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Influence of annealing on structural, morphological, compositional and surface properties of magnetron sputtered nickel–titanium thin films

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ABSTRACT

Thin films of NiTi were deposited by DC magnetron sputtering from an equiatomic alloy target (Ni/Ti: 50/50 at.%). The films were deposited without intentional heating of the substrates. The thickness of the deposited films was approximately 2 μm. The structure and morphology of NiTi films annealed at different temperatures were analyzed in order to understand the effect of annealing on physical properties of the films. The compositional investigations of fresh and annealed films were also evaluated by energy dispersive X-ray spectroscopy (EDS) and X-ray photo-electron spectroscopy (XPS) techniques. X-ray diffraction (XRD) studies showed that as-deposited films were amorphous in nature whereas annealed films were found to poly-crystalline with the presence of Austenite phase as the dominant phase. AFM investigations showed higher grain size and surface roughness values in the annealed films. In annealed films, the grain size and film roughness values were increased from 10 to 85 nm and 2–18 nm. Film composition measured by EDS were found to 52.5 atomic percent of Ni and 47.5 atomic percent of Ti. XPS investigations, demonstrated the presence of Ni content on the surface of the films, in fresh films, whereas annealed films did not show any nickel. From HR-XPS investigations, it can be concluded that annealed NiTi films have higher tendency to form metal oxide (titanium dioxide) layer on the surface of the films than fresh NiTi films.

1. Introduction

Shape memory alloys (SMA's) exhibit an array of desirable properties viz. pseudo-elasticity, high damping capacity, good corrosion resistance and bio-compatibility [1–3]. These unusual properties have attracted tremendous interest in research of SMAs as functional materials. NiTi SMA thin films are now recognized as the most promising and high performance materials in the field of micro-electromechanical systems (MEMS) and bio-MEMS applications [4–8]. In comparison to bulk materials, NiTi films demonstrate fast cooling rates because of their higher surface/volume ratio and substantial increase in the heat transfer rate, and, therefore, lower the response time. Phase transformation in SMA thin films are mainly associated with a significant change in physical, thermal, optical, electrical and mechanical properties. In addition to its transformation behavior and mechanical properties [9–13], surface characteristics of SMA films are one of the important aspects in view of bio-medical applications [14].

Primarily, the mechanical and surface characteristics of thin-films are affected by the compositions of the films, sputtering conditions, deposition and post-annealing temperatures. The proper understanding and adequate optimization of deposition conditions along with the knowledge of surface characteristics play a very important role enabling the usage of NiTi films in specific micro-device applications. In recent years, in spite of the development of advanced deposition techniques, some unresolved issues still remain, which limit precise control during the deposition in SMA films. In order to standardize these deposition techniques, further improvements in SMA properties based on advanced understanding of the underlying process-property relationships are needed. Moreover, the influence of deposition and post-deposition conditions of SMA films on film-structure, morphology, phase transformation and mechanical properties are extensively described in literature [9–13,15,16], but reports on investigations on the evolution of surface property correlations of SMA films are not satisfactory. In the present paper, the influence of annealing on film-structure, micro-structure and composition along with surface property of SMA films is described.

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2. Experimental

2.1. Film deposition

DC magnetron sputtering of an equi-atomic (50/50 at.%) alloy target was employed to deposit NiTi thin films onto silicon (1 0 0) substrates. These substrates were ultrasonically cleaned with Acetone and immersed in 1:20 HF and DI water for one minute. Freshly cleaned silicon substrates were immediately loaded into the sputtering chamber. Argon gas with 99.999% purity was used as sputtering medium at a constant working pressure of 1.5×10^{-3} mbar. Base pressure of the main chamber was $\sim 1.0 \times 10^{-6}$ mbar. Prior to sputtering process, the target was sputter cleaned for ~15 min in a closed shutter situation. Film deposition rate of 33 nm/min was calibrated by surface profile measurements. Films with a thickness of ~2.0 μm were deposited. All films were deposited without intentional heating of the substrates, but during deposition some substrate heating was detected using a thermocouple, and found to be around 80 °C. After the deposition, some films were kept as fresh (as-deposited) films, while other set of films were post-annealed at 400, 500 and 600 °C for four hours in high vacuum condition at a base pressure $\sim 1.0 \times 10^{-6}$ mbar. These samples were classified into two categories, viz. fresh and annealed films. But in the present discussion, only one set of fresh (as-deposited) and another set of annealed (i.e. post-annealed to 600 °C) films are considered.

2.2. Film characterizations

The structure and morphology of the NiTi films were analyzed by X-ray diffraction (BRUKER INSTRUMENT using Cu Kα (1.541 Å) radiation from 40 kV X-ray source running at 30 mA) and scanning electron microscopy (SEM), respectively. The XRD measurements were carried out in Bragg–Brentano geometry. A field emission scanning electron microscope FE-SEM, SIRION 200 was used. The composition of the films was determined by energy dispersive X-ray spectroscopy (EDS) attachment of FE-SEM. Atomic force microscope (Agilent Technologies make Agilent 5500) was used for determining grain size and surface roughness.

The films were characterized for their surface characteristics using X-ray photoelectron spectroscopy (XPS). XPS survey spectra were recorded in the range of 0–1000 eV at 20 eV constant pass energy. A Thermo Scientific Multilab 2000 instrument using Al-Kα radiation (energy of 1486.6 eV) was used. C (1s) spectrum at a binding energy of 284.6 eV was chosen as reference with ±0.1 eV accuracy. The residual pressure inside the chamber during analysis was maintained at 10^{-8} mbar. XPS high resolution spectra (HR-XPS) were also studied for all the dominant elements viz. Ti (2p), Ni (2p), O (1s), and C (1s), in their binding energy ranges, to ensure chemical environments onto the surface of the films. Additionally, HR-XPS was used for assessment of the chemical state as well as for quantification. In order to obtain a better interpretation of the data, the experimental spectra were fitted with Gaussian-peak fitting model.

3. Results and discussions

3.1. Structural and morphological characteristics of the films

The effect of post-annealing on structural and morphological characteristics of NiTi films is described in the following subsection.

3.1.1. X-ray diffraction

Fig. 1 shows the X-ray diffraction pattern plotted for fresh and annealed films at room temperature. Fresh films are indicating a broad hump starting from 35 to 50°, which is centered

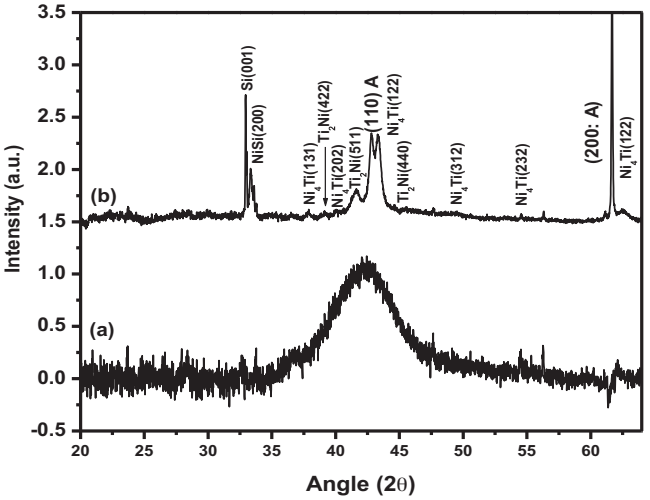

Fig. 1. XRD pattern plotted for (a) fresh and (b) annealed NiTi films.

on $2\theta \sim 42°$. The appearance of broad hump in XRD pattern is suggestive of amorphous nature, of these films [17,18]. In case of annealed films, the films showed crystallinity and introduced distinct film-structure, in spite of similar film-composition. The existence of several diffraction peaks after annealing is indication of poly-crystalline nature. The XRD pattern showed the presence of Austenite phase as the major constituent. Two sharp diffraction peaks observed at $2\theta = 42.83°$ and 61.67° are indexed for (1 1 0) and (2 0 0) planar reflections of the Austenite phase of NiTi [17–19]. In addition to major Austenite phase, XRD pattern showed the presence of some diffraction peaks corresponding to precipitates of Ni-rich, which are identified as Ni_4Ti_3. The diffraction peaks located at 37.81°, 39.10°, 43.34°, 51.26°, 55.71° and 62.71° positions are assigned to (1 3 1), (2 0 2), (1 2 2), (3 1 2), (2 3 2) and (4 2 2) planes of Ni_4Ti_3 precipitates. The appearance of Austenite phase and Ni_4Ti_3 precipitates in Ni-rich NiTi films are in agreement with Martins et al. [20]. They reported the presence of Ni-rich precipitates (Ni_3Ti) along with Austenite phase of NiTi in Ni-rich NiTi films. The evolution of Ni-rich precipitates may be either due to high temperature holding or high temperature post-annealing [20–24]. Interestingly, a few lower intensity diffraction peaks corresponding to $NiTi_2$ precipitates are also observed. The peaks centered at $2\theta = 38.28°$, 41.59° and 45.63° are assigned to (4 2 2), (5 1 1) and (4 4 0) planner reflections, respectively. Appearance of such $NiTi_2$ precipitates is also consistent with the reported literature that NiTi films form precipitates above 500 °C [17,18,25,26]. Lower intensity of $NiTi_2$ peaks can be explained on the location of these precipitates, which is close to the film–substrate interface. However, a first order reflection of Si (0 0 1) substrate at ~34° is also observed. The diffraction peak associated with nickel–silicide phase, i.e. NiSi (2 0 0), is also seen [27–30]. NiSi peak can appear due to migration of Ni into Si wafer at high temperature annealing. Interestingly, no Martensite and R-phase peaks are seen in the spectra. The existence of Martensite and R-phase in annealed films is also cross-examined with electrical resistivity studies. Two step transformation behavior during heating (B19′ – R-phase – B2) as well as cooling (B2 – R-phase – B19′) thermal cycle is observed. The transformation temperature is found to be below the room temperature, which is also supported by DSC studies (details are presented in supplementary material). The crystallite size calculations are carried out by using Scherrer's formula and was found to be 25 nm, corresponding to the (1 1 0) peak broadening of austenitic phase [31].