Results in Physics 10 (2018) 612–615

Contents lists available at ScienceDirect

Results in Physics

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

Excellent near-infrared transmission of Zr-based thin film metallic glasses

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ARTICLE INFO

Keywords:
Thin film metallic glass
Zr-based alloys
Transmittance
Near infrared

ABSTRACT

$Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ thin film metallic glasses (TFMGs) were prepared by pulsed laser deposition (PLD) on glass substrates at room temperature. The effect of thickness on the electrical and optical properties of the Zr-based TFMGs was investigated. It was found that the resistivity of the Zr-based TFMGs basically decreased as the thickness varied from 10 nm to 40 nm. Interestingly, while the transmittance in the visible region decreased significantly with the increase of thickness, the transmittance in the near-infrared range still remained at a high level of larger than 80%. Through the characterization of electrical properties, the high transmittance of the Zr-based TFMGs in the near-infrared range was attributed to their rather low carrier concentration. Our findings provided the possibility for TFMGs to be used as transparent electrodes in the field of near infrared sensors and solar cells.

Introduction

Due to the disordered atomic structure and the absence of grain boundaries, bulk metallic glasses (BMGs) have attracted much attention for decades because of their unique properties such as high yield strength, high elastic strain, high corrosion resistance, high magnetic permeability, temperature-independent electrical resistivity and excellent surface finishing et al. [1–3]. Therefore, BMGs have an extensive range of potential applications in the industrial, electronics and biomedicine field. Traditionally, BMGs have been synthesized almost exclusively by rapid quenching methods from liquid to solid state. In addition, three empirical rules for BMGs were proposed by Inoue [4]: (1) multi-component structures consisting of at least three elements, (2) atomic size mismatches of at least 12% among the three main elements, and (3) negative heats of mixing among the three main elements. Nevertheless, the processing and material composition windows for fabricating the BMGs would be broader if they are prepared from the vapor to solid state. For example, sputtering or evaporation deposition can be proceeded at much higher cooling rates (10^{10}–10^{12} K/s) than that of rapid solidification (10^3–10^8 K/s). The thin film metallic glasses (TFMGs) formed accordingly show better surface roughness [5] and other unique properties [6,7], which make TFMGs being able to improve the mechanical properties for a wide variety of applications.

Because of the good corrosion resistance and mechanical properties, multi-component TFMGs have gradually received much attention in scientific research for potential applications. For example, in the 1990s and the early 21th century, Zr-Cu-Al and Pd-Cu-Si ternary TFMGs were sputter deposited for MEMS applications such as conical spring linear micro-actuator [8]. Also, Zr-Al-Cu-Ni TFMGs prepared by sputter deposition and focused ion beam patterning are reported for nano-device applications [9]. Recently, Lee and co-workers prepared indium tin oxide (ITO)/ZrCu TFMG bi-layer films onto the PET substrate by sputtering process and found that ZrCu TFMG could form a continuous and smooth film in thickness lower than 6 nm and the ITO(30 nm)/ZrCu (12 nm) films exhibited a rather good sheet resistance of 20 Ω/sq [10]. Cheng et al. prepared Al-doped ZnO (AZO)/$Zr_{50}Cu_{50}$/AZO tri-layer transparent conductive films by using pulsed laser deposition and the AZO/$Zr_{50}Cu_{50}$/AZO tri-layer films showed good transmittance (~80%) in the range of 400–2000 nm and sheet resistance of 43 Ω/sq [11]. Ultrathin (~ 0.98 nm) $Cu_{47}Zr_{42}Al_7Ti_4$ TFMGs were employed to enhance the optical properties of ZnO nanostructures and the photoresponse performance of the coated few-layers Cu-TFMG samples was enhanced 1680–7700% compared with the noncoated sample [12]. Lin et al [13] found that after annealing treatment, the CuMg TFMG/ITO bi-layer has a transmittance of 77.5% and a sheet resistance of 26.5 Ω/sq. These findings indicated that TFMGs also have potential applications in the fields of transparent conductive films, infrared sensors and solar cells.

Among all kinds of TFMGs, Zr-based TFMG has been widely investigated due to its good mechanical, tribological, and fatigue

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https://doi.org/10.1016/j.rinp.2018.07.019
Received 7 June 2018; Received in revised form 13 July 2018; Accepted 13 July 2018
Available online 19 July 2018

properties, corrosion resistance and excellent adhesion [14-19]. However, until now, little research has been done on the optical and electrical properties of Zr based TFMGs. In the present study, $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs were prepared on glass substrates by PLD and the effect of thickness on the electrical and optical properties of the Zr-based TFMGs was studied.

Experimental

The Zr-based alloy targets were prepared by copper mold casting. First, ingots with nominal compositions of $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ were prepared by arc-melting the mixtures consisting of pure elements with purities above 99.9% in a Ti gettered high-purity argon atmosphere. To achieve chemical homogeneity, then all ingots were re-melted at least four times, and then suction-cast into copper molds with a dimension of $20 \times 20 \times 3\,mm^3$.

The $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs with different thickness were deposited on $10 \times 10 \times 0.5\,mm^3$ glass substrate by PLD (COMPexPro 203, Coherent; wavelength 248 nm, pulse width 25 ns) using the prepared Zr-based alloy targets under room temperature. The glass substrates were ultrasonically cleaned in an ethanol/acetone solution and then rinsed in deionized water. Prior to all depositions the base pressure was pumped down to 1.0×10^{-3} Pa and the distance between target and substrate was kept at 10 cm. The rotation speed of target and substrate were set at 30 rpm. During the deposition process, the laser was operated at a repetition rate of 5 Hz and with energy of 200 mJ/pulse. Besides, the AZO (50 nm)/$Zr_{50}Cu_{50}$(10 nm)/AZO(50 nm) and AZO(50 nm)/Ag(10 nm)/AZO(50 nm) tri-layer films were also deposited on glass substrate by PLD using AZO ceramic target (99.999% purity, ZnO:Al_2O_3 = 98:2 wt %), $Zr_{50}Cu_{50}$ alloy target (99.95% purity, Zr:Cu = 50:50 at%) and Ag target (99.99% purity) with various $Zr_{50}Cu_{50}$ thicknesses under room temperature.

The deposition rates of $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$, $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs and AZO thin films were measured by α-step profilometer (Dektak XT, Bruker). The structures of the samples were characterized X-ray diffraction (XRD) using the Cu Kα radiation. The resistivity and Hall coefficient measurements were carried out by the Hall Effect Measurement System (HMS 5300, Ecopia). The optical transmittance was measured using an ultraviolet–visible–infrared (UV–VIS–IR) spectrophotometer (UV-3600, Shimadzu) in the range of 200–2000 nm.

Results and discussion

Fig. 1 demonstrated the XRD diffraction patterns of the as-deposited $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ metallic films prepared at room temperature. It can be seen that there were two typical broad diffraction peaks in the vicinity of 14 degrees and 30 degrees respectively, of which the former corresponds to the glass substrate and the latter corresponds to the as-deposited Zr- based metallic films. For comparison, the XRD pattern of the glass substrate was also shown in Fig. 1. It suggested that fully amorphous structure of the as-deposited Zr- based metallic films was formed on the glass substrates at room temperature. Fig. 1(b) shows the SEM image of the as-deposited $Zr_{50}Cu_{50}$ TFMG with a thickness of 10 nm, from which we can see that the $Zr_{50}Cu_{50}$ TFMG has a rather smooth surface and exhibits good continuity.

As shown in Fig. 2, the thickness dependencies of $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs on electrical resistivity was investigated. The results showed that as the thickness of the films increased from 10 nm to 50 nm, the resistivity of $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs decreased from 24.56 Ω·cm, 47.3 Ω·cm, 33.58Ω·cm and 29.69 Ω·cm to 4.45 Ω·cm, 8.37 Ω·cm, 20.52 Ω·cm and 5.18 Ω·cm, respectively. In 2010, Lee et al. [10] reported the ZrCu ultrathin TFMG deposited on PET substrate by co-sputering and the resistivity of ZrCu layer nearly maintained at the region of 150 μΩ·cm (much lower than that deposited on glass substrate in our experiment) after the thickness was greater than 3 nm. It gave us an inspiration that the resistivity of Zr-based TFMGs can be further reduced by choosing suitable substrate materials.

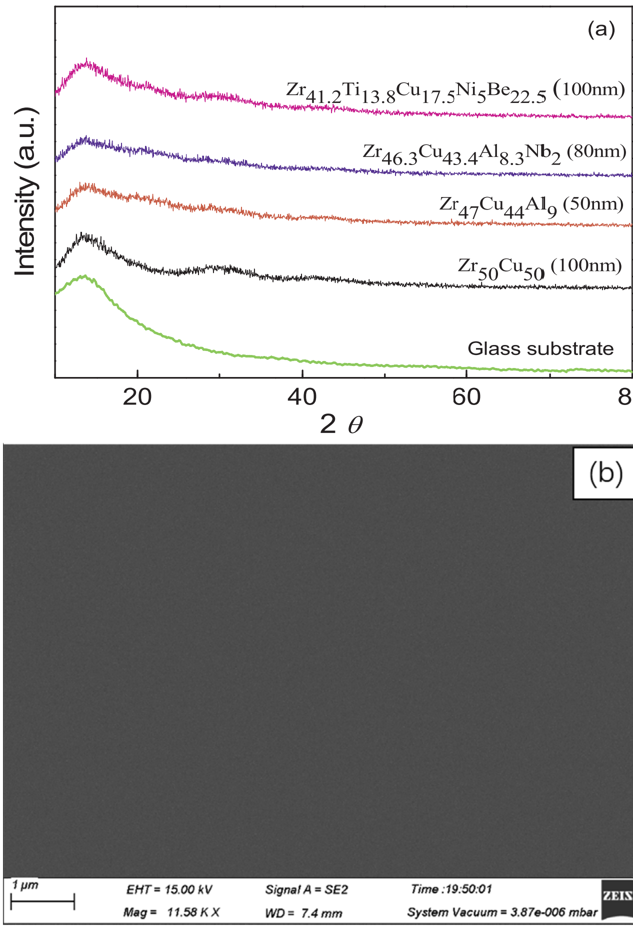

Fig. 1. (a) XRD diffraction patterns of the glass substrate, the as-deposited $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs prepared at room temperature; Fig. 1(b) SEM image of $Zr_{50}Cu_{50}$ TFMG with a thickness of 10 nm.

The optical transmittances for $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs on the glass substrate were shown in Fig. 3, as a function of thickness. In the visible region, the transmittance decreased from ~40% to ~20% for $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$ and $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ TFMGs with the thickness increased from 10 nm to 40 nm. For $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMG, the visible light transmittance was much better and decreased from ~75% to ~50% as the thickness increased. Interestingly, in the near infrared (NIR) spectral range, all samples exhibited excellent transmittance (~80%). Especially for $Zr_{47}Cu_{44}Al_9$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs, the transmittance in NIR waveband maintained above 80% while the thickness increased from 10 nm to 40 nm. In comparison with crystalline metallic film (Ag, Cu and Ni etc), the Zr-based TFMGs studied in the present work showed high transmittance rather than high reflectivity in the NIR region. In order to make a longitudinal contrast, we compared the electrical and optical properties of $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and $Zr_{41.2}Ti_{13.8}Cu_{17.5}Ni_5Be_{22.5}$ TFMGs with the same thickness (20 nm). The detailed bulk concentration, mobility, resistivity and the average transmittances in both visible and NIR regions for $Zr_{50}Cu_{50}$, $Zr_{47}Cu_{44}Al_9$, $Zr_{46.3}Cu_{43.4}Al_{8.3}Nb_2$ and