# THE EFFECT OF ANNEALING TEMPERATURE ON THE OPTICAL AND MECHANICAL PROPERTIES OF INTERMETALLIC NiTi THIN FILMS USING DC MAGNETRON SPUTTERING TECHNIQUE

**B. Naveen Kumar Reddy**[1]**, N. K. Udayashankar**[2]

[1,2]*Nano Materials Laboratory, Department of Physics,*
*National Institute of Technology Karnataka-575 025,( India).*

## ABSTRACT

*Intermetallic Nickel-Titanium shape memory alloys (SMA) is a relatively new material that has attracted immense research interest for micro-electro-mechanical systems (MEMS) and biomedical applications. Large displacement and actuation force, higher surface to volume ratio, higher power density and compatibility with batch processing technologies of silicon micromachining make these films a better option for MEMS. Intermetallic NiTi thin films were prepared by dual source DC magnetron oblique angle sputtering technique from separate elemental Ni and Ti targets. The as-deposited film vacuum annealed for 1hour at a temperature range of 350 ºC-650 ºC. The composition and uniformity of the films were carried out by energy dispersive X-ray spectroscopy in a scanning electron microscope. The optical response of the films was studied using UV-Vis spectrophotometer. The mechanical properties of these films were studied using Hysitron Triboindenter. The optical band gap of the films increased with respect to annealing temperature. The nano scratch and nano wear performance of the intermetallic NiTi thin films are strongly dependent on annealing temperature. The point of delamination and friction measurements of these thin films was studied. It was found that the intermetallic NiTi thin film vacuum annealed at a temperature range of 350 ºC-550 ºC show delamination (failure event) but in the case of higher temperature, i.e. at 650 ºC these films does not show a delamination for the subjected load conditions. However, the nano wear resistance of the film decreases with increase in annealing temperature.*

***Keywords: Annealing, Delamination, Intermetallic, Nano Scratch, Nano Wear.***

## I INTRODUCTION

Thin film shape memory alloys show inherent shape memory effect and superelasticity, offer great potential in the field of micro-electro-mechanical-systems (MEMS) since they can be patterned with standard lithography techniques and can be fabricated by batch processing [1-6]. Large displacement and actuation force, higher power density, higher surface to volume ratio, low voltage requirements makes these films a better option for MEMS and BIO-MEMS, such as microwaves, microgrippers, micropositioner, micropumps, clipping microelectrodes and micro capsules [7-10]. Thin film SMAs attracted much attention to the research field of functional and smart (intelligent) materials. In recent years, intermetallic thin films are shown to be promising and high performance material for oil lubricated, rolling and sliding contact applications (bearings and gears) [11]. Several fabrication methods have been used to prepare intermetallic NiTi thin films including laser ablation, ion beam deposition, melt spinning, sputter-deposition, plasma spray, flash evaporation, etc. [12]. Intermetallic NiTi thin films are ideal materials for optical components such as polarizors, monochromators, supermirror, etc. [13]. In the present work intermetallic NiTi thin films were produced from Bi-layer thin films using oblique angle DC magnetron sputtering technique. Multilayer structure exhibits many new electrical, magnetic, optical, structural and transport properties [14-18]. At low temperature the intermetallic NiTi thin films produced by sputtering deposition technique are usually amorphous in nature. Therefore, intermetallic NiTi thin films have to be vacuum annealed above their crystallization temperature to bring crystalline order. In the present work, we have investigated the effect of annealing temperature on the optical and mechanical properties of sputter deposited intermetallic Ni/Ti Bi-layered thin films. We have prepared Ni-rich (Ni-60 at. pct Ti) NiTi thin films by DC magnetron oblique angle sputtering. The Bi-layer Ni/Ti thin films were prepared by using separate elemental Ni and Ti targets. The film composition was controlled precisely by adjusting the powers supplied to each target. However, in the case of intermetallic NiTi thin films the characteristics of films can vary significantly depending on the annealing temperature and microstructure (phase transformation) [19-20].

## II EXPERIMENTAL

Intermetallic NiTi thin films were deposited on glass substrates of dimension 10 mm x 10 mm by direct current DC magnetron sputter-deposition method which is a two gun oblique angle sputter down set up. The sputter chamber was maintained to a base pressure, lower than 3.75 x $10^{-6}$ Torr using a rotary pump and diffusion pump. The thin films were deposited using separate elemental targets of Ni and Ti of purity 99.99%. The glass substrates were cleaned thoroughly in an ultrasonic bath for 20 minutes with double distilled water and then washed with acetone and 2-propanol. The targets were pre-sputtered 15 min before the deposition to eradicate contamination from the target surface. The substrate to target distance (S-T distance) strongly affects the sputter deposition rate, uniformity of composition of the substrate surface and therefore the S-T distance were carefully maintained at 50 mm. During the deposition time the substrate holder was rotated at 10 rpm to maintain the homogeneity of composition. During the sputter deposition process, argon gas (purity 99.999%) at a flow rate of 30 sccm was allowed into the sputter chamber through an AALBORG GFC 17 mass flow controller. The deposited films were solution treated or annealed for 1 hour in the temperature range of 350 °C-650 °C. The annealing temperature was chosen from the TTT (time-temperature-transformation) diagram established by Nishida et al. [21] for bulk Ti-52 Ni alloy.

The composition of the thin films was determined by energy dispersive X-ray spectroscopy analysis (EDXA) in a scanning electron microscope. The intermetallic thin film thickness was measured using step height on masked glass substrates using a Dektak 150 surface profilometer (Veeco Instruments Inc., Tucson, AZ). The optical transmittance of the NiTi thin films was recorded using UV-Vis spectrophotometer (Ocean optics Spectrophotometer USB4000 Series) in the wavelength range 300-850 nm.

A TI 950 TriboIndenter equipped with Hysitron Standard 2-D transducer was used to perform a set of nanomechanical tests on intermetallic NiTi thin films deposited over the glass substrate and annealed at four different temperatures. The adhesion properties of the films were determined by performing the nanoscratch test. Nanoscratch experiments were conducted using diamond 60° conospherical probe with a 0.228 µm radius of curvature. Each scratch test was performed by moving the probe laterally a distance of 6 µm in 20-second duration, while simultaneously ramping the normal force from 0 to 3000 µN. To assure the repeatability of the obtained results, four load-controlled ramping force scratch experiments were performed in intermetallic NiTi thin films at different locations. Nanowear experiments were performed to obtain the wear resistance of the deposited films and for the quantification of the wear volume. Scanning Wear tests were performed in intermetallic NiTi thin films using diamond 60° Conospherical probe with 0.228 µm radius of curvature. Each test consisted of eight passes at a scan rate of 1 Hz with a scan size of 5 µm. 50 µN normal load was used for the wear tests. After each wear test was completed, the wear areas were imaged using in-situ SPM imaging facility.

## III RESULTS AND DISCUSSION

### 3.1 Optical properties

Fig. 1 shows the optical transmittance spectra of sputter deposited NiTi thin film vacuum annealed at different temperatures and recorded in the wavelength range 350 - 850 nm. The films annealed at higher temperature (at 650 ºC) showed about 95 % transmittance. The annealed NiTi thin films showed an average transmittance of 83 % (at wavelengths > 600 nm). The optical absorption coefficient (α) of the intermetallic NiTi thin films was calculated using the following equation [22-23],

$\alpha = (1/t) \ln T$……….. (1)

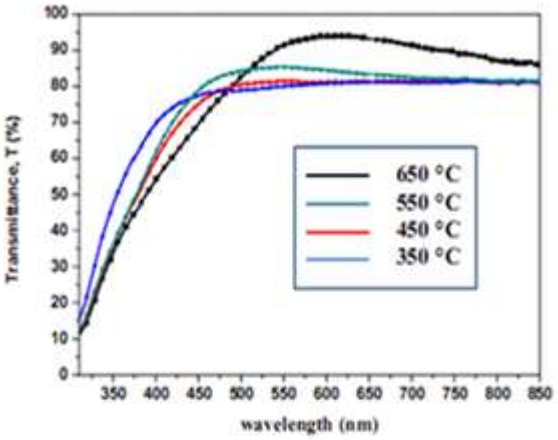


**Fig. 1. Optical transmittance spectra of intermetallic NiTi thin film vacuum annealed for 1 hour at four different temperatures.**

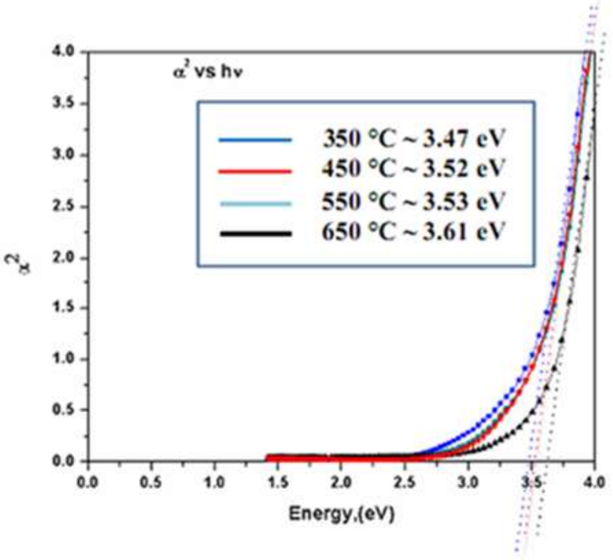


**Fig. 2. Plots of ($\alpha^2$) versus Energy for band gap calculation.**

Where t is the film thickness and T is the optical transmittance. The optical band gap of the films was determined by the Tauc's plots [24] of ($\alpha^2$) versus photon energy (hυ) by assuming a direct transition takes place in thin films. The optical band gap is extracted by extrapolating the linear portion of the plot to the energy axis (x-axis) yielded the direct band gap value as shown in Fig. 2. With the increase of annealing temperature the optical band gap increased and the optical band gap of the annealed films was in the range of 3.47-3.61 eV (Fig. 2). The increase in the band gap with annealing temperature is attributed to the increase in the packing density of thin film and comprising very larger grains in the film. When the crystallite size increases and grain boundaries decrease minimizing the scattering and resulting with energy bandgap increasing.

### 3.2 Nano Scratch

Scratch testing has been employed as a way to evaluate the interfacial adhesion of thin film/substrate systems. Failure events can be found where the indenter probe generates fracture, delamination or breakthrough at the film/substrate interface. The failure or delamination events of the film are normally noticed by a combination of sudden changes in the slope of the lateral force and normal displacement data. The normal force applied to the scratch probe at the time when failure is detected is called as critical load and can be determined by analyzing the scratch data. The adhesion failure of the critical load gives a relative measure of a system's interfacial adhesion strength. In general, a higher critical load denotes a higher interfacial adhesion. However, the true relation between critical load and interfacial adhesion is moderately complicated and can be affected by many factors such as the film thickness, fracture toughness of the materials involved, and scratch testing parameters A normal force is applied to the indenter probe while it is moved laterally, and both the normal and lateral motion is controlled as a function of time according to a specified load function in nano scratch mode. Four parameters: normal force, normal displacement, lateral force, and lateral displacement are measured and recorded continuously during the test. From these parameters, comprehensive information about a material’s nano scratch properties can be characterized. Friction, mar resistance, and critical failure load is commonly characterized nano scratch properties.

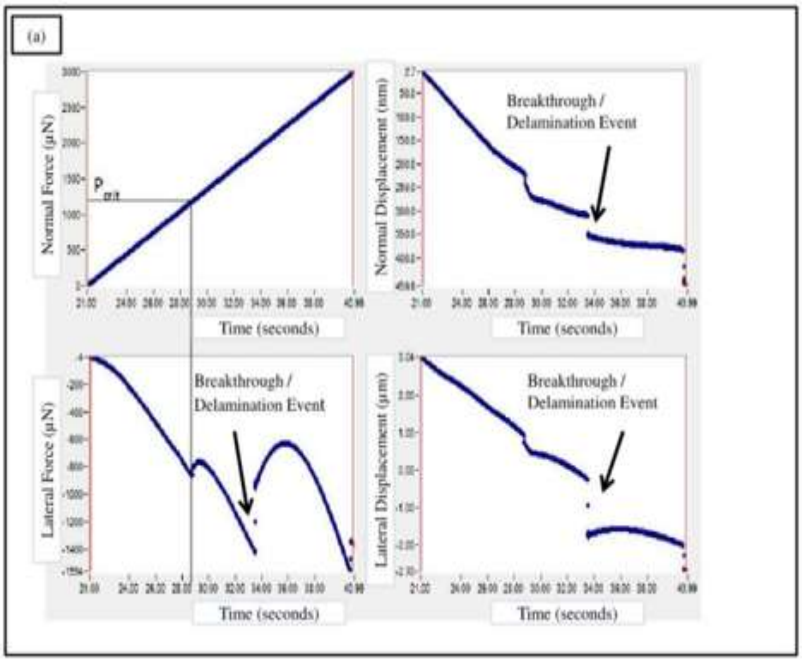
The plots of normal load, normal displacement, lateral force and lateral displacement as a function of time during the scratch are presented in intermetallic NiTi thin films in Fig. 3 (a, b, c and d). The corresponding friction plots are shown in Fig. 4 (a, b, c and d). In nano scratch tests, as the normal force increases, the probe sinks deeper into the material, increasing the lateral force and placing increasing stress on the film/substrate interface. At a certain applied load, the film delaminates from the substrate. The normal load which causes the film to delaminate from the substrate is referred as critical load ($P_{crit}$) or when performing a progressive load test, the smallest load at which the recognizable failure occurs is defined as critical load. The critical load corresponds to the load at which a regular occurrence of such failure along the track is observed in the case of a constant load test.

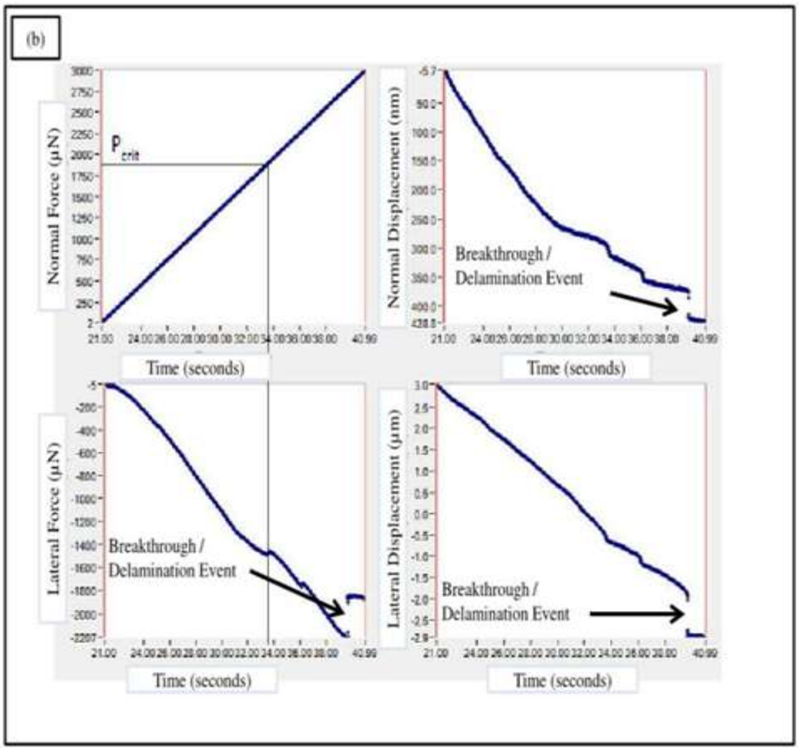
It is clearly observed that the critical load is around 1100 µN for film annealed at 350 °C, 1900 µN for film annealed at 450 °C and 2000 µN for film annealed at 550 °C. This failure event is shown in the data as a sudden decrease in the lateral force combined with an increase in normal displacement. The in-situ SPM imaging capability was used to confirm that the initial failure event in the plots Fig. 3 (a, b and c) and Fig. 4 (a, b and c) corresponds to film delamination while the much larger event that follows may be due various events as a result of delamination like film spallation. Film annealed at 650 °C does not show a failure event for the load conditions applied (Fig. 3(d) and Fig. 4(d)). The nanoscratch behavior of intermetallic NiTi thin films is temperature dependant. This is mainly due to the increase in strength by grain boundaries and dislocation interactions. Therefore, this behavior is attributed to the elemental composition change and phase segregation occurring in the films on thermal annealing [25].

### 3.3 Nano wear

Scanning wear is an important tribological tool for comparing the wear resistance of oxide layers or protective coatings at nanoscale. Wear tests can be performed using Hysitron TI 950 Triboindenter™ nanomechnical test instrument in in-situ Scanning Probe Microscopy (SPM) mode. In this mode, while maintaining a relatively small normal force the instrument can capture images of the sample surface by raster scanning the probe across the surface. Nanowear tests can be performed simply by increasing the contact force maintained by the probe as it scans in the in-situ Scanning Probe Microscopy (SPM) mode. The increased normal load causes the probe to wear away the surface, creating a square region where material has been worn away. An image of the region and its surroundings can be immediately captured using the same probe when the wear test has been completed. This captured image can then be analyzed to determine the average wear depth of the region and the volume of material removed. Fig. 5 and Fig. 6 show the effect of post annealing treatment on the wear performance of the intermetallic NiTi thin films. It is clearly observed that the wear performance of the intermetallic NiTi thin films is strongly influenced by thermal annealing temperature and its wear resistance decreases with an increase in annealing temperature. Nanda Kumar et. al. confirmed from the TEM analysis that the films are in the Austenite

(B2) phase with a substantial amount of segregation of $Ni_3Ti$ [25]. The phenomenon can be endorsed by following two reasons [26]: (a) the phase transition induced by requiring thermal annealing temperature or the stress (which can accommodate the deformation increases with temperature). (b) Nucleation and grain growth at high temperatures can cause adverse effects.





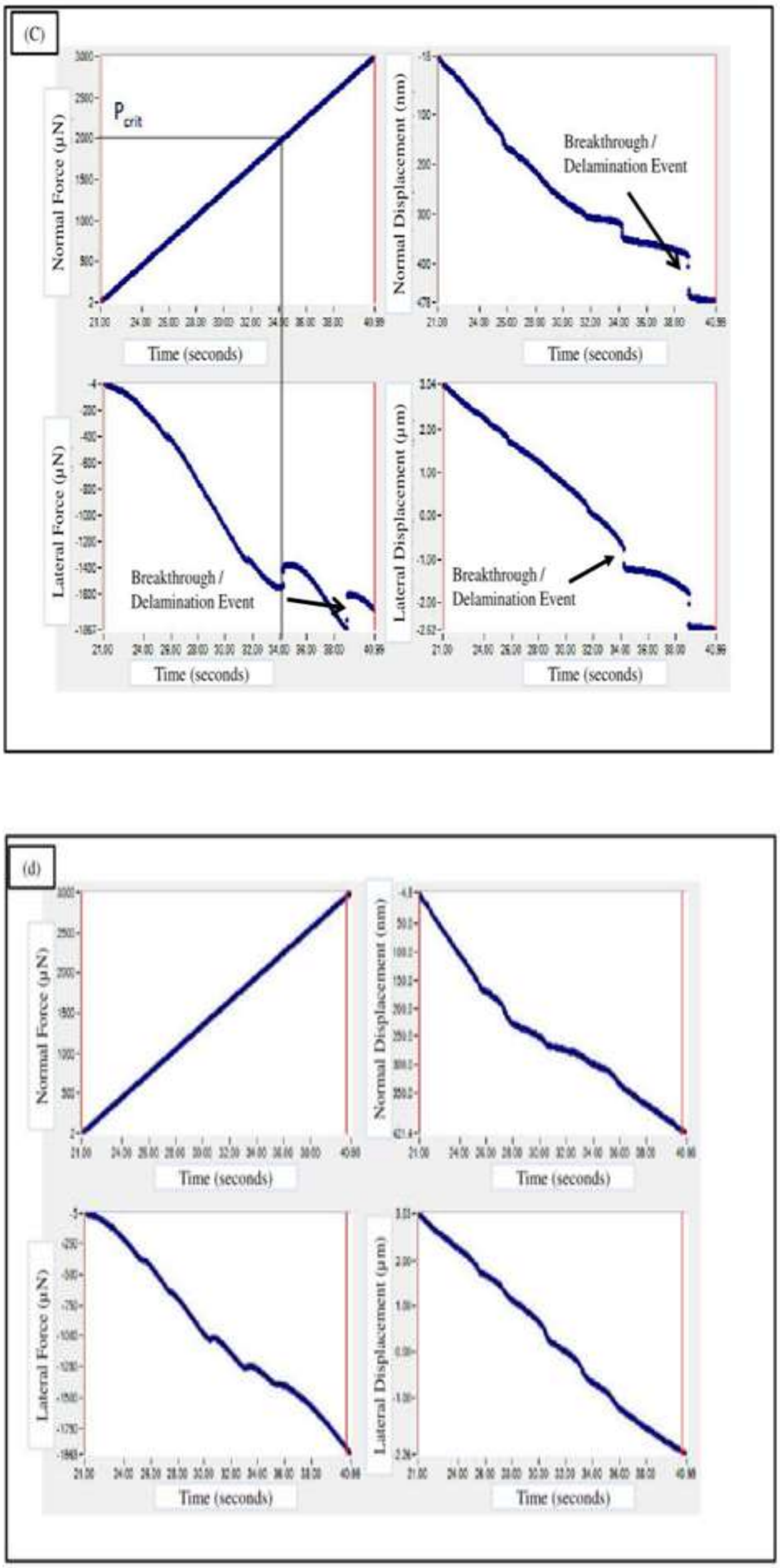


**Fig. 3. Scratch segment analysis of intermetallic NiTi thin films (a) annealed at 350 °C (b) annealed at 450 °C (c) annealed at 550 °C and (d) annealed at 650 °C.**

In this work we have mainly focused on nucleation and grain growth at various annealing temperatures. The films annealed at 350 °C shows feature less microstructure, the resultant microstructure is merely dependant on the conditions of annealing. As the annealing temperature is increasing from 350 °C to 450 °C the crystallization takes place by nucleation of crystals from amorphous state and the growth of these crystals (grain formation). As the annealing temperature is increasing further from 450 °C to 550 °C the microstructure is contributed by coalescence of grains with adjacent grains. At 650 °C an enhanced surface diffusion of adatoms causes a low activation energy ensuing in denser and more compacted film. The microstructure is caused by agglomeration of the few grains with the surrounding ones leads to the larger grain growth [27-28]. It is clearly noticed in SPM images of Fig. 5 and Fig. 6.

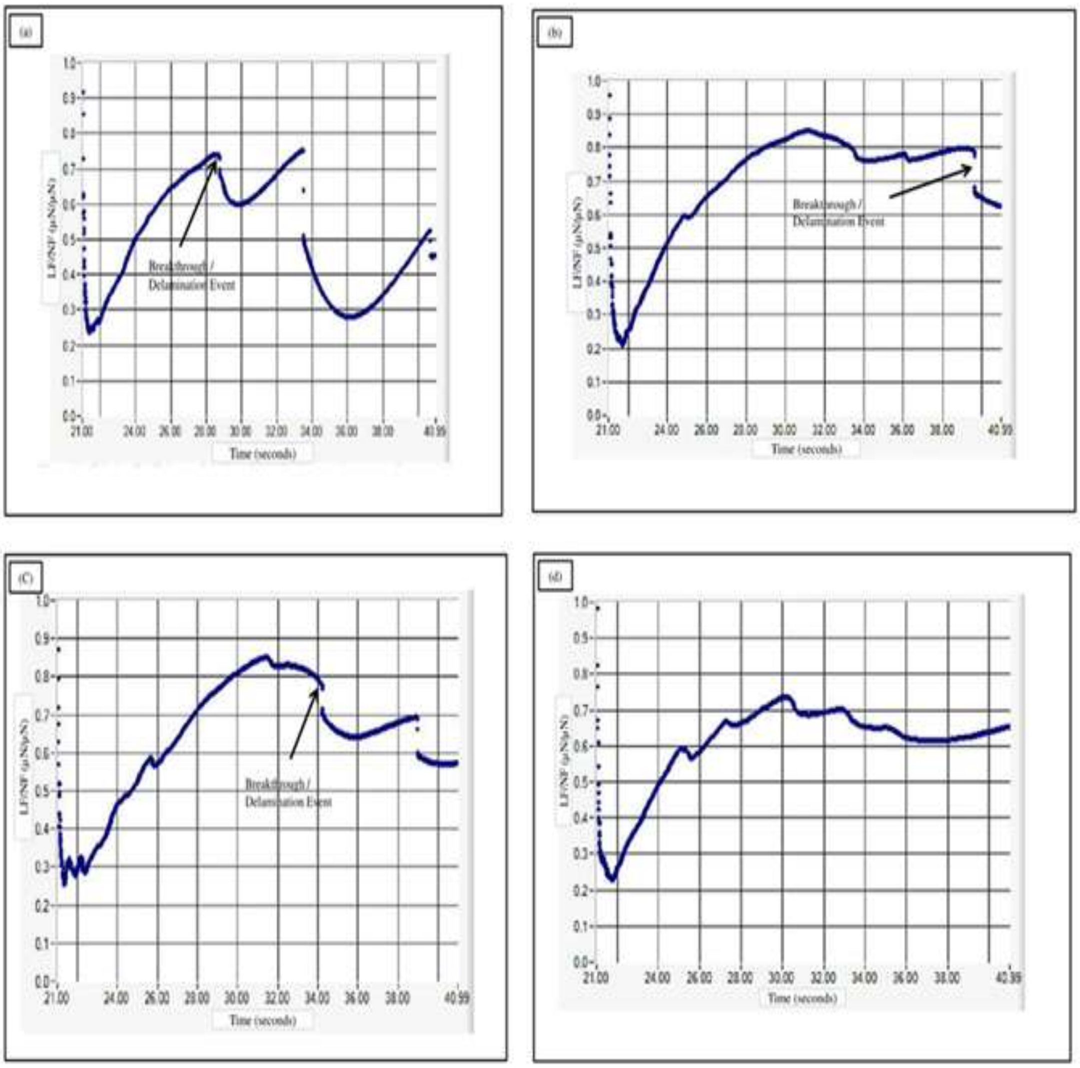


**Fig. 4. Friction Coefficient as a function of time for the scratch segment for intermetallic NiTi thin films (a) annealed at 350 °C (b) annealed at 450 °C (c) annealed at 550 °C and (d) annealed at 650 °C.**

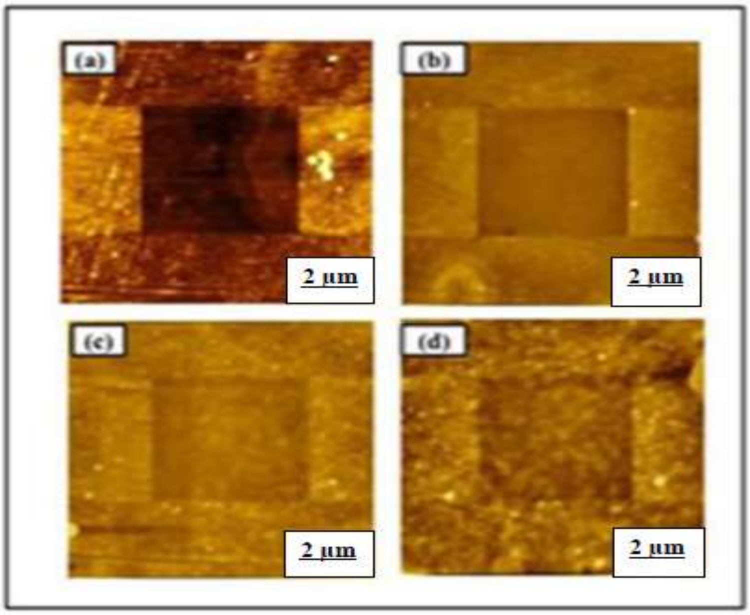


**Fig. 5. 10 µm 2-D in-situ SPM images of intermetallic NiTi thin films (a) annealed at 350 °C (b) annealed at 450 °C (c) annealed at 550 °C and (d) annealed at 650 °C surfaces after nanowear tests using peak load 50 µN.**

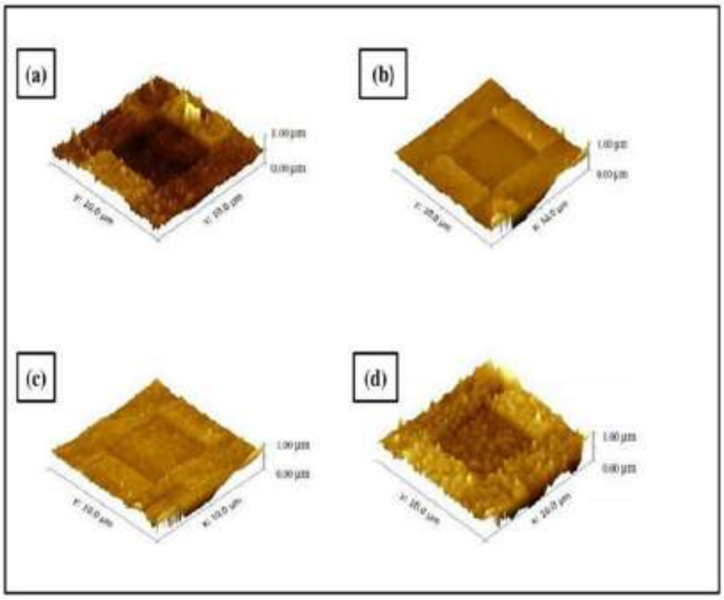
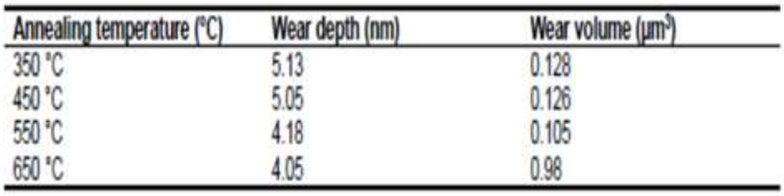


**Fig. 6. 10 µm 3-D in-situ SPM images of intermetallic NiTi thin films (a) annealed at 350 °C (b) annealed at 450 °C (c) annealed at 550 °C and (d) annealed at 650 °C surfaces after nanowear tests using peak load 50 µN.**

**Table 1. Wear depth and wear volume for the intermetallic NiTi thin films after nanowear tests at various annealing temperatures.**



| Annealing temperature (°C) | Wear depth (nm) | Wear volume ($\mu m^3$) |
|---|---|---|
| 350 °C | 5.13 | 0.128 |
| 450 °C | 5.05 | 0.126 |
| 550 °C | 4.18 | 0.105 |
| 650 °C | 4.05 | 0.98 |

## IV CONCLUSIONS

In the present work, we have prepared intermetallic NiTi thin films using dual-source oblique angle DC magnetron sputtering system by Ni/Ti Bi-layer deposition technique. The effect of annealing temperature on the optical response, nano scratch and nano wear properties of these films have been studied. The following conclusions were attained. The optical band gap of the films has increased with increase in annealing temperature. The nano scratch and nano wear behavior of these films are strongly influenced by the thermal annealing temperature. The films annealing at 350°C, 450 °C and 550 °C show delamination or a failure event, but at 650 °C do not show a failure event for the subjected load conditions. At higher annealing temperatures the nucleation and growth rate of the grains in the films are higher. The wear resistances of intermetallic NiTi thin films are decreases with increase in annealing temperature [26]. The intermetallic NiTi thin films are structurally and chemically stable phase even at higher temperatures. This is due to the formation of intermediate metastable states by the incomplete alloying process [25].

## V ACKNOWLEDGEMENTS

The authors are thankful for the financial support provided by the National Institute of Technology Karnataka (NITK), India.

## REFERENCES

[1] A. Ohta, S. Bhansali1, I. Kishimoto, and A. Umeda, Novel fabrication technique of TiNi shape memory alloy film using separate Ti and Ni targets, *Sensors and Actuators A: Physical*, 86, 2000, 165-170.

[2] A. Ishida, M. Sato, and S. Miyazaki, Mechanical properties of Ti-Ni shape memory thin films formed by sputtering, *Materials Science and Engineering A*, 273-275, 1999, 754-757.

[3] Nitin Choudhary, D.K. Kharat, and Davinder Kaur, Structural, electrical and mechanical properties of magnetron sputtered NiTi/PZT/$TiO_x$ thin film heterostructures, *Surface & Coatings Technology*, 205, 2011, 3387-3396.

[4] H. Cho, H.Y. Kim, and S. Miyazaki, Fabrication and characterization of Ti–Ni shape memory thin film using Ti/Ni multilayer technique, *Science and Technology of Advanced Materials*, 6, 2005, 678-683.

[5] K.S.S. Eswar Raju, S. Bysakh, M.A. Sumesh, S.V. Kamat, and S. Mohan, The effect of ageing on microstructure and nanoindentation behaviour of dc magnetron sputter deposited nickel rich NiTi films, *Materials Science and Engineering A*, 476, 2008, 267-273.

[6] A. Kumar, S.K. Sharma, S. Bysakh, S.V. Kamat, and S. Mohan, Effect of Substrate and Annealing Temperatures on Mechanical Properties of Ti-rich NiTi Films, *Journal of Material Science & Technology*, 26 (11), 2010, 961-966.

[7] A.J. Cavaleiro, R.J. Santos, A.S. Ramos, and M.T. Vieira, In-situ thermal evolution of Ni/Ti multilayer thin films, *Intermetallics*, 51, 2014, 11-17.

[8] R.M.S. Martins, N. Schell, K.K. Mahesh, L. Pereira, R.J.C. Silva, and F.M. Braz Fernandes, Texture Development and Phase Transformation Behavior of Sputtered Ni-Ti Films, *Journal of Materials Engineering and Performance*, 18 (5-6), 2009, 543-547.

[9] Y. Motemani, M.J. Tan, T.J. White, and W.M. Huang, Rapid thermal annealing of Ti-rich TiNi thin films: A new approach to fabricate patterned shape memory thin films, *Materials and Design*, 32, 2011, 688-695.

[10] A.J. Muir Wood, S. Sanjabi, Y.Q. Fu, Z.H. Barber, and T.W. Clyne, Nanoindentation of binary and ternary Ni–Ti-based shape memory alloy thin films, *Surface & Coatings Technology*, 202, 2008, 3115-3120.

[11] C. Della Corte, S.V. Pepper, R. Noebe, D.R. Hull, and G. Glennon, Intermetallic Nickel-Titanium Alloys for Oil-Lubricated Bearing Applications, *www.powertransmission.com (powertransmissionengineering)*, Aug 2009, 26-35.

[12] Yongqing Fu, Hejun Du, Weimin Huang, Sam Zhang, and Min Hua, TiNi-based thin films in MEMS applications: a review, *Sensors and Actuators A: Physical, 112*, 2004, 395-408.

[13] Suzana Petrovic, D. Perusko, M. Mitric, J. Kovac, G. Drazic, B. Gakovic, K.P. Homewood, and M. Milosavljevic, Formation of intermetallic phase in Ni/Ti multilayer structure by ion implantation and thermal annealing, *Intermetallics*, 25, 2012, 27-33.

[14] Patrick Surbled, Catherine Clerc, Bruno Le Pioufle, Manabu Ataka, and Hiroyuki Fujitaa, Effect of the composition and thermal annealing on the transformation temperatures of sputtered TiNi shape memory alloy thin films, *Thin Solid Films*, 401, 2001, 52-59.

[15] T. Lehnert, H. Grimmer, P. Boni, M. Horisberger and R. Gotthardt, Characterization of shape-memory alloy thin films made up from sputter-deposited Ni/Ti multilayers, *Acta mater., 48, 2000*, 4065-4071.

[16] Sohrab Sanjabi, Sayed K. Sadrnezhaad, Karen A. Yates and Zoe H. Barber, Growth and characterization of $Ti_xNi_{1-x}$ shape memory thin films using simultaneous sputter deposition from separate elemental targets, *Thin Solid Films*, 491, 2005, 190-196.

[17] Rachana Gupta, Mukul Gupta, S.K. Kulkarni, S. Kharrazi, A. Gupta, and S.M. Chaudhari, Thermal stability of nanometer range Ti/Ni multilayers, *Thin Solid Films*, 515, 2006, 2213-2219.

[18] N. Frantz, E. Dufour-Gergam, J.P. Grandchamp, A. Bosseboeuf, W. Seiler, G. Nouet, and G. Catillon, Shape memory thin films with transition above room temperature from Ni-rich NiTi films, *Sensors and Actuators A: Physical*, 99, 2002, 59-63.

[19] Yongqing Fu, and Hejun Du, Effects of film composition and annealing on residual stress evolution for shape memory TiNi film, *Materials Science and Engineering A*, 342, 2003, 236-244.

[20] B. Geetha Priyadarshini, S. Aich, and M. Chakraborty, An investigation on phase formations and microstructures of Ni-rich Ni-Ti shape memory alloy thin films, Metallurgical and Materials Transactions A, 42A, 2011, 3284-3290.

[21] M. Nishida, C.M. Wayman, and T. Honma, Precipitation processes in near-equiatomic TiNi shape memory alloys, *Metallurgical Transactions A*, 17A, 1986, 1505-1515.

[22] M.C. Jeong, B.Y. Oh, O.W. Nam, T. Kim, and J.M. Myoung, Three-dimensional ZnO hybrid nanostructures for oxygen sensing application, Nanotechnology, 17, 2006, 526.

[23] R. Subba Reddy, A. Sreedhar, A. Sivasankar Reddy, and S. Uthanna, Effect of film thickness on the structural morphological and optical properties of nanocrystalline ZnO films formed by RF magnetron sputtering, *Advanced Materials Letters*, 3(3), 2012, 239-245.

[24] J. Touc, *amorphous and liquid semiconductors* (London and New York: Plenum press, 1974).

[25] A.K. Nanda Kumar, C.K. Sasidharan Nair, M.D. Kannan, and S. Jayakumar, TEM and nanoindentation studies on sputtered $Ti_{40}Ni_{60}$ thin films, *Materials Chemistry and Physics*, 97, 2006, 308-314.

[26] K.L. Ng, Q.P. Sun, M. Tomozawa and S. Miyazak, Wear behavior of NiTi thin film at micro-scale, *International Journal of Modern Physics B*, 24 (1&2), 2010, 85-93.

[27] B. Geetha Priyadarshini, S. Aich and M. Chakraborty, Structural and morphological investigations on DC magnetron-sputtered nickel films deposited on Si (100), *Journal of Material Science*, 46, 2011, 2860-2873.

[28] Xu Huang, and Yong Liu, Surface morphology of sputtered NiTi-based shape memory alloy thin films, *Surface & Coatings Technology*, 190, 2005, 400- 405.