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Ti–Ni–Cu shape-memory alloy thin film formed on polyimide substrate

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Abstract

Ti–Ni–Cu shape-memory alloy (SMA) thin films were sputter-deposited on heated polyimide substrates. Ti–Ni–Cu films deposited at substrate temperatures of 543 and 583 K were found to be crystalline. Especially, a $Ti_{48}Ni_{29}Cu_{23}$ film deposited at 583 K exhibited a high martensitic transformation temperature above room temperature and a narrow transformation temperature range, which enable the film to be used at room temperature. Double-beam cantilevers made of 8 μm thick $Ti_{48}Ni_{29}Cu_{23}$ films deposited on 12.5 and 25 μm thick polyimide substrates displayed a repeatable shape-memory effect by a battery of 1.5 V and it was verified that the composite film consisting of an 8 μm thick $Ti_{48}Ni_{29}Cu_{23}$ film and a 25 μm thick polyimide film is capable of moving 0.18 g wings of a dragonfly toy up and down. These results offer the prospect for using an SMA/polyimide actuator as a convenient small actuator, which will find wide-ranging applications.

Keywords: Actuator; Shape-memory alloy; Polymer; MEMS; Sputtering; Ti–Ni–Cu; Thin film

1. Introduction

Shape-memory alloy (SMA) thin films formed by sputtering have been attracting great interest as powerful actuators in microelectromechanical systems (MEMS) such as microvalves, microfluid pumps, and micromanipulators because of their large force and displacement [1]. Such microdevices are usually fabricated by the silicon micromachining process and hence SMA thin films are always deposited on Si wafers [2,3]. Unless a substrate is intentionally heated during sputtering, as-sputtered films are amorphous and require a crystallization treatment at temperatures exceeding 773 K in vacuum [4]. This annealing process is generally not a problem in the case of silicon substrates, but poses difficulty for temperature-sensitive materials such as polymers and metals that tend to rapidly diffuse into a film. However, if crystalline SMA films could be formed on flexible polymeric substrates, they would find wide-ranging applications as convenient small actuators.

It has been already reported by several researchers [5–7] that deposition on heated substrates allows Ti–Ni films to be crystallized at a deposition temperature lower than the crystallization temperature of amorphous Ti–Ni films, thus eliminating a high-temperature annealing. This effect is explained by sputtering atoms reaching the growing surface with a high energy of movement [5]. At a high substrate temperature, the arriving atoms will acquire high energy when they touch on the hot substrate, which could be an efficient crystal nucleation sites. Substrate temperature can also enhance the diffusion thus promote the crystallization. The feasibility of producing SMA thin films on conventional polymeric substrates was demonstrated by Hou et al. [6]. They produced crystalline TiNi films of 3 μm thick on 7.6 μm thick Kapton polyimide substrates by heating the substrates at 698 K during the deposition. The films were patterned to produce a prototype electrically-excitable thin film actuator and exhibited a robust shape-memory effect. These films were, however, manually bent at liquid nitrogen temperature and recovered by heating in cold nitrogen gas.

In the present paper, we demonstrate that Ti–Ni–Cu thin films sputter-deposited on heated polyimide substrates exhibit a repeatable shape-memory effect above room temperature. An example of the application of the SMA/polyimide actuator is presented.

2. Experimental procedures

Three kinds of thin films (Ti-rich Ti–Ni, Ti-rich Ti–Ni–Cu and (Ni, Cu)-rich Ti–Ni–Cu films) were deposited on glass substrates and polyimide films with a carrousel-type magnetron-

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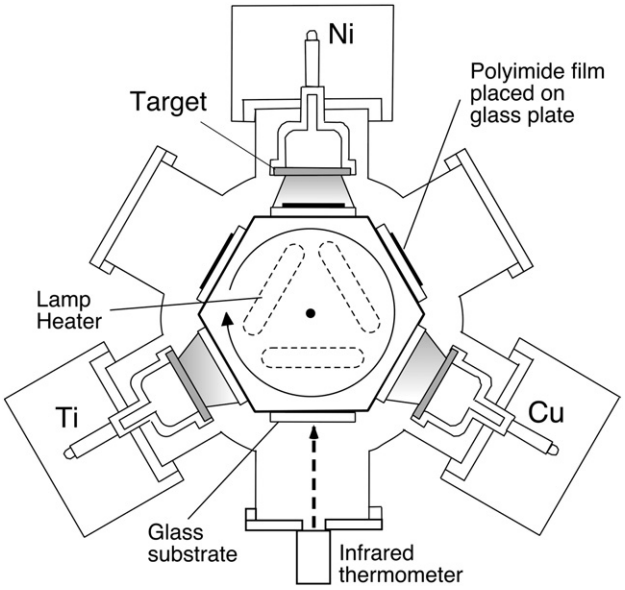

Fig. 1. Schematic illustration of carrousel-type magnetron-sputtering apparatus (view from above).

sputtering apparatus [8]. Three targets of pure Ti, Ni and Cu were used to obtain a desired composition. The direct current power applied to each target was controlled independently; the powers of Cu and Ni targets were varied from 0 to 98 W and from 280 to 177 W respectively, while that of a Ti target was kept at 1000 W. The chamber was evacuated to a base vacuum of 3×10^{-5} Pa and then Ar gas at a working pressure of 0.2 Pa was introduced. The surface temperature of a glass substrate was measured with an infrared thermometer, as shown in Fig. 1, and this substrate surface temperature was kept at 483, 543, 583 and 613 K prior to deposition. The substrate holder was rotated at 60 min^{-1} to obtain composition homogeneity during sputtering. Ti–Ni–(Cu) thin films were deposited on glass substrates for 150 min and the final thickness was 8 μm. The film compositions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be $Ti_{55}Ni_{45}$, $Ti_{52}Ni_{33}Cu_{15}$, $Ti_{51}Ni_{34}Cu_{15}$, $Ti_{49}Ni_{28}Cu_{23}$, and $Ti_{48}Ni_{29}Cu_{23}$. The $Ti_{48}Ni_{29}Cu_{23}$ thin films were also deposited onto Dupont–Toray Kapton 100H and 50H polyimide films with thicknesses of 25 and 12.5 μm respectively, which were placed on glass substrates. For outgassing [6], the polyimide films were baked at 543 K for 100 h prior to deposition.

The phases in the films attached to the glass substrates were identified by X-ray diffraction using Cu Kα radiation. Some deposited films were peeled off the glass substrates for composition analyses, differential scanning calorimetry (DSC) measurements and transmission electron microscopy (TEM) observation. DSC measurements were carried out by cooling and heating at the rate of 10 K min^{-1}. The microstructure of the films was observed with a transmission electron microscope (JEM-2000FXII) at an accelerating voltage of 200 kV. Thin foils for the TEM observation were prepared by double-jet electropolishing in an electrolyte solution consisting of 95% acetic acid and 5% perchloric acid by volume. The shape-memory effect of films deposited on polyimide films was evaluated by making a simple actuator driven by a battery.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of the films sputter-deposited on heated glass substrates. The $Ti_{55}Ni_{45}$ film deposited at 613 K (Fig. 2a) displays many peaks indicative of a crystalline film. The main phase of this film is considered to be a B2 phase, though several peaks due to B19' and Ti_2Ni phases are detected. Gisser et al. [5] reported that Ti–Ni thin films, 2–10 μm thick, deposited on (100) silicon substrates at 733 K were crystalline and had a strong ⟨110⟩ texture. They reported that the diffraction pattern from the film showed a peak intensity ratio of 50,000:1:<0.01 for 110, 200 and 211 reflections of the B2 phase, respectively. A similar texture was also reported for 3.1–9.2 μm thick $Ti_{1-X}Ni_X$ (X=50.8~53.9) films deposited on either quartz or polyimide substrates at 623 K or higher by Hou et al. [6] and for a 6.5 μm thick $Ti_{48.4}Ni_{51.6}$ film deposited on a glass substrate at 623 K by No et al. [9]. All the films in the present study, however, do not show a significant texture, as seen in Fig. 2. The reason for this difference is not clear and further work is necessary, since it seems that there are many factors affecting the texture of crystalline films such as substrate temperature, substrate material, film composition, film thickness and sputtering method.

In Fig. 2b, the $Ti_{55}Ni_{45}$ film deposited at 543 K shows a broad peak characteristic of an amorphous phase around 41.5°. That is to say, a temperature higher than 543 K is required to obtain a crystalline film of $Ti_{55}Ni_{45}$. In contrast, the Ti–Ni–Cu films deposited at the same temperature are found to be crystalline, as is apparent from Fig. 2c and e. This suggests that the replacement of Cu for Ni is effective to reduce the substrate temperature required to obtain a crystalline film. Craciunescu

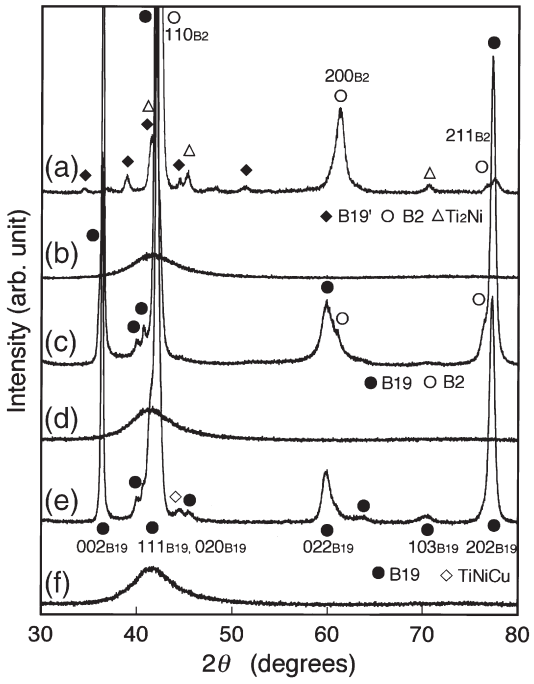

Fig. 2. X-ray diffraction patterns of (a)$Ti_{55}Ni_{45}$ film deposited at 613 K, (b)$Ti_{55}Ni_{45}$ film deposited at 543 K, (c)$Ti_{52}Ni_{33}Cu_{15}$ film deposited at 543 K, (d)$Ti_{52}Ni_{33}Cu_{15}$ film deposited at 483 K, (e)$Ti_{49}Ni_{28}Cu_{23}$ film deposited at 543 K and (f)$Ti_{49}Ni_{28}Cu_{23}$ film deposited at 483 K.