



Review

Shape memory alloy thin films and heterostructures for MEMS applications: A review

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ABSTRACT

In recent years, shape memory alloy (SMA) thin films have attracted significant attention from the scientific community and industry for their potential applications in the field of smart sensors and actuators, micro- and nano-electromechanical systems, aerospace, automobile, and biomedical. The present article focuses on the recent developments in the field of SMA thin films and their heterostructures with other materials for potential microelectromechanical systems (MEMS) applications. Various microdevices such as microgrippers, micropumps, microvalves, and cantilevers fabricated from binary and ternary SMA films have been discussed in detail. SMA thin films combined with various nitrides, oxides, and ferroelectric layers offer excellent surface modification and vibration damping at microscale for their use in harsh environments. The article encompasses the new paradigms in the field of SMA thin films that have been essentially developed by the authors and co-workers during the past 6 years.

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1. Introduction

During the last decade, smart, structural, or intelligent materials have captivated great interest due to their potential scientific and technological importance [1–4]. A material which has built-in or intrinsic sensor (s), actuator (s), and control mechanism (s)

whereby it is capable of sensing an external stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields, responding to it in a predictable or controllable manner, in an appropriate time, and reverting to its original state as soon as the stimuli are removed is known as “smart material.” Varieties of smart materials already exist and are being researched extensively. These include SMAs, piezoelectric materials, magnetostrictive materials, electrostrictive materials, and pH-sensitive polymers [5–7]. Each individual type of smart material has one or more properties such as shape, stiff-

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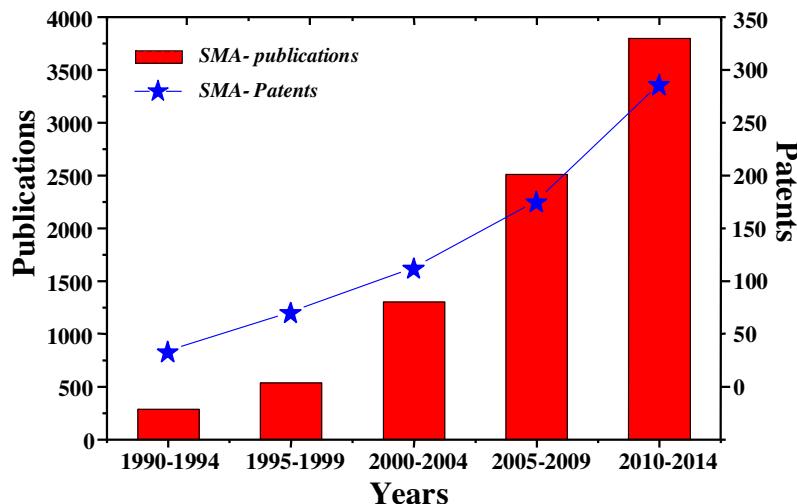


Fig. 1. Number of publications and patents based on temperature driven SMA thin films (Ref: Scifinder (<http://scifinder.cas.org>), Google Scholar (<https://scholar.google.com/>) US Patent & Trademark Office (<http://patft.uspto.gov/>), 09/17/2015).

ness, viscosity, volume, and temperature that can be significantly altered. Because of their special ability to respond to stimuli, they are being used in numerous applications in the field of sensors and actuators [8,9]. Among them, SMAs have been widely used as smart and functional materials because of their unique properties of shape memory effect (SME), pseudoelasticity (superelasticity), high power to weight ratio, high damping capacity, good chemical resistance, and biocompatibility [10–13]. Nickel-Titanium (NiTi) is the most widely used and commercially available SMA for both active and passive applications owing to its superior mechanical and shape-memory properties [14–16].

With the recent advents in MEMS, NiTi-based thin films are potentially desirable for microscale devices such as accelerometers, gyroscopes, microvalves, microphones, micro pressure sensors, microscanners, optical switches for their potential applications in the field of automotive, aerospace, biomedical, industrial process control, electronic instrumentation, telecommunications, and military applications [17–19]. NiTi thin films are a promising material for these applications as the work output per unit volume of NiTi exceeds that of other micro actuation mechanisms, and it can be patterned with standard lithography techniques in batch process [20–23]. A large number of micro-sensors and micro-actuators such as microswitches, microrelays, micropumps, microvalves, micro-grippers, and micropositioners can be made using NiTi thin films [24–26]. In addition, a high damping capacity makes NiTi SMAs an attractive functional material for vibration damping applications at microscale [27]. However, there are some potential problems associated with NiTi thin films including low energy efficiency, low dynamic response speed, large hysteresis, and fatigue problems [28,29]. Fig. 1 shows the growth in the number of publications on temperature and magnetic field driven SMA thin films since 1990.

The present article explores the research progress in the field of binary and ternary SMA thin films conducted in our research laboratory and worldwide, over the last decade. The successful demonstration of various MEMS devices utilizing SMA thin films has been discussed in detail in previous reports. Our research group has made significant progress in the domains of structural, electrical, mechanical, and damping properties of NiTi-based thin films and heterostructures. We studied the influence of grain size, thickness, and composition on phase transformation behavior of NiTi-based thin films. Surface modified NiTi showed significant improvement in mechanical, corrosion, bioactivity, and vibration damping properties at microscale. First, however, we provide some

Table 1
Various properties of NiTi SMA [32,33].

Melting point	1240–1310 °C
Density	6.4–6.5 g/cm ³
Thermal conductivity (austenite)	18 W/m.K
Thermal Conductivity (martensite)	8.6 W/m.K
Specific Heat	470–620 J/Kg K
Latent Heat	24,200 J/Kg
Transformation Range	–200 to 110 °C
Transformation Hysteresis	30–50 °C
Damping capacity, Q ^{−1}	~10 ^{−2}
Yield Strength (austenite)	200–800 Mpa
Young's Modulus (austenite)	50–90 Gpa
Yield strength (martensite)	150–300 Mpa
Young's Modulus (martensite)	28–41 Gpa
Ultimate Tensile Strength	750–960 Mpa
Shape Memory Strain (max.)	~8.0%
Resistivity (austenite)	70–110 μΩ cm
Resistivity (martensite)	40–70 μΩ cm

introductory background on SMAs, which we hope will facilitate our review and analysis of the literature.

2. Shape memory alloys

SMAs are the metals that “remember” their original shapes due to their unique properties of shape memory effect (SME) and superelasticity (pseudoelasticity). The unique shape memory behavior was first observed in AuCd alloy by Chang and Read in 1951, while pseudoelasticity had been seen in this alloy by Olander in 1932. In the early 1960s, Buehler and co-workers discovered the shape memory effect in an equiatomic alloy of nickel and titanium (NiTi) named as Nitinol, which is considered a breakthrough for engineering applications of shape memory materials [30,31]. The term “NITINOL” was coined from its composition and its place of discovery: (Nickel-Titanium-Naval Ordnance Laboratory). Until now, Nitinol has been the alloy showing superior shape memory characteristics among all SMAs. NiTi can exist in two different temperature-dependent crystal structures (phases) called martensite (lower temperature) and austenite (higher temperature or parent phase). The various properties of NiTi SMA are summarized in Table 1 [32,33].

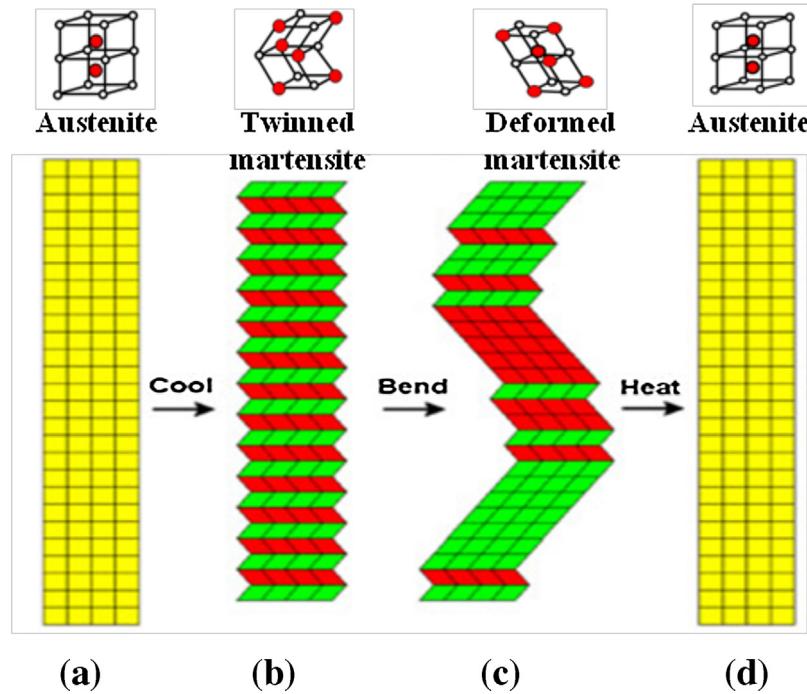


Fig. 2. Schematic diagram illustrating the phenomenon of shape memory effect [36].

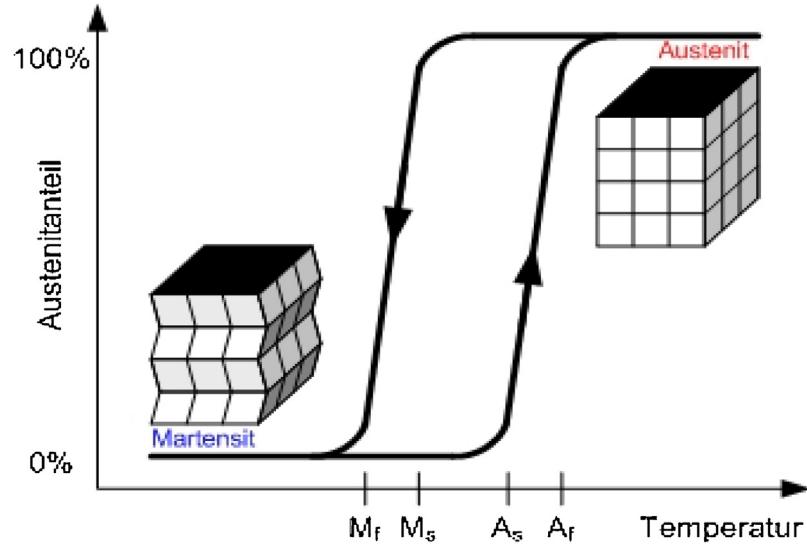


Fig. 3. Generic graph showing transformation between austenitic and martensitic phases of a shape memory material [37].

2.1. Shape memory effect

Shape memory effect (SME) refers to the ability of a SMA, such as NiTi, to recover its initial shape through subsequent heating after significant deformation in its ‘martensitic’ lower temperature state. The basic mechanism in this effect is a diffusionless solid state phase transformation also known as martensitic transformation (MT) occurring because of the nucleation and growth of martensite phase from a parent austenite phase, referring to a low temperature phase and a high temperature phase, respectively [34,35]. A diffusionless transformation is a phase change that occurs by cooperative, homogeneous movement of many atoms that results in a change in the crystal structure. These movements are small, usually less than the interatomic distances, and the atoms maintain their relative relationships such that the material remains a solid.

Shape memory effect can be explained by the schematic diagram shown in Fig. 2 [null][36]. The parent austenitic phase (usually with a cubic symmetry) as shown in Fig. 2(a), in the absence of applied stress will transform upon cooling to a set of differently oriented martensite twin variants (up to 24 variants for cubic-to-monoclinic transformation) in a random orientation usually with a monoclinic structure as indicated by Fig. 2(b). The martensite is relatively soft and can easily be deformed by an external loading, a de-twinning process starts and the growth of certain favorably oriented martensitic variants take place at the expense of other variants (Fig. 2(c)). If the martensitic material is deformed exclusively by twin boundary migration, the parent shape can be regained by re-heating the deformed martensite into highly symmetric austenite phase, as seen in Fig. 2(d). The transformations between austenitic and

variants (up to 24 variants for cubic-to-monoclinic transformation) in a random orientation usually with a monoclinic structure as indicated by Fig. 2(b). The martensite is relatively soft and can easily be deformed by an external loading, a de-twinning process starts and the growth of certain favorably oriented martensitic variants take place at the expense of other variants (Fig. 2(c)). If the martensitic material is deformed exclusively by twin boundary migration, the parent shape can be regained by re-heating the deformed martensite into highly symmetric austenite phase, as seen in Fig. 2(d). The transformations between austenitic and

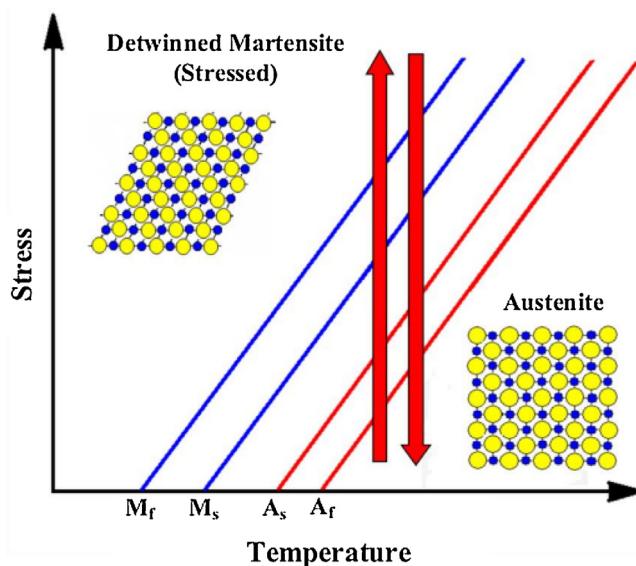


Fig. 4. Schematic of pseudoelastic loading–unloading paths in SMA [43]. Material returns to its original position after the load is removed.

martensitic phases occur over a range of temperatures and are described by a hysteresis loop in Fig. 3 [37]. Hysteresis occurs because an extra driving force is required to overcome the stored elastic strain energy that arises when a region undergoes a shape change as it transforms. The energy penalty associated with this elastic strain continues to rise as large volumes of material transform. The transformation temperatures are defined by: (i) A_s , the austenite start temperature; (ii) A_f , the austenite finish temperature; (iii) M_s , the martensite start temperature; and (iv) M_f , the martensite finish temperature. The hysteresis, ΔT , is defined as the temperature difference between a phase transformation upon heating and cooling. The austenite phase of NiTi with a cubic B2 structure has a lattice parameter of 0.3015 nm [38], while the martensite phase with monoclinic B19' structure has lattice parameters of $a = 0.2889$, $b = 0.4120$ and $c = 0.4622$ nm [39]. Sometimes, SMA undergoes a phase transformation from austenite to martensite and vice versa via self-accommodated intermediate phase, i.e. rhombohedral or R-phase, which is related to the alloy composition, heat treatment, and small grain size [40]. The R-phase crystal structure in NiTi can be thought of as a rhombohedral distortion along the [111] direction of the B2 parent lattice; the R-phase is often described by a hexagonal unit cell with lattice parameters of $a = 0.738$ and $c = 0.532$ nm [41].

2.2. Superelasticity

Superelasticity (SE), or sometimes called pseudoelasticity, is an elastic (reversible) response to an applied stress, caused by a phase transformation between the austenite and martensite phases of a SMA [42]. Unlike the shape memory effect, pseudoelasticity occurs without a change in temperature. SE takes place at sufficiently high temperature where stable austenite phase exists and the alloy is in its parent phase and original shape. When a mechanical strain is imposed, this can stimulate the transformation of an austenite phase to a stable de-twinned martensite phase, sometimes called “stress-induced martensite”. The associated shear of local regions accommodates this strain. Upon unloading, the generated strain is fully recovered and the alloy finally returns to its original austenite phase. This process is shown in Fig. 4 [43]. With NiTi SMAs, relatively large strains (up to about 8%) [44] can be accommodated without being plastically deformed, which is much higher than what would normally be possible during conventional elas-

tic deformation (up to ~0.5% for most metals) [45]. However, this phenomenon is only possible if all of the deformation has been accommodated by martensitic phase transformations. If an excessive strain is imposed, then it is likely that some conventional plastic flow (dislocation glide) will occur and the process will be irreversible.

3. SMA thin films

3.1. Binary SMA films (NiTi)

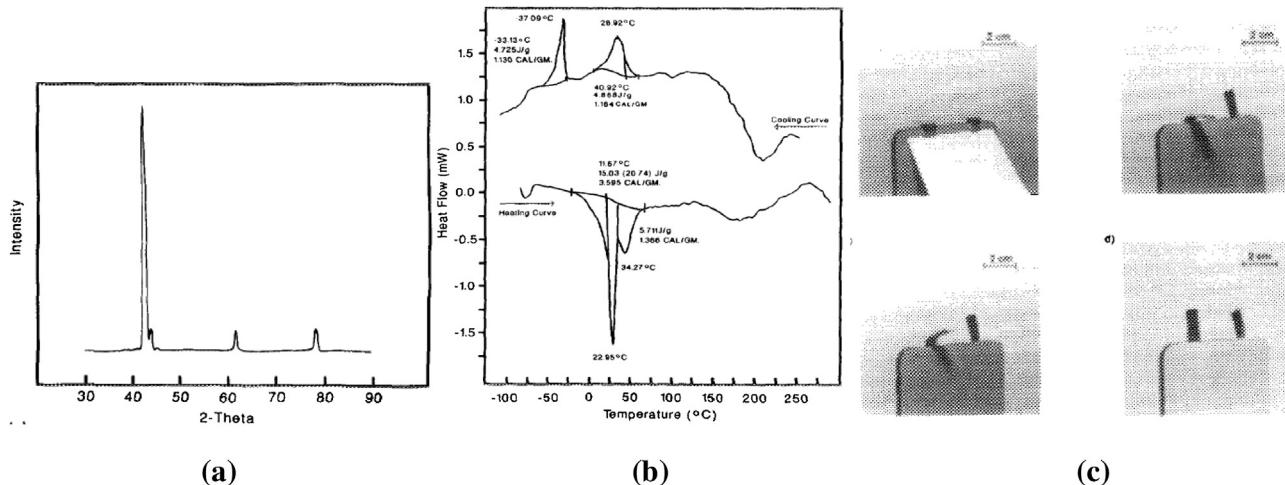
At the end of 1980s, SMA thin films received more attention as new intelligent and functional materials because of their unique properties. This new research area was motivated by the progress of MEMS made at the same era [46,47]. Amongst the shape-memory alloys, NiTi thin films have been the most widely studied materials because of several reasons like ability to recover large transformation stress and strain upon heating and cooling, great shape-restoring force, high damping capacity, good chemical resistance, and biocompatibility. NiTi thin film exhibits small thermal mass to heat or cool as compared to NiTi bulk and results in the reduced response time and increased operation speed [48]. The large surface to volume ratio in NiTi films results in fast natural cooling and large retention of actuation stresses and strains in thin film form [49]. Table 2 compares NiTi-based microactuators with other materials for their work/volume ratio, operating voltage, cycling frequency, power used for operation, and actuation displacement [50–59]. It is evident from Table that microactuators fabricated with NiTi films show the highest energy density (work/unit volume), on the order of 6 J/cm³. Besides this, NiTi microactuators require a very low voltage for their operation and results in large actuation displacements.

Various physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques have been extensively employed to fabricate SMA thin films and heterostructures. These include laser ablation, ion beam deposition, arc plasma ion plating, plasma spray, and flash evaporation [60–62]. But these techniques have some intrinsic problems, such as non-uniformity in film thickness and composition, low deposition rate, or non-batch processing, incompatibility with MEMS process, etc. In comparison to above techniques, magnetron sputtering showed the way to deposit SMA films with good adhesion, high hardness, reproducibility and flexibility, and it also enables the fabrication of large scale uniform coatings with a low/high density [63,64]. In addition, magnetron sputtering is capable of depositing multi-component films such as binary and ternary SMAs. Hence, most of the research on SMA thin films and heterostructures has been carried out by sputtering technique. Busch et al. [65] first fabricated NiTi thin films using sputter deposition technique in 1990. The X-ray diffraction (XRD) and Differential scanning calorimetry (DSC) results in Fig. 5(a) and (b) clearly confirms the formation of NiTi phase and a good shape memory effect, respectively. They also demonstrated the SME in 10 µm thick NiTi actuating element as shown in Fig. 5(c). Since then, a large number of studies have been done to explore the different aspects of NiTi thin films. Miyazaki et al. [66] showed that shape memory effects are associated with both the R-phase (rhombohedral phase) and martensitic transformations in NiTi thin films. Crystal structures of the austenite, martensitic (M), and R phases were also determined to be cubic, monoclinic, and rhombohedral, respectively, by X-ray diffractometry [67]. However, the potential problem observed in the deposition of useful SMA films is the different sputtering yields of depositing elements which cause compositional deviation between alloy target and deposited films. NiTi-based thin films are found to be very sensitive to composition variation and 1 at.% deviation near the equiatomic composition can

Table 2

A comparison of different microactuators [50–59].

S.No	Microactuators	Work/Volume (J/cm ³)	Operating Voltage (V)Approx.	Power use	Response Time (ms)	Displacement(μm)	Temperature Sensitive
1.	SMA (NiTi)	6	5	Medium	30	10–570	Yes
2.	Muscle	0.018	–	Low	150	0.6–10	No
3.	Electromagnetic	0.9	100	Very Low	1	~10 ³	No
4.	Electrostatic	0.4	100	Very Low	1	0.1–30	No
5.	Piezoelectric	0.02	90	Low	20	~10	No
6.	Solid-liquid phase change	4	15	Medium	300	~100	Yes
7.	Micro-bubble	0.00034	5	Medium	1	~140	Yes
8.	Thermo-mechanical	0.02	12	Medium	100	10–100	Yes

**Fig. 5.** First demonstration of NiTi SMA thin films by Busch (a) XRD pattern showing the formation of NiTi phase (b) DSC curves demonstrate a good SME in NiTi films and (c) shape memory behavior in NiTi thin film microactuator [65,72].

shift the transformation by around 100 °C [68]. As inferred from the NiTi phase diagram [69], there is a very narrow composition window for stoichiometric NiTi films and a slight deviation in stoichiometry causes the transformation temperatures of NiTi films to drop, even below room temperature, which makes it difficult to use for successful MEMS applications. For example, sputtering of NiTi thin films from an equiatomic NiTi alloy target invariably leads to Ni-rich films (films may be Ti poor with respect to the target by around 2–4 at.%) because the sputtering yield for Ni is higher than that for Ti [70,71]. Busch et al. [72] observed that NiTi film transformation temperatures decrease by approximately 25 °C per 0.2 at.% rise in nickel content. Similarly, Wibowo et al. [73] optimized RF and DC sputtering conditions to produce nearly equiatomic NiTi films. In an another approach, Shih et al. [74] fabricated equiatomic TiNi films with high transformation temperatures (~100 °C) by using co-sputtering of TiNi and with Ni and Ti targets. Other research groups employed either the elemental targets (Ni and Ti) [75,76], or Ti mesh [77,78] on NiTi target to mitigate the non-stoichiometry in NiTi films. Humbeeck research group [79] proposed hot target sputtering approach to control the microstructure and composition of Ni-Ti films across the thickness. Since, NiTi films deposited at room temperature are amorphous in nature and therefore post annealing treatments or high temperature depositions of thin films are required to observe the typical martensitic transformations. Improper post annealing treatment could also be detrimental to the quality of the films [80,81]. Jarrige et al. [82] investigated the influence of NiTi/Si annealing at 500 °C for 30 min. Their results showed that under annealing conditions, an interfacial layer of NiSi₂ was formed in between NiTi and Si over several tens of nanometers. Vestel et al. [83] used post annealing treatment to crystallize thick, free-standing amorphous NiTi films at 400 °C. However, a good crystalline phase with lamellar microstructure was observed in their films but a Ti-rich precipitate (Ti₂Ni) was also formed at the

columnar/plate grain interface. On the other hand, films deposited at high substrate temperatures (400–600 °C) are crystalline and do not require any post-annealing treatments [84]. But, these temperatures are disadvantageous for the substrates that become unstable at high temperatures and the growth is accompanied by the formation of precipitates due to interfacial chemical reactions [85,86]. These films are more prone to cracking and high surface roughness [87]. Some research groups used localized laser annealing to crystallize certain areas of NiTi amorphous films [88,89].

As the phase transformation in SMA thin films is accompanied by significant changes in the mechanical, physical, chemical, electrical, and optical properties, these changes can be fully used for the design and fabrication of microsensors and micro-actuators. However, due to the lack of full understanding of the SMA thin film together with the controlling of the deposition parameters, effect of nano-grain or nanocrystalline structure on shape memory behavior, film thickness effect, surface chemistry, surface adsorption, and biocompatibility, they cannot get the best place as micro-actuators in MEMS. Therefore, full understanding of these issues will make these films more promising for MEMS devices. Significant efforts have been devoted to explore the effect of grain refinement over martensitic transformation in NiTi bulk by several research groups [90,91]. But the knowledge of such a phenomenon in NiTi thin films is sparse. Improving the understanding of the microstructural development would enable better control of actuation properties. Ramirez et al. [92] studied real time in situ heating of NiTi films in TEM to examine the microstructure evolution with crystallization temperature. They found that equiatomic amorphous NiTi crystallizes by polymorphic mechanisms, and there is a strong dependence of crystallization and phase transformation on the stoichiometry of NiTi films. Fu et al. [93] developed NiTi films with a grain size of about 500 nm and studied its influence on the crystal structure and phase transfor-

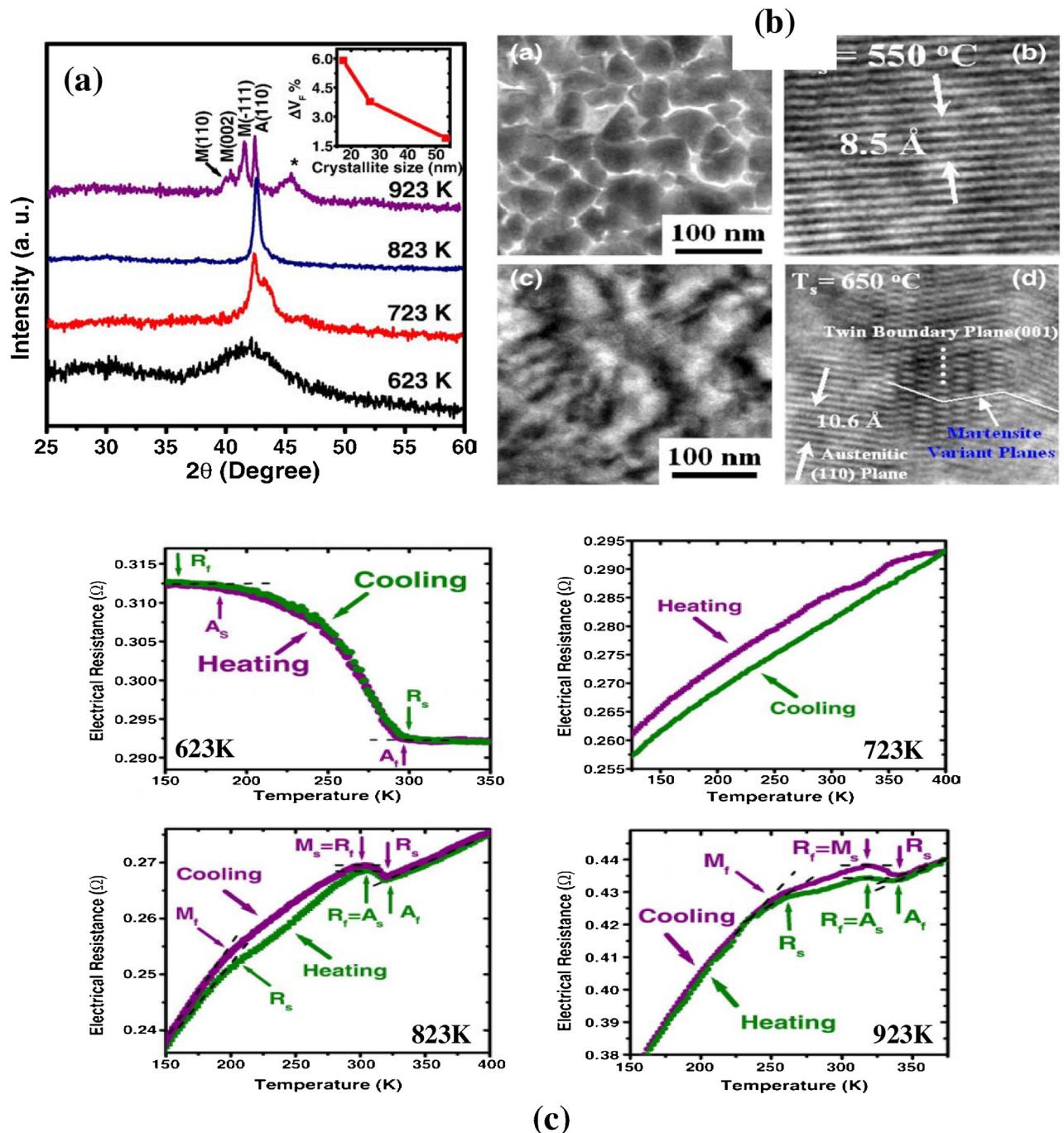


Fig. 6. (a) XRD pattern of NiTi films at different substrate temperatures (b) HRTEM images showing the formation of austenite and austenite + martensite phase in NiTi films deposited at 823 K and 923 K, respectively (c) Resistivity versus temperature (R-T) curves showing phase transformation behavior in NiTi films [94].

mation behavior. Their results from DSC, in-situ XRD, and curvature measurement revealed a clear martensitic transformation in NiTi films. These films were further utilized to fabricate micro-gripper and microvalve on micro-machined silicon cantilever structures with large deformation due to shape-memory effect. In this direction, our research group examined the effect of grain size on the crystal structure, surface morphology, and phase transformation behavior of NiTi thin films [94]. Fig. 6(a) shows the XRD pattern of NiTi thin films deposited on Si (100) substrate at various substrate temperatures (room temperature–923 K) using magnetron sputtering. NiTi films deposited below 623 K were found to be amorphous while they were crystalline and highly oriented along (110) plane of austenite parent phase at deposition tempera-

tures ≥ 723 K. A dominance of martensite phase peaks could be observed in the XRD pattern of NiTi films deposited above eutectic temperature (~ 923 K). HRTEM images of NiTi films deposited at 823 K and 923 K clearly confirm the formation of austenite phase and mixed (austenite + martensite) phase, respectively (Fig. 6(b)). The phase transformation behavior in NiTi films deposited at different substrate temperatures was confirmed by resistance versus temperature (R-T) measurements results as shown in Fig. 6(c). NiTi films deposited at 623 and 723 K resulted in a non-metallic behavior without any indication of SME. On the other hand, R-T plots of NiTi films deposited at 823 K and 923 K clearly indicate a phase transformation from martensite to austenite phase via R-phase during subsequent heating and cooling cycles. The suppression of

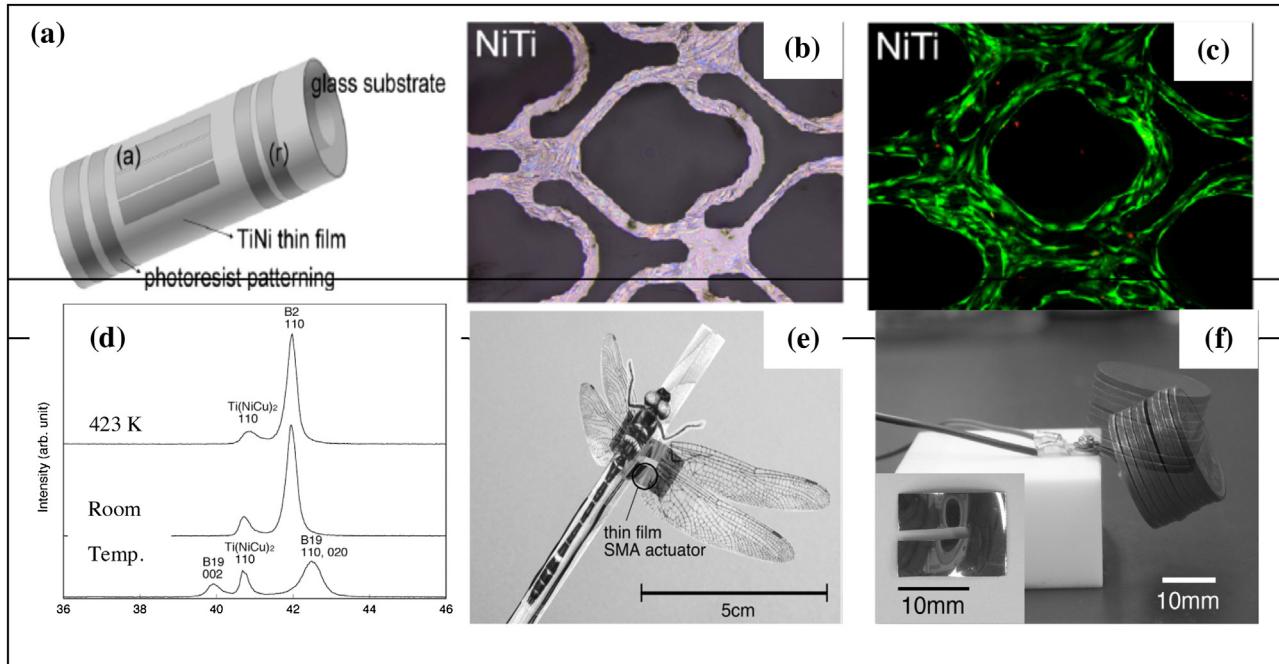


Fig. 7. (a) Cylindrical NiTi films deposited in radial and axial directions (b) Optical micrograph of NiTi thin film stents and (c) fluorescence micrograph of hMSC growth on the surface of NiTi HMSC were incubated for 7 days. [95] (d) XRD patterns of Ti–Ni–Cu/polyimide composite films measured at different temperatures. NiTiCu/polyimide microactuators show (e) wing movement of toy dragonfly and (f) lifting nine coins [98].

phase transformations at low deposition temperatures could be attributed to very small grain sizes causing higher number of grain boundary interfaces and associated excess free volume.

There are several recent developments in NiTi thin films, including fabrication of NiTi-based composites, flexible SMAs, and energy applications. Habijan et al. [95] demonstrated the viability of sputter deposition method to directly produce NiTi thin film stents. Fig. 7(a) demonstrates the deposition of NiTi films on cylindrical glass substrates. Three dimensional (3D) lithography followed by wet etching was employed to produce NiTi tubes for vascular stents as shown in Fig. 7(b). The specimens were further tested in human mesenchymal stem cells (hMSC) to examine the biocompatibility. After 7 days of cell culture, the presence of green fluorescence on NiTi stent surface (Fig. 7(c)) clearly indicate the survival of HMSC and thereby a good biocompatibility. In another effort, Hu et al. [96] prepared NiTi-Sn thin film composites for high performance anode materials in lithium-ion batteries. The presence of NiTi in NiTi-Sn composite offered an excellent tolerance to the mechanical stresses arising from the volumetric expansion of Sn during lithiation-delithiation process. Their electrodes exhibited a high reversible capacity and better retention as compared to previously reported Sn-carbon matrix electrodes. The direct deposition of crystalline NiTi films on flexible substrates is expected to widen the scope of flexible MEMS and bio-MEMS devices. Kotnur [97] successfully fabricated high quality NiTi and NiTiCu SMA films on flexible polyimide substrates at very low deposition temperatures of 350 °C. The as-grown films displayed typical martensitic transformations. In another study, Ishida et al. [98] fabricated NiTiCu films on polyimide substrates even at low substrate temperatures of 270 °C. The XRD pattern of Ti₄₉Ni₃₃Cu₁₈ film in Fig. 7(d) confirms the formation of TiNi (B2) and Ti(NiCu)₂ crystalline phases. They further utilized the SMA/polyimide composite films to fabricate actuators as shown in Fig. 7(e) and (f). These actuators were able to move a 0.18 g wing of the dragonfly up and down and lifted 9 coins weighing 4.5 g each.

3.2. Ternary SMA thin films

In spite of large recovery stress and strain in NiTi thin films, they cannot be used for high temperature applications due to their low transformation temperatures (i.e., ≤ 100 °C). The MEMS devices that require high transformation temperatures are used in automobile industry, where the transformation temperatures are up to 150 °C. Another example is high temperature gas chromatography that requires the operation temperatures up to 180 °C. The substitution of a third element for Ni or Ti (Ni-Ti-X; where X = Pd, Pt, Hf, Au) has been proved to be an effective way to increase the transformation temperatures of NiTi-based SMAs to meet the requirements of high temperature applications [99–101]. Among them, TiNiPd and TiNiHf films are also effective in decreasing the temperature hysteresis, thus promising for quick movement at higher temperatures. There are several reports showing the composition dependence of transition temperatures in ternary SMAs. Sanjabi et al. [102,103] studied the effect of Hf content on binary near equiatomic NiTi thin films using sputtering. They showed that the substitution of Hf for Ti up to 24.4 at.% significantly raised the transformation temperatures to 414 °C, whereas lower Hf contents (5 at.%) showed reduction in transformation temperature (Fig. 8 (a and b)). Fig. 8(c) and (d) are the surface morphology of NiTi and NiTiHf films. The formation of larger grain size in NiTiHf as compared to pure NiTi was responsible for their higher transformation temperatures. Similarly, Tong et al. [104,105] studied in detail the crystallization behavior, microstructure, and martensitic transformations in NiTiHf thin films. They showed that a nanocrystalline structure was formed in RTA-processed thin films and grain size was found to increase with increasing annealing temperature. However, at high annealing temperature at 973 K for 25s, the precipitates could be easily seen in the films. Konig et al. [106] investigated the exact composition region exhibiting reversible phase transformations, structural and fatigue properties in NiTiHf films by using combinatorial and high-throughput methods. A high recovery stress and improved functional fatigue properties were observed by them,

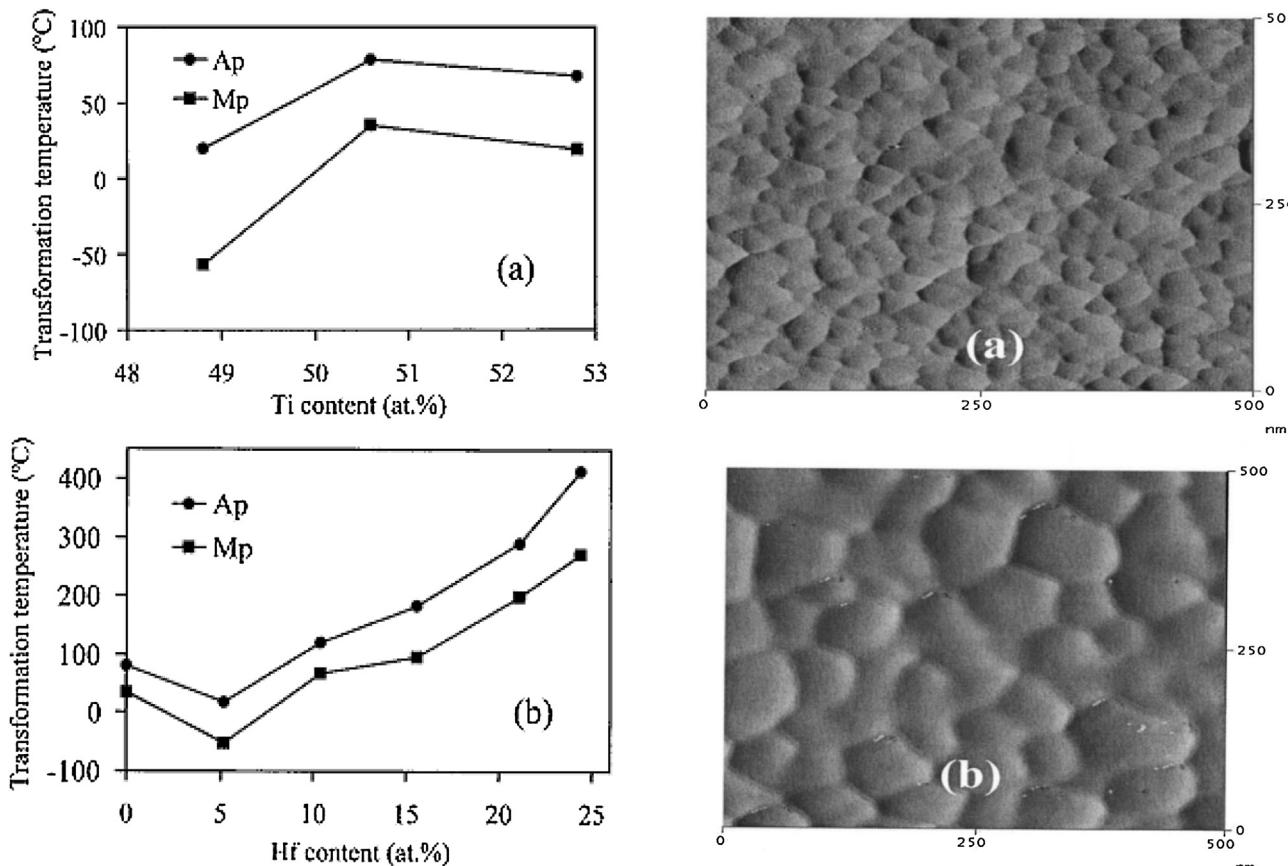


Fig. 8. Transformation temperature as a function of (a) Ti composition in $\text{Ni}_{100-x}\text{Ti}_x$ and (b) Hf content in $\text{Ni}_{50}\text{Ti}_{50-x}\text{Hf}_x$. Mp and Ap refer to Martenite and Austenite phase, respectively. Surface morphology of (c) equiatomic $\text{Ni}_{49.4}\text{Ti}_{50.6}$ and (d) $\text{Ni}_{49.5}\text{Ti}_{34.9}\text{Hf}_{15.6}$ [102,103].

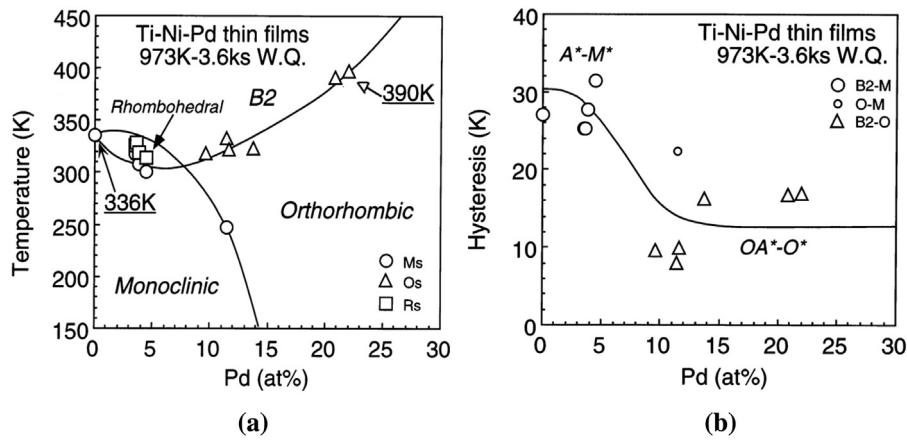


Fig. 9. Influence of Pd content on the (a) transformation temperature and (b) hysteresis width of Ti-Ni-Pd SMA thin films [110].

and it was attributed to the presence of Laves phase precipitates. The substitution of Ni with Pd also increases the transformation temperatures of the films up to 550 °C [107,108]. Schlossmacher et al. [109] investigated the effect of crystallization temperature on the microstructure of the Ti-Ni-Pd films by TEM analysis. They found that the low crystallization temperature (~773 K) results in fully crystalline but brittle films without any shape memory behavior, whereas an expected shape memory behavior was observed at high crystallization temperatures (973–1023 K) with the formation of high density $\text{Ti}_2\text{Ni}(\text{Pd})$ precipitates with diameter ~50–200 nm. Miyazaki and Ishida [110] showed the effect of Pd content on the transformation temperature and hysteresis width in NiTiPd thin

films annealed at 973 K (Fig. 9(a)). An increment in transformation temperatures up to 390 K was observed with an increment in the Pd content up to 22 at.%. The hysteresis width was also found to decrease (down to 10 K) with increasing Pd-content as shown in Fig. 9(b).

Another major drawback in pure NiTi thin films is its acute compositional sensitivity, i.e. a small compositional shift causes a large transformation-temperature change. Compared to traditionally used NiTi, the ternary NiTiCu alloys have shown less composition sensitivity and exhibit a narrower temperature hysteresis [111]. A significant change in the hysteresis width (up to 10 °C) with fast response have been achieved in NiTiCu thin films

with Cu content of 5–12 at.% [112]. Xu et al. [113] studied the crystallization behavior in NiTiCu thin films with small addition of Cu (1.3 at.%). In-situ TEM measurements revealed that NiTiCu films exhibit a higher growth rate and a lower nucleation rate with larger grain size as compared to pure NiTi films. Hashinaga et al. [114] showed a strong dependence of Cu content on the phase transformation behavior and hysteresis in NiTiCu thin films. The hysteresis width was found to decrease from 27 K to 10 K with increasing Cu-content 0 at.% to 9.5 at.%. A two-stage transformation, i.e. $B_2 \leftrightarrow$ Orthorombic \leftrightarrow Monoclinic was observed in 9.5 at.% Cu thin film with a perfect shape memory behavior. A significant improvement in the critical stress from 55 MPa to 350 MPa was also observed with increasing Cu-content.

Other less studied ternary SMA thin films are NiTiPt and NiTiAu. Fu et al. [115] first reported the $Ti_{50}Ni_{40}Pt_{10}$ thin films using co-sputtering of TiNi and Pt targets at 723 K. The films were grown with strong (111) orientation with transformation temperature close to room temperature. In another report by Rios et al. [116], a linear increase in transformation temperature along with a significant increase in hardness was found on the addition of Pt greater than 10 at.%. Mohanchandra et al. [117] showed the influence of crystallization temperature on TiNiPt thin films deposited on Si substrates using RF sputtering of a single target. The films crystallized at 550 °C and 600 °C for about an hour, resulting in an increase of the austenite and martensite transformation temperatures, which was attributed to the presence of large precipitates at higher crystallization temperatures. In this context, Kaur and Kaur [118] in our research group studied the grain refinement in NiTi films by co-sputtering them with tungsten (W) to form ternary NiTiW SMA thin films. Addition of W into NiTi matrix leads to a significant grain refinement that induces B_2 –R single step transformation with reduced thermal hysteresis width (ΔT) from 28 K (pure NiTi) to 11 K (NiTiW). Hardness and elastic modulus were also increased to maximum values of 32.87 ± 2.76 GPa and 167.837 ± 8.64 GPa respectively, with increasing W. Such SMAs are expected to show quick response in microactuators using R-phase transformation. Very recently, Buenconsejo et al. [119] explored new ternary SMA (i.e., Au–Cu–Al) thin films in a large composition range using combinatorial sputter-deposition. The films exhibited reversible phase transformations over a wide range of compositions with excellent thermal cyclic stability due to the presence of β -AuCuAl phase and its components. Besides this, there were other phases like Au–Cu, Al–Cu, and Al–Au that were responsible for limiting the range of phase-transforming composition.

3.3. SMA thin film applications

In the mid '90s, there had been a great research focus on the development of microactuators employing NiTi films deposited on silicon substrates. The fabrication techniques were adopted from microelectronics manufacture like IC, VLSI, etc. to MEMS processes. A common question was raised at the very beginning of the interrogation: why should there be the development of shape memory microdevices? The answer is quite straightforward: the ordinary MEMS devices have drawbacks due to limited actuation technologies and lack of force and displacement. NiTi micro-actuators, on the other hand, can be fabricated down to micro dimensions and still produce relatively large force and displacement compared to other mechanisms. The industries that are particularly interested in NiTi thin film based microactuators include biomedical, aerospace, automotive, and consumer market. NiTi based micropumps and microvalves are attractive for the application of drug delivery, thermal switches, micro-fluidics, chemical analysis, and analytical instruments. The potential uses of micro-valves include flow regulation, on/off switching and sealing of liquids, gases, and vacuums. There are different designs for

NiTi film based micropumps/microvalves using NiTi membranes or diaphragm in the form of free-standing and constrained NiTi thin films [120,121]. Fig. 10 shows the various microdevices fabricated either by binary or ternary SMA thin films. Levi et al. [122] constructed a heart valve made from NiTi thin film and nitinol wire framework (Fig. 10(a)). Makino et al. [123] developed a micropump made of NiTi diaphragm structure by using diffusion and anodic bonding processes. Shin et al. [124] also developed a 10 μm thick NiTi film based actuator pump to generate high output force at large velocities (Fig. 10(b)). Their results showed that at an optimum operating load of 98 N, blocking force was 198 N. Fu et al. [125] fabricated microtweezers and microcages by using free-standing TiNiCu (3.5 μm thick) films. Their devices utilized two-way shape memory effects to show both horizontal and vertical displacements. The microactuators were capable of operating at a maximum temperature of 90 °C and a power less than 5 mW, with a maximum frequency of 100–300 Hz. However, these microdevices were actuated by free-standing SMA thin films, and a special bias structure was required to realize shape memory effect and a special structure to separate working fluid from electronic currents. These requirements complicate the structure design and fabrication of the whole pump extraordinarily. To overcome these complexities, TiNi/Si bimorph membrane based micropumps and valves have been developed because of their large actuation force, simplicity in process while silicon substrate provides the necessary bias force. Xu et al. [126] fabricated a novel NiTi/Si composite diaphragm micropump that showed superior performance with high pumping yield ($\approx 340 \mu\text{l}/\text{min}$), high working frequency (up to 100 Hz), and long fatigue life time ($< 4 \times 10^7$ working cycles) (Fig. 10(c)). Ishida et al. [127] proposed simple graphical designs for bridge-type and diaphragm-type actuators and predicted their performance on the basis of stress-strain curves of an SMA film. They proposed that the diaphragm-type actuators are important from the viewpoint of practical applications, since they are used to fabricate pumps and valves for micro fluid systems. Ternary SMA thin films like NiTiHf, NiTiPd, and NiTiAu are promising for automotive, aerospace, and energy applications where high transformation temperatures are required [128]. Kohl et al. [129] fabricated gas microvalves of about $3 \times 3 \times 5 \text{ mm}^3$ size actuated by NiTiPd ternary SMA (Fig. 10(d)). These microvalves were capable of operating at adjustable temperatures below 405 K. The transformation temperature of the micro device was adjusted by the composition of sputtering target and the crystallization temperature. The brittleness problem that occurred at high Pd content was overcome by the use of stress-optimized SMA microdevices and hybrid integration technology.

NiTi thin films are promising in making microgrippers because of their large gripping force and sufficient opening distance for assembling works due to large actuation. Seidemann et al. [130] and Lee et al. [131] fabricated 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. The force and displacement generated can be very large. A novel micro-wrapper was fabricated using free-standing TiNi films with out-of-plane movement [132] (Fig. 10(e)). 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. Gill et al. [133] fabricated the NiTi microwrapper and discusses the fabrication issues in wet and dry etching techniques (Fig. 10(f)). Results showed that wet etching of the amorphous NiTi film produces a cleaner pattern, while the breakage in the film at sacrificial layer steps was less pronounced in dry etching and ion-milling techniques. There are several reports on the use of ternary NiTiCu thin films for making microgrippers. Bellouard et al. [134] demonstrated a micro-gripper that uses the

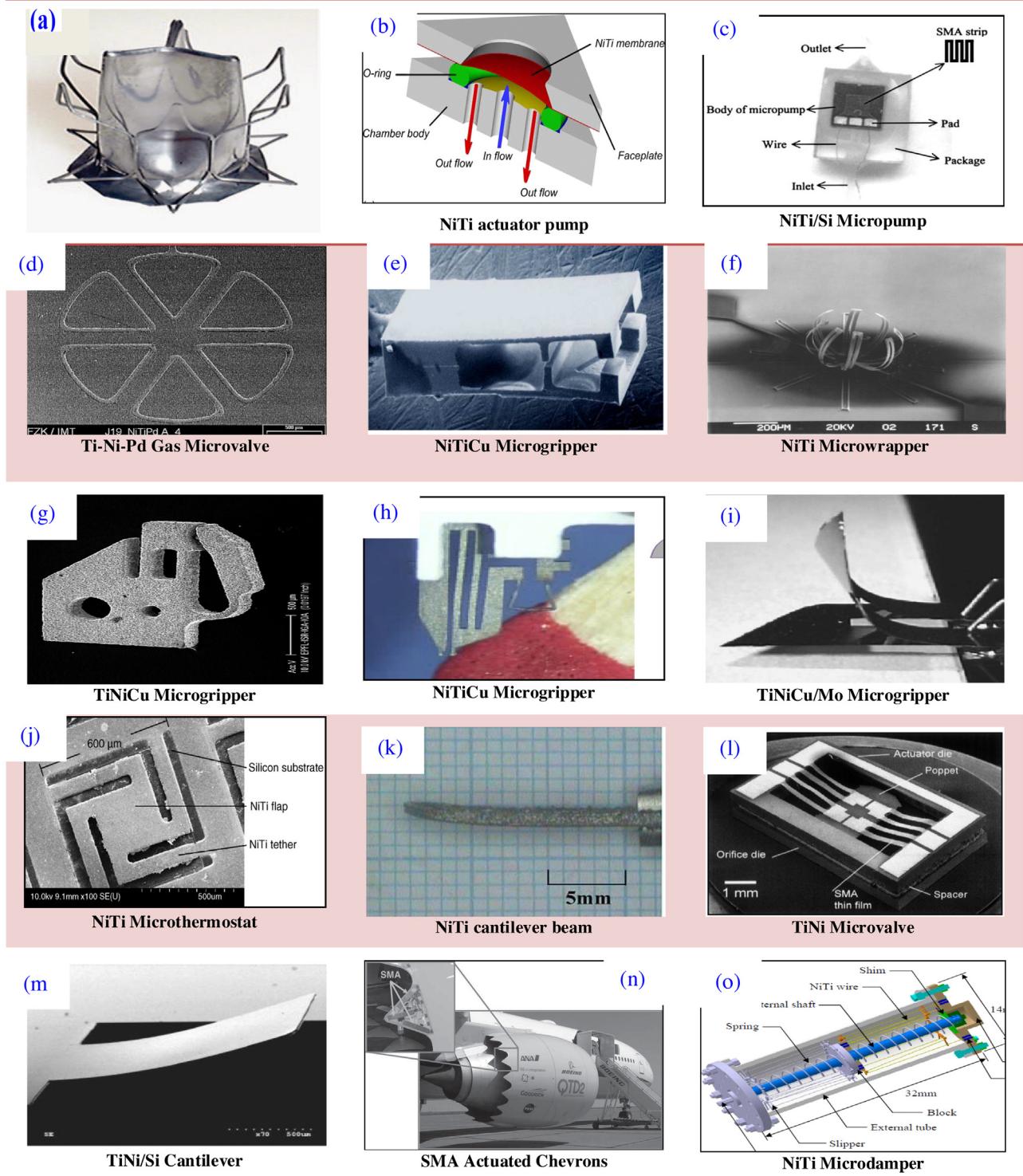


Fig. 10. (a-o) Various microdevices made of binary and ternary SMA thin films for MEMS applications [122,124,129,132–142].

two-way shape memory effect (TWSME) using a single piece of metal laser cut from a $180\text{ }\mu\text{m}$ thick Ni-Ti-Cu cold-rolled sheet (**Fig. 10(g)**). The micro-gripper showed excellent fatigue properties (>200,000 cycles) and stability regarding mechanical perturbations. Similarly, Zhang et al. [135] used cold rolled Ni-Ti-Cu (5 at.% Cu) sheet to develop a laser-annealed micro-gripper (**Fig. 10(h)**). This microdevice was designed for the manipulation of scaffold parts used in bone reconstruction therapy. Winzek et al. [136] developed tweezer-like microgrippers with TiNiCu/Mo thin film actuators on

Si-structures (**Fig. 10(i)**). These microgrippers will find potential applications in handling micro objects under electron beam and/or optical microscopy. In the near future, NiTi thin film based micro-actuators will definitely become the actuator of best choice in many aspects in the rapidly growing field of MEMS and Bio-MEMS. Several other MEMS devices such as microthermostats, chevrons, and microdampers fabricated by SMA thin films are presented in **Fig. 10(j-o)** [137–142]. The various aspects of shape memory alloy

microactuators have been discussed in detail in a book by Kohl [143].

Integration of SMAs with silicon-based microsystems is an important task for their proper functioning and widespread use. The traditional approaches like pick and place is an expensive way of integration [144], whereas the direct sputtering of SMAs on microstructures involves the issues of reproducibility [145]. Fischer et al. [146–148] proposed a standard wire bonding technique to integrate SMAs into silicon based MEMS structures. They utilized this approach for the fast, reliable and accurate integration of NiTi-based SMA wires to silicon-based MEMS that cannot be wire bonded by traditional means. Similarly, polymer based microsystems are highly attractive for biomedical applications due to their low cost and easily tailored chemical properties. However, the realization of active polymer microsystems requires their integration with transducer materials like SMA films. Kohl et al. [149,150] demonstrated the ultrasonic welding and heat-activated bonding methods for the batch integration of micro-machined polymer layers with SMA foils or films.

4. Surface modification of SMA thin films

NiTi based MEMS devices such as pumps, grippers, and valves require good surface treatments for their widespread applications [151]. Interfacial adhesion, large coefficient of friction, and potential stress are other major concerns for their tribological applications [152,153]. Besides this, the corrosion of NiTi surface and possible release of toxic Ni ions from its surface inhibits its use in biomedical applications. Hence, surface modification of NiTi-based SMAs is a promising way to mitigate the above problems. There have been some surface irradiation methods using electrons, ions (Ar, N, He, Ni or O ions), laser beams, neutrals to modify the surface physical, mechanical, wear, corrosion, and biological properties for applications in hostile environments and to cause lattice damage and/or alter the phase transformation behaviors along thickness of film, forming novel two-way shape memory actuation [154–156]. However, these surface treatments are costly, resulting in possible surface or ion-induced damage, amorphous phase formation, or degradation of shape memory effects [157]. Other methods include the surface oxidation of Nitinol using heat treatments in air, argon, and partially reduced atmosphere to prevent the Ni release [158,159]. The drawbacks of heat treatment are that they modify the phase composition along with the formation of Ti- or Ni-rich surface sub-layers. It is also observed that the heat treatments in different environments lead to the formation of various chemical compounds such as Ni_xTi_y , binary and ternary metal oxides and oxi-carbides on NiTi surface and makes them more prone to galvanic corrosion. Titania (TiO_2) coatings have also been demonstrated to be a corrosion resistant and biocompatible material for surface modification of NiTi alloys [160,161]. Liu et al. [162] deposited a 205 nm thick TiO_2 layer on NiTi surgical alloy sheet using sol-gel method. However, their results showed improved corrosion resistance and better blood compatibility. But, the presence of defects in TiO_2 layer and high amount of sub-surface Ni can make them vulnerable to allergic reactions. Recently, Li et al. [163] used magnetron sputtered tungsten (W) films to passivate NiTi for biomedical applications (Fig. 11(a)). The hydrophilic nature of W films facilitated better cell adhesion, reduced hemolysis rate, and inhibited Ni release. Fig. 11(b) shows a significant reduction in Ni^{2+} ion release in W coated NiTi films after the samples were immersed in Hank's solution for 60 days. In another report, Gill et al. [164] studied the influence of alloying (Ti, Ta and Cr) and magnetoelectropolishing (MEP) Nitinol for stent applications. Fig. 11(c) shows that MEP Ni-Ti-Cr alloy exhibited a negative hysteresis in the cyclic potentiodynamic polarization curves and was more resis-

tant to corrosion with less Ni ion release as compared to Ni-Ti and Ni-Ti-Ta. The formation of Ni oxide on the surface of MEP treated alloys allowed a non-toxic behavior and good biocompatibility. Fig. 11(d) displays the endothelial cell growth on NiTi, NiTiTa, and NiTiCr. A well-defined cell-to-cell growth on MEP SMAs represents an improved cytotoxicity and cellular viability.

To date, TiN surface coatings have been the most commonly used technique to modify the surface of NiTi based alloys and thin films, due to its superior mechanical properties, excellent corrosion, wear resistance, and excellent biocompatibility. TiN shows intrinsic biocompatibility and hemocompatibility and therefore is used as surface layers and electrical interconnects in orthopedic prostheses, cardiac valves, and other biomedical devices [165,166]. Cheng et al. [167] reported significant improvement in the wear resistance of NiTi alloy coated with a uniform and adhesive TiN layer by using PIID technique. The presence of TiN passivation layer on the top of NiTi films helps in improving the overall hardness, load bearing capacity, and tribological properties without sacrificing the shape memory effects. Also, the adhesion of TiN film on NiTi film is very good as it forms metallurgical bonds that will not flake, blister, chip, or peel. Fu et al. [168,169] explored the deposition of functionally graded TiN/TiNi coatings. Their experimental results of GIXD and DSC show that TiN physically resides on top of the TiNi film without any noticeable effect on the shape memory effect and martensite transformations. Friction tests showed significant improvements in the load bearing capacity and wear resistance in surface-modified TiNi films.

Our research group studied the influence of TiN passivation layer on the mechanical, corrosion, and electro-catalytic properties of NiTi thin films [170,171]. Fig. 12(a) and (b) are the field emission scanning electron microscope (FESEM) surface morphology and cross-section images of TiN/NiTi heterostructure. The grain size and thickness of TiN layer coated on NiTi was ~ 56 nm and 140 nm, respectively. The R-T curve in Fig. 12(c) clearly indicates that a complete phase transformation takes place in NiTi films even after the presence of TiN passivation layer. Mechanical properties showed that TiN/NiTi films exhibited a higher hardness (12.0 ± 0.8 GPa) as compared to NiTi films with hardness values of 7.3 ± 0.6 GPa. An improved corrosion resistance was found in TiN coated NiTi films as inferred by the shift of whole polarization curve towards low current density and high potential of the potentiodynamic polarization results shown in Fig. 12(d). It was observed that TiN/NiTi electrodes exhibited an excellent electrochemical sensing of dopamine, which has a critical physiological importance in Parkinson's disease. Fig. 12 (e and f) compares the electrochemical behavior of different electrodes (Si, NiTi/Si, TiN/Si, and TiN/NiTi) in dopamine. Pure NiTi electrode did not show any sign of oxidation peaks in dopamine, while the oxidation peaks in TiN/NiTi films were prominent. In another study by Kaur et al. [172], copper nitride (Cu_3N) layers were used to passivate NiTiCu films. Fig. 12(g) shows an interesting Cu nanodot structure that was formed at the surface of NiTiCu films when Cu_3N layer was deposited at a substrate temperature of 450°C . Electrochemical tests revealed that nanodot structure promotes a higher corrosion resistance in $\text{Cu}_3\text{N}/\text{NiTiCu}$ heterostructures as compared to pure NiTiCu. Moreover, the antibacterial and cytotoxicity tests were conducted using green fluorescent protein expressing *Escherichia coli* bacteria and human embryonic kidney cells. It is apparent from Fig. 12(h) that the density of bacteria was lower and deformed in case of Cu_3N nanorods passivated NiTiCu films as compared to pure NiTiCu. The high antibacterial activity and non-cytotoxicity will make them suitable for potential bio-MEMS applications. In a recent effort, Tillmann and Momeni [173] proposed that the performance of TiN coatings could be improved by incorporating carbon atoms to its matrix. The TiCN/NiTi composite films fabricated by

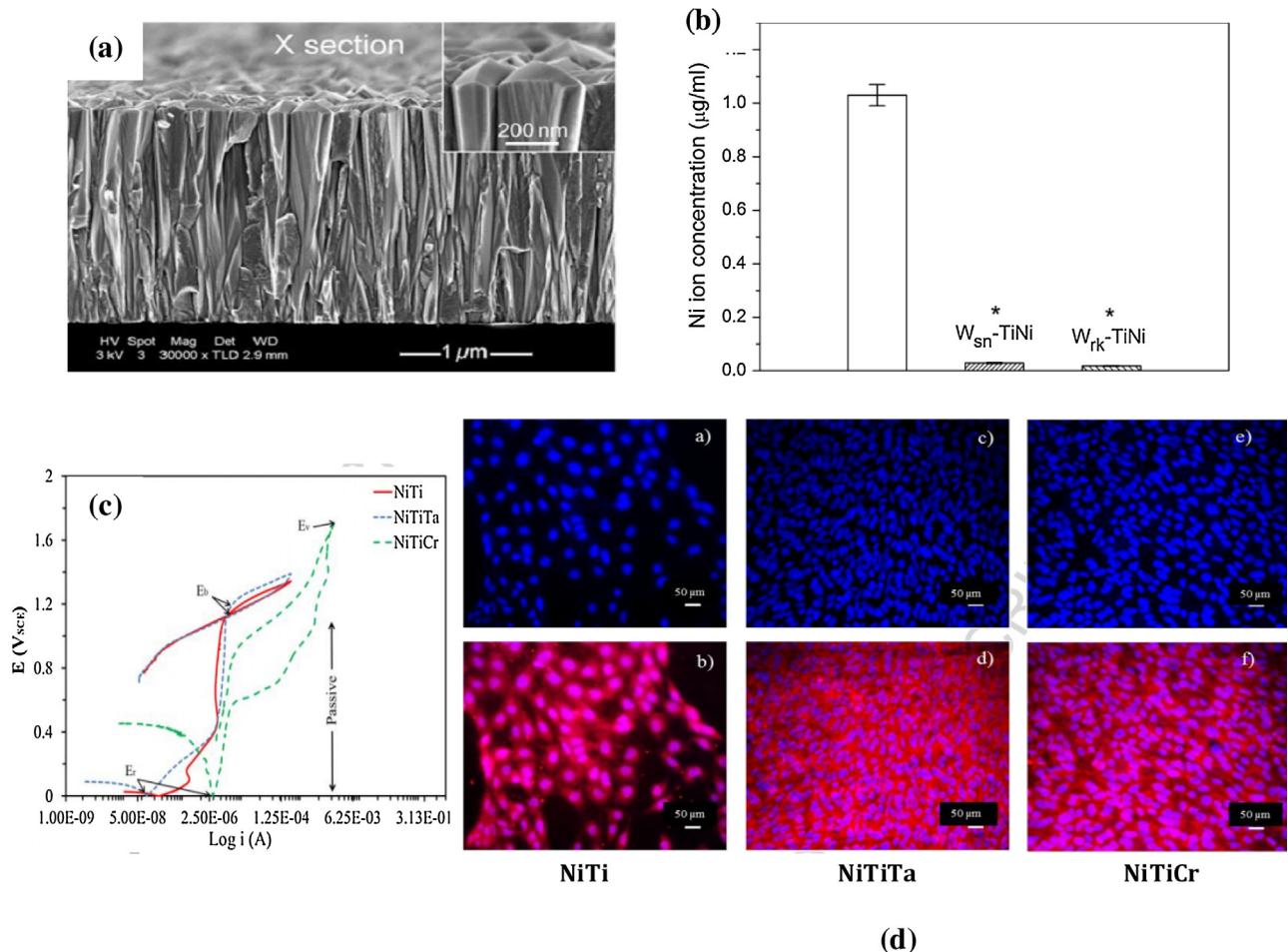


Fig. 11. (a) Cross-sectional SEM image of W film coated on TiNi substrate (b) comparison of Nickel- ion release from NiTi and W coated NiTi into Hank's solution after 60 days immersion [163] (c) cyclic voltammetry curves for MEP alloys (NiTi, NiTiTa, NiTiCr) (d) endothelial cell growth on untreated NiTi and MEP NiTiTa and NiTiCr [164].

them resulted in high mechanical hardness and reduced coefficient of resistance.

5. SMA/ferroelectric heterostructures

Macroscale vibration damping materials such as viscoelastic materials, metal-matrix composites, and smart materials have made enormous progress for a wide range of vibration damping applications including aerospace, automotive, machine tools, ships, satellite structures, space station, turbines, electronics, and optical equipment [174–177]. However, in recent decades there has been a great deal of interest in developing advanced vibration damping materials/approaches to protect MEMS devices (accelerometers, gyroscopes, microvalves, microphones, and micro pressure sensors) from mechanical vibrations and shocks [178–180]. Fig. 13 depicts the different MEMS devices used in different working environmental conditions. Smart munitions/missile systems (Fig. 13(a)) suffer from the severe inaccuracies of target-hit-positions due to MEMS device (angular rate sensors) failure in harsh environment conditions [181]. Similarly, phased array antennas (Fig. 13(b)) need accurate measurement of the signals in hostile environments. Fig. 13(c) represents a typical MEMS engine that utilizes delicate mechanical structures such as rotating gear, micro-cantilevers, and micro-resonators, which are prone to shock vibrations [182]. Fig. 13(d) shows a clear damage to comb drive resonators due to shock mechanical vibrations [183]. Hence, there is a need to develop vibration damping approaches compatible with micro-scale devices.

The basic requirements for a successful vibration damping approach for MEMS applications are high performance, lightweight, compatible, low cost, and reliable in operational environment without impeding MEMS performance, precision, and/or control. Although, some efforts have been undertaken by research groups towards microscale damping such as air damping [184], thermoelastic damping [185], squeeze film damping [186], and constrained layer damping [187], but all these approaches provided a marginal damping at microscale and were found to be incompatible with standard MEMS processing. A combination of SMA with piezoelectric materials in the form of thin film heterostructure presented an advanced, reliable, and compatible vibration damping approach for MEMS devices. NiTi, SMA, and lead zirconate titanate (PZT) are the best choice for these heterostructures owing to their excellent characteristic properties and are extensively studied materials [188,189]. Although, piezoelectric (PZT) and SMA (NiTi) films can offer favorable damping properties when used independently, but they suffer from the apparent weaknesses of small displacement and small response time, respectively [190–193]. Humbeeck et al. [194] have discussed and compared the active and passive damping aspects of various binary and ternary shape memory alloys. The logic of vibration damping by NiTi/PZT heterostructure when attached with a MEMS structure can be explained by considering an approaching mechanical vibration/wave as shown in Fig. 14. When the vibration hits the NiTi layer, the hysteretic movement and reorientation of martensite variant interfaces and twin boundaries produce martensitic-austenitic phase transformation in which some of the

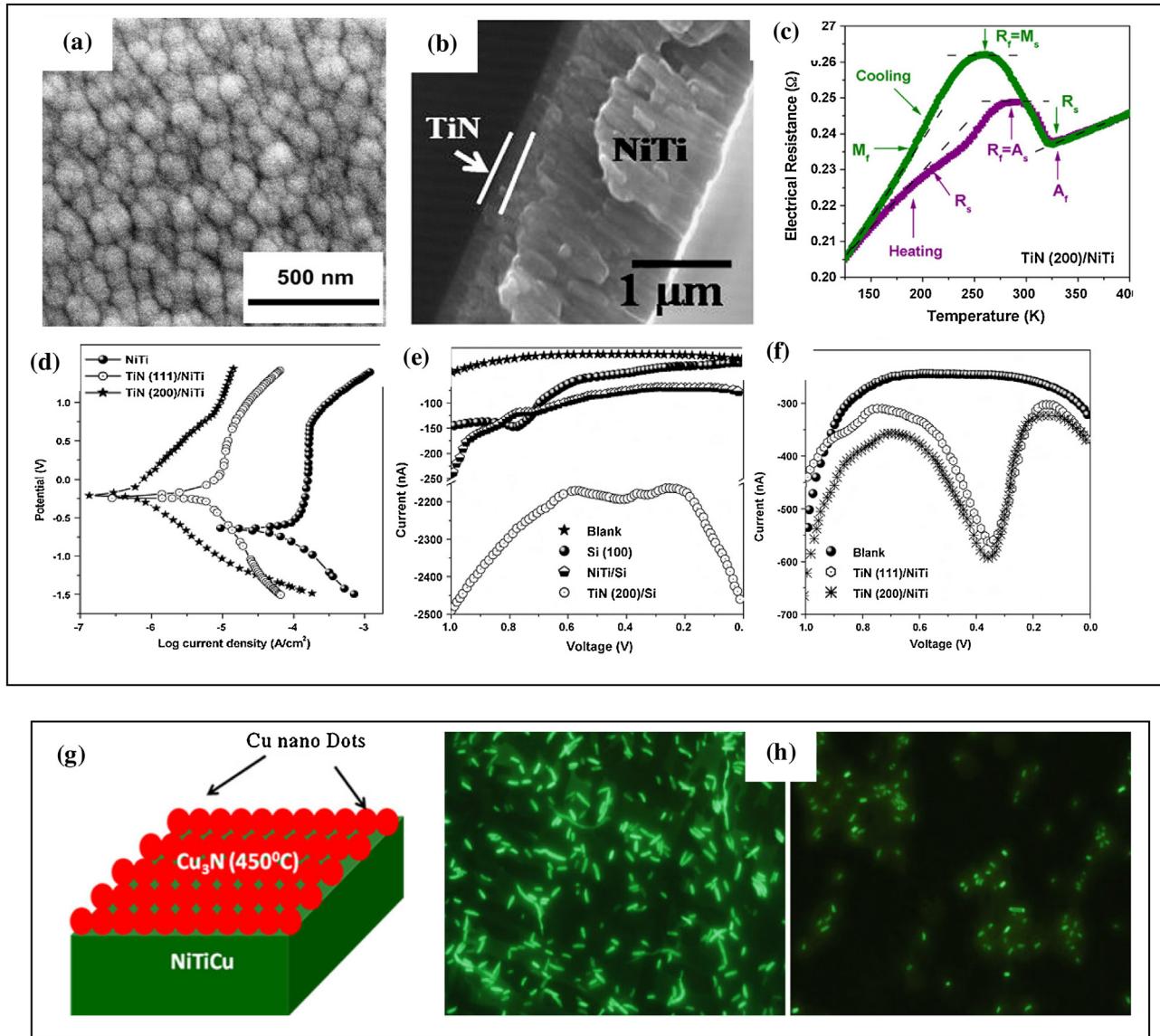


Fig. 12. (a) Surface morphology (b) cross-section FESEM and (c) R-T curve of TiN coated NiTi films (d) comparison of potentiodynamic polarization tests results in 1 M NaCl and (e and f) catalytic activity in dopamine of NiTi and TiN/NiTi films as working electrodes [170,171]. (g) Schematic diagram of Cu nano dots formation on Cu_3N /NiTiCu heterostructure (h) Fluorescent microscopic images of Pure NiTiCu and Cu_3N (450 °C)/NiTiCu treated GFP *E. coli* [172].

energy is converted into heat [195]. Vibrations that are not damped by NiTi continue to propagate through the PZT layer, which directly converts the mechanical energy of vibration into electrical energy by generating electric charges on the surfaces (piezoelectric effect), and this electrical energy may be dissipated by load resistance as joule heat [196].

There are limited reports on the fabrication of NiTi/PZT heterostructures due to severe constraints such as fabrication processing, interfacial diffusion, and the ability to generate the appropriate crystalline phases of each material without losing their individual properties [197–199]. Jardine et al. [200] fabricated an amorphous PZT/TiNi heterostructure on quartz substrates by a combination of the sol-gel processing and direct current sputtering and crystallized them at an optimized temperature of 873 K. Although their XRD result showed minimal chemical interaction between B2 TiNi substrate and the perovskite PZT ceramic phase, the ferroelectric properties were found to be poor as compared to literature values (Fig. 15(a)). Similarly, Chen et al. [201] had prepared the NiTi/PZT film by the sol-gel method, but the crack on the ferroelectric ceramic film was serious due to bad interfacial adhesion. T.J.

Zhu and X.B Zhao [202] used the pulsed laser technique to deposit PZT/TiNi heterostructure. They found that TiNi films deposited at different temperatures exhibit different crystal structures, and the B2 austenite structure favors the growth of perovskite PZT thin films (Fig. 15(b)). Kumar et al. [203] adopted the same technique to grow TiNi films on technically practical Si substrates with ferroelectric (BaTiO_3) underlayers, but TiNi/ BaTiO_3 films were significantly less uniform as compared to TiNi/PZT films. Other research groups used seeding layers to facilitate the nucleation of the perovskite phase of ferroelectric layer [204], while others used expensive Pt barrier layer between PZT and NiTi to mitigate the inter-diffusion at their interface (Fig. 15(c)) [205]. There are reports that show the use of other ferroelectric layers integrated with NiTi to produce vibration damping structures. Cole et al. [206] fabricated a passive damping structure with a NiTi thin layer overlying a BaSrTiO_3 (BST) ferroelectric fabricated on Si substrate having $\text{SiO}_2/\text{Ti}/\text{Pt}$ adhesion layers. Their structure resulted in a polycrystalline BST and martensite NiTi phase. Also, the high annealing temperatures (750 °C) resulted in the formation of reaction phases such as Ni-silicide and Ni-Ti silicide (Fig. 15(d)). On the other hand, Liu et al. [207] utilized

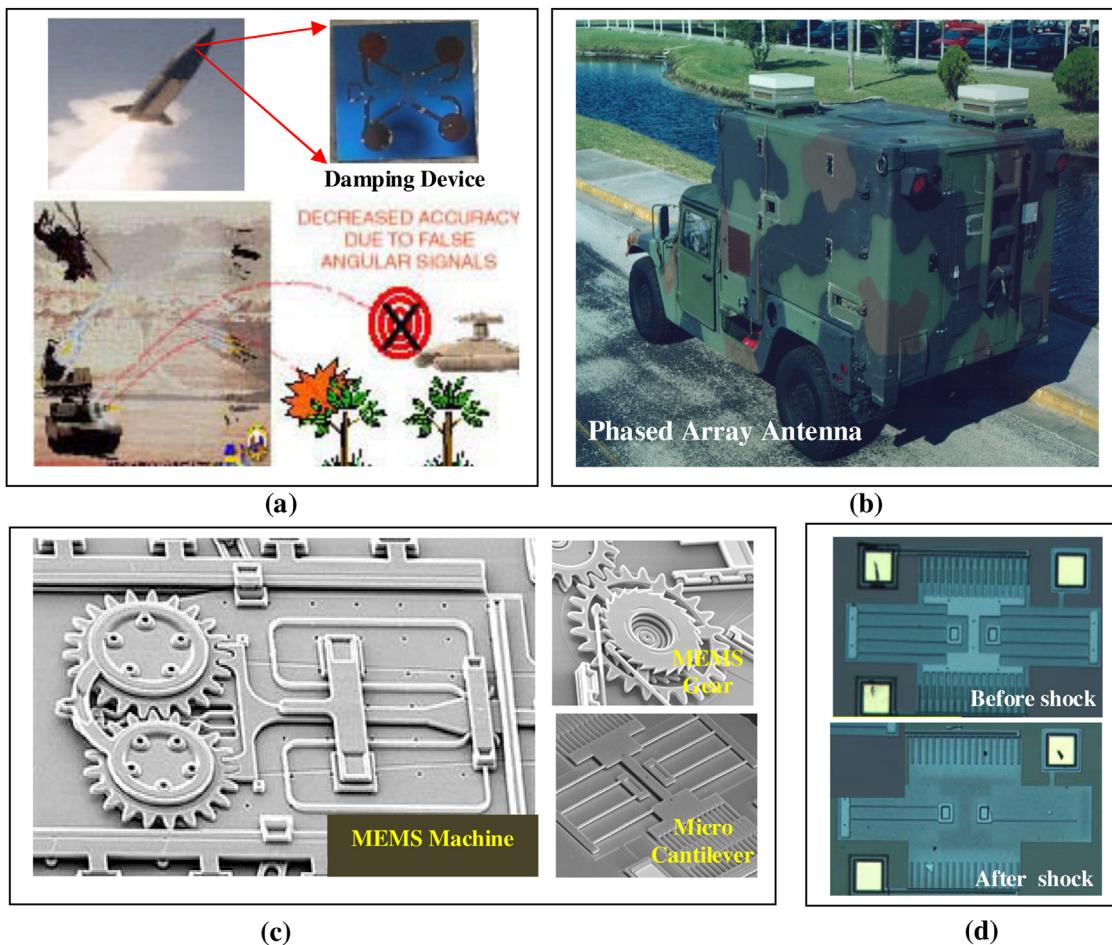


Fig. 13. (a) Smart missile systems require vibration damping device for precise target-hit position in harsh environments [181] (b) phased array antenna (c) MEMS machine composed of various MEMS components such as rotating gear, cantilever, and transducer [182] (d) Demonstration of comb-drive resonators in shock environment [183].

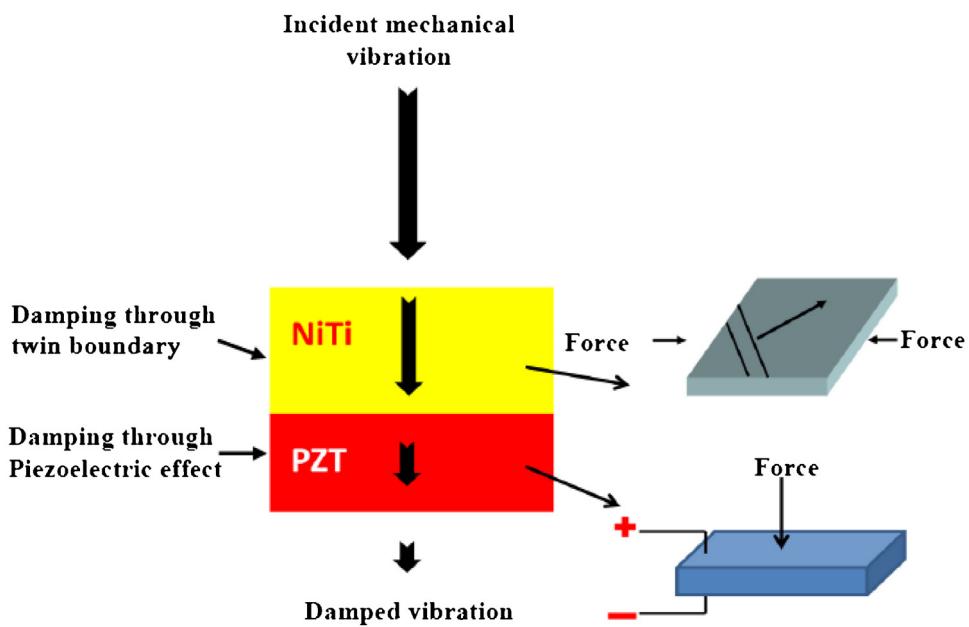


Fig. 14. Schematic representing the vibration damping in NiTi/PZT heterostructure.

hydrothermal reaction method to fabricate PbTiO_3 film on NiTi substrates. Their studies revealed a crack-free outer ceramic layer with an adhesion strength of 65 N between NiTi and PbTiO_3 . Hence, there

are only very few attempts on the fabrication, interfacial adhesion, and microstructure of SMA/piezoelectric structures, but there are no studies concerning the optimal thickness of individual material,

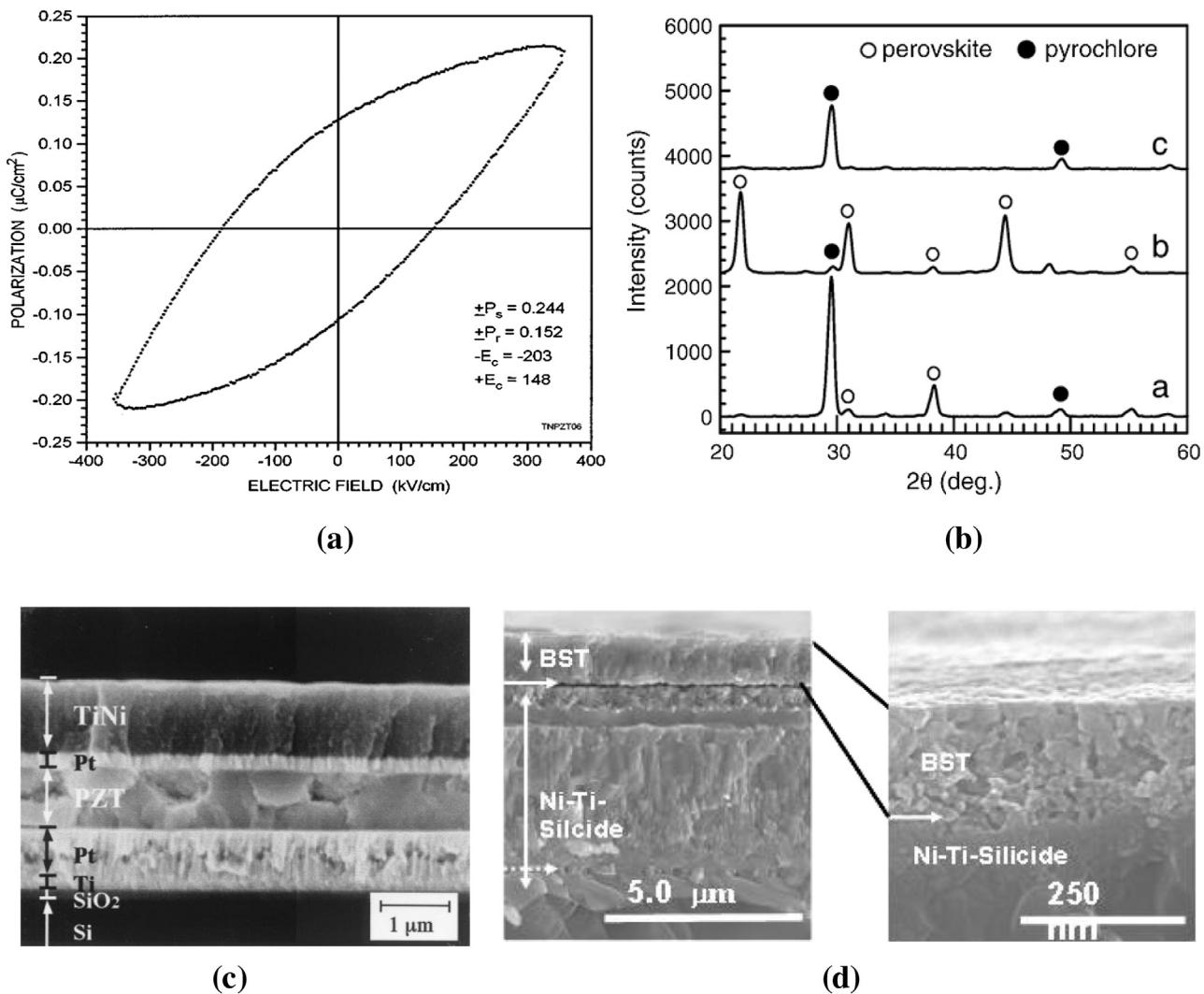


Fig. 15. (a) The poor ferroelectric properties in PZT by Jardine [200] (b) XRD pattern of PZT films deposited on NiTi underlayers [201] (c) cross-sectional SEM image of TiNi deposited on PZT with Pt barrier layers [205] (d) BST/NiTi heterostructure by Cole et al. [206].

phase transformation behavior, and evaluation of mechanical and vibration damping properties of these heterostructures.

For the first time, we fully explored the structural, electrical, mechanical, and damping properties of NiTi/PZT heterostructures by in-situ fabrication using magnetron sputtering technique. In our initial attempts, we optimized high quality NiTi and PZT films without any interfacial diffusion and impurity phases of either material. It was observed that NiTi film with 1.7 μm thickness and PZT (1 μm) exhibited the excellent structural, electrical, mechanical properties in NiTi/PZT heterostructures [208–210]. Fig. 16(a) shows the FESEM image of the cross-section and surface morphology of NiTi/PZT heterostructure. High quality NiTi and PZT films were obtained without any inter-diffusion at the interface. In order to enhance the limited hardness, wear resistance and chemical stability of top NiTi layer, we further modified the existing NiTi/PZT heterostructure by depositing thin protective coatings of AlN, CrN and CrTiN films and studied their impact on mechanical and corrosion properties in detail. Fig. 16(b) shows the hardness and plasticity index of pure and surface modified NiTi/PZT heterostructures [211]. A significant increment in the hardness from 7.8 GPa (min) for NiTi/PZT/ TiO_x heterostructure to 18.1 GPa (max) for CrTiN coated NiTi/PZT/ TiO_x heterostructure was observed. A high corrosion resistance with a protective efficiency of 96.8% was reported in

our surface modified NiTi/PZT heterostructures. Finally, we report the mechanical and damping properties of NiTi/Si, NiTi/PZT and CrTiN/NiTi/PZT heterostructures using Nanoindentation (creep and impact tests) as an alternative approach to DMA [212]. Fig. 16(c) shows the nanoindentation impact test results on NiTi, NiTi/PZT and CrTiN/NiTi/PZT heterostructures. It is clear from the curves that CrTiN/NiTi/PZT heterostructures absorb the impact energy most effectively and the percentage of energy dissipated during impact test was 67.5%, 86.3% and 91% for NiTi/Si, NiTi/PZT and CrTiN/NiTi/PZT, respectively. The enhanced damping capacity of NiTi/PZT and CrTiN/NiTi/PZT as compared to pure NiTi films could be due to the presence of efficient damping layers (PZT and CrTiN). The Figure of Merit (product of E_f and $\tan\delta$) obtained in CrTiN/NiTi/PZT (~0.75) heterostructure was found to be much higher than corresponding bulk materials of NiTi (0.14), PZT (0.24) and traditionally used high damping materials like Mn–Cu (0.48), Ni_2MnGa (0.35) [213]. Based on the same approach, we successfully determined the vibration damping properties in Ni-Mn-Sn FSMA thin films [214]. Nanoindentation approach for vibration damping calculations will definitely trigger important applications in MEMS devices. Kaur and Kaur [215] also utilized the nanoindentation technique to determine the vibration damping capacity in NiTiCu/AlN/NiTiCu heterostructures.

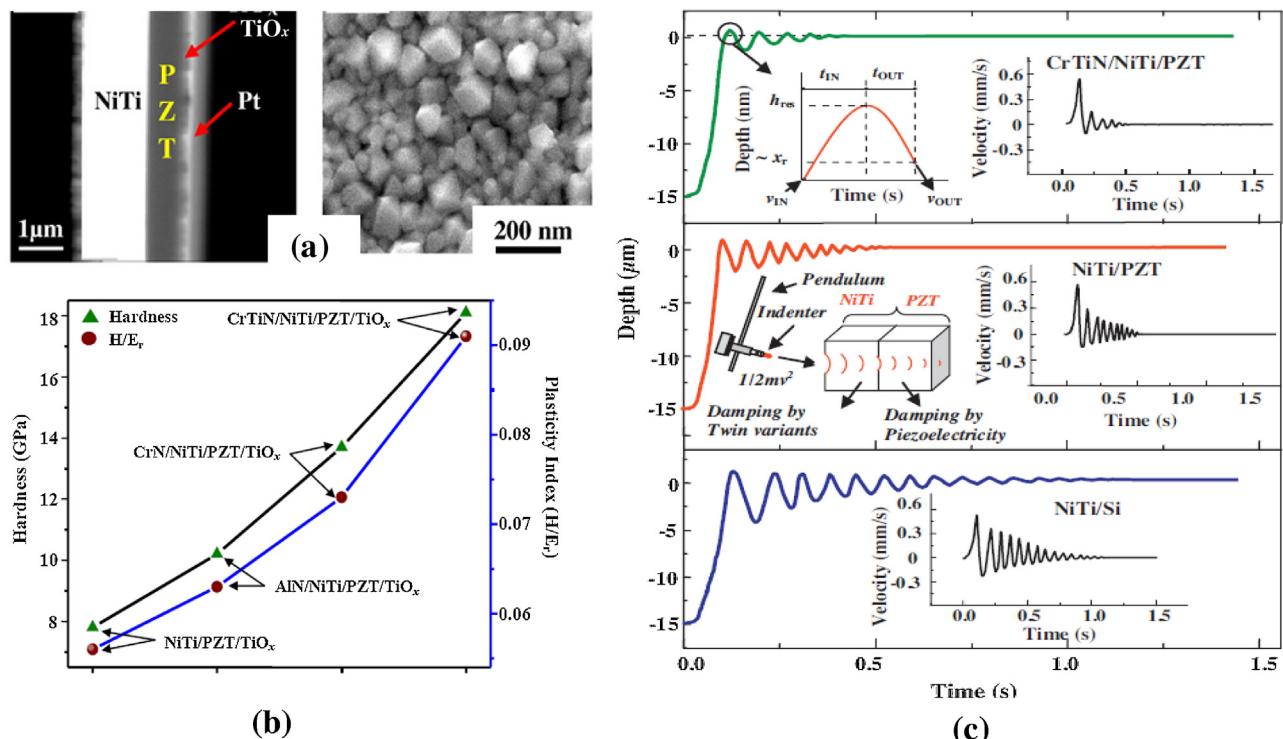


Fig. 16. (a) FESEM cross-section and surface morphology of NiTi/PZT heterostructure [208,209]. A clear interface was observed without any inter-diffusion (b) Hardness and Plasticity Index of NiTi/PZT heterostructures with different passivation layers (AlN, CrN, CrTiN) [211] (c) Impact test analysis of NiTi/Si, NiTi/PZT and CrTiN/NiTi/PZT heterostructures [212]. High vibration damping could be noticed in CrTiN/NiTi/PZT.

6. Conclusions & future directions

The present article gives an overview of the recent developments in temperature-driven SMA thin films and heterostructures for their potential applications in the field of sensors, actuators, biomedical, MEMS, automobile, military, and aerospace. The issues related with SMA thin film deposition, influence of annealing temperatures, film thickness and grain size effect on the structural, electrical, mechanical, magnetic, and shape memory properties were discussed in detail. The successful fabrication and operation of several binary and ternary NiTi-based micropumps, microgrippers, and microvalves is reported. Surface modified SMA films and their heterostructures with oxides and nitrides materials are finding potential applications in the field of Bio-MEMS and vibration damping in harsh environments. We believe that the current review will help researchers to gain insight about the current issues and developments in SMA thin films and heterostructures and will definitely trigger some new research areas for further technological applications.

Ferromagnetic SMAs (FSMAs) are the new class of smart materials exhibiting multifunctional properties like shape memory effect, pseudoelasticity, and ferromagnetism. They have the ability to show shape memory effects both in temperature as well as magnetic fields. The large output strain and fast dynamic response in FSMAs make them better MEMS candidates as compared to SMAs. The integration of SMAs with FSMAs in the form of hybrid heterostructures could be of significant importance for novel and advanced MEMS devices. Surface modification of SMAs is another research area that needs to be developed for their prolong and reliable operations. Graphene, an atomic layer thick sheet of carbon atoms exhibits extraordinary physical, chemical and structural properties, such as high elasticity, mechanical strength and large surface area. Therefore, it could be an interesting passivation layer for surface modifications of body implants such as scaffolds and

stents. Direct deposition of large area graphene on body implants would involve immense scientific and technical challenges.

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