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Effect of plasma treated Ag/indium tin oxide anode modification on stability of polymer solar cells

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ABSTRACT

The most commonly used hole transporting layer (HTL) in conventional polymer solar cells is poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) PEDOT:PSS. The acidic nature of this HTL is responsible for etching of the indium tin oxide (ITO) layer which is the anode in polymer solar cells and leads to degradation of efficiency in polymer solar cells in the long run. In this article we explored the effect of plasma treated Ag as an intermediate layer between ITO and PEDOT:PSS for over one month period. It was found that the devices with plasma treated Ag as an intermediate layer with thickness of 5 nm resulted in only 30% degradation over one month and did not decrease the initial power conversion efficiency (PCE) compared to the cell without the anode modification, whereas the devices without the intermediate layer, degraded up to 66% of the initial PCE. The mechanism was analyzed using XPS measurements and found out that indium from ITO etches out and diffuses to the subsequent polymer layer. Further, the experiment revealed that the presence of plasma treated Ag layer restricted the rapid indium diffusion, which accounted to enhanced device stability.

1. Introduction

In recent years, there has been an increased interest in polymer solar cells or organic photovoltaic cells (OPV). This is due to the fact that it allows fast, simple, low cost and large-volume processing. Although OPV field is developing quickly, there are still issues that are not fully resolved: the improvement of device power conversion efficiency (PCE), the extension of lifetime and large scale production. There are number of degradation mechanisms that result in low PCE, and currently, most research in the field are struggling to overcome these mechanisms. Many procedures to protect the cells from external degrading factors such as moisture and air have already been implemented but more focus on research is needed for protecting the devices from internal degrading factors due to acidity of the constituent polymer layer. In this article, our efforts are focused on improving the device lifetime by reducing internal degradation.

The high thermal stability, transparency, conductivity, and ease of processing makes poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate)(PEDOT:PSS), the most widely used hole transporting layer (HTL) in organic photovoltaic devices (OPV).

The poly(3,4-ethylenedioxythiophene) or PEDOT [1] is attached with PSS (styrene sulfonic acid) because PEDOT in its undoped state is not soluble in usual solvents [2]. PEDOT:PSS has a pH value between 1 and 3 at 20 °C, hence PEDOT:PSS is acidic which makes the interface between ITO and PEDOT:PSS unstable [3]. The instability comes from the fact that ITO has a relatively high solubility in acidic solution [4]. The degradation caused by acidic PEDOT:PSS on top of Indium Tin Oxide (ITO) is the kind of internal degradation which is considered to be crucial because most of the other degrading factors [5,6] can be limited by encapsulation of the devices. When the device ages, the acidic nature of PEDOT:PSS is responsible for etching of the ITO anode which is the lower layer [3].

The etching of ITO can result in degradation of anode and incorporation of indium impurities in to all the subsequent layers, which will in turn accelerate the degradation of the active layer, thus decreasing its efficiency in the long run. One of the method to solve the problem is by the use of neutralized PEDOT:PSS, but during the neutralization process, many of the favorable electrical properties are lost. Due to its low oxidation potential, the neutralized PEDOT:PSS will rapidly oxidize in air and thus is very unstable [7,8]. Moreover there are harmful additives present in the polymer to make it neutralized, which makes processing in air very difficult. In this

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article, we describe a very simple method to protect ITO anode from degradation. It is done by the insertion of a suitable inter layer of plasma treated Ag. The method has the advantage of being simple, efficient, and stable compared to the usual method.

2. Experimental

2.1. Materials and device fabrication

The hole transporting layer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (Clevios PEDOT:PSS) was supplied by H.C. Stark. The glass substrates with patterned ITO stripes were supplied by Thin Film Devices, Inc. (TFD). The square glass substrate with the dimension of 6.25 cm^2 was covered in the middle part with a 1.3 cm ITO stripe. The ITO thickness was 150 nm and had 20 Ω/sq sheet resistance. The substrates were first cleaned with acetone followed by isopropanol and methanol. A thin layer of silver was deposited on top of the ITO by the vacuum vapor deposition method. Then it was plasma treated by Plasma PREEN II-862 asher (60 W, flow rate 4-5SCFM), for 5 min. Following this PEDOT:PSS was spin coated at 5200 RPM for 1 min and consequently dried under a vacuum at 120 °C for 1 h. After drying the substrate, the active layer was spin coated on top.

Poly(3-hexylthiophene-2,5-diyl)(P3HT) was supplied by Sigma Aldrich and Phenyl-C71-butyric acid methyl ester ($PC_{70}BM$) was supplied by NanoC. The P3HT:$PC_{70}BM$ active layer blend was formed by making the solution in the ratio 1:0.8 with a concentration of 30 mg/ml, dissolved in 1,2-dichlorobenzene. The solution was stirred at 55 °C overnight.

The active layer blend was then spin coated at 450 RPM for 2 min inside a glove box [9]. After drying the sample for 1 h at room temperature in the nitrogen-filled glove box, the film was annealed at 160 °C for 30 min [10]. Then a 0.6 nm lithium fluoride and a 120 nm aluminum layer were deposited respectively as electrodes by vacuum vapor deposition at 10^{-7} Torr [11]. The finished cell module made contained 5 working solar cells with an active area of 15 mm^2 each. There were 3 such cell modules fabricated for each configuration, making altogether 15 cells.

2.2. Device characterization

The surface analysis (contact angle measurement) was performed in order to acquire information about influence of plasma treatment on Ag layers. For surface energy measurement and calculation, the static sessile-drop contact-angle measurement method was applied by using Kruss DSA100 system.

In order to calculate the surface energy, two fluids were used: distilled water and ethylene glycol. For each fluid five contact angle measurements were performed and results averaged. Importantly, the measurement was done separately for plasma-treated and untreated samples.

The transmittance measurement of the samples with the ITO layer and with additionally plasma-treated Ag layers was performed using spectrophotometer system (Optoelectronics Laboratory, USA) in the range of 300–900 nm.

For measuring photovoltaic characteristics, we employed an Air Mass 1.5 Global (AM1.5G) class AAA (Oriel Inc.) solar simulator as the light source, and light intensity was calibrated to 100 mW/cm^2 by using a NREL calibrated crystalline silicon reference cell. The measurements were done inside a nitrogen-filled glove box inorder to have an inert atmosphere, thus the other degrading factors such as moisture and oxygen are avoided. The devices were not encapsulated since it was in inert condition.

The OPV cells were stored in the dark and the measurements by illumination were done inside the glove box. The parameters such as Open Circuit Voltage (Voc), short circuit current (Isc), fill factor (FF), power conversion efficiency (PCE) were obtained from corresponding current density(*J*)–voltage(*V*) curves. The lifetime studies for OPV cells were done for 41 days inside the glove box. The lifetime measurements of the OPV cells were an analysis of variation in parameters such as PCE, Voc, Jsc and FF with time. The measurements were an average of 3 cell modules which contained 5 working solar cells thus making a total of 15 solar cells, made for each of the corresponding configurations and the standard deviation for each corresponding measurement was also calculated.

The indium diffusion due to ITO etching by PEDOT:PSS was investigated using X-ray photoelectron spectroscopy (XPS). The XPS experiments were performed in a UHV system equipped with VG Microtech Multilab ESCA 3000 electron spectrometer. Non-monochromatized Mg Kα X-rays (1253.6 eV) were utilized for excitation, and the detection area was set to 600 μm in diameter. The chemical states of compounds were identified and relative atomic concentrations quantified by analyzing the photoelectron transitions of C 1s, O 1s, S 2p, In 3d, Ag 3d, and Na 1s. The Shirley algorithm was used for background subtraction, and the spectral components were fitted with a combination of Gaussian (70%) and Lorentzian (30%) line shapes. XPS spectra were acquired at emission angles of 0° and 74° to probe different depths of the layered structure. Theoretically, on a flat and non-porous surface, the sampling depth of the In 3d signal in PEDOT:PSS is 7.4 nm at normal emission, and 2.0 nm at 74° emission (7.4 nm × cos 74° = 2.0 nm).

3. Results and discussion

3.1. Contact angle measurement

The Ag layer is plasma treated in order to have better wettability by PEDOT:PSS. The measurements revealed that the plasma treatment of Ag thin layer increased its surface energy significantly from 36.6 mN/m to 75.2 mN/m. Therefore plasma treatment increased the hydrophilicity of the treated Ag surface. Results from the surface analysis are in agreement with results from other groups, that plasma treatment increases the surface energy of treated materials. This helps in better deposition of PEDOT:PSS on its surface.

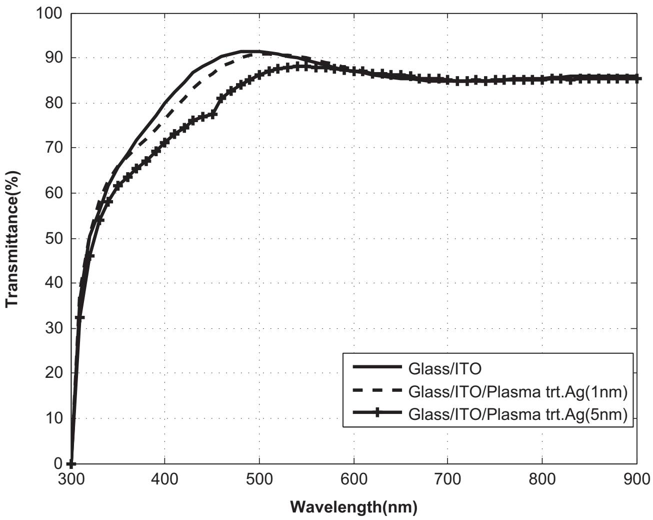

Fig. 1. Optical transmittance of the plasma-treated Ag modified ITO.