## Evolution of surface morphology in TiNiCu shape memory thin films

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A transition of film surface morphology between wrinkling and surface relief during heating/cooling is reported for a sputtered TiNiCu thin film shape memory alloy. The mechanisms for this transition are discussed based on film stress evolution. During annealing surface wrinkling occurs to relieve compressive stress in the film, while the surface relief morphology occurs during cooling due to the martensitic transformation, which relieves tensile stress. © 2006 American Institute of Physics. [DOI: 10.1063/1.2361275]

Phase transformation in shape memory alloy (SMA) thin films is accompanied by significant changes in mechanical, physical, chemical, electrical, and optical properties.<sup>1-3</sup> Significant surface relief (or surface upheaval), caused by the displacive martensitic transformation, is commonly observed in TiNi bulk materials and has recently also been reported in sputtered TiNi thin films.<sup>3,4</sup> During the martensitic transformation, the atomic displacement introduces stacking faults that lead to surface relief morphology on the SMA. A flat surface in austenite transforms to twinned martensite upon cooling and becomes rough, without a macroscopic shape change, and vice versa. However, the detailed evolution of this surface relief morphology, as a function of temperature or composition, in TiNi-based films has not been systematically studied. In this letter we report on the surface morphology transition between film wrinkling and surface relief during heating and cooling of TiNiCu films deposited onto silicon wafers, and the mechanisms are discussed.

Films of  $Ti_{49.5}Ni_{47.5}Cu_3$  were deposited on standard 4 in. (100) silicon wafers (without intentional substrate heating) by magnetron sputtering of a Ti(55 at. %)Ni(45 at. %) target (3 in. diameter, rf, 400 W) and a pure Cu target (3 in. diameter, dc, 2 W). The film deposition rate was 14.6 nm/min, and the final film thickness was 3.5  $\mu$ m. During deposition the substrate holder was rotated for uniformity. The argon pressure was maintained at 0.8 mTorr. After deposition the films were annealed in vacuum (2  $\times 10^{-7}$  Torr) at a temperature of 450 °C for 1 h for crystallization. Film surface morphology was characterized using optical microscopy, scanning electron microscopy (SEM, JEOL-JSM 5800 LV), and atomic force microscopy (AFM, Digital Instruments Nanoscope III). Film composition was determined using energy dispersive x-ray microanalysis, and film microstructure was studied using transmission electron microscopy (TEM, Philips CM200) and x-ray diffraction (XRD, Siemens D500 with Cu  $K\alpha$  x-ray source) with a specimen heating stage. The phase transformation behavior was evaluated using a differential scanning calorimeter (DSC, TA instrument 2920) at a heating/cooling rate of 10 K/min. Crystallization and martensitic transformation behavior was also evaluated based on a curvature method: wafer curvature was measured using a Tencor FLX-2908 laser system, and residual stress was calculated from the change of radius of curvature. The stress change was measured as a function of temperature, from which the martensitic transformation could be observed.<sup>5</sup>

As-deposited TiNiCu films showed featureless surfaces, which were smooth, shiny, and reflective to the naked eye. XRD analysis indicated that these as-deposited films were amorphous. After annealing at 450 °C for 1 h the film surface became slightly opaque and cloudy to the naked eye. SEM observation, after cooling to room temperature, revealed that clusters of circular islands had appeared on the film surface, surrounded by a featureless matrix [see Fig. 1(a)]. These islands had diameters ranging from a few microns to 30  $\mu$ m. A detailed study using AFM [see Fig. 1(b)] showed that the islands consist of interweaving martensite plates, causing an undulating surface relief morphology. TEM observation, shown in Fig. 2, confirmed that these islands are single crystalline in nature, with some grains as large as 20  $\mu$ m, whereas the surrounding areas are amorphous, as revealed from diffraction patterns (see Fig. 2).

In situ optical microscopy observation using a hot stage revealed that, with increasing temperature (up to 90  $^{\circ}$ C), the

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FIG. 1. Surface morphology of martensite relief morphology. (a) SEM image showing surface relief morphology (circular martensite clusters). (b) AFM image showing martensite cluster in amorphous matrix.

interweaving martensite plate structure [shown by the surface relief in Fig. 3(a) disappeared, leaving typical features of radial surface wrinkling within the original martensitic islands [see Figs. 3(b) and 3(c)]. Further heating up to 250 °C did not lead to any apparent change in these wrinkling patterns. On subsequent cooling to room temperature, the twinned martensite plates reformed exactly within the wrinkling patterns as shown in Fig. 3(d). XRD analysis at room temperature confirmed the presence of crystalline martensite and amorphous material (a broad peak between 10° and  $25^{\circ} 2\theta$ ). In situ XRD analysis over the temperature range of 20-80 °C revealed that the martensite (B19', monoclinic) peaks gradually disappeared with increasing temperature, and austenite (B2) became dominant (above 80 °C), and vice versa. DSC results from a freestanding film confirm a one-stage transformation between martensite and austenite during heating and cooling, with no other transformation observed below 300 °C.

To understand the mechanisms for the morphology transition between the surface relief and wrinkling patterns on cooling/heating, an amorphous TiNiCu film on a Si substrate was heat treated in a nitrogen atmosphere, and the stress evolution was recorded *in situ*, as shown in Fig. 4. The compressive stress in the as-deposited amorphous film was 290 MPa. During initial heating the expansion of the TiNiCu film would be expected to be nearly five times higher than that of the Si substrate, and hence the net compressive film stress increased. The compressive stress peaked at about 200 °C (with a maximum value of 410 MPa) and then decreased slightly on further heating as a result of film densification. At higher temperatures (between 300 and 440 °C)



FIG. 3. Evolution of surface morphology between surface relief and wrinkling patterns during heating/cooling; (a) heating to 40 °C, (b) heating to 55 °C, (c) heating to 90 °C, and (d) cooling down to 30 °C.

rapid densification and crystallization of the TiNiCu film resulted in a significant decrease in compressive stress, while above 440 °C thermal stress dominates, resulting in a linear increase in net compressive stress. During cooling, tensile thermal stress increased linearly with decreasing temperature until reaching the martensitic transformation, at which the tensile stress decreased sharply due to the formation of twinned martensite (a shear-induced displacive phase transformation which significantly relieves the tensile stress).<sup>3,5</sup>

For comparison, Fig. 4 also shows the stress evolution of a crystalline TiNiCu film (i.e., a film which had been vacuum-chamber-annealed at 450 °C) with a thermal cycle between 20 and 120 °C. Tensile stress increased significantly (to a maximum value of 430 MPa) during heating, due to the reverse (martensite-austenite) transformation, and then decreased (to 40 MPa) during cooling, due to the martensitic transformation. Repeated heating and cooling, between 20 and 100 °C, led to repeated surface morphology change between wrinkling (at the higher temperature) and surface relief (at room temperature).

According to Fig. 4 there are two critical regions of stress relief during temperature cycling. That during cooling, at about 40-60 °C, is well understood and can be attributed to the formation of the twinned martensitic structure. This relieves the tensile film stress and leads to the observed platelike surface relief morphology (see Fig. 1). The other





FIG. 2. TEM image and diffraction patterns showing the existence of crystallized phase and amorphous matrix.

FIG. 4. Stress evolution of TiNiCu film annealed up to 650 °C using curvature measurement method.

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FIG. 5. (Color online) Schematic drawing showing the formation of wrinkling patterns and transition to surface relief morphology during annealing (a) after film deposition, (b) during annealing, (c) upon cooling  $(>M_s)$ , and (d) further cooling  $(<M_s)$ .

critical region is between 300 and 400 °C during annealing, where film wrinkling occurs to relieve the high compressive stress resulting from thermal mismatch between film and substrate.

It is well known that in-plane compressive stress in a thin elastic film on a soft substrate can lead to spontaneous circular wrinkled patterns in order to relieve stress.<sup>6,7</sup> During annealing, crystalline TiNi grains nucleate randomly at the surface and subsequently grow laterally as the parent amorphous phase is consumed.<sup>8</sup> It was reported that, for very smooth film surfaces, nucleation and lateral growth are quite quick, but the growth inward was apparently more sluggish.<sup>8</sup> In this study, because the annealing temperature for the Ti-NiCu film (450 °C) is slightly above the crystallization temperature (about 440 °C, obtained from Fig. 5), the activation energy for nucleation may not be large, but some crystals nucleate and grow radially on the surface layer of the amorphous matrix. X-ray photoelectron spectroscopy study in Ref. 9 reveals that there is 100 nm thick oxide and interfacial diffusion layer on the TiNi-based film surface [as illustrated in Fig. 5(a)]. Once crystalline NiTi is nucleated, this surface oxide layer is compressively stressed and surface wrinkling occurs by elastic buckling of the layer on top of the crystal-line TiNi, as shown in Fig. 5(b).<sup>7,10</sup> Formation of the wrinkles induces normal and shear tractions on the film surface, which can relieve the film stress. The energy required for activation of this wrinkling process is supplied from the large compressive strain energy stored in the annealed films. The wrinkling accompanies the radial growth of the nucleated crystalline phase.

During cool down, following crystallization, the wrinkling pattern is frozen and may not disappear until the martensitic transformation occurs, during which significant surface relief occurs inside these wrinkles, as illustrated in Fig. 5(c) and 5(d). In the austenite phase, the NiTi film is isotropic, so that a symmetric circular buckling shape results, while the anisotropy of the martensite plates leads to a dramatic surface relief pattern.

According to Ref. 11, the smallest circular zone diameter  $a_m$  for wrinkling (rather than in-plane expansion) to occur in a TiO<sub>2</sub> thin layer with thickness of  $h_f$  can be described using Eq. (1).

$$a_m = 1.106 h_f \sqrt{\frac{E_f}{(1-v)|\sigma_f|}}.$$
 (1)

Assuming that Young's modulus  $E_f$  and Poisson ratio  $\nu$  of the TiO<sub>2</sub> are 200 GPa and 0.28, respectively, and using a film compressive stress of 400 MPa and estimated oxide/ interdiffusion layer thickness of 100 nm,<sup>9</sup> the calculated minimum diameter of a wrinkled zone is about 2.9  $\mu$ m. This estimate is comparable with our observations that only wrinkled zones larger than 2–3  $\mu$ m form and may confirm that the wrinkling patterns are formed by the upper oxide layer.

In summary, we have reported on the film morphology evolution between wrinkling patterns and a martensitic surface relief structure during heating/cooling of NiTiCu films on silicon. There are two stress relief mechanisms: (1) surface wrinkling to relieve the compressive stress formed during heating and film crystallization; (2) the martensitic transformation relieves the large tensile stress formed during cooling, leading to a distinct surface relief morphology.

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