FABRICATION AND CHARACTERIZATION OF FUNCTIONALLY GRADED Ni–Ti MULTILAYER THIN FILMS

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A functionally graded multilayer Ni–Ti thin film was deposited on a SiO2/Si substrate by d.c. sputtering using a ramped heated Ni–Ti alloy target. The stand-alone films were crystallized at 500 °C in vacuum better than 10−7 Torr. Transmission electron microscopy micrographs taken along the film cross section show two distinct regions, thin and thick, with weak R and B2 phases, respectively. The film compositions along the thickness were measured and quantified using the standard-less EELSMODEL method. The film deposited during the initial thermal ramp (thin regions) displays an average of 54 at.% Ni while the film deposited at a more elevated target temperature (thick regions) shows about 51 at.% Ni.

Keywords: Functionally graded Ni–Ti, shape memory alloys, heated target, EELSMODEL, thin film, multilayer, TEM

The shape memory effect and superelasticity represent unique properties of Ni–Ti thin films. The temperature at which these properties exist is primarily dependent upon film composition. Several studies have been conducted on the effect of film composition on shape memory and superelastic properties.1–6 In 2000, Ho and Carman introduced a new process parameter, the so-called “hot” target, to modify the composition of the film to achieve a more uniform in-plane composition when compared to conventional sputter deposited Ni–Ti film.7 During that study, they also found that the film composition varied through the thickness as measured using Rutherford Backscattering Spectroscopy.8 This observation suggests the “hot” target approach could be used to fabricate functionally layered or graded material if a better understanding could be developed. These functionally layered or graded materials could exhibit two way shape memory properties as well as provide superior properties for certain applications when compared to homogeneous thin film solutions. The approach presented in this paper provides such a functionally graded multilayer film from a single target system. Functionally layered Ni–Ti thin films are produced using a custom designed Denton d.c. magnetron sputtering system equipped with a Stanford Research Systems® residual gas analyzer (RGA). The Ni–Ti films are deposited on 10 cm diameter silicon substrates covered with a 0.5 μm thick wet thermal oxide. A single alloy target with composition 49.5 Ni at.% is used for the deposition. The films are deposited on the substrate under “hot” target conditions. This is achieved by reducing the thermal paste between the target and the copper chill block allowing the target to heat during deposition.9 The target temperature profile as a function of sputtering time is shown in Fig. 1. During sputtering, the target temperature ramps to 546 °C in approximately 240 seconds before reaching a steady state temperature of 625 °C. Prior to each deposition run, residual gas pressures are measured with RGA to ensure significant contamination is absent from the chamber. During deposition, the base pressure is kept below 4×10−8 Torr while the Ar pressure is maintained.

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Fig. 1. Plot of target temperature versus deposition time. The first deposition is performed between 321 and 546 °C for 120 s followed by one for 600 s after reaching 625 °C.

at 1.5 × 10⁻³ Torr. The substrate-to-target distance is 4 cm and 300 W of dc power are used. A shutter is placed between the substrate and the target to shield the substrate from the target during deposition. By shielding the substrate, one is able to produce different compositions of film, i.e., film composition is dependent upon target temperature.7–9 For this study, the substrate was shielded from the target during the first 2 min of sputtering. Following this, the shield is rotated out of the deposition path allowing Ni–Ti to be deposited as the hot target ramps from 320–546 °C in 120 s. This is followed by Ni–Ti film deposited by a hot target with a relatively constant 625 °C for 600 additional seconds (see Fig. 1). Following this deposition run, the target is cooled back to room temperature which takes approximately 90 min and the deposition process is repeated. This sequence is repeated a total of four times. The deposition rate under these conditions is approximately 2.7 nm/sec. This produces a multilayer film consisting of four alternating layers of 0.3 µm (ramped temperature) and 1.6 µm (625 °C) with a total film thickness of approximately 8 µm thick. Following deposition, the amorphous film is removed from the wafer and subsequently crystallized under high vacuum better than 10⁻⁷ Torr at 500 °C for 1 h.

Transmission electron microscopy (TEM) is used to study the microstructure along the cross section of the film. The TEM sample is prepared by a focused ion beam technique using a Ga⁺ beam and a Pt protection layer. Figure 2 shows a bright field image of the sample. The total thickness of the resulting film is approximately 7.6 µm. The image clearly shows 7 distinct layers along the thickness. From left to right, the image crosses the entire film and the thickness of the layers is 1.9, 0.3, 1.6, 0.3, 1.6, 0.3 and 1.6 µm. A portion at the bottom of the film (left) is lost while preparing the TEM sample and the increased thickness in the first layer (left) might be due to a substrate effect. The sharpest interfaces can be seen where a thin layer is deposited on top of a thick one, i.e., after the 90 min cooling period, which could allow for a relaxation of the amorphous surface. The opposite interfaces are more irregular and appear to induce a region during crystallization of about 0.25 µm width with more irregularly shaped grains in the thick layers, the rest of these layers being filled with larger grains. Without actual in situ information, the real growth kinetics are difficult to envisage. The width of the grains in the lateral direction is between 0.5 and 1 µm, which is close to the sizes measured in thinner films by Lee et al.10 but substantially smaller than the 10 µm measured by Wang et al.11 Figure 3 shows selective area diffraction (SAD) patterns viewed along two different zone axes, [001] and [012], from the thick odd numbered layers (No. 1, 3, 5 and 7 in Fig. 2). These layers have the ordered austenite B2 phase with some domain formation. Figure 4 shows SAD patterns viewed along [001] and [−113] zone axis in the thin even numbered layers (No. 2, 4 and 6 in Fig. 2). The patterns show that the grains have a bcc lattice with virtually no ordering, but with some diffuse intensity along with some very weak B2 spots as well as some R-phase intensities at 1/3 positions, as seen from the accompanying line trace.

Figure 5 shows a high resolution TEM (HRTEM) image of a domain-like structure in layer no. 5, revealing some lattice
Fig. 3. Diffraction patterns from the odd numbered (thick) layers viewed along (a) [011] and (b) [012] zone axes.

Fig. 4. Diffraction patterns from the even numbered (thin) layers viewed along (a) [011] and (b) [−112] zone axes including a line trace revealing intensity enhancements at $n/3$ R-phase positions.
defects in the ordered austenite B2 phase. These defects could possibly be anti-phase boundaries formed during the coalescence of separately nucleated islands.

The composition of the different layers was first measured by electron energy loss spectroscopy (EELS) using spot sizes of approximately 250 nm diameter, i.e., covering several grains with different orientations but staying within the limits of a single layer. The experimental data were quantified by the standard-less EELSMODEL method developed by Verbeeck,\textsuperscript{12} which has been shown to yield accurate results for Ni–Ti structures\textsuperscript{13} independent of thickness or other artefacts. Figure 6 and Table 1 show an overview of the resulting Ni concentrations with standard deviations obtained from sets of 50 measurements for a given layer. From these, it is clear that the thin layers have about 3 at.% more Ni than the central thick layers.

Nanoprobe EELS measurements were also performed within layers 3 and 4 to evaluate the effect changing target conditions have on a given layer, especially the thin layers. The results shown in Fig. 7 indicate a gradual decrease over about 1 at.% in the growth direction of the thick layer 3 when considering standard deviations of the same order of magnitude (around 0.3 at.%) as in the previous experiment. The average of 51.6 ± 0.4 at.% Ni corresponds well with the value shown in Fig. 6, confirming the earlier measurement. For the thin layer 4, the situation is less clear. Indeed, point 1 was taken very close to the interface with layer 3, which thus may decrease the measured result. Moreover, taking similar precisions into account as obtained from Fig. 6, substantive conclusions regarding the evolution of the remaining points cannot be drawn.

The effective transformation temperatures for the entire film are measured with a Shimadzu® DSC. A stand-alone film weighing approximately 10 mg is measured in the temperature range from −30 to 80°C with a constant heating and cooling rate of 10°C min\textsuperscript{−1}. The constant cooling rate is achieved using a liquid nitrogen trap. The DSC plot is shown in Fig. 8. The observed endothermic and exothermic peaks are used to determine the transformation temperatures. The temperatures at which the endothermic peak ends and exothermic peak starts are very close to each other and the enthalpy change during transformation is only about 4.8 J/g when applied to the whole weight of the sample. However, according to the composition given in Fig. 6 and Table 1, it can be concluded that the thin layers 2, 4 and 6 will not transform since Ms is far below room temperature, following Tang \textit{et al.}\textsuperscript{14} The same holds for the thick layers 1 and 7. On the other hand, the B2 structure in layers 3 and 5 can transform in the present temperature range. As a result the volume fraction to be used in the enthalpy calculation is only 42% of the total volume, yielding an enthalpy of 11.4 J/g. Based on this value, the very small hysteresis and the measured compositions, it is concluded that the observed transformation in the DSC curve is a B2 to R-phase transformation in the thick 3 and 5 layers. The other layers all have a higher Ni content and thus much lower transformation temperatures, i.e., their transformation will not show up in a DSC run between −30 and 80°C.

In summary, a hot target sputtering approach was used to fabricate a multilayered functionally graded film from a single composition target. The expected compositional gradations between different layers of the film were confirmed.
experimentally and some crystallographic differences were also observed. The origin of the small measured compositional gradient in the thick layer 3 is still unclear, but could be due to the fact that in practice, when depositing the first part of the thick layer, the steady state temperature of 625°C has not been fully reached. In this case the Ni concentration will indeed be slightly higher, as for the thinner layers. The effective transformation temperatures were measured and found to be within expected bounds based on available literature. The present process provides a new avenue to control the microstructure and composition of Ni–Ti films through the thickness.

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