

CHAPTER-3

Ti AND TiN THIN FILMS

Abstract

In this chapter, structure, microstructure, mechanical optical and electrical properties of 150 and 220 nm metallic Ti and stoichiometric TiN thin films are studied. Thin films are deposited at room temperature on single crystalline Si (311) and polycrystalline 316 LN nuclear grade stainless steel (SS) substrates using RF reactive magnetron sputtering in 100% Ar atmosphere for Ti films and 100% N₂ for TiN films. Ti films are crystallized into hexagonal structure with (100) orientation and exhibits complex microstructure, which consists of obelisk-like, lenticular-like and flower-like structures. On the other hand TiN thin films are crystallized in to cubic structure with (111), (200) and (220) orientations and display good microstructure, which consists of spherical grains and pyramid-like structures. TiN films have higher hardness and Young's modulus than that of Ti films. The maximum values of hardness and Young's modulus for Ti thin films were obtained on SS substrate for 220nm film and the values are 12 and 132 GPa respectively. Similarly, the values for TiN thin films on SS substrate are 27 and 250 GPa respectively. The reflectance percentage was increase in the visible region for Ti films and it exhibits a reflectance minimum for TiN films. Polycrystalline TiN films have higher electrical resistivity than that of single crystalline Ti films. TiN films on Si substrate of thickness 220 nm has maximum resistivity and the values is 210 $\mu\Omega$ -cm and similarly, Ti films on Si substrate of thickness 220 nm has minimum resistivity i.e., 54 $\mu\Omega$ -cm.

3.1 Introduction

Transition metals in groups IVb and Vb and the first row elements, carbon and nitrogen, together make strong solids in the rocksalt structure. Titanium nitride is the one among them which exhibits interesting physical and chemical properties. The close packed structure, an fcc Ti sub-lattice with N filling all octahedral sites, is due to the relatively small size of the N atoms compared to Ti (0.74 \AA^0 vs. 1.47 \AA^0). In order to accommodate the interstitial nitrogen, Ti must transform from a bcc or hcp structure to fcc, and N_2 must decompose to atomic nitrogen. The sublimation energy for nitrogen molecule to nitrogen atom is 4.897 eV [137]. In this chapter, we present the results of studies on physical properties of pure Ti and stoichiometric TiN thin films. The significant variations in structure, microstructure, mechanical, optical and electrical properties of Ti and TiN thin films were observed. Some of the physical properties of metallic Ti and TiN compound are presented in the table 3.1

Table 3.1 some important physical properties of metallic Ti and TiN compound

Properties	TiN	Ti
Structure	Fcc (NaCl)	hcp
Space group	Fm3m	P6 ₃ /mmc
Range of composition	TiN _{0.6-1.1}	N/A
Color	Golden	Grey
Density	5.40 g/cm ³	4.54g/cm ³
Melting point	2950 °C	1940 °C
Thermal conductivity	30 Watt/m.K	13 Watt/m.K
Thermal expansion	9.36×10 ⁻⁶ /K	11×10 ⁻⁶ /K
Electrical resistivity	20±10 μΩ-cm	39 μΩ-cm
Hall constant	-6.7×10 ¹¹ m ³ /C	-7.7×10 ¹¹ m ³ /C
Vickers Hardness	21-24 GPa	0.55-2.5GPa
Young's modulus	590GPa	120GPa

3.2 Experimental conditions

Table 3.2 Experimental conditions being used to deposit Ti and TiN thin films

Experimental parameter	Ti	TiN
Deposition method	RF magnetron sputtering	RF magnetron sputtering
Target material	2 inch diameter Ti	2 inch diameter Ti
Substrates	Single crystal Si (311) and 316 LN stainless steel	Single crystal Si (311) and 316 LN stainless steel
Ultimate pressure	3×10^{-6} mbar	3×10^{-6} mbar
Working pressure	5×10^{-2} mbar	5×10^{-2} mbar
Sputtering gas	100 % Argon	100 % nitrogen
RF power	100 Watt	100 Watt
Distance between target and substrate	60 mm	60 mm
Substrate temperature	Room temperature	Room temperature
Deposition time	120 and 180 min	120 and 180 min

For the 120 and 180 min deposition time, thickness of the films was 150 and 220 nm determined using surface profilometer. The error in the thickness calculation was about ± 10 nm for 150 nm films and is about ± 16 nm for 220 nm films.

3.3 Crystal structure of Ti and TiN thin films

XRD patterns of metallic Ti thin films on SS and Si substrates are shown in figure 3.1 (a). Films on both substrates crystallized into the hexagonal closed pack structure with preferred orientation only (100) plane. The intensity of the reflection from (100) decreased with increase

in thickness and it was also accompanied by a shift in the peak position to lower diffraction angle. Compared to the film on Si substrate the FWHM increased and the shift is more significant for the films on SS substrate. XRD patterns of Ti films, in the present case, are different from the other reported studies [138-140] with respect to preferred orientation. Titanium films deposited by physical vapor deposition technique at low substrate temperature found to have highly (200) orientated h.c.p structure. Films deposited at high substrate temperature of the order of 800°C on the contrary have been found randomly orientated structure [141]. Ti films deposited using RF bias sputtering by Sundgren *et al.* [142] also had random crystalline orientations with relative intensities of reflections being different from that of the bulk material. This has been attributed to an effect of preferential growth during deposition. Films prepared by arc deposition have been reported to have a prepared (110) orientation under conditions of high negative bias [143]. The crystalline orientation of the films is a process dependent and a generalization of the behavior cannot be made very easily. Beside this, Y. H. Song *at al.* [144] demonstrated that the crystal orientation is also dependent on the surface free energy and the crystal structure of substrates.

A first-order estimation of the stresses in the films was made from the shifts in the positions of the reflections from their standard values. The standard value of 2θ position of (100) reflection of the stress free h.c.p Ti is appears at 35.170° (JCPDS file No: 89-5009). In the present case, films with lower thickness, the diffraction angle of (100) plane is appeared at the same position as the standard value. However, in films with higher thickness the diffraction angles appeared at 34.96° and 34.67° for the films on Si and SS substrate respectively. The shift in the

peak position is attributed to the presence of compressive stress in the films for higher thickness. The difference in lattice parameter between the deposited Ti films and substrate results the presence of stress.

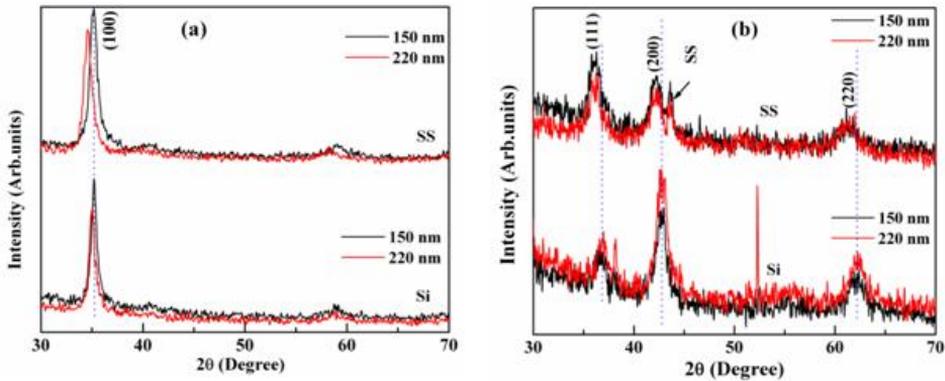


Figure 3.1 X-ray diffraction patterns of 150 and 220 nm thin (a) Ti films (b) TiN films on Si and SS substrates.

XRD patterns of TiN thin films on Si and SS substrates are shown in figure 3.1 (b). From the figure, it is evident that the films are crystallized into cubic structure with (111), (200) and (220) orientation. Films on Si substrate exhibits a (200) preferred orientation, whereas, films on SS substrate did not show any preferred orientation. Comparing the XRD patterns on Si and SS substrates, it is observed that all diffraction planes are shifted to lower diffraction angles for the film on SS substrate independent of the film thickness. The shift is attributed to the presence of residual stress in the films. The calculated lattice parameter of the films on Si substrate is 4.24\AA , which is equal to the bulk stress free lattice parameter. On the other hand, the lattice parameter of the films on SS is 4.28\AA which is greater than the standard value.

Volvada [145] had observed that the lattice parameter of TiN decreases with increasing film thickness. Kiran *et al.* [146] reported that the structural properties such as crystallographic orientations, lattice parameter variation and the level of stress states of TiN thin films are dependent on the structure and properties of substrates. Variations in stresses in TiN were studied by Machunze *et al.* [147] using x-ray diffraction technique and they reported that the average film stress is highly compressive in thin films and less compressive in thicker films. Mismatch of the lattice parameter and the thermal expansion coefficient between the film and substrate result in residual stress in the films. The intrinsic component of the total residual stress is due to contributions from the process parameters, whereas the extrinsic contributions are due to lattice constant or thermal expansion coefficient mismatches [148, 149]. If the extrinsic contributions had dominated, then the direction and magnitude of stress would have been completely predictable from an examination of the differences between the lattice constants and thermal expansion coefficients of the film and the substrate. The lattice mismatches between the film-substrate combinations that TiN-SS and TiN-Si are -21 % and 20.5 % respectively. The thermal expansion coefficient of TiN is $9.4 \times 10^{-6}/^{\circ}\text{C}$ and this value for Si and SS is $4.68 \times 10^{-6}/^{\circ}\text{C}$ and $17.3 \times 10^{-6}/^{\circ}\text{C}$ respectively [145]. The thermal expansion coefficient mismatch between TiN-SS is higher than that of TiN-Si. Therefore, the thermal expansion mismatch and the lattice mismatch between TiN-SS should lead to a compressive stress, which results in the shift of lattice planes to lower diffraction angles.

3.4 Microstructure of Ti and TiN thin films

The microstructure of the films was determined using field emission-scanning electron microscopy. The microstructure evolution of Ti films on Si and SS substrates are shown in figure 3.2. From the figure, it is evident that the surface of the films consists of complex microstructure. Films on Si substrates possess obelisk-like nanostructure and this feature is transformed into flower-like structure with increase in film thickness. On the other hand, films on SS substrates possess lenticular-like structures and the shape is turned to flower-like structure for 220 nm film. On both Si and SS substrates the flower-like structure with relatively little variation could be observed for 220 nm film.

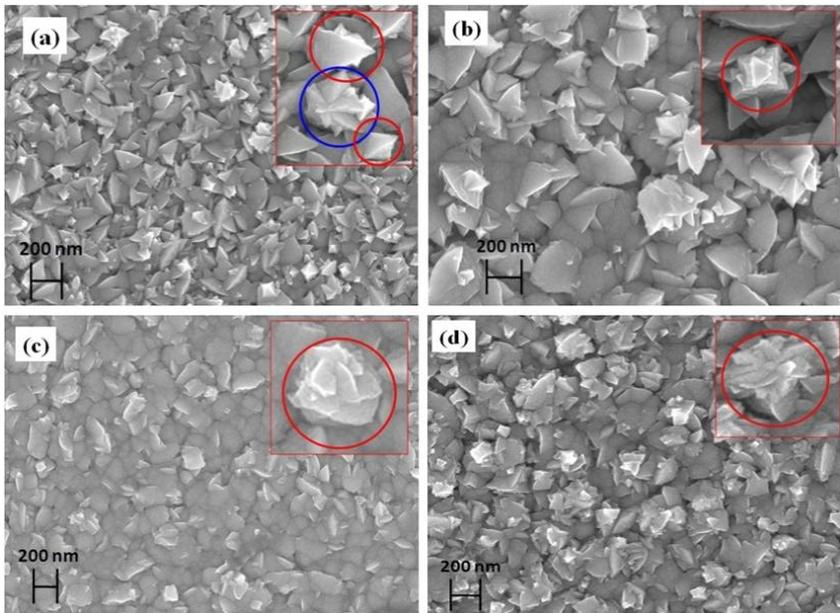


Figure 3.2 Field-emission scanning electron microscopy images of Ti thin films on Si and SS substrates. (a) 150 nm on Si (b) 220 nm on Si and (c) 150 nm on SS (d) 220 nm on SS. The magnified features are shown as insert.

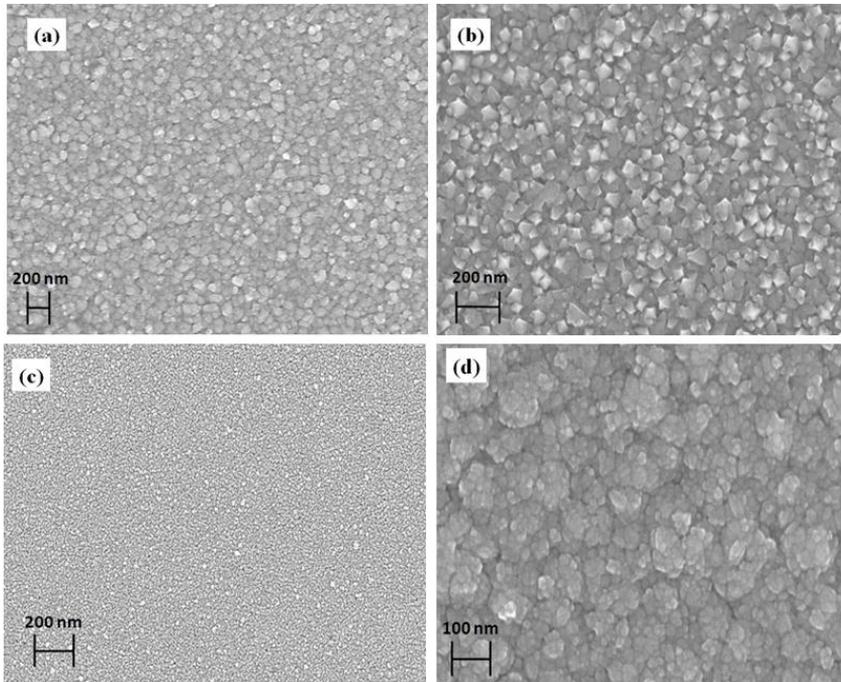


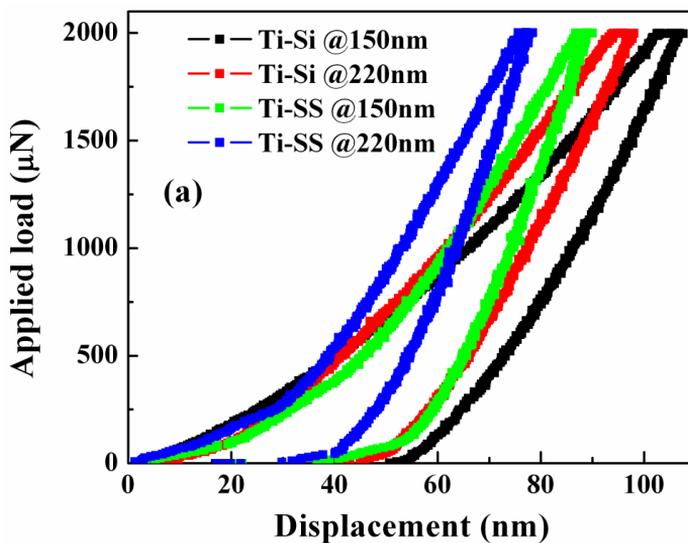
Figure 3.3 Field-emission scanning electron microscopy images of TiN thin films on Si and SS substrates. (a) 150 nm on Si (b) 220 nm on Si and (c) 150 nm on SS (d) 220nm on SS.

The microstructure of TiN thin films on Si and SS substrate is shown in figure 3.3. The morphology of the films on Si substrate changes from circularly shaped fine grains to a pyramid-like structure with increase the film thickness. The mean grain size in the 150 nm films is 80 nm and the diagonal distance of the pyramids in the 220 nm film is about 54 nm. In contract, the microstructure of TiN films on SS substrate consists of fine grains of spherical shape. The grain size in 150 nm film is 35 nm and the size increased to 50 nm for the film with thickness of 220

nm. It is evident that the microstructure evolution of Ti and TiN thin films are dependent on the substrate and the thickness of the films. The microstructure corresponds to zone-I type of the structure zone model, where the films growth temperature is much less than that of melting temperature of Ti and TiN thin films.

3.5 Mechanical properties

The hardness (H) and Young's modulus (Y) of Ti and TiN films were determined using nanoindentation technique. Figures 3.4 (a) and (b) shows the load-displacement curves of Ti and TiN thin films of two different thicknesses (150 and 220nm) on Si and SS substrates respectively. The hardness and Young's modulus of the films were calculated from load-displacement curves using Oliver-Pharr method [150]. The detailed analysis of hardness and Young's modulus of the films was presented in table 3.3.



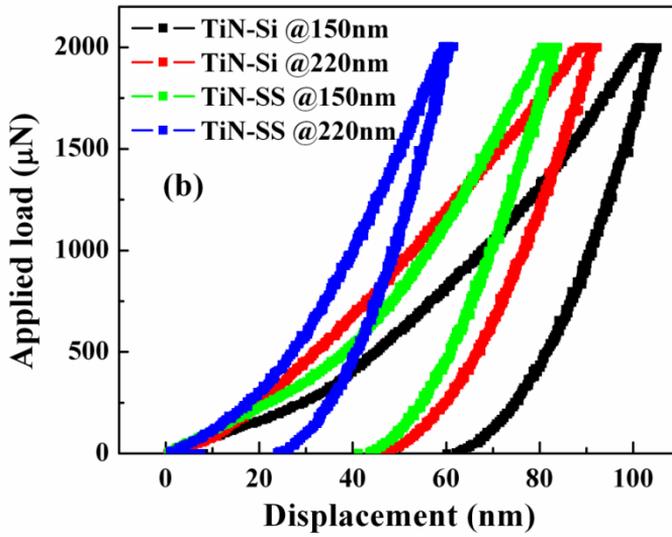


Figure 3. 4 load-displacement curves of 150 and 220nm (a) Ti and (b) TiN thin films on Si and SS substrates.

Table 3.3 Nanoindentation analysis of Ti and TiN thin films on Si and SS substrates

Film	Ti				TiN			
	Si		SS		Si		SS	
Thickness (nm)	150	220	150	220	150	220	150	220
Hardness (GPa)	8	10	10	12	16	21	20	27
Young's modulus (GPa)	82	105	100	132	200	230	220	250

The data revealed that the hardness of 150 and 220 nm thin Ti films on Si substrate is in the range of 8-10GPa and the value on SS substrate is in the range of 10-12GPa. Similarly, the Young's modulus on Si substrate is in the range 82-105GPa and on SS substrate is in the range 100-132GPa. There is a consistency in the data on both substrates in that the films with high thickness (220nm) have higher values of hardness and Young's modulus. Heterogeneous character of coating microstructure, elastic anisotropy, growth texture, and the underlying substrate including the interface have to be accounted for in the interpretation of nanoindentation measurement results. Previously Chang *et al.* [138] studied the structural and mechanical properties of RF sputtered Ti thin films. They reported that with variations in substrate temperature during film growth, the hardness values are spanning in the range 2-6 GPa and similarly the elastic modulus in the range 100-130 GPa for (002) textured films with residual stresses are presented. In the present case films with (100) orientation have higher hardness and Young's modulus than that of previously reported values. In addition, films on polycrystalline SS substrate with high compressive stress have higher values of hardness and Young's modulus. Stresses in a film promote the texture evolution during film growth and hence the plastic yielding in anisotropic materials [151]. Therefore, films on SS substrate have high stress and exhibit enhanced mechanical properties as the films on Si substrates.

Nanoindentation data of TiN thin films revealed that the hardness on Si substrate is in the range 16-21GPa and the value is on SS substrate is in the range 20-27GPa for 150 and 220nm films respectively. Similarly, Young's modulus on Si substrate is in the range 200-230GPa and on SS substrate is in the range 220-250GPa. Levy *et al.* [152]

reported that the mechanical properties of transition metal nitride are depends on the electronic structure, in addition to structure, microstructure and composition. In transition metal compounds, the chemical bond and cohesion energy relate to the mechanical properties, like Young's modulus and hardness [153]. High cohesion energy and high hardness values normally correlate with a covalent character of the bonding. Previously, it is reported that TiN films become harder with increasing N content because the covalent bonding between Ti and N atoms [154]. However, TiN films on SS substrate have higher hardness and Young's modulus than the films on Si substrates. This could be due to improved microstructure of the films on SS substrate.

3.6 Optical properties

The reflectance spectra of Ti and TiN thin films in the wavelength range 200-1500nm are shown in figures 3.5 (a) and (b). The reflectance spectra of Ti films on both Si and SS substrates show similar features. On both substrates with different thicknesses, the percentage of reflectance increased in visible region and saturated at about 35-45% in the near infrared region. In ultraviolet region (200-350 nm), the reflectance is less than 10% for all films. The reflectance spectra of TiN films exhibit a minimum in the visible region, beyond which the reflectance increases in the infrared region. In TiN thin films the reflectance minimum is strongly depended on the nitrogen composition. For stoichiometric TiN experimentally it is observed centered around 2.33 eV, which corresponding to charge transfer between the Ti3p and N2s states [155]. The reflectance minima of all films are centered on 2.30eV. However, in

the entire wavelength region the reflectance is higher for the 150nm thickness than for the 220nm thickness films on both substrates.

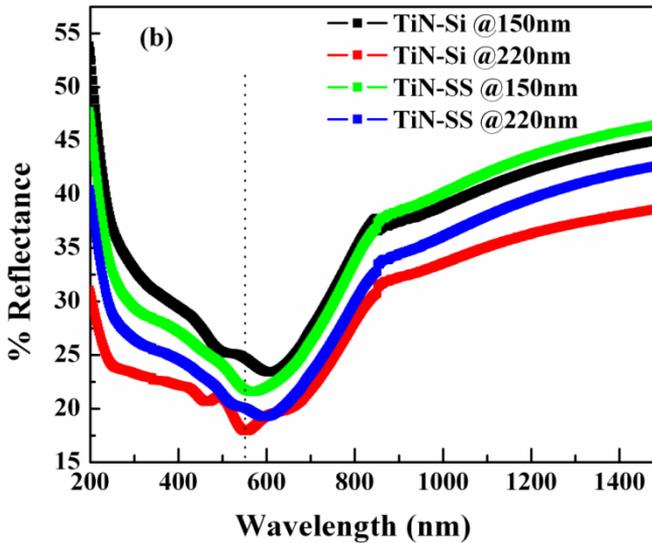
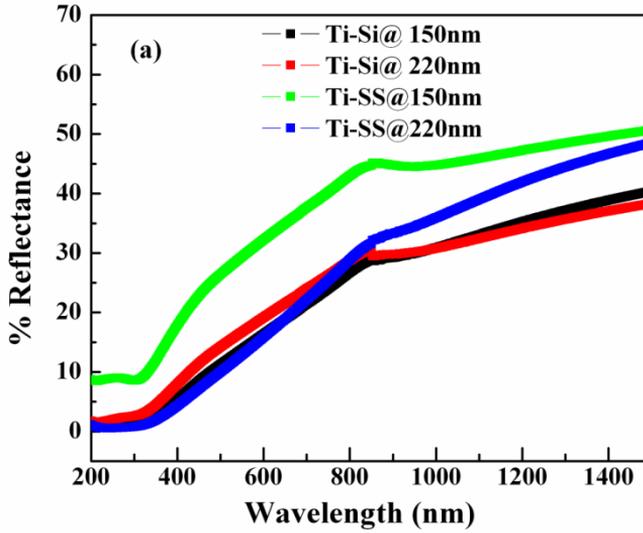


Figure 3.5 Reflectance spectrums of 150 and 220nm thin (a) Ti (b) TiN films on Si and SS substrates.

3.7 Electrical properties

The electrical resistivity of Ti and TiN thin films are determined using four probe method and the data revealed that the films are highly conducting. The calculated values of electrical resistivity of Ti and TiN thin films are presented in table 3.4

Table 3.4 Analysis of electrical resistivity of 150 and 220nm thin Ti and TiN films on Si and SS substrates.

Film	Ti				TiN			
Substrate	Si		SS		Si		SS	
Thickness (nm)	150	220	150	220	150	220	150	220
Resistivity ($\mu\Omega$ -cm)	64	54	80	72	160	210	120	180

On both substrates Ti films exhibits low resistivity in the range 54-80 $\mu\Omega$ -cm and there is a marginal variation in the resistivity with film thickness. On the other hand, TiN films exhibits higher resistivity in the range 120-210 $\mu\Omega$ -cm. It is observed that Ti films on both substrates of 150 nm thickness exhibit higher resistivity than the 220nm film. In contract, TiN films of thickness 150 nm exhibit lower resistivity than the 220 nm films. It has been reported that the electrical resistivity of TiN thin film is less than that of pure Ti and that is because of the intersection of the valence band of the Ti 3d electrons' with the Fermi level [5, 154]. But in the present case, the resistivity of TiN films is higher than that of Ti films; this could be polycrystalline nature of TiN thin films. It is known that the electrical resistivity of TiN_x thin films depends on defects, microstructure, composition and structure [156]. In polycrystalline TiN

films the resistivity arises due to grain boundary scattering [67]. From XRD studies it is observed that TiN films on Si and SS substrates are polycrystalline and Ti films is single crystalline. Therefore, grain boundary scattering could be the reason for higher resistivity of TiN films than for Ti films.

3.8 Summary

Pure metallic and stoichiometric TiN thin films of thicknesses 150 and 220 nm were deposited on single crystalline Si (311) and polycrystalline 316 LN nuclear grade stainless steel substrate by RF reactive magnetron sputtering. From the results presented above, it is observed that the addition of nitrogen to titanium makes new compound, which shows different structure, microstructure, mechanical, optical and electrical properties than that of pure titanium. For example, crystal structure of h.c.p Ti transform into cubic TiN. Cubic TiN shows polycrystalline nature and exhibits (111), (200) and (220) plane orientations, where as h.c.p Ti is a single crystalline and exhibit (100) orientation. Covalent bond between Ti and N make the compound stronger, as a result TiN film displays higher hardness and Young' modulus than that of Ti films. The charge transfer from Ti3p to N2s during compound formation is responsible for exhibit reflectance minimum in the reflectance spectrum and it occurred around 2.35eV for TiN films on Si and SS substrates. Grain boundary scattering is major reason for increase in resistivity of polycrystalline TiN films than that of single crystalline Ti films.