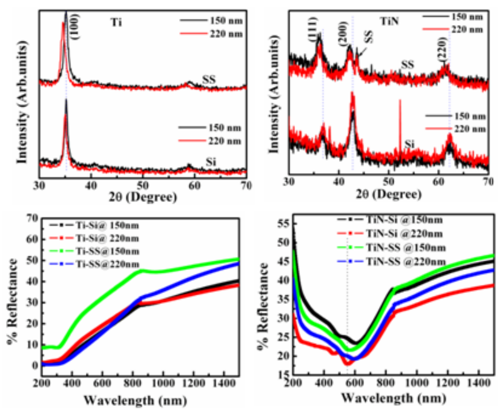
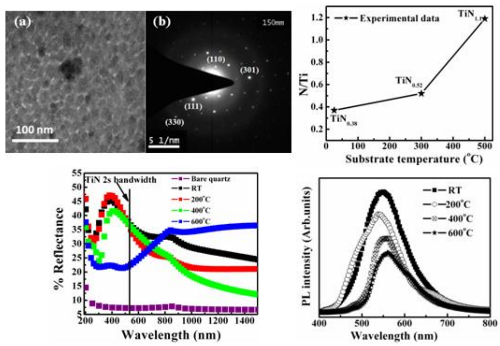
CHAPTER-7

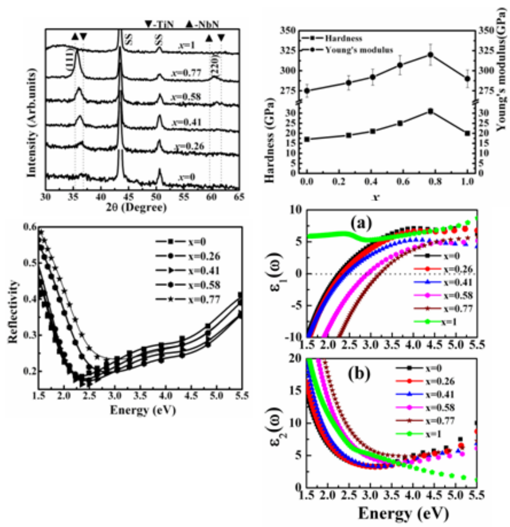
SUMMARY AND SCOPE FOR FUTURE WORK

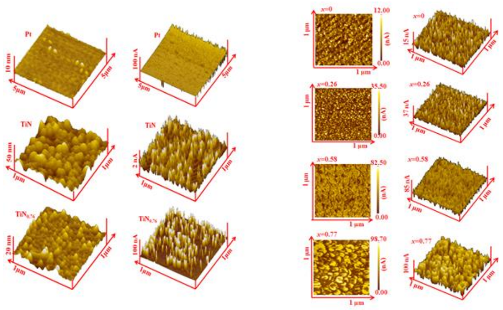
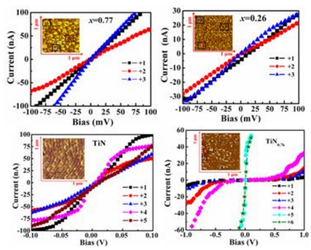
7.1 Summary

Summarizing, the research presented in this dissertation is centered around the structure, microstructure, mechanical, optical and electrical properties of sub-stoichiometric and Nb-substituted titanium nitride thin films. The main object of the present thesis is demonstrate the multifunctional properties of TiN thin films in sub-stoichiometric and metal-substituted forms. Study the microstructure dependent local electrical and electron transport properties of these films is another aspect covered by this thesis. Films are deposited using RF magnetron sputtering on various substrates in 100% nitrogen plasma. The salient conclusions of the thesis with some of the representative figures from chapters-III, IV, V and VI are presented in the table given below.

Ti and TiN thin films 1. Metallic Ti films crystallized into hexagonal structure with (100) orientation. The maximum values of hardness and Young's modulus for Ti thin films are 12 and 132 GPa, respectively. 2. TiN films crystallized into cubic structure with (111), (200) and (220) orientations and the highest values of hardness and Young's modulus are 27 and 250 GPa, respectively	XRD pattern and optical reflectance spectra of metallic Ti and TiN thin films 

***TiN$_x$* thin films** 1. Substrate temperature dependent composition and structure change in TiN$_x$ thin films was observed. N/Ti ratio increased and the crystal structure changed from tetragonal Ti$_2$N to cubic TiN with increase in the substrate temperature. 2. The measured highest values of hardness and Young's modulus were 17.5±1GPa and 120±6 GPa for the film deposited at 600^{o}C. 3. Optical reflectance minima of the films shifted from the ultra-violet region having energy of 4.83 eV to the visible region corresponding to energy of 2.47 eV 4. Films exhibited a single photoluminescence band in the middle of the visible region	TEM (SAED) image of Ti$_2$N film, variation of N/Ti ratio with substrate temperature, PL spectra and reflectance spectra of TiN$_x$ thin films (Clockwise) 

$Ti_{1-x}Nb_xN$ thin films 1. X-ray diffraction studies of $Ti_{1-x}Nb_xN$ thin films revealed that the Nb is completely soluble in TiN and forms a stable ternary solid solution in cubic structure with (111) orientation. 2. The highest hardness achieved was 31GPa for *x*=0.77, at the same Nb concentration, the friction coefficient was 0.15 and the elastic recovery was 60%. 3. The real part of the dielectric function is characterized by screened plasma energy of 2.25 eV for values of *x* <0.5 and 3.2 ± 0.2 eV for *x* >0.5 4. The electrical resistivity of $Ti_{1-x}Nb_xN$ films decreased from 206 to 56 μΩ-cm as increase *x* from 0 to 0.77	XRD pattern, variation of hardness with *x*, real (a) and imaginary (b) parts of dielectric function and fitted reflectance spectra of $T_{i-x}Nb_xN$ films (Clockwise) 

C-AFM study on TiN_x and $Ti_{1-x}Nb_xN$ films 1. C-AFM study on the surface of TiN_x and $Ti_{1-x}Nb_xN$ indicates that the grains in stoichiometric TiN are electrically conductive but those of sub-stoichiometric $TiN_{0.76}$ film are electrically resistive. In $Ti_{1-x}Nb_xN$ films, current on the grain interior is higher than the grain boundary and grain boundaries act as potential barrier for electron transport. 2. The I-V characteristics of TiN film with grain size 73±12 nm is almost linear, but for the sub-stoichiometric $TiN_{0.76}$ film having grain size 50±5 nm, the I-V curve is non linear. 3. I-V characteristic of $Ti_{1-x}Nb_xN$ thin films exhibits linear variation which indicates ohmic contact between tip and films.	3D current images and I-V characteristics of TiN, $TiN_{0.76}$ and $Ti_{1-x}Nb_xN$ thin films (Clockwise)  

7.2 Scope for future work

There are many issues that still need to be resolved and could form part of future work

***Ex situ* annealing**

The metallic Ti films exhibit a variety of microstructures which can be modified by *ex situ* annealing leading to change in their mechanical, optical and electrical properties. Annealing of $Ti_{1-x}Nb_xN$ thin films could also result in the change in structure, microstructure, mechanical, optical and electrical properties. Therefore, a study of the properties of Ti and $Ti_{1-x}Nb_xN$ thin films as a function of *ex situ* annealing temperature is a possible area for future work.

TiN/SiN and TiN/NbN multilayer

Nanostructured multilayer coatings of transition metal nitrides are an emerging class of superhard materials. These multilayers exhibit properties such as high hardness, wear resistance, high corrosion resistance and higher thermal stability. The properties exhibited by nanolayered multilayer coatings depend upon the modulation wavelength and nature of the interface structure which, in turn, can be tailored depending upon the choice, and layer thickness of the constituent materials and by judicious control of the deposition parameters. Nanocrystalline/amorphous TiN/Si_3N_4 multilayer films are one of the important candidates for next-generation materials in high temperature tribological applications. Similarly, TiN/NbN multilayer system is technologically important since it is expected to have lower residual stresses apart from superior mechanical properties. These coatings exhibit hardness in the range 50-90 GPa, which is equal to the diamond hardness. Therefore, deposition and characterization of TiN/Si_3N_4 and TiN/NbN multilayers can be taken up in future.

Kelvin Force Microscopy (KFM)

Using conductive atomic force microscopy, the local electrical and electron transport properties of TiN_x and $Ti_{1-x}Nb_xN$ films were successfully studied. Kelvin force microscopy (KFM) is extensively used to map the local surface potential of metallic and semiconductor thin films. It is also possible to measure local work function of the surfaces at nanometer length scale. Therefore, measurement of the surface potential and work function of TiN_x and $Ti_{1-x}Nb_xN$ films using KFM could form another area of future work.

List of Publications relevant to this thesis

1. K.Vasu, M.S.R.N.Kiran, M.Ghanashyam Krishna, K.A.Padmanabhan
"Effect of substrate on the crystallographic texture and microstructure evolution in titanium nitride thin films" *Proceedings of the DAE-SSPS-2008, **53** (2008) 681*

2. K.Vasu, M.Ghanashyam Krishna, K.A.Padmanabhan
"Substrate temperature dependent structure and composition variations in RF sputtered titanium nitride thin film" *Appl. Surf. Sci.* **257** (2011)3069-3074

3. K.Vasu, M.Ghanashyam Krishna, K.A.Padmanabhan
"Conductive atomic force microscopy study of local electron transport in nanostructured titanium nitride thin films" *Thin Solid Films* **519** (2011) 7702-7706

4. K.Vasu, M.Ghanashyam Krishna, K.A.Padmanabhan
"Effect of Nb concentration on the structure, mechanical, optical and electrical properties of nanocrystalline $Ti_{1-x}Nb_xN$ thin films" *J. Mater. Sci.* **47** *(2012)* 3522

5. K.Vasu, G.M.Gopikrishnan, M.Ghanashyam Krishna, K.A.Padmanabhan
"Optical and electronic properties of $Ti_{1-x}Nb_xN$ thin films" AIP. Conf. Proc.**1447** (2012) xxxx

6. K.Vasu, M.Ghanashyam Krishna, K.A.Padmanabhan
"**Nanomechanical and nanotribological properties of Nb substituted TiN thin films"** AIP. Conf. Proc.**1451** (2012) xxxx

7. K.Vasu, G.M.Gopikrishnan, M.Ghanashyam Krishna, K.A.Padmanabhan
"Reflectance, dielectric function and phonon-vibrational modes of reactively sputtered Nb substituted TiN thin filsms" (2012) (Under review)

8. K.Vasu, M.Ghanashyam Krishna, K.A.Padmanabhan

"Microstructure dependent local electrical and electron transport properties of $Ti_{1-x}Nb_xN$ thin films" (2012) (Under review)