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Modification of structure and property in Zr-based thin film metallic glass via processing temperature control

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ABSTRACT

The aims of this study are to fabricate the Zr–Cu–Ni–Al thin film metallic glass (TFMG) on silicon substrates by DC magnetron sputtering with single target and to investigate the characteristics of coatings with various substrate temperatures. All the coatings exhibit similar structural and thermal properties, yet the hardness increases with processing temperature. It is demonstrated that amorphous matrix and cluster structure are slightly affected by the processing temperatures due to high cooling rate during deposition and superior glass-forming ability. Besides, atoms and clusters can acquire extra energy via heating substrate to stabilize each cluster, and the amount of free volume is reduced. Thus, the hardness increases with substrate temperature owing to the resistance to the shear band propagation. In summary, this study integrates the correlations among microstructure, thermal and mechanical properties, providing a convenient approach to tune TFMG coating performance.

1. Introduction

Metallic glass (MG), amorphous metal lacking long range structural order, is well-known for its high strength, good glass forming ability (GFA), superior corrosion resistance, and biocompatibility [1]. Owing to structural disorder and absence of grain boundaries, amorphous alloys are competitive in micro-electro-mechanical system (MEMS) and micro/nano imprint technique, which can be fabricated by superplastic characteristics of MG in the supercooled liquid region [2,3]. However, the major concern in MG is the limited specimen size, although there are significant improvements in the recent advent of MG [4]. For practical applications, thin film metallic glass (TFMG) coatings via sputter deposition technology seem to be an alternative strategy for the development of MG [5–7].

Zr-based bulk metallic glass (BMG) is an appropriate candidate as a sputtering target, due to its superior glass forming ability and relatively low cost [5,8,9]. In order to expand the life time of MEMS and master molds, better mechanical properties of TFMG are undoubtedly needed [10]. One of the effective solution is to add immiscible elements into Zr-based MG, producing inhomogeneous phases, deterring the propagation of shear band, and further improving the hardness and elastic modulus of the original MG [11,12]. On the other hand, annealing treatment is also used to increase the film hardness as the temperature up to the glass transition temperature (T_g). The enhancement of hardness is mainly attributed to the formation of short range order (SRO) clusters and the annihilation of free volume during annealing process [6,13,14]. As compared to the traditional heat treatment by rapid thermal annealing, substrate heating control provides another pathway, which can significantly reduce time and costs for fabrication processes in single target systems in which properties are strongly dependent on the temperature. In this study, the mechanical and thermal properties of Zr-based TFMG prepared via processing temperature control are highlighted. The effects of the substrate temperature on the microstructure, mechanical and thermal properties are discussed.

2. Experimental procedures

Zr–Cu–Ni–Al TFMG with 1 μm in thickness was fabricated onto silicon wafers using a DC magnetron sputtering system with 1.3×10^{-4} Pa base pressure and 4.5×10^{-1} Pa working pressure. Substrate heating was applied to the substrate holder from room temperature (R.T.) to 400 °C during sputtering deposition. All the substrates were pre-sputtered for 10 min to remove unwanted contamination at 6.6 Pa argon pressure with a substrate bias of −500 V. The sputtering was performed at 80 W (DC power, ADVANCED ENERGY-MDX 500) with a $Zr_{52.2}Cu_{30.4}Ni_{8.6}Al_{8.8}$ bulk metallic glass target (2-in. in diameter). The substrate holder was

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Table 1
Chemical compositions of the Zr–Cu–Ni–Al target and TFMG.

Substrate temperature (°C)	Composition (at.%)			
	Zr	Cu	Ni	Al
R.T.	51.4 ± 0.7	29.5 ± 0.8	12.3 ± 0.1	6.8 ± 0.1
100	52.0 ± 0.5	29.3 ± 0.5	12.0 ± 0.2	6.7 ± 0.2
200	51.5 ± 0.3	30.0 ± 0.1	11.6 ± 0.2	6.9 ± 0.1
300	51.3 ± 0.3	29.6 ± 0.3	12.2 ± 0.5	6.9 ± 0.1
400	51.0 ± 0.2	30.9 ± 0.2	11.1 ± 0.3	7.0 ± 0.1
Target	52.2 ± 0.5	30.4 ± 0.2	8.6 ± 0.4	8.8 ± 0.1

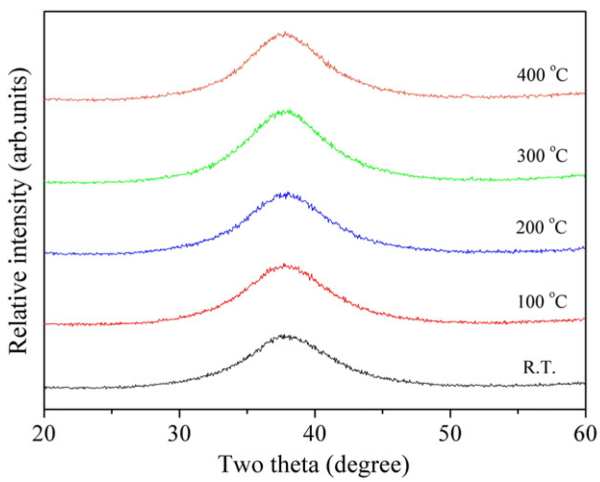

Fig. 1. The GIXRD patterns of Zr–Cu–Ni–Al TFMG.

kept at a distance of 8 cm to the target and the deposition rate was approximately 10 nm per minute for Zr–Cu–Ni–Al TFMG. The chemical compositions of Zr–Cu–Ni–Al TFMG were determined by a field emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Japan). The average composition is obtained from measurements carried out at five different positions on each sample. A grazing incidence X-ray diffractometer (GIXRD, TTRAX III, Rigaku, Japan) using Cu Kα with a wavelength of 1.54 Å operated at 50 kV and 300 mA was used to study the amorphous structures of all TFMG. The incident angle was 1° and the scan rate of GIXRD was 0.02°/min. The cross-sectional samples for transmission electron microscope (TEM, JSM-2010, JEOL, Japan) were prepared with a focused ion beam system. The microstructures of Zr–Cu–Ni–Al TFMG were examined with selected area diffraction (SAD) and high resolution transmission electron microscope (HRTEM) images. The surface morphologies and cross-sectional micrographs were observed by field-emission scanning electron microscope (SEM, JSM-7600F, JEOL, Japan). The glass transition temperature (T_g) and the crystallization temperature (T_x) of all TFMG were determined by a differential scanning calorimeter (DSC, 404 F3 Pegasus, Netzsch) in an argon atmosphere with heating rate of 40 °C/min. Nanoindentation (Nano Hardness Tester, CSM Instrument, Switzerland) test with a Berkovich diamond probe at a maximum applied load of 3 mN was used to assess the hardness and elastic modulus of the TFMG.

3. Results and discussion

3.1. Composition and microstructure analysis of Zr–Cu–Ni–Al alloy thin films

The chemical compositions of as-deposited coatings are shown in Table 1. It is revealed that Zr-based thin films with various substrate temperatures exhibit almost identical composition of $Zr_{51.4}Cu_{29.5}Ni_{12.3}Al_{6.8}$, which is quite close to the target composition of $Zr_{52.2}Cu_{30.4}Ni_{8.6}Al_{8.8}$. Fig. 1 shows the GIXRD patterns of all the coatings at various temperatures. The GIXRD pattern of Zr–Cu–Ni–Al TFMG exhibits a typical broad diffraction hump, indicating that the films are amorphous or nanocrystalline structure within amorphous matrix. To further probe the effects of the processing temperatures on local microstructure, the bright-field TEM images and corresponding SAD patterns of Zr–Cu–Ni–Al TFMG deposited at R.T. and 400 °C are explored and illustrated in Fig. 2. The cross-sectional images of films show a uniform, featureless structure without crystalline grains or particles, even in that of the 400 °C sample. The amorphous microstructure is also confirmed by the SAD pattern on the upper right corner in Fig. 2 of two specimens.

Fig. 3 shows the cross-sectional and top-view SEM morphologies of TFMG with various deposition temperatures. All the films reveal a typical columnar structure with sizes approximately of 20, 30, 40, 70, and 90 nm for films prepared at R.T., 100, 200, 300, 400 °C, respectively. As reported in other amorphous systems, such as Al–Mo [15] and Si-based [16] films, the similar columnar structure is observed. When the substrate is heated up to 400 °C, the thermal energy is sufficient to rearrange atoms locally and vanish the free volumes. Dense columnar structures are observed in TFMG at 400 °C, therefore the vein-pattern is more prone, as shown in Fig. 3(e). The vein-pattern here, which is specific to metallic glass, might have resulted from the local melting of the material at the fracture surface [17]. Furthermore, all the thin films exhibit a "grain-like" surface morphology, and the growth of grainy structures is associated with substrate temperature. It is considered that more stable structure (polygon-like shapes) is formed during substrate heating.

3.2. Mechanical properties and microstructure of Zr–Cu–Ni–Al alloy thin films

Fig. 4 depicts the relationship among hardness, elastic modulus and processing temperature in Zr–Cu–Ni–Al TFMG. When the temperature is increased from R.T. to 200 °C, a slightly enhancement in

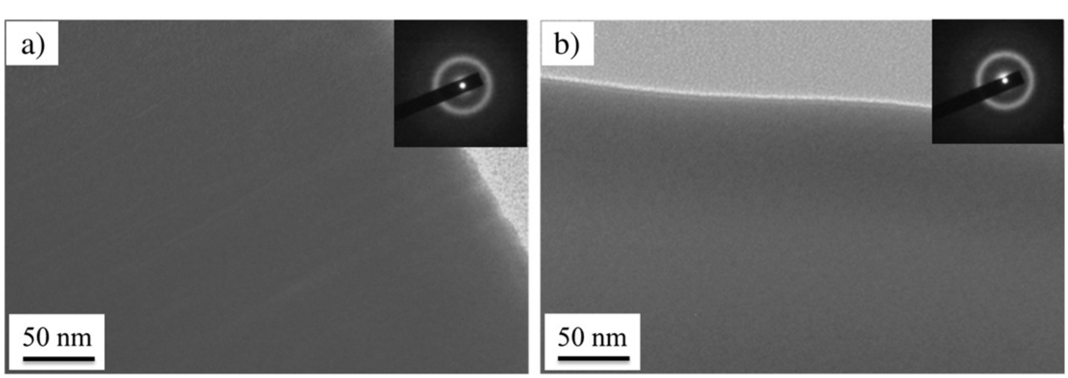

Fig. 2. Bright-field TEM images and corresponding SAD patterns of Zr–Cu–Ni–Al TFMG at (a) R.T. and (b) 400 °C.