Available online at www.sciencedirect.com

SCIENCE DIRECT®

Sensors and Actuators A 112 (2004) 395–408

SENSORS AND ACTUATORS A PHYSICAL

www.elsevier.com/locate/sna

TiNi-based thin films in MEMS applications: a review

Yongqing Fu [a,b,*], Hejun Du [a,b], Weimin Huang [a], Sam Zhang [a], Min Hu [a]

[a] *School of Mechanical and Production Engineering, Nanyang Technological University, Singapore 639798, Singapore*
[b] *Advanced Materials for Micro and Nano Systems Programme, Singapore–Massachusetts Institute Technology (MIT) Alliance, 4 Engineering Drive 3, Singapore 117576, Singapore*

Received 12 February 2004; received in revised form 12 February 2004; accepted 17 February 2004

Abstract

TiNi thin films have attracted much attention in recent years as intelligent and functional materials because of their unique properties. TiNi thin film based micro-actuators will become the actuator of choice in many aspects in the rapidly growing field of micro-electro-mechanical systems (MEMSs). In this review paper, 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, modeling of behavior as well as functionally graded or composite thin films. Comparison is made of TiNi SMA micro-actuation with other micro-actuation methods. Different types of TiNi thin film based microdevices, such as microgrippers, microswitches, microvalves and pumps, microsensors, etc. are also described and discussed.

Keywords: Shape-memory; TiNi; Thin films; MEMS

1. Introduction

Shape-memory alloys (SMAs) possess an array of desirable properties: high power to weight (or force to volume) ratio, thus the ability to recover large transformation stress and strain upon heating and cooling, peudoelasticity (or superelasticity), high damping capacity, good chemical resistance and biocompatibility [1,2], just to name a few. This attracted much attention to the research of SMAs as smart (or intelligent) and functional materials [3]. More recently, thin film SMA has been recognized as a promising and high performance material in the field of micro-electro-mechanical system (MEMS) applications, since it can be patterned with standard lithography techniques and fabricated in batch process [4–8]. Thin film SMA has only a small amount of thermal mass to heat or cool, thus the cycle (response) time can be reduced substantially and the speed of operation may be increased significantly. The work output per volume of thin film SMA exceeds that of other micro-actuation mechanisms. Application of SMA films in MEMS also facilitate simplification of mechanisms with flexibility of design and creation of clean, friction free and non-vibration movement. The phase transformation in SMA thin film is accompanied by significant changes in the mechanical, physical, chemical, electrical and optical properties, such as yield stress, elastic modulus, hardness, damping, shape recovery, electrical resistivity, thermal conductivity, thermal expansion coefficient, surface roughness, vapor permeability and dielectric constant, etc. These changes can be fully made use of the design and fabrication of microsensors and micro-actuators. However, due to the lack of full understanding of the thin film SMAs together with the controlling of the deposition parameters, they have not received as much attention in the MEMS technology as other micro-actuator technologies.

In this paper, recent advances and development for TiNi SMA thin films were reviewed. Different types of MEMS applications (such as microgrippers, micropumps, micromirror, etc.) were reviewed and the prospects for future advances in fabrication process and device development were discussed.

2. MEMS requirements for TiNi-based thin films

Successful implementation of TiNi micro-actuators requires a good understanding of the relationship among processing, microstructure and properties of TiNi films. The enabling technologies for TiNi films required include:

---

* Corresponding author. Tel.: +65-67904264; fax: +65-67911859.
E-mail address: myqfu@ntu.edu.sg (Y. Fu).

0924-4247/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.sna.2004.02.019

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

Some basic requirements for TiNi films used in MEMS applications are listed as follows:

1. low residual stress to prevent deformation of MEMS structure;
2. high actuation speed and fast response with precise control of deformation and strain;
3. good adhesion on substrate (free of cracking, delamination and spallation);
4. durable and reliable shape memory effects;
5. wide range choice of working temperatures (from below zero to several hundred degree Celsius);
6. good resistance to surface wear and corrosion;
7. biocompatible and good corrosion resistance (in case of application in bio-MEMS).

3. TiNi thin film processing and characterization

3.1. Sputtering deposition of high quality TiNi films

TiNi-based films are the most frequently used thin film SMA materials and they are typically prepared using sputtering method [4,5]. Laser ablation, ion beam deposition, arc plasma ion plating, plasma spray and flash evaporation were also reported but with some intrinsic problems, such as non-uniformity in film thickness and composition, low deposition rate, or non-batch processing, incompatibility with MEMS process, etc. Transformation temperatures, shape memory behaviors and superelasticity of the sputtered TiNi films are sensitive to metallurgical factors (alloy composition, contamination, thermo-mechanical 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.) [4,5,9]. Systematic studies on the detailed effects of all the above parameters are necessary. The sensitivity of TiNi films to all these factors is seemingly 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 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 substrate and along cross-section thickness of the coating, as well as wear, erosion and roughening of targets during sputtering [10]. To combat these problems, co-sputtering of TiNi target with another Ti target, or using two separate single element (Ti and Ni) targets [4,10,12], or adding titanium plates on TiNi target are widely used [5,11,12]. Substrate rotation, good configuration of target position and precise control of sputtering conditions, etc. are also helpful. Varying the target temperature can also produce the compositional modification: sputtering the heated TiNi target can limit the loss of Ti, thus improving the uniformity of film properties [13,14]. Since contamination is a big problem to good mechanical properties of the sputtered TiNi films, it is important to limit the impurities, typically oxygen and carbon, to prevent the brittleness, deterioration or even loss of shape memory effect. For this reason, the purity of 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, 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 (0.5–5 mTorr) is essential [5]. Application of bias voltage during sputtering could modify the film microstructure, texture and stress, thus is also important, but few studies have been reported on this topic so far.

3.2. Post-sputtering annealing

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 higher than 450 °C) is a must because SMA effect only occurs in materials of crystalline form. However, Martensite transformation and superelasticity of TiNi films are sensitive to post-annealing and/or aging temperature and duration [15,16], 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 [17]. 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) is crystallized in situ, thus there is no need for post-annealing. Films can be deposited at relatively high temperatures (400–500 °C) at initial sputtering to form 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 [4].

Recently, a localized laser annealing method was studied for TiNi films in our group [18], where only certain areas of the film are annealed by laser beam to exhibit shape memory effect, and the other non-annealed areas remain amorphous, thus acting as a pullback spring during cooling process. This method opens a new way for fabrication of microdevices [19]. The advantages of the localized laser annealing process include: (1) precision in selection of the areas to be annealed, as small as micrometer meter; (2) non-contact and efficiency; (3) free of restrictions on design and processing; (4) ease in integration in MEMS processes; (5) ease in cutting of the final structure using the laser beam. However, still some problems exist that include: (1) energy loss. TiNi film surface is usually smooth and reflection loss of laser beam energy is a big problem. Possible solutions include selection of excimer laser beam, choice of suitable parameters (e.g. wavelength of laser) and surface treatment or roughening of film surface to improve laser adsorption. (2) Difficulty in duration control. Crystallization of 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 protection environment such as Ar gas or vacuum condition, which adds complexity and cost to the process.

3.3. *Characterization of TiNi films*

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 strain–temperature responses of freestanding films are commonly evaluated using tensile tests [5,20,21]. Results show that the stress–strain–temperature relationship, the 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 (micrometer or sub-micrometer size in thin films as compared with tens of micrometers for bulk materials) [22–24]. The difficulties in tensile testing of TiNi thin films include: (1) to obtain free-standing films without pre-deformation; and (2) to clamp tightly the films on a tester grips. For MEMS applications, the TiNi films are usually deposited on Si or other related substrates. One of the important issues in characterization of the 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 (ER) measurements are widely used [4,25]. Some new methods based on MEMS testing [26], such as bulge testing [27], TiNi/Si diaphragm [28,29], cantilever bending or damping [30] are more appropriate for micro-actuator 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, thus is also promising for characterization of superelasicity, phase transformation, shape memory effect and mechanical properties of the constrained thin films [31–33]. Also indentation of Ti–Ni based films is strongly dependent on the materials resistance to dislocation, and dislocation is closely related to fatigue properties of films, thus indentation characterization is particularly useful for MEMS applications, where optimization of fatigue performance is critical.

In our group, an AFM based in-situ testing method have recently been applied to characterize the phase transformation behavior of the constrained films. Fig. 1 shows two micrographs of AFM surface morphology of TiNi films on Si at a low temperature (martensite) and a high temperature (austenite), respectively. The surface roughness of the martesnite phase is much higher than that of the austenite. With the change of temperature, the surface roughness values change drastically when transforming between the marteniste and the austenite phases, thus clearly reveal the occurrence of phase transformation (see Fig. 2). The advantages of this method are its nondestructive nature and applicability to very small size films (down to nanometers). Moreover, the optical reflection changes caused by the changes in the surface roughness and reflective index can also be used to characterize the transformation behaviors of TiNi films.

There are usually some discrepancies in transformation temperatures obtained from different characterization methods [4,34]. The possible reasons include: (1) the phase transformation and mechanical behaviors of the constrained TiNi films could be different from those of free-standing films, due to substrate effect, residual stress, strain rate effect, stress gradient effect and temperature gradient effect; (2) the intrinsic nature of testing method (thus the response of 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 film composition over whole substrate and along cross-section thickness of coating. Therefore, it is necessary to identify whether the application is based on the free-standing film or constrained film/substrate system, so that a suitable method can be chosen.

In film characterization, there are still many important issues unresolved: (1) Nucleation and growth mechanisms of TiNi thin films and substrate effects; (2) effects of precipitation [35], point defects and dislocations; (3) grain size effect, nano-grain and nanocrystalline structure on shape memory effect and phase transformation [36]. The refinement of grain size can strongly modify the struc-

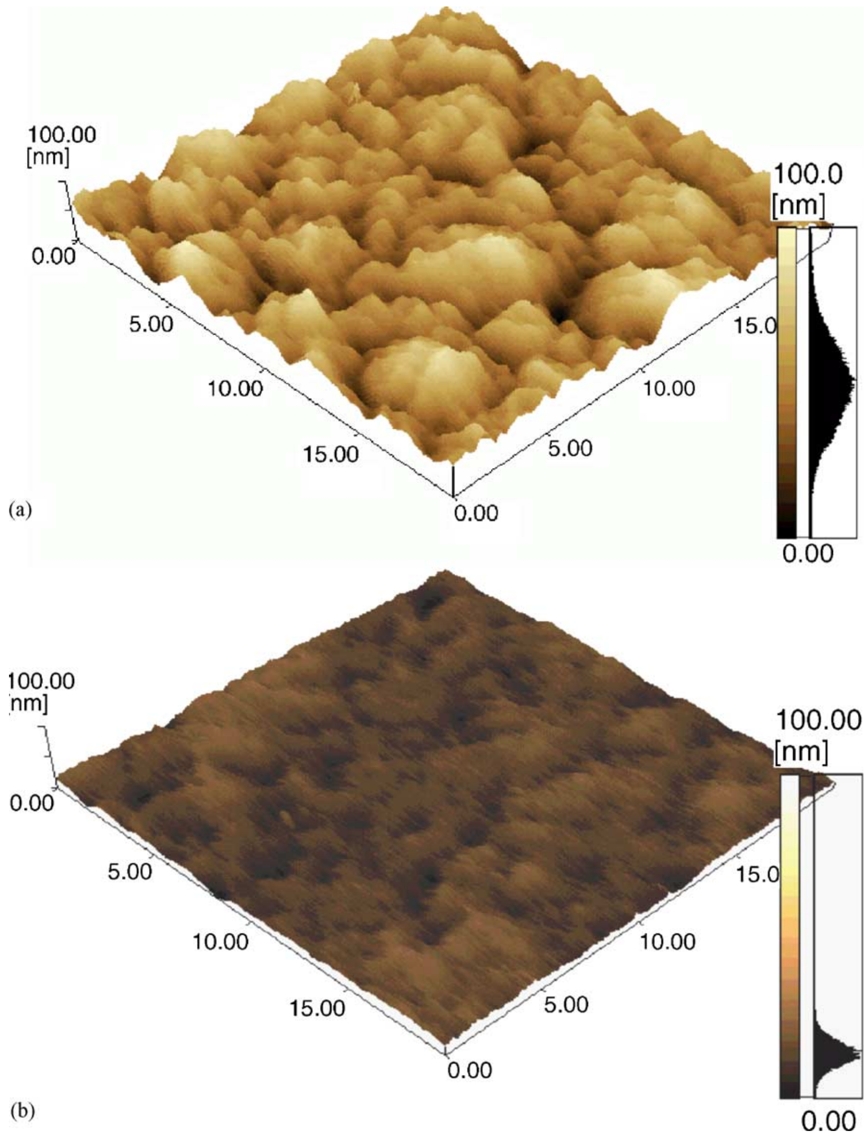


Fig. 1. AFM surface morphology of TiNi films: (a) low temperature in martensite state; (b) high temperature in austenite state.

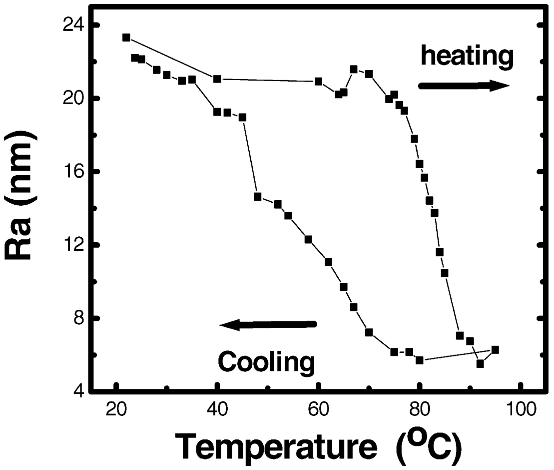


Fig. 2. Surface roughness evolution vs. temperature for TiNi thin film obtained from AFM analysis.

tural and thermodynamic properties, and improvement of mechanical properties of SMAs; (4) film thickness effect (since a minimum thickness is required for the optimized shape memory effect). Surface oxide and oxygen diffusion layer will have dominant effect if the TiNi film is too thin [37]; (5) formation of film texture and its control, and the effects on shape memory effect [38]; (6) internal and external stress on the arrangement of martensite variants, stress induced martensite and its shape memory phenomenon, etc. [39,40]; (7) surface chemistry, surface adsorption and biocompatibility of TiNi films with small grain size.

3.4. *Residual stress and stress evolution*

Residual stress and stress evolution in the films could pose potential problems in applications, as it may influence not only adhesion between film and substrate, but also

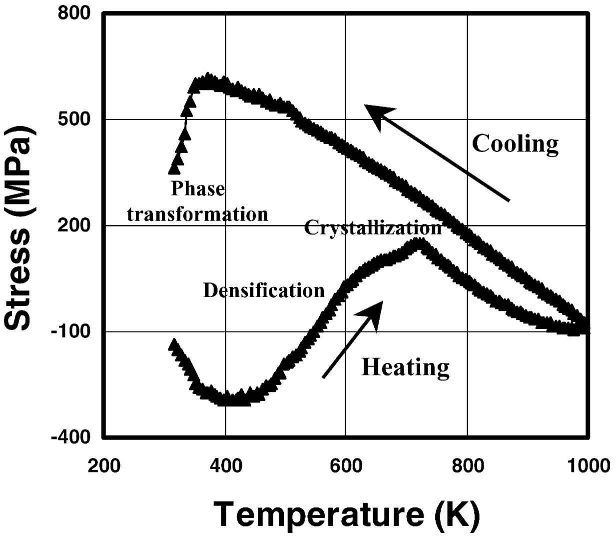


Fig. 3. Residual stress evolution with the temperature heating up to 923 K for as-deposited amorphous TiNi film [42].

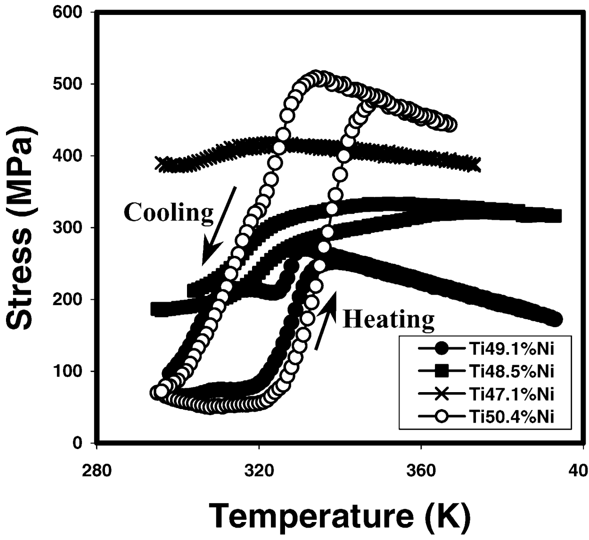


Fig. 4. Stress evolution TiNi film with different Ti/Ni ratios deposited at a temperature of 723 K [42].

deformation of MEMS structure, mechanics and thermodynamics of transformation and superelasticity effects, etc. [25,41]. Large residual stress could lead to either film cracking or decohesion under tension, or film delamination and buckling under compression [10,42]. A wide range of residual stress levels (either tensile or compressive) were found in the sputtered films. Deposition conditions, post-deposition thermo-mechanical treatment and composition in TiNi films could have important consequences with respect to the development of residual stress [43,44]. For a film–substrate system, possible origins of stress in thin films can be divided into three groups, i.e., thermal stress, intrinsic stress and phase transformation stress. Fig. 3 shows the stress evolution for an amorphous TiNi films during annealing [42]. At room temperature, compressive stress exists in film. With increase in temperature, the compressive stress existing in the amorphous film decreases due to relaxation of thermal stress. However, this trend slows down above 400 K, probably due to the beginning of the densification of the film. The development of compressive stress ends at a temperature around 650 K, after which the rapid development of tensile stress can be found due to densification of TiNi films. There is a transient spike in stress due to the densification of films at a crystallization temperature of 723 K. When the crystallization event completes, the development of compressive stress occurs again as a result of the relaxation of thermal stress. Cooling from high temperature results in the development of tensile stress. Upon cooling below Ms, the tensile stress relieves significantly due to the martensitic transformation.

In crystalline TiNi films, large tensile stress is generated during heating due to the phase transformation from martensite to austenite, while during cooling, the martensitic transformation occurs and the tensile stress drops significantly from the formation and alignment of twins and shear-variant boundary motion, etc. The stress generation and relaxation behaviors upon phase transformation are significantly affected by film composition, deposition and/or annealing temperatures, which strongly control the formation and evolution of intrinsic stress, thermal stress and phase transformation behaviors [43,45]. An example is shown in Fig. 4. The difference in residual stress for films with different Ti contents can be attributed to the differences in phase transformation behavior, intrinsic stress in the films, and/or precipitates in the films [42].

Substrate effect is also significant in the stress generation and evolution, because the difference in thermal expansion coefficients between substrate and TiNi films significantly affects the thermal stress. The film intrinsic stress is also critically dependent on the mismatch between film and substrate. So far, most studies have been focused on Si based substrates for MEMS applications. TiNi deposited on other substrates (with different coefficient of thermal expansion) could have different stress state (compressive or tensile) and stress–temperature evolution behaviors, thus detailed studies of substrate effect and stress state on shape memory effect, phase transformation and mechanical properties of TiNi films deserve more and systematic effort [46].

In order to minimize the residual stress in TiNi films, it is necessary to: (1) precisely control the Ti/Ni ratio; (2) deposit films at a possible lower pressure; (3) select a suitable deposition temperature or annealing temperature, with a compromise between thermal stress and intrinsic stress; (4) use some interlayers (with possible compressive stress) to reduce large tensile stress in some TiNi films; (5) perform post-annealing, ion beam post-modification, or in-situ ion beam modification during sputtering in order to reduce intrinsic stress, (6) select suitable substrate to reduce thermal stress.

3.5. Frequency response

Applications of micro-actuators require not only large recovery stress and large transformation deformation, but also high frequency and fast response (narrow transformation hysteresis). One of the challenges for the successful application of TiNi films is effective reduction of hysteresis and increase in operating frequency. External heat generation and dissipation are necessary in generating phase transformation and actuation, and the response speed of NiTi micro-actuators is mainly limited by their cooling capacities. The binary Ti–Ni alloy films have a large temperature hysteresis of about 30 °C, and TiNi films with small hysteresis are preferred for faster actuation response. The hysteresis could be slightly reduced by decreasing the cyclic temperature amplitude and/or increasing working stress. R-phase transformation usually has a very small temperature hysteresis, which is useful for MEMS applications. However, the problem is that the strain and stress (or force) generated are too small to be of many practical uses. Addition of Cu in TiNi films is effective in reducing the hysteresis [5,47]. Compared with TiNi binary alloy, TiNiCu alloys also show less composition sensitivity in transformation temperatures, lower martensitic yield stress, and superior fatigue property, etc., which makes them more suitable for micro-actuator application. However, the transformation temperatures of TiNiCu films decrease slightly, and the transformation becomes weaker with the increase of Cu contents, in terms of recovery stress, maximum recovery strain and heat generation, etc. Also the film becomes brittle when Cu content is higher than 10 at.% [47].

Generally speaking, the constrained films have smaller hysteresis as compared with freestanding films, and the film with large compressive stress could have much smaller (even almost zero) hysteresis compared with films with large tensile stress [46]. Therefore, selection of a suitable substrate (with larger thermal expansion coefficient than TiNi film) could help generate large compressive stress, thus a smaller hysteresis. Another way is to use external heat sinks. TiNi-based films can be deposited on a suitable substrate with good thermal conductivity, like Cu plate, thus significantly improving thermal dissipation and working frequency. However, this brings in more critical issues, such as integration and compatibility with MEMS batch process, residual stress and adhesion.

3.6. Adhesion and interfacial analysis

When TiNi films are deposited on Si substrate, there exist interfacial diffusion and chemical interactions at the interface whereby titanium and nickel silicides may form during high temperature deposition or post-deposition annealing. These interfacial reaction products could be complex, heterogeneous and metastable [48,49]. Since the TiNi film thickness required in MEMS applications is usually less than a few micrometers, a relatively thin reaction layer could have significant adverse effect on adhesion and shape memory properties. TiNi film adheres well to silicon substrate provided it is clean and pre-chemically etched. TiNi films deposited on a glass substrate can be easily peeled off, which is quite useful to obtain free-standing films. In MEMS processes, there is a need for an electrically and thermally insulating or sacrificial layer. Thermally grown SiO_2 is often used as this sacrificial layer. However, the adhesion of TiNi film on SiO_2 layer (or on glass and polymer substrate) is poor owing to the formation of a thin intermixing layer and the formation of a fragile and brittle TiO_2 layer [50]. In a significant deformation or during a complex interaction involving scratch, this layer is easily broken, thus peel off. Wolf et al. [6] proposed a two-step deposition method to solve this problem: pre-deposition of 0.1 μm TiNi film on SiO_2 at 700 °C to promote interdiffusion of elements, followed by bulk film deposition at room temperature. Adhesion of TiNi film on other substrates (such as Si_3N_4, polysilicon, etc.) is important for its successful MEMS applications, but few studies have been done so far.

3.7. Performance degradation and fatigue consideration

Stability and fatigue have always been concerns in development of TiNi thin films for applications. Fatigue of TiNi films is referred to the non-durability and deterioration of the shape memory effect after millions of cycles. The repeated phase changes will alter the microstructure and hysteresis of the transformation and in turn will lead to changes in transformation temperatures, transformation stresses and strains. The performance degradation and fatigue of thin films are influenced by a complex combination of internal (alloy composition, lattice structure, precipitation, defects, film/substrate interface) and external parameters (thermo-mechanical treatment, applied maximum stress, stress and strain rate, the amplitude of temperature cycling frequency) after long term thermal–mechanical cycles. For freestanding films, there are some studies using tensile tests to characterize the fatigue problems. Results indicated that there need tens of cycles before the stability of shape memory effects [5]. Ref. [4,51] studied the fatigue of the constrained TiNi films using the changes of recovery stress during cycling, and the recovery stress of TiNi films from curvature measurement decreased dramatically in the first tens of cycles, and became stable after thousands of cycles (with one example shown in Fig. 5). This reduction of the recovery stress is believed to result from the dislocation movement, grain boundary sliding, void formation, or partial de-bonding at the film/substrate interfaces, non-recoverable plastic deformation, changes in stress, etc. [4]. Transformation temperatures also changed dramatically during cycling. The repeated phase changes will alter the microstructure and hysteresis of the transformation and in turn lead to changes in transformation temperatures, stresses and strains.

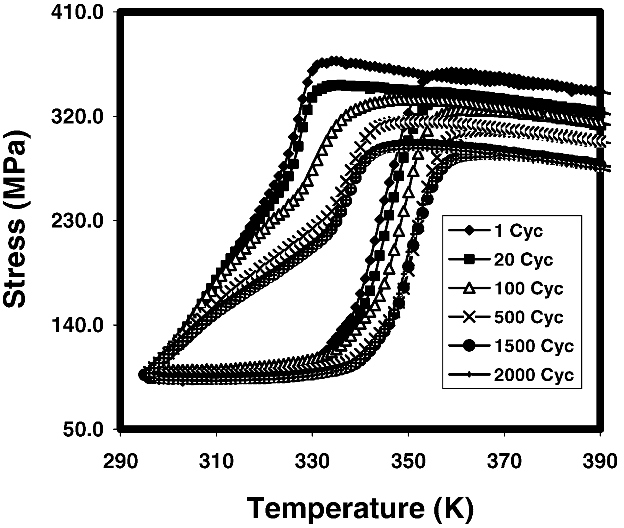


Fig. 5. Hysteresis evolution of Ti52.5Ni film on Si substrate after thermal cycling in different cycles and become stable after 2000 cycles.

3.8. *TiNi-based films with varied transformation temperatures*

The working principle of TiNi micro-actuators renders them very sensitive to environment. The maximum transformation temperature of binary TiNi thin films is usually less than 100 °C. However, a lot of MEMS applications require higher temperatures: in automobile applications, the transformation temperature required is up to 150 °C and in high-temperature gas chromatography the operation temperature is up to 180 °C, etc. Ternary system is the solution: adding a varying amount of a third element, such as Pd, Hf, Zr, Pt, Au, etc., into the binary alloys easily adjusts the transformation temperatures from 100 to 600 °C. TiNiPd and $TiNiH_f$ films are also effective in decreasing the temperature hysteresis, thus promising for quick movement at higher temperatures [52]. The potential problem is that all these high temperature ternary thin films are high cost with poor shape memory effect and thermal stability, as well as brittleness problems [53]. Small amount of Pd or Pt addition (less than 10 at.%) could reduce martensite transformation temperatures rather than increase them [54]. TiNiCu films with Cu content of 5–12 at.% is promising for biomedical devices used in human body because the film transformation temperatures are near body temperature and also the hysteresis is quite small [47]. Slight increase in Ni content in film can dramatically decrease the phase transformation temperatures.

3.9. *Accurate modeling and optimal design of TiNi thin film micro-actuators*

Numerical modeling and computer simulation of behaviors of TiNi films and their micro-actuators, in combination with experimental characterization efforts, will lead to the optimization of technical factors such as structural configuration, geometry and processing procedures and further improvement in the overall performance of TiNi thin film based micro-actuators [55]. There are two levels of simulations. The first level is the simulation and modeling of thermomechanical behaviors of TiNi films, and the second is the design of geometry and structures as well as performance of TiNi mocroactuators. There are many models describing the constitutive behaviors based on thermodynamics and continuum mechanics [56], but only a few have been used in engineering practice. It is difficult to obtain an accurate constitutive relationship for stress–strain of a TiNi film. The intrinsic hysteresis, nonlinearity and history dependent behaviors make it more difficult to accurately predict the response of a TiNi thin film micro-actuator. At present, only phenomenological models appears to be realistic for engineers, and the transformation can be assumed as either a linear or a sine/cosine function [57–59]. There are several special issues in simulation of TiNi films as compared with bulk TiNi materials: (1) smaller grain size in TiNi films and constraint effect on substrates; (2) large film biaxial stress after deposition and stress evolution during phase transformation process; (3) possible textured structure in the thin films. Ref. [60–62] reported different thermodynamic modeling for TiNi thin films. Jin and Weng [63] developed a relaxed self-consistent model to simulate the thermomechanical behavior of TiNi films, and it is confirmed that thermally induced phase transformation has a narrower range of transformation temperatures for the films, and the work hardening characteristics is lower than the bulk material due to geometrical relaxation. For TiNi thin film based microdevices, the non-uniform stress and temperature distribution could affect the prediction of deformation and lead to inaccurate position control.

4. MEMS applications of TiNi films

Table 1 compares the properties of some common micro-actuation mechanisms. The main advantages of TiNi thin film include high power density, large displacement and actuation force, low operation voltage, etc. The main problems 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) high cost of TiNi films and difficulty in control of composition and mechanical properties; (4) potential degradation and fatigue problems. Even with the above disadvantages, TiNi thin film is still considered as a core technology for actuation of some MEMS devices, where large force and stroke are essential and in conditions of low duty cycles or intermittent operation, and in extreme environment, such as radioactive, space, biological and corrosive conditions.

Freestanding films usually show intrinsic "two-way" shape memory effect, with large displacement, but relatively small force in actuation. This is applicable in microsen-

Table 1
Comparison of micro-actuation mechanisms [4,5]

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

sors, microswtiches or micropositioners. The nature of this "two-way" shape memory effect could be due to: (1) intrinsic residual stress in TiNi films [45]; (2) compositional gradient through film thickness [64,65]; (3) existence of R-phase; (4) hot shaping and aging of TiNi film resulting in Ti_3Ni_4 precipitates [66]. The constrained film/substrate actuators could provide large actuation force, but sacrifice the deflection (or strain). The substrate may act as an effective biasing force, thus creating a mechanical "two-way" shape memory effect.

4.1. *Micro-actuators*

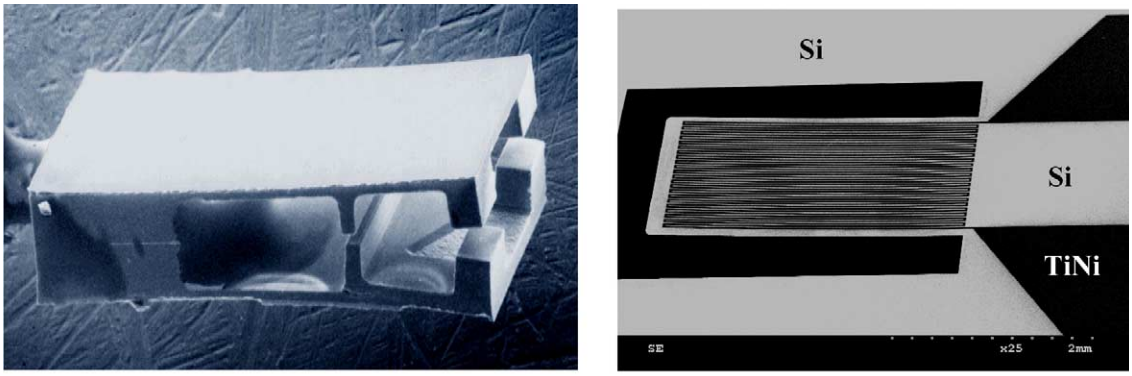
Since TiNi films can provide large forces for actuation and large displacement, therefore, most applications of TiNi films in MEMS are focused on micro-actuators, such as micropumps, microvalves, microgrippers, springs, microspacers, micropositioners, and microrappers, etc.

4.1.1. *Micropumps and microvalves*

MEMS based micropumps and microvalves are attractive for many applications such as implantable drug delivery, chemical analysis and analytical instruments, etc. TiNi thin films are suitable for building microvalves and pumps. There are different designs for TiNi film based micropumps or microvalves, and most of them use TiNi membrane (or diaphragm, microbubble, etc.) for actuation [7,67–69]. Both freestanding TiNi films and constrained TiNi films are used. Although freestanding TiNi film has intrinsic two-way effect, in order to maximize this effect, extra process, such as 3-D hot-shaping of TiNi film (membrane) and externally biased structure (such as a polyimide layer [70], or a bonded Si cap [29] or glass cap [71]) have often been applied. Ref. [68] also reported a design using two active TiNi membrane films to improve actuation. All of these extra processes could result in complicated structure and difficulty in MEMS processing. Another concern is the effective thermal isolation between the heated TiNi films and the fluid being pumped. TiNi/Si bimorph membrane based micropumps and valves are more commonly reported. The advantages of using TiNi/Si membrane as the driving diaphragm include [72]: (1) large actuation force; (2) simplicity in process and no special bias structure needed because the silicon substrate can provide bias force; and (3) no isolating structure is needed because silicon structure can separate the working liquid from SMA film completely.

4.1.2. *Microgrippers*

Grasping and manipulating small or micro-objects with high accuracy is required for a wide range of important applications, such as the assembly in microsystems, endoscopes for microsurgery, and drug injection micromanipulators for cells. There are some basic requirements for microgrippers, for example, large gripping force, sufficient opening distance for assembling works, etc. TiNi films are promising in these applications. So far, two types of TiNi film based microgripper designs are available. The popular design is out-of-plane bending mode, mostly with two integrated TiNi/Si cantilever (or other substrate, such SU-8 or polyimide, etc.) with opposite actuation directions (see Fig. 6(a)) [73,74]. Fig. 6(b) shows the patterned TiNi electrodes on silicon cantilevers. When the electrodes are electrically heated, the cantilever bends up due to the shape memory effects of TiNi films, thus generating gripping force. These types of gripper designs usually need further bonding process to combine two cantilevers to form gripping movement. The force and displacement generated can be very large. A novel micro-wrapper as shown in Fig. 7 was fabricated using freestanding TiNi films with out-of-plane movement [75]. The overall dimension of the micro-wrapper arms is 100 μm, approximately the diameter of a human hair. The micro-wrapper has a small current passing through it to maintain the flat shape. Upon removal of the current, the small arms close to form a cage. This micro-wrapper can be used to manipulate micro-organisms or possibly in minimally invasive surgery to remove anomalies such as tumors. Ref. [76] reported a novel microelectrode with TiNi clipping structure, which can be used for minimally invasive microelectrodes to clip a nerve cord or other living organisms. The TiNi film is actuated when a current is applied to the electrode. The clipping force of the electrode to the nerve is enhanced by a hook structure and two C-shaped probes as shown in Fig. 8(a) and (b). Another gripper design is in-plane mode, in which the deformation of two arms (using freestanding TiNi films or TiNi/Si beams) is within a plane realized by compliant structure design [77]. Ref. [78] reported a microtweezer structure, in which residual stress in TiNi film is used as a bias force load. This can eliminate the need for providing bias force for device



(a) (b)

Fig. 6. TiNi/Si microgripper with cantilever structure with out-of-plane bending mode: (a) microgripper [4]; (b) the patterned TiNi electrodes on silicon cantilevers.

operation. However, the force from the deformation of the free-standing films is not large enough to grasp large objects. The other problem in this type of design is how to prevent out-of-plane bending, beam deformation and fracture during operation caused by intrinsic film stress.

4.2. Micro-sensors, microswitches and microrelays

TiNi thin films are sensitive to environmental changes such as thermal, stress, magnetic or electrical fields thus should be ideal for applications in microsensors. However, only a few studies and applications are reported in this respect. Possible reasons for the lack of studies include: (1) the sensing function is limited only within the appropriate temperature range; (2) low response speed and frequency inherent to the thin film SMA. TiNi film was reported as a gate of metal-on-silicon (MOS) capacity sensor, for detecting the increase in capacitance of TiNi films during heating and cooling [79]. Other potential applications as switches

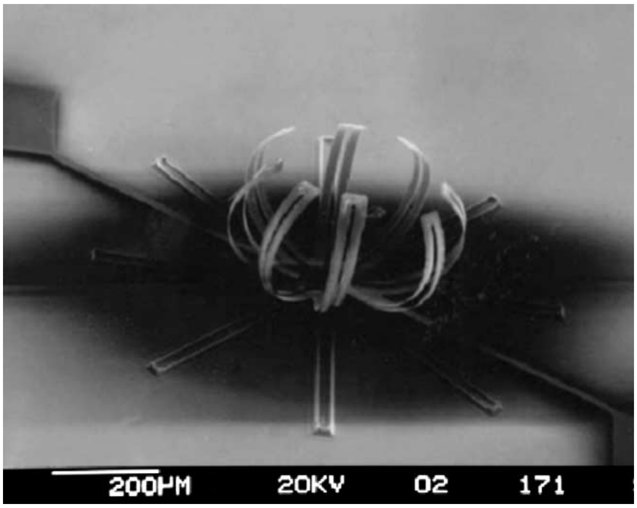
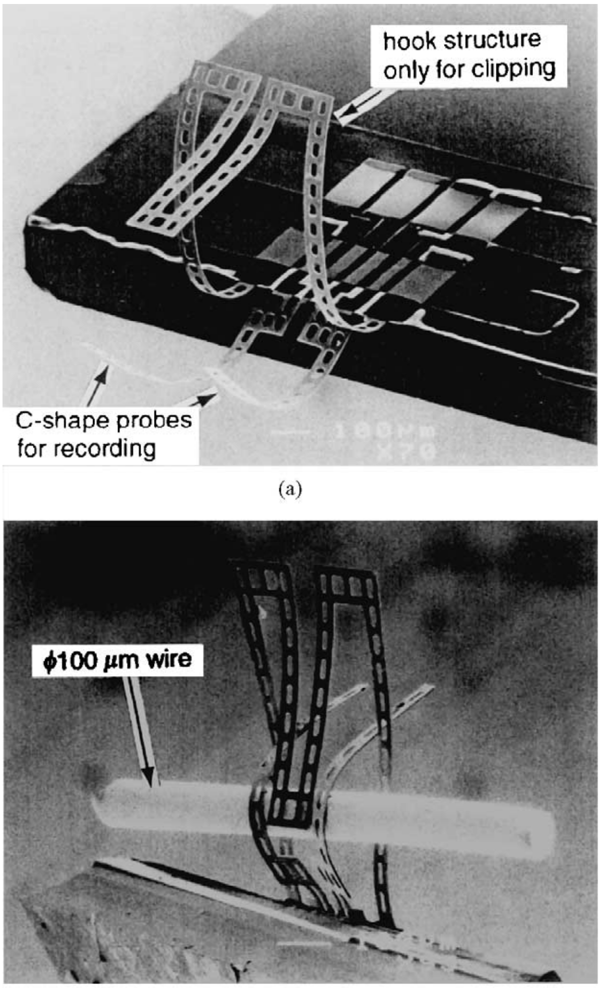


Fig. 7. The micro-wrapper made of freestanding TiNi films [75].



(a)

(b)

Fig. 8. (a) A TiNi electrodes with the hook structure is returned to its memorized shape when it is heated, while two C-shape probes for recording are not heated; (b) the microelectrode clipping a wire (100 µm) after the hook structure is heated [76].

or microrelays include on-chip circuit breakers against overheating caused by short circuit or overload, probe tips for automatic test equipment, fiber optics switching, automotive fuel injectors, micro-lens positioner, etc. [80]. However, the environment stimulus must reach to a critical temperature value to trigger the operation. Also the exact relationship between external heat or electrical current and movement is difficult to control.

When TiNi film undergoes a phase transformation, both its surface roughness (corresponding to light scattering) and its refractive index change [81,82]. The reflection coefficient of the austenite phase is higher than that of the martensite phase by more than 45%, thus it is possible to use TiNi films as a light valve or on–off optical switch for spatial light modulators [82]. TiNi film can also be used as a lever to move optical lens up or down (instead of left or right), thus forming an out-of-plane micro-actuator for optical switches [83]. The potential areas of applications include field emission flat panel displays technology, in which TiNi film based micro-actuators can erect a large number of micromachined spacers between the pixels [83]. Ref. [84] reported a far infrared radiation (FIR) imaging sensor based on a TiNi film cantilever. One side of the cantilever is coated with a FIR absorbing layer, and the other side is coated with a reflecting layer of gold. Upon adsorption of FIR, the temperature of TiNi cantilever changes, causing the large tilting effect. The detection of the mechanical movements in the cantilever is realized by illuminating the reflective gold side with a laser beam. Fig. 9 shows a TiNi micromirror structure, in which a Si cap acts as top mirror, and the arms for actuating Si cap (40 μm) were fabricated with TiNi/Si beam structure. The TiNi/Si beams can be actuated using joule heating of TiNi electrodes, thus causing the beam bending and tilting the Si mirror. The problem is that the tilting angle is rather limited, because silicon cannot be deformed more than about 1–3% strain before fracture. The other problems existing for these optical applications include: (1) low speed, hysteresis and nonlinear deformation of TiNi films, although this can be improved by appropriate design; (2) the sensitivity of optical reflection on film composition, light wavelength, substrate temperature, distance from fiber optic tip to TiNi film surface, etc.; (3) control of stress to prevent undesirable deformation.

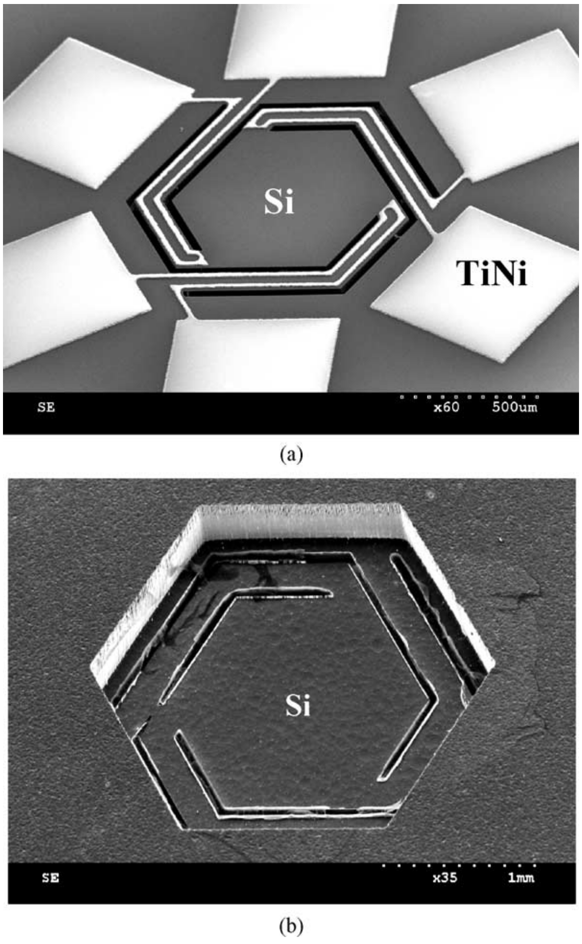


Fig. 9. TiNi micromirror structure with a Si cap acts as top mirror and the arms fabricated with TiNi/Si beam structure: (a) top view; (b) bottom view.

5. Future directions for TiNi films and micro-actuators

5.1. Functionally graded and composite TiNi-based films

To further improve the properties of TiNi films, multi-layer, composite or functionally graded TiNi-based films can be designed. So far, there are different design models for the functionally graded TiNi thin films. The first type is through the gradual change in composition (Ti/Ni ratio), crystalline structures, transformation temperatures, and/or residual stress through film thickness [66,85]. As the Ti or Ni content changes in the micrometer-thick film, the material properties could change from pseudo-elastic (similar to rubber) to shape memory. The seamless integration of pseudo-elastic with shape memory characteristics produces a two-way reversible actuation, because residual stress variations in thickness will enable biasing force to be built inside the thin film. These functionally graded TiNi films can be easily prepared by slightly changing the target powers during deposition [25]. Another novel way is to vary the target temperature during sputtering [13,14], and the films produced by hot targets have compositions similar to that of the target while films produced from cold target are Ti deficient. In order to successfully develop functionally graded TiNi thin films for MEMS application, it is necessary to characterize, model and control the variations in composition, thermomechanical properties and residual stress in these films.

The second type of functionally graded films involves new materials and functions other than TiNi films. Recently, we [86,87] explored the deposition of a functionally graded TiN/TiNi layer to fulfill this purpose. The presence of an adherent and hard TiN layer (300 nm) on TiNi film (3.5 μm) formed a good passivation layer (to eliminate the potential Ni release), and improved the overall hardness, load bearing capacity and tribological properties without sacrificing the shape memory effect of the TiNi film. Also TiN layer is able to restore elastic strain energy during heating and to reset the martensite phase on subsequent cooling, forming a two-way SMA effect. In order to improve biocompatibility and adhesion of TiNi films, a functionally graded Ti/TiNi/Ti/Si graded layer could be proposed. A thin layer of surface Ti layer can improve biocompatibility (prevent potential Ni allergic reactions), while the Ti interlayer is used to improve film adhesion. Using co-sputtering with multi-targets, or controlling the gases during sputtering, these graded film designs can be easily realized.

Some surface modification methods, such as irradiation of TiNi films by electrons, ions (Ar, N, He, Ni or O ions), laser beams, neutrals can be used (1) to modify the surface physical, mechanical, metallurgical, wear, corrosion and biological properties for application in hostile and wear environment; (2) to cause lattice damage and/or alter the phase transformation behaviors along thickness of film, forming novel two-way shape memory actuation [88–90]. The problems of these surface treatments are high cost, possible surface or ion induced damage, amorphous phase formation, or degradation of shape memory effects [88]. Surface oxidation of TiNi bulk materials have often been reported to prevent the Ni ion release and improve its biocompatibility [91,92], and it is possible to do the same process for TiNi films with the sacrifice of shape memory effect.

Other functionally graded or composite designs include the combination of TiNi films with piezoelectric, ferromagnetic, or magnetostrictive thin films [93]. Response time of the piezoelectricity mechanisms (PZT films) is fast (see Table 1), but the displacement is relatively small. TiNi film, on the other hand, has a large force-displacement, but with slow response frequency. By coupling TiNi and PZT films to fabricate a new hybrid heterostructure composite or functionally graded films, it is possible to tune or tailor the static and dynamic properties of TiNi thin films, which may generate a larger displacement than conventional piezoelectric or magnetrostrictive thin films and have an improved dynamic response compared with that of single layer TiNi films. Both PZT and TiNi films can be prepared by sputtering methods, or PZT film by sol-gel methods and TiNi film by sputtering. Either TiNi or PZT films can be the bottom layer. However, the complexity of the fabrication processing, the interfacial diffusion and adhesion, and dynamic coupling of dissimilar components remain tough issues for these types of composite thin films.

5.2. Potential new applications

High passive and active damping capacity is considered as one of the important functional properties of SMAs [94]. Since the process involves the hysteresis movement of interfaces (martensite variant interfaces, like twin boundaries, phase boundaries, lattice defects), thus a large amount of energy is dissipitated upon cycling. The changes of damping capacity of TiNi films have been used to study their phase transformation behaviors [30]. Damping capacity is temperature and frequency dependent and peaks in the vicinity of the martensitic transformation temperature, thus these factors can be explored for the design of anti-vibration damping structures. In hard disk drives, the positioning accuracy of the read/write heads strongly depends on the inherent dynamic characteristics of the head actuator assembly (i.e., vibrations of the head actuator assembly system). TiNi film with large damping property is promising in minimizing the vibrations during the operations of the hard disk drive. However, fabrication of the actual damping devices must take into account factors of economics, reliability, versatility and construction needs. Also important to be considered are film stress and potential distortion of structures.

Good wear resistance is an important property required of some MEMS and biomedical applications, such as pumps, grippers, valves, etc. It was reported that bulk TiNi alloys in austenite exhibit good wear resistance (due to its rapid work hardening and pseudo-elastic properties) [95]. However, poor wear resistance of B19′ (martensite) and high coefficient of friction are potential problems. In the case of SMA films, interfacial adhesion, large coefficient of friction and potential stress are other major concerns for their tribological application [96,97]. Functionally graded layer design (TiN/TiNi) or surface modifications as discussed in Section 5.1 could provide viable solutions.

Bulk TiNi is a common and well-known material for the medical industry [98]. At present, increasing attention has also been paid to use TiNi thin film into minimally invasive surgery, microstents and bioMEMS applications. Some micro-actuators made from TiNi thin films may be used to infuse drugs, or placed in strategic locations in the body to assist circulation. Glass, silicon and polymers are the mostly common used substrates for biological applications. However, high deposition or annealing temperatures for preparation of TiNi films and the poor adhesion on these substrates pose the potential problems. Superelasticity of TiNi, a non-linear peudoelasticity as much as 7–10% strain, has already found many applications for bulk materials, but few explorations are carried out in MEMS applications so far using thin films. TiNi thin film SMA in its super-elastic state is promising for some compliant elements in MEMS devices.

Since thin films with nanometer grains (about tens or hundreds of nanometers) still show shape memory effect, it is promising to fabricate nano-scale SMA thin film structures with the aid of precision tools (such as focused ion milling or FIB). These structures may be able to perform physical actuation (push, pull, etc.) at nano-scale. Possible difficulties of TiNi films in nanoscale structures may include: (1) large amount of oxygen and carbon adsorption on TiNi surface due to the extremely reactive nature of Ti elements, and the oxide and oxygen diffusion depth could be as large as tens of nanometers [50]; (2) the difficulty in fabrication and manipulation of these nanostructure, although laser beam, or FIB is promising.

6. Summary

Development of TiNi-based SMAs thin films and mciroactuators witnessed a considerable progress in recent years. Some important issues pertaining to the preparation of high performance shape memory TiNi films using sputtering methods and their MEMS applications were reviewed in this paper. Successful application of TiNi thin films in MEMS requires consideration of the following issues: preparation and characterization, residual stress and adhesion, frequency improvement, fatigue and stability, patterning and modeling of behavior. At microscale, TiNi actuators out-perform other actuation mechanisms in work/volume (or power/weight) ratio, large deflection and force, but with a relatively low frequency (less than 100 Hz) and efficiency as well as non-linear behavior. More functional and complex designs based on TiNi film devices are needed with multiple degrees of freedom and compact structure. TiNi film based micoractuators will find potential applications in medicine, aerospace, automotive, and consumer products. Miniature TiNi actuated devices based on sputtered TiNi films are ready for the huge commercial market, especially for medical microdevices and implantable applications.

References

[1] K. Otsuka, X. Ren, Recent developments in the research of shape-memory alloys, Intermetallics 7 (1999) 511–528.

[2] J.V. Humbeeck, Non-medical applications of shape-memory alloys, Mater. Sci. Eng. A273–A275 (1999) 134–148.

[3] A. Ishida, V. Martynov, Sputter-deposited shape-memory alloy thin films: properties and applications, MRS Bull. 27 (2002) 111–114.

[4] P. Krulevitch, A.P. Lee, P.B. Ramsey, J.C. Trevino, J. Hamilton, M.A.M.A. Northrup, Thin film shape-memory alloy micro-actuators, J. MEMS 5 (1996) 270–282.

[5] S. Miyazaki, A. Ishida, Martensitic transformation and shape memory behavior in sputter-deposited TiNi-base thin films, Mater. Sci. Eng. A273–A275 (1999) 106–133.

[6] R.H. Wolf, A.H. Heuer, TiNi (shape memory) films on silicon for MEMS applications, J. MEMS 4 (1995) 206–212.

[7] H. Kahn, M.A. Huff, A.H. Heuer, The TiNi shape-memory alloy and its applications for MEMS, J. Micromech. Microeng. 8 (1998) 213–221.

[8] Y.Q. Fu, W.M. Huang, H.J. Du, X. Huang, J.P. Tan, X.Y. Gao, Characterization of TiNi shape-memory alloy thin films for MEMS applications, Surf. Coat. Technol. 145 (2001) 107–112.

[9] A. Ishida, M. Sato, A. Takei, K. Nomura, S. Miyazaki, Effect of aging on shape memory behavior of Ti–51.3 at.% Ni thin films, Metall. Mater. Trans. A 27A (1996) 3753–3759.

[10] C.L. Shih, B.K. Lai, H. Kahn, S.M. Philips, A.H. Heuer, A robust Co-sputtering fabrication procedure for TiNi shape-memory alloys for MEMS, J. MEMS 10 (2001) 69–79.

[11] A. Ohta, S. Bhansali, I. Kishimoto, A. Umeda, Novel fabrication technique of TiNi shape memory alloy film using separate Ti and Ni targets, Sens. Actuators A 86 (2000) 165–170.

[12] P. Krulevitch, P.B. Ramsey, D.M. Makowiecki, A.P. Lee, M.A. Northrup, G.C. Johnson, Thin Solid Films 274 (1996) 101.

[13] K.K. Ho, K.P. Mohanchandra, G.P. Carman, Examination of the sputtering profile of NiTi under target heating conditions, Thin Solid Films 413 (2002) 1–7.

[14] K.K. Ho, G.P. Carman, Sputter deposition of NiTi thin film shape-memory alloy using a heated target, Thin Solid Films 370 (2000) 18–29.

[15] T. Lehnert, S. Crevoiserat, R. Gotthardt, Transformation properties and microstructure of sputter-deposited Ni–Ti shape-memory alloy thin films, J. Mater. Sci. 37 (2002) 1523–1533.

[16] P. Surbled, C. Clerc, B.L. Pioufle, M. Afaka, H. Fujita, Effect of the composition and thermal annealing on the transformation temperatures of sputtered TiNi shape-memory alloy thin films, Thin Solid Films 401 (2001) 52–59.

[17] A. Isalgue, V. Torra, J.-L. Seguin, M. Bendahan, J.M. Amigo, V. Esteve-Cano, Shape memory NiTi thin films deposited at low temperature, Mater. Sci. Eng. A273–A275 (1999) 717–721.

[18] W.M. Huang, Q. He, M.H. Hong, Q. Xie, Y.Q. Fu, H.J. Du, On the fabrication of NiTi shape-memory alloy micro devices using laser, in: Proceedings of the Photonics Asia 2002, Shanghai, China, 14–18 October 2002, SPIE vol. 4915, 2002, pp. 234–240.

[19] Y. Bellouard, T. Lehnert, J.E. Bidaux, T. Sidler, R. Clavel, R. Gottardt, Y. Bellouard, Local annealing of complex mechanical devices: a new approach for developing monolithic microdevices, Mater. Sci. Eng. A273–A275 (1999) 795–798.

[20] A. Ishida, M. Sato, S. Miyazaki, Mechanical properties of Ti–Ni shape memory thin films formed by sputtering, Mater. Sci. Eng. A273–A275 (1999) 754–757.

[21] A. Ishida, A. Takei, M. Sato, S. Miyazaki, Stress–strain curves of sputtered thin films of Ti–Ni, Thin Solid Films 281–282 (1996) 337–339.

[22] Y.Q. Fu, H.J. Du, S. Gao, S. Yi, Mechanical properties of sputtered TiNiCu shape-memory alloy thin films, Mater. Sci. Forum 437 (2003) 37–40.

[23] A. Ishida, M. Sato, S. Miyazaki, Mechanical properties of Ti–Ni shape memory thin films formed by sputtering, Mater. Sci. Eng. A 275 (1999) 754–757.

[24] T. Matsunaga, S. Kajiwara, K. Ogawa, T. Kikuchi, S. Miyazaki, High strength Ti–Ni-based shape memory thin films, Mater. Sci. Eng. A 273–275 (1999) 745–748.

[25] D.S. Grummon, J.P. Zhang, T.J. Pence, Relaxation and recovery of extrinsic stress in sputtered titanium–nickel thin films on (1 0 0)-Si, Mater. Sci. Eng. A 273–275 (1999) 722–726.

[26] H.D. Espinosa, B.C. Prorok, M. Fischer, A methodology for determining mechanical properties of freestanding thin films and MEMS materials, J. Mech. Phys. Solids 51 (2003) 46–67.

[27] S. Moyne, C. Poilane, K. Kitamura, S. Miyazaki, P. Delobelle, C. Lexcellent, Analysis of the thermomechanical behavior of Ti–Ni shape-memory alloy thin films by bulging and nanoindentation procedures, Mater. Sci. Eng. A273–A275 (1999) 727–732.

[28] E. Makino, T. Shibata, K. Kato, Dynamic thermo-mechanical properties of evaporated TiNi shape memory thin film, Sens. Actuators A 78 (1999) 163–167.

[29] E. Makino, T. Mitsuya, T. Shibata, Micromachining of TiNi shape memory thin film for fabrication of micropump, Sens. Actuators A 79 (2000) 251–259.

[30] C. Craciunescu, M. Wuttig, Extraordinary damping of Ni–Ti double layer films, Thin Solid Films 378 (2000) 173–175.

[31] W. Ni, Y.T. Cheng, D.S. Grummon, Recovery of microindents in a nickel–titanium shape-memory alloy: a “self-healing” effect, Appl. Phys. Lett. 80 (2002) 3310–3312.

[32] G.A. Shaw, D.D. Stone, A.D. Johnson, A.B. Ellis, W.C. Crone, Shape memory effect in nanoindentation of nickel–titanium thin films, Appl. Phys. Lett. 83 (2003) 257–259.

[33] X.G. Ma, K. Komvopoulos, Nanoscale pseudoelastic behavior of indented titanium–nickel films, Appl. Phys. Lett. 83 (2003) 3773–3775.

[34] Y.Q. Fu, H.J. Du, RF magnetron sputtered TiNiCu shape-memory alloy thin film, Mater. Sci. Eng. A 339 (2003) 10.

[35] S. Kajiwara, T. Kikuchi, K. Ogawa, T. Matsunaga, S. Miyazaki, Strengthening of Ti–Ni shape-memory films by coherent subnanometric plate precipitates, Phil. Mag. Lett. 74 (1996) 137–144.

[36] A.L. Mckelvey, R.O. Ritchie, On the temperature dependence of the superelastic strength and the prediction of the theoretical uniaxial transformation strain in Nitinol, Philos. Mag. A 80 (2000) 1759–1768.

[37] A. Ishida, M. Sato, Thickness effect on shape memory behavior of Ti–50.0 at.%Ni thin film, Acta Mater. 51 (2003) 5571–5578.

[38] S. Miyazaki, V.H. No, K. Kitamura, A. Khantachawana, H. Hosoda, Texture of Ti–Ni rolled thin plates and sputter-deposited thin films, Int. J. Plasticity 16 (2000) 1135–1154.

[39] R.X. Wang, Y. Zohar, M. Wong, The effects of process-induced stress on the microstructures and the phase transformation characteristics of sputtered titanium–nickel thin-film shape-memory alloys, J. Micromech. Microeng. 11 (2001) 686–691.

[40] M. Wuttig, Y. Zheng, J.S. Slutsker, K. Mori, Q. Su, Stress induced martensite in NiTi corrugated films, Scripta Mater. 41 (1999) 529–533.

[41] C. Craciunescu, J. Li, M. Wuttig, Thermoelastic stress-induced thin film martensites, Scripta Mater. 48 (2003) 65–70.

[42] Y.Q. Fu, H.J. Du, S. Zhang, Sputtering deposited TiNi films: relationship among processing, Surf. Coat. Technol. 167 (2003) 120–128.

[43] Y.Q. Fu, H.J. Du, Relaxation and recovery of stress during martensite transformation for sputtered shape memory TiNi film, Surf. Coat. Technol. 153 (2002) 100–105.

[44] D.S. Grummon, J.P. Zhang, Stress in sputtered films of near-equiatomic TiNiX on (1 0 0) Si: intrinsic and extrinsic stresses and their modification by thermally activated mechanisms, Physica Status Solidi A 186 (2001) 17–39.

[45] Y.Q. Fu, H.J. Du, Effects of film composition and annealing on residual stress evolution for shape memory TiNi film, Mater. Sci. Eng. A 342 (2003) 236–244.

[46] B. Winzek, E. Quandt, Shape-memory Ti–Ni–X-films (X = Cu, Pd) under constraint, Z. Metallkd. 90 (1999) 796–802.

[47] H.J. Du, Y.Q. Fu, Deposition and characterization of $Ti_{1-x}(Ni,Cu)_x$ shape-memory alloy thin films 176 (2004) 182–187.

[48] S. Stemmer, G. Duscher, C. Scheu, A.H. Heuer, M. Ruhle, The reaction between a TiNi shape memory thin film and silicon, J. Mater. Res. 12 (1997) 1734–1740.

[49] S.K. Wu, J.Z. Chen, Y.J. Wu, J.Y. Wang, M.N. Yu, F.R. Chen, J.J. Kai, Interfacial microstructures of rf-sputtered TiNi shape-memory alloy thin films on (1 0 0) silicon, Phil. Mag. A 81 (2001) 1939–1949.

[50] Y.Q. Fu, H.J. Du, S. Zhang, Adhesion and interfacial structure of magnetron sputtered TiNi films on Si/SiO_2 substrate, Thin Solid Films 444 (2003) 85–90.

[51] Y.Q. Fu, H.J. Du, S. Zhang, Curvature method as a tool for shape memory effect, in: A. Kumar, Y.W. Chung, J.J. Moore, G.L. Doll, K. Yahi, D.S. Misra (Eds.), Surface Engineering: Science and Technology II Symposium at TMS 2002 Annual Meeting, TMS, Seattle, WA, USA, 17–21 February 2002, pp. 293–303.

[52] T. Sawaguchi, M. Sato, A. Ishida, Microstructure and shape memory behavior of Ti–51.2 (Pd27.0Ni21.8) and Ti–49.5 (Pd28.5Ni22.0) thin films, Mater. Sci. Eng. A 332 (2002) 47–55.

[53] D.S. Grummon, Thin-film shape-memory materials for high-temperature applications, JOM 55 (2003) 24–32.

[54] Y.Q. Fu, H.J. Du, Magnetron sputtered Ti50Ni40Pt10 shape-memory alloy thin films, J. Mater. Sci. Lett. 22 (2003) 531–533.

[55] F. Auricchio, R.L. Taylor, J. Lubliner, Shape-memory alloys: macromodelling and numerical simulations of the superelastic behavior, Comput. Methods Appl. Mech. Eng. 146 (1997) 281–312.

[56] A. Bhattacharyya, M.G. Faulkner, J.J. Amalraj, Finite element modeling of cyclic thermal response of shape-memory alloy wires with variable material properties, Comput. Mater. Sci. 17 (2000) 93–104.

[57] W.M. Huang, Modified Shape-memory alloy (SMA) model for SMA wire based actuator design, J. Intell. Mater. Sys. Struct. 10 (1999) 221–231.

[58] X.Y. Gao, W.M. Huang, Transformation start stress in non-textured shape-memory alloys, Smart Mater. Struct. 11 (2002) 256–268.

[59] W.M. Huang, J.J. Zhu, To predict the behavior of shape-memory alloys under proportional load, Mech. Mater. 34 (2002) 547–561.

[60] B. Gabry, C. Lexcellent, V.H. No, S. Miyazaki, Thermodynamic modeling of the recovery strains of sputter-deposited shape-memory alloys Ti–Ni and Ti–Ni–Cu thin films, Thin Solid Films 372 (2000) 118–133.

[61] C. Lexcellent, S. Moyne, A. Ishida, S. Miyazaki, Deformation behaviour associated with the stress-induced martensitic transformation in Ti–Ni thin films and their thermodynamical modeling, Thin Solid Films 324 (1998) 184–189.

[62] K. Bhattacharya, R.D. James, A theory of thin films of martensitic materials with applications to micro-actuators, J. Mech. Phys. Solids 47 (1999) 531–576.

[63] Y.M. Jin, G.J. Weng, Micromechanics study of thermomechanical characteristics of polycrystal shape-memory alloy films, Thin Solid Films 376 (2000) 198–207.

[64] A. Gyobu, Y. Kawamura, T. Saburi, M. Asai, Two-way shape memory effect of sputter-deposited Ti-rich Ti–Ni alloy films, Mater. Sci. Eng. A 312 (2001) 227–231.

[65] J.J. Gill, K. Ho, G.P. Carman, Three-dimensional thin-film shape-memory alloy micro-actuator with two-way effect, J. MEMS 11 (2002) 68–77.

[66] E. Quandt, C. Halene, H. Holleck, K. Feit, M. Kohl, P. SchloBmacher, A. Skokan, K.D. Skrobanek, Sputter deposition of TiNi, TiNiPd and TiPd films displaying the two-way shape-memory effect, Sens. Actuators A53 (1996) 434–439.

[67] D. Reynaerts, J. Peirs, H. Van Brussel, An implantable drug-delivery system based on shape-memory alloy micro-actuation, Sens. Actuators A 61 (1997) 455–462.

[68] W.L. Benard, H. Kahn, A.H. Heuer, M. Huff, Thin-film shape-memory alloy actuated micropumps, J. MEMS 7 (1998) 245–251.

[69] M. Kohl, K.D. Skrobanek, S. Miyazaki, Development of stress-optimised shape memory microvalves, Sens. Actuators A72 (1999) 243–250.

[70] M. Kohl, D. Dittmann, E. Quandt, B. Winzek, S. Miyazaki, D.M. Allen, Shape memory microvalves based on thin films or rolled sheets, Mater. Sci. Eng. A273–A275 (1999) 784–788.

[71] E. Makino, T. Mitsuya, T. Shibata, Fabrication of TiNi shape memory micropump, Sens. Actuators A 88 (2001) 256–262.

[72] D. Xu, L. Wang, G.F. Ding, Y. Zhou, A.B. Yu, B.C. Cai, Characteristics and fabrication of NiTi/Si diaphragm micropump, Sens. Actuators A 93 (2001) 87–92.

[73] V. Seidemann, S. Butefisch, S. Buttgenbach, Fabrication and investigation of in-plane compliant SU8 structures for MEMS and their application to micro valves and micro grippers, Sens. Actuators A 97–98 (2002) 457–461.

[74] A.P. Lee, D.R. Ciarlo, P.A. Krulevitch, S. Lehew, J. Trevino, M.A. Northrup, A practical microgripper by fine alignment, eutectic bonding and SMA actuation, Sens. Actuators A54 (1996) 755–759.

[75] J.J. Gill, D.T. Chang, L.A. Momoda, G.P. Carman, Manufacturing issues of thin film NiTi microwrapper, Sens. Actuators A93 (2001) 148.

[76] S. Takeuchi, I. Shimoyama, A three-dimensional shape-memory alloy microelectrode with clipping structure for insect neural recording, J. MEMS 9 (2000) 24–31.

[77] Y.Q. Fu, H.J. Du, Fabrication of micromachined TiNi-based microgripper with complaint structure, in: Smart Sensors, Actuators, and MEMS, 19–21 May 2003, Gran Canaria, Spain, SPIE-Int. Soc. Opt. Eng, USA, SPIE vol. 5116, 2003, pp. 38–47.

[78] R.X. Wang, Y. Zohar, M. Wong, Residual stress-loaded titanium–nickel shape-memory alloy thin-film micro-actuators, J. Micromech. Microeng. 12 (2002) 323–327.

[79] M. Bendahan, K. Aguir, J.L. Seguin, H. Carchano, NiTi thin films as a gate of MOS capacity sensors, Sens. Actuators 74 (1999) 242–245.

[80] A.D. Johnson, Nitinal thin film three dimensional devices-fabrication and 3-D TiNi shape meory alloy actuators, Micromach. Devices 4 (1999) 1.

[81] M. Tabib-Azar, B. Sutapun, M. Huff, Applications of TiNi thin film shape-memory alloys in micro-opto-electro-mechanical systems, Sens. Actuators 77 (1999) 34–38.

[82] B. Sutapun, M. Tabib-Azar, M. Huff, Applications of shape-memory alloys in optics, Appl. Opt. 37 (1998) 6811–6815.

[83] A.D. Johnson, TiNi Alloy Company, 1619 Neptune Drive, San Leandro, CA, Web: http://www.tinialloy.com.

[84] H.P. Ho, C.Y. Chung, K.C. Ng, K.L. Cheng, S.Y. Wu, in: E.C. Harvey, D. Abbott, V.K. Varadan (Eds.), Smart Structures, Device and Systems, SPIE 4935 (2002) 65–73.

[85] S. Takabayashi, E. Tanino, S. Fukumoto, Y. Mimatsu, S. Yamashita, Y. Ichikawa, Functionally gradient NiTi films fabricated by sputtering, Jpn. J. Appl. Phys. 35 (1996) 200–204.

[86] Y.Q. Fu, H.J. Du, S. Zhang, Deposition of TiN layer on TiNi thin films to improve surface properties, Surf. Coat. Technol. 167 (2003) 129–136.

[87] Y.Q. Fu, H.J. Du, S. Zhang, Functionally graded TiN/TiNi shape-memory alloy films, Mater. Lett. 57 (2003) 2995–2999.

[88] F. Goldberg, E.J. Knystautas, The effects of ion irradiation on NiTi shape-memory alloy thin films, Thin Solid Films 342 (1999) 67–73.

[89] D.S. Grummon, R. Gotthardt, Latent strain in titanium–nickel thin films modified by irradiation of the plastically-deformed martensite phase with 5 MeV Ni^{2+}, Acta Mater. 48 (2000) 635–646.

[90] T.B. Lagrange, R. Gotthard, Microstructrual evolution and thermo-mechanical response of Ni ion irradiated TiNiSMA thin films, J. Optoelectron. Adv. Mater. 5 (2003) 313–318.

[91] G.S. Firstov, R.G. Vitchev, H. Kumar, B. Blanpain, J. Van Humbeeck, Surface oxidation of NiTi shape-memory alloy, Biomaterials 23 (2002) 4863–4871.

[92] L. Tan, W.C. Crone, Surface characterization of NiTi modified by plasma source ion implantation, Acta Mater. 50 (2002) 4449–4460.

[93] C.M. Craciunescu, M. Wuttig, New ferromagnetic and functionally graded shape-memory alloys, J. Optoelectron. Adv. Mater. 5 (2003) 139–146.

[94] J. Van Humbeeck, Damping capacity of thermoelastic martensite in shape-memory alloys, J. Alloys Comp. 355 (2003) 58–64.

[95] D.Y. Li, A new type of wear-resistant material: pseudo-elastic TiNi alloy, Wear 221 (1998) 116–123.

[96] T. Girardeau, K. Bouslykhane, J. Mimault, J.P. Villain, P. Chartier, Wear improvement and local structure in nickel–titanium coatings produced by reactive ion sputtering, Thin Solid Films 283 (1996) 67–74.

[97] J.L. He, K.W. Won, C.T. Chang, K.C. Chen, H.C. Lin, Cavitation-resistant TiNi films deposited by using cathodic are plasma ion plating, Wear 233–235 (1999) 104–110.

[98] T. Duerig, A. Pelton, D. Stockel, An overview of nitinol medical applications, Mater. Sci. Eng. A273–A275 (1999) 149–160.

Biographies

Yongqing Fu obtained his PhD degree from Nanyang Technological University, Singapore. Now he is a research fellow in Singapore–Massachusetts Institute Technology (MIT) Alliance, Nanyang Technological University. His research interests include thin films and surface coatings, shape-memory alloy MEMS and nanocomposite coatings.

Hejun Du obtained his BEng and MEng from Nanjing University of Aeronautics and Astronautics, China in 1983 and 1986, respectively, and obtained his PhD degree from Imperial College of Science, Technology and Medicine, UK. He is currently an associate professor in the School of Mechanical and Production Engineering, Nanyang Technological University, Singapore. Prof. Du's research interests mainly include three areas: (1) numerical and computational methods for engineering applications; (2) MEMS sensors and actuators; (3) smart materials and their engineering applications.

Weimin Huang received his BEng and MEng degrees in structural engineering from the Southeast University, China. After obtained his PhD degree from the University of Cambridge, UK, he joined the School of Mechanical and Production Engineering, Nanyang Technological University, Singapore. His main research interest is on shape memory materials.

Sam Zhang is the director and associate professor of the Thin Film Technology Strategic Research Program at the School of Mechanical and Production Engineering, Nanyang Technological University. Prof. Zhang received his PhD degree in Ceramics in 1991 from The University of Wisconsin-Madison, USA. Prof. Zhang's major subjects of research are nano-composite thin films for wear resistance, electronics and biomedical and MEMS applications.

Min Hu (member, IEEE) received his BSc and MEng degrees from the Central South University, China in 1990 and 1993. He received his PhD degree from Tsinghua University, China, in 1997. After that, he joined Nanyang Technological University, Singapore, as a research fellow. His favorite research areas include MEMS, micro-sensors and actuators, miniature linear/spherical actuators, precision motion control, and intelligent mechatronic systems.