DEFORMATION BEHAVIOR
OF
NiTi THIN FILMS
Research Proposal

By

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Summery:

The research proposal explains intentional plan of research to study deformation behavior of TiNi thin films for microelectromechanical systems (MEMS) applications. The possible fabrication process and possible effect of various processing parameters affecting the structural, electrical and mechanical properties of NiTi thin film is discussed in context of earlier work. State-of-art characterization techniques to assess the quality of films in general and specifically its deformation behavior are discussed. The effect of deposition parameters and the application of loading on the deformation of NiTi thin film are stated. Various aspects of film characterization and model development are noted. An intended research is proposed to contribute to the ongoing development of TiNi thin film for MEMS application.

Table of Contents

Introduction

This research proposal is in support of the application by Rahul Thorat for the PhD position (Topic: Deformation of thin films of NiTi shape memory alloy, 3ME08.48, AT96623) within the group of Surfaces and Interfaces at the faculty of Mechanical, Maritime and Materials Science, TU Delft.

In the section 1, we will describe theory behind the shape memory alloy thin films in detail. It contains information of special characteristics of shape memory alloy TiNi, their fabrication as a thin film and their application in microelectromechancial systems (MEMS). In section 2, the techniques used to study the response of thin films to external thermal and /or mechanical stimulus are stated. In section 3, the current research on the fabrication of TiNi thin film and their thermo-mechanical behavior is explained. The current research describes the effect of various deposition parameters on the microstructure of the films and relation between microstructure and mechanical properties of the material. The research proposal in section 4 looks at the intended studies on the deformation behavior of TiNi shape memory alloy thin film. The research areas fabrication, characterization, mechanical testing and modeling are stated. We have stated the research goals and explain how this research will be conducted.

Section 1 NiTi Shape Memory Alloy Thin Films

Shape memory effect can be described as follows: Suppose an alloy is deformed in its martensitic phase (lower temperature phase). Upon heating to its austentic phase (higher temperature phase), it partially or fully recovers its original shape or form. This behavior of “remembering” its shape from a certain (higher) temperature is called shape memory behavior and the alloy exhibiting such behavior is called a shape memory alloy. Similarly, if such an alloy is loaded with constant force, it undergoes martnesitic phase transformation. If it is unloaded at this stage (when the material is in martensitic phase), the alloy recovers partial or full strain. This property of recovering its dimensions upon unloading, just like rubber, is called pseudoelasticity (Otsuka & Waymen _1998).

1.1 Mechanism of shape memory and pseudoelasticity

Upon cooling below the martensite temperature M_f, unstrained SMAs have a twinned martensite structure. In this phase, deformation of the material is accommodated by preferential alignment of variants, i.e. different twinning planes detwin and align to accommodate the deformation. Unlike permanent deformations associated with dislocations, deformations due to detwinning are partially/fully recoverable when heated to the austenite phase. This is a simplified working of shape memory effect. Uniaxial stress assists in martensitic transformation of a material in austenitic phase. Under constant loading conditions, the twin orientation in martensitic phase is reorganized along the direction of stress and the reorganization propagates through the structure, involving an easy deformation under low stress. As this stress induced martensite is unstable, when unloaded, the material regains austenitic phase with partial/full strain recovery resulting into pseudo elastic behavior (Otsuka_1998 & Surbled_2001). Alloys that exhibit shape memory effect and pseudoelasticity are for example Au-Cd, Cu-Zn based alloys, Fe based alloys (Fe-Pt, Fe-Pd) and NiTi alloys.

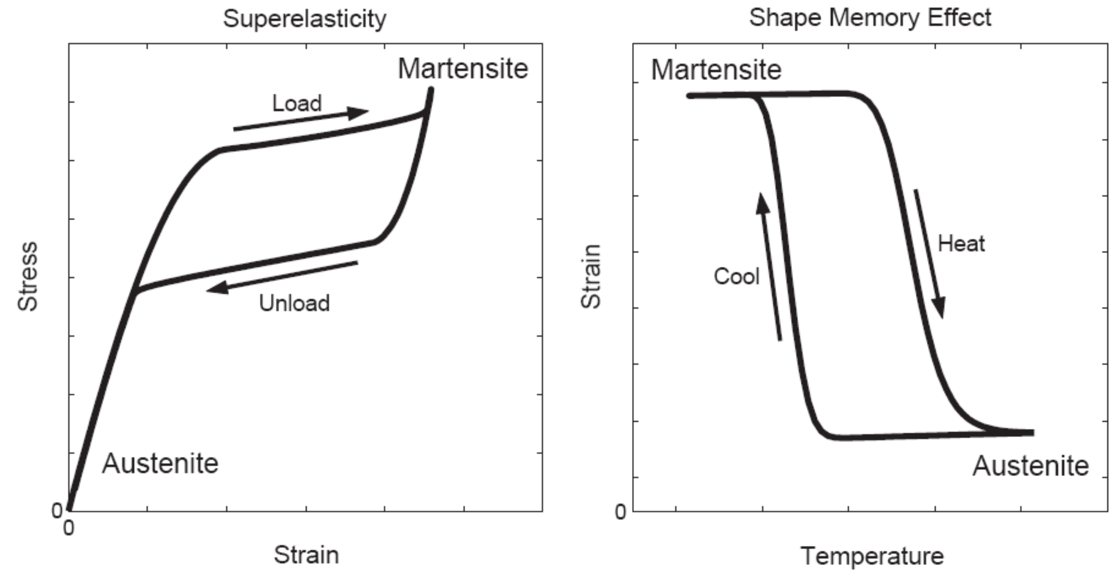


Fig.1 Hysteresis associated with superelasticity (pseudoelasticity) (fixed temperature) and the shape memory effect (fixed load) (Massad_2005)

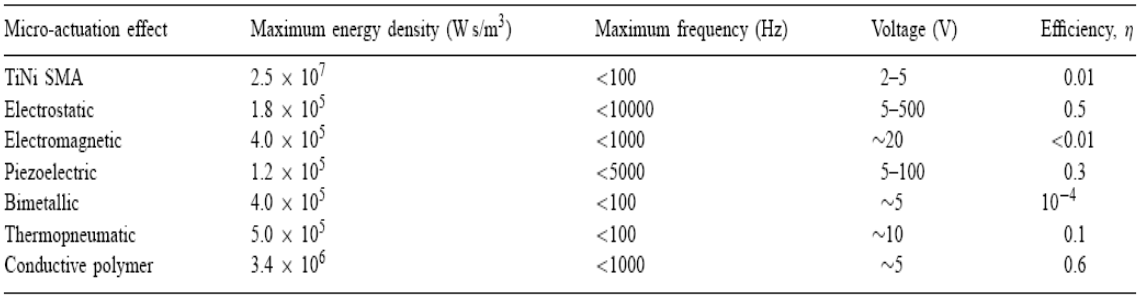
1.2 Advantages of NiTi shape memory alloy as a thin film in microelectronics

The phase transformation in SMA thin film is accompanied by significant changes in the mechanical, physical, chemical, electrical and optical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, electrical resistivity, thermal conductivity, thermal expansion coefficient, surface roughness, vapor permeability and dielectric constant, etc. These changes can be fully made use of the design and fabrication of micro-sensors and micro-actuators (Gupta_2002). Small device cross sections and high surface-to-volume ratios provide effective heating at minimum currents and homogeneous, fast cooling of the micro-actuators (Quandt_1996). In comparison with other shape memory alloys (SMAs), NiTi possess an array of desirable properties suitable for Microelectromechanical systems (MEMS) applications. Thin film SMA has only a small amount of thermal mass to heat or cool, thus the cycle (response) time can be reduced substantially and the speed of operation may be increased significantly. However there are also some disadvantages. Because of its high sensitivity to external stimulus and internal variables, SMAs are difficult to fabricate and tune to certain applications. Table 1 summarizes the advantages and disadvantages of NiTi for sensors and actuators while table 2 gives the comparison between various actuation mechanisms.

Table 1: Advantages and disadvantages of NiTi for MEMS applications (Wilson_2007, Fu_2001, Gupta_2002, Quandt_1996)

Advantages	Disadvantages
High power/weight ratio, Peudoelasticity (or superelasticity), high damping capacity, Noiseless and friction free operation, Excellent chemical resistance, Simple and compact actuator mechanics, produced by standard lithography techniques	Low energy efficiency: Max 10%, Limited bandwidth due to heating and cooling restrictions, Degradation and fatigue under the strain > 5 %, Complex control, SMA behavior is controlled by large number of parameters

Table 2 Comparison between various actuation mechanisms (Fu_2001)



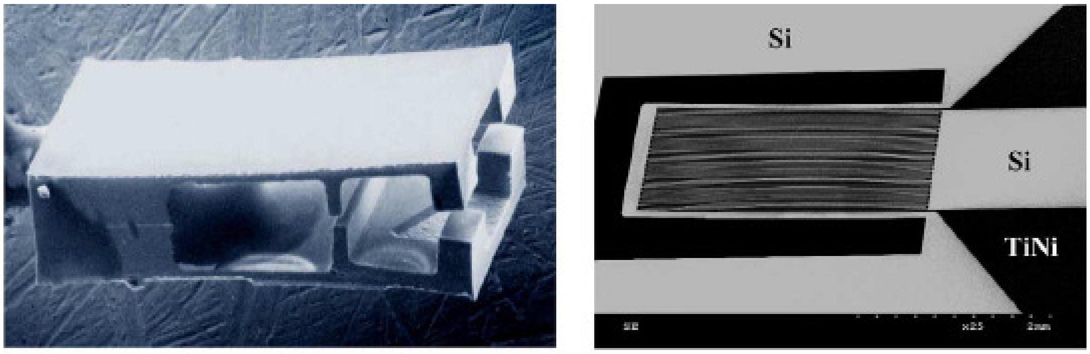
Micro-actuation effect	Maximum energy density (W s/m^3)	Maximum frequency (Hz)	Voltage (V)	Efficiency, η
TiNi SMA	2.5×10^7	<100	2–5	0.01
Electrostatic	1.8×10^5	<10000	5–500	0.5
Electromagnetic	4.0×10^5	<1000	~20	<0.01
Piezoelectric	1.2×10^5	<5000	5–100	0.3
Bimetallic	4.0×10^5	<100	~5	10^{-4}
Thermopneumatic	5.0×10^5	<100	~10	0.1
Conductive polymer	3.4×10^6	<1000	~5	0.6

1.3 Mechanism of microactuation by shape memory alloys:

A successful microactuator must develop a large work output from smaller and smaller volume, and therefore work output per unit volume is a key figure of merit for any actuator material. In order to obtain maximum work output, the devices have to be operated at complete transformation cycles. This requires effective heating and cooling of the device regions of maximum strain. In particular, these general criteria have been met for thin-film devices (Bhattacharya_2003). There are broadly two strategies to use shape memory alloy in microactuation. The first is to deposit on a flexible substrate in such a manner that there is a residual stress when the film is in austenite and use this as a bi-material strip. The residual stress causes the bi-material strip to bend while in austenite. But when it is cooled, the film transforms to martensite and deforms by the arrangement of variants thereby relaxing the residual stress and straightening out the bi-material strip. Most of SMA MEMS (microelectromechanical systems) devices rely on this mechanical design to produce the two-way effect rather than material design (Ho_2000). While this strategy can produce impressive curvatures and displacements, it produces very low forces and energies of actuation. The second strategy is to take advantage of the stretching and shearing by using the films of shape memory alloy as a membrane. The free standing films come into this category. The film is in martensitic form when it is free standing though still attached to substrates in the corners. When subjected to a back pressure, the film bulges out in the martensite state, but becomes flat when heated and transformed to the austenite (Bhattacharya, 2003). Sputtered TiNi films show one way shape memory behavior. There have been some efforts to get the two way effect by changing the microstructure. Graded films with changing crystalline structure and transformation temperature across the film thickness are developed in such a way as to produce films with a bimorph structure exhibiting two-way shape memory effect (Ho_2000, Martins_2005). Gotthardt_2004 discussed ion irradiation as a surface-modification technique to make a novel thin film SMA actuator, which exhibits a reversible out-of-plane bending.

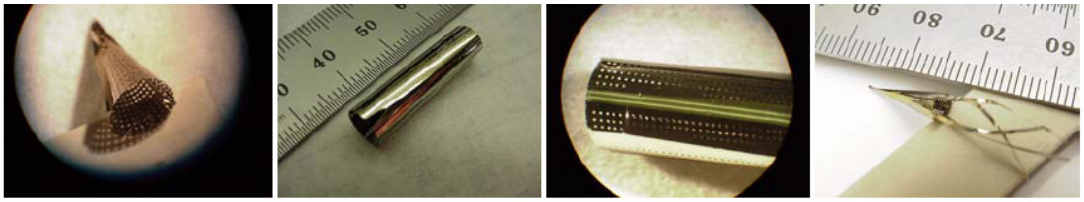
1.4 Current MEMS application of TiNi

The possibility of fabricating integrated micro-actuators on Si wafers by using optical lithography opens the way for TiNi thin films to applications, such as microvalves or micro-cantilevers (Lehnert_2000). TiNi thin films see the applications for various cases: loading conditions, ambient temperature and environment, heat dissipation, heating/cooling rate, strain rate, etc. (Fu_1996). Figure 2 shows an example of applications of TiNi thin films as an actuator like microgripper (Fu_2004). Amongst other applications, micron-scale fenestration patterns fabricated using MEMS techniques enable to design and fabricate wide spectrum of nitinol thin film devices for medical industries and others. Using thin film shape memory alloys one can make such three-dimensional devices as shown in fig.3 (Gupta_2002).



(a) (b)

Fig. 2. TiNi/Si microgripper with cantilever structure with out-of-plane bending mode: (a) microgripper; (b) the patterned TiNi electrodes on silicon cantilever (Fu_2004)



(a) (b) (c) (d)

Figure 3: (a) TiNi thin film cone, (b) cylinder fabricated using multi- layer sputter deposition method (c) Magnified optical image to illustrate micron-scale fenestration patterns on TiNi structures (d) Image of a TiNi cone structure with strings as integral parts made from multi-layer method (Gupta_2002)

1.5 Fabrication of TiNi thin film

TiNi-based films are prepared typically by using physical vapor deposition. The first thin films of NiTi of amorphous nature were developed during 1990’s. The way to anneal the film to crystallize and thereby exhibit shape memory alloy was done by Bush and Johnson (Ho_2000). Further, it is found that the films deposited at higher substrate temperature needs no annealing to exhibit shape memory behavior. From the literature review, it is observed that sputtering is the most widely used fabrication process for TiNi thin films. Table 3 gives an example of parameters used for fabrication of TiNi thin film by sputtering (Fernandes_2002).

DC Magnetron sputtering and RF diode sputtering (Isalgue_1999) are known to be better for the quality of deposition than other techniques. The magnetron sputtering provides low levels of impurities, easy control of the deposition rate, and the production of thin films of various morphology and crystallographic structure of the thicknesses of 2 to

20µm (Quandt_1996, Kumar_SCT_2009). Laser ablation, ion beam deposition, arc plasma ion plating, plasma spray and flash evaporation were also reported but with some intrinsic problems, such as non-uniformity in film thickness and composition, low deposition rate, or non-batch processing, incompatibility with MEMS process, etc.(Quandt_1996, Isalgue_1999, Fu_2004). A typical sputtering system for the fabrication of TiNi thin film is shown in figure 4

Table3 Parameters used for the deposition of TiNi thin film (Fernandes_2002)

Sputtering		
	Cold substrate	Heated substrate T = 673 K
Distance target/substrate (mm)	100-150	50
Initial pressure (mbar)	1E-6 to 6.4 E-6	3E-5 for 673 K
Argon pressure (mbar)	1E-3 to 2.1 E-3	1.9E-3
Deposition pressure (mbar)	1.1 to1.2 E-2	1.1E-2

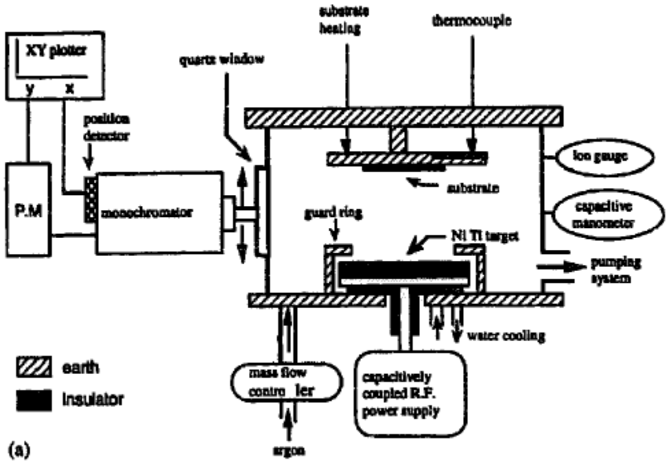


Fig.4 Example of sputtering process to deposit TiNi thin film (Bandahan_1996)

Section 2 Characterization Techniques

The developed NiTi thin films are characterized to evaluate the effect of processing parameters on the structural, electrical and mechanical properties of the film. Different characterization techniques like X-RD, DSC, microscopies are used to study phase transformation of the TiNi thin films. Some times it is possible to get the discrepancies in the measurement. For example, the crystallization temperature of TiNi films has been variously determined by differential scanning calorimetry to be 464ºC, by *in situ* transmission electron microscopy (TEM) to be 477ºC and by *ex situ* TEM to be 400ºC (Kahn_1998). To overcome this problem, the measurement needs to be taken carefully and confirmed by several other techniques.

2.1 X-ray spectroscopy (X-RD, EDX)

In the literature, X-Ray Diffraction (X-RD) is used to check the crystallization, phases of the sample (as sputtered or annealed) and precipitates at room temperature. It is also used during in situ heating/cooling to follow phase transformations. The composition of the film is determined by wavelength- or energy-dispersive X-ray microanalysis (WDX, EDX) (Fu_2006). Table 4 shows example of use of X-RD from literature to study thin film structure. In latest cases (Martins_2005), X-ray diffraction in grazing incidence geometry off-plane (GIXD) at a synchrotron-radiation beam line patterns is used during the annealing process of the Ni–Ti polycrystalline films to reveal austenitic structure (B2 phase) and the precipitation of Ni_4Ti_3.

Table 4 some examples of X-RD use for TiNi thin film characterization

Author	X-RD use
Isalgue_1999	Crystallinity and effect of different target heating conditions to check phase transformation
Fernandes_2002	Phases and Crystallization of the austenite phase during in situ heating at 723 K
Ho_2000	To show relation between the straining of the lattice and widening of the peaks at X-ray diffraction
Martins_2005	In situ studies to understand time dependent crystal reorientation and metastable phase formation or strain evolution

2.2 Differential Scanning Calorimetry (DSC):

Differential scanning calorimetry (DSC) has been used to determine the transformation temperature of the TiNi thin film. It is also used to study the crystallization curve during annealing process (Lehnert_2000).

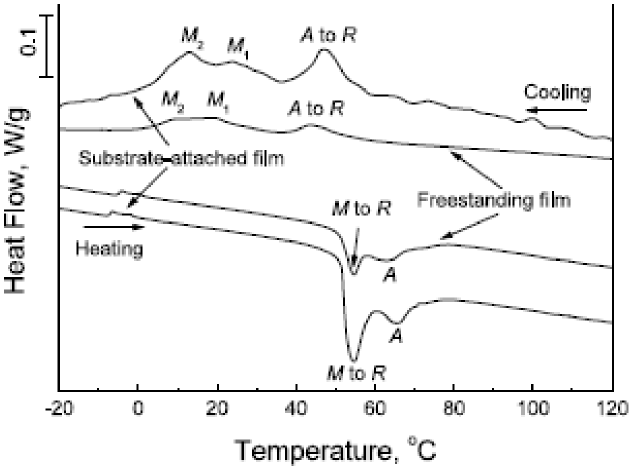


Fig. 5 Example of use of DSC: Transformation behavior of substrate-attached film and freestanding Ti_ 50.5at.%Ni deposited thin films (Huang_2003)

2.3 Microscopic characterization:

Microscopic characterization is used to study the quality of the film, the phases present at the given temperature and in situ phase transformation happening on the surface during heating or cooling process. Field emission scanning electron microscopy (e.g. FEI Quanta 200F), high resolution transmission electron microscopy are the methods used to study the microstructure (Fig.6, Kumar_SCT_2009). The large amount of contrast within TEM images of TiNi thin film grains (Fig.7, Ho_2000) shows large amount of strain due to crystal defects or possible precipitates. Atomic Force Microscope (e.g. NT-MDT: NTEGRA Model) based in-situ testing method has been applied to characterize the phase transformation behavior of the constrained films (Kumar_SCT_2009, Fu_2001). With the change of temperature, the surface roughness values change drastically when transforming between the martensite and the austenite phases, thus clearly reveal the occurrence of phase transformation. The advantages of this method are its nondestructive nature and applicability to very small size films (down to nanometers). Moreover, the optical reflection changes caused by the changes in the surface roughness and reflective index can also be used to characterize the transformation behavior of TiNi films. Study of the crystallographic texture of the Ni–Ti thin films assumes in this way major importance, since the texture has a strong influence on the extent of the strain recovery, the manipulation of the crystallographic orientations of Ni–Ti thin films is also important studies (Martins_2008).

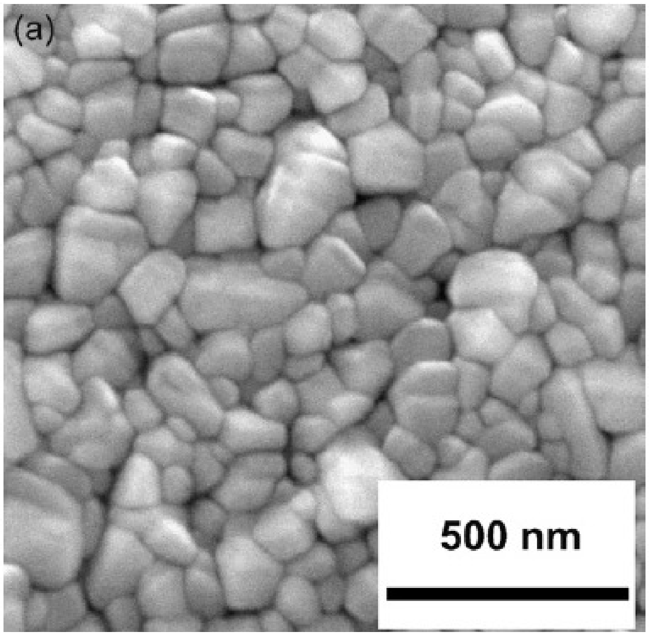


Fig.6 FESEM image of NiTi thin film (Kumar_JAC_2009)

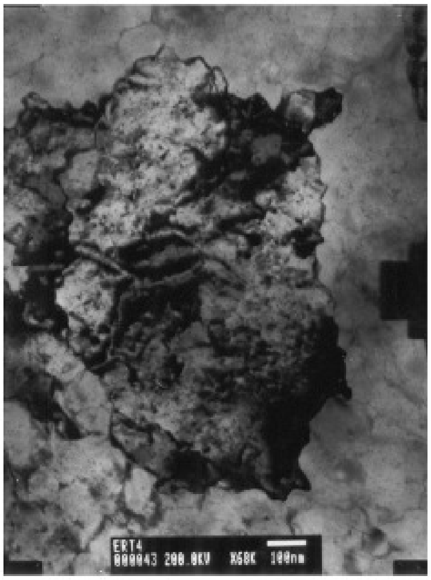


Fig.7 TEM of the NiTi thin film sample showing presence of subgrains and a large amount of strain fields (Ho_2000)

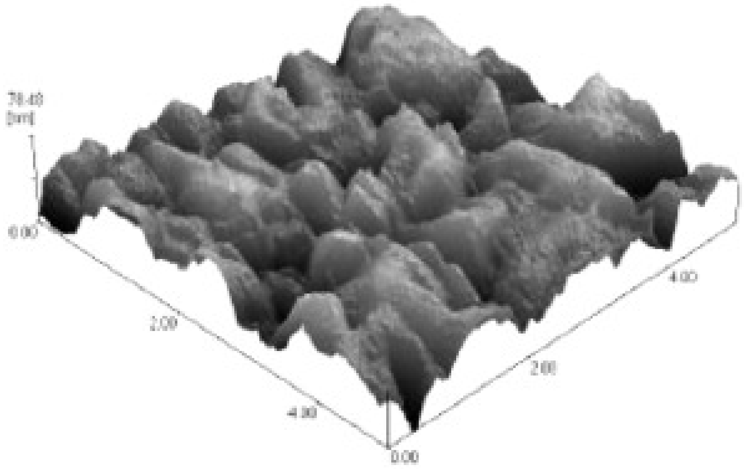


Fig.8 Surface morphology of the deposited NiTi film obtained using AFM (Fu_2001)

2.4 Nano-indentation testing

Indentation of Ti–Ni based films is strongly dependent on the materials resistance to dislocation, and dislocation is closely related to fatigue properties of films. Thus indentation characterization is particularly useful for MEMS applications, where optimization of fatigue performance is critical. Nano-indentation testing with/or without changes of temperature is being used to reveal the different elastic and plastic deformation behaviors of austenite and martensite. Kumar_SCT_2009 (fig.9) investigated the elastic modulus and hardness of thin films to measure the behavior of wear resistance by using a nano-indentation tester with different indentation depths from 100 to 400 nm.

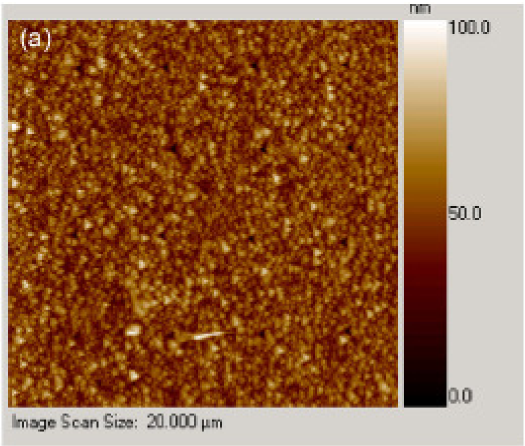


Fig.9 Surface topographical in situ images taken over 20µm × 20µm using AFM in conjunction with nanoindenter for NiTi thin film (Kumar_SCT_2009)

2.5 Rutherford Back Scattering (RBS) spectroscopy:

RBS can give composition through the thickness of a film if the film is sufficiently thin, such that the RBS signal penetrates through the film and detects the substrate reference <1μm (Ho_2000).

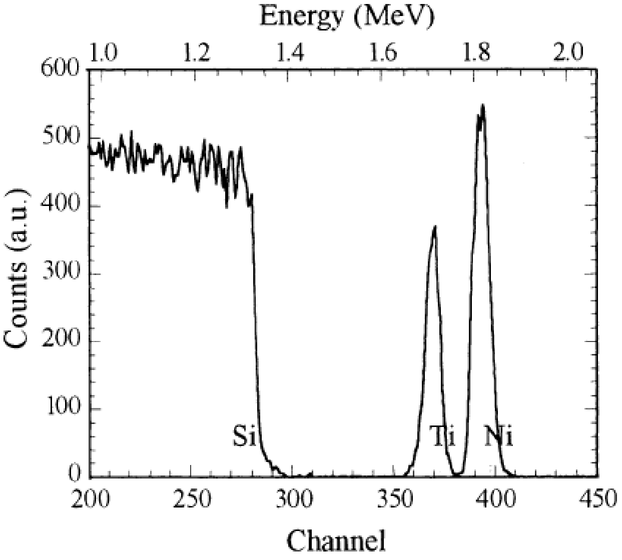


Fig.10 Typical RBS spectrum of Ti Ni thin films (2.4 MeV He^+ on a 40-nm thick film) (Surbled_2001)

2.6 Film thickness measurement:

Film thickness is measured by mechanical surface profile analyzer (Isalgue_1999, Huang_2003).

2.7 Thermal straining of thin films

In contrast to on-chip test structures, wafer curvature experiments of thin films on substrates provide stress–strain data by using the differences in thermal expansion coefficients between the film and substrate material. The biaxial film stress σ is calculated based on Stoney's equation:

$$\sigma = \frac{Mt^2}{6h}K$$

The curvature, K, of the film/substrate system, film thickness, h, and substrate thickness, t, must be measured and the biaxial modulus M of the substrate (with M = E/(1 _ ν); E: Young's modulus, ν: Poisson's ratio) must be known (Dehm_2009).

2.8 Mechanical testing:

Thin film samples are difficult to handle and align in general mechanical testing machines. To overcome this problem, sample positioning is either done by lithographic techniques, such as for micro-electromechanical systems (MEMS), or by taking advantage of the resolution of light optical or electron microscopes. Tensile testing of freestanding films is usually performed by using micromechanical testing equipments (Fig.11, Dehm_2009) with facility to measure the transformation strain/shape memory force at different temperature (Legrange_2004, Rumpf_2006, Gupta_2002).

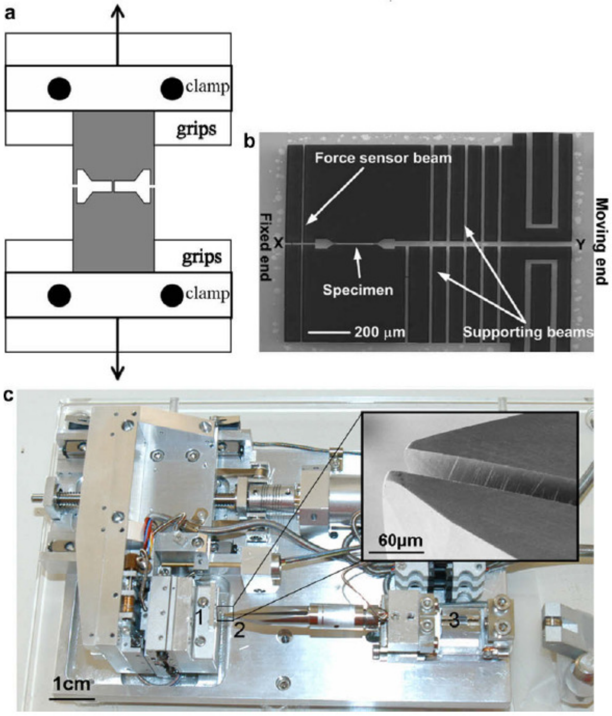


Fig.11 (a) Schematic of a tensile sample made by lithography techniques consisting of a several hundred microns long freestanding metal film on an mm-sized Si support. The Si support can be attached to a tensile apparatus and after cutting the Si frame the free-standing metal film can bet strained (b) Micro-tensile testing chip for in situ experiments in electron microscopes. From Ref.(Haque/Dehm_2009). (c) Photograph of a commercial micro-tensile stage for use in a SEM. The sample is mounted on a piezo-driven stage (1), clamped by a tweezers (2, see also inset for magnified view on the tip of the tweezers), and load measured by a pre-strained wire (3) connected with the tweezers. For details see Ref. (Yang/Dehm_2009)

Section 3 Current Research

This section gives information about the current research being done to study the effect of processing parameters variation on the microstructure and mechanical properties of TiNi thin film. Roughly the research can be grouped in following three areas: Fabrication, deformation behavior and modeling of thermo-mechanical behavior of TiNi thin films

3.1 Fabrication of TiNi thin film

Ni–Ti films are quite sensitive to diverse process conditions like target power, gas pressure, target/substrate distance, deposition temperature, substrate bias voltage as well as inherent characteristics of thin film like passivation layer, contamination, thermo-mechanical treatment, annealing and aging processes, etc.(Martins_2009). Sputtering parameters interactively affects the composition and thereby pseudo-elasticity of TiNi thin films. Some of the important governing parameters are discussed here.

Table 5 some TiNi thin film sputtering research from literature

Author	**Lehnert_2000**	**Ho_2000**	**Surbled_2001**	**Martins_2005**	**Kumar_2009**
Process	Magnetron	Ultra high vacuum	Magnetron	Magnetron	Magnetron
Substrate	Si	Si	Si	Si	Si
Target	Separate pure Ni & Ti	NiTi	NiTi & Ti mesh	NiTi & Ti	Separate pure Ni & Ti
Presputtering time(min)	10	------	30	15	5
Specific	substrate moved near Ni & Ti alternatively			No bias voltage	
Temperature Conditions (K)	Substrate below 350 K	Various conditions	Ambient substrate temp.	Substrate 723 K	623,723, 823 & 923 K
Target/substrate distance (mm)	--	40	40	100 angled 30^0	50 angled 45^0
Deposition rate(nm/min)	---	225	-------	6	
Annealing temp (K)	973-1073, 30 min	773, 10 min	973-1373, 15 min	------	
Base pressure	5E-5 Pa	5E-8 Torr	8E-5 Pa	2E-5 Pa	1E-7 Torr
Gas pressure	0.13 Pa	2 m Torr	0.4 Pa	0.42 Pa	

3.1.1 Effect of substrate on the film growth

Substrate properties such as (material, temperature, microstructure, surface conditions) play an important role in deciding the quality of the film.

3.1.1.i Material of the substrate

Si is the most popular substrate in depositing TiNi thin film for MEMS applications due to ease of deposition and its presence in microelectronics. TiNi film adheres well to silicon substrate provided it is clean and pre-chemically etched. In addition to Si, glass has been used due to easiness of peeling off the film for free standing applications (Kahn_1998). Substrate selection (Si, Si/SiO2, MgO) affects crystallographic orientation of NiTi thin films (Martins_2008) and thereby pseudoelastic behavior.

3.1.1.ii Surface conditions of the substrate

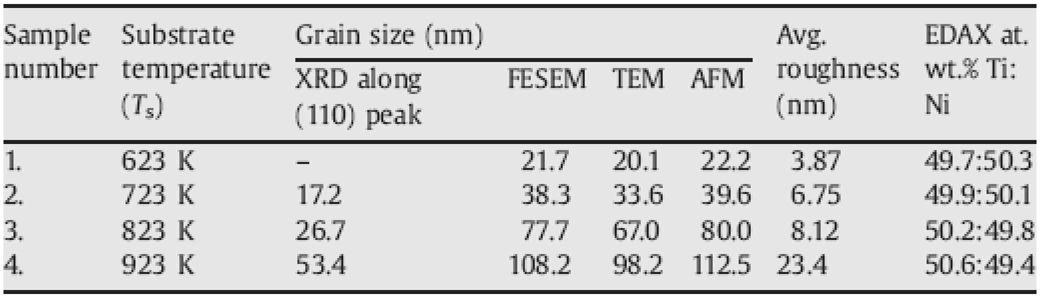
The condition of the deposition surface plays an important role in the growth and final quality of the film. The combined constraining effects from both surface oxide and interfacial diffusion layers in a very thin film will be detrimental to the phase transformations among austenite, R-phase and martensite, giving rise to the degraded phase transformation and shape memory performance (Fu_2006). The trend is to modify surface by treatment or to use coated surface for the deposition. Some of the cases of improving the quality of the film by engineering deposition surface are given here.

In MEMS processes, there is a need for an electrically and thermally insulating or sacrificial layer. Various layers like silicon oxide, TiN, Si_3N_4, pure Au (Martins_2007, Rumpf_2006) are used to build TiNi thin film. Silicon oxide surface offers good adhesion with TiNi and also acts as a barrier layer to prevent any diffusion of TiNi atoms into silicon. Presence of an intermediate layer of Si_3N_4 on naturally oxidized Si enhances the crystallization process of the NiTi sputtered films when compared to the films deposited directly on single-crystal Si (with native oxide) due to possible surface energy minimization (Martins_2007, Martins_2009). TiN layer has also been developed to induce crystallographic orientation and to act as a diffusion barrier (Martins_ 2007). In some cases (Isalgue_1999), a sacrificial layer of Boron nitride is used on Si substrate for the easy detachment of NiTi film. The in situ deposition of hard and adherent nanocrystalline TiN protective coating of 200 nm thickness on NiTi thin films improves the top surface quality of NiTi films while retaining the phase transformation effect (Kumar_JAC_2009). In order to reduce contaminants (principally Ti oxide precipitates) in the film which could adversely affect the SME, very low base pressure in the sputtering chamber is maintained before the admittance of the argon sputtering gas (Kahn_1998).

3.1.1.iii Temperature of the substrate

Substrate temperature influences the thin film fabrication in a large way. Films deposited onto unheated substrates are amorphous as deposited and are usually crystallized by annealing while still under vacuum (Kahn_1998). As shown in table 6 the grain size, avg. roughness and at. Wt. % Ti increases with increase in substrate temperature (Kumar_SCT_2009). Martensitic phase is observed in the microstructure due to higher temperatures of substrate during deposition as shown in figure 12. Ho (Ho_2000) observed that deposition of samples on a hot substrate while keeping the target cold results into precipitate growth.

Table 6: Various parameters of NiTi thin film deposited at different substrate temperature



Sample number	Substrate temperature (T_s)	Grain size (nm)				Avg. roughness (nm)	EDAX at. wt.% Ti: Ni
		XRD along (110) peak	FESEM	TEM	AFM		
1.	623 K	–	21.7	20.1	22.2	3.87	49.7:50.3
2.	723 K	17.2	38.3	33.6	39.6	6.75	49.9:50.1
3.	823 K	26.7	77.7	67.0	80.0	8.12	50.2:49.8
4.	923 K	53.4	108.2	98.2	112.5	23.4	50.6:49.4

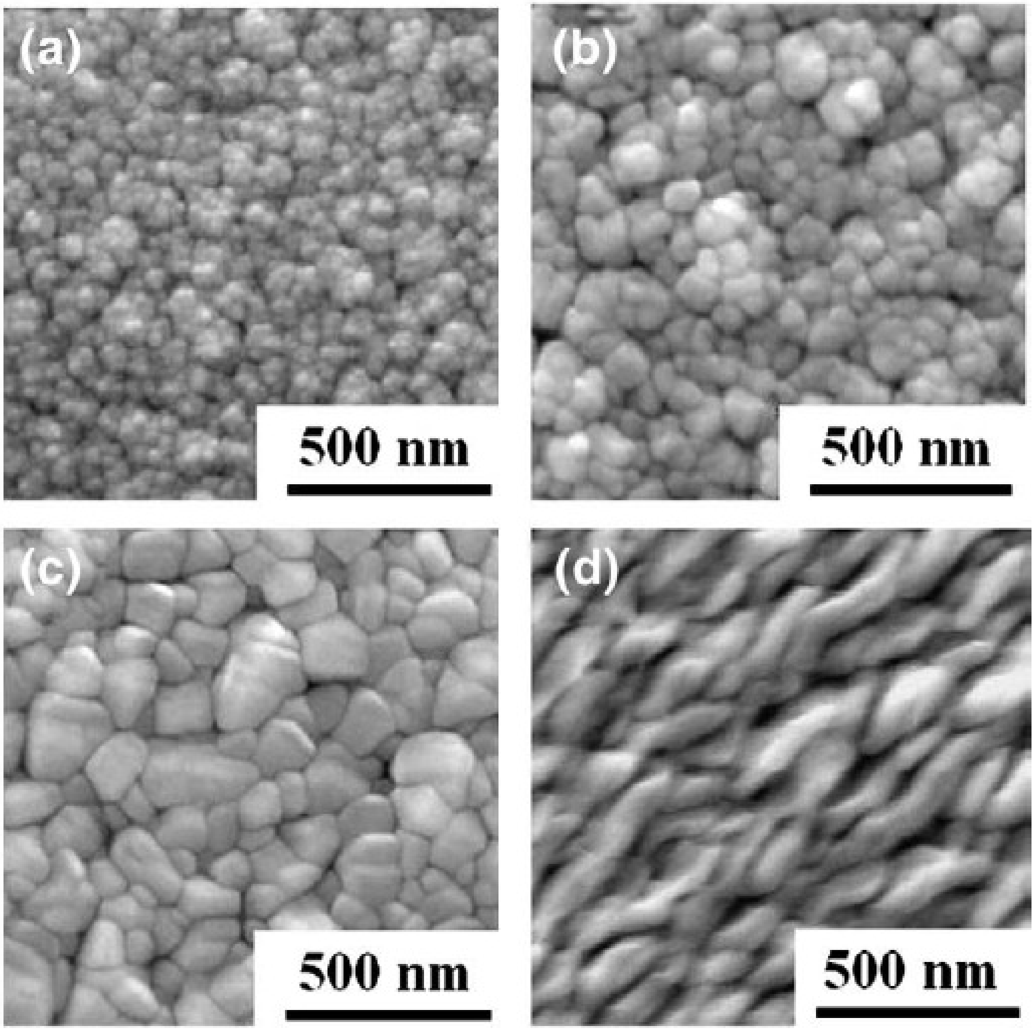


Fig.12 FESEM images of NiTI thin film with substrate temperature (a) 623 K (b) 723 K (c) 823 K (d) 923 K(Kumar_SCT_2009)

3.1.2 Effect of target material on the deposition of TiNi thin film

The shape memory effect in TiNi film is only evident with Ni and Ti ratio within narrow region. The working temperature range for TiNi thin film is even tighter (Fernandez_2002). The reason for this compositional sensitivity lies in the narrow intermetallic region on the Ni–Ti phase diagram (Fig.13, Murray/Kahn_1998, Okamoto_1996). Therefore, it is in practice to select the target material of predetermined composition to exhibit shape memory effect. However it is found that it is difficult to get the composition of TiNi thin film same as of the target material; specifically, the films are Ti poor with respect to the target (by ~2–4 percent).

Few reasons (Kahn_1998, Ho_2000 and Fernandes_2002) are mentioned:

1. Difference in the sputtering rates of the two elements from an alloy target;
2. Difference in re-sputtering rates from the substrate and capture by reactive contaminants;
3. Change in the target geometry due to wear resulting into the change in the sputtering profile and ejection angle, consequently composition change

It has been shown that the polar angular distribution of Ti is wider than that of Ni during sputtering. This means that the Ti:Ni ratio is larger at low angles from the target surface plane and is smaller at perpendicular from the surface plane. Also, this difference in angular distribution will be more pronounced the further the substrate is from the target. This problem of unequal ratio has been solved by putting additional pieces of pure Ti onto the target (Miyazaki_1994, Wolf_1995, Gyobu_1996), by using Ti-rich target (Quandt_2001), or by using a multigun co-sputtering system (Krulevitch_1996). Control of composition is also achieved by measuring peak intensity ratio of NiTi in plasma. The composition of NiTi can be controlled by maintaining the product *Pd* (*P* gas pressure and *d* substrate–target distance) (Bendahan_1995, Isalgue_1999, Fu_2004).

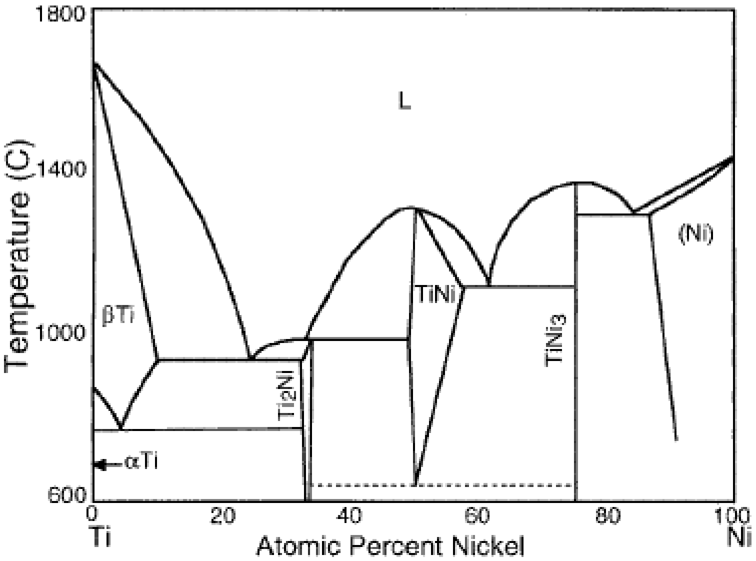
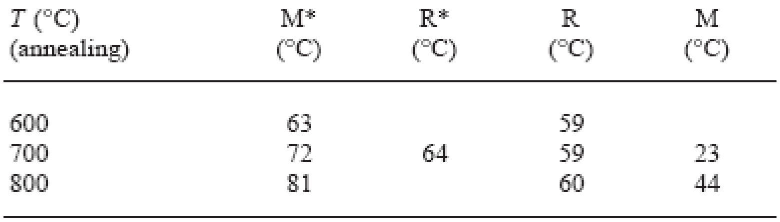


Fig.13. Titanium–nickel binary equilibrium phase diagram: Equiatomic TiNi could exist in equilibrium below 630^0C in a very narrow composition region (Murray/Kahn_1998)

3.1.3 Effect of annealing on the transformation temperature of TiNi thin film

Thin films deposited at room temperature are of amorphous nature; hence they are required to be annealed to get into crystalline shape memory form. Annealing temperature, above which the crystallized film shows shape memory effect, depends on the composition of the film (Isalgue_1999 and Surbled_2001). Ni-rich films and Ti rich films show different response to the same annealing temperatures (Kahn_1998). However by doing annealing and post annealing processes, there is a hug risk of creating damages to microstructure, thereby ultimate properties of TiNi thin films. The shift of transformation temperatures is attributed to a modification in the matrix composition and/or microstructure of the films after annealing at different temperatures. Annealing also leads to grain growth and precipitation which subsequently influences phase transformation (Lehnert_2000). It is seen that higher temperature annealing increases the transformation temperature, suppresses R-phase formation and increases precipitation (Surbled_2001, Kahn_1998). Ramirez_2006 examined the microstructural development of thin film NiTi during the annealing process and provided a correlation between annealing temperature and average grain size. Ramirez_2006 also pointed that slight increase in annealing temperature for the crystallization of NiTi thin films results into drastically lower crystallization time. The films produced from multiple Ni and Ti separate layers shows similar transformation behavior due to annealing as that of regularly developed films (Lehnert_2000). In addition the films produced by this method shows two way shape memory effect as compared to one way shape memory effect by other techniques.

Table 7 Phase transformation temperatures as a function of annealing temperatures by (Lehnert_2000)



T (°C) (annealing)	M* (°C)	R* (°C)	R (°C)	M (°C)
600	63		59	
700	72	64	59	23
800	81		60	44

M*, R* are the peaks during heating

Table 8 inter-relation between annealing and microstructure

Annealing Process	**Initial parameters**	**Affecting microstructure**	**Final properties**
Annealing temp, rate of heating	Initial composition (Equiatomic, Ti rich or Ni rich)	Composition, Transformation temperature	One way shape memory effect
		Phases (R-phase, especially)	Two way shape memory affect
			Pseudoelastic behavior
	Single layered or multi layered	Crystallization	
		Grain growth	
		Precipitation	

3.2 Deformation of TiNi thin films

The plastic deformation in ordinary metal happens via dislocation movement on the application of sufficient load. In case of TiNi Shape memory alloys, the application of load in addition to cause dislocation movement, results into changing the stable austenite phase into martensite via rearrangement of atoms to accommodate the stress. Under microstructural and operating conditions, applied load can convert whole material into martensitic (soft) phase and the material shows ductile mechanical behavior upon further loading. NiTi when used as thin films show similar deformation behavior in addition to characteristic deformation features of thin solid films.

3.2.1 Thermomechanical behavior of TiNi thin films

The behavior of TiNi thin films under tensile testing depends on various factors: microstructure, composition, operating conditions (temperature, load) etc.(Legrange_2004). In principle, the mechanical behavior of the film can be deducted from the phase of the film and temperature at the start of the loading. Typical mechanical behavior of the film in martensitic phase can be seen in fig.14 (a) from (Rumpf_2006).

The film when deformed in martensite phase for a certain strain, can recover some strain upon unloading. When the material in austenitic phase is loaded there can be generation of stress induced martensite. This can be seen in next fig.14 (b) where full recovery of the strain with closed loop hysteresis shows superelastic behavior of the material. This elastic recovery behavior on account of stress induced martensite transformation depends on temperature, amount strain and the phase at the time unloading. Rumpf showed in figure 14(c) that this particular behavior of superelasticity continues till certain temperature which is also dependent on the phase of the film and strain rate. The superelasticity also depends on amount optimum stress, below which it is possible to get some or full strain recovered. If applied stress is higher than this optimum value, it will induce permanent plastic deformation of the martensite via slip-dislocation motion, and the hysteric profile will not be closed looped. There is, thus, a limiting stress to avoid plastic deformation of martensite and to get a limited amount of recoverable strain. The maximum recoverable strains reported for TiNi films range from 2.6 to 6% for recovery forces of 117 to 600 MPa (Kahn_1998). NiTi thin film in pure austenitic state shows typical stress–strain behavior of typical metallic material in fig.14(d). It is also found that R-phase produces lesser volume change, hence has less force to apply in case of MEMS applications.

3.2.2 Stresses in NiTi thin films

Stresses in the TiNi thin film can be divided into three components: thermal, transformation and intrinsic stresses. The thermal stress is originated from the difference in the coefficient of thermal expansion (CTE) between NiTi films and the substrate. The intrinsic stress critically depends on mismatch between film and substrate, deposition rate, substrate temperature, working gas pressure, and impurities level, etc.. Transformation stress is the stress exhibited by the film during transformation. The thermal and intrinsic stress can be classified as residual stresses. Lower residual stress is required to prevent unwanted deformation of MEMS structure while high recovery stress is desirable for the intended deformation. In order to minimize the residual stress in TiNi films, it is necessary to: (1) precisely control the Ti/Ni ratio; (2) deposit films at a possible lower pressure; (3) select a suitable deposition temperature or annealing temperature, with a compromise between thermal stress and intrinsic stress; (4) use some interlayers (with possible compressive stress) to reduce large tensile stress in some TiNi films; (5) perform post-annealing, ion beam post-modification, or in-situ ion beam modification during sputtering in order to reduce intrinsic stress, (6) select suitable substrate to reduce thermal stress.

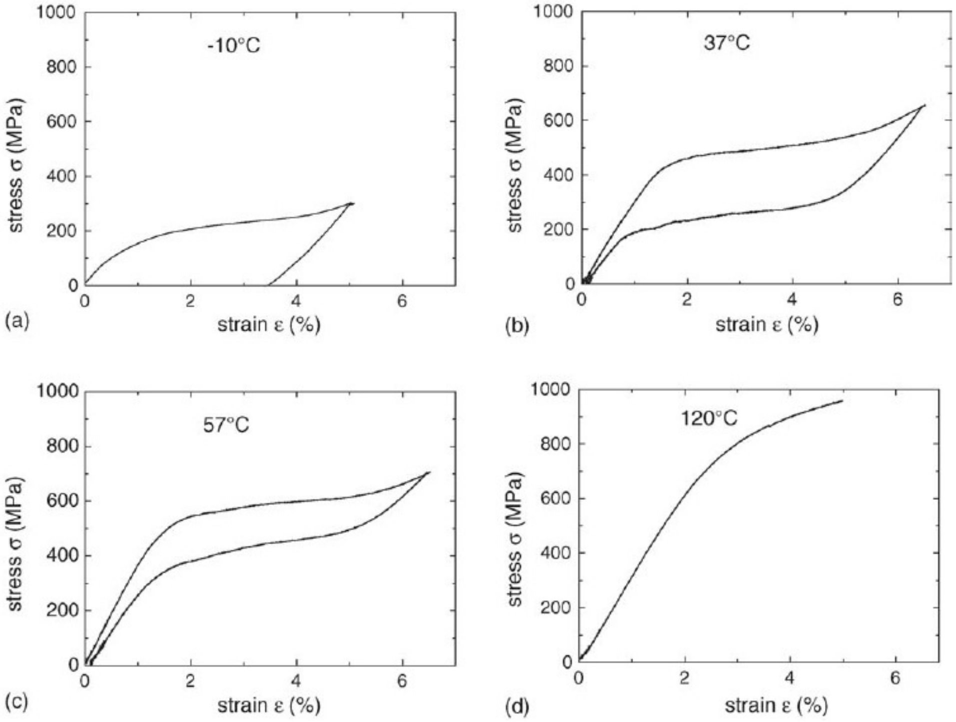


Fig.14. Stress–strain diagrams for tensile testing experiments of sputtered thin films at different temperatures (a–d) (Rumpf_2006)

3.2.3 Effect of film thickness on the stresses in TiNi thin films

The thickness of the NiTi thin film affects the stresses and consequently, pseudo elasticity (Fu_2006). As shown in figure 15, the recovery stress increases and residual stress decreases with the increase in film thickness. As the thickness increases, grains become bigger resulting into higher recovery stresses by allowing martensitic transformation while relieving thermal and intrinsic stresses (Martins_2008). Film thickness also affects transformation temperatures and shape memory effect. Shape memory behavior is observed within certain thickness range and is optimum (highest recovery stresses and strain rate) for a value of thickness depending on its composition (Martins_2008, Fu_2006). In general, as thickness increases, the transformation shifts to slightly higher temperature. Yang (Yang_1995) found that the decrease in film thickness leads to the increase in precipitation due to lesser requirement of activation energy. Compositional variation through the film thickness by gradually heating the target leads two way shape memory effect (Ho_2000).

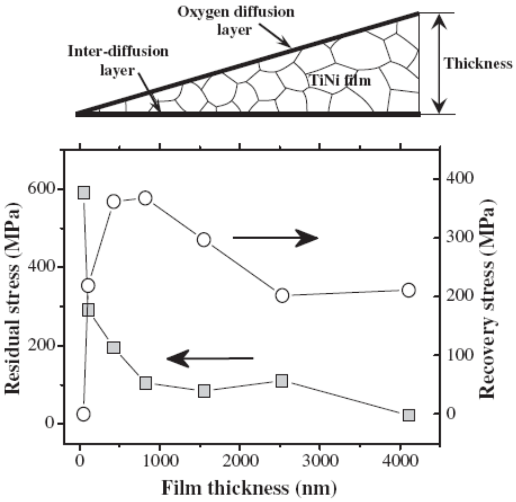


Fig. 15 Residual stress and recovery stress for films with different thicknesses (Fu_2006)

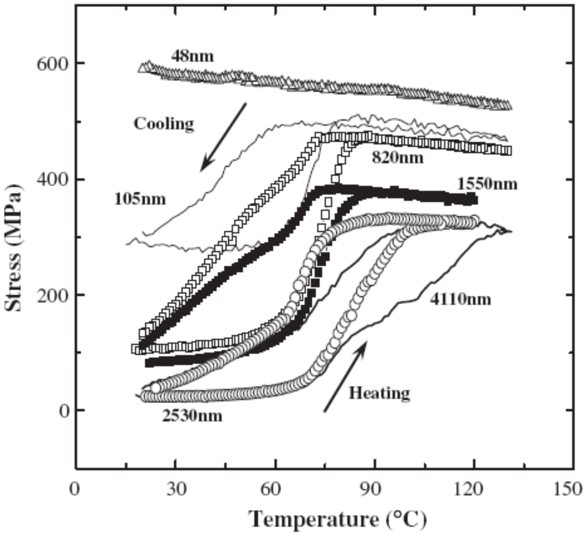


Fig. 16 Stress-temp evolution curves for the TiNi films with different thicknesses (Fu_2006)

Table 9: Film thickness: parameters affecting and parameters affected

	Affected by	Affects
		Transformation temperature
		Pseudoelasticity
Film thickness	Deposition rate	Recovery Stress and strain rate
	Substrate conditions	Grain and grain boundaries

3.2.4 Effect of grain size on the deformation of NiTi thin films

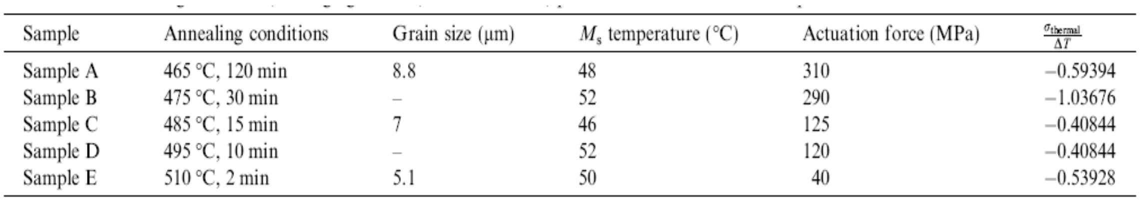
Grain size affects the mechanical behavior of the NiTi thin films by phase transformation and by slip planes as like in ordinary polycrystalline metals. In general, smaller grain sizes leads to the better mechanical properties by hindering dislocation movement. However, smaller grain size suppresses martensitic transformation because of number of grain boundaries impeding phase transformation. Hence, for a smaller grain size, the loading of stable austenite microstructure leads to R-phase transformation than martensite. Hence, such materials with R-phase shows smaller displacement as compared to martensite phased material (Legrange_2004, Lee_2009).

Table 9 Grain size: parameters affected by and parameters affecting grain size

	Affected by	Affects
	Deposition parameters	Mechanical properties
Grain size	Annealing (Crystallization) temp, time	Phase transformation
	Composition, phase transformation	Actuation force

However as there are other parameters like temperature and stress which plays an important role in deformation, it is seen in some cases that smaller grain size is associated with acceptable shape memory behavior and upgraded mechanical properties(Rumpf_2006). In fact, Otsuka (Otsuka_1998) notes that reduction in grain size improves the pesudoelasticity. In recent work it is shown that grain size depends on the phase transformation. (Kumar_SCT_2009). Table 10 shows interrelation between grain size and other variable for actuation force.

Table 10: The annealing conditions, average grain size, actuation force, phase-transformation start temperature and thermal stress rate (Kumar_SCT_2009).



Sample	Annealing conditions	Grain size (μm)	M_s temperature (°C)	Actuation force (MPa)	$\frac{\sigma_{\text{thermal}}}{\Delta T}$
Sample A	465 °C, 120 min	8.8	48	310	−0.59394
Sample B	475 °C, 30 min	–	52	290	−1.03676
Sample C	485 °C, 15 min	7	46	125	−0.40844
Sample D	495 °C, 10 min	–	52	120	−0.40844
Sample E	510 °C, 2 min	5.1	50	40	−0.53928

3.2.5 Fatigue in TiNi films

Fatigue of TiNi films is referred to the non-durability and deterioration of the shape memory effect after millions of cycles. The repeated phase changes will alter the microstructure and hysteresis of the transformation and in turn will lead to changes in transformation temperatures, transformation stresses and strains. For freestanding films, there are some studies using tensile tests to characterize the fatigue problems. Results indicated that there need tens of cycles before the stability of shape memory effects. Prolonged cycling reduces the recovery stress of constrained TiNi thin film which is believed to result from the dislocation movement, grain boundary sliding, void formation, or partial de-bonding at the film/substrate interfaces, non-recoverable plastic deformation, changes in stress, etc. (Kahn_1998)

Table 11 Fatigue parameters affected and parameters affecting

	Affected by parameters		Affects	
	Internal	External	Microstructure	Performance
Fatigue	(alloy composition, lattice structure, precipitation, defects, film/substrate interface)	thermo-mechanical treatment, applied maximum stress, stress and strain rate, the amplitude of temperature cycling frequency)	Composition, transformation temperatures	Recovery stresses, recoverable strains

3.3 Modeling the deformation behavior of NiTi thin films

SMA hysteresis models can be roughly categorized as being microscopic, mesoscopic, or macroscopic, depending on which material level they base their method of predicting constitutive behavior. Liang's model (Liang_1993) gives simple explanation of thermomechanical behavior without considering internal variables like internal stress. Massad (Massad_2005) gave the thermo-mechanical model based on free energy principle to explain the shape memory and super-elasticity effect in thin film SMAs. It starts with the construction of a thermoelastic free energy relation for SMAs followed by modeling the evolution of the phase fractions as a function of stress and temperature. It predicts rate-dependent, polycrystalline SMA behavior, and it accommodates heat transfer issues pertinent to thin-films. Bhattacharya (Bhattacharya_2003) developed the theory of deformation of thin film with the calculation of effective energy including the term for interfacial energy. He also discussed the deformation with one variant or one phase and deformation with two variants or two phases. In case of single variant, the only possible deformations of one variant or phase is one where the rotation is constant. In case of multiple variant, it is required to find a line in the plan of the film that is deformed equally by the two variants of martensite. Bhattacharya has given the solutions to the problem of formation of interfaces between martensite and austenite. Bhattacharya also found that each pair of martensite variants is compatible in a cubic to tetragonal and a cubic to orthorhombic transformation.

Section 4 Research Plan

4.1 Motivation

While sputtering is a well understood deposition process, the fabrication of TiNi films suitable for MEMS applications is still complex. Due to the lack of full understanding of properties of thin film SMAs together with the controlling of the deposition parameters, they have not received as much attention in the MEMS technology as other micro-actuator technologies.

4.2 Thesis description

This research will be spread over for four years and possibly end up with a thesis for an academic PhD degree awarded to the researcher. We have discussed all the important background information for this research, so we now state the research goal.

4.2.1 Research Goal

Research goal of this research is to develop the NiTi thin film via sputtering process and mechanically test it for the intended application in microelectromechanical systems (MEMS). In the course realizing this goal, it is expected to understand the scientific reasons behind the pseudoelastic deformation behavior of the NiTi as a thin film. Because the main goal of the research is very broad, we will split it into several sub goals which can be met by answering the related research questions.

4.2.1.i SubGoal One: Fabrication of NiTi SMA thin film

Research will include fabrication of TiNi thin film on a sputter deposition system at TU Delft. Effect of variation of parameters (Substrate, target, sputtering gas, bias voltage, post-sputtering treatment) on the microstructure of the film will be systematically studied. The research will be focused on arranging the interrelated dependence of various parameters to get the final microstructure of desirable transformation characteristics. It is desirable to find two or three combination of parameters to optimize the sputtering conditions. The transformation behavior and crystallanity of NiTi thin films will be studied via X-RD, DSC. Microstructure will be analyzed for phase transformation and grain growth by characterization techniques like SEM, TEM and AFM with nano-indentation testing. Mechanical spectroscopy (Internal friction) is an excellent choice to study defects and phase transformation in TiNi thin films. TU delft has a mechanical spectrometer at Reactor Institute (RI) and it has been used for study transformation behavior in NiTi sheets of 0.5 mm thickness. It is also possible to check if it can be used for TiNi thin films.

4.2.1.ii SubGoal two: Micromechanical testing of thin film

In this research stage, we will investigate the connection between the microstructure and the mechanical properties of NiTi thin films. A better understanding of such a relationship will illuminate the conditions for optimizing properties and enable improved fabrication methods for more reliable MEMS devices. Stresses in the film affect the thermo-mechanical behavior and lifetime of fabricated devices but also can cause the unwanted deformation of the deposited films. Thus, it is important to investigate the stress in the deposited NiTi film in order to optimize and control its performance. To correctly evaluate the shape memory effects and mechanical properties of the constrained thin films on substrates, curvature and electrical resistivity (ER) measurements will be used. Some new methods based on MEMS testing cantilever bending or damping (internal friction) are more appropriate for micro-actuator applications, which are compatible with small dimensions and high sensitivities. An important part of the research is the micro-mechanical testing of SMA TiNi thin film inside the SEM at TU Delft. With the in situ micromechanical testing, the progress of phase transformations and pseudoelastic behavior of TiNi thin films on the application of temperature and load will be studied. Some of the points which needs attention in relating microstructure and mechanical properties of TiNi thin films are

1. Interface between (substrate and film) to understand film properties
2. Effect of annealing conditions on the deformation behavior of TiNi thin films
3. Grain size effect on the TiNi transformation and thereby pseudoelasticity, formation of film texture and its control, and the effects on shape memory effect
4. Study of internal and external stress on the arrangement of martensite variants, stress induced martensite and its shape memory phenomenon, etc.

5. Effect of precipitation, point defects and dislocation on the mechanical properties of the film
6. Stress evaluation studies of TiNi thin films to various modes of deformation (bending, stretching, twisting)
7. Effect of film thickness effect on pseudo-elasticity (Shape induced martensite, recovery stresses), deformability
8. Transformation fatigue

4.2.1.iii Subgoal three: Modeling of thin film deformation behavior

Depending on the analysis of the data observed in testing of NiTi thin films, a model would be proposed to describe deformation behavior of thin NiTi films for desired thermo-mechanical conditions. Modeling and simulation of thermal behavior of TiNi films and an optimized design for TiNi MEMS actuators are necessary outcomes of this part of the research for possible use of NiTi thin films for MEMS applications.

4.2.3 Schedule

For now we have the following global schedule in mind, which needs to be refined during meetings with the supervisors.

Date	Phase	Description
01-09-2009 - 01-01-2010	1	Read literature and discuss the possibilities
01-01-2010 - 31-03-2010	2	Start first deposition and characterization expt. TU Delft.
01-04-2010 - 31-08-2010	3	Develop optimum processing parameters
01-08-2010 - 31-12-2010	4	First conference/writing of maiden manuscript
01-01-2011 - 31-03-2011	5	Deposition and further characterization expt. TU Delft.
01-04-2011 - 31-08-2011	6	Result/analysis of characterization techniques
01-08-2011 - 31-12-2011	7	Second manuscript/second conference
01-01-2012 - 31-03-2012	8	Modeling based on experimental observations.
01-04-2012 - 31-08-2012	9	Literature review complete/modeling results
01-08-2012 - 31-12-2012	10	Third manuscript on the modeling of SMA behavior
01-01-2013 - 31-03-2013	12	Write thesis report and supportive experiments
01-04-2013 - 31-08-2013	13	Corrections, Submission and Presentation of thesis report

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