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Influence of moisture out-gassing from encapsulant materials on the lifetime of organic solar cells



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ABSTRACT

The results of a study on the effects of encapsulant pre-conditioning (drying) on the durability of “conventional” and “inverted” bulk-heterojunction organic solar cells based on P3HT:PCBM are presented. The architectures of the conventional and inverted devices were ITO/PEDOT:PSS/P3HT:PCBM/Al and ITO/ZnO/P3HT:PCBM/MoO₃/Ag, respectively. Quantitative analysis of the moisture content, moisture out-gassing, and re-absorbing properties of flexible barrier encapsulant films under ambient conditions was conducted. The effect of moisture out-gassing from the encapsulation materials on device performance was studied and the lifetime of conventional and inverted devices was found to decline significantly for the devices encapsulated using materials without pre-conditioning. This study reveals the essential role of pre-conditioning of materials in the encapsulation of organic photovoltaic devices. Current-voltage characteristics exhibit a clear increase in the series resistance of the devices during storage under ambient conditions, and Spectroscopic Impedance analysis indicates that charge-transport resistance within the devices increases significantly during the degradation process. The results are consistent with the primary degradation mechanism being corrosion at the metal-electrode surface.

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1. Introduction

The field of Organic Photovoltaics (OPVs) has attracted worldwide attention over the past two decades due to potential advantages such as flexibility, large-scale printability, light weight and potential utility in a wide variety of products. Through gradual developments in new active polymers and electrode materials, together with improvements in interfacial properties, proven energy conversion efficiencies of more than 10% have been reported for laboratory-scale OPV devices [1–3]. At present, this emerging technology is at a pre-commercial stage of development and there are several challenges that must be addressed before it can be realized commercially.

Foremost among these challenges are improving efficiency, scalability, and the durability of the devices. It is well known that OPV device performance is highly sensitive to oxygen and moisture which can cause interfacial instabilities as well as permanent physical or chemical changes to the active polymer and other layers resulting in reduced device lifetime [4,5]. Irradiation of OPV

devices can lead to even more complex degradation mechanisms involving factors such as oxidation and de-lamination of metal electrodes and other deposited layers, [6] photo-oxidation of the active polymer material, [7,8] photo-oxidation of inorganic oxide nanocomposite films, [9] degradation of the PEDOT:PSS layer, [10,11] and chemical degradation of metal electrodes and the ITO electrode [12]. To reach sufficiently long lifetimes for commercial applications OPV devices require encapsulation using barrier materials having low permeability towards atmospheric oxygen and moisture. As such, developing improved flexible and transparent barriers and new encapsulation methodologies are critical steps for improving the stability of such devices.

Flexible barrier materials displaying water vapour transmission rates (WVTR) of less than 10^{−4} g m^{−2} day^{−1} are considered essential for durable printed flexible organic solar cells [13]. Materials displaying such ultra-high barrier properties have been reported and are now available commercially [14–17]. Furthermore, sealing materials such as pressure-sensitive adhesives, [18] UV-curing cements [19], and hot-melt adhesives are often used to bond the barrier films onto the devices. Among these, the use of pressure-sensitive transfer adhesives has attracted much attention as they can be used readily in roll-to-roll lamination systems to encapsulate solar-cell modules fabricated on

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flexible substrates [20]. Although the barrier films applied to OPV devices are designed to protect against the ingress of atmospheric moisture into the device, 'out-gassing' of residual dissolved moisture and oxygen from these materials after device encapsulation can also lead to device degradation. For example, in preliminary work, we found that a number of polymer-based encapsulation materials readily absorbed moisture when exposed to ambient conditions, and that even trace levels of moisture absorbed and retained within the barrier films and adhesive materials appeared to cause significant reduction in the stability of OPV devices.

In the present work, we discuss the results of a detailed study of the effects of retained moisture in encapsulation materials comprising commercially-available flexible barrier films and transfer-adhesives on the shelf-life of OPV devices having so-called "conventional" or "inverted" architectures. The results of this work highlight the importance of thorough and systematic drying of encapsulation materials prior to use in encapsulation of OPV devices.

2. Experimental

2.1. Device fabrication and encapsulation

The OPV device structures discussed in this work are shown schematically in Fig. 1(a) and (b). The pre-patterned indium tin oxide (ITO)-coated glass substrates (Kintec Company) were cleaned by successive ultrasonic treatments in acetone and isopropyl alcohol for 20 min followed by UV-ozone treatment for 10 min. For the preparation of conventional devices, cleaned substrates were spin-coated with an aqueous solution of poly-3,4-ethylenedioxythiophene-poly(styrenesulphonate) (PEDOT:PSS) in air at 5000 rpm for 20 s using a Laurell single-wafer spin processor (WS-400B-6NPP-LITE) and then annealed at 150 °C for 5 min on a hotplate in a N₂-filled glove box. For the active layer, poly-3-hexylthiophene-2,5-diyl (P3HT, Merck, 30 mg/ml) and 6,6-phenyl-C61-butyric acid methyl ester (PCBM, nano-C, 24 mg/ml) in chlorobenzene were stirred for an hour at 70 °C inside the glove box. PEDOT-coated ITO-glass substrates were spin-coated with the P3HT:PCBM (1:1) blend solution at 2000 rpm for 30 s. The devices were then transferred without exposure to air to an evaporator (Angstrom Engineer EvoVac) with a base pressure below 10⁻⁶ mbar. A layer of aluminium having 100 nm thickness was evaporated through a shadow mask to define six separate devices each having an active area of 10 mm². The conventional OPV devices were then annealed at 150 °C for 10 min on a hotplate in the glove.

Inverted devices were prepared first by spin coating a ZnO colloidal solution onto cleaned ITO-glass substrates at 1000 rpm for 30 s followed by an annealing step at 200 °C for 10 min to remove residual solvents and to form a dense ZnO thin film. The ZnO solution

was prepared as described by Jasieniak et al. [21] For the active layer, a solution of P3HT (15 mg/ml) and PCBM (15 mg/ml) in chlorobenzene was stirred for an hour at 90 °C inside the glove box. ZnO-coated ITO substrates were spin coated with the P3HT:PCBM (1:1) blend solution at 1000 rpm for 30 s and then were annealed at 150 °C for 10 min. A 10-nm thick MoO₃ anode buffer layer was evaporated through a shadow mask followed by evaporation of a 100 nm-thick Ag metal electrode. Each device had an active area of 10 mm².

Viewbarrier[®] (Mitsubishi Plastic, Inc) was used as the plastic barrier encapsulant film for the metal electrode side of the device. According to the manufacturer, the WVTR, overall thickness, and transparency in the visible spectrum of this material are 5 × 10⁻³ g m⁻² day⁻¹, 85 μm and 89%, respectively. A transfer-adhesive film pre-coated on a paper liner (3M, 467MP Adhesive) was first laminated onto the barrier film which then was cut into the required size (2 cm × 2.5 cm). Following the removal of the paper liner, the barrier film integrated with the adhesive was then laminated at 110 °C onto the devices using an office-type laminator (Peach 3500) as illustrated in Fig. 2(a). A photographic image of the metal-electrode side of the OPV device encapsulated with the laminated barrier film is shown in Fig. 2(b).

2.2. Moisture content analysis

The moisture content and absorption/desorption properties of encapsulation materials was determined using a highly sensitive moisture content analyser (Computrac Vapour Pro, Arizona Instruments). Firstly the encapsulant films with the integrated transfer adhesive layer were pre-conditioned at 100 °C under vacuum (~10⁻³ mbar in a BINDER vacuum oven) for various time intervals to remove absorbed moisture. The moisture content of the films was quantitatively analysed using the moisture analyser which can detect moisture levels as low as 1 ppm utilising a moisture/relative humidity sensor. During the moisture analysis, samples having known weight and area (2.1 g, ~5 cm²) were subjected to a drying step at 140 °C and the residual moisture content of the samples was determined in units of ppm and mg m⁻². Quadruplicate encapsulant samples from each batch of encapsulant materials dried for different time periods were subjected to this analysis and the average moisture content was calculated. Moisture gain in encapsulation materials was studied by analysing the moisture content of fully dried samples on exposure to ambient conditions for known time intervals.

2.3. Durability performance and impedance spectroscopy analysis

The objective of this study was to investigate the effect of the moisture content of the encapsulant films on the durability of OPV

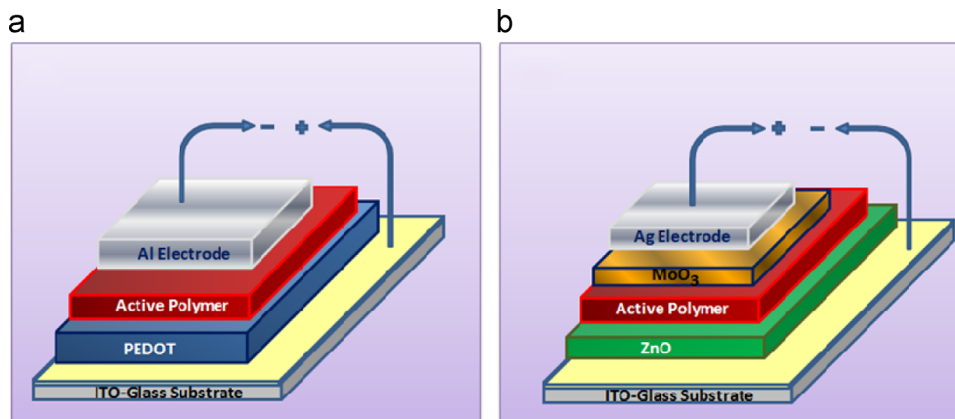


Fig. 1. Schematic representation of (a) conventional and (b) inverted device structures.

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