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Fabrication and Characterization of NiTi-based Shape Memory Thin Films

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Abstract

NiTi-based shape memory thin films have attracted much attention in recent years as intelligent and functional materials in the rapidly growing field of Micro-Electro-Mechanical-Systems (MEMS) and Bio-MEMS. In this paper the fabrication of NiTi and NiTiHf thin films by a DC magnetron sputtering using simultaneous deposition from elemental targets is reported. The characterization of the films were performed using a differential scanning calorimetry (DSC) and X-ray diffractometry (XRD) to explore transformation temperatures and structure as a function of film composition. The results showed that film composition is a critical issue to control transition temperatures. The proposed technique can be considered as a flexible fabrication method to control precise film composition, which leads to manufacturing of shape memory microactuators in a wide range of applications.

Keywords: NiTi-based thin films; sputtering; shape memory effect.

1 Introduction

In the past decade, considerable commercial and military interest in MEMS has been developed. In the most general form, MEMS is the integration of mechanical elements, sensors, actuators and electronics on a common silicon substrate through the utilization of silicon microfabrication technology. While the electronics are fabricated using integrated circuit (IC) processes, the micromechanical components are fabricated using compatible micromachining processes that selectively etch away parts of the silicon wafer or add new structural layers to form mechanical and electromechanical devices [1]. In these systems, the microelectronics process the information derived from the microsensors which gather information from the environment through measuring mechanical, thermal, biological, chemical, optical and magnetic phenomena and pass the decided information to the microactuators to respond by moving, thereby controlling the environment for some desired outcome or purpose [2].

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A crucial topic for the continued maturation of MEMS technology is the development of suitable actuator materials for practical applications. Various types of microactuators used are based on electrostatics, magnetic, piezoelectric, bimetallic and thermopneumatic phenomena. Although there are a considerable number significant advantages render them suitable for many applications, in particular, many applications require an integrated microactuation mechanism that is compatible with microfabrication, and able to provide a large displacement and a large actuation energy density. None of these microactuator technologies is capable of simultaneously satisfying these requirements.

NiTi shape memory alloy (SMA) thin films have been recognized as a promising and high performance material from which to make MEMS microactuators [3]. Thin film SMAs requires only a small amount thermal mass to heat or cool, thus the cycle (response) time can be reduced substantially and the speed of operation increases significantly. The work output per volume of thin film SMA exceeds that other micro-actuation mechanisms [4]. Applications of shape memory thin films in MEMS also facilitate simplification of mechanisms with flexibility of design and creation of clean, friction free and non-vibration movements.

Transformation temperatures, shape memory behaviors and superelasticty of NiTi films are sensitive to metallurgical factors (e.g. chemical composition and heat treatment), and fabrication conditions (e.g. in sputtering: target power, gas pressure, deposition temperature, etc.) which are accompanied by significant changes in the physical, mechanical, electrical, optical and chemical properties. These changes can be fully made use of design and fabrication of microactuators.

We have used a new method to fabricate binary $Ni_{100-x}Ti_x$ and ternary $Ni_{50}Ti_{50-x}Hf_x$ films by simultaneous deposition from separate pure Ni, Ti, and Hf targets, controlling the film composition by adjusting the ratio of powers supplied to each target. This technique is cost effective (fabrication from pure elements), can easily be optimized under varying sputtering parameters and can be developed to deposit other ternary shape memory thin films for MEMS applications. Results show that the film quality is comparable with bulk material.

2 Experimental procedures

NiTi films were deposited by an ultra high vacuum DC magnetron sputtering onto unheated Si (100) substrates, of dimension 10 mm× 5 mm. The deposition system allowed three magnetrons (target size: 35 mm×55 mm) to deposit two and three elements simultaneously (Ni, Ti, and Hf with a purity of 99.9%) [5]. A substrate support rotated in the horizontal plane during film deposition in order to achieve a uniform film composition. The power to each target was controlled precisely by computer. A base vacuum of $< 10^{-6}$ Pa was achieved after overnight bake-out and subsequent liquid nitrogen cooling of the chamber walls prior to deposition. A constant flow of Ar (99.999%) was controlled with a leak valve during film deposition, and various sputtering gas pressures (~0.6 to 1.2 Pa) were set by throttling the gate valve. A range of Ar sputtering gas pressures between 0.6 and 1.2 Pa was used to explore the effect of working gas pressure on the film microstructure and shape memory properties[6].

The composition of as deposited films was determined by Electron Dispersive X-ray Spectroscopy (EDS) using a JEOL JSM-5800LV operating at 15 keV. The thickness of the films was measured by surface profilometry around 2 μm. As-deposited films were subsequently annealed in a vacuum furnace (base pressure $< 10^{-5}$ Pa) with heating and cooling rates of approximately 50 ºC/min. A Philips PW1060 X-ray diffractometer (XRD) with Cu-Kα (λ=1.54056Å) X-ray source was used to identify the film structure. Transformation temperatures of annealed films were determined by Differential

Scanning Calorimetry, DSC (Q1000, TA instrument, with the minimum required mass = 0.5 mg) at heating and cooling rates of 10 ºC/min.

3 Results and discussion

Important parameters which affect the quality of the films are target power (and hence the deposition rate), Ar gas pressure, substrate-target distance, substrate temperature, and purity of the targets and the deposition environment. The Ar pressure and the target-substrate distance affect the energies of the depositing species and hence film density, structural integrity and stress. At high Ar pressures films often show low density, containing structural defects, whilst at low pressures the structure is denser with fewer defects [7]. Films spanning a range of composition, prepared at high Ar pressures (>1 Pa) had a brittle structure and cracks were observed on the film surface: Figure 1(a) shows the extensive delamination at the NiTi/Si interface and cracks caused by in-plane, biaxial tensile stresses. This figure also reveals a wavy fracture morphology, indicating that the interface cracks have penetrated into the Si substrate near the NiTi/Si interface, implying that the interface toughness is greater than the bulk toughness of the single crystal silicon substrate [8]. Films covering a similar range of composition, prepared at low Ar pressures exhibited a smooth, featureless surface structure: Figure 1(b) shows the SEM picture a film deposited at 0.6 Pa revealed acceptable ductility after removing from Si substrate.

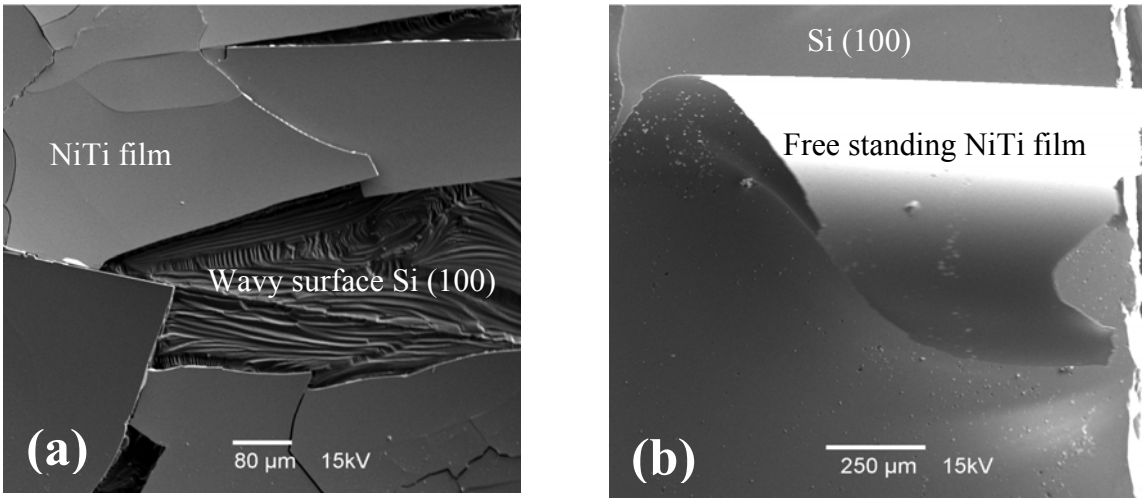

Figure 1: Scanning electron micrographs of films deposited at different Ar gas pressures: (a) plan view of a film deposited at 1.2 Pa, showing severe surface delamination, and (b) a smooth surface film deposited at 0.6 Pa.

The as-deposited films exhibited no crystalline XRD peaks, suggesting an amorphous structure. A broad peak around 2θ= 42° and 40° was observed for NiTi and NiTiHf films respectively and the structure is expanded by introducing Hf into the NiTi binary system [9].

Figure 2(a) shows the room temperature X-ray diffraction patterns of a typical annealed near-equiatomic NiTi. The peak positions show that at room temperature the phase structure of annealed film corresponds to monoclinic martensitic structure. The peaks at 2θ= (38.2˚, 39.1˚, 41.3˚, 44.05˚, 45.1˚, 60.2˚), indexed as 110, 002, -111, 020, 012, and 022 planes, respectively. The peak positions and intensity of the NiTiHf film

are slightly different from those of the NiTi film. The lattice parameters *a*, *b*, *c*, and the monoclinic angle β were calculated for NiTi as 2.89, 4.11, 4.62 Å, and 97.07° respectively, whilst those for NiTiHf with 15.6 at.% Hf were 3.01, 4.07, 4.79 Å and 101.86°, similar to the reported data for (15 at.%) NiTiHf bulk alloy [10]. These results indicate that the Hf addition causes an increase of *a*, *c*, and β, and a decrease of *b*.

Annealed films undergo a martensitic phase transformation when cooled below their transformation temperature. Figure 2(b) shows a typical DSC curves during heating and cooling for a near-equiatomic NiTi which show a one-stage transformation is observed during heating, corresponding to B19′ to B2 transformation. The transformation enthalpy of 22.3 J/g confirms that this peak is related to a direct transformation from martensite to austenite phase: the transformation starts from 71 ºC and finishes at 86 ºC. During cooling, a two-stage transformation is observed, corresponding to transformation between B2, R-phase and B19′ phases. The austenite phase starts to transform to R-phase at around 60 ºC .The R-phase starts to change to the martensite phase at a temperature around 50 ºC and finishes at 30 ºC. This evaluation indicates that the martensite structure is dominant at room temperature, as indicated by XRD, Figure 2(a).

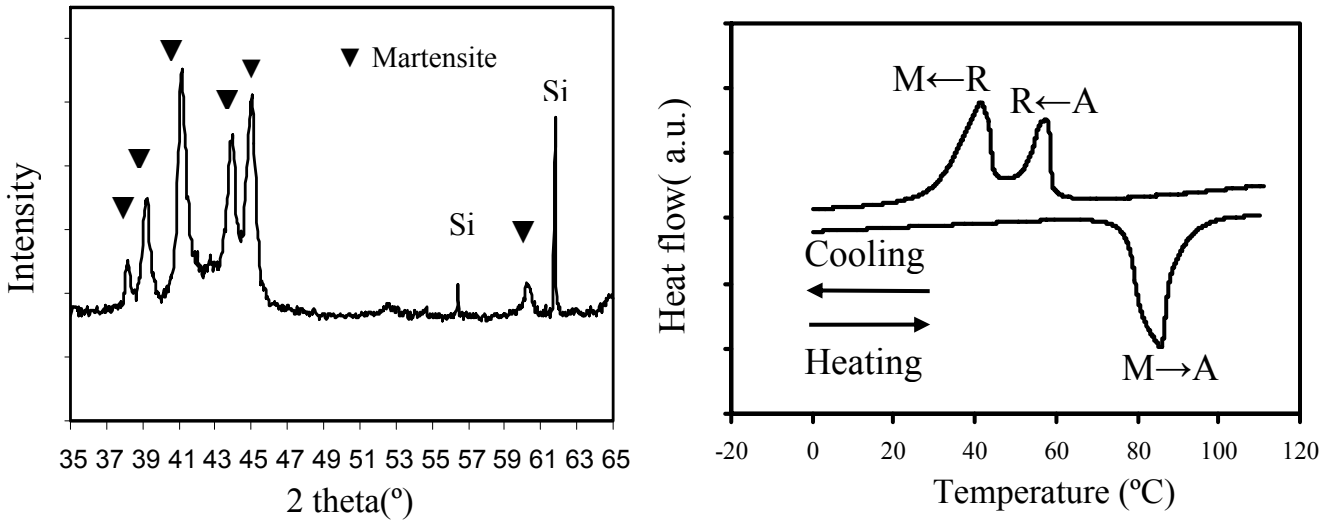

Figure 2: (a) XRD trace and (b) DSC plots of crystallized $Ni_{49.4}Ti_{50.6}$ film

Transformation temperatures were dependent upon film composition. Figure 3 shows the peak phase transformation temperatures (Ap and Mp) as a function of composition for both binary NiTi and ternary NiTiHf thin films [11]. In Figure 3(a) the transformation temperatures are seen to be very sensitive to Ti content: deviation of around 1at.% from near equiatomic composition causes the transformations to take place below room temperature (e.g. a Ti content of 48.8 at.% had a martensitic transformation (Mp) around -50 ºC). Similar results have been reported elsewhere for NiTi bulk material [12]. As can be seen from Figure 3(b), by adding Hf the transformation temperatures are at first decreased (below 5 at.%Hf), but for higher Hf additions, the transformation temperatures are increased considerably. An austenitic transformation temperature (Ap) around 414 ºC is achieved by replacing Ti in NiTiHf with Hf content about 24.4 at.%. For NiTiHf alloy, it has been reported elsewhere that

the transformation temperatures increase with increase in the Hf content and that the highest phase transformation temperature (above 500 ºC) is reached with a Hf content of around 30 at.%[13]. In Table 1 and 2, in addition to transformation temperatures, the energy for each phase transformation is included.

Following deformation, shape memory materials return to their high temperature shape upon heating, and may retain this shape upon cooling (the one way shape memory effect). Alternatively, they may spontaneously return to their low temperature (deformed) configuration upon cooling (two-way shape memory effect). This two-way shape memory effect is often the result of defects, such as dislocations and precipitate interfaces, leading to internal stresses during the deformation, or training treatment. In this case the martensite formed upon cooling is no longer fully self accommodated, but adopts a preferred configuration with regard to the stress distribution. As a consequence there is a shape change on cooling (to form martensite) as well as heating (to form austenite).

Figure 4 illustrates the observed shape memory effect in a free-standing $Ni_{49.5}Ti_{34.9}Hf_{15.6}$ film. After removal from the Si substrate the film was observed to curl up, due to strains resulting from the deposition and annealing treatments. To illustrate qualitatively the shape memory effect, the film (in the martensitic state) was deformed into a flat shape at room temperature (Fig.4 a). By warming to about 200 ºC it returned to its curled shape (Fig. 4 b) and remained curled when cooled back to room temperature, showing one-way shape memory behavior.

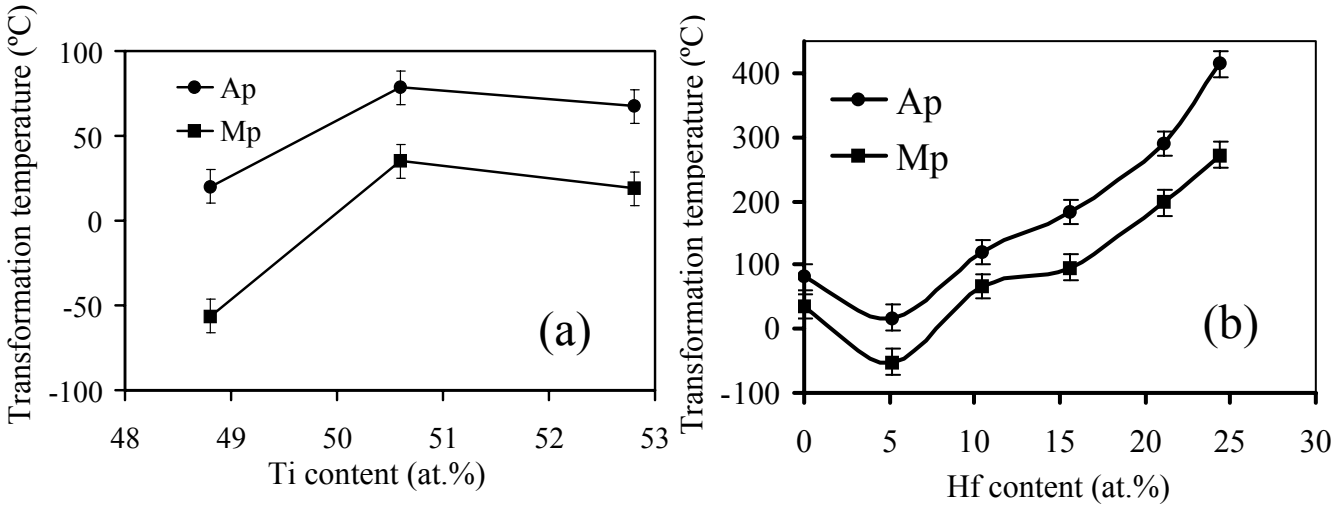

Figure 3: Transformation temperature as a function of composition: (a) $Ni_{100-x}Ti_x$ binary, and (b) $Ni_{50}Ti_{50-x}Hf_x$ (Mp and Ap refer to exothermic and endothermic peak in DSC graph)

Table1: Phase transformation temperatures and transformation enthalpy as a function of film composition (p refers to the maximum or minimum in the heat flow peak).

Film composition	**Heating**				**Cooling**			
	Rp (˚C)	$\Delta H_{M\rightarrow R}$ (J/g)	Ap (˚C)	$\Delta H_{M\rightarrow A}$ (J/g)	Rp (˚C)	$\Delta H_{A\rightarrow R}$ (J/g)	Mp (˚C)	$\Delta H_{R\rightarrow M}$ (J/g)
Ti-rich ($Ti_{52.8}Ni_{47.2}$)			71	17.3	57	5.8	19	4.5
NiTi ($Ti_{50.6}Ni_{49.4}$)			78	22.3	52	5.9	35	14.3
Ni-rich ($Ti_{48.8}Ni_{51.2}$)	20	5.28	35	1.4*	26	4.1	-56	5.9

* In Ni-rich film this number is corresponded to $\Delta H_{R\rightarrow A}$

Table 2: Transformation temperatures and enthalpies of NiTiHf thin films as a function of Hf content (p refers to the maximum or minimum in the heat flow peak).

Hf (at%)	**Heating**		**Cooling**			
	Ap (˚C)	$\Delta H_{M\rightarrow A}$ (J/g)	Rp (˚C)	$\Delta H_{A\rightarrow R}$ (J/g)	Mp (˚C)	$\Delta H_{R\rightarrow M}$ (J/g)
0	81	22.3	52	5.9	35	14.3
5.2	17.3	4.9	7.2	0.8	-51.6	3.6
10.4	120	12.2	101	1.3	67	9.2
15.6	183	11.0	114.2	0. 9	96.02	8.7
21.1	290	14.9			198.8	10.8†
24.4	414	8.3			272	6.1†
28.7	-	-			-	-

†The enthalpy of transformation from A→M

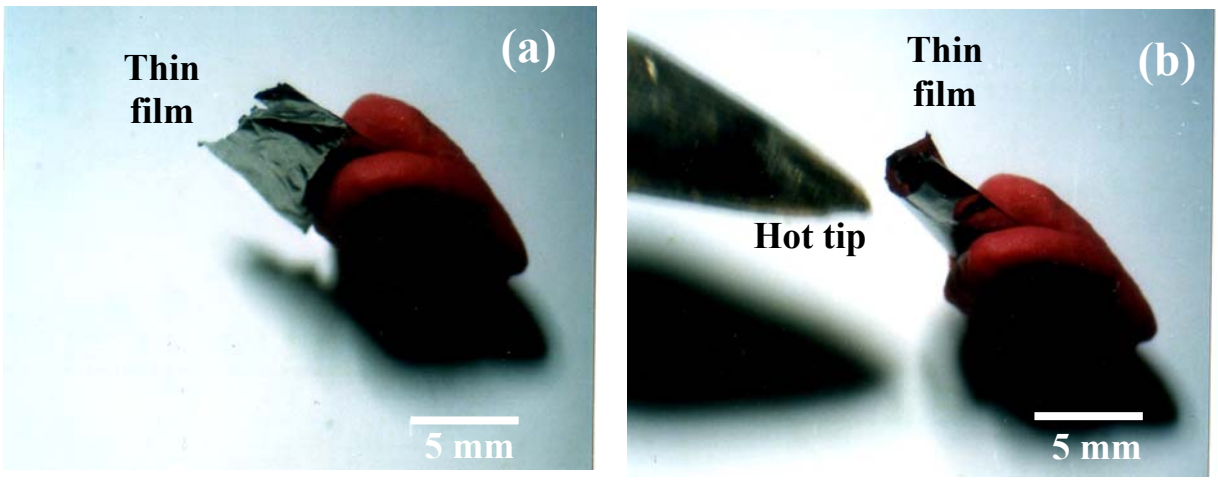

Figure 4: Free-standing $Ni_{49.5}Ti_{34.9}Hf_{15.6}$ film exhibiting the one way shape memory effect: (a) RT and b (>200ºC).

Conclusions

A technique was used to deposit binary and ternary NiTi-based shape memory thin films using simultaneous sputter deposition from separate elemental targets. Characterization of the films was carried out using XRD and DSC. Transformation temperatures were shown to be as a function of film composition: in NiTi films the transformation temperature was sensitive to composition around the equiatomic Ni/Ti ratio, and Hf additions led to austenitic transformation temperatures (Ap) up to 414 ºC at 24.4 at.% Hf. The advantages of this method are the ability to control the film composition precisely with any chosen sputtering parameters, and the lack of a requirement to fabricate binary, or ternary, alloy targets.

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