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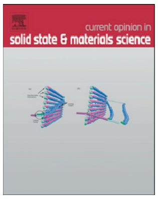

Thin film metallic glasses in optoelectronic, magnetic, and electronic applications: A recent update

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ABSTRACT

Thin film metallic glass (TFMG) is a new class of metallic thin film with unique characteristics, including smooth surface, absence of grain boundaries, second-order glass transition, annealing-induced amorphization, soft magnetic properties, and high thermal stability. Hence, with these properties, TFMGs are found very useful and promising in many areas, ranging from structural, biomedical to electrical components. This review provides an update on future challenges and opportunities associated with the further development of TFMG.

1. Introduction

Since the discovery of amorphous Au–Si alloys by Duwez et al. in 1959, interest in metallic glass (MG) has grown, particularly over the last decade [1]. Metallic glass can be produced in the form of thin film metallic glass (TFMG) using many deposition techniques such as evaporation [2], sputtering [3] and electroplating [4,5]. Thin films prepared by vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes [6]. This is expected to further improve the glass forming ability (GFA) and widen the composition range for amorphization [7,8]. An amorphous structure can be obtainable using various methods; nevertheless, MGs have been shown to undergo second-order glass transition and first-order crystallization at temperatures of T_g, and T_x, respectively, upon heating toward melting. In the 1980s and 90s, Inoue et al. developed numerous multi-component MGs with good GFA using Mg-, Ln-, Zr-, Fe-, Pd-, Cu-, Ti-, and Ni-based systems [9]. At that time, research on TFMGs was focused primarily on immiscible binary systems, including Cu–Ta and Cu–W deposited by evaporation [2], as well as Cu–Zr [3] and Al–Fe, Bi–Fe and Bi–Ti [10] produced by sputtering. A number of early studies on binary systems focused on the annealing-induced solid-state amorphization (SSA) of multilayer films [11–14]. In 1983, Schwarz and Johnson [11] reported the first La–Au TFMG by SSA during annealing of evaporated La/Au multilayer films. In 1986, Newcomb and Tu [13] and Cotts et al. [12] characterized the SSA of crystalline Ni/Zr multilayer thin films prepared by sputtering. In 1999 and 2000, Zr–Cu–Al and Pd–Cu–Si ternary TFMGs were sputter deposited for applications in micro-electro-mechanical systems (MEMS) [15,16].

Owing to its amorphous nature, TFMGs are thought to be free from crystalline defects, such as dislocation and grain boundaries. Accordingly, TFMGs possess exceptional mechanical properties adopted from its bulk form such as high strength, large elastic limits, and excellent corrosion and wear resistances. For the electrical properties, TFMGs are also expected to have distinctive properties, *e.g.* less electron scattering and minimal leakage problem for the absence of grain boundaries. Amorphous materials have captured attention as a promising candidate due to the presence of homogeneously distributed defects in the grain boundary-free structure. Unlike crystalline counterparts, there is no size effect for the amorphous structure, which is especially important in order to cope with the downscaling of electronic devices. In addition, because of their viscous flow in the supercooled liquid region (SCLR), they are beneficial for miniaturization and complicated shape material fabrication. Consequently, TFMG has been gaining a great interest in recent years [6]. More recently, attention has been focused on the development of TFMGs for specific applications [6]. Compared to conventional crystalline films, Zr- and Pd-based TFMGs have excellent three-dimension forming ability, good corrosion resistance, and mechanical properties suitable for MEMS applications, such as conical spring linear micro-actuators. Zr–Al–Cu–Ni TFMGs prepared by sputter deposition have been used in nano-devices [17], in the fabrication of tools used in biomedicine [18–20], and

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as a means to improve fatigue properties of various substrates [21–23].

Extensive reviews have been published focusing on the mechanical properties and development of bulk metallic glass (BMG) [24–29]. The first short review of TFMGs was published in 2010 and discussed their properties and preparation techniques [30]. This was followed by an article published in 2012 thoroughly reviewing their unique properties and potential applications [6]. The present review is to call attention to recent developments in TFMG research in the fields of optoelectronics, magnetics, and electronics.

2. Optoelectronic applications

The optoelectronic properties of TMFGs have been evaluated in a number of studies [23,31–33]. In particular, these studies have focused on the optical transmittance and reflectivity of TFMGs when applied to various substrates, such as polyethylene terephthalate (PET) and glass. The smooth surface, negative heat of mixing, and absence of grain boundaries of TFMGs make them ideal for applications aimed at improving the optical transmittance or reflectivity of devices used to harvest solar energy.

2.1. Improvements in optical transmittance

Indium tin oxide (ITO) is a transparent conductive material used in numerous applications [34–36]. Huang et al. [31] reported the use of TFMG ($Zr_{54}Cu_{46}$, ZrCu) in a bilayer structure of ITO/ZrCu (IZC films) to produce transparent conductive electrodes on a PET substrate in order to avoid the high cost of indium without deteriorating the optical transmittance of ITO. That study also introduced a layer of pure Ag to form ITO/Ag (IA films) for comparison. The aim was to develop a metal layer with good transparency and conductivity for a sandwich structure of ITO–metal–ITO. The authors of the study suggested that in order to form a continuous metal layer in thickness less than 6 nm as a transparent conductor, an alloy system with lower resistivity and negative of mixing heat between atoms might be an alternative choice. In this respect, TFMG is thought to be a promising transparent conductor.

Fig. 1 presents optical transmittance and reflectivity as a function of metal thickness in IZC and IA films on the PET substrate [31]. The transmittance of IZC films was similar to that of pure single-layer ITO films (83% at a visible wavelength of 550 nm); however, transmittance was shown to decrease with an increase in the thickness of the ZrCu layer. The transmittance of IZC films with a ZrCu layer 3 nm thick was 73% at 550 nm, varying little at wavelengths up to 1000 nm. The maximum transmittance of IA films with a 6 nm thick pure Ag film was 73% at wavelengths of 480–540 nm, which gradually decreased to 54% at longer wavelengths. Thicker Ag films (9 nm) were shown to be more susceptible than thinner Ag films (6 nm) to a loss of transmittance at a wavelength of 500 nm. The reflectivity of IZC films in conjunction with ZrCu films of various thicknesses was maintained in the range from 10% to 23%. In contrast, the reflectivity of IA films at wavelengths exceeding 550 nm showed a gradual increase with an increase in the thickness of the Ag layer.

The apparent differences between Ag and ZrCu TFMG layers were attributed to the microstructures they form when produced in very thin layers. ZrCu presents a smooth, continuous film even when applied in layers only 3 nm thick. Ag layers of similar thickness tend to present discontinuous island structures, which promote the scattering of incident light. The negative mixing heat between elements in TFMGs has led some researchers to postulate that these materials may provide the means to obtain thin (<6 nm) continuous metal layers for ITO–metal–ITO transparent conductive electrodes.

2.2. Improvements in optical reflectivity

Hu et al. studied the optical reflectivity of TFMGs in the ultraviolet, visible, and infrared regions [32]. This study compared the optical reflectivity of amorphous and crystalline Ag-based alloy films (250 nm in thickness) grown on glass substrates. They suggested that in all multi-component alloys, the reflectivity is a function of electrical resistivity, and amorphous alloys show a higher scaling coefficient as compared to their crystalline counterparts. This is mainly because of a longer mean free time for charge carriers in the amorphous alloys.

As shown in Fig. 2, reflectivity (*R*-value) measurements of crystalline and amorphous multi-component AgMgAl alloys were performed at wavelengths ranging from 190 to 1000 nm, the results of which are presented in Fig. 2(a) and (b). *R*-values for pure Ag, Mg, and Al are presented in Fig. 2(c). Among the pure metals, Ag showed the highest *R*-value in the visible and infrared regions; however, deep *d*-like valence electron absorption was observed at wavelengths below 320 nm. Al had the lowest *R*-value and Mg presented a relatively flat curve without *d*-like valence electron absorption.

A sudden drop in reflectivity was observed in crystalline alloys with high Ag content at ultraviolet wavelengths, as shown in Fig. 2(a). Alloys with low Ag content did not present this drop in reflectivity. The amorphous alloys in Fig. 2(b) presented reflectivity values (<0.8) lower than those of crystalline alloys. However, the reflectivity-wavelength curves were relatively smooth and no drop in reflectivity was observed in the near ultraviolet region, indicating that the *d*-like chemical bond was disrupted by the random lattice structure, which resulted in a reduction in absorption at ultraviolet wavelengths. Differences in the optical reflectivity of amorphous alloys were mainly due to a longer mean free time for charge carriers [32]. In this respect, the amorphous structure of TFMGs as well as their high mean free time for carriers provide superior optical reflectivity.

3. Magnetic properties of TFMGs: annealing effects

The excellent soft magnetic properties of MGs have led to their widespread uses in sensors, actuators, amorphous metal transformers, and magnetic recording heads [37,38]. Fe- and Co-based TFMGs with low coercivity, high saturation magnetization, and high electrical resistivity are well suited to applications involving miniaturization, particularly when operating at high frequencies [39]. In addition, the formation of nano-crystallites in a glassy matrix after thermal annealing is reported to further improve their soft magnetic properties [38,40–43]. In the following, we will examine the effects of thermal annealing on the magnetic properties of Fe- and Co-based TFMGs [41,42].

3.1. Magnetic properties: Fe-based TFMGs

Chu et al. [42] reported the magnetic properties of sputtered $Fe_{65}Ti_{13}Co_8Ni_7B_6Nb_1$ TFMG in as-deposited and annealed conditions. Thermal analysis of as-deposited film measured by differential scanning calorimeter showed T_g at 758 K and two exothermic peaks with crystallization onset temperatures at 814 K and 911 K (denoted as T_{x1} and T_{x2}), as shown in Fig. 3. The difference in temperature between T_g and T_{x1} was defined as the supercooled liquid region (ΔT). A slight decrease in hardness occurred when the stress was released at an annealing temperature of 673 K (Fig. 3). With the exception of small drops at T_{x1} and T_{x2}, strengthening was