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SURFACE METROLOGY AND OPTICAL PROPERTIES OF THIN FILM SHAPE MEMORY ALLOYS

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
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Acknowledgment

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Abstract

Shape memory alloys (SMA) have many interesting characteristics induced by the phase transformation upon thermal cycling or mechanical loading/unloading. In recent years, with the development of Micro-Electro-Mechanical-System (MEMS), NiTi SMA thin films have received more attention due to their high work output per unit volume, good biocompatibility and durability. These properties enable NiTi SMA thin films to be widely considered as a good candidate for powerful microactuators. Upon the austenite $\rightarrow$ twined martensite transformation, the significant surface morphology change (i.e. surface relief) reveals another potential feature for optical micro-devices.

In this project, the optical properties of NiTi based SMA thin films for possible optical MEMS applications are investigated. NiTi and NiTiCu thin films with different compositions are prepared and characterized. A temperature controlled atomic force microscopy (AFM) is used to measure the surface roughness during the phase transformation. Thermally induced reversible trenches are found in both NiTi and NiTiCu thin films, which are identified as the result of the elastic buckling in the top surface oxidation layer. With the existence of these reversible trenches, surface morphology of these thin films changes significantly upon thermal cycling.

Furthermore, optical properties of the thin films are characterized by means of polarization and reflection studies. Two contributors for reflection change, namely surface roughness and refractive index, are quantitatively investigated and

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separated. It is proved that the transition temperature of SMA thin films can be determined from the reflection vs. temperature relationship in a thermal cycle.

A good understanding of the NiTi/NiTiCu optical performance is achieved. It is concluded that the existence of reversible trenches can greatly enhance the potential applications of thin film SMAs in micro optical devices.

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Chapter 1 Introduction

1.1 Background

“Shape Memory Alloys” (SMAs) is a group of metallic materials which have the ability to return to a previously defined shape or size after an appropriate thermo-mechanical training procedure. Generally, these materials can be plastically deformed at a relatively low temperature. Upon heating to a high temperature, usually called the austenite finish temperature (A_f), they will return to their shape prior to the deformation. This phenomenon is well known as the shape memory effect (SME) (Figure 1-1(a)). On the other hand at a temperature above A_f , after a large deformation, the SMA can fully recover its original shape upon unloading. This is called pseudo-elasticity (PE) or super-elasticity (SE) (Figure 1-1(b)) (Fremond and Miyazaki 1996, Hodgson et al¹).

1.1.1 Fundamentals of SMA

The SME was first found in an Au-47.5at%Cd alloy by Chang and Read, and then in In-Tl alloy in 1953 (Otsuka and Wayman 1998). However, the possibility of using SME in actual applications was realized after the SME was found in a NiTi alloy in 1963. Although a relatively wide variety of alloys are known to exhibit the SME, only those that can recover substantial amounts of strain or generate significant stress upon changing shape are essentially of commercial interest. To date, this has been

¹ <http://www.sma-inc.com/information.html>

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identified in some NiTi and NiTi based alloys and Cu-base alloys, such as, CuZnAl and CuAlNi. Table 1-1 lists a few materials with the shape memory phenomenon.

Figure 1-1 Typical behaviors of SMAs

It is well known that the SME is related to two kinds of transformations, i.e., the phase transformation and martensite re-orientation. The martensitic transformation and its reverse transformation are a diffusionless structural change in solids, in which atoms move cooperatively, and often accompanied by a large shear-like deformation. The amount of deformation is generally about 20 times more than the elastic deformation. Usually the austenite phase (high temperature phase, hard) is cubic, and the martensite phase (low temperature phase, soft) has a lower symmetry. The difference in free energy between these two phases drives the transformation.

In order to induce the austenite $\Rightarrow$ martensite transformation, the chemical free energy of martensite must be lower than that of austenite. However, since the transformation requires also non-chemical free energy, such as, the transformation

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strain energy, friction energy, etc., the transformation can happen only when the difference between the chemical free energies of these two phases is greater than the necessary non-chemical free energy. Similarly, the transformation from martensite to austenite will occur when the difference between these two energies, with their signs reversed, is sufficiently large. Thus, a distinguishing characteristic of SMAs is hysteresis, i.e., difference is observed between the forward and reverse transformation paths.

Table 1-1 Alloys with shape memory phenomenon (Shimizu and Tadaki 1987).

Alloy	Composition	Transformation temperature range (°C)	Transformation hysteresis range (°C)
Ag-Cd	44/49 at.% Cd	-190 to -50	15
Au-Cd	46.5/50 at.% Cd	30 to 100	15
Cu-Al-Ni	14/14.5 wt.% Al, 3/4.5 wt.% Ni	-140 to 100	35
Cu-Sn	approx. 15 at.% Sn	-120 to 30	
Cu-Zn	38.5/41.5 wt.% Zn	-180 to -10	10
Cu-Zn-X (X= Si,Sn,Al)	a few wt.% of X	-180 to 200	10
In-Ti	18/23 at.% Ti	60 to 100	4
Ni-Al	36/38 at.% Al	-180 to 100	10
Ni-Ti	49/51 at.% Ni	-50 to 110	30
Fe-Pt	approx. 25 at.% Pt	approx.-130	4
Mn-Cu	5/35 at.% Cu	-250 to 180	25
Fe-Mn-Si	32 wt.% Mn, 6 wt.% Si	-200 to 150	100

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In the martensitic transformation, to ensure that the lattice of the two phases matches perfectly on the inter-phase surface, the exact orientation of an austenite crystal depends on the orientation of its neighboring martensite crystals. Upon cooling, even in a single austenite grain, up to 24 martensite variants may be formed. In Nitinol² (NiTi based SMA), there are only 12 variants. These variants are crystallographically equivalent, but they have different orientation and different planes of shearing. Different martensite variants arrange themselves into twinning groups (Figure 1-2) in order to minimize the internal stresses (Christian 1982). All transformations, free from external stress, tend to be self-accommodating since the deformation in any group produces a stress field favoring the formation of some particular variants. Macroscopically there is almost no shape change in the material. Such phase is called twinned martensite (TM) (Wayman and Duerig 1990).

On the other hand, the transformation induced by external stress tends to produce only these variants that have the most favorable orientation to the applied stress, which is the sum of the external stress and the internal stress resulting from the geometrical constraints of inter-phase and grain boundaries (for polycrystals) etc. However, as shown by Patoor et al. (1996), in the case of polycrystals, in order to satisfy the grain boundary constraints, even in a uniaxial tension test several martensite variants groups are found in a grain. These variant groups are different from the twinned martensite produced by external stress-free cooling.

² The word Nitinol was derived by the initial letters of Nickel and Titanium, by its discoverers (Dye 1990) at the Naval Ordnance Laboratory.

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Figure 1-2 Schematic plot of a twinned martensite, where A, B, C and D stands for different twinning groups, and 1, 3, 4, 5 and 6 are different martensite variants (Saburi and Nenno 1982).

As there are up to 24 martensite variants, the conversion from one single-variant martensite into another is possible. Such process is called martensite re-orientation. This transformation is always stress-related and the corresponding recoverable strain is associated with the conversion among those possible variants.

Figure 1-3 Relationship among different phases. (a) Austenite, (b) TM, (c) DM (Hodgson et al, Shape Memory Applications, Inc.).

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As the stress level increases, similar conversions will take place among martensite groups until the entire specimen consists of only those dominant variants. In the martensite, a large macroscopic strain is produced. This process is called detwinning, and the resultant martensite is usually called detwinned martensite (DM). At a certain thermomechanical condition, austenite, TM and DM may exist together. The relation among different phases is schematically illustrated in Figure 1-3.

In the transformation process, the atomic displacement introduces stacking fault that results in relief on the surface of a SMA. A flat surface in the austenite phase becomes rough upon cooling to TM phase without macroscopic shape change, vice versa (Figure 1-4) (Huang et al. 2002, Tabib-Azar et al. 1999, Xiong et al. 2000).

Figure 1-4 Surface of CuAlNi single crystal of different phases.

1.1.2 SMA Applications

There are a wide variety of applications of bulk SMAs by utilizing their unique thermomechanical characteristics, such as, the blood –clot filter developed by Simon

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(Lipscomb and Nokes 1996), cryofit hydraulic couplings by Raychem Corporation (Harrison and Hodgon 1975, Funakubo 1987), circuit board edge connector made by Beta Phase Inc. (Krumme 1987) , etc.

Micro-Electro-Mechanical Systems (MEMS) is an integration of mechanical elements, sensors, actuators, and electronics on a common silicon substrate normally through the utilization of microfabrication technology on a millimeter scale with micrometer resolution. MEMS enable the development of “smart” products by augmenting the computational ability of microelectronics with the perception and control capabilities of microsensors and microactuators. The microsensors gather information from the surrounding environment through measuring a change in mechanical, thermal, biological, chemical, optical and magnetic properties; the microelectronics process the information derived from the sensors and, through some decision-making capability, direct the microactuators to respond by moving, positioning, gripping, cutting, regulating, pumping or filtering, thereby controlling the environment for some desired outcome or purpose.

Now one of the hottest topics for the continued maturation of MEMS technology is the development of suitable microactuators for practical applications. Various types of microactuator devices have been reported in the literature, including microvalves (Jerman 1990, Obnstein et al. 1990, Robertson and Kensall 1994), micropumps (Folta et al. 1992, Rapp et al. 1993, Ahn and Allen 1995), optical switches (Walker et al. 1995), imaging displays (Van Alstyne 1984, Van Kessel et al. 1998), etc. Each of these devices uses one of a variety of integrated actuator mechanisms based on

electrostatic, magnetic, piezoelectric, bimetallic or thermopneumatic phenomena. Among these actuator materials, thin film NiTi SMAs receive more attention due to the larger energy density, high work output per volume, shape memory effect, excellent biocompatibility and durability even at the microscale (Wolf et al. 1995, Benard et al. 1998, Krulevitch et al. 1996).

Details of equations used for evaluating the work out put per volume for each actuator are shown in Table 1-2. Ideal values against cycling frequency (hollow diamonds), represent the energy available for actuation are plotted, in Figure 1-5. Other values (filled diamonds) are based on actual microactuator data (Krulevitch et al. 1996).

Figure 1-5 Work per volume versus cycling frequency for various microactuators (Krulevitch et al. 1996).

According to Figure 1-5, among these microactuators, SMA films can generate the greatest work per volume at a reasonably fast cycling frequency.

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Table 1-2 Work per unit volume for various microactuators (Kruevitch et al 1996).

Actuator Type	W/V (J/m ³)	Equation	Comments
1. NiTi SMA	2.5×10 ⁷	$\sigma \cdot \epsilon$	Max. one-time output: $\sigma = 500\text{MPa}$, $\epsilon = 5\%$
	6.0×10 ⁶		Thousands of cycles: $\sigma = 300\text{MPa}$, $\epsilon = 2\%$
2. Solid-Liquid Phase Change	4.7×10 ⁶	$\frac{1}{3} \left(\frac{\Delta V}{V} \right)^2 k$	k = bulk modulus = 2.2 GPa (H ₂ O) 8% volume change (acetamide)
3. Thermo-pneumatic	1.2×10 ⁶	$\frac{F \cdot \delta}{V}$	Measured values: F = 20N, $\sigma = 50\mu\text{m}$, V = 4mm × 4mm × 50μm
4. Thermal Expansion	4.6×10 ⁵	$\frac{1}{2} \frac{(E_s + E_f)}{2} (\Delta\alpha \cdot \Delta T)^2$	Ideal, nickel on silicon, s = substrate, f = film, $\Delta T = 200^\circ\text{C}$
5. Electro-magnetic	4.0×10 ⁵	$\frac{F \cdot \delta}{V} \quad F = \frac{-M_s^2 \cdot A}{2\mu}$	Ideal, variable reluctance: V = total gap volume, $M_s = 1 \text{ V sec/m}^2$
	2.8×10 ⁴	$\frac{F \cdot \delta}{V}$	Measured values, variable reluctance: F = 0.28mN, $\delta = 250\mu\text{m}$, V = 100 × 100 × 250μm ³ .
	1.6×10 ³	$\frac{T}{V}$	Measured values, external field: Torque = 0.185 nNm, v = 400 × 40 × 7μm ³
6. Electrostatic	1.8×10 ⁵	$\frac{F \cdot \delta}{A \cdot \text{gap}} \quad F = \frac{\epsilon V^2 A}{2\delta^2}$	Ideal: V = 100volts, $\delta = \text{gap} = 0.5\mu\text{m}$
	3.4×10 ³	$\frac{F \cdot \delta}{V}$	Measured values, comb drive: F = 0.2mN (60 volts), v = 2 × 20 × 3000μm ³ (total gap), $\delta = 2\mu\text{m}$
	7.0×10 ²		Measured values, integrated force array: v = device volume, 120 volts
7. Piezo-electric	1.2×10 ⁵	$\frac{1}{2} (d_{33} E)^2 E_f$	Calculated, PZT: $E_f = 60\text{GPa}$ (bulk), $d_{33} = 500$ (bulk), E = 40kv/cm.
	1.8×10 ²		Calculated, ZnO: $E_f = 160\text{GPa}$ (bulk), $d_{33} = 12$ (bulk), E = 40kv/cm
8. Muscle	1.8×10 ⁴	$\frac{1}{2} (\sigma \cdot \epsilon)$	Measured values: $\sigma = 350\text{kPa}$, $\epsilon = 10\%$
9. Micro-bubble	3.4×10 ²	$\frac{F \cdot \delta}{V_b}$	Measured values: bubble diam. = 71μm, F = 0.9μN, $\delta = 71\mu\text{m}$

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Till now, the main usage of SMA in MEMS is to use the SME for large deformation and high recovery force, such as microvalves (Kohl et al. 2000), micropumps (Benard et al. 1998, Makino et al. 2000), and microwrapper (Gill et al. 2001). With the phenomenon of reversible surface morphology change upon the phase transformation, SMA thin films may be used for many interesting optical applications and devices, such as, optical switches and optical attenuators.

1.2 Objectives and Scopes

This project aims to investigate the possibility of using NiTi based thin film SMA for optical MEMS applications. The focus is on their surface and optical properties.

NiTi and NiTiCu thin films with different compositions sputter-deposited atop silicon wafers were studied. All films were characterized. Their surface roughness during the phase transformation was measured using a temperature controlled atomic force microscopy (AFM). The mechanism behind the surface morphology evolution upon thermal cycling was identified. A mathematical model was proposed to investigate the surface topography and reflection angle dispersion.

Subsequently, optical polarization and reflection were investigated for the influence of phase transformation on the optical properties of NiTi and NiTiCu thin films, in order to quantitatively separate the contribution from refractive index and surface morphology.

1.3 Outline of the dissertation

Chapter 2 reviews the technique for thin film deposition and discusses the influential parameters. The traditional methods for characterization of the shape memory behavior are also reviewed. As an approach to measure the surface topography, AFM is introduced. Optical properties of thin films and some optical MEMS applications are presented.

In Chapter 3, the sputter deposition procedure and characteristics of six different types of SMA thin films are presented.

Chapter 4 presents the measurement of surface roughness of SMA thin films by a temperature controlled AFM.

Chapter 5 investigates the mechanism behind the thermally induced reversible trenches in a thermal cycle.

In Chapter 6, optical studies by means of polarization and reflection measurement in the phase transformation of SMA thin films are presented.

Chapter 7 is the conclusions and future work.

Chapter 2 Literature Review

In this chapter, background information is reviewed for a better understanding of the project. First, the techniques for the fabrication of NiTi based SMA thin films are reviewed. Then, the traditional techniques for characterization of the shape memory behaviour are summarized. Subsequently, atomic force microscopy (AFM) as a powerful 3-D surface scanning tool is introduced. The last two sections are about the optical property of thin films and existing optical MEMS applications.

2.1 Fabrication of SMA Thin Films

SMAs have many unique properties which enable them for a variety of applications. Among these currently available SMAs, equiatomic NiTi alloys in bulk or sheet forms are the most widely used. Melting, casting, hot- and cold-working processes are commonly used to fabricate bulk SMAs.

With continuous demands for miniaturization of functional materials in modern technologies, the fabrication of SMA thin films has been intensively investigated and developed in the past decades. Due to the ability to exert strong recovery stress over a large distance, NiTi shape memory thin films turn out to be ideal for microactuators. The first reported work on the integration of NiTi shape memory thin films into the silicon micromachining process is probably the one by Walker et al. (1990). They sputter-deposited NiTi films atop polyimide/gold coated substrates, patterned the NiTi films with a wet chemical etchant containing hydrofluoric and nitric acids,

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removed the polyimide/gold sacrificial layer, and then post-annealed to produce free standing NiTi shape memory thin film springs. At about the same time, Johnson (1991) vacuum-sputter-deposited NiTi shape memory films on heated substrates to fabricate valves which can be cycled at a rate of 20 Hz for more than two million times.

Nowadays, there are several techniques to fabricate SMA films, namely sputtering deposition (Walker et al 1990, Miyazaki and Ishida 1992), pulse laser deposition (Ciabattari et al. 1997, Gu et al. 1998), flash evaporation (Makino et al. 1998), ion beam sputter deposition (Davies and Tsuchiya 1999), and electron beam evaporation (Noh et al. 2000). However, sputter deposition is the main method, yielding the best SMA thin films.

During sputtering, a substrate is placed inside a vacuum chamber with a target of the material to be deposited. A plasma is generated in a passive source gas (i.e. Argon) in the chamber, and the ion bombardment is directed towards the target, causing material to be sputtered off the target and condensed on the chamber walls and the substrate. A strong magnetic field (magnetron), DC or R.F. (radio frequency), can be used to concentrate the plasma near the target to increase the deposition rate.

Sputter-deposited NiTi thin films exhibiting shape memory characteristics were demonstrated by Miyazaki et al. (1992). They found the phase transformation temperatures are strongly affected by film composition, sputtering condition and post-deposition annealing (or “post-annealing”) (Ishida et al. 1993, Ishida et al. 1995,

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Ishida et al. 1996, Miyazaki et al. 1992, Miyazaki et al. 1994, Miyazaki et al. 1995, Miyazaki et al. 1996).

The deposition result is determined by the source and transport factors and together with the conditions of the deposition surface (Donald 1995). There are three major surface factors which determine the deposition behavior, namely the substrate surface condition, the reactivity of the arriving material, and the energy input. In the sputtering process, the factors, such as R.F./DC, Ar gas (as passive source gas) pressure, substrate-target distance, substrate temperature and alloy composition of targets used, affect the quality of the thin films and their characteristics.

The R.F./DC power energy input greatly influences the chemical composition of the resultant thin films in a relationship with the target composition. Because the sputtering yield (number of atoms sputtered per passive plasma gas ion) for Ni is higher than that for Ti, a pure Ti chip is usually used as an additional target to control the alloy content of the sputter-deposited films. In the actual process, these two parameters are strongly influenced by the condition of the sputtering machine.

Transformation temperatures and microstructures of deposited SMA thin films are greatly affected by the sputtering temperature and working gas pressure. If the substrate is not heated, as-sputtered thin films are amorphous and post-sputtering heat treatment is required for crystallization. High temperature sputtering can simplify the process and result in fine-grained structures with good SME (Ishida 2002).

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From previous researches, it is known that most NiTi thin films crystallize at above 600K (327°C) (Patrick et al. 2001). With the increase of annealing temperature, the film becomes more brittle (Ishida et al. 1999) and less reflective, and has a cloudy appearance (Patrick et al. 2001).

The working gas pressure is also an important factor in sputtering process. High gas pressure easily produces a porous columnar structure, resulting in brittleness (Ishida et al. 1993). With low gas pressure, films undergo tensile residual stress, which affects the phase transformation and hysteresis (Ren et al. 2000). High vacuum is needed to avoid oxygen contamination, which leads to brittleness and composition shift. A value of 1×10^{-4} mTorr (1.33×10^{-5} Pa) or better is recommended in pre-sputtering.

Ternary Ti-Ni-Cu alloys have been investigated extensively in order to improve the shape memory and pseudo-elasticity characteristics. Substitution of Cu for Ni affects the transformation behavior and the associated shape memory characteristics in many aspects. As a candidate for MEMS, Ni-Ti has limitations of large transformation hysteresis (20 ~ 40K) (Suzuki et al. 1992), and the extreme sensitivity of the transformation temperature to slight changes in composition (Nomura 1993). The addition of copper as substitution for 5 ~ 10at.% Ni is found to narrow the transformation hysteresis (10 ~ 15K), keep transformation temperature less dependent on concentration variations, and lower the martensitic yield strength effectively (Moberly et al. 1990), while change the crystal structure and the

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transformation temperatures of thin films only slightly. In this project, three different NiTiCu thin films are deposited by sputtering with a Cu target.

2.2 Characterization of SMA Thin Films

2.2.1 Chemical Composition

Traditionally X-ray microanalysis is used to investigate the crystal structure and the chemical composition of materials. Electron bombardment is used to generate X-rays which penetrates into a sample. The wavelength and the intensity of the lines in the X-ray spectrum allow us to identify the elements presented, and give an estimation of their concentrations. Computer controlled scanning electron microscopy (SEM) in connection with image processing and energy dispersive x-ray spectrometry (EDX) is commonly used in chemical composition measurement.

The SEM works by scanning a focused beam of high energy electrons across a sample surface. The interaction between the beam and the specimen produces a number of signals including secondary electrons, back scattered electrons and X-rays. The secondary electrons are collected to form the standard image and the back scattered electrons provide an image with atomic number contrast. X-rays are produced by the interaction of the electron beam with atoms in the specimen. These X-rays are characteristic of the elements present and they may be separated out in an energy spectrum to allow the identification of the elemental composition of the specimen. Quantitative analysis may be accurately carried out by using prepared

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standards. The X-rays can also be mapped back to their original position in the sample to provide a map of the distribution of the elements in the sample.

2.2.2 Phase Transformation and Crystal Structure

The martensitic transformation that occurs in SMAs yields thermoelastic martensite which develops from a high-temperature austenite phase with long-range order. The transformation, although a first-order phase change, does not occur at a single temperature but over a range of temperatures that varies depending on the exact alloy system. In order to precisely describe the transformation, several definitions are involved. M_s is where the martensite starts to form upon cooling and M_f is where martensite finishes; A_s marks the start of austenite formation upon heating; while A_f identifies the finish of the transformation to austenite and completion of shape recovery (Figure 2-1). The transformation also exhibits hysteresis, i.e. the transformations upon heating and upon cooling do not overlap (Figure 2-1). This transformation hysteresis also varies from one alloy system to another.

There are several ways to measure the transformation temperatures of SMAs, such as the active A_f (or functional A_f) test, the resistivity change measurement, or the differential scanning calorimetry (DSC).

DSC is a technique for measuring the temperature, direction, and magnitude of thermal transitions in a material sample upon heating and cooling, and comparing the amount of energy required to maintain its rate of temperature increase or decrease with an inert reference material under similar conditions. DSC yields excellent,

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repeatable result on fully annealed samples. But one important drawback of the DSC method is that for partially cold worked materials, such as those used to optimize superelasticity, the result may be poor and inconclusive. This same drawback also may apply to uneven samples that have undergone an uncompleted heat treatment at a low temperature or partially annealed materials.

Figure 2-1 Typical transformation length versus temperature curve of a SMA under a constant load (stress) in a thermal cycle (Hodgson et al, Shape Memory Applications, Inc.).

X-ray diffraction (XRD) analysis can be employed to characterize the crystalline structure of the deposited NiTi thin films.

2.2.3 Curvature and Stress Evolution

Thin films are deposited atop a substrate. The deposition of these films can create residual stress due to thermal mismatch between the film and the underlying

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substrate, and intrinsic stress built up during crystal growth. For SMA thin films deposited atop silicon wafers, monitoring the curvature change upon thermal cycling in the wafer produced by the residual stress in the films is an alternative method to measure the transformation process.

Figure 2-2 Schematic illustration of curvature change in silicon wafer with a single layer of thin film atop.

As schematically shown in Figure 2-2, the evaluation of stress upon thermal cycling can be estimated by measuring the curvature change. The thicknesses of the film and the substrate are named as t and h , respectively. The width of the substrate is b . R is the radius of the curvature of substrate. Since the radius is very large as compared with the thicknesses of the substrate and film, the difference of radius of the film and substrate can be ignored. P is the force. And,

$$P_f = P_s = P \quad (2.1)$$

where the subscribes, “ f ” and “ s ” stand for the film and substrate, respectively. The bending moments generated in the film and substrate about the interface are:

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$$\begin{cases} m_f = P_f \times \frac{t}{2} = P \times \frac{t}{2} \\ m_s = P_s \times \frac{h}{2} = P \times \frac{h}{2} \end{cases} \quad (2.2)$$

On the other hand, since the substrate is much thicker than the thin film, the bending moment can be obtained from the radius as following,

$$m_s = \frac{E_s I_s}{R} \quad (2.3)$$

where $I_s = (bh^3)/12$ is the inertia moment of the substrate, and E_s is the Young's modulus of substrate. Substituting the expression of I_s and Eqn.(2.3) into Eqn.(2.2), results in

$$P = \frac{E_s b h^2}{6R} \quad (2.4)$$

This P is also the force in the thin film. If the biaxial elastic modulus of the substrate is used, the film stress can be obtained as following

$$\sigma = \frac{E h^2}{(1-\nu) 6 R t} \quad (2.5)$$

where $\frac{E}{(1-\nu)}$ is the biaxial elastic modulus of the substrate, h is the substrate thickness, t is the film thickness, R is the substrate radius of curvature, σ is the average film stress.

This equation is suitable for estimation of the nominal stress in SMA thin films. Using the stress-temperature measurement mode, from the change of curvature before and after deposition, we can measure the stress changes as a function of temperature, from which the phase transition can be determined.

2.3 Surface Morphology

2.3.1 Surface Roughness - R_a and R_{ms} (Precision Devices, Inc.¹)

There are many aspects and parameters used to describe or measure a surface. Roughness, which includes the finest (shortest wavelength) irregularities of a surface, is the most important parameter to describe the surface profile in sputter deposited thin films.

R_a , average roughness, is the most commonly used roughness parameter. It is also known as the arithmetic average (AA) and the center line average (CLA), and it is the arithmetical mean deviation of the profile.

Mathematically, R_a is the area between the roughness profile and its mean line, or the integral of the absolute value of the roughness profile height over the evaluation length, i.e., (Figure 2-3)

$$R_a = \frac{1}{L} \int_0^L |r(x)| dx \quad (2.6)$$

When evaluated from digital data, the integral is normally approximated by a trapezoidal rule,

$$R_a = \frac{1}{N} \sum_{n=1}^N |r_n| \quad (2.7)$$

R_a alone cannot describe the surface profile completely. If we want to distinguish between surfaces that differ in shape or spacing, we need additional parameters that measure peaks and valleys and profile shape and spacing.

¹ <http://www.predev.com/smg/index.html>

Figure 2-3 Average roughness (R_a)².

R_{ms} (root-mean-square roughness) is another important parameter to describe the surface roughness. It is calculated from an integral of the surface profile,

$$R_{ms} = \sqrt{\frac{1}{L} \int_0^L r^2(x) dx} \quad (2.8)$$

The digital equivalent normally used is,

$$R_{ms} = \sqrt{\frac{1}{N} \sum_{n=1}^N r_n^2} \quad (2.9)$$

For a pure sine wave of any wavelength and amplitude, R_{ms} is proportional to R_a and about 1.11 times larger.

2.3.2 AFM (atomic force microscope)

For surface roughness measurement, there are two main methods, namely optical interferometry and stylus profiling. Atomic force microscope (AFM) is a miniaturized, rastering stylus profiler, and is widely used in surface measurement (Donald 1995).

² www.predev.com

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The AFM may work by scanning a fine ceramic or semiconductor tip over a surface, very close to the sample. The small probe-sample separation (on the order of the instrument's resolution) makes it possible to take measurements over a small area. The tip is positioned at the end of a cantilever beam shaped much like a diving board. As the tip is repelled by or attracted to the surface, the cantilever beam deflects. AFM operates by measuring attractive or repulsive forces between a tip and the sample (Binnig et al. 1986). The magnitude of the deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever. A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface (Figure 2-4). The AFM can also work with the tip touching the sample (contact mode), or otherwise the tip can tap across the surface (tapping mode) (Albrecht et al. 1991).

Figure 2-4 Schematic of atomic force microscope (University of Toledo³).

AFMs can achieve a resolution of 10 pm. Unlike electron microscopes, they can image samples in either air or liquid. Three types of tips are generally used (Figure 2-5). The "normal tip" (Albrecht et al. 1990) is a 3 μm tall pyramid with ~ 30 nm end

³ <http://www.che.utoledo.edu/nadarajah/webpages/whatsafm.html>

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radius. The electron-beam-deposited (EBD) tip or "supertip" (Keller and Chih-Chung 1992) improves on this with an electron-beam-induced deposit of carbonaceous material made by pointing a normal tip straight into the electron beam of a scanning electron microscope. Especially if the user first contaminates the cantilever with paraffin oil, a supertip will form upon stopping the raster of the electron beam at the apex of the tip for several minutes. The supertip offers a higher aspect ratio. Since it is long and thin, it is good for probing pits and crevices. Finally, Park Scientific Instruments offers the "Ultralever", based on an improved microlithography process. Ultralevers offers a moderately high aspect ratio and up to a ~ 10 nm end radius.

Figure 2-5 Three common types of AFM tips⁴. (a) Normal tip (3 μm tall); (b) supertip; (c) ultralever (3 μm tall).

2.4 Thin Films Optical Property (Heavens 1991, Abeles 1972)

The root-mean-square roughness, R_{ms} , is widely used in optical applications, since it is more directly related to the optical quality of a surface. Scattering loss at a gently sloped surface with a Gaussian distribution of the surface height (mirror like surface),

⁴ [http:// stm2.nrl.navy.mil/how-afm/afm.html](http://stm2.nrl.navy.mil/how-afm/afm.html)

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is related to the surface R_{ms} roughness. The scattered power is expressed as (Beckmann and Spizzichino 1987),

$$\eta = 1 - \exp \left[- \left(\frac{4\pi R_{ms} \cos \theta_i}{\lambda} \right)^2 \right] \quad (2.10)$$

where η is the percentage of the scattering loss, θ_i is the incident angle, and λ is the light wavelength.

In an optical study, the characteristics of a material are determined by measuring how the material samples interact with light. Optical techniques can measure the optical constants of a material, the thickness, and the roughness of a thin film sample. Optical constants determine how light propagates through and reflects from the surface of a material.

Optical studies of metals and alloys can be performed on either thin films or bulk samples. For both states of materials, there are different aspects to address. For the bulk materials, due to absorption, the electromagnetic field is rapidly attenuated. Light probes only a very thin region in the vicinity of the top surface of the sample. Therefore the quality of a surface and of a thin layer in the vicinity is of great importance. Thin films do not suffer from this inconvenience, because they can be deposited atop substrates, which are well polished. Hence the thin films, if not too thick, are as smooth as that of the substrate. The absorption of electro-magnetic waves in a metal is due to both free electrons and bound electrons. In certain regions of the spectrum, one of them may be dominant. The contribution of free electron absorption in films consisting of aggregates will be considerably higher than that in a

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bulk metal, because of the much larger extent of scattering at the particle boundaries. The contribution of the bound electrons changes slightly with the state of aggregation. As observed, silver and aluminum have the maximum absorption over a range of thickness for all wavelengths. Copper and gold films have similar behavior for wavelengths above 550 nm. Films of antimony, nickel, palladium and chromium show only slightly variation of absorption with thickness for visible wavelengths.

The structural perfection of thin films is not the same as that of bulk specimens. The principle defects which are found in thin films are grain boundaries, whereas the thick ones contain mainly dislocations and stacking faults. To have an estimate of the importance of defects in thin films, it is reported that the mean free path at liquid helium temperature is 100 times shorter than that of a pure bulk specimen (Heavens 1991). Only for thick films (1 μm or above) this ratio can be reduced to about 10. However their surface is rougher.

For thin films, there is another problem: inhomogeneity, i.e. the refractive index varies in a direction normal to the film surface. In general, it is assumed that the films are homogeneous except on a very small scale. The theory developed for a film with a constant index has been elaborated to deal with the structural character of evaporated films with the assumption that the properties of the layer next to the substrate are identical to those next to the air (Heavens 1991). It might be reasonable to say that a large difference of this kind does not exist in evaporated films of a single pure material.

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In practice, the preservation of a good surface is difficult. Most of the metals undergo a superficial oxidation at atmospheric pressure even at room temperature. Two solutions are possible, namely, either preventing this oxidation by maintaining the samples in a very high vacuum during the experiments or taking into account the presence of the superficial layer when working under normal conditions. The former is applied in investigations extending into the vacuum ultraviolet region, where the influence of a very thin oxide film (around 1 nm thick) may have a dramatic effect on complex dielectric constant. In the visible and infrared regions, a superficial thin layer has very little influence on the measured optical quantities because it is virtually nonabsorbing since its thickness is so small as compared with the wavelength of the light wave. In the vacuum ultraviolet, the oxide layers are often more absorbing than the underneath metals. As indicated by Beaglehole et al. (1966), for bulk materials, even a 0.5 nm oxide layer can cause error as large as 10% in the reflectance at 100 nm of wavelength.

There are two commonly used optical measurement methods for thin films, namely spectral reflectance and ellipsometry. Spectral reflectance measures the amount of light reflected from a thin film over a range of wavelengths, with the incident light normal (perpendicular) to the sample surface. Ellipsometry is similar, except that it measures reflectance at non-normal incidence and at two different polarizations.

A plane electromagnetic wave traveling in a medium can be represented from Maxwell's equations,

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$$\begin{cases} \text{curl } \vec{E} = -\frac{\partial \vec{B}}{\partial t} \\ \text{curl } \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \\ \text{div } \vec{D} = \rho \\ \text{div } \vec{B} = 0 \end{cases} \quad (2.11)$$

where $\vec{E}$ and $\vec{D}$ are the vectors of the electric-field strength and the dielectric displacement, $\vec{H}$ and $\vec{B}$ are the corresponding magnetic vectors, ρ is the charge density and $\vec{J}$ is the density of the electric current.

As a solution of Maxwell's equations, the equation of propagation of light in an absorbing medium can be presented as,

$$E = E_0 \exp i\omega \left\{ t - \frac{(n - ik)(\lambda x + \mu y + \nu z)}{c} \right\} \quad (2.12)$$

where, n is the refractive index of the absorbing medium and k is the extinction coefficient, also called attenuation index. The light is traveling in the direction (λ, μ, ν) in the absorbing medium. The direction of maximum damping coincides with the direction of propagation.

We consider a plane wave incident on a boundary separating two media (Figure 2-6), at $z=0$. This boundary is infinite in extent so that it may accommodate the necessarily infinitely wide plane wave of unique frequency. The plane of incidence is the plane xOz . The angle of incidence is φ_0 and the angle of refraction is φ_1 . The amplitudes of the electric vectors of the wave approaching the surface are presented by E_{op}^+ and E_{os}^+ for two components. The reflected waves are denoted by E_{op}^- , E_{os}^- and the

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transmitted waves by E_{1p}^+ , E_{1s}^+ . The phase factors associated with the incident and reflected waves are of the form,

$$\begin{cases} \exp i \left(\omega t - \frac{2\pi n_0 x \sin \varphi_0}{\lambda} - \frac{2\pi n_0 z \cos \varphi_0}{\lambda} \right) (\text{incident}) \\ \exp i \left(\omega t - \frac{2\pi n_0 x \sin \varphi_0}{\lambda} + \frac{2\pi n_0 z \cos \varphi_0}{\lambda} \right) (\text{reflected}) \\ \exp i \left(\omega t - \frac{2\pi n_1 x \sin \varphi_1}{\lambda} - \frac{2\pi n_1 z \cos \varphi_1}{\lambda} \right) (\text{transmitted}) \end{cases} \quad (2.13)$$

At the boundary ($z=0$), the point of incidence is the origin of co-ordinates. The components of the electric vectors in the x- and y- directions are obtained as,

$$\begin{cases} E_{0x} = (E_{0p}^+ + E_{0p}^-) \cos \varphi_0 \\ E_{0y} = E_{0s}^+ + E_{0s}^- \\ E_{1x} = E_{1p}^+ \cos \varphi_1 \\ E_{1y} = E_{1s}^+ \end{cases} \quad (2.14)$$

Applying the boundary conditions, the reflectance and transmittance are obtained as,

$$\begin{cases} R_p = \frac{(E_{0p}^-)^2}{(E_{0p}^+)^2} = \left(\frac{n_0 \cos \varphi_1 - (n_1 - ik) \cos \varphi_0}{n_0 \cos \varphi_1 + (n_1 - ik) \cos \varphi_0} \right)^2 \\ R_s = \frac{(E_{0s}^-)^2}{(E_{0s}^+)^2} = \left(\frac{n_0 \cos \varphi_0 - (n_1 - ik) \cos \varphi_1}{n_0 \cos \varphi_0 + (n_1 - ik) \cos \varphi_1} \right)^2 \\ T_p = \frac{(n_1 - ik)(E_{1p}^+)^2}{n_0 (E_{0p}^+)^2} = \frac{(n_1 - ik)}{n_0} \frac{2n_0 \cos \varphi_0}{n_0 \cos \varphi_1 + (n_1 - ik) \cos \varphi_0} \\ T_s = \frac{(n_1 - ik)(E_{1s}^+)^2}{n_0 (E_{0s}^+)^2} = \frac{(n_1 - ik)}{n_0} \frac{2n_0 \cos \varphi_0}{n_0 \cos \varphi_0 + (n_1 - ik) \cos \varphi_1} \end{cases} \quad (2.15)$$

In the case of normal incidence, R_p is equal to R_s . Hence,

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$$R_p = R_s = \frac{(n_0 - n_1)^2 + k_1^2}{(n_0 + n_1)^2 + k_1^2} \quad (2.16)$$

For other incidence, exact expression for the reflectance is cumbersome and approximation is often used.

Figure 2-6 Sketch drawing of light reflected and transmitted at a boundary.

2.5 Optical MEMS

During the phase transformation occurring in the SMA thin films the change in roughness and in electronic configuration would affect the optical properties of the thin film, particularly its transmittance and reflectance. As such we think that it may be possible to build devices that could benefit from this effect, and we will now review a few existing micro-optical devices to decide how this technique could be used.

Micro-Electro-Mechanical Systems (MEMS) is an integration of mechanical elements and electronics on a common (silicon) substrate through micro-fabrication

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technology. Sometime, micro-optics and micromagnetics elements are also integrated into MEMS. Optical MEMS, also called MOEMS for Micro-Opto-Electro-Mechanical Systems⁵. In contrast to conventional optomechanical systems that employ bulk mechanical parts, the micromechanical elements in MOEMS are batch fabricated by micromachining techniques. They are smaller, lighter, faster, and cheaper than their bulk counterparts, and can often be monolithically integrated together with some optical components. An illustration to reveal the concept of MOEMS is in Figure 2-7.

Figure 2-7 MOEMS relation concepts⁶.

MEMS ranges in size from 10s of millimeters to 10s of microns. For MOEMS, small size and ability to integrate movable opto-mechanical parts with microactuators have

⁵ Introduction to the Issue on Microoptoelectromechanical Systems (MOEMS), *IEEE Journal of Selected Topics in Quantum Electronics*, Vol. 5, No.1, pp.2-3, 1999.

⁶ <http://www.darpa.mil/MTO/MOEMS/index.html>

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opened up many new opportunities. A small displacement (or rotation) can produce a large effect in optical systems. Optical techniques and MEMS mutually benefit from each other. The “optical” range of wavelength is taken in its broad sense, from 0.2 μm in the ultraviolet to 12 μm in the far infrared region.

In the last two decades, MOEMS has been quickly developed and changed remarkably. From micromirror arrays and fiber switches to sensors and bio-photonics applications, many MOEMS devices have been realized. In the last few years, with the great commercial interesting in the telecommunications and internet industries, more and more MOEMS devices in fiber-optic communication and switching are produced. These exciting developments also indicate that MEMS fiber switches join the MEMS projection displays as the second commercial success stories of MOEMS technology⁷.

The Digital Micromirror Device (DMDTM) is a showpiece of MOEMS (Hornbeck 1995). It is a culmination of years of development at Texas Instruments. It is an array of mirrors, which are independently addressable and can deflect light through a tri-stable range of motion ($+10^\circ$, 0° , -10°), as indicated in Figure 2-8. These devices can be used in a variety of optical systems. The current commercial applications are for projection devices. The DMD is used as a reflective element in the optical path of a system. A light source is directed onto the DMD while a signal is input to the device. Each individual mirror is placed in a binary mode. The mirrors that are “on” will

⁷ Introduction to the Issue on Microoptoelectromechanical Systems (MOEMS), *IEEE Journal of Selected Topics in Quantum Electronics*, Vol. 5, No.1, pp.2-3, 1999

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reflect the light into the optical path and onto the projection surface. The mirrors in the “off” state will reflect the light into a baffle, and the associated pixel on the projection surface will appear dark.

Figure 2-8 DMD cutaway view showing two mirrors in opposite tilted positions (Texas Instruments).

Six photo-mask layers build a complex, multilayer, aluminum structure. Each pixel in the DMD array is independently addressable by digital signals from the CMOS memory circuit substrate.

Undoubtedly MOEMS will play a significant role in the future of the communications industry. It is clear that fiber optics is a major player. Integrated MEMS switches and lasers for wavelength division multiplexing (WDM) will be a common standard in the future.

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Figure 2-9 Colorized micrograph of a micromirror near the end of an optical fiber (Bishop and Giles 1998).

Fiber switches are classified into two basic categories, namely, on/off switches and $n \times n$ switches. “on/off” switches can block the light that propagates along the fiber. They may be simple in design and manufacture (Figure 2-9). A mechanical shutter, which blocks the light transmitted through a gap between fiber ends, is a good example of a simple on/off switch. A vertical polysilicon surface is coated with gold to form a mirror that is inserted between two closely-spaced optical fibers. With passive assembly, the coupling loss is 16%, while active alignment reduces the loss to 10%. The mirror is on the end of hinged and erected surface, which passes over a pivot to a plate parallel to the substrate. A few volts is adequate for driving the actuation, and only 2 μW of power is required, even for frequent reconfiguration of optical routers containing these MEMS switches.

Devices that switch optical signals from one fiber to another are called “ $n \times n$ ” switches. The 1×2 switch is the simplest. A novel approach to the waveguide coupler

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(Boysel et al. 1993) uses a suspended metal membrane to selectively inhibit one path of the coupler and create a 1×2 switch. Designs that perform $n \times n$ optical switching may involve redirecting the light path or translating the fiber. The most common optical switches are designed so a mirror can be actuated in and out of the light path and act as a switch, such as the cross-bar switch illustrated in Figure 2-10. The translating action of the mirror can be done with a linear actuator that drives the mirror into a desired position. Crossbar switches have been made using deep reactive ion etching (Marxer et al. 1997) and bulk micromaching (Toshiyoshi and Fujita 1996). Scratch drive actuators (Lee et al. 1997) and PZT meander (Riza and Polla 1992) have been implemented as actuators. Another common method for switching a mirror is to mount one edge of the mirror on a torsion spring and electrostatically move it. This method has been realized with both vertical (Lee and Wu 1997) and horizontal (Miyachi et al. 1997) torsion springs, as well as cantilever leaf spring (Mita et al. 1998). These methods achieve a switching time that is suitable for slow speed applications, such as network reconfiguration switching, but is too slow for high-speed multiplexing applications.

Figure 2-10 Cross-bar switch.

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There are also many other designs for fiber switching which involve a variety of geometries and optical components. The idea of microprism arrays (Goring et al. 1996) has been adapted for fiber switching. In this design, a PZT driven microprism is used to redirect light from an input fiber to as many as nine output fibers for a 1×9 fiber switch. This device shows less than 1dB insertion loss and greater than 50 dB isolation between output channels. Thermo-capillary optical switches using total internal reflection (TIR) have also been achieved to switch optical paths in a waveguide structure (Sato et al. 1997).

Optical grating is also widely used in MOEMS. Micro-opto-mechanical gratings are very attractive for implementing WDM switches, as reflection grating is often used to disperse incident light into angular directions determined by the incident light's wavelength and the period of the grating. The MEMS gratings can also be used as light modulators. A display device has been developed as an electronically-controlled light modulator (Solgard 1997).

A grating light valve (GLV) (Gudeman 2002) is made of thin deformable ribbons of silicon or Si_3N_4 and SiO_2 or Nitride. Each pixel is composed of two sets of ribbons. One set is fixed. The interleaved movable set is suspended over an air gap (Figure 2-11). In the on-state, the ribbons form a flat mirror, while in the off-state the suspended ribbons are pulled down by one quarter of a wavelength, as such, a grating is formed. The incident light is diffracted by the grating into the plus and minus first order of the grating.

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Figure 2-11 Sketch drawing of grating light valve (Gudeman 2002).

Variable blaze gratings (VBGs) (Burns and Bright 1997) with adjustable blaze angles are designed as $1 \times N$ multiplexer using MEMS technology. A diffractive grating without any movable mechanical part can be used to produce a diffraction spot pattern for optical interconnection (Hinton 1993).

From the progress made so far, it is clear that optical MEMS has great potential in the future. Commercial production of Digital Mirror Devices by Texas Instruments exceeds ten thousand units annually. Fiber optical crossbar and other switches, especially reconfigurable MEMS devices for wavelength division multiplexing, are poised for large-scale production and widely used in communication networks.

Chapter 3 Sample Preparation and Characterization

3.1 Sample Preparation

Two series of SMA thin films, namely NiTi and NiTiCu, were investigated in the course of this project. They were fabricated with the help from Dr. Y.Q. Fu, in the Micromachines Center, School of Mechanical and Production, Nanyang Technological University.

SMA thin films were sputter deposited atop 4-inch (100) silicon wafers (with a thickness of 0.45 mm) at around 360°C. One 0~600W RF generator and two 0~1 KW precision DC power supplies were used. The RF magnetron power was used for the NiTi alloy target, while the DC power was applied on the Cu/Ti targets. In order to obtain a better composition control, a series of high purity targets (99.99%) were used, namely, 45at.%Ni-Ti, 50at.%Ni-Ti, 40at.%Ni-Ti, pure Ti and pure copper targets.

The base pressure of the main chamber was 10^{-4} mTorr (1.33×10^{-5} Pa) before deposition. Other basic parameters in the sputtering process are summarized as follows,

- Distance between target and wafer is 100 mm;
- Deposition time > 10 hours;
- Ar gas pressure is 2.3 mTorr (0.3 Pa).

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The NiTi thin films were deposited with a 45at.%Ni-Ti target and a pure Ti target. The NiTiCu series were deposited with a Ni-Ti target of different composition and a pure copper target. For one sample, Ni_{45.2}Ti_{50.3}Cu_{4.5}, after the curvature measurement, one hour post annealing was performed at 440°C. Table 3-1 lists the deposition parameters of all thin films for easy reference.

Table 3-1 Parameters for deposition of NiTi and NiTiCu thin films.

Sample (thin film)	Target Power			Temp. (°C)	Post- annealing
	NiTi (at%), RF (W)	Ti DC (W)	Cu DC (W)		
Ni ₅₄ Ti	Ni ₄₅ Ti ₅₅ , 300W	0	0	360	No
Ni ₅₀ Ti	Ni ₄₅ Ti ₅₅ , 300W	15	0	360	No
Ni ₄₈ Ti	Ni ₄₅ Ti ₅₅ , 300W	20	0	360	No
Ni _{45.2} Ti _{50.3} Cu _{4.5}	Ni ₅₀ Ti ₅₀ , 300W	0	2.5	360	Yes
NiTiCu ₉	Ni ₄₀ Ti ₆₀ , 400W	0	8	370	No
NiTiCu ₁₅	Ni ₄₀ Ti ₆₀ , 400W	30	15	370	No

3.2 Characterization

3.2.1 Chemical Composition

Chemical compositions of the resultant thin films were investigated by an energy dispersive X-ray spectrometry (EDX) attached to a JEOL JSM-5600LV scanning electron microscopes (SEM). In each sample, the composition was measured five times on different areas. The mean value was taken as the nominal composition.

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Table 3-2 Chemical Compositions (at.%) of (a) NiTi thin films; (b) NiTiCu thin films.

	Ni ₅₄ Ti		Ni ₅₀ Ti		Ni ₄₈ Ti	
	Ni	Ti	Ni	Ti	Ni	Ti
1	53.10	46.90	50.75	49.25	48.48	51.52
2	53.44	46.56	50.40	49.60	47.96	52.04
3	52.87	47.13	50.31	49.69	47.86	52.14
4	53.50	46.50	50.94	49.06	48.70	51.30
5	53.68	46.32	50.29	49.71	49.46	50.54
Mean	53.32	46.68	50.54	49.46	48.49	51.51
Deviation	0.33		0.29		0.64	

(a)

	NiTiCu _{4.5}			NiTiCu ₉			NiTiCu ₁₅		
	Ni	Ti	Cu	Ni	Ti	Cu	Ni	Ti	Cu
1	44.83	50.25	4.92	40.62	50.58	8.80	33.3	49.95	16.76
2	46.26	49.67	4.07	41.13	49.80	9.07	32.57	49.63	17.8
3	45.79	50.43	3.78	40.80	50.12	9.09	32.2	49.91	17.88
4	45.13	50.35	4.52	40.39	50.87	8.75	32.1	50.21	17.68
5	43.84	50.9	5.26	40.53	49.68	9.79	32.7	49.35	17.95
Mean	45.17	50.32	4.51	40.69	50.21	9.10	35.02	50.22	14.76
Deviation	0.93	0.44	0.6	0.29	0.51	0.42	0.48	0.33	0.49

(b)

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The chemical compositions of these NiTiCu thin films are listed in

Table 3-2. The deviation, σ , is obtained from

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (3.1)$$

Small deviation was found in both NiTi and NiTiCu thin films, ranging from 0.29 at% to 0.9 at%. This difference can be attributed to the EDX measurement itself, but of course it also includes the tolerance of sputtering uniformity. From now on, the mean value will be used to present the chemical composition of all thin film samples. Tiny oxygen element was measured in all thin films, which indicates that the thin films were slightly oxidized. As observed, their surfaces all have a cloudy appearance. In NiTiCu thin films, Ti-content is all around 50.0 at%.

3.2.2 Phase Transformation and Crystal Structure

A Differential Scanning Calorimeter (DSC, TA instrument 2920) was used to investigate the phase transformation in the thin films. Based on the resultant heat flow vs. temperature relationship, one can determine the transformation temperatures. The samples were peeled-off from the silicon wafer and then thermally cycled between -20°C and 120°C at a heating/cooling rate of 10°C/min.

X-Ray Diffraction (XRD, Philips PW3719 XRD, Cu-K α , 40 KV/30 mA) was used to find the diffraction spectra of the deposited thin films at some different temperatures upon heating from the room temperature (about 23°C) up to 100°C. Based on that,

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one can identify not only the lattice structures of martensite (*M*) and austenite (*A*) (and *R*-phase, if any), but also the phase transition process. In XRD tests, the samples were tested on top of the silicon wafer.

Figure 3-1 and Figure 3-2 present the DSC and XRD results of all NiTi and NiTiCu films, respectively. As one test was done with the films on the substrate (XRD), while the other was not (DSC), it is expected that there is some difference in terms of the transformation temperatures.

As indicated in Figure 3-1, at room temperature (about 23°C), Ni₄₈Ti is *R*-phase upon cooling from high temperature, or after pre-cooling. At room temperature, Ni₅₀Ti is martensite after pre-cooling by liquid nitrogen. But upon cooling from high temperature to room temperature, the *R*-phase to martensite transformation is not complete. Martensite and *R*-phase coexist in Ni₅₄Ti at room temperature, even after pre-cooling by liquid nitrogen. Upon cooling to room temperature, the films are not 100% martensite, i.e., the phase transformation is not complete.

As shown in Figure 3-2, one-stage martensite to austenite transformation happens in all NiTiCu thin films. After pre-cooling by liquid nitrogen, all of them are 100% martensite at room temperature.

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Figure 3-1 DSC and XRD results of NiTi thin films. (a) Ni_{48}Ti ; (b) Ni_{50}Ti ; (c) Ni_{54}Ti .

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Figure 3-2 DSC and XRD results of NiTiCu thin films. (a) NiTiCu_{4.5}; (b) NiTiCu₉; (c) NiTiCu₁₅.

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3.2.3 Curvature and Internal Stress

Since the deposited thin film and silicon substrate are bonded together, upon thermal cycling, the difference in their thermal expansion coefficients will modify the deflection of the composite structure and the internal stress. The internal stress in the thin films can be very high, which may damage the film after a certain numbers of cycles.

A Tencor FLX-2908 laser system was used to evaluate the stress by means of the wafer-curvature method at a heating/cooling rate of $0.5^{\circ}\text{C}/\text{min}$. The measured curvature vs. temperature relationships of both NiTi and NiTiCu films are plotted in Figure 3-3 and Figure 3-4, respectively. Note that all samples were pre-cooled by liquid nitrogen before experiments to ensure that they are 100% martensite.

No closed-loop can be found in Figure 3-3 in NiTi thin films, as all phase transformations are not complete at room temperature (refer to Figure 3-1). In contrast, all curves of NiTiCu films are closed-loop, as a complete transformation can be obtained upon cooling to room temperature (refer to Figure 3-2).

Subsequently, the internal stress in the shape memory film can be determined roughly by Eqn. 2.4 (Grummon and Zhang 2001, Grummon 2000, Krulevitch et al. 1996, Fu and Du 2002, Rong et al. 2001).

Based on the stress vs. temperature relationship, not only the transformation temperatures and hysteresis, but also the multi-stage transformation, magnitude of

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stress generation and relaxation rate can be obtained (Grummon and Zhang 2001, Grummon 2000, Krulevitch et al. 1996).

Figure 3-5 and Figure 3-6 plot the stress vs. temperature relationships of NiTi and NiTiCu films in a thermal cycle, respectively.

Figure 3-3 Curvature evolution upon thermal cycling in NiTi thin films. (a) Ni₄₈Ti, (b) Ni₅₀Ti, (c) Ni₅₄Ti.

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Figure 3-4 Curvature evolution upon thermal cycling in NiTiCu films. (a) NiTiCu_{4.5}, (b) NiTiCu₉, (c) NiTiCu₁₅.

As we can see in Figure 3-5, all stresses in NiTi thin films are tensile stress. The highest one is in Ni₄₈Ti, about 1000 MPa, which is high and may result in damage to the material, e.g., plastic deformation. The stress in Ni₅₄Ti is also very high, around 600 MPa. The stress in Ni₅₀Ti varies from about 600 MPa to close to 0 MPa in a thermal cycle. According to Huang (2002), in NiTi shape memory bulk materials, the fatigue strength (for 10⁶ cycles) is about 350 MPa. Hence, it does not appear that

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these Si/NiTi films structures are very suitable for real applications, although thin films often have better fatigue characteristics than bulk material.

Figure 3-6 shows good SME in all NiTiCu thin films upon thermal cycling between room temperature and about 100°C. The internal stresses in these NiTiCu thin films are much smaller as compared with those in NiTi films. Especially, the stress in NiTiCu_{4.5} is compressive (-50MPa) at room temperature. This is unique among all the shape memory films that we have studied.

Figure 3-5 Stress evolution upon thermal cycling in NiTi films.

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Figure 3-6 Stress evolution upon thermal cycling in NiTiCu films.

3.3 Summary

After sputter deposition, six different SMA thin films were characterized by means of DSC, XRD and curvature measurements. From the experimental results, it can be seen that under the given deposition conditions, NiTiCu thin films show better shape memory behavior than NiTi thin films. After pre-cooling, all NiTiCu thin films are martensite at room temperature with a small internal stress. In NiTi thin films, only Ni₅₀Ti is martensite at room temperature after pre-cooling, and the internal stress is relatively small as compared with other NiTi thin films.

Among these thin films, NiTiCu_{4.5} appears to be rather unique, as it presents a great shape memory behavior and the internal stress is compressive at room temperature.

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In order to quantitatively investigate the surface morphology change in SMA thin films, a temperature controllable AFM (SFT-9800, Shimazu) was used. The AFM was operated in contact mode with an OMCL-TR800PSA tip (Micro cantilever produced by OLYMPUS)¹.

Unless otherwise stated, in each test, the surface of a same area of $10\ \mu\text{m} \times 10\ \mu\text{m}$ was measured at room temperature (RT, about 22°C) and at a high temperature (HT, slightly higher than A_f , at which the transformation is finished). For NiTiCu_{45} , the surface was measured with three different area sizes, i.e., $50\ \mu\text{m} \times 50\ \mu\text{m}$ for a full transformation cycle, $20\ \mu\text{m} \times 20\ \mu\text{m}$ and $10\ \mu\text{m} \times 10\ \mu\text{m}$ for RT/HT measurement. In a heating/cooling cycle, each measurement was taken after the temperature was stabilized by means of holding for about five minutes before scanning.

Before each test, the sample was pre-cooled by immersion into liquid nitrogen to reach 100% martensite and then heated to room temperature in air.

4.1 NiTi Thin Films

Figure 4-1 shows the AFM results of three NiTi thin films at RT and HT. In general, there is no significant change in surface morphology upon heating, but the films become smoother. At this point, the small features on the surfaces, about 500 nm to 1

¹ <http://www.olympus.co.jp/en/insg/probe/en/outlineproductE.html>

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μm in size, seem to be the grains of the thin films. With the increase of Ni content, the grain size seemingly decreases. At RT, there is no apparent pattern, which can be normally found atop the surface of bulk SMAs due to the appearance of twinned martensite. This is because the twinned martensite inside NiTi grains is too small to be observed at this point of time.

Two commonly used roughness parameters, namely R_a and R_{ms} of these NiTi thin films at RT and HT, are obtained and listed in Table 4-1. Note that the value at HT of each film is taken as reference to compute the relative change of roughness in %.

Table 4-1 R_a and R_{ms} of NiTi thin films (value at HT taken as reference for relative change computation).

	Ni ₄₈ Ti	Ni ₅₀ Ti	Ni ₅₄ Ti
R_a (RT) (nm)	30.1	18.4	14.1
R_a (HT) (nm)	21.9	13.1	9.9
Change of R_a (nm)	8.2	5.3	4.3
Relative change of R_a	37.5%	40.1%	43.2%
R_{ms} (RT) (nm)	37.5	22.9	17.9
R_{ms} (HT) (nm)	27.2	16.2	12.3
Change of R_{ms} (nm)	10.2	6.6	5.5
Relative change of R_{ms}	37.6%	40.7%	44.8%

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(a) at RT (22.1°C)

(b) at HT (90°C)

(1)

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(a) at RT (22.7°C)

(b) at HT (100°C)

(2)

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(a) at RT (21.4°C)

(b) at HT (80°C)

(3)

Figure 4-1 AFM results of NiTi thin films at RT and HT. (1) Ni₄₈Ti, (2) Ni₅₀Ti, and (3) Ni₅₄Ti.

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Figure 4-2 shows the change of surface roughness upon heating from RT to HT in NiTi thin films with different composition. It reveals that with the increase of Ni content, R_a and R_{ms} at both RT and HT decrease. The absolute difference in ΔR_a and ΔR_{ms} also decreases with the increase of Ni content. However, in contrary, the relative change of ΔR_a and ΔR_{ms} increases.

(a)

(b)

(c)

Figure 4-2 Variation of surface roughness against Ni content in NiTi thin films. (a) R_a and R_{ms} , (b) ΔR_a and ΔR_{ms} , and (c) relative change of ΔR_a and ΔR_{ms} (value at HT is taken as reference for relative change computation).

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4.2 NiTiCu Thin Films

Figure 4-3 and

Table 4-2 show the surface morphology/roughness of NiTiCu_{4.5} upon heating in three different area sizes, namely, 50 $\mu\text{m} \times 50 \mu\text{m}$, 20 $\mu\text{m} \times 20 \mu\text{m}$ and 10 $\mu\text{m} \times 10 \mu\text{m}$. Different from that of NiTi thin films, there are many apparent trenches, about 3.8 μm in width, atop the surface of NiTiCu_{4.5} at RT (Figure 4-3(1-2)). Upon heating, these trenches disappear at HT. After cooling back to RT, the trenches appear again in a pattern similar to the original configuration.

According to

Table 4-2, with these trenches, the surface becomes rougher at RT, which results in a significant change in surface roughness between RT and HT, much higher than that in NiTi thin films (Table 4-1).

It is well-known that significant surface relief (or surface upheaval) caused by the displacive martensitic transformation can be observed in sputtered NiTi thin films (Fu et al. 2004, He et al. 2004). During the martensitic transformation, a flat film surface at austenite becomes rough upon cooling due to the formation of twinned martensite striations. During the reverse transformation, the rough surface of martensite changes back to smooth surface at a high temperature of austenite state.

For comparison, a 10 $\mu\text{m} \times 10 \mu\text{m}$ flat area without any trench was selected for further test. As shown in Figure 4-3(3), its surface is very smooth. There is no obvious twinned martensite striation existence.

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(a) at RT (21.5°C)

(b) at HT (100°C)

(c) return to RT' (22.3 °C)

(1)

(a) at RT (22 °C)

(b) at HT (92°C)

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(c) return to RT' (23°C)
(2)

(a) at RT (23.5°C)

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(b) at HT (95°C)

(3)

Figure 4-3 AFM results of NiTiCu_{4.5}. (1) 50 μm × 50 μm, (2) 20 μm × 20 μm, and (3) 10 μm × 10 μm.

Table 4-2 R_a and R_{ms} of NiTiCu_{4.5} (value at HT is taken as reference for relative change computation).

	50×50 (μm ²)	20×20 (μm ²)	10×10 (μm ²)
R_a (RT) (nm)	16.5	19.0	11.4
R_a (HT) (nm)	3.7	4.3	7.2
Change of R_a (nm)	12.8	14.7	4.2
Relative change of R_a	345.9%	341.9%	58.3%
R_{ms} (RT) (nm)	20.1	23.3	14.6

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R_{ms} (HT) (nm)	4.9	5.5	9.1
Change of R_{ms} (nm)	15.2	17.8	5.5
Relative change of R_{ms}	310.2%	323.6%	60.4%

Figure 4-4 (and Table 4-3) shows the surface morphology and roughness of NiTiCu_9 and NiTiCu_{15} thin films at RT and HT upon heating. As we can see, at RT the surfaces of NiTiCu_9 and NiTiCu_{15} are also very smooth, only 6.1 nm and 11.1 nm in term of R_{ms} , respectively. Upon heating to HT, the surface roughness does not change much. For example, in NiTiCu_9 , the change is as small as 0.3 nm.

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(a) at RT (21.6°C)

(b) at HT (70°C)

(1)

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(a) at RT (21.7°C)

(b) at HT (70°C)

(2)

Figure 4-4 AFM results of NiTiCu₉ and NiTiCu₁₅. (1) NiTiCu₉, and (2) NiTiCu₁₅.

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Table 4-3 R_a and R_{ms} of NiTiCu₉, NiTiCu₁₅ (value at HT is taken as reference for relative change computation).

	NiTiCu ₉	TiNiCu ₁₅
R_a (RT) (nm)	4.9	8.8
R_a (HT) (nm)	4.9	8.4
Change of R_a (nm)	0	0.4
Relative change of R_a	0%	4.8%
R_{ms} (RT) (nm)	6.1	11.2
R_{ms} (HT) (nm)	6.4	10.5
Change of R_{ms} (nm)	-0.3	0.7
Relative change of R_{ms}	-4.7%	6.7%

Figure 4-5 plots the relationship of the surface roughness at RT and HT against the composition in NiTiCu thin films. Note that for NiTiCu_{4.5}, a size of 50 $\mu\text{m} \times 50 \mu\text{m}$ is considered here. Different from other NiTiCu thin films, the trenches in NiTiCu_{4.5} cause the surface to become much rougher, and thus a more significant change between RT and HT.

For confirmation, a scanning electron microscope (SEM) (JEOL JSM-5600LV) was used to observe the surface of NiTi and NiTiCu thin films. Figure 4-6 shows the surface morphology of NiTi and NiTiCu thin films measured by SEM at room temperature. It reveals the almost same result as that of the AFM measurement. At RT, NiTi thin films have a larger grain size than that of NiTiCu thin films. In Figure

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4-6 (d) (a zoom-in view of NiTiCu₄₅), the grains are observed. As such, it can be concluded again that the reversible trenches are not surface relief resulting from martensite striations.

Figure 4-5 Variation of R_a and R_{ms} against composition in NiTiCu thin films. (a) R_a and R_{ms} , (b) ΔR_a and ΔR_{ms} (absolute value), (c) relative change of ΔR_a and ΔR_{ms} (value at HT is taken as reference).

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(a)

(b)

(c)

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(d)

(e)

(f)

Figure 4-6 Surface morphology of NiTi and NiTiCu thin films at RT scanned by SEM. (a) Ni₄₈Ti, (b) Ni₅₀Ti, (c) Ni₅₄Ti, (d) NiTiCu_{4.5}, (e) NiTiCu₉, and (f) NiTiCu₁₅.

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(1) 22°C

(2) 60°C

(3) 75°C

(4) 80°C

(5) 85°C

(6) 92°C

(7) 80°C

(8) 75°C

(9) 62°C

(10) 52°C

(11) 35°C

(12) 23.7°C

(a)

(b)

Figure 4-7 Evolution of surface morphology and roughness in a $\text{NiTiCu}_{4.5}$ thin film upon thermal cycling. (a) AFM results. (1)-(6): heating, (6)-(12): cooling; (b) evolution of R_a and R_{ms} .

As the change of the surface roughness in $\text{NiTiCu}_{4.5}$ is the highest among all films, the evolution of surface morphology in $\text{NiTiCu}_{4.5}$ during a full thermal cycle was measured to reveal more details by AFM over an area of $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ (Figure 4-7). Figure 4-7(a) presents the evolution of surface morphology in a full thermal cycle. According to Figure 4-7(b), at the very beginning of heating and cooling, there is not much change in surface roughness as no apparent phase transformation occurs. A clear hysteresis can be observed in the full cycle.

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Since DSC and AFM measure different properties of SMAs, i.e., one is the heat flow and the other is the surface roughness, a new parameter the transformation fraction (ξ) is used to compare the phase transformation progress measured by both tests.

Referring to the heat flow versus temperature relationship in Figure 4-8, the areas S_c and S_h are the total entropies in the phase transformations. In a cooling process, at a temperature T_x , the entropy $S_c(T_x)$ over S_c is the transformation fraction (ζ) of the forward transformation. Similarly, in a heating process, at a temperature T_x , the entropy $S_h(T_x)$ over S_h is the fraction of the reverse transformation ($1 - \zeta$).

As for the AFM test, ζ can be estimated by

$$\xi = \frac{R(T_x) - R_{\min}}{R_{\max} - R_{\min}} \quad (4-1)$$

where $R(T_x)$ is the value of R_a or R_{ms} at a temperature T_x , $R_{\min}$ the minimum value of R_a or R_{ms} (pure austenite phase), and $R_{\max}$ the maximum value of R_a or R_{ms} (pure martensite phase).

Figure 4-9 presents the fraction curves of DSC and AFM results of NiTiCu4.5 thin film. As shown in Figure 4-9, it is clear that these two curves match fairly well. We note that the DSC and AFM measurement are not performed over the same piece of thin film at the conditions. For DSC test, the film was peeled off from the substrate. But in AFM test, the film sample was still atop the substrate. Due to the influence of substrate, which provides an elastic constraint to the film, some difference in the thermo-mechanical response is expected. Additional difference is also expected if the material is not perfectly uniform. Actually we think that AFM is a suitable

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alternative for local characterization of SMAs at a very small size, whereas DSC is used for global characterization of the entire SMA film.

Figure 4-8 Illustration of a DSC result.

Figure 4-9 Comparison of DSC integral curve and AFM integral curve for NiTiCu_{4.5}.

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4.3 Summary

The surface morphology of NiTi and NiTiCu thin films upon thermal cycling was thoroughly studied by AFM.

We have observed that

- 1) Upon heating, surface roughness decreases in most SMA thin films, except NiTiCu₉. For Ni₄₈Ti and Ni₅₄Ti, that is due to the R→austenite transformation, and for Ni₅₀Ti and other two NiTiCu thin films, it is the reverse martensitic transformation.
- 2) At RT, the surface roughness of NiTi thin films is greater than that of NiTiCu thin films due to their bigger grain size. From Figure 3-1(DSC and XRD results), it is observed that NiTi thin films have weak shape memory behavior, and at RT Ni₄₈Ti and Ni₅₄Ti are R-phase, while NiTiCu thin films all have good shape memory behavior and are martensite at RT (Figure 3-2). According to the curvature measurement (Figure 3-5), a large residual stress was in NiTi thin films at RT. A low residual stress in Ni₅₀Ti is due to the formation of martensite at RT, which also causes a rougher surface. The addition of Cu may result in smaller grain size in NiTiCu thin films, and thus, to the lower surface roughness.
- 3) With the increase of Ni content, R_a and R_{ms} of martensite and austenite all decrease. The difference of R_a and R_{ms} at high and low temperature also decreases. But the relative difference increases. Also shown in Figure 3-5, it is noted that, with the same deposition environment, the residual stress decreases with the increase of Ni content. The small residual stress in Ni₅₀Ti

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is because it is martensite at room temperature.

- 4) For NiTiCu₉ thin film, there is no remarkable change in surface roughness upon thermal cycling.
- 5) Thermally induced reversible trenches are observed in NiTiCu_{4.5} thin film upon thermal cycling. As proved, these reversible trenches are not surface relief caused by twin martensite striations. A compressive stress (-50MPa) at RT (Figure 3-6) may be the cause of these trenches but this unique phenomenon requires further investigations that will be performed in Chapter 5.

Chapter 5 Thermally Induced Reversible Trenches

Chapter 5 Thermally Induced Reversible Trenches

As revealed in Chapter 4, thermally induced reversible trenches were found in NiTiCu_{4.5} thin film, which was deposited at 360°C, then post-annealed at 440°C for one hour. It seems at first that the reversible trenches make NiTiCu_{4.5} distinct from the other films, but it is not clear yet if it is due to its composition or due to some processing steps.

To further investigate the trenches formation and its origin, a series of new NiTi/NiTiCu thin films were fabricated under different conditions and studied.

5.1 Reversible Trenches

We first tried to investigate the process that lead to reversible trenches formation and particularly the role of an intermediate oxidation step in air between the deposition and the annealing.

We investigated different SMA films composition as well as the effect of pre-patterning of the substrate.

a) NiTiCu-S1

We first deposited NiTiCu films on a substrate that had been scratched along different direction in three quarter and left smooth in the fourth quarter as shown in Figure 5-1.

Chapter 5 Thermally Induced Reversible Trenches

Figure 5-1 Illustration of scratches on wafer substrate.

A 4-hour sputter deposition was performed at 370°C using one Ti-50at%Ni target and one Cu target. After deposition, the samples were taken out for characterization. Curvature upon thermal cycling was measured by a Tencor FLX-2908 laser system to determine the evolution of internal stress. As shown in Figure 5-2, it was confirmed that the film is with good SME.

Figure 5-2 Stress evolution upon thermal cycle before and after post-annealing of NiTiCu-S1.

Chapter 5 Thermally Induced Reversible Trenches

Optical inspection was carried out to check the surface profile. Figure 5-3 reveals that no trenches appear in both with/without pre-scratched samples, at RT.

Figure 5-3 Comparison of typical surfaces of NiTiCu-S1 at RT, (a) with 1 μm and 3 μm scratches; (b) without scratches.

Subsequently, the NiTiCu-S1 sample was placed into a vacuum chamber for post annealing at 440°C for one hour. After this, curvature measurement and optical inspection were taken out again.

After post-annealing, the NiTiCu-S1 sample still has good SME, as shown in Figure 5-2. However the internal stress is lower and the phase transformation temperatures shift to a low temperature range.

Optical observation, Figure 5-4, reveals the reversible trenches on the film surface after post-annealing. AFM measurement was performed at RT for further detailed analysis. A cross-sectional line of the film surface at room temperature is presented in Figure 5-5, which reveals that the trenches are around 119 nm deep and 6.5 μm wide.

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(a) RT (~22°C) (b) HT (over 100°C)

Figure 5-4 Surface morphology of NiTiCu-S1 at RT (a), and HT (b) after post-annealing.

Figure 5-5 Surface morphology of NiTiCu-S1 at RT after post-annealing.

EDX test was carried out, and the results measured at two places (Table 5-1), reveal that the composition is about $\text{Ni}_{45.2}\text{Ti}_{54}\text{Cu}_{0.8}$.

This first experiment reveals that the composition is not the unique factor in the trench formation as a $\text{Ni}_{45.2}\text{Ti}_{54}\text{Cu}_{0.8}$ film shows the same trenches as the $\text{NiTiCu}_{4.5}$ films. Moreover, it shows that the presence of surface relief on the substrate is not

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directly linked with the trenches apparition as they appear on the whole surface of the wafer, whether they are with/without surface scratches.

Table 5-1 Chemical compositions (at.%) of NiTiCu-S1 thin film.

	Ni	Ti	Cu
1	45.33	53.79	0.88
2	45.11	54.14	0.76
Mean	45.22	53.965	0.82

b) NiTi-F6

The NiTi-F6 film with a completely different composition did also show, at least locally, reversible trenches.

NiTi-F6 was sputter deposited at RT (~22°C) with one Ti-45at.%Ni target and one pure Ti target. After deposition, the sample was placed in air for natural oxidation. In the end, one-hour post-annealing was carried out at 440°C. Curvature measurement result (Figure 5-6) shows the good SME.

In the optical inspection, reversible trenches were found atop the film surface, but not over the whole film area, and only within some small portions as presented in Figure 5-7. Figure 5-7 (b) and (c) are zoom-in view which clearly shows martensite variant groups. By comparing with Figure 5-7 (a) and the position of the trenches, it is confirmed again that the thermally induced reversible trenches are not surface relief formed by martensite striations.

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Figure 5-6 Stress evolution upon thermal cycle after the post-annealing of NiTi-F6.

Between the area where trenches form and the normal area, a clear difference in chemical composition is revealed by the EDX test (Table 5-2). As we know that the SME is strongly affected by the chemical composition of NiTi thin films, the reason why only some portions have trenches seems to be explained as the result of the significant variation in chemical composition. The area without trenches probably has a less strong SME being either Ni-rich or Ti-rich films.

Table 5-2 Chemical Compositions (at.%) of NiTi-F6 thin film in a trench area and two normal areas (1&2).

	Trench area		Normal area 1		Normal area 2	
	Ni	Ti	Ni	Ti	Ni	Ti
1	49.65	50.35	50.27	49.73	49.19	50.81
2	49.78	50.22	50.11	49.89	49.31	50.69
Mean	49.72	50.28	50.19	49.81	49.25	50.75

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(a) 100 μm x 100 μm

(b) 50 μm x 50 μm

(c) 10 μm x 10 μm

Figure 5-7 Surface of NiTi-F6 with reversible trenches under RT, (a) 100 μm x 100 μm , (b) 50 μm x 50 μm , (c) 10 μm x 10 μm .

c) Summary

It is observed that reversible trenches can be formed atop NiTi or NiTiCu thin films. According to the summary of the fabrication and treatment procedures listed in Table 5-3, it can be concluded that all the films with reversible trenches were placed in air and then post-annealed. Without the exposure to air and the following post-annealing, no trenches can be observed on the film surfaces.

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Table 5-3 Fabrication and treatment procedure of NiTiCu_{4.5}, NiTiCu-S1 and NiTi-F6 thin films.

	Fabrication & Treatment	Effects
NiTiCu_{4.5}	1. 360°C deposition	Good SME
	2. Exposure to air	
	3. 440°C post annealing	Good SME and with reversible trenches
NiTiCu-S1	1. 360°C deposition	Good SME; no trenches on surface.
	2. Exposure to air	
	3. 440°C post annealing	Good SME and with reversible trenches.
NiTi-F6	1. Room temperature deposition	No SME, no trenches.
	2. Exposure to air	
	3. 440°C post annealing	Good SME and some areas with reversible trenches.

5.2 Stress and Strain Analysis

We want to investigate the stress/strain characteristics of the films, but first we should determine the composition of the layer. We will particularly test its surface where the exposure to air and following thermal treatment could have changed the composition of the film.

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5.2.1 Characterization of top surface layer

X-ray photoelectron spectroscopy (XPS) analysis can identify the composition of top surface layer of a material and also measure its relative thickness.

XPS analysis was performed using a Kratos AXIS spectrometer with monochromatic Al K α (1486.71eV) X-ray radiation. Wide-scan spectra were recorded in 1eV step. Detailed core level spectra of different elements were recorded in 0.1eV step. Curve fitting was performed after a Shirley background subtraction by a non-linear least square fit. The spectra were calibrated using the C 1s (284.6eV) peak as a reference. The XPS depth profiles were recorded by sputtering progressively the thin film using an ion gun (Kratos MacroBeam) of 4keV energy with high purity Ar gas. The sputtering rate of SiO₂ under the same experimental condition was approximately 0.05nm/s. Only typical results of NiTi-F6 are represented and discussed here.

At the top surface, three elements, Ti, O and C, were observed. The amount of Ni element cannot be identified by XPS. Figure 5-8 shows the XPS narrow scan spectra of Ti, O and C elements. Ti 2p_{3/2} spectra have two distinct peaks at 454.4eV and 458.8eV corresponding to Ti in NiTi and in TiO₂. Ti 2p_{1/2} peak at 464.5eV also reveals the existence of Ti in TiO₂. O 1s peak at 530.3eV shows the existence of metal oxides, corresponding to TiO₂. The slight shoulder around 532.7eV and 529.2eV seems to correspond to hydroxide and oxygen bound to carbon.

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(a) Ti 2p

(b) O 1s

(c) C 1s

Figure 5-8 XPS narrow scan spectra on NiTi-F6 top surface, (a) Ti 2p, (b) O 1s, (c) C 1s.

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After slightly etching, the XPS peaks of Ni showed up, at around 870eV, 859.7eV and 853.2eV, corresponding to oxidation of Ni and Ni-enriched metallic layer.

Table 5-4 Surface composition (at%) of NiTi-F6 sample at different etching time.

Etching Time (s)	Ni 2p	Ti 2p	O 1s	C 1s
0	1.3	21.26	48.68	28.76
60	3.99	37.97	50.01	8.02
120	11.57	37.45	42.7	8.27
180	23.05	39.35	33.03	4.57
240	37.38	39.37	17.3	5.94
300	48.2	32.05	15.86	3.9
360	52.23	36.23	11.54	0
420	56.74	31.81	9.59	1.87
480	57.53	36.46	5.44	0.57
540	59.39	36.32	4.3	0

Figure 5-9 XPS depth profile of NiTi-F6 oxidation depth at RT.

Table 5-4 and Figure 5-9 reveal that the NiTi-F6 sample is covered by a thin layer of TiO₂ about 10 nm to 20 nm thick. After removing the oxide layer, a steady-state in chemical composition was identified.

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5.2.2 Stress and strain analysis

It is now clear that the samples are three-layer structure, namely 10 nm ~ 20 nm TiO_2 , 3.5 μm ~ 4.5 μm NiTi or NiTiCu thin film, and 450 μm Si substrate.

As the TiO_2 layer is very thin and on top of NiTi or NiTiCu thin film, the strain in TiO_2 can be considered as the sum of three parts, i.e. the strain of NiTi or NiTiCu thin film (ε_f), the thermal mismatch between TiO_2 layer and NiTi or NiTiCu thin film (ε_{th}), and the strain induced by the stress between TiO_2 layer and NiTi or NiTiCu thin film ($\frac{\sigma_o}{E_o}$). As such, one has that,

$$\varepsilon_o = \varepsilon_f + \varepsilon_{th} + \frac{\sigma_o}{E_o} \quad (5-1)$$

where the subscript o stands for the oxide layer, TiO_2 .

As the SMA thin film is much thinner than the substrate, the stress and strain in the thin film, σ_f and ε_f , are almost uniform (Huang et al. 2004) and can be obtained from the measured curvature (K) versus temperature variation (ΔT) relationship through (Huang et al. 2005)

$$\begin{cases} \sigma_f = \frac{K \bar{E}_s t_s^3}{6 t_f (t_f + t_s)} \\ \varepsilon_f = -\frac{1}{6} K \left[4 t_s + t_f \left(5 + \frac{t_f}{t_f + t_s} \right) \right] + \alpha_s \Delta T \end{cases} \quad (5-2)$$

where $\bar{E} \left(= \frac{E}{1-\nu} \right)$ is the biaxial modulus (E is Young's modulus and ν is Poisson ratio), α is the coefficient of thermal expansion (CTE), and t is the thickness. Here, subscripts s and f stand for the silicon substrate and NiTi or NiTiCu thin film,

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respectively. The initial temperature should be taken roughly as the later on annealing temperature (440°C). In the above-analysis, the contribution of the TiO₂ layer is ignored, since it is much thinner than the other layers.

By surface scanning, such as AFM and WYKO, the exact length of surface lines can be measured. Figure 5-10 shows a typical surface profile line of the NiTiCu_{4.5} at RT.

Figure 5-10 Surface profile of NiTiCu_{4.5} at RT.

As at annealing temperature, the film surface should be flat and smooth. Comparing with the hundreds nanometer depth irregular surface trenches, NiTi or NiTiCu film layer can be regarded as a flat basement. As such the relationship between the length of TiO₂ and that of NiTi or NiTiCu film layer can be presented by,

$$\delta_{local} = \frac{L_o}{L_f} \quad (5-3)$$

Here, δ_{local} is the ratio between the true length of a TiO₂ line, L_o , over that of NiTi or NiTiCu thin film, L_f .

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If scanning through the whole wafer line by line, L_f can be calculated from the strain of NiTi/NiTiCu, ε_f , and the original length, L_{origin} , at the annealing temperature, when there is no internal stress among the layers. Thus

$$L_f = (1 + \varepsilon_f) \times L_{origin} \quad (5-4)$$

Combining Eqn. (5-3) and Eqn. (5-4), the strain in TiO₂, ε_o , can be expressed as

$$\varepsilon_o = \delta_{local}(1 + \varepsilon_f) - 1 \quad (5-5)$$

The thermal mismatch between TiO₂ layer and NiTi/NiTiCu thin film, ε_{th} , is

$$\varepsilon_{th} = (\alpha_o - \alpha_f)\Delta T \quad (5-6)$$

where α_o and α_f are the coefficients of thermal expansion (CTE) of TiO₂ and NiTi or NiTiCu thin film respectively.

Combining Eqns. (5-1), (5-5) and (5-6), the stress in TiO₂ layer, σ_o , can be obtained as,

$$\sigma_o = \bar{E}_o \left[(\delta_{local} - 1)(1 + \varepsilon_f) - (\alpha_o - \alpha_f)\Delta T \right] \quad (5-7)$$

5.2.3 Strain and stress calculation

5.2.3.1 Strain and stress in SMA thin film

According to Eqn. (5-2), the stress and strain in the NiTi or NiTiCu thin films, σ_f and ε_f , can be calculated from the measured curvature (K) versus temperature variation (ΔT). Table 5-5 lists the typical material properties of TiO₂, NiTi SMA and Si substrate, which are used in the calculation below.

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Table 5-5 Typical values of some thermo mechanical properties of bulk TiO₂ (Shackelford and Alexander 2001), NiTi (Huang 2002) and Si (Yasumasa and Yozo 1984).

		α ($^{\circ}\text{C}^{-1}$)	E (GPa)	ν
TiO ₂		9×10^{-6}	282.76	0.28
NiTi	Austenite	11×10^{-6}	83	0.33
	Martensite	6.6×10^{-6}	20	
Silicon (100)		2.6×10^{-6}	130.2	0.28

The post annealing temperature, 440°C, is taken as the equilibrium point for stress and strain in our calculations. NiTiCu_{4.5} is selected as a typical sample for study. The film thickness, t_f , is taken as 4.2 μm. Wafer thickness, t_s , is taken as 450 μm. The curvature, K , has been reported in Chapter 3. Substituting all the data into Eqn. (5-2), the stress and strain in the NiTiCu_{4.5} sample can be worked out.

Figure 5-11 shows the evolution of NiTiCu_{4.5} film stress and strain in a thermal cycle.

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(a)

(b)

Figure 5-11 Stress and strain in NiTiCu_{4.5} film in a thermal cycle. (a) stress and strain evolution in a thermal cycle; (b) stress – strain curve.

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5.2.3.2 Strain and stress in oxide layer

a) CTE (α) of SMA in phase transformations.

During the phase transformation, α_f of a SMA is a variable. Refer to Table 5-5, α_f of martensite and austenite NiTi is available. As discussed in Chapter 4, transformation fraction (ξ) can be calculated from the DSC result. Subsequently, the fraction of martensite or austenite during the phase transformation is able to be worked out. With the phase fraction, the evolution of α_f upon transformation can be obtained. Figure 5-12 shows the evolution of α_f in NiTiCu₄₅ in a thermal cycle. Here, 20°C and 100°C are taken as the start/finish points respectively.

Figure 5-12 Evolution of CTE in NiTiCu₄₅ film in a thermal cycle.

Hence,

- i. Upon cooling:

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$$\left\{ \begin{array}{ll} \alpha_f \Delta T = \alpha_A (T - 440) & T \geq 100 \\ \alpha_f \Delta T = \alpha_A (100 - 440) + \int_{100}^T (\alpha_A \xi + \alpha_M (1 - \xi)) dT & 100 > T > 20 \\ \alpha_f \Delta T = \alpha_A (100 - 440) + \int_{100}^{20} (\alpha_A \xi + \alpha_M (1 - \xi)) dT + \alpha_M (T - 20) & 20 \geq T \end{array} \right. \quad (5-8)$$

ii. Upon heating

$$\left\{ \begin{array}{ll} \alpha_f \Delta T = \alpha_A (100 - 440) + \int_{100}^{20} (\alpha_A \xi + \alpha_M (1 - \xi)) dT + \alpha_M (T - 20) & 20 \geq T \\ \alpha_f \Delta T = \alpha_A (100 - 440) + \int_{100}^{20} (\alpha_A \xi + \alpha_M (1 - \xi)) dT + \int_{20}^T (\alpha_A \xi' + \alpha_M (1 - \xi')) dT & 100 > T > 20 \\ \alpha_f \Delta T = \alpha_A (T - 440) + \int_{100}^{20} (\alpha_A \xi + \alpha_M (1 - \xi)) dT + \int_{20}^{100} (\alpha_A \xi' + \alpha_M (1 - \xi')) dT & T \geq 100 \end{array} \right. \quad (5-9)$$

b) δ_{local}

An interferometer, WYKO NT2000, was used for the surface profile measurement, which can provide a larger inspection area than that of AFM. A Peltier device was used for temperature control. Eighteen different temperatures were selected for the surface profile evolution in a full thermal cycle, but only seven of them are shown in Figure 5-13. Figure 5-14 indicates that the surface morphology changes tremendously during thermal cycling, which is the result of the apparition of the thermally induced reversible trenches.

225 $\mu\text{m} \times 296 \mu\text{m}$ profiling area was measured by WYKO, as shown in Figure 5-13. Surface lines are obtained along X and Y axis in the whole profiling area. A 736 $\times$ 480 sampling matrix was used to work out the surface line length ratio, δ_{local} , for every profiling result.

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(a) 20°C

(b) 50°C

(c) 70°C

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(d) 100°C

(e) 80°C

(f) 57°C

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(g) 19°C

Figure 5-13 Surface morphology evolution of NiTiCu_{4.5} in a thermal cycle measured by WYKO. Upon heating: (a) 20°C, (b) 50°C, (c) 70°C (d) 100°C; upon cooling: (e) 80°C, (f) 57°C, (g) 19°C.

Figure 5-14 Comparison of surface morphology. (a) Before heating at 20°C, (b) heated to 100°C, (c) cooling back to 19°C. Same scale bar is used for a better view.

With the values of α_f and δ_{local} , σ_o and ϵ_o are obtained by Eqn. (5-7). From Figure 5-15, it is clear that the top TiO₂ layer is always in compression during thermal cycling.

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Figure 5-15 Calculated stress evolution in TiO_2 layer upon thermal cycling.

5.3 Trench Formation Mechanism

The surface morphology of materials can be altered by, for instance, the phase transformation [e.g., surface relief in SMAs (He et al. 2004)] or wrinkling [e.g., heating/cooling of thin metallic films atop of elastomeric polymers (Bowden et al. 1998, Zhang et al. 2004)], and in thermal cycling of oxidized viscous thin films atop of elastic substrates (He et al. 2000, Parry et al. 2004). One of the particular interesting points of this phenomenon is that the formed patterns can be at micron scale and highly in order (Bhattacharya and James 2005, Liang et al. 2002, Yoo and Lee 2003, Chen and Hutchinson 2004, Im and Huang 2004). These surface morphology could be removed, for instance, in the reversible phase transformations (e.g., in SMAs) and in heating of polymer materials (Chen and Hutchinson 2004). However, in ceramic and metallic materials, the wrinkling patterns are normally permanent and/or even grow with further thermal cycles (Im and Huang 2004).

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Significant surface relief (or surface upheaval) caused by the displacive martensitic transformation has been observed in sputtered NiTi thin films (e.g. Fu et al. 2004, He et al. 2004). During the martensitic transformation, a flat film surface in austenite phase becomes rough upon cooling due to the formation of twinned martensite striations. During the reverse transformation, the rough surface of martensite changes back to smooth surface at a high temperature of austenite phase.

Figure 5-16 Cross-section of a trench in NiTiCu_{4.5} upon heating.

From NiTiCu_{4.5} SEM pictures (Figure 4-6 (d)), and NiTi-F6 AFM images (Figure 5-7), it is clear that the reversible trenches are not the surface relief resulted by the martensitic transformation. Figure 5-16, cross-sectional view of a trench upon heating, suggests the occurrence of a kind of elastic buckling at RT, which is seemingly similar to the thermally induced ratcheting that requires (Im and Huang 2004): 1) An elastic-plastic metallic layer underneath the elastic thin layer; 2) An elastic thin layer, which is under compression.

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Figure 5-17 Evolution of stresses in NiTiCu_{4.5} thin film and atop TiO₂ layer upon thermal cycling.

From the top surface study by XPS in Section 5.2.1, we know that a thin oxide layer of TiO₂, 10-20 nanometers thick, was formed on the surface of NiTi and NiTiCu thin films. Upon cooling, the martensitic transformation, in which the harder austenite phase transforms to the soft martensite phase, occurs in those NiTi or NiTiCu SMA thin films. Consequently, the film becomes soft and serves as the elastic-plastic metallic layer, in which a large *plastic* strain can easily occur. Figure 5-17 shows the stress evolutions in the NiTiCu_{4.5} and atop TiO₂ layers upon thermal cycling. The compressive stress in the TiO₂ layer atop softer martensite substrate enables surface wrinkling to happen at RT. And opposite to what happens in ordinary metals, the *plastic* deformation in SMAs is fully recoverable upon heating. As such, the trenches disappear upon heating.

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To further verify the role of TiO_2 in the thermally induced reversible trench phenomenon, one half of a $\text{NiTiCu}_{4.5}$ sample was immersed into an etching solution (40% nitric acid, 1.5% hydro fluoric, diluted by de-ionized water) for about 12 seconds to remove the oxide layer. After another thermal cycle, at room temperature, no trench, except pitting due to etching, can be observed on the surface of the etched part, while trenches persist in the part without etching (Figure 5-18). It proves that the oxide layer, TiO_2 , is indeed a requirement for the trenching phenomenon.

Figure 5-18 Comparison of surface at RT with etching (left part) and without etching (right part).

As studied in Section 5.1, those thin films deposited atop of a heated wafer do not show any trench at RT, even after being left in air for a long period. After a following post-annealing, the reversible trenches are formed. It may further be concluded that the subsequent annealing step is another requirement for the appearance of trenches.

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5.4 Conclusion

Thermally induced reversible trenches are observed in NiTi or NiTiCu thin films.

Following conclusions are obtained from this study:

1. Thermally induced reversible trenches are the result of elastic buckling of a top oxidation layer (TiO_2).
2. Air exposure (forming TiO_2) and a following annealing are two necessary conditions for the occurrence of the thermally induced reversible trenches.

Chapter 6 Optical Measurements

To investigate the optical properties of SMA thin films, we carried out polarization and reflection measurement.

6.1 Background

The optical properties of a solid are determined by how light is transmitted, reflected, or absorbed as it passes through the solid. Since light is an electromagnetic wave, the interaction between light and solid is considered as the interaction between the electric-field component of the light and the charged particles, namely, the electrons and ions in the solid (Kwok 1997). Absorption occurs when light falls on a solid. If the solid is sufficiently thin, we can actually measure the amount of attenuation after light has passed through. Light absorption in a solid usually involves either the excitation of the electronic states or the vibrational states.

For a metal which does not have an energy gap, light absorption starts with the polarization of the atoms or ions. At low frequency, the electric-field component of light polarizes the valence electrons with respect to the nuclei, which increases the dielectric constant of the solid. Any increase in the dielectric constant also increases the index of refraction and, hence, the reflectance. Thus, the change of crystal structure upon the phase transformation will affect the absorption.

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Measuring the optical properties of a surface or solid can be achieved by ellipsometry. Ellipsometry is a very old technique for studying surface and thin films. It is used extensively in various areas, including surface science, electrochemistry, corrosion science, microelectronics manufacturing and development, and biology etc. Ellipsometry is the measurement of the state of polarization of a light beam after it has interacted with a medium to obtain information about that medium (Figure 6-1). It is well known that the polarization of a beam can be modified by reflection, transmission, and scattering (Herman 1995). The result of an ellipsometric measurement can be the complex refractive index of the reflecting materials, or if the reflecting material is a film-coated substrate, the thickness and optical constant of the film can be determined. Ellipsometry is sensitive to several material characteristics, such as layer thickness, optical constant, surface roughness, composition and optical anisotropy. The most common application of ellipsometry is the analysis of very thin films, thinner than the wavelength of the light itself, down to a single atomic layer.

Figure 6-1 Schematic of the geometry of an ellipsometry experiment¹.

¹ <http://www.uta.edu/optics/research/ellipsometry/ellipsometry.htm#Related%20Pages>

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In this technique, a simple polarization measurement is performed by using a variable angle ellipsometer. The polarization of the linearly polarized incident light is modified upon reflection and becomes elliptic. From the resulting polarization, it is possible to find the property of the material.

6.2 Polarization Measurement

6.2.1 Experimental Setup

A variable angle ellipsometer (L115C WAFERSKAN™ Ellipsometer) was used to create the linearly polarized laser beam, and detect the polarization direction and corresponding intensity of the reflected light.

Figure 6-2 Experimental setup of polarization measurement.

The experimental setup is schematically illustrated in Figure 6-2. A low-power (Class II) laser source (helium-neon laser with a wavelength of 632.8 nm) was used. A minimum 15-minute warm-up of the 632.8 nm laser was applied before any

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measurement. It allows the laser tube to reach its thermal equilibrium, and the intensity and wavelength of the laser to stabilize. The laser light is first passed through a $\lambda/4$ plate to make its polarization circular, and then through a polarizer (locked at 45°), to obtain linearly polarized light with the desired orientation. The reflective light, with its polarization altered by the optical properties of the sample, passes through an analyzer (i.e. a polarizer that can be rotated) and is then measured by a photo-detector, which converts the light energy into an electric current proportional to the intensity of the reflected light passing through the analyzer. The analyzer is rotated continuously which allows measuring the intensity of the light for all polarization direction. The output current of the photo-detector is thus recorded as an analog-voltage varying sinusoidally in amplitude with the analyzer orientation and proportional to the intensity of the reflected light. An optical interference filter between the analyzer prism and the photo-detector blocks all of the wavelengths other than that of the laser beam, thus eliminating the effects of ambient illumination.

The samples were cut into small pieces, about $2\text{ cm} \times 2\text{ cm}$ in size. A Peltier heater was placed right underneath the samples for heating. 6-8 W was required for the Peltier heater to induce a complete martensite to austenite transformation in the sample. A thermometer was attached to the surface of the Peltier heater, very close to the sample in order to indicate the real temperature of films. A multi-meter was connected to the LI15C WAFERSKANTM Ellipsometer to record the output of analog voltage, which is proportional to the intensity of reflected light.

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Three different incident angles were selected, 45° , 60° and 70° , which are commonly used in Ellipsometry. The measurement was taken under RT (room temperature, about 22°C) and HT (high temperature, little higher than A_f). Every sample was measured twice (by rotating the sample by 90° after the first test). Before each test, the samples were cleaned and pre-cooled by immersed into liquid nitrogen to reach 100% martensite and then heated to room temperature in air.

During the operation, the analyzer drum was rotated manually to measure the directions corresponding to the maximum and minimum voltage outputs, which indicate the long axis and short axis of the elliptical polarization light, respectively. The voltage output of long axis can partially represent the intensity of the reflected light.

6.2.2 Result and Analysis

From Table 6-1, Table 6-2 and Table 6-3, it can be seen that there is no apparent change of the polarization in reflected light in two perpendicular directions in all samples. It indicates that the surface morphology of all samples is uniform without any favorable direction. In terms of signal amplitude, NiTi thin films result in weaker signal than that of NiTiCu thin films. This is consistent with the results reported in Chapter 3, i.e. cloudy appearance on the surface of NiTi thin films, suggesting they have a lower reflection coefficient. Ni_{48}Ti has the weakest reflection performance. On the other hand, all NiTiCu thin films have a clear surface.

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Table 6-1 Polarization and reflection intensity at RT with 70° incident angle. (a) NiTi series, (b) NiTiCu series. (“2” is taken after “1” by rotating the sample by 90°)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	1	90	1.835	0	0.343
	2	90	1.819	0	0.315
Ni ₅₀ Ti	1	90	2.026	0	0.388
	2	85	2.024	-5	0.378
Ni ₅₄ Ti	1	99	2.25	7	0.217
	2	99	2.34	7	0.228

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	1	97	2.406	7	0.533
	2	97	2.398	7	0.528
NiTiCu ₉	1	104	2.638	14	0.464
	2	105	2.633	15	0.462
NiTiCu ₁₅	1	105	2.649	15	0.501
	2	104	2.623	14	0.497

(b)

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Table 6-2 Polarization and reflection intensity at room temperature with 60° incident angle. (a) NiTi serious, (b) NiTiCu serious. (“2” is taken after “1” by rotating the sample 90°)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	1	107	0.726	17	0.113
	2	107	0.725	17	0.111
Ni ₅₀ Ti	1	107	1.61	17	0.249
	2	107	1.59	17	0.245
Ni ₅₄ Ti	1	104	1.475	14	0.222
	2	104	1.474	14	0.219

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	1	116	2.354	26	0.311
	2	116	2.329	26	0.308
NiTiCu ₉	1	119	2.662	29	0.229
	2	119	2.651	29	0.222
NiTiCu ₁₅	1	120	2.783	30	0.192
	2	120	2.761	30	0.19

(b)

In NiTiCu thin films, the polarization direction and reflection intensity of NiTiCu₉ and NiTiCu₁₅ are similar, but different from that of NiTiCu_{4.5}. From the AFM results (Tables 4-2, 4-3 and Figures 4-3, 4-4), it appears that the surface morphology in NiTiCu_{4.5} is different from that in NiTiCu₉ and NiTiCu₁₅, indicating the influence of surface roughness on reflection properties. Similar phenomenon is also found for other incident angles (60° and 45°).

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Table 6-3 Polarization and reflection intensity at RT with 45° incident angle. (a) NiTi series, (b) NiTiCu series. (“2” is taken after “1” by rotating the sample by 90°)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	1	121	0.383	31	0.048
	2	121	0.382	31	0.048
Ni ₅₀ Ti	1	121	1.586	31	0.107
	2	121	1.581	31	0.105
Ni ₅₄ Ti	1	124	1.478	34	0.073
	2	124	1.480	34	0.077

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	1	126	2.428	36	0.104
	2	126	2.404	36	0.102
NiTiCu ₉	1	128	2.771	38	0.086
	2	128	2.767	38	0.081
NiTiCu ₁₅	1	128	2.904	38	0.076
	2	128	2.890	38	0.076

(b)

With the decrease of the incident angle from 70° to 45°, the difference in polarization direction of the reflected light between NiTi and NiTiCu films becomes smaller.

As shown in Table 6-4, Table 6-5 and Table 6-6, there is no significant change in polarization in the reflected lights from RT to HT for all thin films. It means that the phase change does not have any apparent influence on the polarization of reflected light, at the used wavelength (632.8nm).

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Table 6-4 Polarization and reflection intensity under RT and HT with 70° incident angle. (a) NiTi serious, (b) NiTiCu serious.

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	Rt: 23.2°C	90	1.835	0	0.343
	Ht: 80.1°C	90	1.839	0	0.346
Ni ₅₀ Ti	Rt: 23.5°C	85	2.024	-5	0.378
	Ht: 100°C	85	2.024	-5	0.357
Ni ₅₄ Ti	Rt: 23.6°C	99	2.25	7	0.217
	Ht: 80.3°C	99	2.27	7	0.215

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	Rt: 23°C	97	2.406	7	0.533
	Ht: 95°C	97	2.438	7	0.518
NiTiCu ₉	Rt: 23.1°C	104	2.638	14	0.464
	Ht: 71°C	105	2.64	15	0.467
NiTiCu ₁₅	Rt: 22.9°C	105	2.649	15	0.501
	Ht: 68°C	105	2.626	15	0.492

(b)

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Table 6-5 Polarization and reflection intensity under RT and HT with 60° incident angle. (a) NiTi series, (b) NiTiCu series.

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	Rt: 22.6°C	107	0.726	17	0.113
	Ht: 80.7°C	107	0.743	17	0.115
Ni ₅₀ Ti	Rt: 22.4°C	107	1.61	17	0.249
	Ht: 100°C	107	1.647	17	0.239
Ni ₅₄ Ti	Rt: 23.5°C	104	1.475	14	0.222
	Ht: 80.9°C	104	1.472	14	0.219

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	Rt: 23.6°C	116	2.354	26	0.311
	Ht: 97.2°C	116	2.427	26	0.304
NiTiCu ₉	Rt: 22.6°C	119	2.662	29	0.229
	Ht: 71.2°C	119	2.614	29	0.228
NiTiCu ₁₅	Rt: 23.4°C	120	2.783	30	0.192
	Ht: 71.2°C	120	2.854	30	0.195

(b)

In comparison, the signal amplitude shows some notable variation. For all three incident angles, the voltage output in the long axis of NiTiCu_{4.5} increases about 1.3%-3.5% upon heating as compared with the value at RT. But NiTiCu₉ is different and the amplitude decreases by 1.4%-1.8% (taking the result at RT as reference). Other thin films show very little change upon heating. From the AFM study in Chapter 4, it is known that NiTiCu_{4.5} has the biggest surface morphology change from RT to HT, and NiTiCu₉ shows almost no difference between RT and HT. As such, for NiTiCu_{4.5}, a combination of both surface scattering and refractive index change may contribute to the reflection coefficient. As for NiTiCu₉, it mainly

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comes from the refractive index. Therefore, the result here seemingly indicates that upon heating the change of refractive index of NiTiCu₉ causes a decrease of reflection coefficient.

Table 6-6 Polarization and reflection intensity under RT and HT with 45° incident angle. (a) NiTi series, (b) NiTiCu series.

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
Ni ₄₈ Ti	Rt: 22.3°C	121	0.383	31	0.048
	Ht: 80°C	121	0.407	31	0.048
Ni ₅₀ Ti	Rt: 21.9°C	121	1.586	31	0.107
	Ht: 100°C	121	1.579	31	0.105
Ni ₅₄ Ti	Rt: 21.3°C	124	1.478	34	0.073
	Ht: 81°C	124	1.5	34	0.074

(a)

		Maximum		Minimum	
		Direction (°)	Voltage (V)	Direction (°)	Voltage (V)
NiTiCu _{4.5}	Rt: 22.1°C	126	2.428	36	0.104
	Ht: 97.3°C	126	2.513	36	0.104
NiTiCu ₉	Rt: 23.1°C	128	2.771	38	0.086
	Ht: 71°C	128	2.731	38	0.085
NiTiCu ₁₅	Rt: 22.5°C	128	2.904	38	0.076
	Ht: 70°C	128	2.969	38	0.076

(b)

A cyclic temperature test was performed on a NiTiCu_{4.5} thin film. As shown in Figure 6-3, hysteresis was found in the intensity change curve along the reflected light long axis. As compared with the surface roughness measurement and DSC result, we can see that the revealed phase transformation temperatures are very

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close. It demonstrates that the change of surface roughness has a strong influence on the reflection intensity.

Figure 6-3 Reflection intensity change along the maximum direction in a thermal cycle of NiTiCu₄₅. (a) Relative change (taking the value of RT as reference for comparison); (b) fraction (in comparison with the change of surface roughness change); and (c) fraction (in comparison with DSC result).

In conclusion, a study of the ellipsometer results reveals that the polarization of the reflected beam is not affected by the phase change for a wavelength of 632nm, but that the reflected intensity is affected. We will now study in more details the reflection change using a spectrometer.

6.3 Reflection Measurement by Spectrometry

6.3.1 Experimental Setup

In order to investigate the reflection change upon thermal cycling, a spectrometer (SD2000 fiber optic spectrometer, Ocean Optics) was used for the reflection coefficient measurement.

Figure 6-4 Experimental setup.

Figure 6-4 illustrates the setup of the reflection measurement. A Tungsten-Halogen light source (HL-2000-HP-FHSA, Ocean Optics) was selected to provide a flat-top white light with a wavelength range from 360 nm to 2 μ m. A minimum 5-minute warm-up of Tungsten-Halogen light source was applied in all experiments to ensure the light source to be stable. The reflection probe (RP200-7, Ocean Optics) was located perpendicular to the sample, which is made up of seven individual optical fibers, six illumination fibers around one read fiber, with the same specifications, namely, 200 μ m diameter, 0.22 numerical aperture and 250 nm – 800 nm optimization range. The white light passed through the six illumination

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fibers to hit on the sample. Then the reflection from the surfaces was collected by the spectrometer and analyzed. In order to decrease the temperature shift due to airflow and background reflection, a big piece of black cloth was used to cover all instruments during experiment.

The measurement was taken at four different distances, namely, 0.55 mm, 1.4 mm, 3.4 mm and 6.4 mm. Every sample was measured at RT, HT and RT'². Aluminum, Gold and Chromium thin films were also tested for reference and comparison. They were deposited by sputtering as well. Table 6-7 lists the key parameters in sputtering. As we did before, all samples were cleaned and pre-cooled before the experiment.

Table 6-7 Parameters for deposition of aluminum, gold and chromium thin films.

Sample (thin film)	Target, Power	Sputtering Time
Aluminum	Aluminum, 200 W(R.F)	8 minutes
Gold*	Chromium, Gold, 200 W (R.F)	5 min (Chro.)+8 min (Gold)
Chromium	Chromium, 200 W(R.F)	10 minutes

* For gold thin film deposition, chromium was deposited as base layer to enhance the adhesion of gold.

During thermal cycling, the Peltier heater changes its thickness, which results in the distance changing between the sample and the optical fiber. Consequently, the reflection result is strongly influenced by this thermal expansion. So before the reflection measurement, the thickness change of Peltier heater upon heating was studied using a dial micrometer. We found a 0.045 mm thickness increase upon heating from RT to 95°C.

² RT': room temperature after cooling down from HT.

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6.3.2 Result and Analysis

First, the reference films were characterized.

Figures 6.5-6.8 show the reflection change of three reference thin films at four different distances (D). From Figure 6-5 and Figure 6-6, it can be found that in the reference thin films measurement, the reflection decreases upon heating at $D=0.5$ mm and 1.4 mm, and there is no significant difference between them. From Figure 6-7 and Figure 6-8, it can be seen that the reflection increases upon heating at $D=3.4$ mm and 6.4 mm, and there is also no significant difference between them. For further investigation, thermal cycles were done for these three references at four different distances. The wavelength 625.51 nm was selected in these thermal cycles. Figure 6-9 shows the measured results. From Figure 6-9, it can be found that the reflection change in these references is quite similar. It seems that this change is most probably caused by the specific configuration of the optical probe. As shown in Figure 6-4, the optical fiber is made up of seven individual fibers, six illuminations around one read fiber. For further analysis, a geometric model was built up for investigating the reflection evolution upon distance change in this specific probe configuration (refer to Appendix).

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Figure 6-5 Reflection change of references at $D=0.55$ mm. Right column: absolute value; left column: relative in percent (taking the value of RT as reference). (a) Aluminum, (b) gold, (c) chromium.

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Figure 6-6 Reflection change of references at $D=1.4$ mm. Right column: absolute value; left column: relative in percent (taking the value of RT as reference). (a) Aluminum, (b) gold, (c) chromium.

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Figure 6-7 Reflection change of references at $D=3.4$ mm. Right column: absolute value; left column: relative in percent (taking the value of RT as reference). (a) Aluminum, (b) gold, (c) chromium

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Figure 6-8 Reflection change of references at $D=6.4$ mm. Right column: absolute value; left column: relative change (taking the value of RT as reference). (a) Aluminum, (b) gold, (c) chromium.

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Figure 6-9 Reflection relative change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle. (a) $D=0.55$ mm; (b) $D=1.4$ mm; (c) $D=3.4$ mm; (d) $D=6.4$ mm.

Figure 6-10 shows the reflection evolution upon distance change at $NA=0.04$, which is computed from a purely geometric model.

Since the heating substrate will move up upon heating, it causes a decrease in the probe-film distance. Figure 6-10 reveals that for a short distance, the reflectance decreases with the decrease of distance. But for a large distance, the change in

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reflectance is opposite. This shares the same trends as in all reference films, although the exact distance does not fit precisely. The error is most probably due to the manual distance adjustment, the probe placement and the approximate nature of the geometrical model.

Figure 6-10 The reflectance evolution upon distance change from geometric model at $NA=0.04$.

From Figure 6-6(b) to 6-8(b), it can be seen that there is a bump near 475 nm – 500 nm in the spectrum of gold at HT. It has been reported (Syms et. al. 1977) that for thermally modulated reflectance spectrum of gold between 50°C and -166°C, there is a shift of +0.050eV (486.2 nm, relative to 495.9 nm) or -0.004eV (496.7 nm, relative to 495.9 nm) in the position of the principal peak at 2.5eV (495.9 nm), and a corresponding shift of -0.075 eV (431.2 nm, relative to 420.2 nm) in the subsidiary peak at 2.95eV (420.2 nm) . So the bump near 475 nm - 500 nm is caused by the temperature shift in the reflectance spectrum. Due to the noise near 420 nm, the temperature shift in the subsidiary peak is inconspicuous. The reflectance of gold is more than 92.5% over 2.1eV (590.3 nm). Thus the

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temperature change, from RT to 95°C, has only a very little influence on its reflectance, and the reflectance changes in reference films as shown in Figure 6-6 to Figure 6-8 are mainly due to the specific probe configuration.

The change in reflectance of the reference films upon heating can be considered as the baseline for the reflection measurement with SMA thin films.

Three SMA thin films, Ni_{50}Ti , $\text{NiTiCu}_{4.5}$, and NiTiCu_9 , were selected for this study and we conducted the experiments for different probe-sample distance.

Figure 6-11 shows the reflection change at a distance of 0.55 mm. Figure 6-11 reveals that in all three SMA thin films, the reflection decreases upon heating. However, there is no significant difference between the SMA thin films and the reference films. In the case of a very short distance between the probe and the sample, a large fraction of the scattered light will return to the illumination fibers. As such, at a very short distance, the contribution of scattering from the change of surface roughness is very small. As for the probe, there is only a very little portion of the reflected light received by the read fiber. As compared with the significant change caused by the specific configuration, the variation due to the change in the refractive index and surface roughness is not obvious.

According to Figure 6-11, it seems that the reflection coefficient of Ni_{50}Ti thin films is smaller than that of $\text{NiTiCu}_{4.5}$ and NiTiCu_9 thin films, which is consistent with the results of our previous polarization measurement.

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Figure 6-11 Reflection change at $D=0.55$ mm. Right column: absolute value; left column: relative in percent (taking the value of RT as reference). (a) Ni_{50}Ti ; (b) $\text{NiTiCu}_{4.5}$; (c) NiTiCu_9 .

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For a further investigation, a thermal cycle was done on $\text{NiTiCu}_{4.5}$, which has the greatest change of the surface roughness upon thermal cycling, and on the reference films. In the thermal cycle test, the wavelength of 625.51 nm, which gives the maximum reflection in the 400 nm to 800 nm range, was selected.

Figure 6-12 shows the reflection change in a thermal cycle. The curves of $\text{NiTiCu}_{4.5}$ and other three references are almost identical. The hysteresis in $\text{NiTiCu}_{4.5}$ is not visible. Actually, the large reflectance change due to the decrease of the probe-sample distance upon heating (Figure 6-10) is probably hiding the smaller effect that could be induced by the surface roughness change.

Figure 6-12 Reflection change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle at $D=0.55$ mm. (a) Comparison with reference films, (b) detail of $\text{NiTiCu}_{4.5}$.

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Figure 6-13 Reflection change at $D=1.4$ mm. Right column: absolute value, left column: relative in percent (taking the value of RT as reference). (a) Ni_{50}Ti ; (b) $\text{NiTiCu}_{4.5}$; (c) NiTiCu_9 .

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Figure 6-13 shows the reflection change at a distance of $D=1.4$ mm. Similar to that of $D=0.55$ mm, the reflection decreases in all films upon heating and reverses back after cooling down to RT'. But as the probe-sample distance is larger the decrease is less than that of $D=0.55$ mm, only amounting to 8% - 25%. The curves of the three references are very close, with a change of reflection about 6% to 8%. But, the change in SMA thin films is much larger, especially in Ni_{50}Ti , near 24%.

As before, a thermal cycle was carried out on $\text{NiTiCu}_{4.5}$. Significant hysteresis is now observed (Figure 6-14), which counter-balances the decrease of reflection upon heating. Obviously the hysteresis is caused by hysteresis in the change of surface roughness induced by the phase transformation.

Figure 6-14 Reflection change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle at $D=1.4$ mm. (a) Comparison with reference films; (b) detail of $\text{NiTiCu}_{4.5}$.

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Figure 6-15 Reflection change at $D=3.4$ mm. Right column: absolute value, left column: relative in percent (taking the value of RT as reference). (a) Ni_{50}Ti ; (b) $\text{NiTiCu}_{4.5}$; (c) NiTiCu_9 .

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Different from the previous two experiments, at $D=3.4$ mm, the reflection increases upon heating, and decreases upon cooling. Actually, we are now past the peak in Figure 6-10 and as the distance probe-sample is increased, a large fraction of the reflected light will not be guided back to the measurement fibers. Hence, at this distance, the decrease of surface roughness will contribute positively for an apparently better reflection. From Figure 6-15, it can be found that $\text{NiTiCu}_{4.5}$ has the largest change of the relative value, about 24.3%. It is associated with the change of surface roughness.

Figure 6-16 Reflection change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle at $D=3.4$ mm. (a) Comparison with reference films; (b) detail of $\text{NiTiCu}_{4.5}$.

Figure 6-16 plots the reflection change in $\text{NiTiCu}_{4.5}$ and three reference films. There is a significant difference between the heating and cooling processes in $\text{NiTiCu}_{4.5}$, i.e. hysteresis, similar to those in DSC, Curvature and AFM measurement upon the phase transformation. It can be seen in Figure 6-16(a) that the curves of three references are very close and fit well with the curve of $\text{NiTiCu}_{4.5}$ in the low temperature regime. After removing the “base line”, the

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reflection change due to the phase transformation is only about 5%, very close to the value 3.5% obtained with the ellipsometer.

Figure 6-17 Reflection change at $D=6.4$ mm. Right column: absolute value; left column: relative in percent (taking the value of RT as reference). (a) Ni_{50}Ti ; (b) $\text{NiTiCu}_{4.5}$; (c) NiTiCu_9 .

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With the further increase of distance D , the change of reflection coefficient decreases. But $\text{NiTiCu}_{4.5}$ still has the maximum reflection change (Figure 6-17).

Figure 6-18 shows the results at $D=6.4$ mm in a thermal cycle, which is very much similar to Figure 6-16. It is found that the reflection change due to the phase transformation in $\text{NiTiCu}_{4.5}$ is also about 5%, same as that of $D=3.4$ mm. Hence, surface roughness should be the main player, rather than the change of refractive index.

Figure 6-18 Reflection change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle at $D=6.4$ mm. (a) Comparison with reference films; (b) detail of $\text{NiTiCu}_{4.5}$.

For confirmation, NiTiCu_9 , which has a very small change of surface roughness upon the phase transformation, was selected for a thermal cycle at $D=3.4$ mm. As shown in Figure 6-19, the change of reflection due to the transformation has a small opposite effect, about -1.5% in NiTiCu_9 . It is again very much similar to the result obtained by the ellipsometer. The curve of NiTiCu_9 at the low temperature regime is close to the curves of references; while at the high temperature regime, it

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is close as well after deduction of the contribution from the phase transformation. For NiTiCu₉, the change in surface roughness is quite small. Hence, its refractive index change is the main player in the reflection change, and has the opposite effect on the reflection.

Figure 6-19 Reflection change (taking the value at RT as reference) for wavelength 625.51 nm as a function of temperature in a thermal cycle at $D=3.4$ mm. (a) Comparison with reference films; (b) detail of NiTiCu₉.

For a further study, the mean value of reflection change from 600 nm - 650 nm upon heating is calculated for all thin films as listed in Table 6-8. At a distance of 0.55 mm, the values of NiTi thin films are less than the corresponding reference values. At a distance of 3.4 mm and 6.4 mm, the values of NiTi thin films are close to the corresponding values of reference, only a little bit higher. For NiTi thin film, there is about 40% surface roughness change in the phase transformation. But the reflection change is almost zero. This confirms that the change of refractive index of SMA thin films upon the phase transformation has the opposite effect.

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As further revealed in Table 6-8, the change of refractive index upon the phase transformation in NiTi thin films is greater than that of NiTiCu thin films measured at a short distance.

Table 6-8 Mean value of reflection change from 600 nm to 650 nm upon heating (taking the value at RT as reference).

	0.55 mm	1.4 mm	3.4 mm	6.4 mm
Ni ₄₈ Ti	-85.8%	0.4% ¹	13.6%	8.8%
Ni ₅₀ Ti	-99.2%	-25.2%	19%	11.8%
Ni ₅₄ Ti	-90.7%	-13.5%	14.7%	9.1%
NiTiCu _{4.5}	-92.8%	-12.3%	24.3%	15.6%
NiTiCu ₉	-83.2%	-14.9%	9.3%	5.3%
NiTiCu ₁₅	-75.2%	-11.1%	8.6%	5.7%
Aluminum	-91.9%	-8.1%	19.8%	10.7%
Aluminum (70°C) ²	-63.3%	-1.3%	10.4%	5.6%
Aluminum (80°C) ²	-77.1%	-2.9%	13.6%	7.3%
Gold	-93%	-7.6%	17.1%	8.7%
Chromium	-94.7%	-6%	19.4%	11.1%

1. This value is strange. Further investigation is needed in future.
2. Because HT of Ni₄₈Ti and Ni₅₄Ti is 80°C, HT of NiTiCu₉ and NiTiCu₁₅ is 70°C, the values of Aluminum at 70°C and 80°C are taken as reference for comparison.

Figure 6-20(a) shows that the transformation temperatures derived from $D=1.4$ mm, 3.4 mm and 6.4 mm are more or less the same. Figure 6-20(b) confirms that the change of surface roughness in the phase transformation is the domain factor for the change of reflection in NiTiCu_{4.5} thin film. The transformation temperatures obtained at different distances are close, and they are also close to the ones derived from DSC and roughness measurement. The good agreement in Figure 6-20(d)

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reveals the possibility to measure the transformation temperature by optical method as an alternative.

Figure 6-20 Comparison of transformation temperatures in a thermal cycle measured by various techniques or distances (for current technique). (a) Comparison of NiTiCu_{4.5} at distances of 1.4 mm, 3.4 mm and 6.4 mm; (b) comparison with R_{ms} curve of NiTiCu_{4.5} (at 3.4 mm); (c) comparison with DSC curve of NiTiCu_{4.5} (at 3.4 mm); (d) comparison with DSC curve of NiTiCu₉ (at 3.4 mm).

From Figure 6-10 and Figure 6-20(a), we can see that there is an optimal distance for this reflection measurement. Near the peak position, the influence from the

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specific configuration is minimal, and the reflectance change induced by surface roughness and refractive index change can be observed more clearly.

6.4 Mathematical Analysis

A mathematical analysis was performed to evaluate the influence of 3-D surface topography on reflection quantitatively.

6.4.1 Surface Topography Analysis

(a) Mathematical model

According to the current experimental configuration, the scanning sizes are $10\ \mu\text{m} \times 10\ \mu\text{m}$, $20\ \mu\text{m} \times 20\ \mu\text{m}$ and $50\ \mu\text{m} \times 50\ \mu\text{m}$. There are 256×256 pixels with equal adjacent distance in the horizontal XY plane, and every pixel corresponds to a Z (height) value. So a $10\ \mu\text{m} \times 10\ \mu\text{m}$ area can be divided equally into 255×255 patches. The size of each patch is $\frac{10}{255}\ \mu\text{m} \times \frac{10}{255}\ \mu\text{m}$. For $20\ \mu\text{m} \times 20\ \mu\text{m}$ and $50\ \mu\text{m} \times 50\ \mu\text{m}$ area, the size is $\frac{20}{255}\ \mu\text{m} \times \frac{20}{255}\ \mu\text{m}$ and $\frac{50}{255}\ \mu\text{m} \times \frac{50}{255}\ \mu\text{m}$, respectively. Figure 6-21(a) illustrates the coordinates of a 255×255 patch matrix.

Any complicated surface can be estimated as a combination of many tiny triangles. In this case, a real surface can be replaced by $255 \times 255 \times 2$ triangles. The triangles $P_1P_2P_4$ and $P_1P_3P_4$ in Figure 6-21(b) are examples. By studying these triangles, the topography of each sample can be calculated quantitatively.

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Figure 6-21 Model for surfaces. (a) Over-all view, (b) an element.

Refer to Fig. 6.21 (b), the vector $\vec{n}$ is the normal of the triangle $P_1P_2P_4$ and the vector $\vec{m}$ is the normal of the triangle $P_1P_3P_4$. The angle between a triangle and the overall XY plane equals to the angle of the normal of the triangle with the Z axis, $\vec{z}$ (unit vector). Assume that θ_i is the angle for the triangle $P_1P_2P_4$ and θ_{i+1} for the triangle $P_1P_3P_4$.

Consider triangle $P_1P_2P_4$ (Figure 6-21),

$$\begin{aligned} \vec{n} &= P_1P_4 \times P_1P_2 \\ \theta_i &= \arccos \left(\frac{\vec{n} \cdot \vec{z}}{|\vec{n}| |\vec{z}|} \right) \end{aligned} \quad (6.1)$$

and

$$\begin{aligned} P_1P_2 &= (x_{i+1} - x_i, 0, z_{(i,j+1)} - z_{(i,j)}) \\ P_1P_4 &= (x_{i+1} - x_i, y_{j+1} - y_j, z_{(i+1,j+1)} - z_{(i,j)}) \end{aligned} \quad (6.2)$$

Thus,

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$$\begin{aligned}
\vec{n} &= P_1 P_4 \times P_1 P_2 = \begin{vmatrix} I & J & K \\ x_{i+1} - x_i & y_{j+1} - y_j & z_{(i+1,j+1)} - z_{(i,j)} \\ x_{i+1} - x_i & 0 & z_{(i,j+1)} - z_{(i,j)} \end{vmatrix} \\
&= (y_{j+1} - y_j)(z_{(i,j+1)} - z_{(i,j)})I + (x_{i+1} - x_i)(z_{(i+1,j+1)} - z_{(i,j+1)})J - (x_{i+1} - x_i)(y_{j+1} - y_j)K \\
&= dy(z_{(i,j+1)} - z_{(i,j)})I + dx(z_{(i+1,j+1)} - z_{(i,j+1)})J - dxdyK \\
&= a_x I + a_y J + a_z K
\end{aligned}$$

$$\theta_i = \arccos \left(\frac{\vec{n} \cdot \vec{z}}{|\vec{n}| |\vec{z}|} \right) = \arccos \left(\frac{a_z}{\sqrt{a_x^2 + a_y^2 + a_z^2}} \right) \quad (6.3)$$

From an AFM result, the corresponding $z_{(i,j)}$ value can be obtained,

and $dx = dy = \frac{10}{255} \mu m$, we can work out the angle for each individual triangle.

(b) Result and analysis

Three SMA thin films, Ni₅₀Ti, NiTiCu_{4.5} and NiTiCu₉ were studied. From the statistic results, the angle distribution and accumulation are plotted at RT and HT.

For AFM SFT-9800, the vertical resolution is approximately 0.1 nm. So the minimal surface angle, reliable in the mathematic analysis, can be obtained by

$$\theta_{\min} = \arccos \left(\frac{\vec{n}_{\min} \cdot \vec{z}}{|\vec{n}_{\min}| |\vec{z}|} \right) = \arccos \left(\frac{a_z}{\sqrt{a_x^2 + a_y^2 + a_z^2}} \right) = \arccos \left(\frac{d^2}{\sqrt{(d \times z_{\min})^2 + d^4}} \right) \quad (6.4)$$

where d is the side length of each patch, $z_{\min}$ the vertical resolution of SFT-9800.

For a $10 \mu m \times 10 \mu m$ area, the minimal reliable angle is 0.15° . For $20 \mu m \times 20 \mu m$ and $50 \mu m \times 50 \mu m$ areas, they are 0.07° and 0.03° , respectively.

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Figure 6-22 Surface angle dispersion. Left column: distribution of surface angle; right column: accumulation of surface angle. (a) Ni_{50}Ti ; (b) $\text{NiTiCu}_{4.5}$; (c) NiTiCu_9 .

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Figure 6-22 shows the surface angle distribution of Ni_{50}Ti , $\text{NiTiCu}_{4.5}$ and NiTiCu_9 . Most surface angles in NiTiCu_9 , about 90%, are less than 7° at RT. Upon heating there is a very little change in the angle distribution. In Ni_{50}Ti and $\text{NiTiCu}_{4.5}$, a large amount of surface angles are from 2° to 9° , about 53.4% and 56.8% respectively, at RT. Upon heating to HT, in $\text{NiTiCu}_{4.5}$, the amount of surface angles, which less than 9° , increases greatly, from 62.3% to 83.1%; while that of Ni_{50}Ti changes from 57.9% to 69.6%. This result indicates that the trenches and large grain size all can produce a rough surface. After heating to HT, the disappearance of trenches results in a more surface roughness change.

6.4.2 Dispersion of Reflection Angle

(a) Mathematical model

When a light beam hits the surface of a SMA thin film, the intensity of the reflected beam is dependent on two factors, namely the refractive index which is associated with the material property, and the surface roughness. In the following discussion, the reflective angle dispersion is studied.

Figure 6-23 is an illustration of the reflective angle dispersion. The incident light $\vec{I}_{inc}(\sin\theta_i, 0, \cos\theta_i)$ from a fiber or some other light source hits on the surface of the SMA thin film and is reflected. If the surface is perpendicular to Z, the ideal reflective beam $\vec{R}_{ideal}$ is in the direction of $(-\sin\theta_i, 0, \cos\theta_i)$. However, due to surface roughness, patch surface angles distribute widely and the reflected light direction $\vec{R}_r$ will vary by a shift angle θ_r with the ideal reflection direction $\vec{R}_{ideal}$.

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In the study below, the distribution of θ_r , i.e. the angle between $\vec{R}_{ideal}$ and $\vec{R}_r$, is calculated for different incident light.

Figure 6-23 Reflective angle dispersion.

Assume that

$$\begin{cases} \vec{I}_{inc} = a_1\vec{i} + b_1\vec{j} + c_1\vec{k} \\ \vec{n}_i = a_2\vec{i} + b_2\vec{j} + c_2\vec{k} \\ \vec{R}_r = a_3\vec{i} + b_3\vec{j} + c_3\vec{k} \\ \vec{R}_{ideal} = -a_1\vec{i} - b_1\vec{j} + c_1\vec{k} \end{cases} \quad (6.5)$$

For a triangle surface, the incident beam $\vec{I}_{inc}$, the surface normal $\vec{n}_i$ and the reflective beam $\vec{R}_r$ are in one plane, and the angle (θ_i) between $\vec{I}_{inc}$ and $\vec{n}_i$ equals to the angle (θ_r) between $\vec{R}_r$ and $\vec{n}_i$ (Figure 6-24).

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Figure 6-24 Relation between $\vec{R}_r$, $\vec{I}_{inc}$ and $\vec{n}_i$.

Thus

$$\begin{cases} a_1 + a_3 = k \frac{a_2}{\sqrt{a_2^2 + b_2^2 + c_2^2}} \\ b_1 + b_3 = k \frac{b_2}{\sqrt{a_2^2 + b_2^2 + c_2^2}} \\ c_1 + c_3 = k \frac{c_2}{\sqrt{a_2^2 + b_2^2 + c_2^2}} \end{cases} \quad (6.6)$$

and

$$\begin{cases} k = 2 \cos \theta_i \cdot |\vec{I}_{inc}| = 2 \cos \theta_i \cdot \sqrt{a_1^2 + b_1^2 + c_1^2} \\ \cos \theta_i = \frac{\vec{n}_i \cdot \vec{I}_{inc}}{|\vec{n}_i| \cdot |\vec{I}_{inc}|} = \frac{a_1 a_2 + b_1 b_2 + c_1 c_2}{\sqrt{a_1^2 + b_1^2 + c_1^2} \cdot \sqrt{a_2^2 + b_2^2 + c_2^2}} \end{cases} \quad (6.7)$$

A combination of Eqns. (6.5), (6.6) and (6.7), results in,

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$$\begin{cases} a_3 = 2 \frac{(a_1 a_2 + b_1 b_2 + c_1 c_2) a_2}{a_2^2 + b_2^2 + c_2^2} - a_1 \\ b_3 = 2 \frac{(a_1 a_2 + b_1 b_2 + c_1 c_2) b_2}{a_2^2 + b_2^2 + c_2^2} - b_1 \\ c_3 = 2 \frac{(a_1 a_2 + b_1 b_2 + c_1 c_2) c_2}{a_2^2 + b_2^2 + c_2^2} - c_1 \end{cases} \quad (6.8)$$

The angle θ_r between $\overline{R_r}$ and $\overline{R_{ideal}}$ can be expressed as

$$\theta_r = \arccos \left(\frac{-a_3 a_1 - b_3 b_1 + c_3 c_1}{\sqrt{(a_3^2 + b_3^2 + c_3^2)(a_1^2 + b_1^2 + c_1^2)}} \right) \quad (6.9)$$

If the angle between $\overline{n_i}$ and $\overline{I_{inc}}$ equals or exceeds 90° , the incident light will be reflected back to the source directly or will not hit on the patch. Hence, the incident beam will not result in a useful reflection.

(b) Result and analysis

Six different incident angles were considered, namely 70° , 60° , 45° , 30° , 20° and 0° . For every incident angle, the statistic analysis was performed twice, one with an incident beam in the XZ plane and another in the YZ plane (Figure 6-23). The distribution of shift angles (θ_r) between real reflected light ($\overline{R_r}$) and ideal reflection beam ($\overline{R_{ideal}}$) was calculated.

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(a)

(b)

(c)

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Figure 6-25 Shift angle θ_r distribution of Ni_{50}Ti . Left column: distribution of reflection angle; right column: accumulation of reflection angle. (a) 70° ; (b) 60° ; (c) 45° ; (d) 30° ; (e) 20° ; (f) 0° .

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(a)

(b)

(c)

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Figure 6-26 Shift angle θ_r distribution of $\text{NiTiCu}_{4.5}$. Left column: distribution of reflection angle; right column: accumulation of reflection angle. (a) 70° ; (b) 60° ; (c) 45° ; (d) 30° ; (e) 20° ; (f) 0° .

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(a)

(b)

(c)

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Figure 6-27 Shift angle θ_r distribution of NiTiCu₉. Left column: distribution of reflection angle; right column: accumulation of reflection angle. (a) 70°; (b) 60°; (c) 45°; (d) 30°; (e) 20°; (f) 0°.

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Figure 6-25, Figure 6-26 and Figure 6-27 present the distributions of θ_r in Ni_{50}Ti , $\text{NiTiCu}_{4.5}$ and NiTiCu_9 at RT and HT. We can see that the distributions of θ_r in Ni_{50}Ti and $\text{NiTiCu}_{4.5}$ decreases upon heating to HT, which results in a smaller dispersion cone. This is because the surfaces of Ni_{50}Ti and $\text{NiTiCu}_{4.5}$ become smoother upon heating to the austenite phase. For NiTiCu_9 , the change is not that significant.

Figure 6-28 Shift angle θ_r distribution of $\text{NiTiCu}_{4.5}$ with 70° incident angle. Left column: distribution of reflection angle; right column: accumulation of reflection angle. (a) $50\ \mu\text{m} \times 50\ \mu\text{m}$; (b) $20\ \mu\text{m} \times 20\ \mu\text{m}$.

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For NiTiCu_{4.5}, when the incident beam angle θ_i is large, the distribution of θ_r is different between XZ incident plane and YZ incident plane. With the decrease of θ_i , the difference decreases and becomes insignificant, particularly at below 45°. With the increase of the reflection area, the orientation dependence is averaged (Figure 6-28). For 50 $\mu\text{m} \times 50 \mu\text{m}$ area size, the difference between RT and HT in two incident planes is similar, although the distribution along two orientations is different. It is expected that with the further increase of reflection area, eventually there will be no orientation dependence in NiTiCu_{4.5}.

For all three SMA thin films, when incident beam tilts from 70° to 0°, the distribution of θ_r becomes stable, especially when the incident angle is less than 45°.

In order to compare in the distribution of θ_r between RT and HT in these three thin films, incident angles 70° and 20° were selected for statistic analysis.

Table 6-9 shows the change of θ_r distribution between RT and HT at incident angles of 70° and 20°, for Ni₅₀Ti, NiTiCu_{4.5} and NiTiCu₉ thin films. It is clear that NiTiCu_{4.5} has the biggest θ_r distribution change among them, and the change is bigger at the small shifting angle range. Upon heating, θ_r distribution becomes narrow due to surface change in NiTiCu_{4.5}. At 20° incident light angle, the change of θ_r distribution is even more significant, which may be resulted by the scattering effect.

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Table 6-9 Change of reflection angle dispersion between RT and HT with (1) 70° and (2) 20° incident angle (taking RT value as reference). (a) Ni₅₀Ti; (b) NiTiCu_{4.5}; (c) NiTiCu₉.

Incident Plane	θ_r	Accumulation		Change ratio(%)	Incident Plane	θ_r	Accumulation		Change ratio(%)
		RT(%)	HT(%)				RT(%)	HT(%)	
XZ	2°	2.93	4.93	68.55	YZ	2°	2.44	6.25	156.53
	6°	25.22	30.98	22.84		6°	21.20	41.16	94.17
	10°	46.99	47.85	1.82		10°	47.83	77.19	61.37
	30°	84.98	87.54	3.01		30°	99.33	99.90	0.57
(a) Ni ₅₀ Ti									
XZ	2°	4.76	13.85	191.03	YZ	2°	4.64	16.90	264.43
	6°	23.82	39.21	64.65		6°	35.11	80.59	129.52
	10°	39.15	59.03	50.77		10°	70.29	97.63	38.89
	30°	88.68	98.33	10.88		30°	99.92	99.86	-0.06
(b) NiTiCu _{4.5}									
XZ	2°	12.69	10.89	-14.18	YZ	2°	22.27	25.87	16.18
	6°	64.95	53.11	-18.23		6°	71.19	84.14	18.19
	10°	84.86	69.73	-17.82		10°	91.64	97.33	6.21
	30°	99.71	99.07	-0.64		30°	99.99	99.98	-0.01
(c) NiTiCu ₉									

(1) incident angle 70°

Incident Plane	θ_r	Accumulation		Change ratio(%)	Incident Plane	θ_r	Accumulation		Change ratio
		RT(%)	HT(%)				RT(%)	HT(%)	
XZ	2°	1.34	2.16	61.76	YZ	2°	1.34	2.16	61.76
	6°	10.61	18.07	70.37		6°	10.61	18.06	70.27
	10°	27.27	41.98	53.95		10°	26.73	40.70	52.27
	30°	83.34	87.44	4.92		30°	84.84	89.56	5.57
(a) Ni ₅₀ Ti									
XZ	2°	1.56	8.22	427.38	YZ	2°	1.56	7.52	380.88
	6°	14.08	35.38	151.17		6°	13.85	38.29	176.53
	10°	31.48	56.66	79.96		10°	32.95	59.36	80.18
	30°	87.95	98.22	11.67		30°	89.74	98.66	9.94
(b) NiTiCu _{4.5}									
XZ	2°	7.78	8.70	11.82	YZ	2°	7.78	8.70	11.82
	6°	46.65	47.57	1.98		6°	46.65	47.57	1.98
	10°	78.81	68.63	-12.91		10°	75.63	68.27	-9.74
	30°	99.69	99.04	-0.65		30°	99.83	99.45	-0.38
(c) NiTiCu ₉									

(2) incident angle 20°

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6.4.3 Discussions

From the mathematical analysis of the surface topography and reflection angle dispersion, a quantitative comparison is achieved.

- 1) NiTiCu_{4.5} (with trenches) and Ni₅₀Ti (large grain) all induce rougher surface at RT. Upon heating to HT, the disappearance of trenches results in a larger change in the surface angle.
- 2) Trenches in NiTiCu_{4.5} result in the reflection orientation dependence at a incident angle larger than 60°. With the increase in scanning area, this effect can be averaged out.
- 3) Upon heating to HT, a larger change in θ_r distribution is observed in NiTiCu_{4.5}, especially within the small shifting angle cone ($< 2^\circ$). At 20° incident light angle, the change in θ_r distribution is even more significant, which may be resulted by the scattering effect.

6.5 Summary

Polarization and reflectance measurements were carried out to characterize the optical properties of NiTi/NiTiCu thin film. It is found that:

- 1) The phase transformation does not cause any significant change in polarization in the reflected light at 632.8nm. There is no orientation dependence in the sputter deposited SMA thin films if the examined spot size is not too small.
- 2) The phase transformation does have contribution to the overall optical reflection. In our probe configuration, the change of surface roughness increases reflection, but the change in refractive index provides the

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opposite effect. This is in contrary to the previous result reported by Tabib-Azar et al. (1994).

- 3) The change of refractive index in NiTiCu thin films is smaller than that of NiTi thin films upon the phase transformation.
- 4) Reflection measurement can be used as an alternative method to determine the phase transformation temperatures of thin film SMAs.
- 5) The existence of reversible trenches results in a large surface angle distribution change from RT to HT. As a consequence, the distribution of reflection shift angle (θ_r) also changes more, especially for shifting angle less than 2° .

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In this project, we have systematically studied the surface morphology and associated optical properties of thin film SMAs deposited atop a silicon wafer during the phase transformation upon thermal cycling.

In addition to traditional techniques, two alternative approaches based on the change in optical and surface properties were developed and shown to be interesting for the characterization of the phase transformation in SMA thin films.

Additionally, we observed reversible trenches during thermal cycling atop some of the thin films. The mechanism behind this new phenomenon was worked out and the necessary conditions for this interesting behavior to happen were identified.

7.1 Conclusion

Six different sputter deposited SMA thin films of two types, NiTi and NiTiCu, were investigated. Conventional techniques, i.e. DSC, EDX, XRD and curvature measurement, were applied for characterization of the films' chemical composition, transformation temperatures, crystalline structure and stress evolution upon thermal cycling. A temperature controllable AFM was used to investigate the surface morphology evolution upon the phase transformation during thermal cycling. Films topography was measured in these NiTi/NiTiCu thin films, and a new phenomenon, the presence of reversible trenches, was observed for the first time in NiTiCu_{4.5} thin

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films. The existence of reversible trenches results in large surface roughness change during the phase transformation. By comparing DSC and AFM results, a close relationship was found between surface roughness and phase transformation. It reveals the possibility to use AFM as a reliable and useful tool for nondestructive *in situ* characterization of shape memory films, especially for small size samples ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m} \sim 125\text{ }\mu\text{m} \times 125\text{ }\mu\text{m}$).

To further study the mechanism behind the trenches formation a series of NiTi/NiTiCu thin films were fabricated under different conditions. Reversible trenches were obtained in both NiTi and NiTiCu thin films. From the AFM result, it is confirmed that the reversible trenches are not surface relief formed by martensite striations. On NiTi samples, supposedly due to the extreme sensitivity to chemical composition, only some local zones are occupied by trenches. Thermally induced reversible trenches were confirmed to be the result of the elastic buckling in the top oxidation layer. Actually, surface oxidation and subsequent post annealing were identified as two necessary conditions for the formation of reversible trenches. Within the post-annealing, the internal stress is largely removed at the annealing temperature. Upon cooling, compressive stress is generated and accumulated on the oxidation layer. Upon martensitic transformation, SMA films turn to be soft and easy to deform. With the growth of compressive stress, surface wrinkling occurs as a result of elastic buckling of the oxidation layer on top of the NiTi/NiTiCu film.

Two optical measurement methods were used to study the optical property of the films, namely ellipsometry and reflectometry. Both NiTi and NiTiCu thin films do

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not show any polarization change upon phase transformation within the wavelength range of the study. In the reflection measurement, the refractive index changes upon heating reveals a negative effect on the reflection coefficient. With the reversible trenches, the surface roughness changes upon heating resulting in a remarkable change in reflection. With these findings, we established an alternative *in situ* approach to determine the phase transformation temperatures of sputter deposited NiTi/NiTiCu films using only reflection measurement.

A mathematical analysis on the surface topography and reflection angle dispersion was carried out on NiTiCu_{4.5}. With the existence of reversible trenches, which brings large surface morphology change, the distribution of the reflection angle changes significantly between RT and HT, especially for small angles ($2^\circ \sim 6^\circ$).

Through these studies, a good understanding on the optical performance of NiTi/NiTiCu thin films is achieved. The thermally induced reversible trenches observed during the course of this project reveal the potential of NiTi/NiTiCu films for applications in optical engineering.

Significant surface roughness change due to the reversible trenches is observed in NiTi or NiTiCu thin films. With the increasing of surface roughness, the reflection decreases especially at big incident angles. With these properties, a grating light valve can be structured using reversible trenches atop a NiTi or NiTiCu thin film deposited on silicon base to form grating structure. By controlling the phase at different positions, different grating pattern can be achieved.

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7.2 Future Work

In the future we will need further theoretical study and quantitative calculation on reversible trenches formation to be able to fully control the production of required trench pattern. A theoretical model for this elastic buckling of the top oxidation layer will be developed. The driving conditions, i.e. compression force on oxidation layer, elastic property of martensite and austenite, will be quantitatively studied with the theoretical model.

After the development of this tool to obtain full control over the trenches formation, we will be able to design and fabricate devices using this new principle. One possibility would be to develop an optical grating attenuator by using NiTi/NiTiCu thin film, in which reversible trench pattern plays the role of the grating. The corresponding fabrication process will be studied with embedded circuitry for thermal control at high working frequency.

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Appendix

Multimode fiber coupling - a geometric model

A purely geometric model is based on the computation of the surface of the read fiber illuminated by the illumination fiber and multiplying it by the irradiance in the plane of the illumination fiber. We consider a uniform illumination in the illumination fiber plane, whereas it is clearly not the case (at least we should consider the diffraction by a circular aperture and use Bessel function for the intensity profile, or more probably approximate them with Gaussian, or even better look at the mode coupling). However this simple model should give some of the features of the phenomenon.

Because the arrangement of fibers is symmetric, only the effect of one illumination fiber to the read fiber is concerned. It is assumed that a is the radius of the read and illumination fiber cores, b is the radius of the area (uniformly) illuminated by the illumination fiber, d is the offset between the illumination and read fibers centre, z is the separation between the read fiber and the mirror, I is the uniform illumination intensity, and 0.22 is used as the NA of the fiber (concerning the NA we could note that because the fiber have the same NA, there is, in theory, no light that could be lost in the coupling because they would become leaky rays: the maximum ray angle

Appendix

in the source is also limited by the NA, thus all the ray falling on the receiving fiber core will be propagated).

Figure A.1 Sketch drawing of optical fiber. (a) specific configuration of optical probe, (b) relationship in computation.

Corresponding to different b , the computation for the illuminated area of read fiber is divided in three different types of conditions.

1. $d - a < b < \sqrt{d^2 + a^2}$

Appendix

Figure A.2 Condition 1.

From Figure A.2, the illumination area of read fiber is obtained as

$$S = S_a + S_b = \theta_a a^2 - a^2 \sin \theta_a \cos \theta_a + \theta_b b^2 - b^2 \sin \theta_b \cos \theta_b \quad (\text{A1})$$

and

$$\begin{aligned} \sin \theta_a &= \frac{h}{a}, \quad \cos \theta_a = \sqrt{1 - \left(\frac{h}{a}\right)^2}, \quad \sin \theta_b = \frac{h}{b} \\ \cos \theta_b &= \sqrt{1 - \left(\frac{h}{b}\right)^2}, \quad h = \sqrt{a^2 - \left(\frac{d^2 + a^2 - b^2}{2d}\right)^2} \end{aligned} \quad (\text{A2})$$

Combining Eqns. (A1) and (A2) yields

$$\begin{aligned} S &= a^2 \arcsin\left(\frac{h}{a}\right) + b^2 \arcsin\left(\frac{h}{b}\right) - hd \\ &= a^2 \arcsin\left(\frac{\sqrt{a^2 - \left(\frac{d^2 + a^2 - b^2}{2d}\right)^2}}{a}\right) \\ &\quad + b^2 \arcsin\left(\frac{\sqrt{a^2 - \left(\frac{d^2 + a^2 - b^2}{2d}\right)^2}}{b}\right) - \sqrt{a^2 - \left(\frac{d^2 + a^2 - b^2}{2d}\right)^2} d \end{aligned} \quad (\text{A3})$$

Appendix

Thus the reflection coefficient η is

$$\eta = \frac{SI}{\pi b^2 I} = \frac{S}{\pi b^2} \quad (\text{A4})$$

$$2. \sqrt{d^2 + a^2} < b < d + a$$

Figure A.3 Condition 2.

From Figure A.2, the illumination area of read fiber is obtained as

$$S = S_a + S_{ab} + S_b = \theta_a a^2 + h\sqrt{a^2 - h^2} + \theta_b b^2 - b^2 \sin \theta_b \cos \theta_b \quad (\text{A5})$$

and

$$\sin(\pi - \theta_a) = \frac{h}{a}, \quad \sin \theta_b = \frac{h}{b}, \quad \cos \theta_b = \sqrt{1 - \left(\frac{h}{b}\right)^2} \quad (\text{A6})$$

Here the relation between h and other parameters is

$$d = \sqrt{b^2 - h^2} - \sqrt{a^2 - h^2} \quad (\text{A7})$$

Similar with condition one, the reflection coefficient is η

$$\eta = \frac{SI}{\pi b^2 I} = \frac{S}{\pi b^2} \quad (\text{A8})$$

Appendix

Then combining the Eqns. (A5), (A6), (A7) and (A8), the η can be obtained.

3. $d + a < b$

Figure A.4 Condition 3.

In this condition,

$$\eta = \frac{\pi a^2 I}{\pi b^2 I} = \frac{a^2}{b^2} \quad (\text{A9})$$

From Figure A.1(b), b can be presented as

$$b = a + 2 * z * \tan(\arcsin 0.22) \quad (\text{A10})$$

Combining these three conditions, the geometric model is established.

Here, we consider the fibers are bundled without cladding

Appendix

The program is written by using Maple.

Program:

```
> restart;

> assume (a>0, b>0, d>0);

> f:=x->piecewise(b>d-a and b<sqrt(d^2+a^2),
(a^2*arcsin(1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2)/d/a)+b^2*arcsin(1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2)/d/b)-1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2))/Pi/b^2, b<d+a and b>sqrt(d^2+a^2),
(a^2*(Pi-arcsin(1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2)/d/a))+b^2*arcsin(1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2)/d/b)-1/2*(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)^(1/2))/Pi/b^2, b>d+a, a^2/b^2);

f:=x->piecewise(d-a<b and b<sqrt(d^2+a^2),
(a^2*arcsin(1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)/d/a)
+b^2*arcsin(1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)/d/b)
-1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4))/(pi*b^2), b<d+a and sqrt(d^2+a^2)<b,
(a^2*(pi-arcsin(1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)/d/a)
+b^2*arcsin(1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4)/d/b)
-1/2*sqrt(2*a^2*d^2-d^4-b^4+2*b^2*d^2+2*b^2*a^2-a^4))/(pi*b^2), b>d+a, a^2/b^2);
```

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$$-\frac{1}{2}\sqrt{2a^2d^2-d^4-b^4+2b^2d^2+2b^2a^2-a^4}\bigg)/(\pi b^2), d+a < b, \frac{a^2}{b^2}\bigg)$$

```
>plot(subs(b=a+2*z*tan(arcsin(0.22)),
a=100e-6,d=200e-6,f(b)), z=0..6.4e-3);
```

```
>plot(subs(b=a+2*z*tan(arcsin(0.12)),
a=100e-6,d=200e-6,f(b)), z=0..6.5e-3);
```

```
>plot(subs(b=a+2*z*tan(arcsin(0.08)),
a=100e-6,d=200e-6,f(b)), z=0..6.5e-3);
```

Appendix

```
>plot(subs(b=a+2*z*tan(arcsin(0.04)),  
a=100e-6,d=200e-6,f(b)), z=0..6.4e-3);
```

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