On the lower thickness boundary of sputtered TiNi films for shape memory application

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Abstract

In this paper, we study the effects of film thickness on phase transformation of constrained Ti50.2Ni49.8 films deposited onto silicon substrates. When the film is too thin, surface oxide and interfacial diffusion layers exert dominant constraining effect that renders high residual stress and low recovery capabilities in the film. The surface oxide and inter-diffusion layer restricts the phase transformation, alters stoichiometry of the remaining TiNi film, and reduces volume of the material available for phase transformation. As a result, a lower thickness boundary (about 100 nm) exists for TiNi films to remain “shape remembering”. Results indicate that a maximum recovery stress and actuation speed can be realized with a thickness of about 800 nm. Based on the curvature measurement results, the relationship between the relative stress and strain of the films (during phase transformation with change of temperature) can be derived.

Keywords: TiNi; Thin film; Thickness; Sputtering; Shape memory

1. Introduction

TiNi thin film based shape memory alloys (SMAs) are promising for applications in micro-electro-mechanical system (MEMS) [1–3] because of these desirable properties: high work output per volume thus the ability to recover large transformation stress and strain upon heating and cooling, superior elasticity, good chemical resistance and biocompatibility [4–6]. TiNi materials with grain size of hundreds of nanometers [7] and TiNi powder with grain size of tens of nanometers show apparent shape memory effect [8], which spark preparation of nano-layer SMA thin film and fabrication of nano-scaled structures with the aid of precision tools (such as MEMS processing, e-beam lithography, or focused ion beam milling, etc.). Potential applications include sampling of molecules, manipulating of proteins and genetic components using TiNi nano-actuators [9]. These actuators may be able to perform effective physical actuation (push, pull, move, place, etc) at nano-scale local heating with electron-beam or photon-beam instead of the traditional Joule heating. However, so far, most studies were conducted with TiNi films of a thickness of several microns while only a few on films of thickness or features size down to into sub-micron [10,11]. TiNi films usually undergo a high temperature between 400 and 650 °C (during deposition or post-annealing). At these temperatures, the surface oxidation and interfacial diffusion between the film and substrate could be significant to affect the phase transformation behavior if the film is too thin [10]. It is important to know how thin the TiNi-based film can go or how small the TiNi structure can be without losing the shape memory effect. Another problem related to the sub-micron TiNi layer is how to correctly evaluate the shape memory effect and phase transformation of constrained thin film on Si-based substrates. Curvature method and electrical resistance measurement are sensitive to slight changes in phase transformation, thus are frequently used [2,11] for this purpose. In this study, TiNi films with an array of thickness have been prepared by magnetron sputtering. The phase transformation behaviors of these films are characterized using the curvature...
method to assess the effect of film thickness and its lower boundary.

2. Experimental details

Ti$_{50.2}$Ni$_{49.8}$ Films were prepared by co-sputtering of a Ti$_{32}$Ni$_{48}$ (at.%) target (RF, 400 W) and a pure Ti target (70 W, DC) without intentional substrate heating. Commercially obtained 4-in. (100)-type silicon wafers were used as the substrates. Before deposition, the Si substrates were ultrasonically cleaned in acetone, methanol and then de-ionized water, successively. The base pressure of the main chamber was 2.67 $\times$ 10$^{-5}$ Pa. The substrate holder was rotated during the deposition for uniformity. The substrate-to-target distance was 100 mm, and argon gas flow rate was 15 sccm and the working pressure was 0.11 Pa. All the films were post-annealed at 650 °C for one hour in the sputter chamber in vacuum (2.67 $\times$ 10$^{-5}$ Pa). The composition analysis using energy dispersive X-ray spectroscopy showed that the variation in Ti content is about ±0.5 at.%. The deposition duration was varied thus the TiNi films with different thicknesses were obtained as listed in Table 1.

The crystalline structure of the films was characterized using X-ray diffraction (XRD, Philips PW3719 with thin film attachment, and Siemens D500 with hot stage, Cu K$_\alpha$, 40 kV/30 mA). The curvatures of the wafer before and after deposition were measured using a Tencor FLX-2908 laser system. The residual stress $\sigma_f$ was calculated from the radius of wafer curvature using:

$$\sigma_f = \frac{E_S t_s^3}{(1-v)6R t_f (t_f + t_s)} \quad (1)$$

where, $E_S/(1-v)$ is the biaxial elastic modulus of the Si substrate, $t_s$ is the substrate thickness, $t_f$ is the film thickness, $R$ is the substrate radius of curvature. $R$ can be calculated through:

$$R = \frac{R_1 R_2}{(R_1 - R_2)} \quad (2)$$

where, $R_1$ and $R_2$ are the radius of curvature of wafer before and after film deposition. The stress change as a function of temperature was measured in situ, from which martensitic transformation temperatures and hysteresis, multi-stage transformation, magnitude of shape recovery can be obtained from the stress–temperature curves, and the details can be found from Refs. [12–14]. Heating and cooling were performed at a rate of 1 °C/min. An estimation of the film mechanical strain $\varepsilon_m$ can be done based on the curvature changes:

$$\varepsilon_m = \varepsilon_t - \varepsilon_{\text{thermal}} \quad (3)$$

where, $\varepsilon_t$ is the total strain calculated from the curvature change and $\varepsilon_{\text{thermal}}$ is the thermal strain. Since the film is thin compared with the Si substrate, it is assumed that the total strain in the Si substrate is the same as that of thin film. The total strain in Si substrate can be expressed using Eq. (4) [15]. Combining Eqs. (3), (4) and (5), the mechanical strain in the film can be calculated using Eq. (6) [15].

$$\varepsilon_t = \frac{1}{6} R \left(4t_s + 5t_f + \left(\frac{t_f^2}{t_f + t_s}\right)\right) + \alpha_s \Delta T \quad (4)$$

$$\varepsilon_{\text{thermal}} = \alpha_f \Delta T \quad (5)$$

$$\varepsilon_m = \frac{1}{6} R \left(4t_s + 5t_f + \left(\frac{t_f^2}{t_f + t_s}\right)\right) + (\alpha_s - \alpha_f) \Delta T \quad (6)$$

where, $\Delta T$ is the variation in temperature, $\alpha_f$ and $\alpha_s$ are the coefficient of thermal expansion (CTE) of the film and the Si substrate. For TiNi thin film, the mechanical strain does not simply follow Eq. (6) due to phase transformation. $\xi$ is used here to represent the coefficient of transformation (or how many percentage of the initial phase remained, $\xi=1$ means no transformation, and $\xi=0$ means full transformation). For example, the calculation of $\xi$ value during heating can be expressed using Eq. (7).

$$\xi = \frac{C(T_s) - C_{\min}}{C_{\max} - C_{\min}}\quad (7)$$

where, $C(T_s)$ is the value of curvature at temperature $T_s$, $C_{\min}$ is the minimum curvature (or in pure austenite phase), and $C_{\max}$ is the maximum curvature (or in pure martensite phase). Using the film mechanical strain at the room temperature as the reference point, the relative strain change during heating and cooling can be calculated, with one example of heating shown in Eq. (8). Therefore, the relationship between relative strain and temperature can be obtained. In the same way, relative stress change with temperature can also be obtained using Eq. (1) if the film stress at the room temperature is used as the

<table>
<thead>
<tr>
<th>Deposition durations (min)</th>
<th>Film thickness (nm)</th>
<th>Residual stress (MPa)</th>
<th>Recovery stress (MPa)</th>
<th>Stress increase rate (heating) (MPa/min)</th>
<th>Stress increase rate (cooling) (MPa/min)</th>
<th>Transformation temperatures (°C)</th>
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<tr>
<td>5</td>
<td>48</td>
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reference point. As such, the relationship between the relative stress $\sigma_f$ vs. relative strain $\epsilon_f$ of the film can be established based on Eqs. (1)–(8). The parameters used in the calculation are listed in Table 2.

$$
\epsilon_{f} = \begin{cases} 
\frac{\epsilon_t - \epsilon_M T}{T_0 - T} & (T < A_t) \\
\frac{\epsilon_t - \epsilon_M A_t}{T_0 - T} + \int_{T_0}^{T} \left[ \epsilon_M + (1 - \xi) \epsilon_A \right] dT & (A_t \leq T \leq A_f) \\
\frac{\epsilon_t - \epsilon_M A_f + \epsilon_f}{T_0 - T} + \int_{T_0}^{T} \left[ \epsilon_M + (1 - \xi) \epsilon_A \right] dT + \epsilon_A (T - A_f) & (A_f < T)
\end{cases}
$$

(8)

X-Ray Photoelectron Spectroscopy (XPS) analysis was performed using a Kratos AXIS spectrometer with monochromatic Al K$\alpha$ (1486.71 eV) radiation. The survey spectra in the range of 0–1100 eV was recorded in 1 eV step followed by high-resolution spectra over different element peaks in 0.1 eV steps, from which detailed compositions were calculated. Curve fitting was performed after a Shirley background subtraction using Lorenzian–Gaussian curve fit. The pressure of the analysis chamber was lower than $10^{-7}$ Pa, which was increased to approximately $5 \times 10^{-5}$ Pa during ion bombardment. For elemental depth profiling of the interfacial structure, an ion gun (Kratos MacroBeam) of 4 keV was used at a sputtering rate of 0.05 nm/s with high purity Ar gas.

3. Results and analysis

Fig. 1(a) plots thin film XRD patterns of the as-annealed TiNi films with different thicknesses. The films show crystalline characteristics with a mixture of martensite, R-phase and austenite [5,14]. The peak intensities increase significantly with film thickness. All the films were then cooled with liquid nitrogen vapor (to bring the sample to below the martensitic transformation finishing temperature, $M_f$). The XRD results are shown in Fig. 1(b). Martensite (B19’, monoclinic) is dominant in all the films, and the peak intensities increase significantly with film thickness. Results confirm that the martensitic transformation does not finish when cooling down to room temperature (22 °C) after post-annealing, while reverse transformation occurs above room temperature. Difference in thickness does not result in apparent change in preferred orientation.

Fig. 2 shows the measured residual stress of the as-annealed TiNi films (i.e., stress at room temperature). The thinnest film (48 nm) experiences the maximum residual stress (590 MPa). With increasing film thickness, the residual stress decreases gradually, and then remains at a low value. Fig. 3 shows the stress–temperature evolution for all the films. The stress–temperature response of the thinnest film is almost linear, i.e., this film experiences only thermal effect (due to the difference in thermal expansion between film and substrate) with no apparent phase transformation. Thicker films, however, undergo stress/temperature hysteresis loops, demonstrating the shape memory effects. During heating, the stress increases significantly due to phase transformation from martensite to austenite. During cooling, martensitic transformation occurs and the tensile stress relaxes significantly due to formation and alignment of twinned martensites [12–14]. Fig. 2 and Table 1 show recovery stresses of these films, defined as the difference between the maximum and minimum stresses during phase transformation. This is an indication of shape memory actuation ability during application. With increase of film thickness, the recovery stress increases significantly, and reaches a maximum at a film thickness of 820 nm before it gradually decreases with further increase in thickness.

![Fig. 1. XRD patterns of the TiNi films with different thicknesses after cooled with liquid nitrogen vapor. (a) as-deposited films; (b) cooled with liquid nitrogen.](image-url)
Fig. 4(a) and (b) show the stress rate for different films as a function of temperature during heating and cooling. The stress rate corresponds to the rate of generation of actuation (or actuation speed). The stress rate can be obtained by differentiating the stress vs. temperature curves shown in Fig. 3. The maximum stress rates are listed in Table 1. From Fig. 4, the detailed martensitic transformation behaviors of the films with different thicknesses can be compared. Results in Fig. 4(a) show that during heating, there is only one peak in each curve, corresponding to the reverse transformation from martensite to austenite. However, the stress rate increases with film thickness, and reaches a maximum value of 26.2 MPa/min at 425 nm, then decreases continuously with further increase in thickness. For a thick film of 4110 nm, the maximum stress rate can be as low as 7.9 MPa/min. During cooling, there are two peaks observed, corresponding to R-phase transformation and martensitic transformation. The R-phase transformation peaks are relatively better defined, whereas the martensitic transformation peaks are much lower and broader (in most cases, the peaks are not fully formed when cooling down to room temperature). The maximum stress rate in cooling curves is significantly lower than those in heating. During cooling there is a maximum value of stress rate of 10.6 MPa/min for the film of 425 nm. In view of MEMS application, where the large recovery stress, quick response or fast actuation and small dimension are required, films with a thickness of several hundred nanometers are promising, but this critical value may
vary according to film composition deposition conditions (mostly vacuum condition). Another observation in Fig. 4 (b) is that for the film of 105 nm, there is no R-phase transformation, indicating that for a thin layer of TiNi, R-phase transformation can be suppressed, which is in agreement with the observation by Ref. [11]. From Fig. 4, the transformation temperatures of the films can be obtained and the results are entered in Table 1 for easy comparison. In general, as film thickness increases, the transformation shifts to slightly higher temperature. This shift is more apparent as the film gets thicker.

Fig. 5 plots relative stress vs. relative strain (during heating) for films of different thicknesses during phase transformation. The curves obtained during cooling follow the similar trend. For the 48 nm film, it is almost linear. The tensile stress decreases (or the compressive stress increases) with the increase in compressive strain. Because there is no phase transformation, the stress–strain curve depicts the elastic deformation of the film under the combined thermal and intrinsic stress. For other films, the relative stress–strain curves show a linear line at a small strain, obviously due to the elastic deformation of martensite structure. However, with further increase in strain, the film stress increases sharply due to formation of austenite upon change of temperature (i.e., restoration of the tensile recovery stress). As the reverse transformation finishes, the tensile stress decreases due to generation of thermal stress in the film.

Fig. 6 plots the in situ XRD analysis for films with thickness of 450 and 4110 nm during heating. Fig. 6 reveals the existence of phase transformation in these films. At room temperature, the film is basically martensitic (B19'). With increase of temperature, martensite gradually changes to austenite as clearly shown in Fig. 6(a) through (b). During cooling, transformation from austenite to R-phase and martensite can be identified in Fig. 6(c). The height and width of (011)B2 peak


As the film thickness increases above a few hundred nanometers, the effects of the surface oxide, oxygen diffusion layer and inter-diffusion layer become relatively insignificant. For a 500 nm thick film, 15 nm thick oxide accounts 15/500 nm = 3% of the total thickness, and it is less than 0.4% in a four-micron thick film. Therefore, phase transformation becomes significant and the recovery stress increases as thickness increases. Due to the significant phase transformation, the films would be similar. Thermal stress can be calculated using Eq. (9):

\[ \sigma_{th} = \left( \frac{E_{TiNi}}{1 - v_{TiNi}} \right) \times (\alpha_{Si} - \alpha_{TiNi}) \times (T_{\text{anneal}} - T_{\text{room}}). \]  

In which \( \sigma_{th} \) is film thermal stress; \( E_{TiNi} \) is the Young’s modulus of the TiNi film (about 78 GPa for austenite); \( v_{TiNi} \) is the Poisson ratio of the TiNi film (about 0.33). The calculated thermal stress is 616 MPa as a result of cooling from annealing temperature of 650 °C to room temperature of 20 °C. For a film with thickness of tens of nanometers, due to the formation of surface oxide and oxygen diffusion layer as well as thick interfacial diffusion layer, the Ti/Ni stoichiometry would be significantly altered, thus shape memory effect of the films deteriorates (i.e., lower recovery stress or even loss of shape memory effect). Therefore, large intrinsic and thermal stress generated after high temperature post-annealing could not be significantly released due to insignificant phase transformation, resulting in the large residual stress in film.

Results in Fig. 3 show that a minimum thickness (about 100 nm) is necessary to guarantee an apparent shape memory effect in the TiNi films. Surface oxide and oxygen diffusion layer as well as interfacial diffusion layer are dominant in films with thickness of tens of nanometers [10,20], which can be clearly verified from XPS analysis shown in Fig. 5. Assuming the surface oxide layer is a mere 15 nm, for films with a thickness of 50 nm, the oxygen layer is 15/50 nm = 30%, which is a huge proportion. The same is true with regard to the effect of the inter-diffusion layer between film and substrate (more than 30% of the total thickness, and the inter-diffusion layer could increase slightly with deposition durations, i.e., film thickness). The combined constraining effects from both surface oxide and interfacial diffusion layers in a very thin film will be detrimental to the phase transformations among austenite, R-phase and martensite, giving rise to the degraded phase transformation and shape memory performance. R-phase transformation is a self-accommodation twinning process, and involves large lattice distortion [11]. For film of 105 nm in thickness, the expected total thickness of the surface oxide and interfacial layer take up about 40% to 50% of the total film thickness, the resistance force from the constraining effect could be large enough to suppress the R-phase transformation, which is also reported in Ref. [11]. With further decrease of film thickness to 48 nm, even the martensitic transformation has been suppressed, thus no phase transformation is observed. From Fig. 5, the nominal modulus of 48 nm thick TiNi film is much higher than those of the other TiNi films, but comparable to that of TiO₂, that show significant constraining effect from both the surface oxide and interfacial layer.

As the film thickness increases above a few hundred nanometers, the effects of the surface oxide, oxygen diffusion layer and inter-diffusion layer become relatively insignificant. For a 500 nm thick film, 15 nm thick oxide accounts 15/500 nm = 3% of the total thickness, and it is less than 0.4% in a four-micron thick film. Therefore, phase transformation becomes significant and the recovery stress increases as thickness increases. Due to the significant phase transformation,
effect, thermal and intrinsic stresses in the films are drastically relieved, resulting in significant decreases in residual stress. The recovery stress and the stress rate peak at certain film thickness (for example, 820 nm for recovery stress, and 425 nm for stress rate in this study), and then decrease slightly with further increase in film thickness. The decrease in recovery stress results from the constraining effects from the neighboring grains. With the increase in film thickness, more and more grain boundaries form in the films (Ref. [10], also see Fig. 2). The grain boundaries are the weak points for generation of large distortion and twinning processes. Therefore, as the film thickness increases, the constraining effect from the neighboring grains becomes more and more significant, causing decrease in recovery stress and stress rate.

The formation of oxide and oxygen diffusion layer also affects the transformation temperatures. Oxygen (or carbon) diffusion into bulk TiNi alloys significantly decreases phase transformation temperatures [21,22]. The alternation of the composition near the surface and interface due to surface oxidation and elemental interlayer diffusion leads to alternation in stoichiometry of the remaining TiNi film, as well as volume of the material available for phase transformation, thus the transformation temperatures are also altered.

5. Conclusions

A minimum thickness (about 100 nm for the TiNi film in this study) is necessary to guarantee apparent phase transformation behaviors in TiNi films. When the film is too thin, surface oxide and interfacial diffusion layers exert dominant constrained effect that renders high residual stress and low recovery stress in the film. The surface oxide and interdiffusion layer restricts the phase transformation, alters the stoichiometry of the remaining TiNi film, and reduces the volume of the material available for phase transformation. A maximum recovery stress and actuation speed can be realized in the film with a thickness of about 800 nm.

References