Thin Solid Films 517 (2009) 5508–5511

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Effects of $(NH_4)_2S_x$ treatment on the electrical and optical properties of indium tin oxide/conducting polymer electrodes

Yow-Jon Lin [a],*, Bei-Yuan Liu [b], Yi-Min Chin [a]

[a] Institute of Photonics, National Changhua University of Education, Changhua 500, Taiwan
[b] Department of Physics, National Changhua University of Education, Changhua 500, Taiwan

ARTICLE INFO

Article history:
Received 1 November 2008
Received in revised form 3 April 2009
Accepted 3 April 2009
Available online 14 April 2009

Keywords:
Defects
Polymers
Oxides
Surface treatment
Transmittance

ABSTRACT

In this study, the effects of $(NH_4)_2S_x$ treatment on the electrical and optical properties of the indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) electrodes were researched. The authors found that $(NH_4)_2S_x$ treatment could result in suppressing the hysteresis-type current–voltage characteristics related to the interfacial capacitance variation and a reduction in the equivalent refractive index of the ITO/PEDOT:PSS electrodes, owing to the improvement in the interfacial stability of the ITO/PEDOT:PSS electrodes and a reduction in the interface trap-states related charge store at the ITO/PEDOT:PSS interface. This implies that the ITO/PEDOT:PSS electrodes fabricated using the $(NH_4)_2S_x$-treated ITO may produce a higher extraction efficiency for ITO/PEDOT:PSS-based optoelectronic devices.

1. Introduction

The development of organic-based devices applicable to optoelectronics and electronics has received considerable attention over the past few years and is leading to commercial products that should appear on the market in the near future. Conducting organic materials are appealing candidates for low-cost, flexible electronics applications, and as possible replacements for conventional metals and inorganic semiconductors, and there has been considerable progress in the fabrication of devices using different semiconductor polymers [1]. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) is a conducting polymer and has advantages over indium tin oxide (ITO) as a transparent anode as well as mechanical flexibility. Waterborne dispersions of PEDOT:PSS have become the established material for the buffer layer [that is, the hole injection layer (HIL)] or electrodes in organic light-emitting diodes (OLEDs) or solar cells [2–6]. Snaith et al. [3] pointed out that the PEDOT:PSS layers improves the hole injection properties and planarizes the rough ITO surface. Kim et al. [7] observed a dependence of injection onset parameters on the treatment conditions of the ITO substrate, despite the presence of a PEDOT:PSS intermediate layer. Chen et al. [8] concluded that the energy barrier difference between the ITO/HIL interface was not the main factor in determining the hole injection efficiency from the ITO anode to HIL. Huang et al. [9] suggested that the performance enhancement of OLEDs is result of the high quality interface between ITO surface and HIL. Hsiao et al. [10] demonstrated that polymer light-emitting diode (PLED), in which the ITO was modified by a self-assembled monolayer, had high efficiency and high brightness. Heil et al. [11] found that the optically induced desorption of oxygen from the ITO could lead to a degradation at the supper yellow–polyphenylenevinylene interface either directly or after diffusion through the Baytron P layer. They suggested that the ITO/polymer interface could be identified as responsible for the degradation effect [11]. On the other hand, it is found that the ITO/PEDOT:PSS interface is not stable due to the etching of ITO by the strongly acidic nature of PSS [4,12,13]. The degraded interface can act as a defect site and lead to deterioration of the ITO/PEDOT:PSS-based device performance. In our previous studies [12,14,15], we found more effective and dependable surface treatment on ITO with $(NH_4)_2S_x$ solution. The procedure of $(NH_4)_2S_x$ treatment follows a simple wet process. The $(NH_4)_2S_x$ treatment technique is very attractive as it can be implemented easily in a laboratory for the passivation of semiconducting thin films. The effects of the $(NH_4)_2S_x$ treatment of indium tin oxide (ITO) on the efficiency of polymer light-emitting diodes (PLEDs) had been investigated, as shown in reference 14. It is worth noting that a suitable sulfide treatment time is an important issue for producing high-external-quantum-efficiency PLEDs. A suitable $(NH_4)_2S_x$ treatment time is 2 min [14]. According to the previously reported result [12], we found that $(NH_4)_2S_x$ treatment could lead to the improvement of the interfacial stability of ITO/PEDOT:PSS samples. The measurement shows ITO/PEDOT:PSS samples products of the etch reaction between the ITO substrate [12]. The In–out diffusion may lead to the formation of indium vacancies (V_{In}) in ITO near the ITO/PEDOT:PSS interface and the small In clusters (or the single In ionic form) at the ITO/PEDOT:PSS interface and the In–out

---

* Corresponding author. Tel.: +886 4 7232105x3379; fax: +886 4 7211153.
E-mail address: rzr2390@yahoo.com.tw (Y.-J. Lin).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.04.023

diffusion-related defects can capture or release holes, resulting in the occurrence of trapping or detrapping of charges at interface defect sites [12]. In addition, the effects of an $(NH_4)_2S_x$ treatment on the surface work function and roughness of ITO had been investigated, as shown in reference 15. We found that the S occupation of oxygen vacancies (V_O) near the ITO surface after $(NH_4)_2S_x$ treatment may result in a marked increase in the surface work function and a slight increase in the surface roughness [15]. On the other hand, charge hopping among the polymer chains is believed to be the dominant conduction mechanism in almost all conducting polymers [16,17]. The interfacial reaction may affect charge injection and charge hopping. Therefore, the actual mechanisms affecting the performance of layered OLEDs (or PLEDs) from PEDOTS:PSS insertion between ITO and hole transport layer (or active layer) remained partially uncertain. However, the effect of the interfacial trap-states on the electrical and optical properties of the ITO/PEDOT:PSS electrodes has never been reported until now. Clearly, knowledge of the charge and the field distribution inside an organic device and of also its variation with the applied voltage is crucial for physically understanding the organic device operation. Therefore, more experimental work is needed to understand the mechanisms behind the improved device performance by surface treatment. In this study, the effects of $(NH_4)_2S_x$ treatment on the electrical and optical properties of the ITO/PEDOT:PSS electrodes have been investigated. We found that $(NH_4)_2S_x$ treatment could result in suppressing the hysteresis-type current–voltage (*I–V*) characteristics related to the interfacial capacitance variation and a reduction in the equivalent refractive index of the ITO/PEDOT:PSS electrodes, owing to the improvement of the interfacial stability of the ITO/PEDOT:PSS electrodes and a reduction in the interface trap-states related charge store at the ITO/PEDOT:PSS interface. Note, the technique mentioned in this paper is simple and does not require complicated processes, implying that it will be suitable for manufacturing ITO/PEDOT:PSS-based optoelectronic devices with $(NH_4)_2S_x$ treatment.

2. Experiment procedure

A glass substrate was first cleaned by ultrasonic agitation in ethanol and subsequently in acetone followed by mechanical scrubbing in deionized water using detergent. The samples were then cleaned in an ultrasonic bath using a water solution of the same detergent and rinsed several times by ultrasonic agitation in water. This was followed by radio frequency magnetron sputtering (using an oxidized target of In_2O_3 and SnO_2 with a weight proportion of 9:1) of ITO as the transparent electrode (referred to as as-grown ITO). The sheet resistance of ITO film, as estimated from four-point probe measurements, was ~20 Ω/□. The area of each ITO electrode was 2.0×0.6 cm^2. The gap spacing between the ITO contact pads was designed to be 0.4 cm. Some of the as-grown ITO samples were next dipped into a yellow 60 °C $(NH_4)_2S_x$ solution (purchased from Nippon Shiyaku) for 2 min [referred to as $(NH_4)_2S_x$-treated ITO]. Next, as-grown and $(NH_4)_2S_x$-treated ITO samples dried under a dry nitrogen flow. Then, PEDOT:PSS was deposited on as-grown or $(NH_4)_2S_x$-treated ITO surfaces by spin coating. Spin casting was accomplished at 3000 rpm for 60 s per cast layer. Each PEDOT:PSS layer was baked at 150 °C for 30 min. The procedures from coating to drying were repeated three times. Au was used as the other electrode, deposited on top of PEDOT:PSS films. Au contacts were formed by an SC5750 sputter coater (Quorum Technologies). The lateral structures of the devices were as-grown ITO/PEDOT:PSS/as-grown ITO and $(NH_4)_2S_x$-treated ITO/PEDOT:PSS/$(NH_4)_2S_x$-treated ITO. The vertical structures of the devices were Au/PEDOT:PSS/as-grown ITO and Au/PEDOT:PSS/$(NH_4)_2S_x$-treated ITO. The area of each device was 2.0×1.6 cm^2. The area of each Au electrode was 2.0×0.6 cm^2. The *I–V* characteristics of the devices were measured with a Keithley Model-4200 semiconductor characterization system. Each device was fabricated three times. We found that the repeatability of the findings was satisfactory.

3. Experimental results and discussion

Fig. 1 shows the *I–V* characteristics of the as-grown ITO/PEDOT:PSS/as-grown ITO and $(NH_4)_2S_x$-treated ITO/PEDOT:PSS/$(NH_4)_2S_x$-treated ITO devices for 2 and 4 V loops. We can see that the *I–V* curves show hysteresis behavior. The voltage was incremented in steps of 25 mV from −4 V (−2 V) to 4 V (2 V) and the reverse direction. The sweep rate was 0.66 V/s in all cases. Brütting et al. [18] pointed out that the observation of hysteresis effects in the *I–V* characteristics is a hint of the presence of trapped charges in the organic device. Lee et al. [19] suggested that the hysteresis occurs mainly because of charges which could be injected from the electrode and trapped in the organic layer. Majumdar et al. [20] pointed out that the charges stored in the polymer layer near the metal/polymer interface control charge injection and result in the hysteresis-type *I–V* characteristics. The contributions by the displacement current (I_d) from the voltage variation and capacitance variation have been considered to explain the hysteresis behavior by Majumdar et al. [20]. Fig. 1 shows, with a sweep voltage of 4 V, the current amplitude at $V=0$ (during the 4 to −4 V sweep or the −4 to 4 V sweep) was higher than with a sweep voltage of 2 V and the voltage amplitude at $I=0$ (during the 4 to −4 V sweep or the −4 to 4 V sweep) was higher than with a sweep voltage of 2 V, meaning more stored charges in the device for a sweep voltage of 4 V [20]. This agrees with the result reported by Majumdar et al. [20]. Majumdar et al. found that the density of stored charges in the polymer layer near the metal/polymer interface depends on the voltage amplitude [20]. They suggested that the contribution of capacitance variation [$V(dC/dt)$] on I_d is therefore much stronger than from the voltage variation [$C(dV/dt)$] and the capacitance can vary due to the formation of space charges at the metal/polymer interface [20]. I_d is represented by $I_d \approx V\frac{dC}{dt}$ [21–24]. With I_r as the resistive part of the current, the total current is given by $I = I_r + I_d \approx I_r + V\frac{dC}{dt}$ [21–24]. In Fig. 1, we find that the current does not vanish at zero bias (a positive current at zero bias for a sweep from negative to positive bias and a negative current at zero bias for the reverse sweep direction), owing to the presence of I_d. In Fig. 1, we find that the hysteresis-type *I–V* characteristics were influenced by $(NH_4)_2S_x$ treatment and the current amplitude at $V=0$ (during the 4 to −4 V sweep or the −4 to 4 V sweep) of the as-grown ITO/PEDOT:PSS/as-grown ITO devices and the voltage amplitude at $I=0$ (during the 4 to −4 V sweep or the −4 to 4 V sweep) of the as-grown ITO/PEDOT:

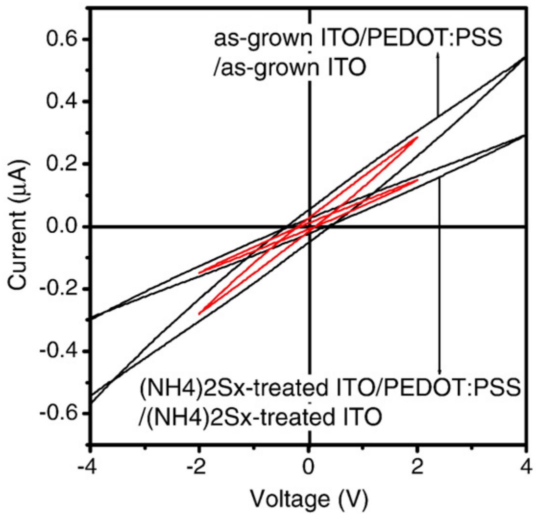

Fig. 1. Hysteresis-type *I–V* characteristics of the as-grown ITO/PEDOT:PSS/as-grown ITO and $(NH_4)_2S_x$-treated ITO/PEDOT:PSS/$(NH_4)_2S_x$-treated ITO devices for 2 and 4 V loops.