Residual Stress of TiNi Shape Memory Alloy Thin Films with (111) Single-crystal Silicon Wafer

Tingbin Wu¹, Bohong Jiang¹, *, Xuan Qi¹, Yushu Liu¹, Dong Xu² and Li Wang²

¹Open Lab of Education Ministry for High-Temperature Materials and Testing, Shanghai Jiao Tong University, 200030, P.R. China
²Key Lab of Education Ministry for Micro-Processing and Technique, Shanghai Jiao Tong University, 200030, P.R. China

As micro-actuator materials, TiNi shape memory alloy thin films with substrate are used more and more in MEMS field. The residual stress in Ti-rich TiNi thin films with silicon substrate prepared by the magnetron-sputtering technique is measured by both X-ray glancing and contour method. The influence of crystallization annealing temperature and film thickness on the residual stress is tested. It is shown that the tensile residual stress decreases from 106 to 37 MPa with increasing annealing temperature from 723 to 923 K. However, it increases again above 1023 K. While increasing the film thickness from 2.4 to 6.5 µm, the residual stress reduces from 323 to 80 MPa. A lot of beautiful sunflower-like structures in crystal grains are observed by OM and TEM. The origin of the residual stress and its affecting factors are discussed. The thermal stress during cooling after annealing is the main factor resulting in tensile stress and the formation of martensite phase will release a part of tensile stress.

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Keywords: residual stress, titanium, nickel, shape memory alloy, thin films.

1. Introduction

TiNi shape memory alloy (SMA) thin films are paid more and more attention in the field of micro-electro-mechanical systems (MEMS).¹ Especially the thin films with substrate are utilized in designing of devices with micrometer size, such as pumps,² valves³-⁴ and grippers⁵-⁶ etc., because the substrate such as silicon can be used as a bias-elastic element that makes the design more simple. In that case the residual stress can be found in the final thin film-substrate composite element, which will inevitably affect the performance of SMA thin film actuators.⁷ Therefore, it is really of great significance to investigate the residual stress in TiNi thin films with substrate. In this paper, both X-ray and contour method are used to measure the residual stress in TiNi thin film prepared by magnetron sputtering, and the origin and influence factors on residual stress are discussed.

2. Experimental Procedure

The titanium-rich TiNi thin films were prepared by ANULVA 210 magnetron sputtering system using a TiNi alloy target with 53 at%Ti. The (111) single-crystal silicon wafers with 50.8 mm diameter and 0.2 mm thickness were used as substrates. The argon pressure during deposition was 3 kV and the power was controlled from 150–300 W in order to get different film thickness changing from 2.4 to 6.5 µm. The deposition time was 80 min. The pre-sputtering and inverse sputtering was performed to clean the target and substrate. After sputtering the amorphous TiNi films with substrate were annealed at various temperatures (723, 823, 923 and 1023 K) in argon atmosphere for 30 min. The final chemical compositions of thin films determined by EDAX were shown in Table 1. The X-ray diffraction analysis of film specimens with wafer was performed by D/max3A with Cu Kα at room temperature (near 300 K). The microstructures of films were observed both by the optical microscope typed of LEIKI MEF4M and by the transmission electronic microscope typed of Hitachi 800. The disc specimens cut from thin films was firstly electro polished using the twin jet method in an electrolyte of 25% HNO3 and 75% methanol in volume and secondly thinned with ion-milling method to produce a central thinned region suitable for TEM observation and selected area electron diffraction experiments.

The residual stress in TiNi films with silicon substrate was measured by both X-ray grazing method and contour method respectively. In X-ray grazing method the residual stress (σ) in thin films can be calculated by following equation:

$$\sigma = \frac{E}{1 + v} \frac{1}{\sin^2 \Psi} \frac{\partial a\Psi}{\delta}$$

where E and v are Young’s modulus and Poisson ratio of films, a₀ is lattice parameter of film at stress-free state. Ψ(= θ – α) is the orientation angle of diffraction plane. θ and α is diffraction angle and the glancing angle respectively. In this paper α was taken as 8°. a₀ is the lattice parameter of film in the Ψ direction.⁹ In the present study, the σ was evaluated with the diffraction pattern of the parent phase.

In the contour method, the curvature radii of samples were measured by a contourgraph before and after sputtering, as well as after crystallization. Thus the residual stress in thin films can be calculated according to the following equation:⁹

$$\sigma = \frac{1}{6} \left[ \frac{E_{f} t_{f}^{2}}{1 - v_{f}} + \frac{E_{s} t_{s}^{3}}{1 - v_{s}} \right] \frac{[l_{f}(t_{f} + t_{s})]}{K}$$

$$K = 88/L^2$$

where t₇ and tₛ, E₇ and Eₛ, v₇ and vₛ are the thickness, Young’s modulus and Poisson ratio of film and substrate respectively shown in the footnote of Table 1, and δ is the
Table 1 Crystallization temperature, phase transformation temperature and residual stress of TiNi thin film on substrate.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Titanium content (at%)</th>
<th>$M_s$ (K)</th>
<th>Crystallization temperature (K)</th>
<th>Film thickness (µm)</th>
<th>Residual stress (MPa)</th>
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<tbody>
<tr>
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<td></td>
<td>Contour method</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>X-ray method</td>
</tr>
<tr>
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<td>6.90</td>
<td>106</td>
</tr>
<tr>
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<td>823</td>
<td>6.45</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>53.79</td>
<td>333.89</td>
<td>923</td>
<td>6.21</td>
<td>37</td>
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<tr>
<td>4</td>
<td>52.59</td>
<td>334.54</td>
<td>1023</td>
<td>7.48</td>
<td>59</td>
</tr>
</tbody>
</table>

Note:
1. Sputtering power: 300 W, deposition time: 80 min;
2. In calculation of X-ray method, elastic modulus $E_f = 30$ GPa, $E_s = 180.5$ GPa and Poisson’s ratio $v_f = 0.3$, $v_s = 0.28$;
3. * means residual stress can’t be calculated because of the interference by diffraction peak of martensite phase

Table 2 Relationship between film thickness and residual stress in TiNi thin film on substrate.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Titanium content (at%)</th>
<th>$M_s$ (K)</th>
<th>Sputtering power (W)</th>
<th>Film thickness (µm)</th>
<th>Residual stress (MPa)</th>
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<tr>
<td>6</td>
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<td>325.44</td>
<td>200</td>
<td>5.0</td>
<td>190</td>
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<tr>
<td>7</td>
<td>53.44</td>
<td>312.80</td>
<td>150</td>
<td>2.4</td>
<td>323</td>
</tr>
</tbody>
</table>

Note: Crystallization temperature: 823 K

amount of needle displacement of countourgraph node, $L$ is the scanning length.

3. Results

The measuring results of residual stress in thin films on Si substrate affected by crystallization temperature and film thickness are listed in Table 1 and Table 2 respectively. It is shown that the tensile stresses are certainly existed in TiNi thin films in all treatment conditions and the value of the stress decreases with increasing crystallization temperature and thickness of films.

The XRD spectrums of film specimens are shown in Fig. 1. It is shown that the structure is mainly composed by B2 parent phase and B19’ martensite phase and small amount of Ti$_2$Ni. It is worth to notice that the martensite phase peak gets stronger when the crystallization temperature raises.

The phase transformation temperatures measured by DSC are shown in Fig. 2. It shows that both $M_s$ and $A_s$ increase with increasing crystallization temperatures. However, the $M_s$ temperature increases only a little while crystallizing at 1023 K.

4. Discussion

4.1 Residual stress in TiNi thin films

It can be considered that the residual stresses in TiNi films with Si substrate may connect with the following factors:

(1) Intrinsic stress. It results from the lattice mismatch between the arrangement of atoms in TiNi film and that in silicon substrate as well as immission of ions in sputtering process. Usually this kind of stress is small. Our experimental results indicate that the stress in as-sputtering state of amorphous TiNi films is less than 7 MPa.

(2) Stress produced in crystallization process. A volume contraction of TiNi thin films occurring in processing from amorphous to crystal state introduces a remarkable tensile...
stress into the TiNi thin films.

(3) Thermal stress $\sigma_t$, the main extrinsic stress, resulted from the difference of expansion coefficient $\Delta \alpha$ between TiNi film and Si substrate. The thermal expansion coefficient of TiNi alloy is $6 \times 10^{-6} \text{K}^{-1}$, which is 2–3 times larger than that of silicon substrate ($3 \times 10^{-6} \text{K}^{-1}$). In the subsequent cooling process after crystallization annealing it will inevitably bring tensile stress into films. It was estimated using the following formula that tensile stress more than 500 MPa could be developed for TiNi film with Si substrate on cooling from 1000 K to room temperature.

$$\sigma_t = \frac{\Delta \alpha \cdot \Delta T \cdot E_f}{1 - v_f}$$

(4) Stress relaxation holding in high temperature. Both intrinsic and extrinsic stresses relax rapidly at the temperature above 873 K due to dislocation motion and diffusion-controlled viscous flow. At higher temperature, a recrystallization process, occurring in those strained grains, causes more internal stresses released.

(5) Stress of phase transformation. Both stress-induced and thermal-induced martensitic transformation will be activated in TiNi film during cooling from crystallization annealing temperature to ambient temperature. The volume expansion due to the martensitic transformation will relax the tensile residual stress partially depending on the amount of martensite formed.

4.2 Effects of crystallization temperature and film thickness on residual stress in TiNi films.

(1) The residual stress at room temperature in TiNi film on silicon substrate decreases with increasing crystallization temperature from 723 to 923 K, however, it increases a little again while annealing at 1023 K, as shown in Fig. 3 derived from the data in Table 1. According to the above analysis the thermal stress during cooling should be higher as annealing at higher temperature, however, the more amount of martensite induced by the higher tensile stress leads to the more thermal stress to be relaxed. XRD experiments confirm that the amount of martensite increases with enhancing crystallization temperature. The phase transformation temperatures ($M_s$ and $A_s$) measured by DSC method also increase with increasing crystallization temperatures as shown in Fig. 2. It is also found that $M_s$ almost doesn’t increase when the crystallization temperature changed from 923 to 1023 K. Therefore the amount of martensite reaches to maximum value and keeps unchanged and so does the released residual stress by martensite formation. However, thermal stress still increases continuously as cooling from such high temperature. Accordingly, the residual stress increases somewhat again while crystallized at 1023 K. The precipitation and solution of Ti$_2$Ni phase during crystallization at different temperature will not affect the $M_s$ temperature and in turn the residual stress so much because in TiNi equilibrium phase diagram the solvability limit of B2 phase in Ti-rich side is nearly unchanged with temperature.

(2) Figure 4 shows that the residual stress in TiNi thin films decreases with increasing film thickness. Residual stress coming from the lattice mismatch and expansion coefficient difference between film and substrate is of course concentrated in the interlayer area, where deformation is restricted and will weaken gradually with growing of film. Thus a residual stress gradient will come into being in the thickness direction of TiNi thin films, which decrease from the interface between substrate and thin film to the outer surface of thin film as shown in Fig. 5. The thicker the film is, the smaller the average residual stress will be.

4.3 Microstructure of TiNi thin films with substrate

A very interesting phenomenon was observed in microstructure of TiNi films with silicon substrate. A lot of beautiful radiate patterns looked like sunflowers can be observed by optical microscope as shown in Fig. 6. In the sam-
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Fig. 5 Stress gradient in TiNi thin film.

Fig. 6 Optical metallograph of TiNi thin film with wafer annealed at different temperatures. (a) 723 K (b) 823 K (c) 923 K (d) 1023 K.

ple crystallized at 723 K nearly every grain becomes a sunflower with the size ranging from 10 to 20 µm or so. At the center of each grain a white core of 2–3 µm as shown in Fig. 6(a) can be noticed.

When the annealing temperature rises to 823 K, these radiate patterns still exist, but its quantity is not as much as that in sample crystallized at 723 K. Meanwhile, in some grains, two white cores and even more appear in one grain at the same time as shown in Fig. 6(b). However, in the sample crystallized at higher temperature such as 923 K and 1023 K, a lot of fine, newly formed recrystallization grains appears in addition to a few remaining sunflower patterns as shown in Fig. 6(c) and (d).

By energy spectrum analysis (EDAX), no chemical composition difference was found between the center part of sunflowers and areas around it. And within the white core, no titanium-rich second phase particle serving as preferred nucleation nuclei of martensitic transformation, as described in literature,15 was found.

TEM image of a single sunflower pattern is showed in Fig. 7(a). The selected area electron diffraction pattern is shown as Fig. 7(b), which is identified as B2 structure. The radiate contrast can be observed both in bright and dark field by using B2 reflection, as shown in Figs. 7(c) and (d), respectively. That means the sunflower pattern is unrelated to the formation of martensite. The exact mechanism on the formation of such sunflower patterns is not yet clear but it should be related to the residual stress existed in TiNi films with wafer. Because the sunflower patterns do not appear in free-standing TiNi thin films due to less residual stress as shown in our previous paper.10 From the optical microscopy in Fig. 6, we find that the higher the crystallization annealing temperature is, the less sunflower patterns could be seen. And a simultaneous decrease of residual stress is observed. This clearly points out that the formation of sunflower-like radiate patterns is closely related with the stress field.

5. Conclusion

(1) Tensile residual stresses exist in Ti–Ni thin films deposited on single crystal silicon substrate.

(2) The residual stress is larger while crystallization annealing at lower temperature. It decreases with increasing crystallization temperature.

(3) While increasing the film thickness the residual tensile stress in TiNi films on Si substrate reduces.

Acknowledgements

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Fig. 7  TEM image and SAED patterns of Ti-Ni thin films crystallized at 723 K for 30 min. (a) single sunflower pattern (b) corresponding SAED pattern (c) bright field image of radiate strip (d) dark field of radiate strip.