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Influence of plasma treatment on Indium Tin Oxide electrodes

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ABSTRACT

Organic Schottky diodes (OSDs) with various plasma treated Indium Tin Oxide (ITO) as anodic electrode are prepared and tested to investigate the effect of plasma treatment on their performance. Oxygen plasma treated ITO (O-ITO), nitrogen plasma treated ITO (N-ITO) and plasma untreated ITO (U-ITO) are used. The current density–voltage analysis and electrochemical impedance spectroscopic analysis are utilized in the study. The frequency-dependent response is interpreted in terms of an equivalent-circuit model consisting of three resistors, two capacitors, and one inductor. Device parameters are extracted by fitting equivalent circuit with obtained impedance data. Capacitance–voltage (*C*–*V*), and ac conductance–voltage (*G*(*ω*)–*V*) features of the OSDs are analyzed in the frequency of 1 kHz. It has been concluded that the OSDs fabricated using N-ITO showed lower impedance and higher capacitance than other devices.

1. Introduction

Indium Tin Oxide (ITO) coated over glass and polyethylene terephthalate (PET) film exhibit high luminous transparency in the visible spectrum while maintaining high conductivity and better work function (∼4.7 eV) [1], and are therefore widely used for manufacturing optoelectronic devices such as organic solar cells (OSCs) and organic light emitting diodes (OLEDs) [2–5] Schottky diodes etc. It has been seen that surface treatment of ITO substrates can alter its physical and chemical properties which in turn affect the performance of the devices of which it forms a part. Plasma treatment of surface promises high potential in this direction with its various advantages. It does not have line of sight problem as compared to the laser and UV radiation. Further, plasma treatment is a safe and environment-friendly alternative to the traditional surface treatment methods such as UV–ozone treatment, solvent annealing, ion-assisted-reaction (IAR) etc. [6–9].

In this context this report describes an attempt made to investigate the effect of plasma treatment on the ITO anode by fabricating organic Schottky diodes (OSDs). Organic Schottky diode (OSD) has triggered renewed interest among the organic device developers due to its low cost and light weight applications [10–13]. Metal–semiconductor (MS) contact is one of the most widely used rectifying contacts in electronic industry. A high volume of experimental efforts are being made to investigate the charge transfer mechanism of this type of devices. The simple and straight forward devices structure of organic Schottky diode motivated to use this structure for investigating the efficiency of oxygen and nitrogen plasma treatment for surface treatment of ITO electrodes. A device with exactly same structure with untreated ITO (U-ITO) electrode is also fabricated for comparing the performance. For all devices aluminium is used as the cathode which is coated using vacuum thermal evaporation technique. Poly (2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH:PPV) is used as the organic semiconductor layer sandwiched between anode and cathode electrodes. A layer of conducting polymer Poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) is coated over the ITO electrode to improve the hole transportation and to protect the device from short circuit [14]. Electrochemical impedance spectroscopy (EIS) is used to analyze frequency dependent electrical properties as this technique is capable to give real and imaginary part of impedance. Capacitance–voltage (*C*–*V*) and ac conductance-voltage (*G*(*ω*)–*V*) measurements are also carried out to determine the diode integrity.

2. Experimental

Indium Tin Oxide (ITO) coated PET substrates with a sheet resistance of 60Ω/□ and Poly (2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH:PPV) were purchased from Sigma Aldrich. 6 mg of MEH: PPV was dissolved in 1 ml of 1,2-dichlorobenzene and stirred for 24 h in a nitrogen filled glove box. ITO coated PET substrates were cleaned for 5 min each in succession in ultrasonic baths of acetone, methanol, and isopropanol. For

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plasma treatment one set of patterned ITO substrates was kept inside the reaction chamber and evacuated to a pressure of 5×10^{-5} mbar. Oxygen gas with 99.999% purity was pumped into the reaction chamber through a needle valve for a duration of 5 min and the chamber was evacuated again to a pressure of 1×10^{-4} mbar. Oxygen was then refilled in the chamber for a duration of 2 min and again evacuated to get a pressure of 1 mbar which allows for a relatively long free path of accelerated electrons and ions. At this point a high potential of 3000 V was applied in between the electrodes to produce oxygen plasma inside the reaction chamber. The oxygen plasma was maintained inside the reaction chamber for 15 min by carefully adjusting oxygen flow and evacuation rate. The same procedure has been carried out on a second set of ITO substrates with nitrogen plasma inside.

Poly (3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) aqueous solution was then spun cast over the ITO substrates and annealed at 80 °C for 20 min. Even though this temperature is not high enough to remove water residue fully, annealing at 80 °C has been made as a compromise to avoid degradation of PET substrate employed here. Further it has been shown [15] that the work function of PEDOT:PSS reduces monotonically with increasing annealing temperature.

Previously prepared MEH:PPV solution was then spun cast over the PEDOT:PSS layer by adjusting the spinning rate to get 170 nm of layer thickness. The samples are then shifted to the vacuum chamber for aluminium coating. The aluminium evaporation was done at $\sim 4 \times 10^{-5}$ mbar through a shadow mask.

Fig. 1 illustrates the final structure of fabricated OSDs. Active area of OSDs was found to be 0.16 cm^2. Current density–voltage (*J–V*) characteristics of the device were measured using a Keithley 2400 source meter which is interfaced to a computer with the help of GPIB cable. All EIS experiments were performed in the air at room temperature, using an IM6ex impedance measurement unit from Zahner electrik. An ac oscillating amplitude of 10 mV (RMS) was applied in order to maintain the linearity of the response. The capacitance–voltage (*C–V*) and ac conductance-voltage ($G(\omega)$–*V*) experiments were performed in a Faraday cage at room temperature. Measurements were made in a wide range of bias and frequency several times, to optimize measurement conditions for *C–V* and $G(\omega)$–*V* analysis of these devices. Optimised measurement conditions were, ac frequency of 1 kHz, and bias voltage of −2 to +2 V.

3. Results and discussions

Fig. 2 illustrated the current density–voltage (*J–V*) characteristics of the fabricated devices using O-ITO, N-ITO and U-ITO as anode electrode. It is observed that the characteristics of OSDs are uniform over different diodes and all devices showed good rectifying property. The *J–V* characteristics of the devices first exhibit a linear regime, where charge transport is injection-limited, followed by a sudden increase for an intermediate range of applied biases. In this region, the performance of the OSDs is controlled by the transport of charge through the organic semiconductor. The extent of this intermediate region is governed by the energetic and spatial distribution of trap states [16–18]. N-ITO device showed better and linear *J–V* characteristics at forward bias conditions and this may be due to that the nitrogen plasma treatment reduces the concentration of traps and defects on the ITO surface.

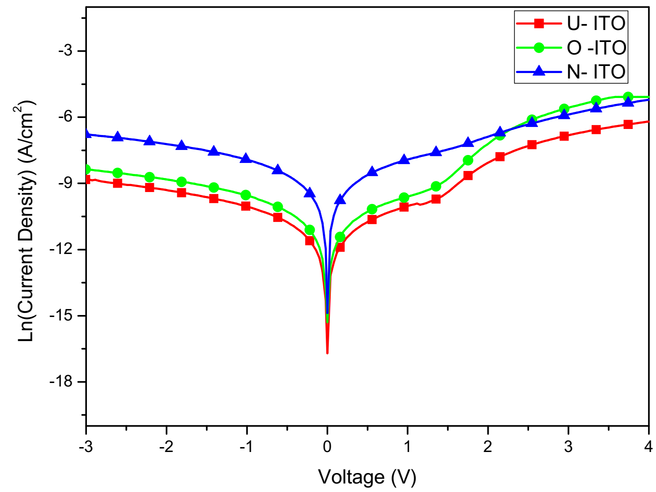

Fig. 2. Semi logarithmic *J–V* curve of OSDs under dark condition.

Forward *J–V* characteristics of the OSDs can be described with the help of the relation [19]

$$J = A^*T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \exp\left[\left(\frac{qV}{nkT}\right) - 1\right] \tag{1}$$

where A^* is the Richardson constant, k is the Boltzmann constant, T is the temperature and ϕ_B is the barrier height. But in the case of bias voltages greater than 3 kT/q, Eq. (1) can be rewritten as

$$J = J_0 \exp\left[\frac{qV}{nkT}\right] \tag{2}$$

$$n = \frac{q}{kT}\frac{dV}{d(\ln I)} \tag{3}$$

where J_0 is the saturation current density and n is the ideality factor. The ideality factor presents how closely the diode follows the ideal diode equation. Values of ideality factor can be determined from the slope of the exponential regime of the *J–V* characteristics on a semi-logarithmic plot by using Eq. (3). The linearly fitted curves with the exponential regime of forwarded bias characteristic gives the values of ideality factor (Table 1). It can be noted that the N-ITO device showed the lowest ideality factor ($n = 14$) which is closer to ideality than all other OSDs. The deviation of ideality factor from unity shows violation of Einstein relation caused by [20] deeply trapped carriers that are not in thermal equilibrium with free carriers in the sites.

Fig. 3 shows the impedance response of the fabricated devices with frequency. DC bias of 1 mV and a frequency range of 100 mHz–1 MHz were used for this analysis. It can be observed

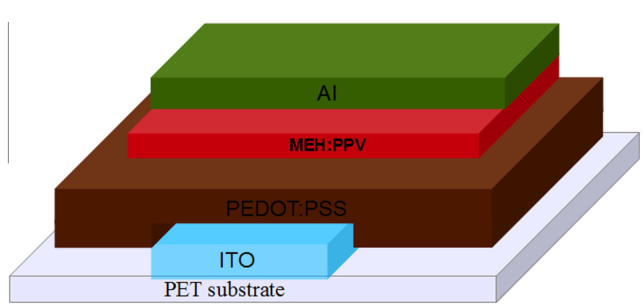

Fig. 1. Structure of organic Schottky device used in this work.

Table 1
Ideality factor of the fabricated devices.

Device name	Slope	Ideality factor
U-ITO	0.46	18.4
O-ITO	0.44	17.6
N-ITO	0.35	14