1 Overview of sputter-deposited TiNi based thin films

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Abstract

The motivation for fabricating sputter-deposited TiNi base shape memory alloy (SMA) thin films originates from the great demand for the development of powerful microactuators, because actuation output (force and displacement) per unit volume of thin film SMA exceeds those of other microactuation mechanisms. Stable shape memory effect and superelasticity, which are equivalent to those of bulk alloys, have been achieved in sputter-deposited TiNi thin films. Narrow transformation temperature hysteresis and high transformation temperatures were also achieved in TiNiCu and TiNi (Pd or Hf) thin films, respectively. In the meantime, unique microstructures consisting of non-equilibrium compositions and nanoscale precipitates in the matrix have been found in Ti-rich TiNi thin films which were fabricated from an amorphous condition by annealing at a very low temperature. Several micromachining processes have been proposed to fabricate the prototypes of microactuators utilizing TiNi thin films. This chapter will review the recent development of the above-mentioned topics relating to sputter-deposited TiNi based thin films. Some critical issues and problems in the development of TiNi thin films are discussed, including preparation and characterization considerations, residual stress and adhesion, frequency improvement, fatigue and stability, and thermomechanical modeling. Recent development in the microdevices based on SMA thin films is also summarized.

1.1 Introduction

A shape memory alloy (SMA) is a metal that can “remember” its geometry, i.e., after a piece of SMA has been deformed from its original shape, it regains its original geometry by itself during heating (shape memory effect) or simply during unloading at a higher ambient temperature (superelasticity). These extraordinary
properties are due to a temperature-dependent martensitic phase transformation from a low-symmetry (martensite) to a highly symmetric crystallographic structure (austenite) upon cooling and a reverse martensitic transformation in the opposite direction upon heating. Shape memory effects have been found in many materials, such as metals, ceramics and polymers. Among all these materials, TiNi based alloys have been extensively studied and found many commercial applications [1, 2, 3, 4]. For microelectromechanical system (MEMS) applications, thin film based SMAs possess many desirable properties, such as high power density (up to 10 J/cm\(^3\)), the ability to recover large transformation stress and strain upon heating, the shape memory effect, pseudoelasticity (or superelasticity) and biocompatibility [5, 6, 7, 8]. The work output per unit volume of SMA exceeds those of other micro-actuation mechanisms. The phase transformation in SMA thin film is also accompanied by significant changes in the mechanical, physical, chemical, electrical and optical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, electrical resistivity, thermal conductivity, thermal expansion coefficient, surface roughness, vapor permeability and dielectric constant, etc. [9, 10]. These changes can be fully utilized in the design and fabrication of microsensors and microactuators [11, 12].

Since the early 1990s, several trials have been made in order to fabricate TiNi thin films using a sputter-deposition method [13]. Some of these results showed that conventional micromachining processes are applicable for making microstructures consisting of a silicon substrate and a TiNi thin film. If the films contain micro-defects, which are characteristic in sputter-deposited films, and other elements such as oxygen and hydrogen, they will become brittle. Application of stress to such films will cause them to fracture. Without information about the characteristics of materials, any trial for an improvement in the sputtering process will be ineffective. Therefore, it was very important both to establish fabrication methods for high quality thin films in enduring high stress applications and to develop mechanical testing methods to evaluate the shape memory characteristics of thin films.

The mechanical behavior of TiNi thin films can be characterized by damping measurement, tensile tests and thermomechanical tests [10]. The crystal structures of the austenite, martensite (M) and R phases were also determined to be B2, monoclinic and rhombohedral, respectively. The transformation and shape memory characteristics of TiNi thin films were shown to depend strongly on metallurgical factors and sputtering conditions. The former includes alloy composition, annealing temperature, aging temperature and time, while the latter includes Ar pressure, sputtering power, substrate temperature and so forth [14, 15]. Conventional mechanical properties such as yield stress, ductility and fracture stress have been investigated by measuring stress-strain curves at various temperatures. The maximum elongation amounted to more than 40% in an equiatomic TiNi thin film. The yield and fracture stresses of the martensite can be as high as 600 MPa and 800 MPa, respectively [6]. These mechanical properties provide good evidence to indicate that sputter-deposited TiNi thin films possess sufficient ductility and stable shape memory characteristics for practical applications.
The stability of shape memory behavior associated with both the R-phase and martensitic transformations against cyclic deformation was investigated in TiNi thin films [6]. The R-phase transformation characteristics showed perfect stability against cyclic deformation because of the small shape change which caused no slip deformation to occur, while the martensitic transformation temperatures increased and temperature hysteresis decreased during cycling because of the formation of internal stress which is due to the introduction of dislocations. However, no slip deformation occurred during cyclic deformation under 100 MPa so that perfect stability of the shape memory effect was also observed in the martensitic transformation. Besides, by increasing the number of cycles under higher stresses, the shape memory characteristics associated with the martensitic transformation were stabilized by a training effect.

TiNi thin films with Ni-rich composition, which were age-treated at intermediate temperatures, showed a strong aging effect on transformation temperatures and shape memory behavior [16]. The aging-treatment induced fine Ti$_3$Ni$_4$ precipitates, which are metastable. The size and density of the precipitates depend on aging temperature and time, hence the shape memory characteristics varied with changing aging conditions. The precipitates with a lenticular shape are formed on {111} planes of the B2 parent phase and have their intrinsic stress fields. The stress fields cancel each other by forming the precipitates on all four {111} planes when the film is aged without any applied stress. If the film is aged under elastic constraint, the precipitates are formed preferentially on one of the {111} planes, causing a specific stress field to be created. The stress field causes two-way shape memory behavior that is mainly associated with the appearance of the R-phase transformation. Since the critical stress for slip is increased by the Ti$_3$Ni$_4$ precipitates, stable superelasticity is achieved as well as a stable shape memory effect in Ni-rich TiNi thin films [17].

Bulk Ti-rich TiNi alloys are characterized by constant and high transformation temperatures. However, when sputter-deposited amorphous Ti-rich TiNi films were subjected to heat-treatment at various temperatures, they showed a strong dependence of the transformation temperatures on the heat-treatment temperature. The heat-treatment dependent characteristics originate from the formation of non-equilibrium Ti-rich plate precipitates that are several atomic layers in thickness on {100} planes [18]. Evolution of the internal structure as a function of heat-treatment temperature was systematically clarified [15], i.e., amorphous below a crystallization temperature, Ti-rich plate precipitates at temperatures a little higher than the crystallization temperature, a mixture of Ti-rich plate precipitates and equilibrium Ti$_2$Ni precipitates at intermediate temperatures, and Ti$_2$Ni precipitates at sufficiently high temperatures. The Ti-rich plate precipitates were found to be the origin of the stability of shape memory behavior.

If a large recovery strain is required for a microactuator, we need to use the martensitic transformation, which has a larger temperature hysteresis of about 30 K in TiNi binary alloys. In order to improve the response, it is necessary to decrease the temperature hysteresis. Addition of Cu is effective in decreasing the transformation...
temperature hysteresis without decreasing transformation temperatures themselves. TiNiCu thin films with Cu-contents varying from 0 to 18 at% were investigated [19, 20, 21, 22]. The martensitic transformation temperatures of all the thin films were around 323 K, decreasing only slightly with increasing Cu-content in the range below 9.5 at%, while slightly increasing in the range beyond 9.5 at%. The hysteresis associated with the transformation showed a strong dependence on Cu-content, i.e., it decreased from 27 K to 10 K with increasing Cu-content from 0 to 9.5 at%. In the 9.5 at% Cu thin film, a two-stage transformation appeared and it was determined as B2→orthorhombic(O)→M-phase by X-ray diffractometry. A perfect two-stage shape memory effect was observed corresponding to these transformations. The addition of Cu caused the maximum recovery strain to decrease from 3.9 % to 1.1 % and the critical stress for slip to increase greatly from 55 MPa to 350 MPa with increasing Cu-content up to 18 at%.

Additions of third elements, such as Pd, Au, Pt, Ag, Hf, etc., are effective for increasing transformation temperatures. In the case of sputter-deposited thin films, Pd and Hf have been added as a third element for this purpose [23]. However, Hf increases transformation temperature hysteresis, while Pd is effective in decreasing the transformation temperature hysteresis in addition to increasing transformation temperatures [24, 25]. For this reason, Pd addition is more promising for applications. The TiNiPd ternary alloy thin films basically show the M-phase and O-phase transformations but not the R-phase transformation in a narrow Pd-content region. The addition of Pd is effective in increasing the O-phase transformation temperatures, e.g., the $O_s$ (O-phase transformation start temperature) of a 21.8 at% Pd thin film is higher than the $M_s$ (M-phase transformation start temperature) of an equiatomic TiNi binary alloy thin film by about 50 K. It was found that Pd addition is also effective in decreasing transformation temperature hysteresis, e.g., 16 K in a thin film with 22 at% Pd content. The achievement of the small transformation temperature hysteresis in TiNiCu thin films or the high transformation temperatures in TiNiPd thin films is promising for achieving quick movement in microactuators made of TiNi base shape memory thin films.

Since TiNi films can provide large forces for actuation and large displacement, most applications of TiNi films in MEMS are focused on microactuators [26, 27], such as cantilevers, diaphragms, micropumps, microvalves, microgrippers, springs, microspacers, micropositioners, and microrappers, mirror actuators, etc., TiNi thin films are sensitive to environmental changes, such as thermal, stress, magnetic and electrical fields. Thus, they should be also ideal for applications in microsensors.

The main potential problems associated with TiNi thin film in MEMS applications include: (1) low energy efficiency, low dynamic response speed and large hysteresis; (2) non-linearity and complex thermomechanical behavior and ineffectiveness for precise and complex motion control and force tracking; (3) potential degradation and fatigue problems. Even with the above disadvantages, the TiNi based thin film is still considered as a core technology for actuation...
of some MEMS devices where a large force and stroke are essential in conditions of low duty cycles or intermittent operation, and in an extreme environment, such as radioactive, space, biological and corrosive conditions.

This chapter reviews the recent development of sputter-deposited TiNi base SMA thin films and fabrication of microsystems [6]. Successful implementation of the TiNi microactuators requires a good understanding of the relationship among processing, microstructure and properties of TiNi films. The required enabling technologies for TiNi films include [10]:

- low-cost, reliable and MEMS-compatible deposition methods with precise control of film composition and quality;
- reliable and precise characterization technologies for various properties (such as shape memory effect, superelasticity and mechanical properties, etc.);
- an appropriate post-deposition annealing (for film crystallization) or aging process compatible with the MEMS process;
- precise etching and patterning of TiNi film compatible with the MEMS process and the possibility of nano-size TiNi structures and actuators;
- prediction and modeling of the non-linear behavior of TiNi films as well as design and simulation of TiNi thin film microactuators.

Some basic requirements for TiNi films in MEMS applications are listed as follows [10]:

- large recovery stress and strain;
- low residual stress to prevent undesired deformation of MEMS structures;
- high actuation speed and fast response with precise control of deformation and strain;
- good adhesion on substrate (free of cracking, delamination and spallation);
- durable and reliable shape memory effects;
- wide range choice of working temperatures (from sub-zero to several hundred degrees C);
- good resistance to surface wear and corrosion;
- biocompatibility and good corrosion resistance (for instance in bio-MEMS applications).

1.2 Fabrication and characterization methods

1.2.1 Film deposition

TiNi based films are the most frequently used thin film SMA materials and they are typically prepared using a sputtering method. Laser ablation, ion beam deposition, arc plasma ion plating, plasma spray and flash evaporation were also reported but with some intrinsic problems, such as non-uniformity in film thickness and composition, low deposition rate, and/or non-batch processing, incompatibility with MEMS process, etc. Figure 1.1 shows a schematic drawing of a
most common radio frequency (RF) magnetron sputtering apparatus [6]. Ar ions are accelerated into the target to sputter Ti and Ni atoms, which are deposited onto the substrate to form a TiNi film. Transformation temperatures, shape memory behaviors and superelasticity of the sputtered TiNi films are sensitive to metallurgical factors (alloy composition, contamination, thermomechanical treatment, annealing and aging process, etc.), sputtering conditions (co-sputtering with multi-targets, target power, gas pressure, target-to-substrate distance, deposition temperature, substrate bias, etc.), and the application conditions (loading conditions, ambient temperature and environment, heat dissipation, heating/cooling rate, strain rate, etc.) [28]. Systematic studies on the detailed effects of all the above parameters are necessary. The sensitivity of TiNi films to all these factors seems an intrinsic disadvantage but, at the same time, this sensitivity provides tremendous flexibility in engineering a combination of properties for intended applications.

Precise control of the Ti/Ni ratio in TiNi films is of essential importance, as has been documented since TiNi film studies started more than a decade ago. The intrinsic problems associated with sputtering of TiNi films include the difference in
sputtering yields of titanium and nickel at a given sputtering power density, geometrical composition uniformity over the substrate and along the cross-sectional thickness of the coating, as well as wear, erosion and roughening of targets during sputtering [29]. To combat these problems, methods of co-sputtering of the TiNi target with another Ti target, or using two separate single element (Ti and Ni) targets, or adding titanium plates on a TiNi target are widely used [30]. Substrate rotation, optimal configuration of target position and precise control of sputtering conditions, etc. are also helpful. Varying the target temperature can produce a compositional modification: sputtering with a heated TiNi target can limit the loss of Ti, thus improving the uniformity of film properties [31, 32]. Good performance TiNi films can also be obtained by post-annealing of a multi-layer of Ti/Ni [33]. Since contamination is a big problem for good mechanical properties of sputtered TiNi films, it is important to limit the impurities, typically oxygen and carbon, to prevent the brittleness, deterioration or even loss of the shape memory effect. For this reason, the purity of the Ar gas and targets is essential, and the base vacuum of the main chamber should be as high as possible (usually lower than $10^{-7}$ torr). Pre-sputtering cleaning of targets before deposition effectively removes the surface oxides on targets, which thus constitutes one of the important steps in ensuring film purity. In order to deposit films without columnar structure (thus with good mechanical properties), a low processing pressure of Ar gas (0.5 to 5 mtorr) is essential. Application of a bias voltage during sputtering could modify the film microstructure, texture and stress, and is thus also important, but few studies have been reported on this topic so far. More information of this topic can be found in Chapter 3.

Important sputtering factors which will affect the quality of the films are r.f. power, Ar gas pressure, substrate–target distance, substrate temperature and alloy composition of the target used. Figure 1.2 shows the fracture surface of as-deposited thin films. The film prepared at a low Ar gas pressure exhibits a flat and featureless structure, while films prepared at high Ar gas pressure exhibit a columnar structure. This columnar structure suggests that the films are porous. This structure seems to be caused by the restricted mobility of deposited atoms on the surface of the growing film. A high Ar gas pressure is likely to decrease the energy of the sputtered atoms by collision with Ar ions, resulting in a decrease in their surface diffusion. Furthermore, under a high Ar gas pressure, Ar ions adsorbed on the film surface can interfere with the surface diffusion of sputtered Ti and Ni atoms. Of the films prepared at a high Ar gas pressure, the fracture surface of the film prepared at an r.f. power of 600 W seems to be less porous than the other films.

Depending on processing conditions, TiNi films can be deposited at room temperature or high temperatures. TiNi films sputtered at room temperature are usually amorphous, thus post-sputtering annealing (usually above 450°C) is a must because the shape memory effect only occurs in materials of crystalline form. However, martensitic transformation and superelasticity of TiNi films are sensitive to post-annealing and/or aging temperature and duration [34, 35], thus post-sputtering annealing should be handled with care. It is suggested that the lowest possible
annealing or aging temperature be used in a bid to conserve thermal processing budgets and more importantly minimize the reactions between film and substrate [36]. A long-term post-annealing and aging process should be avoided since it could trigger dramatic changes in film microstructure (i.e., precipitation), mechanical properties and shape memory effects. Films deposited at a relatively high temperature (about 400°C) are crystallized in situ, thus there is no need for post-annealing. Films can be deposited at relatively high temperatures (400 to 500°C) during sputtering to form the crystallized phase, then at a relatively lower temperature (about 300°C) to maintain a crystalline growth during the later sputtering process. Films can also be deposited at a low temperature (about 300°C) to get partial crystallization, then annealed at a higher temperature (500°C) for a short time to promote further crystallization.

Recently a localized laser annealing method was used for TiNi films [37], where only certain areas of a film are annealed by a laser beam to exhibit the shape memory effect, and the other non-annealed areas remain amorphous, thus acting as a pullback spring during the cooling process. This method, discussed in detail in Chapter 9, opens a new way for fabrication of microdevices [38]. The advantages of the localized laser annealing process include: (1) precision in selection of the areas to be annealed, down to a micron scale; (2) non-contact and high efficiency; (3) freedom from restrictions on design and processing; (4) ease in integration in MEMS processes; (4) ease in cutting of the final structure using the laser beam.

### Table 1.2

<table>
<thead>
<tr>
<th>RF W</th>
<th>0.67 Pa</th>
<th>6.7 Pa</th>
<th>13.3 Pa</th>
</tr>
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<tbody>
<tr>
<td>600 W</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
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<tr>
<td>400 W</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>200 W</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td><img src="image9.png" alt="Image" /></td>
</tr>
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Figure 1.2: Cross-section of TiNi thin films formed under various sputtering conditions [Miyazaki & Ishida, 1999 [6], with permission from Elsevier].
However, still some problems exist that include: (1) Energy loss. The TiNi film surface is usually smooth and reflection loss of laser beam energy is a big problem. Possible solutions include selection of an excimer laser beam, choice of suitable parameters (e.g. wavelength of the laser) and surface treatment or roughening of the film surface to improve laser adsorption. (2) Difficulty in duration control. Crystallization of the film structure is a thermodynamic process, and it is necessary to maintain sufficient treatment time for crystallization to complete. However, over-exposure easily causes surface damage of the thin films. (3) Need of a protection environment such as Ar gas or vacuum condition. This adds complexity and cost to the process.

1.2.2 TiNi film characterization

For freestanding TiNi films, conventional methods, such as differential scanning calorimetry (DSC) and tensile tests (stress–strain curves) are quite applicable to characterize the shape memory effects. The stress–strain and stress–temperature responses of freestanding films are commonly evaluated using tensile tests \[39, 40\]. Results show that the stress–strain–temperature relationship, elongation, fracture stress and yield stress are at least comparable to (if not better than) those of bulk materials, because of the grain size effect (micron or submicron size in thin films as compared with tens of microns for bulk materials) \[41, 42\]. The difficulties in tensile testing of TiNi thin films include: (1) to obtain free-standing films without pre-deformation; and (2) to clamp the films tightly on tester grips. For MEMS applications, the TiNi films are usually deposited on Si or other substrates. One of the important issues in characterization of TiNi films for MEMS applications is how to correctly evaluate the shape memory effects and mechanical properties of the constrained thin films on substrates. For this purpose, curvature and electrical resistivity measurements are widely used \[43\]. Some new methods based on MEMS techniques \[44\], such as the bulge test \[45\], TiNi/Si diaphragm \[46, 47\], cantilever bending or damping \[48\] are more appropriate for microactuator applications, which are compatible with small dimensions and high sensitivities. Nano-indentation testing with or without changes of temperature could reveal the different elastic and plastic deformation behaviors of austenite and martensite, which is also promising for characterization of superelasticity, phase transformation, the shape memory effect and mechanical properties of the constrained thin films \[49, 50, 51\]. Indentation of TiNi based films is strongly dependent on the materials’ resistance to dislocation. Since the dislocation is closely related to the fatigue properties of films, indentation for material characterization is particularly useful for MEMS applications, where optimization of fatigue performance is critical.

Recently, an AFM based in situ testing method has been applied to characterize the phase transformation behavior of constrained films \[10\]. Figure 1.3 shows two micrographs of the AFM surface morphology of TiNi films on an Si substrate at a low temperature (martensite) and a high temperature (austenite), respectively. The surface roughness of the martensite phase is much higher than that of the
austenite. With the change of temperature, the surface roughness changes drastically during transformation between the martensite and the austenite phases, thus clearly revealing the occurrence of phase transformation. The advantages of this method are its non-destructive nature and applicability to very small size films (down to nanometers). Moreover, the changes in optical reflection caused by the changes in the surface roughness and reflective index can also be used to characterize the transformation behaviors of TiNi films. The details relating to this issue can be found in Chapter 19.

There are usually some discrepancies in transformation temperatures obtained from different characterization methods [52]. The possible reasons include: (1) the phase transformation and mechanical behaviors of constrained TiNi films could be different from those of freestanding films, due to the substrate effect, residual stress, strain rate effect, stress gradient effect and temperature gradient effect; (2) the intrinsic nature of the testing method (thus the changes in physical properties will not start at exactly the same temperatures); (3) differences in testing conditions, for example, heating/cooling rate; (4) non-uniformity of the film composition over the whole substrate and along the cross-sectional...

Figure 1.3 AFM surface morphologies of TiNiCu films: (a) low temperature in the martensite state and (b) high temperature in the austenite state [Fu [2004] [10], with permission from Elsevier].