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Improved bending fatigue behavior of flexible PET/ITO film with thin metallic glass interlayer

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ABSTRACT

The thin film metallic glass (TFMG) ZrCu coupled with ITO as a bi-layer electrode has potential to be transparent conductive films due to the promising sheet resistance of 20 Ω/sq (or 1×10^{-4} Ω-cm) and the transmittance of 73% at 550 nm wavelength. In addition, it is demonstrated that, with the TFMG ZrCu interlayer in between PET and ITO under long-termed bending fatigue, the induced micro-cracks can be appreciably reduced, the service cycling fatigue performance can be pronouncedly improved, and a fairly stable electrical property can result in. The relative change of resistivity is below 0.4, significantly lower than that of the commercial PET/ITO product.

1. Introduction

Indium–tin oxide (ITO) has been commonly applied as transparent conducting oxides for optoelectronic devices because of its resistivity, which can reach $1–3 \times 10^{-4}$ Ω-cm and promising optical transmission, which is 80–90% in the visible region, and the easy preparation by wide physical vapor deposition facilities [1–5]. Continuous roll-to-roll fabrication of flexible displays has become possible [6]. Like all other displays, transparent electrode patterns need to be defined as data or scan lines for the color control. However, ITO film is inevitably stiff and brittle, whereas the flexible polymer substrate PET is not. It follows that the PET/ITO laminate, while subjected to tensile or fatigue loading, would be prone to tensile micro-cracks which in turn leads to the increase of the ITO electrode resistivity and the degradation of optical transmission [7,8].

In order to decrease the use of ITO materials, the thickness of the transparent conductor ITO film is typically lowered down to 100 nm or less. In addition, the sandwich multilayered structure of ITO–metal–ITO has verified the performance of good conductivity and transparency in the visible light range due to higher carrier concentration in the middle layer of metal film [9–11]. This thin metal interlayer is often of pure Ag.

The interlayer of crystalline metal is typically required to be very thin (< 8 nm), so as not to degrade the optical transmission. However, it induces the problem of poor electric conductivity due to the discontinuous film of the island structure. All common crystalline metal films in the extra-thin range of 3–6 nm are difficult to form flat and continuous films. Metallic glass is another category of metal materials. In addition to the extensive research on the bulk metallic glasses (BMGs) [7,9,12–15], thin film metallic glasses (TFMGs) have also been explored in recent years [16–18]. ZrCu is the model binary metallic glass system. In order to enhance the mechanical properties of the PET/TCO laminate, a thin ZrCu TFMG interlayer of the thickness of 3–12 nm was deposited, forming the PET/ZrCu/ITO hybrid structure [19]. This ZrCu film could form a continuous and flat interlayer even at the lowest thickness of 3–6 nm. In this study, the fatigue properties of this multilayered hybrid structure are examined and compared to the performance of commercial products.

2. Experimental

The flexible polymer PET substrate was purchased from Nan-Ya company (CH 185), 125 μm in thickness. The transmittance of PET is 91.4% at wavelength of 550 nm. Firstly, the ZrCu TFMG was deposited onto the PET substrate by sputtering and then ITO was sputtered on the ZrCu film. All targets measured 4 in. in diameter and the Ar working pressure is about 5×10^{-3} Torr. The thickness of the ITO layer was fixed at 30 nm and that of the metallic films was varied from 3 to 12 nm. The morphology and components ratio of films were examined by scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), as well as transmission electron microscopy (TEM). The sheet resistance

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was measured using a four-point probe technique. Optical transmittance was measured by the N&K analyzer 1280.

The experimental bending fatigue system, with in-situ measurement of electrical resistivity, can keep on bending the samples from plane to specific curvature radius for customized cycles setting. The bending fatigue specimen measures 45 mm in length, 10 mm in width, and 125 μm in thickness. The bending velocity was defined as 1 cycle/s, and the maximum fatigue bending curvature *R* was varied from 15.5 to 19.5 mm. The bending strain ε can be calculated by $\varepsilon = h_s/2R$, where h_s is the substrate thickness. With a smaller bending curvature, the experienced strain per cycle would be higher. The bending strain per cycle is 0.32%, 0.36%, 0.38% and 0.40% for the curvature of 19.5, 17.5, 16.5 and 15.5 mm respectively.

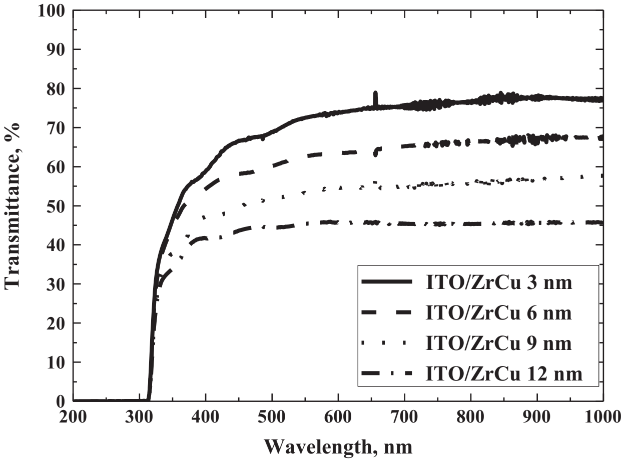

Fig. 1. The optical transmittance of ZCI films on the PET substrate as a function of light wavelength for four metallic glass thicknesses from 3 to 12 nm.

3. Results and discussion

The thin ZrCu layer less than 10 nm is firstly characterized by TEM for its atomic structure, and the thin layer is confirmed to be fully amorphous based on the halo diffraction pattern and lattice image. The transmittance of the pure single-layer ITO film is ~83% in the visible wavelength of 550 nm. The optical transmittance of PET/ZrCu/ITO is shown in Fig. 1, as a function of TFMG thickness. The ZrCu/ITO films (also simplified as the ZCI films) show the similar variation trend in transmittance as pure ITO, and the transmittance would decline with increasing ZrCu layer thickness, as shown in Fig. 1. The transmittance of ZCI films with 3 nm ZrCu layer is ~75% at 550 nm wavelength, and it is relatively fixed from 500 to 1000 nm. The ZCI films could give the sheet resistance of 20 Ω/sq, or a low value of 1×10^{-4} Ω-cm.

When the PET/ZrCu/ITO hybrid structure is subject to bending fatigue loading, micro-cracks and defects would be induced, and the in-situ measured electric resistivity would exhibit scattering and degradation with increasing fatigue cycles. Fig. 2(a) shows that the relative changes of resistivity ($\Delta R/R0$, where $R0$ is the initial resistivity, R is the measured resistivity after certain cycles and ΔR is $R - R0$) of the PET substrate coated with either only ITO film or

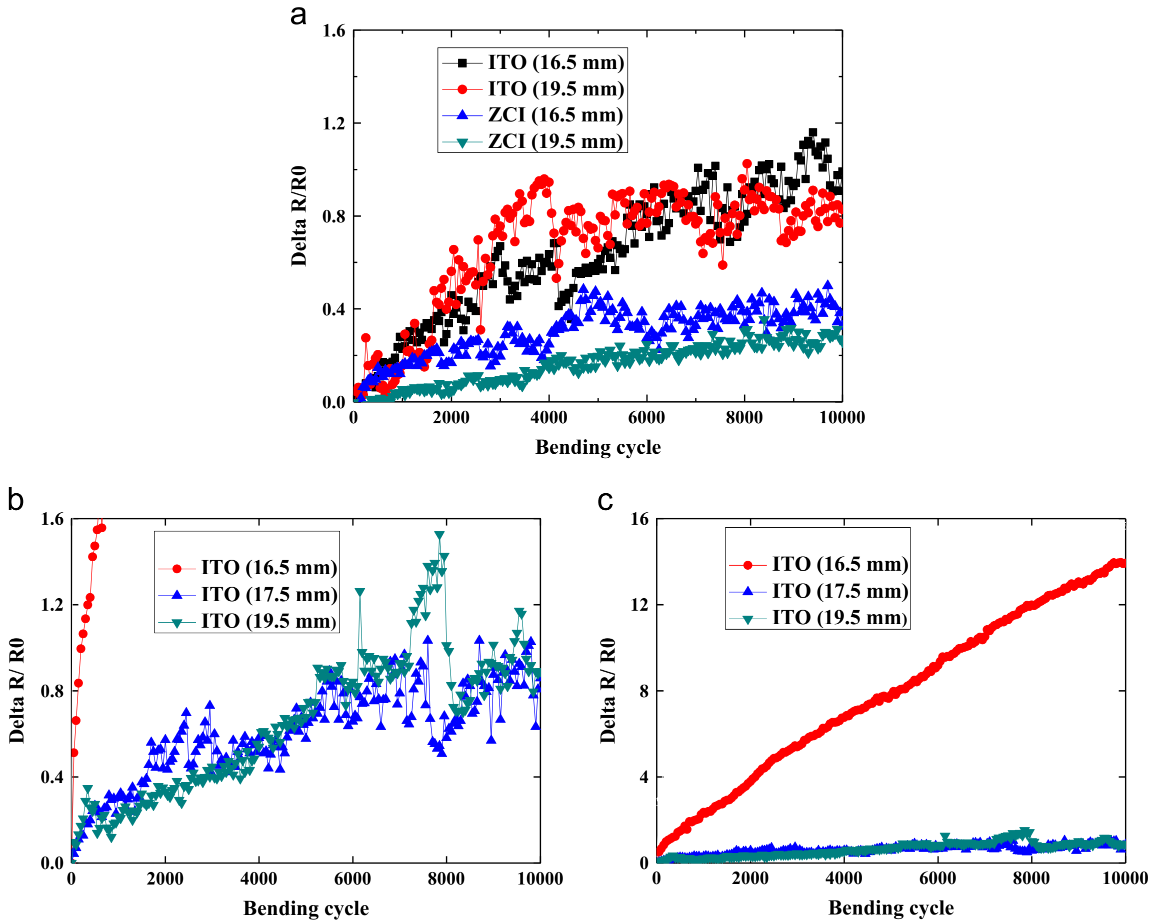

Fig. 2. The relative changes of resistivity as a function of the bending fatigue cycles of (a) our laboratory prepared PET/ITO and PET/ZrCu/ITO with two bending curvatures of 19.5 and 16.5 mm, (b) commercial PET/ITO foils, in the same vertical scale as (a) up to 1.6, and (c) in the reduced scale up to 16, showing the significant increment of relative changes of resistivity for the commercial PET/ITO foil fatigue-tested under a curvature of 16.5 mm.

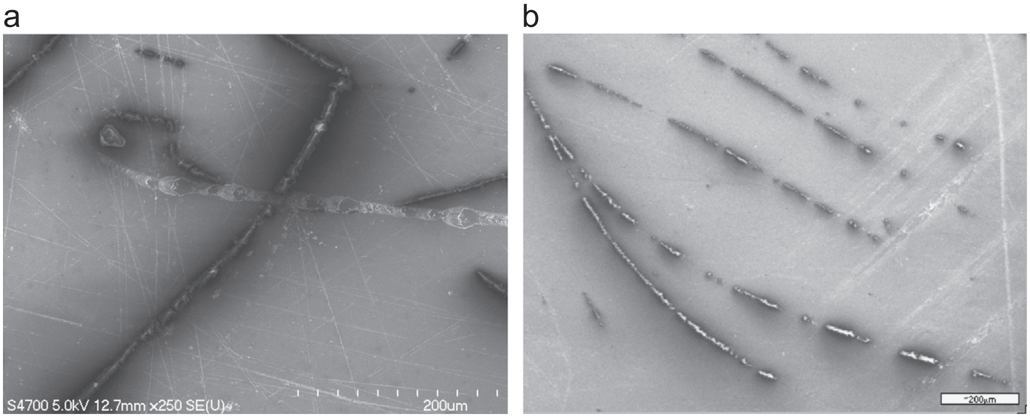

Fig. 3. (a) PET/ITO after 1000 bending cycles with the 15.5 mm curvature radius, and (b) PET/ZrCu/ITO after 10,000 bending cylces with the 15.5 mm curvature radius.

with the ZCI compound films under the maximum bending curvature of 19.5 and 16.5 mm (0.32% and 0.38% strain per bending cycle). It is apparent that a higher degree of micro-cracks would be induced, and in turn a higher degree of electrical resistivity change $\Delta R/R0$ with decreasing bending curvature (i.e., increasing fatigue maximum strain) and increasing fatigue cycles. Especially, a fairly stable electrical property of the ZCI compound film on the PET substrate was obtained during fatigue loading, as compared to the ITO film. The relative change of resistivity $\Delta R/R0$ is below 0.4 for ZCI and over 0.9 for ITO. If the bound line of 0.5 is set, the ZCI compound films would pass the 10,000 cycles fatigue test for the 16.5 mm curvature, and the ITO would not. When the bending curvature is further pushed to 15.5 mm (0.40% strain per bending cycle), the maximum $\Delta R/R0$ would reach 2.0 for ZCI and 2.5 for ITO.

Other than the fatigue tests on the PET/ITO prepared in our laboratory, with a thickness of 125 μm for PET and 30 nm for ITO, a commercial PET/ITO flexible foil, with the same PET and ITO thicknesses, was also examined and compared. The fatigue response as presented in Fig. 2(b) and (c) is found to be significantly worse than our laboratory prepared PET/ITO or PET/ZrCu/ITO. For the commercial foils, the maximum $\Delta R/R0$ under a 16.5 mm curvature after 10,000 cycles would approach 14.0, significantly higher than the ~1.1 for our laboratory prepared PET/ITO and the ~0.4 for our laboratory prepared PET/ZrCu/ITO. The improvement of ΔR/R0 by careful control of sputtering and the incorporation of TFMG ZrCu interlayer can be highly promising for the bending fatigue response.

Fig. 3 shows that SEM images of the PET/ITO and PET/ZrCu/ITO films after the bending fatigue test. The PET/ITO film after the short-termed bending fatigue test (1000 cycles) with the 15.5 mm curvature radius is shown in Fig. 3(a). It can be seen that many long and continuous cracks are already seen after only 1000 cycles. In contrast, Fig. 3(b) shows the PET/ZrCu/ITO hybrid foil after the long-termed bending fatigue test (10,000 cylces) with the same 15.5 mm curvature radius. The cracks in PET/ZrCu/ITO are still discontinuous. It is apparent that with the TFMG ZrCu interlayer in between PET and ITO, the long-termed fatigue resistance would be greatly enhanced.

The toughening for the substrate materials by TFMG coating has been demonstrated in several cases [9]. For example, the fatigue life of the Zr-based TFMG-coated 316L stainless steel can be increased by 30 times and the fatigue strength limit can be improved by 30% [20]. Also, a 200-nm Zr-based TFMG coating can result in pronounced improvement in bending strain [17]. Experimental and numerical modeling results indicate that the thin TFMG coating can (i) flatten the substrate surface and decrease the surface flaw number, and (ii) absorb partially the deformation energy and allow the formation of a high-density of more homogeneously distributed shear bands. Thus, a thin TFMG coating for modifying and improving the surface-sensitive mechanical properties of the substrate materials can be a promising and simple mean. The upgraded fatigue performance of the current PET/TFMG-ZrCu/ITO is another example along this line.

4. Conclusion

The bi-layer structure consisting of a TFMG ZrCu film and an outer ITO layer can be a promising candidate for the transparent conductive film deposited on a PET flexible substrate due to the better sheet resistance of 20 Ω/sq and the transmittance of 73% at 550 nm wavelength. It is demonstrated that, with the TFMG ZrCu interlayer in between PET and ITO under long-termed bending fatigue, the induced micro-cracks can be appreciably reduced, the service cycling fatigue performance can be pronouncedly improved, and a fairly stable electrical property can result in. The relative change of resistivity is below 0.4, significantly lower than that of the commercial PET/ITO product. The improvement of $\Delta R/R0$ by careful control of sputtering and the incorporation of TFMG ZrCu interlayer can be highly promising for the bending fatigue response of flexible optical devices.

Acknowledgments

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