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Research Letter

Structural Characteristics and Crystallization of Metallic Glass Sputtered Films by Using Zr System Target

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Zr-Al-Ni-Cu thin films were deposited by the radio-frequency sputtering method at low substrate temperature using three kinds of targets: $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass target (α-BMG target), crystallized bulk metallic glass target (c-BMG target), and an elemental composite target composed of each Zr, Al, Ni chips, and Cu plate. XRD profiles of the films prepared when using these targets indicated that all of the films showed amorphous structures. While XRD profiles of the films using α- and c-BMG targets revealed a broad peak of $2\theta = 38$ degree in the same way as the α-BMG target indicating amorphous structures, that of the film using elemental composite targets showed a broad peak of $2\theta = 42$ degree, which is higher compared to the latter material. As a result of annealing the films at various temperatures for 900 seconds, the film using the α-BMG target showed a crystallization temperature of 748 K, higher than that of BMG with 723 K, while the other films had lower crystallization temperatures below 723 K. XRD profiles also indicated that the crystallized compounds of the films were different from those of BMG target.

1. INTRODUCTION

Metallic glasses have excellent mechanical properties, which are significantly different from those of organic glasses [1–5], in particular, the powder metallurgy process is more useful to prepare large-scale bulk metallic glass (BMG) materials [6, 7]. BMG shows a high corrosion resistance due to the absence of grain boundaries [8]. Thus, a metallic glass film is a promising candidate for suitable surface treatments to improve the corrosion resistance of poor-resistance materials, such as aluminum, titanium, and magnesium alloys. In this study, it is attempted to form metallic glass thin films by radio-frequency planar-magnetron sputtering. The previous studies on the glass-forming ability which were carried out [9–11], resulted in the superplastic deformation of the Zr-based bulk metallic glass. In this study, $Zr_{55}Al_{10}Ni_5Cu_{30}$ bulk metallic glass (BMG) with a high glass-forming ability [12] was selected as a sputtering target. In addition, the elemental composite targets composed of each pure Zr, Al, Ni, and Cu were employed as low-grade targets compared with the BMG target. Structure, composition, and crystallization temperature of the films deposited by BMG targets and composite targets were investigated.

2. EXPERIMENTAL

Zr-Al-Cu-Ni films were deposited by 13.56 MHz radio-frequency planar-magnetron sputtering [13]. Four kinds of targets were prepared as follows: (i) α-BMG target disk specimen with 74 mm diameter composed of four divided plates of $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG; (ii) c-BMG target, which was the above α-BMG target after annealing at 773 K for 900 seconds in argon gas atmosphere; (iii) Zr-Al-Ni-Cu elemental composite target consisting of Zr, Ni, Al chips set on a Cu disk; (iv) Zr-Al-Cu elemental composite target composed of Zr, Al chips with a Cu disk. The purity of the Cu disk, Zr, Ni, and Al chips used in this study are 99.96%, 99.2%, 99%, and 99.999%, respectively. The sputtering chamber was evacuated to less than 1.0×10^{-4} Pa pressure, and then argon gas (purity 99.999%) was introduced to the chamber as a sputtering gas. SiO_2 glass substrates of 18 mm × 18 mm square were placed on the water-cooled substrate

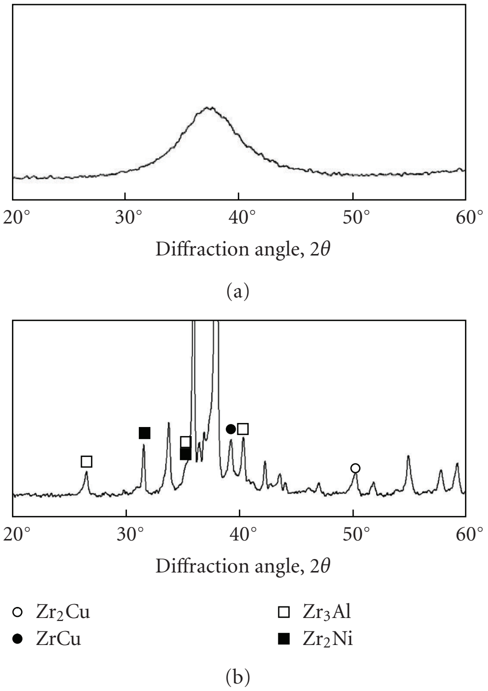

Figure 1: (a) XRD profiles of α-BMG material and (b) its annealed version (c-BMG) at 773 K.

Table 1: Thickness and compositions of as-sputtered films.

Targets	Films	Thickness of films (μm)	Compositions (at.%)			
			Zr	Al	Ni	Cu
BMG target	—	—	55.4	9.9	5.1	29.5
BMG	α-BMG	0.74–0.76	46.0	22.2	10.3	21.5
	c-BMG	0.75–0.80	51.7	14.3	6.9	27.1
Elemental	Zr-Al-Ni-Cu	0.75–0.80	30.7	13.4	2.9	53.1
	Zr-Al-Cu	0.75–0.80	30.0	9.7	—	60.3

holder. Before the film deposition, the presputtering was performed by placing a shutter between target and substrates to remove contaminations on the target surface. Sputtering power, time and gas pressures in this study were fixed at 100 W, 900 seconds and 1.3 Pa, respectively. The structures of the films and BMG targets were analyzed by X-ray diffraction (XRD) using Cu-Kα radiation (Shimadzu, XRD-6100). The composition of the sputtered films and BMG targets were determined by electron probe microanalysis with wavelength dispersive X-ray spectroscopy (JEOL, JXA-8600). In order to determine the crystallization temperature of the films, they were annealed at several temperatures in a nitrogen gas atmosphere using an image furnace, and subjected to XRD analysis.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD profiles of α-BMG and c-BMG materials used as targets. The XRD profile of α-BMG target shows a very broad peak of $2\theta = 38$ degree indicating amorphous

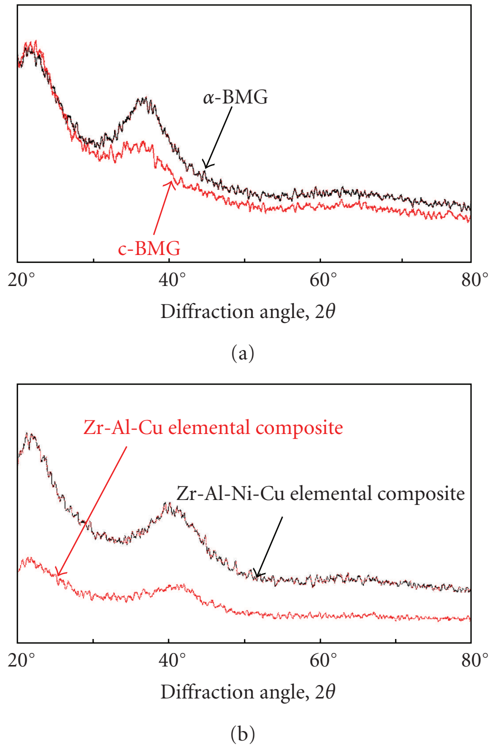

Figure 2: (a) XRD profiles of sputtered films when using BMG targets and (b) elemental composite targets.

structure, which is significantly good agreement with that of the previous study [12]. The c-BMG target annealed at 773 K shows sharp peaks of Zr_2Cu, ZrCu, Zr_3Al, and Zr_2Ni intermetallic indicating crystallization, which also agree with the results of the previous study [12, 14, 15].

Table 1 summarizes the thicknesses and compositions of sputtered films when using BMA material targets and elemental composite versions. The thickness of the films 0.74–0.8 μm is independent of the target species. Using BMG targets, both films, amorphous and crystallized ones, contain higher fractions of Al and Ni compared to raw BMG materials used as a target. This indicates that the rate of sputtering and/or deposition of Al and Ni elements contained in the BMG target easily occur compared to Zr and Cu elements. In the case of the films deposited by two kinds of the elemental composite targets, a larger content of Cu element than that of the BMG target is obtained. This is because this study employs the Cu plate disk, and the deposition of Cu is accelerated compared to the other metal chips on the Cu plate. Therefore, a careful adjustment of the volume of Zr, Al, and Ni chips set on the Cu disk surface is necessary to obtain the required composition of the sputtered film. Figure 2 shows XRD profiles of the films shown in Table 1 by using BMG targets and elemental composite targets. The broad peak of $2\theta = 22$ degree observed in the all films represents the peak of glass substrate. The XRD profiles of α-BMG and c-BMG films indicate a very broad peak of $2\theta = 38$ degree in the same way as the α-BMG target with a completely amorphous structure.

This means that the amorphous structure of the films seems to be almost the same as the structure of BMG material in spite of the different compositions from $Zr_{55}Al_{10}Ni_5Cu_{30}$. The XRD profile of the film deposited by the elemental composite target composed of a Cu base disk containing Zr, Al, and Ni chips shows a very broad peak of $2\theta = 42$ degree, which is higher than that in using BMG material as a sputtered target. When using an elemental composite target of Zr-Al-Cu without Ni chips, the deposited film shows a broad peak the same as that in employing the Zr-Cu-Ni-Al elemental composite target. This means that the films deposited by the elemental composite targets composed of Zr, Al, and Cu, with and without Ni, also indicate amorphous structure, while the structure of the films is dissimilar to that of BMG because of the remarkable difference of the compositions from $Zr_{55}Al_{10}Ni_5Cu_{30}$. When applying heat treatment at 723 K for 900 seconds on the above films shown in Figure 2, XRD profiles are summarized in Figure 3. The XRD profile of BMG material via the same heat treatment is also shown as reference data. The crystallization temperature of $Zr_{55}Al_{10}Ni_5Cu_{30}$ is 770 K from the results of differential scanning calorimetry (DSC) analysis [12], while the XRD profile of BMG annealed at 723 K shows a few small peaks caused by crystallization. The α-BMG film annealed at 723 K, however, shows a broad peak of $2\theta = 38$ degree without any sharp peaks caused by crystallization. The other films after being annealed at 723 K reveal several sharp peaks, corresponding to their crystallization phenomena. That is, the crystallization temperature of the films deposited by c-BMG and elemental composite targets is below 723 K. Degrees of the peaks of the films are almost same, but different from that of BMG. This suggests a crystallization mechanism of the films is different from that of BMG, and further study is necessary to clarify the mechanism of the crystallization at this moment. XRD profiles of α-BMG film and BMG annealed at 748 K for 900 seconds are shown in Figure 4. In the case of BMG, several sharp peaks are distinctly observed, and almost same as that of BMG annealed at 773 K. The XRD profile of α-BMG films annealed at 748 K indicates that several sharp peaks with crystallization and the 2θ values of the peaks are almost the same as those of the films annealed at 723 K deposited by c-BMG and elemental composite targets. This means that the crystallization mechanism of the α-BMG film corresponds to that of the other films, and the crystallization temperature of the α-BMG film is between 723 K and 748 K, higher than that of $Zr_{55}Al_{10}Ni_5Cu_{30}$ BMG material.

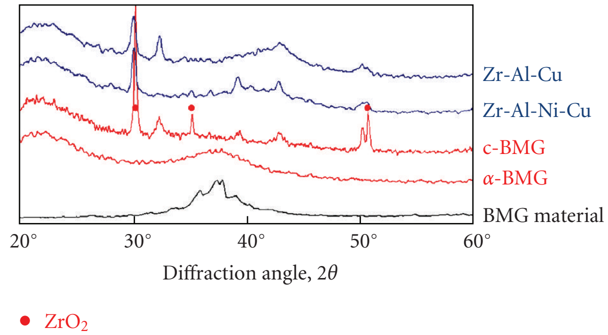

Figure 3: XRD profiles of annealed α-BMG material and various sputtered films when using BMG and elemental composite targets after annealing at 723 K for 900 seconds.

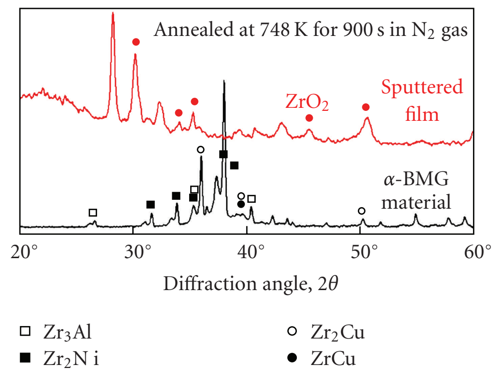

Figure 4: XRD profiles of α-BMG material and its sputtered film after annealing at 748 K for 900 seconds.

4. CONCLUSIONS

In the present study, Zr-Al-Cu-Ni films were deposited on glass substrates by the radio-frequency planar-magnetron sputtering device using four kinds of targets: α-BMG and c-BMG targets, and elemental composite targets composed of Zr, Al, Cu, with and without Ni. Structure, composition, and crystallization temperature of the films were investigated. Both films deposited by amorphous and crystallized BMG targets contain higher fractions of Al and Ni than that of the BMG targets, while both films deposited by elemental composite targets with and without Ni contain higher Cu content compared with $Zr_{55}Al_{10}Ni_5Cu_{30}$ due to using a Cu disk plate. All of the films deposited by BMG and elemental composite targets showed amorphous structures. The films deposited by BMG targets revealed a broad peak of $2\theta = 38$ degree in the same way of that of BMG. On the other hand, when employing the elemental composite target, with or without Ni, XRD profiles indicated a broad peak of $2\theta = 42$ degree higher than that of BMG. Although the crystallization temperatures of the films deposited by c-BMG and elemental composite targets was below 723 K, the temperature of the film deposited by α-BMG target was between 723 K and 748 K, higher than that of BMG material.

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