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In situ crystallization of sputter-deposited TiNi by ion irradiation

Noriaki Ikenaga [a,*], Yoichi Kishi [b], Zenjiro Yajima [b], Noriyuki Sakudo [b]

[a] Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, 3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan
[b] Kanazawa Institute of Technology, 3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan

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ABSTRACT

TiNi is well known as a typical shape-memory alloy, and the shape-memory property appears only when the structure is crystalline. Until recently, the material has been formed as amorphous film by single-target sputtering deposition at first and then crystallized by being annealed at high temperature over 500 °C. Therefore, it has been difficult to make crystalline TiNi film directly on a substrate of polymer-based material because of the low heat resistance of substrate. In order to realize an actuator from the crystallized TiNi film on polymer substrates, the substrate temperature should be kept below 200 °C throughout the whole process. In our previous studies we have found that deposited film can be crystallized at very low temperature without annealing but with simultaneous irradiation of Ar ions during sputter-deposition. And we have also demonstrated the shape-memory effect with the TiNi film made by the new process.

In order to investigate what parameters of the process contribute to the low-temperature crystallization, we have focused to the ion fluence of the ion irradiation. Resultantly, it was found that the transition from amorphous structure to crystal one has a threshold range of ion fluence.

1. Introduction

TiNi shape memory alloy (SMA) has larger work output per volume than those of other ferroic materials like PZT. Thus, SMA is excellent material for actuators. However, when TiNi film is made by sputter deposition, its structure is amorphous. The film has to be crystallized in order to make the shape memory properties appear. Until sometime ago the crystallization of sputtering-deposited TiNi film had been usually realized by high temperature (above 450 °C) annealing process during and/or after the deposition [1–3]. As a special case, it was reported that the crystallization temperature could be lowered by utilizing high-energy sputtered particles with a single-target sputtering deposition [4]. However, the method had a difficulty in freely controlling the energies and/or the composition of sputtered films, which were considered to play the important role in lowering the crystallization temperature and shape memory effect. Especially, the TiNi film composition was the important factor to determine the martensitic phase-transformation temperature [3,5]. On the other hands, the TiNi film composition could be precisely controlled with a multi-target RF magnetron sputtering deposition by separately determining the sputtering condition for each target [6]. In our previous studies, the deposited film can be crystallized at very low temperature without annealing but with assistance of Ar ion irradiation during sputter-deposition in the method [6]. Finally the crystallization temperature could be lowered down to 200 °C by optimizing the deposition conditions including ion irradiation [7,8]. Ar ion irradiation is caused by applying the pulse bias voltage to the substrate in Ar plasma. Then the Ar ion energy can be controlled by changing the pulse bias voltage. Also, the amount of Ar ion irradiation is controlled by changing the plasma density or pulse bias duty ratio. In this paper, we reveal how the ion fluence affects on lowering the crystallization temperature of films deposited by the new process, in which a multi-target RF magnetron sputtering deposition is combined with simultaneous ion irradiation. The Ar ion fluence is calculated from the plasma density and electron temperature measured by a double probe. The deposited TiNi films are examined with an X-ray diffraction (XRD). We discuss the effects of ion fluence on the crystallization temperature of TiNi film.

2. Apparatus and film formation

The TiNi films are deposited on Si substrates with a multi-target RF magnetron sputtering deposition system which is equipped with an ion irradiation system as shown in Fig. 1. The deposition system mainly consists of four separate confocal targets as well as a temperature-controlled substrate holder of 101 mm in diameter. However, the specific difference of this apparatus from traditional

* Corresponding author at: Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, 3-1 Yatsukaho, Hakusan, Ishikawa 924-0838, Japan. Tel.: +81 76 274 8272; fax: +81 76 274 8273.
E-mail address: n-ikenaga@neptune.kanazawa-it.ac.jp (N. Ikenaga).

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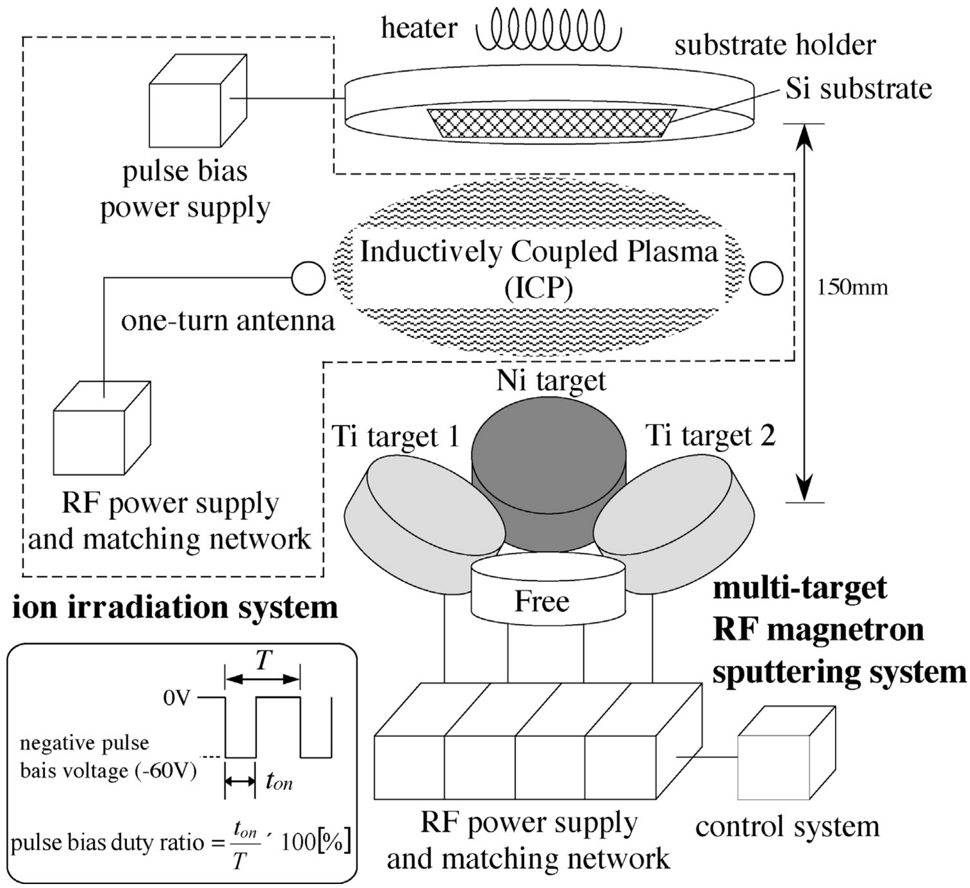

Fig. 1. Schematic illustration of a multi-target RF magnetron sputtering deposition system and ion irradiation system.

sputtering deposition systems is that an ICP (inductively coupled plasma) source is installed between a set of the targets and the substrate. The plasma is generated by an RF power which is independent of the RF powers for sputter sources. Ar ions which are generated by the ICP source with a one-turn antenna of 150 mm in diameter are accelerated to the substrate by applying pulse bias voltages of −60 V to the substrate holder. The ion irradiation and sputtering deposition parameters are shown in Table 1. Ti compositions of the deposited films under these conditions are between 51.5 at.% and 52.8 at.%. The ion energy value expressed in eV is not exactly equal to the pulse bias voltage in *V*, but is added with the plasma floating potential. In order to suppress the plasma-potential variation as much as possible, the pulse bias voltage feeder in vacuum to the substrate holder is coated with ceramics.

In order to realize the film composition of around 50 at.% of Ti/Ni ratio, three sputtering targets of 50 mm in diameter, two of Ti (99.9% in purity) and one of Ni (99.9% in purity) are used, since the ion sputtering ratio of Ni is roughly two times that of Ti. The films of 1 μm in thickness are deposited on Si (0 0 1) substrates of 10 mm × 10 mm in area at a substrate temperature at 200 °C. Ar gas pressure is set at 0.15 Pa by adjusting the gas flow as well as the conductance valve. The target-substrate distance is 150 mm. Since the Ti deposition rate per minute (DR_{Ti}) and the Ni deposition rate (DR_{Ni}) are separately controlled by adjusting the RF power for each target, the ratio of DR_{Ti} to DR_{Ni} was freely selected from 1.3 to 1.6, while the total deposition rate for the TiNi film is kept at 10 nm/min.

The film thickness is measured with a surface profilometry (Dektak150, ULVAC) from the step height at the edge of masked part of Si substrate. An X-ray powder diffraction (XRD; RAD-2R, RIGAKU) with Cu Kα (λ = 1.54056 Å) line is used for estimating the degree of crystallization. The plasma density in ICP is measured by changing the plasma condition with double probe measurement system (L2P, JE Plasma Consult GMbH) which is replaced with the temperature-controlled substrate holder in Fig. 1. The edges of double probe are positioned near the surface of former substrate holder.

The ion fluence is calculated from plasma density and electron temperature. In order to calculate the ion fluence, it is assume that the plasma consists of electrons and singly charged positive ions of a single species. When the velocity distribution of electrons in the plasma is Maxwellian, the ion irradiation density I_i is expressed

Table 1
Ion irradiation and sputtering deposition parameters.

Ion irradiation					Sputtering deposition			
Pulse bias duty ratio (%)	Substrate temperature (°C)	Pulse bias voltage (V)	Pulse bias repetition frequency (Hz)	RF power for ICP generation (W)	Ar pressure (Pa)	RF power Ni (W)	RF power Ti 1 (W)	RF power Ti 2 (W)
15 20 25	200	−60	1k	200	0.15	100	190	190