Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Fabrication of W-Zr-Si thin film metallic glasses and the influence of post-annealing treatment

Chia-Lin Li[a], Jen-Chun Chang[b], Bih-Show Lou[c,d], Jyh-Wei Lee[b,e,f,*], Jinn P. Chu[g]

[a] Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taiwan
[b] Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan
[c] Chemistry Division, Center for General Education, Chang Gung University, Taoyuan, Taiwan
[d] Department of Nuclear Medicine and Molecular Imaging Center, Chang Gung Memorial Hospital, Taoyuan, Taiwan
[e] Center for Thin Film Technologies and Applications, Ming Chi University of Technology, New Taipei, Taiwan
[f] College of Engineering, Chang Gung University, Taoyuan, Taiwan
[g] Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

ARTICLE INFO

Keywords:
W-Zr-Si
Thin film metallic glass
Post-annealing
Hardness
Indentation toughness

ABSTRACT

The amorphous thin film metallic glasses (TFMGs) have been studied widely due to their unique properties and ease of fabrication as compared with the bulk metallic glasses (BMGs). Among the many TFMG systems, the W-based TFMG remains unstudied. In this work, a series of ternary W-Zr-Si TFMGs containing various W content ranging from 49.3 to 66.5 at.% were fabricated using a magnetron co-sputtering system. Increasing the W content of W-Zr-Si TFMG rendered an increase of Young's modulus up to 182 ± 4 GPa with the highest W content of 66.5 at.%. The film hardness was 13 GPa, independent of the W concentration in the as-deposited W-Zr-Si TFMGs. The influence of post-annealing on the microstructure and mechanical properties of TFMGs was studied by a vacuum thermal treatment ranging from 450 to 750 °C under various holding times. The surface roughness increased with increasing annealing temperature, with the sample annealed at the supercooled liquid region exhibited the lowest surface roughness of 1.14 nm. The hardness of TFMGs increased with increasing annealing temperature and longer holding time due to annealing-induced crystallization with a highest hardness of 16.8 ± 0.5 GPa. However, the indentation toughness decreased upon annealing and the lowest value was achieved for the hardest film due to the increasing amount of short range ordered (SRO) clusters.

1. Introduction

For the last decades, the research and development of amorphous bulk metallic glasses (BMG) have been of great interest to academia and industries due to their unique properties of high hardness, as well as excellent wear and corrosion resistances [1,2]. Additionally, the amorphous BMG can be produced into a thin film form, which still provides some unique properties, such as amorphous structure, good mechanical and anticorrosion properties [3–6]. Among BMGs, W-based BMGs have been extensively studied since 1998 for their outstanding mechanical properties and relatively low fabrication cost [7–11]. W-Ru-B and W-Fe-B-C BMGs have extremely high hardness (> 11 GPa), Young's modulus (> 198 GPa), as well as crystallization temperature (> 700 °C) [11,12]. Meanwhile, W-Ni-B thin film metallic glass (TFMG) exhibited a hardness higher than 24 GPa and extraordinary wear resistance [13]. Moreover, a hardness enhancement from 6.9 to 7.6 GPa was also reported through the control of W concentration in a previous study of Zr-W-Ti TFMGs [3].

For TFMGs, the crystallization tends to occur during thermal annealing because the crystalline phases are more thermodynamically favorable than the metastable phases formed in the as-deposited condition. Chu et al. reported an extensive amorphization result for the sputtered Zr-based TFMG when it was annealed at the temperature range between the glass transition temperature, T_g, and crystallization temperature, T_x. Then, annealed above T_x, nanocrystalline phases were observed [14]. Furthermore, it has been reported that heat treatment significantly influenced the microstructure and mechanical properties of W-based BMGs [11]. Influences of annealing on the microstructure, electric resistance, surface roughness and mechanical properties of TFMGs have been well evaluated recently [4,15–18] but a completely understanding on the effect of annealing on the indentation fracture toughness of TFMGs is still lacking, particularly for W-based TFMGs. In this work, W-Zr-Si TFMGs containing various W concentrations were prepared by a magnetron co-sputtering system to provide a better

---

* Corresponding author at: Department of Materials Engineering, Ming Chi University of Technology, New Taipei, Taiwan.
E-mail address: jefflee@mail.mcut.edu.tw (J.-W. Lee).

https://doi.org/10.1016/j.jnoncrysol.2017.12.035
Received 27 September 2017; Received in revised form 16 December 2017; Accepted 18 December 2017

Please cite this article as: Li, C.-L., Journal of Non-Crystalline Solids (2017), https://doi.org/10.1016/j.jnoncrysol.2017.12.035

Table 1
Sample designations, deposition condition, chemical composition, mechanical and thermal properties of as-deposited W-Zr-Si TFMGs.

Sample no.		W1	W2	W3	W4
Pulsed target power density (W/cm^2)	W	2.27	2.73	3.18	3.64
	Zr	2.27			
RF power density (W/cm^2)	Si	2.27			
Base pressure (Torr)		3×10^{-6}			
Working pressure (Torr)		3×10^{-3}			
Ar flows (sccm)		30			
Chemical composition (at.%)	W	49.3 ± 0.2	55.0 ± 0.2	60.9 ± 1.3	66.5 ± 0.3
	Zr	34.6 ± 0.2	30.2 ± 0.1	26.1 ± 0.5	23.3 ± 0.4
	Si	13.7 ± 0.4	12.3 ± 0.2	11.2 ± 0.2	10.2 ± 0.3
	O	2.4 ± 0.5	2.5 ± 0.1	2.7 ± 0.3	–
Ratio of W/(W + Zr + Si)		0.51	0.56	0.62	0.67
Hardness (GPa)		13.0 ± 0.3	13.3 ± 0.2	13.1 ± 0.5	12.8 ± 0.5
Young's modulus (GPa)		164 ± 2	170 ± 1	175 ± 3	182 ± 4
Average atomic distance, d/k		0.232	0.231	0.230	0.229
Glass transition temperature, Tg (°C)		566.8	565.1	563.4	549.1
Crystallization temperature, Tx (°C)		602.0	600.1	598.4	601.3
Supercooled liquid region, ΔT (°C)		35.2	35.0	35.0	52.2

understanding of the microstructure, phase, and mechanical properties of W-Zr-Si TFMGs. The influence of post-annealing on the microstructure and mechanical properties including hardness, Young's modulus, and indentation fracture toughness of the W-Zr-Si TFMGs will be discussed in this work.

2. Experimental procedures

Four ternary W-Zr-Si TFMGs were deposited on Si wafer and glass plate substrates by a co-sputtering system, which has been reported in previous work [3]. Elemental W, Zr, and Si (99.99 wt% in purity) were used as the sputtering targets with the dimension of 127 × 305 × 6 mm. Two pulsed direct current (DC) power supplies were connected to the W and Zr targets. The pulse frequency was kept at 20 kHz with 10% reversed voltage and 90% duty cycle. A radio frequency power supply was connected to the Si target. Background and working pressure, as well as the target power density values of W, Zr, and Si targets and sample designations are listed in Table 1. The deposition time was 2 h. A DC bias voltage was − 100 V and there was no substrate heating during deposition. The chemical composition of as-deposited W-Zr-Si TFMGs were determined using a field emission electron probe microanalyzer (FE-EPMA, JXA-8500F, JEOL, Japan). The thermal characteristic of coatings was evaluated using a differential scanning calorimeter (DSC, NETZSCH DSC 404F3, Germany) at a heating rate of 40 °C/min with a temperature resolution of 0.1 °C under Ar atmosphere. Cross-sectional microstructure observation on the as-deposited film was done by a field emission scanning electron microscope (FE-SEM, JSM-6701, JEOL, Japan).

To understand the influence of post-annealing on the property of W-Zr-Si TFMGs, an as-deposited W-Zr-Si TFMGs with the optimal mechanical property was selected for the annealing treatment. The W4 specimens of W-Zr-Si films were annealed in a furnace at temperatures ranging from 450 to 750 °C with a heating rate of 40 °C/min and a holding time of 60 s. The working pressure of the furnace was pump down to 10^{-6} Torr during annealing treatment. In addition, annealing treatments of thin films at 750 °C with longer holding times from 120 to 300 s were also performed. The sample designations and annealing conditions are listed in Table 2.

The crystallographic analysis of as-deposited and post-annealing

Table 2
Sample designations, annealing condition, surface roughness and mechanical property measurements of post-annealing W4 films.

Sample no.	W4	WA1	WA2	WA3	WA4	WA5	WA6	WA7	WA8	WA9	WA10	WA11
Annealing temperature (°C)	–	450	549 (T_g)	575	601 (T_x)	625	650	700	750	750	750	750
Heating rate	–	40 °C/min										
Holding time (s)	–	60								120	180	300
Ra (nm)	1.53 ± 0.02	1.30 ± 0.05	1.20 ± 0.01	1.14 ± 0.01	1.31 ± 0.03	1.19 ± 0.11	1.54 ± 0.09	1.95 ± 0.13	1.84 ± 0.01	1.70 ± 0.01	2.16 ± 0.04	2.14 ± 0.05
Hardness (GPa)	12.8 ± 0.5	12.3 ± 0.3	12.6 ± 0.4	12.7 ± 1.2	12.8 ± 0.4	14.0 ± 0.3	13.4 ± 0.2	13.6 ± 0.4	14.8 ± 0.4	15.6 ± 0.6	15.9 ± 0.5	16.8 ± 0.5
Young's modulus (GPa)	182 ± 4	177 ± 3	178 ± 3	178 ± 6	180 ± 2	187 ± 5	188 ± 6	192 ± 5	192 ± 3	198 ± 4	205 ± 3	206 ± 3
Indentation fracture toughness (MPa$\sqrt{\mathrm{m}}$)	0.91 ± 0.05	0.62 ± 0.08	0.61 ± 0.03	0.58 ± 0.07	0.55 ± 0.10	0.53 ± 0.06	0.48 ± 0.07	0.53 ± 0.02	0.60 ± 0.05	0.59 ± 0.04	0.47 ± 0.02	0.45 ± 0.03