Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells

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ABSTRACT

The interlayer adhesion of roll-to-roll processed flexible inverted P3HT:PCBM bulk heterojunction (BHJ) polymer solar cells is reported. Poor adhesion between adjacent layers may result in loss of device performance from delamination driven by the thermomechanical stresses in the device. We demonstrate how a thin-film adhesion technique can be applied to flexible organic solar cells to obtain quantitative adhesion values. For the P3HT:PCBM-based BHJ polymer solar cells, the interface of the BHJ with the conductive polymer layer PEDOT:PSS was found to be the weakest. The adhesion fracture energy varied from 1.6 J/m^2 to 0.1 J/m^2 depending on the composition of the P3HT:PCBM layer. Post-deposition annealing time and temperature were shown to increase the adhesion at this interface. Additionally the PEDOT:PSS cells are compared with V$_2$O$_5$ cells whereby adhesive failure marked by high fracture energies was observed.

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1. Introduction

Roll-to-roll (R2R) processed polymer solar cells are promising due to their low cost, light weight, compatibility with flexible substrates, high throughput processing and large area solar cell production [1–6], although concerns exist regarding their reliability. Many failure modes relevant to polymer solar cells have been identified while there is a general agreement that the majority of failure modes remain uncharted. Until now degradation due to chemical reaction with atmospheric components (oxidation and corrosion) has been studied for laboratory devices on rigid substrates. The general polymer solar cell comprise a multilayer structure where mechanical stability is not automatically granted due to the different mechanical properties for each of the layers and their individual response to the processing conditions (temperature, humidity, solvent vapor, strain, etc). Since most research efforts have focused on achieving higher power conversion efficiencies (PCE) for small area devices on rigid and mechanically stable substrates, little is known about the thermomechanical reliability of polymer solar cells. For example, damage processes such as adhesive and cohesive fracture may result from the thin-film stresses present in the organic solar cells [7]. Thin-film stresses can develop during device processing and operation. During processing the evaporation of solvents may give rise to different shrinkage strains and associated stresses [8]. Thermal strain and associated stresses develop during thermal cycles due to the thermal expansion mismatch of the different layers. Other stresses may result from specific film growth processes such as the coalescence of islands of material as the film is deposited. Finally, bending of the flexible polymer solar cells may cause additional mechanical stresses. It is the combination of these film stresses together with other possible mechanical handling and operation stresses that provide the mechanical driving force for the delamination of weak interfaces or cohesion cracking of weak layers. This leads to a loss of mechanical integrity and device performance. Therefore a fundamental understanding of the interlayer adhesion and strategies for improving the adhesion fracture energy must be developed.

We demonstrate how a thin-film adhesion technique can be applied to flexible R2R processed inverted polymer solar cells on polyethyleneterphthalate (PET) substrates. The adhesion energy required to separate adjacent layers can be precisely measured independent of the solar cell film mechanical properties, thickness and stresses, which greatly simplifies the measurement technique [9]. This provides for quantitative analysis of the impact of various processing and structural variables on adhesion and a means for understanding the mechanisms of delamination. Additionally this enables a compositional analysis of the interfaces of the internal layers.

In this work we report on the adhesion between the photo-active region Poly(3-hexylthiophene):Phenyl-C61-butyric acid methyl ester (P3HT:PCBM) BHJ and hole transport layer (HTL)

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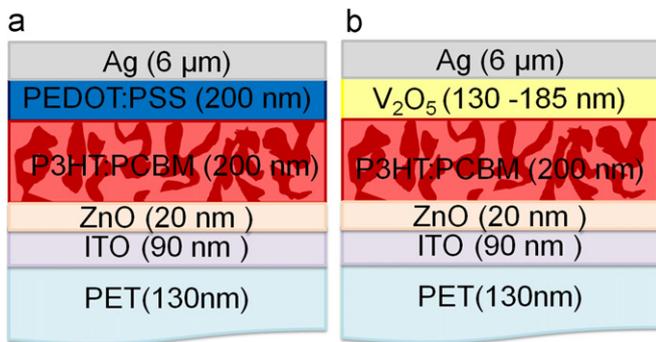dauskardt@stanford.edu, rhd@stanford.edu (R.H. Dauskardt).

Fig. 1. Device structure of P3HT:PCBM solar cells with either PEDOT:PSS (a) or V_2O_5 (b) as hole transport layer.

Poly(3.4-ethylenedioxythiophene): Poly(styrenesulfonate) (PEDOT:PSS). This interface was found to be the weakest in the R2R inverted polymer solar cells. The adhesion fracture energy varied from 1.6 J/m^2 to 0.1 J/m^2 depending on the composition of the P3HT:PCBM layer. Post-deposition annealing was applied to increase the adhesion at this interface. It is shown that the adhesive fracture energies increased with annealing time and temperature. Additionally, delamination in PEDOT-free R2R inverted flexible polymer solar cells has been studied, whereby the conductive polymer PEDOT:PSS has been replaced by a metal oxide HTL, vanadiumoxide (V_2O_5).

2. Experimental

2.1. Solar cell processing

The processing of the R2R inverted polymer solar cells, shown in Fig. 1 has been described elsewhere [10–13]. Briefly, the polymer solar cells were processed using a roll-to-roll automated set-up. A screen printer was used for the ITO and silver electrodes and a slot die coater for the ZnO, BHJ and HTL's. The polymer solar cells were processed on flexible PET substrates covered with transparent ITO electrodes. A thin zinc oxide layer was initially deposited to form an electron selective contact. Then, the photoactive BHJ of an electron donor P3HT (Sepiolid P200 BASF) and electron acceptor PCBM (99%, Solenne B.V.) was deposited. The fraction of PCBM in P3HT:PCBM BHJ was varied between 0 wt% and 100 wt% using a differentially pumped slot die coater. A thin-film of PEDOT:PSS (Agfa 5010) diluted in isopropyl alcohol was slot-die coated on top to serve as the HTL. Additionally cells, whereby the conducting PEDOT:PSS polymer layer was replaced by a hydrated vanadiumoxide layer ($V_2O_5 \cdot (H_2O)_n$), were prepared from a dilution of vanadyl-triisopropoxide (Sigma Aldrich) in isopropanol. The thickness of the V_2O_5 layer was varied between 130 nm and 185 nm, while keeping the composition of P3HT:PCBM at a constant 10:9 ratio. A 6 μm thick silver paste (UV curing Toyo Ink) layer was used as back electrode for both cell structures. Finally, the polymer solar cells were encapsulated using a barrier material (Amcor) and an adhesive (467 MPF, 3M).

2.2. Thin-film adhesion/cohesion testing

The adhesion or cohesion fracture energy is the energy needed to cause delamination at the interface between layers or failure within a layer, respectively. In the case of interface adhesion, delamination occurs if the driving force for debonding, quantified in terms of the applied strain energy release rate, G is larger than a critical value, G_c, the adhesion fracture energy. The fracture energy is determined by two different energy absorbing
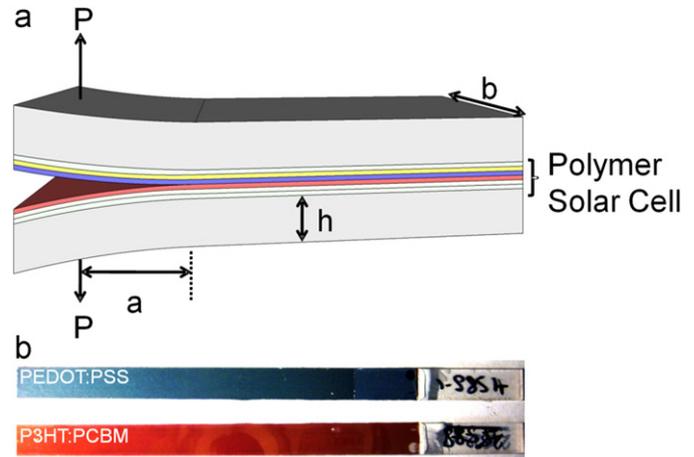

Fig. 2. (a) Illustration of the double cantilever beam (DCB) test specimen. The polymer solar cell is sandwiched between two rectangular elastically stiff beams. (b) Illustration of the debonded surfaces clearly showing adhesive failure between the blue PEDOT:PSS layer (top) and red brown P3HT:PCBM layer (bottom). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

processes: one involves the near-tip work of fracture including processes such as breaking chemical bonds across the interface and creating new surfaces and the other includes energy dissipation in a zone surrounding the crack [9]. G_c is typically strongly dependent on the material, mechanical and processing properties.

To measure the fracture energy, G_c (J/m^2) the flexible solar cells were epoxy bonded in between two elastic beams to form a double cantilever beam (DCB), as illustrated in Fig. 2. The DCB test geometry is a well-established method for measuring the fracture energy in thin-film structures and interfaces [9,14–16]. Silicon, polycarbonate and aluminum were used as beam materials. The specimens were mounted into the adhesion testing system (Delaminator DTS, Menlo Park, CA). Subsequently the DCB specimens were loaded in a mode I tension from which a load versus displacement curve was recorded. Finally, the fracture energy, G_c can be expressed in terms of the critical load at which crack growth occurs, P_c, the corresponding crack length a, the plain strain elastic modulus, E' and the specimen dimensions width, b and half- thickness, h. The fracture energy was calculated from Eq. 1[17].

$$G_c = \frac{12 P_c^2 a^2}{B^2 E' h^3}\left(1 + 0.64 \frac{h}{a}\right)^2$$

All testing were carried out in laboratory air environment at $\sim 25\ ^\circ$C and $\sim 45\%$ relative humidity. Following mechanical testing, x-ray photo spectroscopy (XPS, PHI 5000 Versaprobe) was used to determine the location of the fracture path in the polymer solar cell.

3. Results and discussion

3.1. Composition ratio P3HT:PCBM

The fracture energy, G_c measured versus the weight fraction of PCBM in the P3HT:PCBM layer is shown in Fig. 3. G_c reaches values of 1.6 J/m^2 for a nearly pure P3HT layer (3 wt% PCBM), decreases non-linearly with higher fraction of PCBM in the BHJ and is only 0.1 J/m^2 for a nearly pure PCBM layer (98 wt% PCBM). The PCE of the PEDOT:PSS cells varied from 0.006% for a 100% P3HT going through a maximum of 2.2% for a 1:1 ratio of P3HT:PCBM layer and decreasing to 0.05% for a 100% PCBM layer