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Highly stable Ag–Ni based transparent electrodes on PET substrates for flexible organic solar cells

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ABSTRACT

We report a novel transparent electrode structure made of Ag–Ni bilayer on polyethylene terephtalate (PET) substrates. However, without any adequate countermeasure, such an ultrathin layer would uninvitedly oxidize even at ambient conditions due to permeation of moisture and oxygen through the polymer substrates. A combination of heat and Ar plasma pretreatment was found to significantly increase the stability of the metals layers deposited onto polymer substrates. The 1 nm Ni capping layer provides higher work function together with stability to the underlying Ag conducting layer over time and in harsh conditions of 85 °C and 85% relative humidity. The obtained Ag–Ni bilayer ultrathin films show average transparency of 75% in the visible region and sheet resistance of 11 Ω/sq. To demonstrate its operational potential, the electrode has been used as the transparent anode in an organic solar cell (OSC), which shows an overall photon conversion efficiency of >90% of the indium tin oxide (ITO) based cell which was measured to be 2.67%. With respect to ITO, the proposed transparent electrode has several advantages, including mechanical flexibility, room temperature processing and low cost.

1. Introduction

Flexible optoelectronic devices, such as organic solar cells (OSCs) and light emitting diodes (OLEDs), have seen a recent surge in interest due to the fact that they are lightweight, mechanically robust and can be manufactured using low-cost roll-to-roll fabrication techniques. Transparent Conductive Oxide (TCO) films constitute one of the most important materials that can be used as transparent electrodes in flexible optoelectronic devices, mainly because their properties can be tuned from an insulator to a semiconductor behavior [1–5].

Among TCOs, Indium Tin Oxide (ITO) films are the most widely used since they offer high optical transparency in the visible region and sufficient electrical conductivity required for most of the devices [6,7]. However, the high cost of indium, the poor chemical compatibility of ITO with acid containing layers, the lack of mechanical flexibility due to ITO fragility and the high processing temperatures lead to the search for new transparent electrode materials, such as carbon nanotubes (CNTs), graphene films, thin metal films and metal grids [8–16]. Compared to other alternatives, which are still far from ITO performances in terms of sheet resistance and transparency, ultra thin metal films (UTMFs) (<10 nm) possess the advantage to be highly compatible with nearly all organic and semiconductor materials, high flexibility, transparent to light, still maintaining large electrical conductivity. In addition their deposition technology, physical vapor depositions, is cost-effective since it can be carried out on large scale using roll-to-roll geometry [17–20].

Among UTMFs, noble metals, such as silver (Ag), platinum (Pt) and gold (Au), have been extensively studied since they show high electrical conductivity and relatively high transparency in the visible wavelength range. In particular, Ag has one of the lowest contact electrical resistance. There are various reports on using different forms of Ag as a stand-alone layer or in conjunction with other materials, as transparent electrode for OSCs [9,20–23].

Although UTMFs represent a competitive alternative to ITO, they are strongly subjected to corrosion and oxidation processes which can significantly alter their electrical and optical properties. Especially when UTMFs are deposited on polymer substrates the absorption of moisture or water makes UTMFs to deteriorate very quickly. Therefore, it is essential to find a way to reduce the level of vapor and oxygen diffusion into polymer substrates and protect UTMFs from oxidation. A range of materials, such as SiO_2, SiN_x, TiO_2 and Al_2O_3, have been used as permeation blocking layer

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in order to solve this issue [25]. When made thin, these materials become flexible but remain brittle. Therefore, microdefects can propagate to form top-to-bottom cracks, which render them permeable [26–29]. To retain their excellent barrier properties but suppress crack propagation, inorganic/polymeric multilayer composite films, including Al_2O_3/polyacrylate [30], SiO_xN_y/silicone [31] and SiN_x/parylene-C were developed [32]. Since the polymeric layers mechanically decouple the inorganic layers from each other, the cracks in the inorganic layers are randomly distributed. This random distribution lengthens the permeation paths for atmospheric gases and thereby the device life time [33]. However, the processes for preparing a multilayer barrier for devices can be complicated and costly.

In this work, we propose to combine Ag and Ni UTMFs as stable and highly performing transparent electrodes on flexible substrate. We have studied the electrical, optical characteristics and surface morphology of a thin Ag–Ni bilayer sputtered on a flexible PET substrate and demonstrates its high stability. The results demonstrate that cleaning procedures and pre-treatments of the PET substrates are of crucial importance to obtain a stable electrode on a polymer substrate. In fact, if it is properly treated, the proposed Ag–Ni/PET structure can withstand high temperature and damp heat tests, even without any additional permeation barrier layer. We have also tested the mechanical flexibility of Ag–Ni/PET which shows unchanged properties under repetitive bending. The organic solar cell (OSC) built incorporating this electrode shows similar performances to those with ITO-coated substrates.

2. Experimental details

The ultrathin Ag–Ni bilayers were deposited on a Polyethylene terephtalate (PET) substrate (125 μm thickness, Melinex ST504 Dupont) by DC magnetron sputtering using Ag and Ni targets. Ag and Ni depositions were carried out sequentially on the PET substrate without breaking the vacuum in the main chamber, at a base pressure of 10^{-7}–10^{-8} Torr, room temperature, DC-power 100 W and pure Ar working pressure of 2×10^{-3} Torr. The deposition rates of Ag and Ni were 0.252 nm/s and 0.573 nm/s, respectively, and the target-substrate distance was 30 cm. The electrical and optical properties were measured using a Cascade Michotech 44// S 2749 four-point probe system with a Keithley 2001 multimeter and a Perkin Elmer Lamba 950 spectrophotometer, while the work function of the films was evaluated by Ambient Scanning Kelvin Probe Microscope.

The surface morphology of the prepared samples was studied at room temperature by a digital instrument D3100 Atomic Force Microscope (AFM) and FEI-Scanning Electron Microscopy (SEM). The AFM was used in tapping mode at ambient conditions over a scan sized of 5 μm × 5 μm and at a scan rate of 1 Hz. The damp heat test at standard conditions, 85% relative humidity and 85 °C, was carried out in a Vötsch VCL 7003 climate chamber.The mechanical properties of Ag–Ni films were evaluated by measuring the change in electrical sheet resistance (R_S) as a function of the number of bending cycles. For this purpose a home-made fatigue machine was used and the film on the substrate was bended between curvature radii of 12 mm (maximum) and 4 mm (minimum), respectively.

To demonstrate their effectiveness, the proposed electrodes were used as anode in OSCs according to the following architecture: Anode/MoO_3(5 nm)/ [fluorinated zinc phthalocyanine, F4-ZnPc] ID345: [Fullerene] C60(1:1, 35 nm)/ C60(25 nm)/ [(4,7-diphenyl-1,10-phenanthroline)] Bphen(5 nm)/Ag(100 nm).

The substrates were ozone-treated for 10 min. Afterwards, the different layers were deposited under high vacuum conditions (3.76×10^{-6} Torr) by sublimation in a commercially available evaporation chamber (Kurt J. Lesker Company) through a shadow mask. The evaporation temperature of the ID345 material was 390 °C. The photovoltaic *I*–*V*-measurements were carried out using simulated sun light with standard AM1.5 conditions. The intensity is monitored by a Si diode that is calibrated using a certified reference diode from the Fraunhofer ISE CalLab.

3. Results and discussion

The cleaning procedure and other pretreatments are always a critical step for polymer substrates and influence the stability of the films deposited on them, more specifically UTMFs for OSCs in our case. Prior to any UTMFs' deposition, the PET substrates were ultrasonically cleaned in acetone and ethanol for 10 min, respectively, and subsequently dried by using nitrogen gas.

Ag–Ni UTMFs on PET substrates with different pretreatments were prepared in order to determine the ones with highest stability properties. Considering that Ag nanolayers easily degrade when exposed to the environment, we covered the thin Ag films by a 1 nm Ni top layer. In our previous work, it was shown that Ni capped Cu UTMFs exhibit excellent stability against temperature and oxidation and when used as an anode in OLEDs or OSCs, the devices show similar efficiency as ITO based devices, with satisfactory operation stability over time [34]. The Ni capping layer protects the underlying ultrathin metal layer from oxidation, without affecting significantly its optical and electrical characteristics, and at the same time increases the work function which is an important parameter for OLEDs and solar cells.

Several samples [SX, X=1–7] consisting of 9 nmAg–1 nmNi bilayer UTMFs were deposited onto PET substrates with different pretreatment to assess their stability properties. S1 was without any pretreatment, S2 was pretreated in-situ by Ar plasma for 15 min at a pressure of 8 mTorr and 40 W RF power, S3 was kept at 120 °C in ambient atmosphere for a dwell time of 10 min prior to the loading into the sputtering machine, S4 was pretreated by a combination of heat (120 °C) and Ar plasma treatment, S5 was covered by a blocking layer of 20 nm TiO_2 layer on the back side of the PET substrate, S6 was covered by a blocking layer of 20 nm TiO_2 layer on the side of the PET substrate where the UTMF was deposited, and S7 was the sample which was covered with a blocking layer of 20 nm TiO_2 layer on both sides of the PET substrate. The TiO_2 blocking layer was deposited directly from a titanium dioxide target in the same chamber prior to the deposition of Ag9–Ni1 layer. Except for the sample S5 all other samples were prepared without breaking the vacuum. Details of the different pretreatments performed for the fabricated samples are summarized in Table 1.

Fig. 1 summarizes the results on the change of sheet resistance for all samples as a function of time. From the graph one can see that without any pre-treatment the samples degrade in about 10 day. Depositing a moisture blocking layer on the front side (where

Table 1
Summary of pretreatments for SX samples.

Sample	Pretreatments
S1	Without pretreatment
S2	Ar Plasma (15 min, 8 mTorr 40 W RF power)
S3	Heat (10 min at 120 °C, ambient atmosphere)
S4	Ar Plasma+Heat
S7	TiO_2 Blocking layer (back side)
S6	TiO_2 Blocking layer (in contact with UTMF)
S7	TiO_2 Blocking layer (both sides)