Environmentally stable Al-doped ZnO transparent electrode for organic optoelectronic devices

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Abstract: Al-doped ZnO (AZO) transparent electrodes capped with oxidized ultrathin Ni are proposed. The novel structure show enhanced stability in damp heat and also leads to OLED efficiencies as high as those of similar ITO-based devices.
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1. Introduction

Indium tin oxide (ITO) is the most widely used transparent conductive oxide (TCO) for many optoelectronic devices, such as organic light emitting diodes (OLEDs), photovoltaic cells, flat panel displays, and photodetectors. Despite its maturity, ITO suffers from several drawbacks, including shortage and cost of one of its constituents, indium, and indium migration into active layers during device operation [1, 2]. Al-doped ZnO (AZO) thin films have been considered as a promising alternative to ITO. However, the environmental stability of AZO films is still an unsolved problem, leading to significantly increased electrical resistivity and surface degradation when the TCO being exposed to harsh environment, especially to a combination of temperature and humidity. This drawback prevents AZO films to be deployed in real applications that require long-term reliability of the devices. Therefore, great effort has been dedicated to improve the environmental stability of AZO thin films [3, 4]. Up to now, the majority of the research works are targeting composition modification as well as crystalline quality control to stabilize AZO. Here, we investigate the environmental stability of AZO thin films and report an effective approach to enhance it. By adding an oxidized ultrathin nickel (Ni) capping layer with a thickness in proximity of its percolation threshold (2.5nm thickness), the environmental stability of AZO thin film is greatly enhanced, as it is shown via damp heat (DH) tests at 95ºC and 95% relative humidity. The developed Ni capped AZO (AZO/Ni) transparent conductor was then used as an anode in OLEDs, showing performance similar to those of ITO-based devices.

2. Experimental

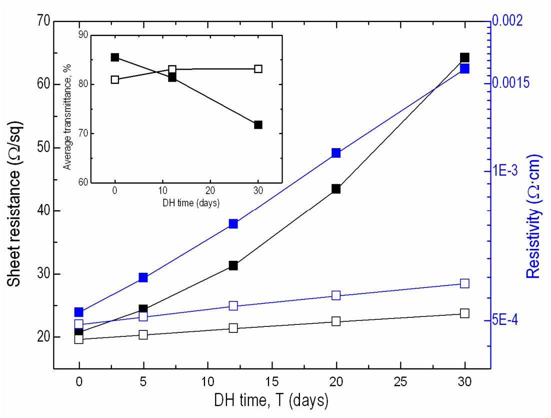
AZO thin films with thicknesses of 250 nm and Ni layer with different thicknesses were deposited by sputtering on fused silica substrates. AZO films were prepared with a substrate temperature of 200 ºC, RF power 150W, and a pure Ar working pressure of 1-1.5 mTorr. A humidity chamber Vötsch VCL 7003 was used for the DH test in harsh conditions of 95ºC and 95% relative humidity. The surface morphology was characterized by AFM and optical interferometry (Veeco Wyko 9800NT). Work function of the films was evaluated by ambient scanning Kelvin probe microscopy. The developed transparent conductors were used as anode electrodes in OLED devices with the following structure: Anode/PEDOT:PSS/SY/Ag.

3. Results and discussion

Fig.1 shows the DH test for AZO and AZO/Ni samples. It is clearly seen that AZO/Ni sample shows electrical properties more stable than those of AZO, with a sheet resistance value still below 24 Ω/sq after 30 days. Moreover, as it can be seen in the inset of Fig.1, the average optical transmittance in the 375-700nm wavelength range for AZO/Ni remains unchanged – in fact it even increases slightly due to additional oxidation of the Ni surface – while that of AZO strongly decreases. The surface morphology of AZO and AZO/Ni samples was also characterized by optical interference microscopy. Before the DH test, a typical image for both samples is featureless. After 30-day DH, the surface morphology of AZO/Ni remains almost unchanged while that of AZO shows spikes and droplet-like spots distributed in a random manner. The morphological degradation of AZO is likely to be intimately correlated with hydrolysis-induced corrosion process occurred possibly at the grain boundaries. From the above results, one can conclude that oxidized Ni capping layers with appropriate thickness can effectively increase the environmental stability of AZO films and strongly reduce otherwise unavoidable degradation in surface morphology, electrical and optical properties.

The as-deposited AZO and AZO/Ni were next used to fabricate OLED devices according to the above mentioned configuration. For a comparison, commercially available ITO (100 nm, 17-21 Ω/sq) was used to realize the same device architecture. Fig. 2 shows the luminance characteristics of OLEDs with AZO, AZO/Ni and ITO anodes. The AZO/Ni anode based device shows an equivalent performance to the ITO-based one, in which the luminance level for both cases is almost identical. The enhanced device performance based on AZO/Ni anode is related to a significant improvement in the injection of charges due to a better work function matching at the anode-organic interface. It is expected that the final device performance can be further improved by optimization of the device stack and cathode (e.g., Ca/Ag instead of pure Ag [5]).

In summary, an ultrathin Ni capping layer with a thickness at percolation threshold can significantly stabilize an underlying AZO layer in harsh environment. The proposed capping layer acts as a blocking layer to inhibit the penetration of oxygen and water at the grain boundaries of AZO. It is also found that the bilayer transparent electrode shows electro-optical performance similar to ITO when used as an anode in OLED devices.



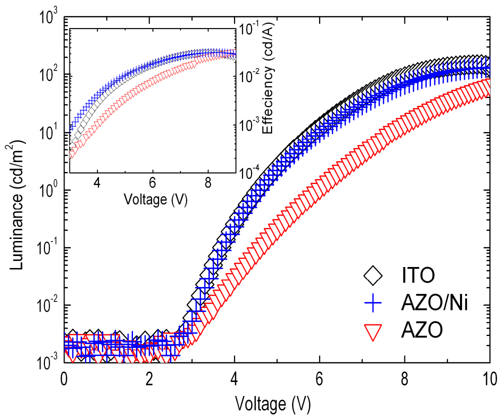


Fig. 1. Evolution of electrical properties of AZO (solid square) and AZO/Ni (open square) films with DH test time, inset is the average transmittance change with DH test time (Left). Fig.2. Luminance versus voltage curves of SY-based OLEDs with the different anodes, inset is the corresponding luminance efficiency curves

4. References

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