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Transformation Behavior of Low Temperature Crystallized TiNi Shape Memory Alloy Films

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Abstract. Transformation behavior of TiNi SMA films sputter-deposited on Si(001) and polyimide substrates was observed. An RF magnetron sputtering apparatus equipped with four separate confocal sources as well as with a heating and ion-irradiating system for substrates was used to make the films crystalline. Without using the system, the films deposited on ambient-temperature substrate have been amorphous. However, crystallized film is deposited even at 473 K of substrate temperature applying pulse bias voltage to the substrate. Shape memory effect of the crystallized film which was sputter-deposited on a polyimide sheet of 0.025 mm in thickness was observed. From the relationship between the normalized curvature of film and temperature, it was recognized that the start and finish temperatures of shape changes were 329 K and 399 K on heating process, respectively. While on cooling process, its reverse shape changes were observed. The shape was recovered to the original curvature at about 315 K.

1. Introduction

TiNi shape memory alloy (SMA) films are expected to be promising material for micro actuators in micro-electro mechanical systems because their work output per volume exceeds that of other micro-actuator materials. The fascinating property in TiNi alloys is caused by a martensitic phase transformation between a B2 type cubic structure (parent phase) and a B19' type monoclinic structure (martensitic phase). Thus, in order to exhibit the shape memory effect, the TiNi films need to be in a crystalline structure. TiNi SMA films are commonly produced by using a high temperature (above 723 K) annealing process during and/or after deposition in order to promote crystallization [1]. Therefore, the films could not be deposited on unstable materials at high temperature.

Transformation temperatures are very sensitive to the alloy composition, since the martensitic transformation start temperature changes more than 100 K for a 1 at% change in composition [2]. Therefore, precision control of the alloy composition of the film is required to improve reliability of micro actuators. Sputter deposition system with a single target is usually applied to fabricate TiNi SMA films [1, 3, 4]. It is well known that the alloy composition of the film is difficult to precisely control by using a single target. Alloy compositions of sputter deposited TiNi films are always Ni-rich when an equiatomic TiNi alloy target is used, because of the difference between deposition rates of Ti and Ni [2].

In order to realize the precision control of the alloy composition of the film and low temperature crystallization, we develop a radio frequency magnetron sputtering apparatus equipped with four separate confocal sources as well as with a heating and ion-irradiating system for substrates [5].

In this study, microstructures of TiNi films that are fabricated by sputter-depositing Ti and Ni simultaneously are examined with X-ray powder diffraction and SEM observation. Shape memory effect of the crystallized film which is sputter-deposited on a polyimide sheet was observed. The optimum conditions for sputter-deposition of TiNi films are discussed based on the experimental results.

2. Experimental Procedure

The experimental set-up used for the deposition of the TiNi films is a radio frequency (RF) magnetron sputtering apparatus. This apparatus consisted of four separate confocal sources as well as with a heating and ion-irradiating system for substrates. The apparatus used in this study is schematically shown in Fig. 1, with three elemental targets (2-Ti and 1-Ni). The substrate holder can be rotated at 12 rpm during film deposition in order to achieve a uniform alloy composition and film thickness. The films of 1 μm in thickness were deposited on (001) silicon wafers and polyimide sheets of 0.025 mm in thickness.

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A constant flow of Ar (99.999%) was controlled with a leak valve during film deposition, and a sputtering gas pressure of 0.1 Pa was set by adjusting the conductance valve. The distance between target and substrate was 150 mm. The total deposition speed of the film was adjusted at 10 nm/min by controlling each RF power for the respective magnetron source so that the alloy composition of the film becomes near equiatomic TiNi. In order to realize the crystallization of as-deposited film at low substrate temperature, ionized Ar, Ti and Ni atoms are irradiated to the substrate and deposited film surface. Inductively coupled coil (ϕ150 mm with stainless tube of ϕ6 mm) was installed between a set of targets and substrate. The inductively coupled plasma (ICP) was generated through supplying RF power to the coil. Ar, Ti and Ni ions, which were ionized passing through the ICP, struck against the substrate and deposited film surface , because negative pulse bias voltage was supplied to the substrate. Supplying conditions for negative pulse bias voltage are also schematically shown in Fig. 1. Based on the previous report [5], pulse repetition frequency, *f*, and negative pulse bias voltage, V_p, were set to 1 kHz and −0.3 kV, respectively. Effect of the pulse duty ratio on the crystallization was examined.

Crystal structures of the films were determined by X-ray diffractometry. X-ray powder diffraction profiles were recorded with an X-ray diffractometer (Rigaku RAD-2R) using Cu-Kα radiation. Surface and cross sectional morphologies were observed by using a scanning electron microscope with a field emission electron gun (Hitachi S-4200, SEM).

Shape memory effect by thermal cycle for the film deposited on a polyimide sheet was observed using a CCD camera. One end of the film was fixed on a sample holder and another end was free. Temperature of the film was measured by using a radiation thermometer. The observation was performed from 294 K (RT) to 433 K.

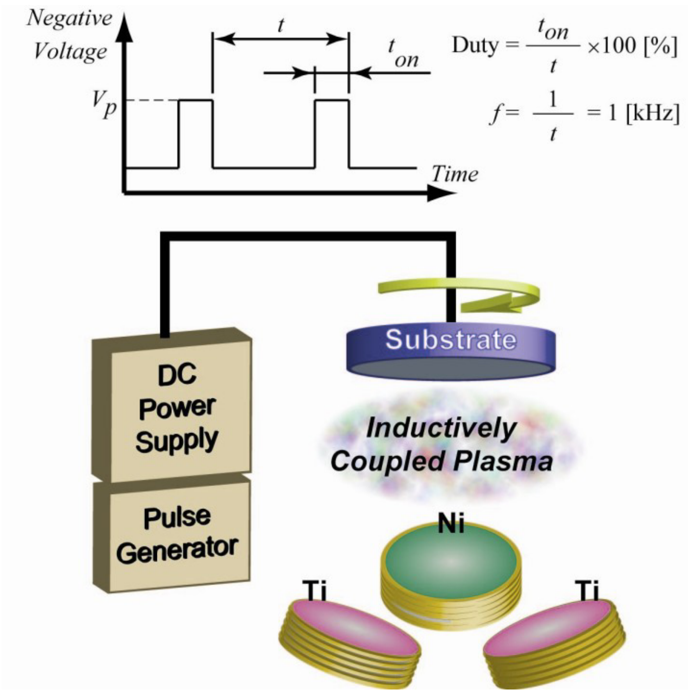

Fig. 1. Schematic illustration of RF magnetron sputtering system using separate elemental targets with PBII (Plasma-Based Ion Implantation) module.

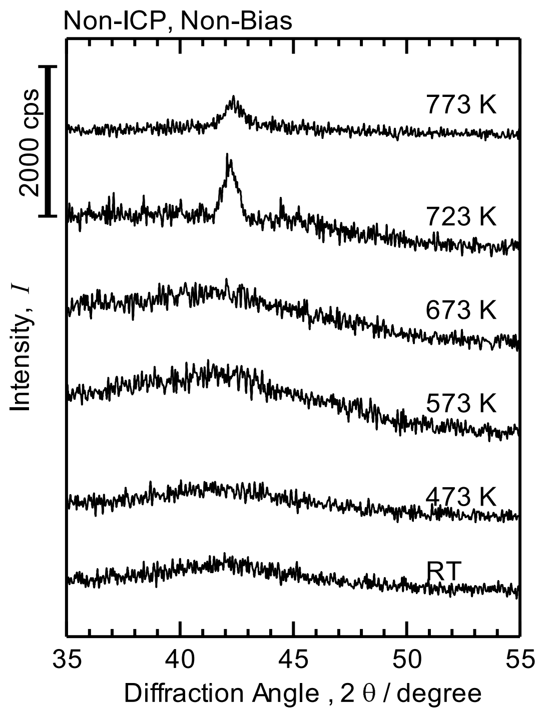

Fig. 2. Room temperature X-ray diffraction profiles of Ti-Ni films formed at various substrate temperatures.

3. Results and Discussion

Figure 2 shows the X-ray diffraction profiles of the films deposited on Si substrates as a function of substrate temperature. The films showed amorphous if the substrate temperature is below 673 K. While above 723 K of the substrate temperature, diffraction peak indexed 110_TiNi-B2 was obtained. Many investigators have reported that crystallization temperature of amorphous TiNi film is about 673 K [6], therefore, the above-mentioned substrate temperatures are reasonable values.

Figure 3 shows the X-ray diffraction profiles of the films deposited on Si substrates and polyimide sheets as

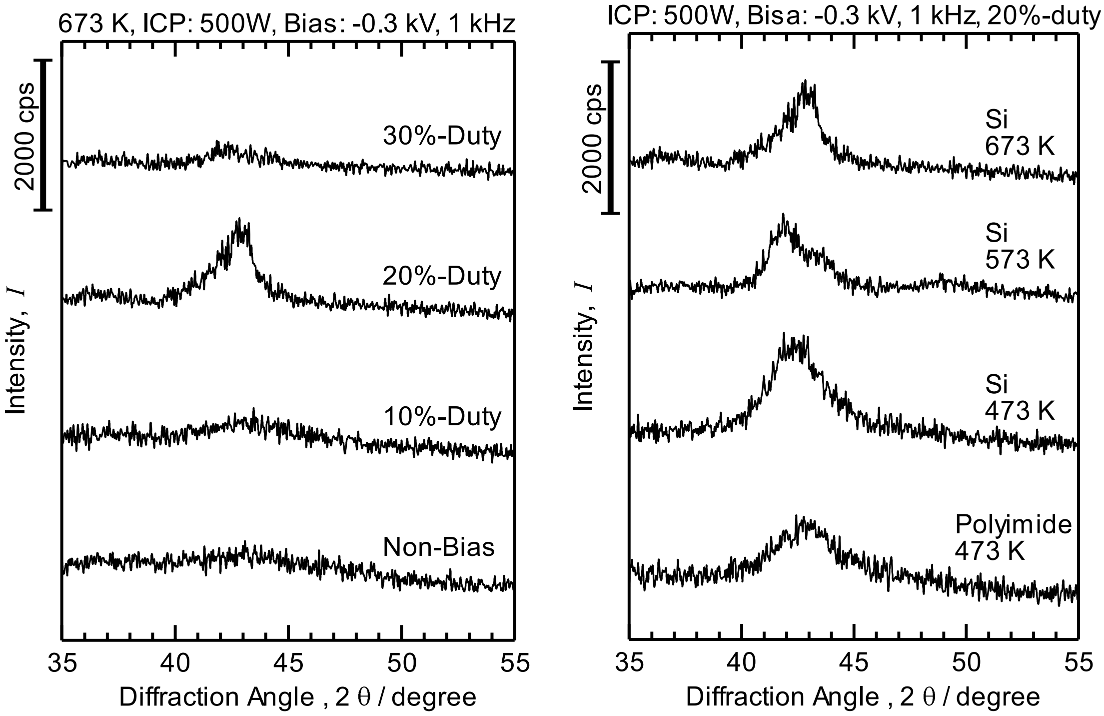

Fig. 3. Room temperature X-ray diffraction profiles of Ti-Ni films formed under various ion irradiation conditions.

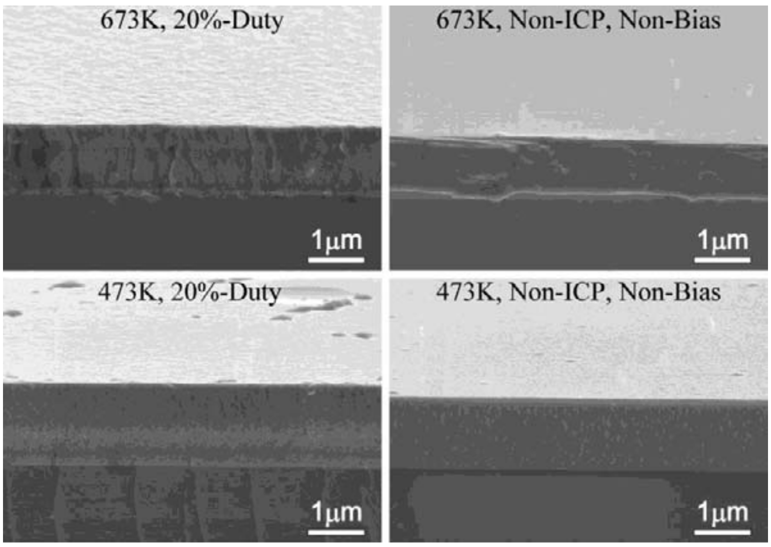

Fig. 4. Cross-sectional SEM images of Ti-Ni films formed under various sputtering conditions.

a function of substrate temperature and ion irradiation conditions. Broad X-ray profile, which was diffracted from martensitic phase, was recorded around 42 degree in 2 theta for the crystallized films. Specific value of the plus duty ratio accelerates the crystallization of the deposited film. For ion-irradiating at 20 % of the pulse duty ratio, crystallized film is deposited even at 473 K of substrate temperature. In the results, the ion irradiation can induce crystallization of deposited TiNi films.

Figure 4 shows the surface and cross sectional morphology of the film deposited under various conditions. The films exhibit a flat and featureless structure at cross-section. The cross sectional morphology of the films seems to be not influenced by ion irradiating conditions. While on surfaces of the film deposited by using ion irradiating system, small dimples, which were caused by the impact of Ar, Ti and Ni ions against the film, are observed. It is well known that the impact of the ions against the film leads to introducing or relieving lattice distortion of the film. Therefore, broad X-ray diffraction profile caused by the martensitic phase was observed on the films deposited by using both substrate heater and ion irradiating system.

Figure 5 shows shape recovery ratio, D_R, versus temperature curves of a TiNi film deposited on a polyimide sheet. In this figure, the photos of the spontaneous shape change of the film are also indicated. The value of D_R increased with increasing the temperature. On cooling process, the value of D_R decreased, and finally recovered original one. It is clear that the film deposited on a polyimide sheet shows two-way motion by thermal cycle. The two-way motion appears to be originated in martensitic and its reverse transformations. The film is in the martensitic phase at ambient (room) temperature. On heating process, the film deposited on a polyimide sheet reverts by means of the reverse transformation, finally the parent phase is completely produced in the film. While on cooling process, parent phase transformed to the martensitic phase, and the shape is recovered original one by elasticity of polyimide sheet acting as a bias force. From the above relationship, start and finish temperatures of shape changes on cooling process, i. e., martensitic transformation start and finish temperatures, were determined to be 399 K and 315 K, respectively.

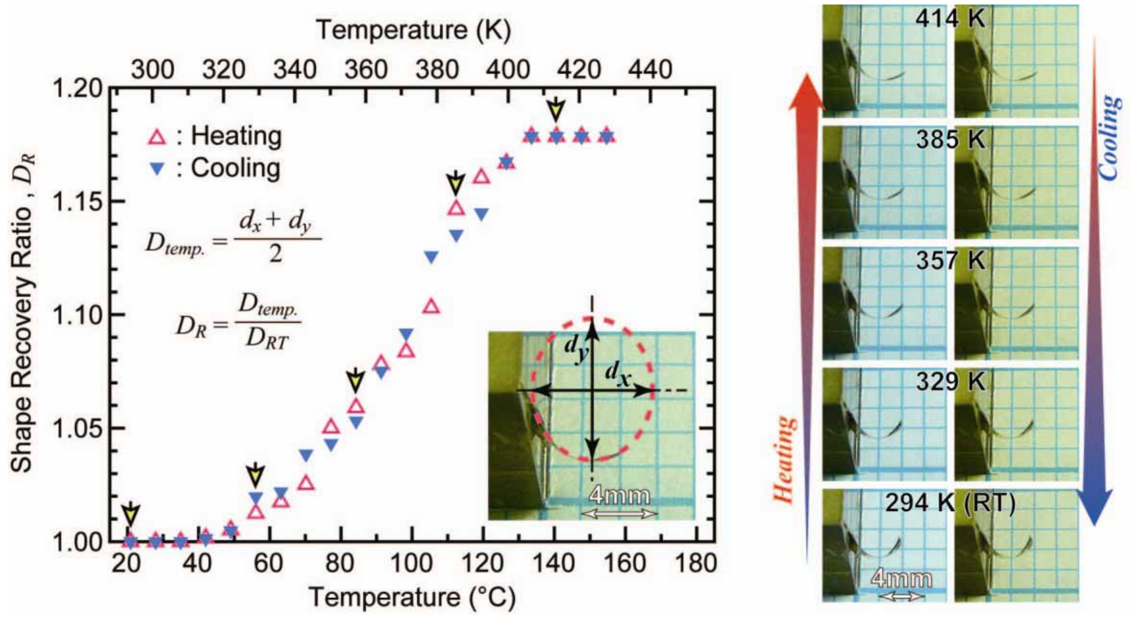

Fig. 5. Shape recovery ratio vs. temperature curves and corresponding shape changes observed during thermal cycling of a TiNi film deposited on a polyimide sheet.

4. Conclusion

TiNi SMA films were deposited on Si and polyimide substrates. An RF magnetron sputtering apparatus equipped with four separate confocal sources as well as with a heating and ion-irradiating system for substrates was used to make the films crystalline. Without using the system, the films showed amorphous if the substrate temperature is below 673 K. However, crystallized film is obtained even at 473 K of substrate temperature by ion-irradiating at 20 % of the pulse duty ratio. Crystallized film deposited on a polyimide sheet shows two-way motion by thermal cycle. From shape recovery ratio versus temperature curves, start and finish temperatures of shape changes on cooling process, i. e., martensitic transformation start and finish temperatures, were determined to be 399 K and 315 K, respectively.

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