si_3N_4 along with oxide additives and TiN powder. They measured creep of samples in air within the range of 1100–1340 °C and they could not find any crack in the specimen's surface tested below 1250 °C by SEM analysis.

Chemical stability of TiN on different conditions of silicon nitride was investigated by Huang et al. [9]. The effect of TiN on mechanical properties and microstructure of Si_3N_4 also scrutinizes in this work. To prepare the sample for experiment, they mixed silicon nitride powder with yttria and alumina in a polyurethane bottle. Highly pure silicon nitride balls were mixed with ethanol for periods of 22 h in this bottle. They milled TiN powders of 5 μm size in this mixture with the help of a PE balls in presence of ethanol with a charge to ball ratio of 1:8. After analysed by SEM micrographs, they could not find any interfacial reaction between TiN and Si_3N_4 and up to 1800 °C interfacial regions between TiN and Si_3N_4 remain intact (Fig. 2).

Huang et al. [10] investigated the mechanical properties, microstructure, morphology and fracture behaviour of hot pressed silicon nitride mixed with two different sizes of TiN particles. They prepared their samples as in [9]. Only exception is that they used high purity alumina balls instead of silicon nitride balls and maintained the ratio of ball, charge and vehicle at 6:1:5. Then they hot pressed the sample at 1800, 1850 and 1900 °C. SEM micrographs reveal intactness between the interfaces of TiN and Si_3N_4 even at very high temperature. This proved chemical stability of TiN in Si_3N_4 at 1850 °C. They also found that width of propagation crack increases with decreasing TiN content.

Metal organic chemical vapour deposition technique is used to grow titanium silicon nitride films. In this work, Smith and Custer [11] maintained temperature between 300 and 450 °C and in this temperature tetrakis titanium, ammonia and silane combined together to form films of average compositions near the tie line of TiN–Si_3N_4. They used thermally oxidized bared wafers of Si to deposit the films.

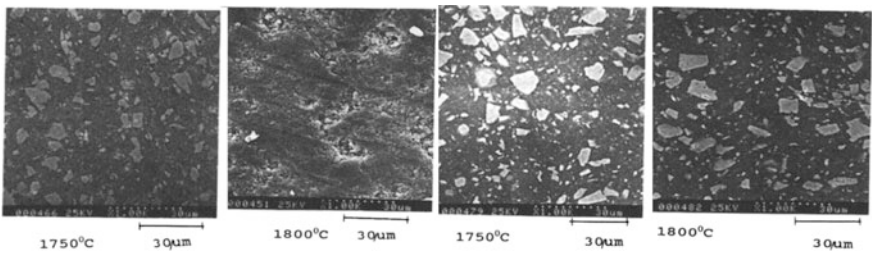

Fig. 2 SEM photograph of microstructure [24]

After analysing the deposited films by SEM, they found that the density of deposited films reduces up to 25% compared to bulk TiN.

In order to compare the R-curve behaviour of Si_3N_4-40 wt% TiN with monolithic Si_3N_4 Choi et al. [21] used indentation strength method. They used Si_3N_4, TiN, Al_2O_3, Y_2O_3 powders as starting materials. For monolithic Si_3N_4, they mixed 97 wt% Si_3N_4, 2 wt% Y_2O_3, 1 wt% Al_2O_3 powders and for Si_3N_4–TiN composites they mixed powders with ratio of 57 wt% Si_3N_4, 40 wt% TiN, 2 wt% Al_2O_3. Then they used chemical routing to prepare the sample. Thin film of gold and moisture free silicon oil deposited on the indentation surface to reduce the moisture-assisted sub critical crack growth. SEM analysis reflects on crack deflection around TiN grains which is bridging by Si_3N_4 grains.

With an objective to improve wear resistance properties of TiN coatings Diserens et al. [13] deposited Titanium silicon nitride films by PVD (reactive unbalanced magnetron sputtering) process. To allow independent regulation of each source, they equipped PVD reactor with titanium and silicon as targets. Cross-sectional morphology of the sample was investigated by SEM analysis. They found that addition of Si into Ti causes transforming of columnar structure into finely grained structure.

Min et al. [22] used metal organic atomic layer deposition technique at 180 °C to grown titanium silicon nitride films. They maintained Si content 18% and Si deposition thickness 0.22 nm/cycles during silane supply. Silane was supplied separately in different pulses (e.g. titanium, ammonia, etc.) within the pressure range of 0.27–13.3 Pa. SEM micrograph of TiSiN films found the step coverage of MOALD even for 0.3 μm films with very less negative slope.

High speed steel is used as a substrate material to deposit TiSiN films by Park et al. [23] with an objective to find the effect of silicon addition on mechanical and microstructural properties of TiN in presence of gaseous mixture (e.g. $SiCl_4$, $TiCl_4$, H_2, N_2 and Ar, etc.). During deposition pressure, temperature and rf power were maintained at 1 Torr, 500 °C and 60 W, respectively and deposition time 120 min. By varying the evaporation pressure, they controlled the inlet gas ratio of $TiCl_4$/$SiCl_4$ while inlet gas ratio of N_2/H_2/Ar was maintained at 15/40/45. SEM micrographs of undoped TiN film show the presence of columnar grains from substrate to surface whereas for Ti–S–N films a fine microstructure with destruction of columnar grains appeared.

Lemus and Drew [15] studied the different directions of diffusion bonding Ti foil interlayer during joining of Si_3N_4. They used Si_3N_4-rod ceralloy-147 31 N and commercially pure Ti foil as starting materials. The combination of Si_3N_4/Ti foil/Si_3N_4 was hot pressed for different holding times at temperature ranging in between 1200 and 1500 °C. Si_3N_4 which is used in hot pressing is β-Si_3N_4 contained of Y_2O_3 and Al_2O_3 as additives. From SEM analysis, they could not find any bonding between Ti and Si_3N_4 up to 1400 °C.

Blugan et al. [24] investigated the effect Ti addition on fracture toughness, strength and wear properties of commercial Si_3N_4. In this work, they varied the TiN wt% (10, 20, and 30) to study the effect on fracture toughness. Alumina (Al_2O_3) and yttria (Y_2O_3) were used as a doping material to dope Si_3N_4 and Si_3N_4–TiN

composite materials. They investigated the microstructure of plasma etched specimen by SEM process. They observed that the average grain size of β-Si_3N_4 increases with increased TiN content up to 20 wt%. But average grain size of TiN maximum for 10 wt% of TiN was observed. They also found that Si_3N_4 can retain their sub micrometre grain size with addition of TiN.

Lee and Lim [25] used ion arc plating technique to deposit TiN films on silicon wafer at 450 °C. Before deposition, they sputtered the surface of substrate using Ar ion at −700 V bias voltages for duration of 10 min. Base and working pressure was maintained at 1×10^{-5} and 3×10^{-3} Torr, respectively. Time of deposition was 20 min. Arc and sputter current was 50 and 1 A, respectively. They also maintained ratio of N_2 gas to Ar gas at 0.3. Produced particles from laser ablation are collected on carbon tape to investigate by SEM process. They observed from FESEM and TEM that size of the particles for first 5 laser shots was within the range of 70–90 nm. Size of particle increases up to 50–100 nm as the laser shots increase. Si substrate was completely exposed by TiN layer after 25–30 laser shots. Silicon particle completely appeared from 30 to 50 laser shots.

Commercially available TiN powders and amorphous silicon nitride (a-Si_3N_4) of 1.7–8.1 mol% had been sintered at 6.5 GPa to prepare dense nano composite. In this experiment, Blab et al. [26] maintained temperature at 1300 °C during high pressure sintering. They also processed the powders in dry N_2 gas because of their high affinity in oxygen. SEM images of the samples reveal the presence of various clusters of pores inside thick matrix at 1300 °C and it decreases with increasing content of Si_3N_4. But there is a presence of cluster pores sporadically with maximum silicon nitride content of 8.1 mol%.

3 Structure of TiSiN

3.1 X-ray Diffraction (XRD)

Bellosi et al. [3] sintered Si_3N_4–TiN composites to study microstructural development of it. They used three different grades of Si_3N_4 powder (e.g. LC 12, Starck, FRG) and TiN powder (grade C, Starck, FRG). Three different densification techniques are used by them for sintering. From XRD analysis, they came to know that hot pressing sintering and gas pressure sintering produce very dense structure but pressure less sintering produces porous structure. They also find out a complete conversion of α to β Si_3N_4 in HP samples only.

Yasutomi et al. [18] mixed TiN and Si powder to produce net-shaped reaction bonded Si_3N_4–TiN. They carried out different steps to produce Si_3N_4–TiN. They found out from X-ray diffractometry that the reaction between metallic Si and nitrogen formed TiN, α and β-Si_3N_4 in nitride bodies.

Grigorov et al. [19] tried to prevent the silicon diffusion in TiN films of columnar [B_o] and fine-grained structure [B_+]. They deposited the titanium nitride films on

silicon substrate by different methodologies. Presence of δ-TiN, α-TiN in B_o layers and δ-TiN, TiN in B_+ layers they found different phase of titanium nitride (TiN) from XRD analysis. Crystalline sizes of B_o layers for pronounced TiN (200) and peaks Ti (011) are 25 and 20 nm, respectively, also they were found from it.

Huang et al. [9] investigated the chemical stability of TiN in Si_3N_4 matrix in different temperature and gaseous environment conditions. They also studied the effect of titanium nitride (TiN) on mechanical properties and microstructure of silicon nitride (Si_3N_4). From XRD analysis, they find that α phase of Si_3N_4 converted into β phase at the temperature of 1800 °C but some α-Si_3N_4 returns back when temperature decreased to 1750 °C.

Huang et al. [10] could not find any phases except Si_3N_4 and TiN from XRD profile of monolithic Si_3N_4 and 20 vol% TiN-containing Si_3N_4 composites up to a temperature of 1900 °C.

Diserens et al. [13] deposited TiSiN films with the help of PVD techniques in quest to improve wear resistance properties of TiN by adding Si into it. PVD reactor equipped with titanium and silicon targets to adjust the Ti:Si ratio in the gas phase. XRD analysis shows that the columnar structure (111) transforms into dense finely grained structure when Si was added to TiN coatings. Park et al. [23] found from XRD analysis that the orientation of undoped TiN film is very strong (200) whereas TiSiN films has some mixed orientation of (111), (220) and (311). Intensity of peak (200) will decrease with increasing gas mixture.

Vaz et al. [27] to investigate and characterize the properties of (Ti,Si)N systems, (Ti,Si)N films deposited on high speed steel and silicon wafers substrate by r.f. reactive magnetron sputtering technique. They carried out deposition in Ar and N_2 gas atmosphere. All the substrates were sputter etched in pure argon gas atmosphere for 15 min in 200 W r.f. powers. The base pressure of deposition chamber was 10^{-4} Pa later raised to 4×10^{-1} Pa during deposition. XRD patterns of the film reveal that both the structures were indexed to cubic structure.

Yokota et al. [14] deposited TiN on alcohol, acetone and solvent naphtha rinsed silicon wafer by ion beam assisted deposition technique. To ionize N, they used an electron cyclotron ion source. Deposition pressure and ratio of N ion beam current to N_2 flow rate were maintained at 10^{-2} Pa and 16.5 mA/20 sccm, respectively. From XRD analysis, strongest and weakest peaks are found at (200) and (111), (220) lattice planes, respectively, for cubic TiN films. They also came to know that cubic TiN increased significantly with increasing temperature when it diffracted from (200) lattice plane.

At the interface of Si_3N_4/Ti foil/Si_3N_4 specimen Lemus and Drew [15] found the presence of Ti_5S_3, TiSi and TiN from XRD analysis. The interface of polished samples was grown thicker parabolically as compared to those samples considered as ground sample.

Shen et al. [16] used reactive unbalanced dc magnetron sputtering technique to grow $Ti_{1-x-y}Si_xN_y$ film on unheated Si (100) substrate. They carried out their deposition in presence of Ar and N_2 gas mixture. Si substrates were ultrasonically cleaned and dried in acetone–methanol mixture and N_2 gas, respectively, before entered into the deposition chamber. The base pressure and working pressure set at 2×10^{-6} Torr and 2 mTorr, respectively. To get homogeneous composition and thickness, they rotated the substrate at a speed of 35 rpm during deposition. They used XRD to determine crystallographic structure of the film. From XRD θ-2θ scan, they observed a single peak for TiN at (111) and this peak broadened with increasing Si content. They found average grain size of pure TiN 50 nm by using XRD peaks and Scherrer equation.

Blugan et al. [24] investigated the crystalline phase of their polished samples with XRD process with CuKα1 radiation. XRD confirmed presence of βSi_3N_4 and TiN as main crystalline phase as there are no Ti-based crystalline phase has been detected.

Blab et al. [26] prepared dense nanocomposite of TiN and 1.7–8.1 mol% silicon nitride by sintering process. They maintained pressure and temperature during sintering at 6.5 GPa and 1300 °C, respectively. After investigating the crystalline structure of samples by XRD, they found that TiN was present as a crystalline form in all specimens. They also observed significant reduction in lattice parameter of titanium nitride.

4 Compositional and Electronic Structure

4.1 X-ray Photoelectron Spectroscopy (XPS)

Diserens et al. [13] tested chemical nature of their samples by XPS technique and presence of silicon, titanium and nitrogen they found in it. Even they also discovered that partial pressure of nitrogen plays the high influential role for nitridation of silicon. They also came to know that, as the partial pressure of nitrogen is increasing it causes changes in chemical state of silicon.

Park et al. [23] were performed XPS operation to verify the behaviour of Si on TiSiN films consist of 7% Si. They found that peak binding energy of Si 2p and Ti 2p were at 455.6 and 101.8 eV, respectively.

Shen et al. [16] produced $Ti_{1-x-y}Si_xN_y$ thin films on unheated Si (100) substrate by PVD (reactive unbalanced dc magnetron sputtering) method in presence of Ar–N_2 gas mixture. The electron bonding configuration of film was characterized by XPS technique. They observed opposite trend between Si and Ti concentration growth with current. Concentration of Si increased with increasing current up to 2 A whereas Ti concentration decreased.

5 Mechanical Properties

5.1 Nano Indentation

Shen et al. [16] used nanoindentation to measure hardness of their samples. They observed significant growth in hardness for TiN films with Si addition. Initial hardness of TiN found 18.8 GPa and it increases up to 32.8 GPa with increasing Si concentration.

6 Conclusion

Some of the nitride-based ternary thin films (e.g. TiSiN, TiAlN, TiMoN) have huge industrial application because of their properties like significant hardness, less coefficient of friction, good wear resistant, corrosion protection and significantly high melting point, etc., as compared to binary-based nitride coatings. The hardness of TiSiN film was found to be 32.8 GPa [16] when deposited by reactive unbalanced dc magnetron sputtering technique in presence of Ar–N_2 gas mixture. From AFM analysis, minimum surface roughness (R_a) of titanium silicon nitride thin film deposited by ion beam assisted deposition technique was found to be 4 nm [17]. Young modulus of dense nano composite of titanium nitride and silicon nitride increased with decreasing temperature [26].

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