In-Situ Observation of Transition Between Surface Relief and Wrinkling in Thin Film Shape Memory Alloys

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Significant surface morphology evolution between relief and wrinkling was observed on a 3.5 μm thick TiNiCu film sputter-deposited on a silicon substrate. At room temperature, variation in surface relief morphology (from separated martensite crystals embedded in amorphous matrix to fully interweaved martensite plates) was observed with slight change in film composition. The phenomenon was attributed to variations in crystallization temperatures of as-deposited amorphous films during annealing because of the compositional difference. During thermal cycling between room temperature and 100 °C, reversible surface morphology changes can be observed between surface relief and wrinkling patterns. The formation of the surface wrinkling is attributed to the large compressive stress in the film during high temperature post-annealing and crystallization, whereas surface relief is caused by the martensitic transformation to relieve the large tensile stress in the film. Compositional effect on this surface morphology evolution is discussed. Results also indicate that there is a critical dimension for the wrinkling to occur, and a small circular island can only relax by in-plane expansion.

Keywords: Shape Memory, Thin Film, TiNiCu, Surface Morphology, Relief, Wrinkling.

1. INTRODUCTION

Recently, significant surface relief (or surface upheaval) caused by the displacive martensitic transformation has been frequently reported in sputter-deposited TiNi thin films.1–3 During the martensitic transformation, a flat film surface in austenite transforms into twinned martensite and becomes rough upon cooling, without a macroscopic shape change. During the reverse transformation, the rough surface of martensite will change back to a smooth, austenite surface at a high temperature of about 100 °C. The mechanism behind this phenomenon is the diffusionless displacive martensitic transformation, and this distinct effect has been proposed to fabricate optical devices.4 In Ref. [5], we reported that film composition variation could cause significant difference in the surface relief morphologies across a TiNiCu film on a four-inch silicon wafer. The edge of the sample features randomly scattered martensite crystals, and the size and density of the crystals increases towards the center area of the sample. Fully interweaved martensite plates were observed in the center of the sample. Apart from surface relief, there are some other phenomena often observed on the TiNi based films, for example, reversible surface trench morphology reported in Ref. [6]. In Ref. [7], a new phenomenon was reported for TiNiCu film: a film surface morphology transition between surface relief and wrinkling during a complete thermal cycle. In this paper, a detailed study of the effect of film composition on the morphology evolution between surface relief and wrinkling is reported.

2. EXPERIMENTAL DETAILS

Films of a nominal composition of Ti50Ni47Cu3 with a thickness of 3.5 microns were sputter-deposited on a 4-inch (100) silicon wafer 500 microns thick (without intentional substrate heating) by magnetron sputtering of a Ti(55 at.%)Ni(45 at.%) target (3-inch diameter, RF, 400 W) and a pure Cu target (3-inch diameter, DC, 2 W). The films were then annealed in vacuum (2 × 10⁻⁷ Torr) at a temperature of 450 °C for one hour for crystallization. Detailed information about the film deposition and annealing technique.
can be found in Refs. [5–7]. The changes in wafer curvature as a function of temperature were measured and used to calculate the residual stress.\(^3\) Surface morphology evolution was characterized using optical microscopy, profilometer, scanning electron microscopy (SEM) and atomic force microscopy (AFM). Crystalline structure of the film was identified using X-ray diffraction (XRD) equipped with a heating stage. Nano-indentation tests were performed at both room temperature (martensite) and 120 °C (austenite) with indentation depth varying from 50 nm to 500 nm.

3. RESULTS AND DISCUSSION

3.1. Surface Relief with Composition Variation

As-deposited amorphous films are smooth and reflective to the naked eye. Annealing at 450 °C for one hour significantly changes the surface morphology. At the edge of the annealed 4-inch wafer, the film surface remains reflective and shiny. However, analysis using optical microscopy and SEM showed that some circular crystals with size ranging from a few microns to 30 microns diameter are embedded...
inside a featureless matrix (see Figs. 1(a and b)). Further TEM and XRD analysis confirmed that these circular patterns are single crystals and the surrounding matrix is amorphous. AFM analysis showed that within one single crystal island, there are interweaving martensite plates with different sizes and orientations (or martensite variants, see Figs. 2(a and b)). Within each martensite plate, the martensite twinning structure (striation patterns and martensite variants) can be identified, and they have different orientations and interspacing (see Figs. 2(c and d)). This may indicate that they form at different stages of martensitic transformation. When the specimen was cooled down to \(-20^\circ C\), there were no apparent morphology changes in the featureless matrix, nor are the crystal sizes and surface relief morphology within the crystals. This also indicates that the matrix is amorphous and not austenitic.

The film surface becomes opaque and cloudy to the naked eye in regions closer to the wafer center. The number and average size of the martensite crystals increase dramatically, with some crystals of relatively small size also observed, as shown in Figures 1(c to e). When two adjacent clusters contact each other, some martensite plates with similar orientation appear to coalesce into one large plate, so that there appears to be no clear boundary between these adjacent clusters (see Figs. 1(c to e)). The morphology of the edge of a martensite crystal is quantified by AFM, with an image shown in Figure 1(c). The undulating and rough edge is due to the formation of martensitic striations. XRD results (not shown here) illustrated that an amorphous phase is still dominant in this region of the film.

In the center area of the film, no amorphous matrix is observed and the entire film surface is covered by

![Fig. 2. AFM images showing the surface relief morphology in the circular crystals (a) crystals embedded inside amorphous matrix; (b) undulate surface morphology inside crystals; (c) morphology of martensite plate; (d) martensite striations and variants inside the martensite plate.](image-url)
significant relief morphology (interweaving martensite plates), as shown in Figure 1(e). The martensite plates have different orientations, dimensions and distribution. AFM measurement reveals significant roughening due to formation of martensite and twinned structures (see Fig. 4), with a surface roughness of 18.5 nm over an area of 10 μm × 10 μm. For comparison, the surface roughness of the as-deposited amorphous film is only 2.6 nm. Martensite plates as long as 100 microns can be occasionally observed from the optical microscopy. XRD analysis in these areas confirmed the fully crystalline and martensite-dominant structure with an almost insignificant amount of amorphous phase and retained austenite.

Surface relief morphology changes with different regions are due to the variation in film composition, as discussed in Ref. [5]. Since the deposition method is based on co-sputtering from two targets, slight misalignment of the two-targets with respect to the center of the wafers could affect the film composition uniformity. This is the intrinsic problem for the co-sputtering deposition method. EDX results confirmed that along the radial direction of the substrate holder, Ti contents can vary by about 2 at.% over the whole Si wafer, and the crystallization temperature varies according to the Ti/Ni ratio in the film. For example, Ni et al.8 found that crystal nucleation and growth rate is much slower and crystal size is much smaller in Ti-rich film than in a stoichiometric Ti50Ni50 film. The anneal-temperature used in our study is 450 °C, which is about the crystallization temperature of the TiNiCu films. Therefore, annealing at this temperature, the edge of the film (Ti rich) only partially crystallized, whereas the center of the film became fully crystallized. In the edge region, the nucleation and growth rates are slow according to Ref. [8]. Depending on the residual stress and the nuclei distribution, some grains may nucleate and then grow significantly before other grains nucleate.9 During subsequent cooling after annealing, martensite only forms inside these nucleated grains, resulting in the structures shown in Figure 1.

Figures 1(a to e) provide a clear picture of crystal nucleation and formation and distribution in TiNiCu films, which have also been recently studied using in-situ TEM and in-situ optical microscopy analysis.10 Our study shows that crystalline grains nucleate randomly and homogeneously on the surface, grow isotropically and laterally as the amorphous phase is consumed during annealing. Growth occurs continuously as new crystals form in the amorphous matrix and all crystals continuously grow laterally until impinging with each other. From both Refs. [8 and 9], the kinetics of crystallization have been found to follow a Johnson-Mehl-Avrami-Kolmogorov model11

\[ \phi = 1 - \exp(-k t^n) \]  

in which \( \phi \) is the fraction of the crystallized material, \( k \) is a temperature dependent constant, \( n \) is the Avrami component, \( t \) is the holding time at a certain temperature.

### 3.2. Evolution Between Surface Wrinkling and Relief

In-situ optical microscopy observation with substrate heated up to 100 °C revealed that the interweaving martensite plate structure (shown by the surface relief in Fig. 3(a)) disappeared. Instead, radial surface wrinkles form within the original martensitic structure as shown in Figure 3(b). Further heating up to 300 °C did not lead to much change in these wrinkling patterns. Upon subsequent cooling to room temperature, the twinned martensite plates or bands reformed as before thermal cycling. Many small round islands less than 10 to 20 microns did not show wrinkling patterns, which may indicate that the formation of wrinkling patterns is size dependent.

Figure 4 shows the detailed morphology evolution from surface relief to wrinkling as heating proceeds. Changes in surface morphology and surface roughness values in a 50 μm scale were monitored using a profilometer, and the results are plotted in Figures 5 and 6 as a function of temperature. At room temperature, significant ridge and valley structures due to formation of the interweaving...
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**Fig. 4.** Surface morphology evolution with temperature for TiNiCu film (a) surface relief morphology (twinning structure) at 25 °C; (b) 55 °C and (c) 65 °C showing the co-existence of martensite plate and wrinkles; (d) 75 °C and (e) surface wrinkles at 100 °C.

Martensite plate structure can be observed as shown in Figures 4(a) and 5. Surface roughness (Ra) is quite high (see Fig. 6). With increasing temperature, the surface relief of the martensite structure gradually becomes flattened when the reverse transformation starts. It is also observable that the size of the martensite plates decreases with temperature (see Figs. 4(b and c)). Some small plates or relief features disappear and become smooth, thus the circular relief patterns become not well-defined. Film surface becomes relatively smooth as shown in Figures 5 and 6. With further increasing temperature, only some large martensite plate can be observed, and wrinkling patterns appear within large circular patterns (see Figs. 4(c and d)). The wrinkles co-exist with the relief patterns (martensite plate structure) at intermediate temperatures. Profilometer results showed that above 65 °C, the surface becomes wavy again and surface roughness also increases, which is mainly due to the formation of wrinkling patterns. At a temperature above austenite transformation finish temperature, the surface shows clearly the wrinkle patterns. According to Figure 6, with the change of temperature, the surface roughness value changes dramatically when transforming between martensite and austenite, corresponding to surface evolution between relief and wrinkling patterns.

Figure 7 demonstrates the evolution of surface morphology of small crystals (at the edge of the film sample) embedded inside the amorphous matrix. When the film was heated to a high temperature, wrinkling patterns can only be observed in crystals with dimension larger than 10 to 20 microns. Results indicate that a critical dimension is required for the wrinkling to occur, and that smaller islands can relax by in-plane expansion without wrinkling.

_In-situ_ XRD analysis of the film in the center of the wafer over a temperature range from 20 to 120 °C is shown in Figure 8. At room temperature, XRD analysis confirmed the fully crystalline and martensite dominant structure with an almost insignificant amount of retained austenite. The
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4. DISCUSSION

The mechanisms behind wrinkling formation in thin films have been extensively studied in recent years. Both experimental evidence and numerical simulation confirmed that large in-plane compressive stress in a thin elastic film on a soft, plastic or viscous substrate can lead to spontaneous circular wrinkled patterns in order to release the large compressive stress. For the TiNiCu film in this study, the film stress evolution as a function of annealing temperature up to 450 °C has been studied. During heating, the net thermal compressive stress increases significantly up to a maximum value of 410 MPa. Densification and crystallization of the TiNiCu film results in a decrease in compressive stress. During cooling, tensile thermal stress increases linearly with decreasing temperature until the martensitic transformation occurs, at which point the tensile stress decreases sharply due to the formation of twinned martensite which relieves the tensile stress significantly.2,4

Wrinkling may occur during nucleation of crystals within the amorphous matrix during high temperature annealing. XPS analysis proved that there is usually a diffusion layer of about 30 to 50 nm rich in Ti and O on a TiNiCu film. Once the nucleated crystalline TiNiCu forms, the compressive stress will apply on the thin surface oxide layer, thus surface wrinkling would occur by the elastic buckling of the elastic oxidation layer on top of crystallized TiNiCu film. The wrinkles can grow radially along the growth direction of crystals. During cooling, the martensitic transformation occurs, and significant surface relief appears inside these wrinkles. As discussed in Ref. [5], the composition variation could cause the differences in the crystallization temperatures during annealing, resulting in the dramatic difference in the nucleation of austenite crystal distributions over the whole 4-inch wafer. Ti rich or Ni-rich regions have higher crystallization temperature, thus only some nucleated crystals are formed and embedded inside the amorphous matrix. Under large compressive stress at a high temperature, the wrinkling patterns form inside these crystals. During cooling after annealing, those surrounding amorphous film areas do not change morphology, whereas the circular wrinkling patterns change to the martensite surface relief morphology due to martensitic transformation. For most of film area, the Ti/Ni ratio is near to 50/50 (at.%), and all the films are crystallized at the annealing temperature of 450 °C, thus the film surface is full of wrinkles. Upon cooling down to room temperature, martensite plates form inside these wrinkles, resulting in a dense surface relief morphology. During heating and cooling between room temperature and 100 °C, surface morphology evolution occurs between surface relief and wrinkling.

To further verify the existence of an oxide surface layer, nano-indentation was carried out on the TiNiCu film. The measured hardness and elastic modulus readings as a function of indentation depth have been tabulated in Table I. The measured hardness and modulus in martensite is much higher compared with those readings from references.16 The reason is partially attributed to the existence of a surface oxide layer from XPS analysis.

The existence of a surface oxide layer, the results from 50 nm indentation differences in the crystallization temperatures during annealing, resulting in the dramatic difference in the nucleation of austenite crystal distributions across the whole 4-inch wafer, Ti rich or Ni-rich regions have higher crystallization temperature, thus only some nucleated crystals are formed and embedded inside the amorphous matrix. Under large compressive stress at a high temperature, the wrinkling patterns form inside these crystals. During cooling after annealing, those surrounding amorphous film areas do not change morphology, whereas the circular wrinkling patterns change to the martensite surface relief morphology due to martensitic transformation. For most of film area, the Ti/Ni ratio is near to 50/50 (at.%), and all the films are crystallized at the annealing temperature of 450 °C, thus the film surface is full of wrinkles. Upon cooling down to room temperature, martensite plates form inside these wrinkles, resulting in a dense surface relief morphology. During heating and cooling between room temperature and 100 °C, surface morphology evolution occurs between surface relief and wrinkling.

<table>
<thead>
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<th>Table I.</th>
<th>Indentation results of TiNiCu3 films at room temperature (25 °C) and 150 °C.</th>
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<td>Depths (nm)</td>
<td>Room temperature 25 °C</td>
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<td></td>
<td>Hardness (GPa)</td>
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increased indentation depth. Apart from the existence of an oxide layer, there are many other possible contributions for the enhanced hardness values, e.g., size effect, surface roughness, gradient theory, etc. At an indentation temperature of 120 °C (austenite is dominant), the enhancement from the hardening effect due to the existence of the oxide layer can be observed but is not so significant. The reason is because austenite has a much higher hardness and modulus values compared with those of martensite.

Theoretical modeling shows that there exists a critical size for the formation of wrinkles under a large compressive stress, below which in-plane expansion prevails over wrinkling. The critical island size $a_c$ for wrinkling (rather than in-plane expansion) to occur in a TiO$_2$ thin layer can be calculated:

$$a_c = \pi \left( \frac{H_o h}{f} \right)^{1/2} \ln \left( \frac{A_o}{A_c} \right)$$

(2)

in which $H_o$ is the film thickness (i.e., 3.5 microns for this study), and $h$ is the oxide thickness (about 50 nm). $A$ is the wrinkling amplitude, and $A_o$ is the initial film surface amplitude. $A/A_o$ can be estimated from the surface roughness measurement. In Eq. (2), $f$ is a function of two variables: $h_o/H_o$ and $e_o(1 + \nu)$, where $e_o$ is the biaxial in-plane strain at which wrinkling occurs and $\nu$ is the Poisson ratio. According to Ref. [14], if the value of $h_o/H_o$ is quite small, then $f$ can be estimated by

$$f = \frac{1}{12} (1 - 4\nu)(1 + \nu)^{1/2}, \quad \text{when } h_o/H_o = 0$$

(3)

In this study, the Young’s modulus $E_f$ and Poisson ratio $\nu$ of the TiO$_2$ are chosen as 200 GPa and 0.28. Since the film is thin compared with the Si substrate, it is assumed that the total strain in the film is the same as that of the underlying Si surface. An estimation of the film strain $\varepsilon_f$ can be obtained based on the curvature changes. The strain in Si substrate at a certain temperature can be expressed using Eq. (4):

$$\varepsilon_f = \frac{1}{6} R \left( 4\varepsilon_o + 5H_o + \frac{H_o^2}{H_o + r} \right) + \alpha \Delta T$$

(4)

Where $r$ is the substrate thickness (500 microns) and $R$ is the curvature at a certain temperature. $\Delta T$ is the temperature change, $\Delta T = T - T_r$, in which $T_r$ is room temperature. $\alpha$ is the coefficient of thermal expansion (CTE) of the Si substrate. Si substrate has a CTE value of 2 × 10$^{-6}$ K$^{-1}$. Based on Eqs. (2) to (4), the estimated critical island diameter which wrinkling could occur is about 70 to 150 microns, depending on the assumptions during calculations. The crystals below this diameter range will relax by in-plane expansion, rather than forming wrinkling patterns. The calculated values are much larger than the experimentally observed critical crystal size for wrinkling occurring, which can be attributed to many assumptions during the theoretical calculation.

In-situ observation on the surface of Ti50Ni50 film annealed at 450 °C has also showed the transition between the surface wrinkling and relief morphology. However, the phenomenon is not as significant as those observed in the TiNiCu films. The reason could be attributed to the large recovery stress in the TiNiCu3 films with one-stage martensitic and reverse transformations. Whereas for the Ti50Ni50 film, there is two stage transformation during cooling, and recovery stress is not as large as that in the TiNiCu3 film.

5. CONCLUSIONS

Significant surface wrinkling and relief was observed on a 3.5 μm thick TiNiCu film, which was sputter-deposited onto a Si wafer at room temperature and posted annealed at 450 °C. Following conclusions are obtained from this study:

(1) Variation in film composition on a four-inch wafer could cause dramatic changes in surface relief morphology in the TiNiCu films (from separately distributed martensite crystals embedded inside the amorphous matrix to fully interweaved martensite plates).

(2) Within a complete thermal cycles with temperatures ranging between room temperature and 100 °C, film surface morphology changed between surface relief and wrinkling patterns.

(3) For relieving large stress in the films, there are two feasible mechanisms: (i) surface wrinkling to relieve large compressive stress during annealing or heating processes; (ii) surface relief to relieve the large tensile stress during the martensitic transformation.

(4) There is a critical dimension for the wrinkling to occur, and a small circular island can only relax by in-plane expansion.

Acknowledgment: This project was partially supported by a European FP6 project PROMENADE (Project No. 507965).

References and Notes
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Received: 20 December 2006. Accepted: 29 March 2007.