Sputter-Deposited SMA Thin Films: Properties and Applications

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Abstract

Shape memory alloy (SMA) thin films formed by sputter deposition have attracted considerable attention in the last decade. Current intensive research demonstrated that thin films' unique fine microstructure is responsible for superior shape memory characteristics in films, compared to that of bulk materials. Simultaneously, much effort has been taken in the development and fabrication of microdevices actuated by SMA thin films. This article reviews the research to date on shape memory behavior and mechanical properties of SMA thin films, in connection with the peculiar microstructures. Furthermore, promising applications such as microvalves are demonstrated, along with the focused discussion on process-related problems. All the results indicate that thin films shape memory actuators are ready to contribute to the development of microelectromechanical systems.

Introduction

In the last decade, shape memory thin films formed by sputtering have been attracting great interest as powerful actuators in microelectromechanical systems (MEMS) such as micro valves, micro fluid pumps and micromanipulators, since the shape memory thin films (SMA thin films) possess a large force and displacement compared with the other type actuators including electrostatic, electromagnetic and piezoelectric ones. (Typically, the available stress and elongation limits for SMA actuators are 600 MPa and 5% as compare to 40 MPa and 0.1 % for piezoelectric ones). Originally, SMA actuators have an advantage of large output as the size decreases¹ (Figure 1). Besides, the response speed which is regarded as a drawback for SMA actuators in normal size is dropped by a large surface to volume ratio. Furthermore, they have potential compatibility with batch processing technology of silicon micromachining, so the actuators could be powered and controlled electrically by resistive heating of the film, utilizing potential of integrated microelectronics.

Such micro devices fabricated by the silicon micromachining process are keenly demanded in a variety of fields such as medicine, biotechnology, semiconductor industry and other applications. The first microvalve with SMA thin films actuator was reported in 1992². Since then, intensive research works have been done to clarify the properties of SMA thin films and, simultaneously, many efforts to fabricate some other micro devices driven by SMA thin films have been made. This article reviews the properties of SMA thin films and introduces promising applications.

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Fig.1 Power weight ratio vs. weight diagram of actuator (From Ikuta¹)

Sputtering process

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SMA thin films with thicknesses ranging from 0.5 to $20 \,\mu\text{m}$ are available by magnetron sputtering. In sputtering process, atoms sputtered from a material target by sputtering gas condense onto various substrates such as silicon wafer, polyimide films and glass plates to form a thin film.

The early difficulties to overcome in fabricating thin films were porous structure, oxygen contamination, composition deviation and so on. The structure and composition of deposited films are affected by sputtering conditions significantly. For example, if substrates are not heated, as-sputtered thin films are in the amorphous state. These films need post-sputtering heat-treatment for crystallization. On the other hand, heated substrates (typically above 600 K) produce crystalline films with $<110>_{B2}$ fiber texture and fine-grained structure³. Sputtering gas pressure is the important factor which influences the film structure. High gas pressure produces porous columnar structure, resulting in brittleness⁴.

Oxygen contamination also causes the brittleness and composition shift of deposited films by the formation of Ti-rich oxide. To avoid this contamination, a high vacuum system (base pressure, less than $2x10^{-5}$ Pa) is, of course, necessary, but more important is presputtering of a Ti target with a shutter closed. Sufficient presputtering prior to sputtering can reduce the oxygen partial pressure effectively, because of the getter effect of titanium.

The deviation of film composition from the target composition and its variation both in the plane and across the thickness are still troublesome problems, since a small shift of film

composition causes a large change of the martensitic transformation temperature. The composition shift arises from the differences in sputtering yield, angular flux distribution, lateral diffusion due to the collision with Ar gas and so on between sputtered species. In addition, the development of localized target wear and the variation in target composition with sputtering time make composition control difficult. After all, precise composition control is experientially achieved based on excellent reproducibility of sputtering. In most cases, the composition of Ti-Ni films shifts to the Ni-rich side because of higher sputtering yield of nickel. The compensation is performed by placing titanium plates on top of the Ti-Ni target or using multiple targets.

Microstructure and shape memory behavior of sputter-deposited thin films

For Ni-rich Ti-Ni thin films, conventional heat-treatment, *i.e.*, solution-treatment followed by aging-treatment, is available to stabilize the shape memory behavior, in the same manner as for bulk materials. This heat-treatment produces the same microstructure as that in bulk materials.



In contrast, Ti-rich Ti-Ni thin films crystallized from the amorphous state show peculiar fine microstructures which have never been reported in bulk materials. Figure 2 summarizes their microstructures⁵. When an amorphous Ti-48.2 at%Ni thin film is heat-treated at various temperatures, the microstructure in the B2 matrix changes drastically in the sequence of (e), (d) plate precipitates along {100} planes of the matrix⁶, (c) plate precipitates and spherical Ti₂Ni

precipitates with moiré fringes and (b) spherical Ti₂Ni precipitates⁷, with increasing heat-treatment temperature. The distribution of the plate precipitates changes depending on the heat-treatment temperature. When the heat-treatment temperature is high, supersaturated B2 phases with the same composition as that of the amorphous phase appear in the amorphous matrix first and then plate precipitates generate uniformly in the B2 grain. On the other hand, when the heat-treatment temperature is low, B2 phases with a near equiatomic composition crystallize in the amorphous phase, ejecting surplus Ti atoms into the amorphous matrix. This process results in localized distribution of plate precipitates⁸. The detailed structure of the plate precipitates is still controversial, but two types of structures have been reported so far: a Guinier-Preston-zone type structure in which excess Ti atoms are clustered on a $\{100\}_{B2}$ plane⁶ and a C11_b type ordered structure⁹ which is different from that of Ti₂Ni. The high-resolution electron microscopy revealed that the plate precipitates have coherency with the matrix⁹, while the spherical Ti₂Ni precipitates are semi-coherent with the matrix⁷.

Besides the oriented Ti_2Ni precipitates, Ti_2Ni particles which do not show any specific orientation relationship form in thin films containing higher Ti content (Fig. 2(a))¹⁰. In these films Ti_2Ni particles crystallize first and then B2 phases surrounding them crystallize.

The drastic change in microstructure shown in figure 2 must affect the shape memory characteristics. Figure 3 demonstrates the useful shape memory characteristics of the thin films containing the plate precipitates. The Ti-47.9at%Ni thin film annealed at 723K for 1h exhibits both a large transformation strain comparable to that of the Ti-50at%Ni thin film and no permanent strain after a cooling-heating cycle which is comparable to that of Ti-45.2at%Ni thin film. It is obvious that the peculiar fine microstructures improve the shape memory effect. Ti-rich Ti-Ni thin films possess higher transformation temperatures than Ni-rich thin films basically. These properties make Ti-rich Ti-Ni thin films more attractive than Ni-rich Ti-Ni thin films, unlike bulk materials.



Ternary shape memory thin films¹¹ such as Ti-Ni-Cu, Ti-Ni-Pd, Ti-Ni-Hf and Ti-Ni-Zr have also been fabricated by sputtering. Substitution of a third element is an attractive mean to raise the transformation temperature or decrease the temperature hysteresis, as for bulk materials. Besides ordinary shape memory effect described above, two-way shape memory effect¹² and a perfect superelasticity¹³ have been achieved in the form of thin film.

Mechanical properties of sputter-deposited thin films

The measurement of stress-strain curves has been performed for thin films¹⁴. A Ti-50.0 at%Ni thin film shows an elongation of more than 50%, while a Ti-51.5 at%Ni thin film containing a large amount of Ti₃Ni₄ shows a fracture stress as high as 1.6 GPa. These values are comparable to those in bulk materials. Especially, a Ti-48.3 at%Ni thin film annealed at a low temperature (773K) shows an elongation of almost 20 %. It is known that a bulk material with the same composition does not show any plastic deformation. This improvement comes from suppression of the coarse grain-boundary precipitates which cause fracture in the bulk materials. In general,

the yield stress for plastic deformation of thin films seems higher than that of bulk materials, owing to the small grain size (less than 4 μ m). The grain size of bulk materials is typically several tens of microns.

Thin film SMA microactuators

Ordinary shape memory effect is one-way, in which a deformed shape in the martensite phase recovers the original shape in the parent phase. To achieve reversible actuation, a bias force is required to deform the film in the martensite phase. Depending on the source a bias force, thin film SMA microactuators can be classified into two types: bimorph and freestanding. For the first one the bias force is provided by a thermal stress exerted from the substrate, while for the last one there is an external source of stress such as bias pressure and a spring. The bimorph actuators can produce large deflections at low forces, while the freestanding ones are capable of exerting large forces over a substantial stroke.

The application of SMA thin films as microactuators produces additional challenging problems. The understanding of stress evolution and relaxation in thin films during film processing and micromachining is inevitable to prevent detachment of films and to control the actuation of SMA thin films especially for bimorph type actuators¹⁵. The stress in SMA thin films consists of intrinsic and extrinsic stresses: the former is caused by deposition and crystallization, while the latter comes from differential thermal expansion. In addition to the stress in films, characteristics of the film/surface interface, such as the presence of reaction products, also affect the film adhesion.

Film thickness is also an important parameter in designing a thin film SMA actuator. Figure 4 shows the thickness effect on the shape memory behavior and mechanical properties of thin films. It is apparent that they change drastically when the film thickness is less than the mean grain size¹⁶.



Application of SMA thin films

The main issues to be addressed to integrate the sputter-deposited TiNi film into a silicon micromachining process are: 1) compatibility with the high annealing temperature (\sim 773 K) of deposited film; 2) compatibility of patterning methods for TiNi films; 3) developing of technique for selective releasing of TiNi film from the substrate. The possibility of integrating TiNi SMA thin films in silicon micromachining process was first demonstrated in 1990¹⁷. The fabrication process of the valve actuator first developed in TiNi Alloy Company is described in figure 5.



Although the number of other micro devices activated with thin film TiNi microactuators (microvalves^{18,19}, micropump²⁰, microreley²¹, micromirrors²², out of

plane spacers²²) have been reported during the last time, the microvalve manufactured by the TiNi Alloy Company (Fig. 6) is the only commercially available device²¹. It consists of an actuator die with a poppet controlled by the 8 TiNi thin film strips $3.5 \,\mu\text{m}$ thick, and 250 μm wide (Fig. 6(b)), a silicon orifice die, a spacer, and a bias spring. All elements are assembled in a plastic package (Fig. 6(a)). The bias spring forces the poppet towards the orifice. Resistive heating of the SMA thin films supporting the poppet causes it to transform from the martensite phase to the parent phase. By this transformation, TiNi strips recover the original length, lifting the poppet against the bias force and opening the valve. This device has a poppet displacement ~100 μm and bias force of 0.5 N. It is operated with an electric current of 50 to 100 mA. The response time is about 10 ms; maximum flow is up to 2000 sccm at 1.3 atm.

Apart from using the SMA thin film for purely technical application, it has also been introduced for medical use. As medical implantable devices made out of TiNi alloys are getting smaller in size, designers are trying to benefit from the combination of sputter deposition of TiNi and photolithography for manufacturing miniature medical devices. The United State Patent²³ proposed a method for fabricating of a rolled sheet thin film TiNi stent for use in the very small (down to 1 mm size) brain vessels (See the article by T. W. Duerig in this issue of *MRS Bulletin* for stent.). The film up to 30 μ m in thickness is deposited onto a flat substrate and released from it by etching away the sacrificial layer. The stent is provided with the dense perforation pattern, created by photochemical machining process, and has the wrap length up to 75 mm.



Future of SMA thin films

After a decade since the first report on shape memory effect in TiNi thin films²⁴, the sputter

deposition technique of SMA thin films has matured into the advanced technology, so today the processing technique of miniature SMA actuated devices is ready to be transferred to manufacturing. The future application of SMA thin films will continue to grow along with the expected progress in development of high temperature (~ 423 K) alloy compositions and three-dimensional deposition and photolithographic fabrication technology. The high transition temperature is essential for the SMA thin films to be used in devices, which operate at elevated temperatures (automotive applications, gas chromatography) and represent substantial part of the potential market. The sputter-deposited SMA devices also will continue to contribute to advances in miniaturizing of medical devices implantable into blood vessels.

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Captions of figures

- Fig. 1 Power weight ratio vs. weight diagram of actuator (From Ikuta¹)
- Fig. 2 Various precipitates in the Ti-Ni matrix of Ti-rich Ti-Ni thin films heat-treated at various temperatures for 1h:
 - \blacksquare Ti₂Ni particles with random orientation (a),
 - \Box Ti₂Ni precipitates with orientation relationship (b),
 - \triangle plate precipitates and oriented Ti₂Ni precipitates (c),
 - plate precipitates (high temperature form) (d) and plate precipitates (low temperature form) (e),
 - O no precipitates and
 - ▲ amorphous
 - (From Kawamura et al.⁵. Some revisions have been made.)
- Fig. 3 Effects of heat-treatment and film composition on strain-temperature curves under a constant stress of 400 MPa for Ti-rich Ti-Ni thin films. Each symbol corresponds to the microstructure in Fig. 2.
- Fig. 4 Thickness effects on the shape memory behavior (▲: transformation strain under a constant stress of 200 MPa) and mechanical properties (•: yield stress at a deformation temperature of 270K, ○: elongation until fracture at a deformation temperature of 360K) of a Ti-50 at% Ni thin film. The illustration of a cross section was depicted based on transmission electron microscopic observation of the cross sections of different thick films.
- Fig. 5 Micromachining steps: (1) back-side anisotropic wet etch, creating thin membranes of silicon (~40μm) for supporting an island of silicon which eventually becomes the poppet of the valve; (2) sputter deposition of layer of TiNi on the front side and subsequent crystallization anneal; (3) sputtering gold at the top of TiNi for facilitating masking in TiNi wet etching and to provide electrical contact to conductive path of the actuator; (4) patterning and wet etching of the gold and TiNi film; (5)removing the gold from the active parts of the actuators. Gold remains only on the contact tabs and interconnecting parts of TiNi; (6) final backside etching for releasing the poppet and active parts of the actuator; (7) assembled micro valve (see Fig.6).
- Fig. 6 Microvalve, (a) exploded view and (b) subassembly of micromachined parts.