Shape Memory Alloy Films Manufactured by Magnetron Sputtering

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Abstract. By transferring the functional properties from bulk alloys to thinner structures in the range of micrometers it becomes possible to manufacture devices that can be used in micro-opto-electro-mechanical systems. Shape memory alloy possess a wide range of functional properties among which the shape memory effect, superelasticity and the high damping are influenced by the martensitic transformation. The current paper shows the results obtained on manufacturing shape memory alloy films by magnetron sputtering and the analysis of the martensitic transformation in the films attached to the substrate.

1. Introduction

The deposition of shape memory alloy films is a technique that is considered for both the fabrication of sensors and actuators [e.g. 1], as well as for the exploration of new and optimized composition based on combinatorial exploration [2]. The common substrate used for the deposition is silicon or glass. Glass is readily available and inexpensive. Over the time, several other substrates have been explored in order to assess the possible use in various applications, based on shape memory alloy films deposited on substrates, such as metallic substrates [3] or substrates / photoresist films that can be dissolved following the deposition or put of which the film may be removed, leading to freestanding films [4].

In most cases, the shape memory alloy films deposited at room temperature need to be annealed in order to show the shape memory effect. In these cases an annealing temperature in the range of 600°C or higher may be needed. For such annealing temperatures it is difficult to find adequate polymeric substrates. Another way is to deposit the films on heated substrates, a technique requiring lower heating temperatures for the substrate. It was shown that for NiTi films deposited on Si substrates, the crystallization starts at temperatures above 250-300°C [5] and for Ni-Mn-Ga freestanding films the sequence of the occurrence of ferromagnetic above and shape memory properties occurs during crystallization by heating.

Ishida et al. [6 ] was successful in depositing crystalline 8 µm films out of Ti, Ni and Cu elemental targets on heated polyimide substrates, using a carrousel-type magnetron-sputtering system, thus opening the path for the use of such substrates for manufacturing shape memory alloy thin film actuators. The peeled-off films out of glass substrates also showed the B2-B19 reversible transformation.
The aim of this work is to further explore the possibility to analyze the deposition of shape memory alloy films Ni-Ti-Cu films using alloyed target and to study the occurrence of the martensite in the as-deposited and further annealed films, respectively.

2. Experimental details
A 2" Ti-Ni-Cu target was used for depositing films using a custom made DC magnetron sputtering equipment on glass substrates, resulting in bimorph film/substrate structures. The deposition was made at room temperature (RT) with the following parameters: 2x10⁻⁶ torr preliminary vacuum, 10 mtorr Ar pressure and 100W power, for a total duration of 10.8 ks. One set of samples was further on annealed at 400°C in high vacuum by placing the glass substrate with the film on it on a K.J.Lesker ultra high vacuum heater module. The temperature was controlled with an OMRON temperature controller. The thickness of the film deposited was measured with a Sloan-Dektak-IID-Profilometer with 5Å vertical resolution.

The composition of the target and the film was analyzed in TESCAN Vega 3LM electron microscope, equipped with a Bruker Quantax 200 Energy Dispersive X-ray Spectroscopy (EDX) system with Peltier-cooled XFlash 410M silicon drift detector. Structural analysis was performed by X-ray diffraction in an X'Pert³ Powder (PANalytical) at room temperature. Monochromatic Cu Kα was used as radiation, with a 1.541840 Å wavelength, 40 mA power at 40 KV, 0.04 mm step with a 0.5 s/step, for a 20° – 55° 2θ range.

3. Results and discussions
The as deposited films had a measured thickness in the range of 1µm, as detailed in Figure 1a, resulting in a deposition rate of about 1Å/s.

![Figure 1](image)

Figure 1. Crosssectional details of the Ni-Ti-Cu films deposited at RT on glass substrate. a) Film thickness profile measured with the stylus profiler, b) Microstructure of the film deposited art RT showing a columnar growth.

The thickness was also confirmed by microstructural analysis of the cross section of the film detached from the substrate. A typical columnar growth is also observed as well as the uniformity of the film thickness.

The analysis of the composition of the film deposited at RT (Figure 2a) shows a composition that has about 12.5 at % Cu, thus positioning the alloy in the compositional range of the structural phase diagram (Figure 2b) where orthorhombic martensite (B19) is present.
Depending on the Cu content, the Ti-Ni-Cu shape memory alloys show different paths for phase transitions from the B2 high temperature phase. According to Figure 2b, for contents below 7.5 at% Cu the phase transformation is B2↔B19' (monoclinic martensite), while for higher contents the transition sequence is B2↔B19'↔B19 (orthorhombic martensite).

The formation of the orthorhombic martensite is further confirmed by the X-ray diffraction data (Figure 3), where B19 peaks are identified.

In fact, the presence of the B19 martensite at room temperature is justified by the fact that the B2↔B19' takes place in a temperature range above 300K for 12 at% Cu content.

Figure 2. EDX analysis of the films deposited and the corresponding position in the phase diagram(structural diagram redrawn after [7]), a) EDX results of the Ti-Ni-Cu film, b) Structural diagram for Ni-Ti-Cu alloys, c) Surface of the as-deposited film.
Also, it is observed that even the film deposited at RT is at least partially crystalline and not amorphous, thus the possibility to obtain crystalline structure for lower deposition temperatures exists.

4. Conclusions
The EDX analysis of the film compositions and of the target shows changes that occurred during the plasma transfer from the target to the substrate.

Films deposited at room temperature showed to be partially crystalline – as investigated by room temperature X-ray diffraction - with B19 orthorhombic martensite and did not show the presence of B19', expected to appear at lower temperature for 12at% Cu. Annealing up to 370°C did not lead to significant changes in the crystallinity of the film.

5. References
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Figure 3. X-ray diffraction profiles for the Ti-Ni-Cu films deposited at RT (top) and subsequently annealed at 370°C.