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Mechanical integrity of hybrid indium-free electrodes for flexible devices

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ABSTRACT

Maintaining electrical conductivity, optical transparency, and mechanical integrity against bending and stretching are key requirements for flexible transparent electrodes. Transparent conducting oxides (TCOs) are widely used thin film electrodes in optoelectronic devices. However, these materials are brittle and reducing film thickness to improve their mechanical integrity compromises their electrical performance. Here we combine TCO thin films with metal grids embedded in a polymer substrate to create hybrid electrodes with low sheet resistance and high resilience to bending. Amorphous zinc tin oxide (ZTO) and aluminum-doped zinc oxide (AZO) films sputtered onto polyethylene-terephthalate (PET) substrates with and without embedded metal grids are studied. The hybrid electrodes have an optical absorptance below 5% in the visible range and their electrical sheet resistance is less than 1 Ω/sq. The critical strain for tensile failure is analyzed through a combination of electrical measurements and *in-situ* observations of crack initiation and propagation during tensile loading. The mean critical strain for failure of the AZO/metal grid is 8.5% and that of the ZTO/metal grid is as high as 10%. The AZO and ZTO films alone present critical strain values around 0.6% and 1% respectively, demonstrating that the addition of the metal grid considerably improves the resistance onset strain of the electrodes far beyond these critical strain limits.

1. Introduction

The growing interest in flexible electronics and energy-efficient lighting has greatly motivated research activities in transparent conductive electrodes (TCEs) that are not only highly conductive and transparent, but also mechanically flexible and made of earth-abundant elements [1,2]. Transparent conductive oxides (TCOs) are the most widely used TCEs, Sn-doped In_2O_3 (ITO) currently being the predominant material used as the transparent electrode in several optoelectronic devices, like touchscreens, photovoltaics and organic light emitting diodes (OLEDs). However, due to the limited supply and consequently high cost of indium, indium-free alternatives are highly desirable [3]. Doped tin oxide (SnO_2) and zinc oxide (ZnO) are the main indium-free TCOs for optoelectronic applications, due to their wide bandgap (>3 eV) and tunable low resistivity ($<10^{-3}$ Ω cm) [4]. Nevertheless, these materials are brittle and the high film thickness required to achieve low sheet resistance restrict their application in flexible devices. Several promising indium-free TCEs alternatives have been proposed in literature for flexible applications, including multilayer TCO/metal/TCO stacks [5,6], metal grids [7,8] and nanowire networks [1]. As a matter of fact, most of these TCEs are presently not available for deposition onto industry-relevant substrate sizes. Recently we have demonstrated that by combining an amorphous zinc tin oxide (ZTO) film with metal grids as the anode, we can fabricate flexible white OLEDs in industry-relevant substrates [9]. The mechanical endurance of these different TCEs remains to be investigated.

Resistance to mechanical bending or stretching is indeed an important parameter when developing electrodes for flexible applications. Micro-crack formation and delamination of thin-film TCOs under mechanical load degrade the electrical and optical performance of the device and may lead to further degradation

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with the formation of e.g., black spots due to moisture ingress through the electrodes [10,11]. The mechanical behavior of brittle thin films deposited on polymer substrates has been widely investigated, particularly using electro-mechanical test methods *in-situ* [12–14]. In this work we evaluate the mechanical properties of amorphous ZTO and polycrystalline aluminum-doped zinc oxide (AZO) films deposited onto PET substrates with and without embedded metal grids (Epimesh 300 by Epigem Ltd). The characterization is conducted using two complementary mechanical test methods, namely the electro-fragmentation *in-situ* in an optical microscope [15] and an electro-mechanical two-point rotation test [16] to monitor the formation of cracks and the correlated change of electrical resistance under tensile stress.

2. Experimental section

Two types of flexible substrates were used, based on a 125 μm thick PET foil coated with a 10 μm thick UV-cured adhesive layer followed by a 4 μm thick epoxy resin layer, without (Fig. 1a) and with a hexagonal nickel + gold grid (Fig. 1b), hereafter called as PET and PET-Ni/Au grid respectively. The 6 μm wide and 4 μm thick metal grid lines are embedded in the epoxy layer, forming a hexagonal grid with a 300 μm pitch size. Both substrates were provided by Epigem Ltd. UK. An optical micrograph of the PET substrate is shown in Fig. 1c. One notices the presence of parallel straight grooves (horizontal lines on the micrograph), which originated from the processing of the flexible PET substrate and randomly oriented ribs, which were within the UV-cured adhesive and did not impact the surface roughness of the substrates. Fig. 1d shows a confocal image of the hexagonal PET-Ni/Au grid substrate. A photograph of a curved PET-Ni/Au grid substrate is depicted in Fig. 1e together with a magnified image of the grid geometry. Fig. 1f shows a scanning electron micrograph of the substrate with the embedded Ni/Au grid.

The optical properties of the samples were measured using a spectrophotometer (Perkin-Elmer Lambda-900) equipped with an integrating sphere. The transmittance (T) and reflectance (R) were measured in the spectral range of 320–1500 nm. The absorptance (A) was calculated from $A = 1 - T - R$. The sheet resistance of the ZTO and AZO was determined by four-point probe measurements, and an Ecopia Hall effect system (HMS 5000) was used to determine the resistivity (ρ), free-carrier concentration (N_e) and Hall mobility (μ_{Hall}) using the Van der Pauw configuration. X-ray diffraction (XRD) patterns were obtained with a Bruker D8 Discovery using Cu-Kα radiation ($\lambda = 1.542$ Å) and AFM images were obtained with a Bruker Dimension Edge system using tapping mode.

For the mechanical test, the substrates were cut into 65×5 mm^2 rectangular samples, which were laminated onto a glass substrate for the sputter deposition of the TCOs. Prior to deposition, the substrates were annealed at 100 °C for 1 h. The ZTO and AZO films were deposited in an Oerlikon Clusterline Sputtering System from a ZTO (94 wt % SnO$_2$) and an Al:ZnO (2 wt % Al$_2$O$_3$) targets respectively, under an argon (Ar) and oxygen (O$_2$) atmosphere, at 60 °C.

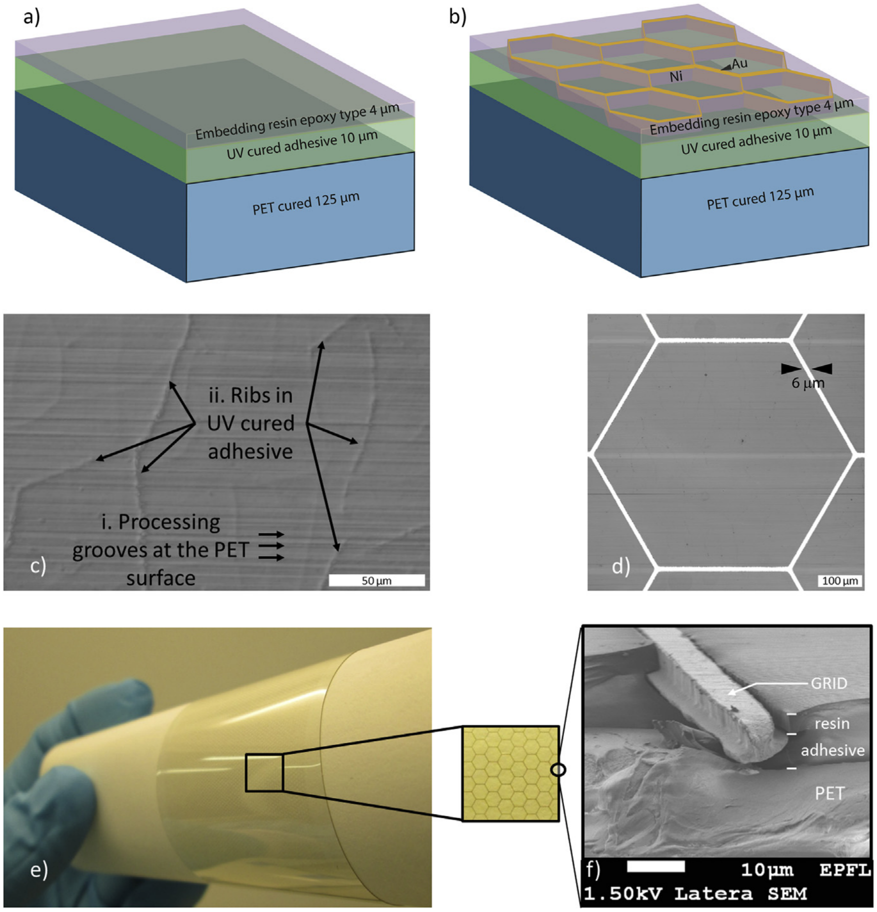

Fig. 1. Schematic diagrams of the flexible substrates with and without embedded grid: a) PET/adhesive/epoxy resin (PET), b) PET/adhesive/embedded grid (Ni+Au) in epoxy (PET-Ni/Au grid), c) Optical micrograph of the PET substrate showing (i) processing grooves at the PET surface and (ii) ribs in the UV-cured adhesive, d) Confocal image of the hexagonal PET-Ni/Au grid, e) Photograph of the curved PET-Ni/Au grid sample and f) SEM micrograph of the PET-Ni/Au grid sample taken with a 55° tilt.