Morphology and interdiffusion control to improve adhesion and cohesion properties in inverted polymer solar cells

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Abstract

The role of pre-electrode deposition annealing on the morphology and the fracture properties of polymer solar cells is discussed. We found an increase in adhesion at the weak P3HT:PCBM/PEDOT:PSS interface with annealing temperature, caused by increased interdiffusion between the organic layers. The formation of micrometer sized PCBM crystallites, which occurs with annealing above the crystallization temperature of PCBM, initially weakened the P3HT:PCBM layer itself. Further annealing improved the cohesion, due to a pull-out toughening mechanism of the growing PCBM clusters. Understanding how the morphology, tuned by annealing, affects the adhesive and cohesive properties in these organic films is essential for the mechanical integrity of OPV devices.

Keywords

Adhesion and delamination, cohesion, reliability, polymer solar cells, annealing, NEXAFS

1. Introduction

Organic photovoltaic (OPV) devices, typically involving materials that are compatible with flexible plastic substrates, have reached over 10 % power conversion efficiency (PCE), one of the critical milestones for market penetration [1-4]. However, organic materials are often mechanically fragile compared to their inorganic counterparts, and devices containing these materials have a higher tendency for adhesive and cohesive failure. For example, the poor adhesion between the poly(3-hexyl)thiophene:[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) and poly(3,4-ethylenedioxythiophene) poly(styrene-sulfonate) (PEDOT:PSS), and the low cohesion of the P3HT:PCBM layer can contribute to low processing yield and poor long-term reliability [5, 6]. Several methods have been used to increase the fracture properties of OPVs, including polymer:fullerene ratio, molecular weight, polymer layer thickness, chemical treatments and post-electrode deposition annealing [6-10]. The role of pre-electrode deposition annealing has not been studied yet, while it is well known that it strongly affects the bulk heterojunction (BHJ) morphology, phase separation, the carrier mobilities and power conversion efficiency (PCE).

Here, we show how to tune the pre-electrode annealing parameters to control the interdiffusion and morphology of the polymer layers and to optimize the fracture properties. Using Near Edge X-Ray Absorption Fine Structure (NEXAFS) and X-ray Photoelectron Spectroscopy (XPS), an increase of P3HT:PCBM and PEDOT:PSS interdiffusion with annealing temperature was found to be the underlying mechanism for effectively improving the interlayer adhesion, similar to the mechanisms that occur during post-electrode deposition annealing, for all samples that were annealed below the cold crystallization temperature, T_c , of PCBM around 120 °C [11, 12].

For annealing above T_c , we found the formation of micrometer large PCBM clusters form, weakening the BHJ layer, even at very short annealing times of 10 minutes. With further annealing time, the PCBM clusters grew and improved the cohesion of the BHJ, related to a pull-out mechanism of the 100 nm's high PCBM clusters. This behavior was modeled with micromechanical bridging theories. We also found that PCBM cluster formation and extensive phase separation decreased the device PCE due to decreased exciton splitting and hindered charge transport. In conclusion, pre-electrode deposition annealing at temperatures below the T_c of the fullerene can be used to effectively improve the adhesion at the P3HT:PCBM/PEDOT:PSS interface, but annealing above T_c should be avoided to preserve the cohesion and efficiency of the OPV devices.

2. Experimental Section

2.1 Solar cell preparation

Inverted OPV devices with ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag architecture were made on 30 mm x 30 mm square glass substrates (Figure 1). The details of the OPV sample preparation have been reported previously [6, 13]. Shortly, ITO coated glass substrates were purchased from Kintec. ZnO was spin coated from a ZnO precursor (zinc acetate dehydrate dissolved in 2-ethoxyethanol, ethonolamine and ethanol). A 250 nm active layer was deposited from a 1:1 wt. % mixture of as purchased P3HT (Rieke Materials) and PCBM (Solenne B.V.) dissolved in o-dichloro-benzene (oDCB). Subsequent to deposition, all blends were annealed at 130 °C for 10 min in an inert atmosphere. A 30 nm PEDOT:PSS layer was deposited from a commercially available water-based dispersion (Baytron PVP AI 4083, Clevios), followed by a pre-electrode deposition annealing treatment, as described below. Then, a silver electrode was thermal evaporated (Ag, 100 nm) on top of the annealed samples. Finally, the solar cells were

encapsulated by bonding an identical glass substrate on top of the silver electrode using a brittle epoxy, resulting in a square glass sandwich.

2.2 Pre-electrode Annealing Treatments

Prior to the deposition of the silver electrode, two different annealing treatments were carried out on the hotplate. Set 1 contained samples that were annealed for 10 min at various temperatures: 45 °C, 65 °C, 85 °C, 105 °C and 130 °C. The samples in Set 2 were annealed at a constant temperature of 130 °C for 10 min, 0.5 h, 1 h, 2 h, 3 h and 24 h. In addition each set contained several non-annealed control samples.

2.3 Characterization before debonding

Photovoltaic characteristics of the OPV devices were measured in ambient atmosphere at room temperature with a Keithley 2602A in two-wire configuration under a Lot Oriel 1000 W Xenon arc lamp filtered by OD0.8 Newport neutral density to obtain 100 mW/cm² illumination intensity and AM1.5G spectrum. The lamps intensity was calibrated with an ISE Fraunhofer certified Si photodiode. Ultra-violet visible absorption measurements were performed on all OPV samples using Perkin Elmer Lambda 900 or 950 UV-VIS spectrophotometer to record morphology and reorganization changes in the P3HT:PCBM layer prior to adhesion testing.

2.4 Adhesion specimen and testing

Double cantilever beam (DCB) adhesion specimens of 5 mm wide, 30 mm long and 1.5 mm thick were machined using a high speed wafer saw with a resin blade. To prevent water coolant diffusing into the OPV structure during dicing and damaging the solar cell materials, trenches were cut on each side of square sandwich. Perfectly aligned trenches on the top and bottom glass substrates of the sandwiched structure made it easy to cleave individual DCB specimens prior to

testing. The DCB specimens were loaded under displacement control in a thin-film cohesion testing system (Delaminator DTS, Menlo Park, CA) from which a load, P, versus displacement, Δ , curve was recorded. The adhesion energy, G_c (J/m²), was measured in terms of the critical value of the applied strain energy release rate, G. G_c can be expressed in terms of the critical load, P_c , at which debond growth occurs, the debond length, a, the plain strain elastic modulus, E' , of the substrates and the specimen dimensions; width, B and half-thickness, h. The adhesion energy was calculated from equation (1) [14]:

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

The debond length was measured directly under an optical microscope and also inferred from measurement of the elastic compliance, $d\Delta/dP$, using the compliance relationship in equation (2):

$$a = \left(\frac{d\Delta}{dP} \times \frac{B E' h^3}{8} \right)^{1/3} - 0.64 \times h \quad (2)$$

All G_c testing was carried out in laboratory air environment at ~25 °C and ~40 % R.H..

2.5 Characterization of the debond path

Following mechanical testing, a survey x-ray photo spectroscopy (XPS, PHI 5000 Versaprobe) scan (0 - 1000 eV) was made of each of the fractured specimens using monochromatic Al K α x-ray radiation at 1487 eV in order to characterize the surface chemistry and to help precisely locate the debond path. Detailed high-resolution XPS scans around the S_{2p} core level (155 - 175 eV) were made for compositional analysis and further identification of the debond path. Optical microscopy was used to locate and determine the nature of the debond path.

Atomic force microscopy (AFM) (XE-70, Park Systems) was used to characterize the surface morphology and roughness in non contact mode.

Carbon K-edge NEXAFS spectra [15] were measured on the bending magnet beam line 8-2 at Stanford Synchrotron Radiation Laboratory (SSRL) [16]. The spherical grating monochromator (500 l/mm) was operated with 40 μm by 40 μm slit with a resulting energy resolution of about 0.3 eV. All samples were mounted on an Aluminum sample bar and electrically connected with carbon tape. The spectra shown in the article were acquired in the Total Electron Yield (TEY) mode, measured via the drain current without bias, i_0 . The incoming flux was normalized by a gold grid with freshly evaporated gold, positioned upstream of the sample chamber, intercepting 10 - 20 % of the beam intensity. The NEXAFS spectra were collected over the range 250 - 340 eV at 54°, close to the magic angle, where no angular dependence of states with high molecular symmetry (assuming azimuthal averaging) is expected [Stohr PRB angular dependence] for the surface composition extraction. Before normalization, both the i_0 and sample current intensity were subtracted by an offset (resulting from amplifiers and a small contribution from the ion pump to the sample current) that was measured before each spectrum. All spectra were then energy normalized to the carbon dip of the beam line (284.7 eV), with an expected precision of ± 25 meV, followed by division of the i_0 . A linear background was subtracted before intensity normalization at 330 - 340 eV, where the intensity is assumed to be atomic. With this atomic normalization, each spectrum corresponds to the average intensity per carbon atom over the sampled area. The TEY probing depth is in the order of 5 nm [17].

The spectra were fitted using a linear combination of reference compounds (measured at the beam line 8-2 with the same settings and with the same atomic normalization described above). In order to increase the precision of the fitting to composition, the region most sensitive

to the different functional groups (in particular the π^* region) was fitted with 10 times increased weight. Moreover, we observed some oxygen functionalization around 288.5 (carbonyl π^*) due to minor oxidation. To reduce the effect of this small but varying oxidation, the fitting was weighted 10 times less (0.1 instead of 1) in the region of 288 to 290 eV. The fitting results in linear contributions of the various compounds in atomic fractions. To translate the atomic fractions to molecular fractions, the atomic C contribution needs to be scaled by the number of carbon atoms in each compound and renormalized.

3. Results

3.1 Annealing Temperature

A pre-electrode deposition annealing treatment of 10 min at various temperatures was carried out on a set of glass/ZnO/ITO/P3HT:PCBM/PEDOT:PSS/Ag/Glass OPV devices. The PCE of the OPV devices and fracture energy, G_c (J/m^2), were measured and shown in Figure 1. We found a linear increase in G_c with annealing temperature. Similarly, device efficiency noticeably increased with annealing above 85 °C, which sufficiently above the glass transition temperature of the blend to enable re-organization in 10 min [12]. Improved performance mostly originates from slightly increased short-circuit current, which corroborates development of an optimal phase segregation (Figure S1).

After delamination, every adhesion specimen split into two sides: one includes the Ag electrode (“Ag side”) and the other includes the ZnO layer (“ZnO side”). In order to understand the interfacial reinforcement mechanism responsible for the increase in G_c , the composition of delaminated surfaces were characterized using NEXAFS and XPS. It was complemented by structural characterization relying on UV-VIS absorption and AFM.

NEXAFS in TEY mode was used to quantify the surface composition at the top few nanometers of the delaminated surfaces [8]. The surface composition of each delaminated surface was extracted from the linear superposition of the P3HT, PCBM and PEDOT:PSS spectra (Figure S2), fit numerically to the NEXAFS TEY spectra of the delaminated surface, as described by equation (3).

$$\text{Surface Composition} = x \text{ P3HT} + y \text{ PCBM} + z \text{ PEDOT:PSS} \quad (3)$$

with x, y and z the atomic fraction (*at.%*) of P3HT, PCBM and PEDOT:PSS, respectively. The composition at the delaminated surfaces is shown as a function of annealing temperature in Figure 2a,b.

For all the samples annealed up to 105 °C, the surface composition on the Ag side was a mix of PEDOT:PSS, P3HT and PCBM, while top surface of the ZnO side was pure P3HT:PCBM. This indicated adhesive failure at the interface between the P3HT:PCBM and adjacent intermix PEDOT:PSS/P3HT:PCBM layer (Figure 1), consistent with previously reported results [8]. The increase in *at.%* P3HT and *at.%* PCBM, and decrease in *at.%* PEDOT:PSS with annealing temperature is indicative for the growth of the intermixed layer. The increased interdiffusion and subsequent increased chemical interaction, such as polymer entanglements, interchain interactions and electrochemical interactions between P3HT and PSS, are responsible for the increase in adhesive strength. The samples were further characterized with XPS, and both survey and high resolution scans near the S_{2p} indicated typical adhesive failure at the P3HT:PCBM/PEDOT:PSS interface, consistent with the literature [6]. Detailed XPS characterization revealed about 85 - 90 *at. %* carbon (C), 6 - 8 *at.%* sulfur (S) and 3.5 - 10 *at.%* oxygen (O) on the Ag electrode side and 90 - 95 *at.%* C, 4.5 - 7 *at.%* S and 0 - 3 *at.%* O on the ZnO side. No significant changes in the elemental concentration were observed with annealing

time or temperature (Figure S3). A decrease in the 168 eV peak intensity or PSS signal, only apparent on the Ag side, was observed with temperature (Figures 2c and S5). The peak around 168 eV corresponds to double sulfur-oxygen bonds in the sulfonic acid group in PSS, while the main peak around 164 eV is associated to single sulfur-carbon or sulfur-oxygen bonds [18]. The observed decrease in 168 eV peak intensity indicates a decrease in the amount of PSS at the delaminated interface compared to the amount of P3HT:PCBM with annealing temperature. Yet another experimental sign of the existence of a growing intermixed layer of P3HT:PCBM and PEDOT:PSS at the interface with annealing, reinforcing the adhesion at the interface.

For the samples annealed at 130 °C, we found cohesive failure with 70 +/-2 *at.%* P3HT and 30 +/-2 *at.%* PCBM at both the Ag electrode and ZnO side. XPS high resolution scans around the S_{2p}, with a penetration depth of 10 nm, indicated a light PSS signal (intensity around the 168 eV), while NEXAFS, sensitive to the first 3 to 5 nm did not show any PEDOT:PSS presence. Combining those results, we can conclude that failure occurred cohesively in the P3HT:PCBM layer, close to the PEDOT:PSS interface. Cohesive failure in the P3HT:PCBM layer for OPV devices annealed at 130 °C is related to the formation of PCBM crystallites, which starts at temperatures of 120 °C [11, 12]. Optical microscopy revealed μm-size PCBM crystallites (Figure 3). Ultraviolet-visible absorption measurements showed a dramatic decrease in the absorption shoulder at 620 nm for annealing at 105 °C and 130°C (around and above the T_c), linked to P3HT interchain disorganization (Figure 2d). This implies that P3HT chain organization is obstructed during the formation of PCBM crystallites [11]. The PCBM clusters act as stress concentrators, weakening the BHJ and causing cohesive failure in the P3HT:PCBM layer, as opposed to adhesive failure at the interface with PEDOT:PSS. It is expected that the crystallites grow further

with annealing at 130 °C [19, 20], but the effect on the cohesion properties of the P3HT:PCBM layer is still unknown and will be discussed below.

3.2 Annealing Time

A set of OPV devices was pre-electrode deposition annealed at 130 °C. We observed a gradual increase in the growth and fraction of PCBM crystals with time using an optical microscope, consistent with the literature (Figure 3a) [19]. The efficiency of the OPV devices and the cohesion energy of the P3HT:PCBM layer was regularly measured and shown in Figure 4a. We added previously published adhesion energy values of the P3HT:PCBM/PEDOT:PSS interface, increasing with post – electrode deposition annealing [8]. An increase in cohesion energy was measured with annealing time, with the greatest relative increase during the first couple of hours. Device performance gradually increased up to 2 h annealing owing to slight increase of the fill factor (Figure S4). However further annealing up to 24 h lead to a severe decrease in all device parameters as severe demixing between the polymer and fullerene (Figure 4) results in reduced exciton harvesting and severely hindered charge transport.

Similar to the OPV devices discussed above, the delaminated surfaces were characterized using NEXAFS and XPS, confirming cohesive failure in the P3HT:PCBM layer (Figures 5a,b). Moreover, the surface composition on both the Ag and ZnO sides slightly increased in *at.%* P3HT and decreased in *at.%* PCBM with annealing, indicating further phase separation. High resolution XPS scans near the S_{2p} peak revealed a clear absence of the PSS peak on the Ag side, which confirms cohesive failure.

The NEXAFS TEY spectra in the range of 282 *eV* to 290 *eV* for the non-annealed, 1 h and 24 h annealed OPV devices are shown in Figure 5 d, e and f to illustrate the clear difference between adhesive and cohesive failure. For the adhesively debonded non-annealed sample, the

TEY spectra on the Ag side clearly depicts a peak around 285.50 eV typical for PEDOT:PSS, while the peaks at 285.0 and 286.46 eV for PCBM and at 285.85 eV for the thiophene group in P3HT are strongly present on the ZnO side. The TEY spectra on the ZnO and Ag side of the cohesively debonded samples (1 h and 24 h annealing) are almost identical. The difference in delaminated surface composition between the 1h and 24h annealed OPV is less *at.%* PCBM for 24 h annealed OPV.

UV-VIS measurements show a gradual decrease in the absorption shoulder at 620 nm with annealing time, implying a decrease in P3HT chain organization (Figure 5c). Significant reduction of fullerene absorption peak at 400 nm is assigned to PCBM cluster formation in agreement with previous morphology studies [19]. Optical microscopy and AFM revealed the pull-out of PCBM crystallites, sticking out of the P3HT:PCBM layer with a height of 200 nm for 30 min and 800 nm for 24h annealing, leaving behind holes on the opposite delaminated sample.

The cohesion of the BHJ layer is greatly determined by the growth, fraction and size of the PCBM clusters. The kinetics and physical understanding of the formation of PCBM clusters has been previously published. Shortly, PCBM crystals formation involves a 3 step process: nucleation, diffusion and growth [20, 21]. The nucleation site is determined by the concentration of PCBM. In the inverted device architecture, the PCBM concentration is the highest at the ZnO interface, the most likely spot for nucleation to happen [22]. During pre-electrode deposition annealing, PCBM diffuses through the amorphous polymer matrix regions to the specific growth fronts. The mobility is greatly affected by the glass transition temperature T_g of the polymer, miscibility and the spatial confinement, i.e. retarded mobility with increased confinement caused by retarded conformational dynamics of the host polymer chains [20, 23]. The growth of the crystals needs unobstructed space to expand. The PCBM crystal is surrounded by a PCBM

depleted region, creating local sinks in which the P3HT collapses, as can be observed on the AFM images (Figure 3c). In case of post-electrode annealing, PCBM cluster formation is suppressed due to the double spatial confinement created by the top glass substrate, causing retarded diffusion rate and hindering the growth itself. PCBM nanocrystals of maximum 80 to 120 nm have been reported [20]. The absence of micrometer sized PCBM crystallites preserves the cohesion, and therefore we observed adhesive failure at the interface with higher G_c values (Figure 4).

For pre-electrode deposition annealing, the growth of μm -size PCBM clusters initially weakened the P3HT:PCBM layer (Figure 4). An increase in crystallites size was found to improve the cohesion of the P3HT:PCBM. This can be understood in terms of a pull-out toughening mechanism. For larger clusters, the cohesive energy or energy required to propagate the debond might be significantly increased due to the energy dissipated by stretching the crystallites. A larger cluster height and fraction of clusters allows for a greater degree of resistance to pull-out as the BHJ is being debonded. The measured cohesive energy can be modeled as the scaled sum of the intrinsic energy necessary to separate the layer, G_o and the pull-out contribution, $G_{\text{pull-out}}$:

$$G_c = [1 - f(t)] \times G_o + f(t) \times G_{\text{pull-out}} \quad (4)$$

where $f(t)$ is the areal fraction of PCBM clusters, inferred by optical microscopy, that increases as a function of annealing time, t . Characterizing the molecular pull-out elements using a stress separation curve, σ - δ , with the maximum molecular-pull-out stress, σ_o , and maximum value of the molecular separation, δ_o , $G_{\text{pull-out}}$ can be approximated by [24]:

$$G_{\text{pull-out}} = \sigma_o \delta_o(t) \int_0^1 \chi(\varepsilon) d\varepsilon \quad (5)$$

where χ describes the shape of the σ - δ curve, which was assumed to be triangular. δ_o was assumed the average height of the PCBM clusters that sticks out of the surface after delamination, which was measured by AFM and increased with time.

The cohesion energy for the samples annealed up to 3 hours was fitted to equation 5, as shown in Figure 4b, and we found that $\sigma_o = 400$ MPa and $G_o = 1.75$ J m⁻². Note that the non-annealed and 24 h annealed G_c data is excluded from this model, because they belong to a different debonding mechanism. The non-annealed data is associated with adhesive failure at the interface. The 24 h annealed sample shows fracture of the PCBM clusters itself, as can be seen on the AFM images in Figure 3c, where the clusters are topped of instead ending in a peak. Additionally the chemistry of the 24h annealed sample is quite different from the other samples, as can be seen by comparing Fig. 5 e and f, with a strong depletion of PCBM in the regions around the PCBM clusters.

4. Summary

Pre-electrode deposition annealing at temperatures below the T_c of the fullerene was effectively used to improve adhesion at the weak P3HT:PCBM/PEDOT:PSS interface. Higher annealing temperatures were found to increase interdiffusion and chemical interaction at the interface, leading to improved adhesion. Annealing above T_c should be avoided to prevent the formation of μ m-sized PCBM crystallites. These do not only weaken the cohesion of the BHJ layer but also dramatically decrease the device efficiencies.

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Figures

Figure 1: The measured adhesion energy, G_c (J/m²) and efficiency, PCE (%) as a function of the 10 min annealing temperature. Insets are illustrations of the OPV device structure with either adhesive or cohesive failure.

Figure 2: The surface composition of the delaminated (a) Ag and (b) ZnO side represented as the atomic fraction of each compound, measured by NEXAFS TEY, as a function of the annealing temperature. (c) XPS scans around the S_{2p} core level on the delaminated surface of the intermixed layer. (d) UV-VIS absorption spectra through the OPV before delamination.

Figure 3: Microscopy and AFM images of the PCBM crystallites in the OPVs annealed at 130C for various annealing time. (a) before delamination illustrating increased fraction and size (b) after delamination on the debonded surfaces indication clusters and holes (c) AFM illustrates clearly holes on the Ag side and PCBM clusters sticking out of the sample surface on the ZnO side with increasing height.

Figure 4: (a) G_c (squares) and PCE (circles) as a function of annealing time for pre-electrode deposition annealed OPVs. Comparison of the G_c values for post-electrode deposition annealing is included (triangles and dashed line). (b) Fit of the bridging toughening model to the experimental data calculated using equation 5.

Figure 5: (a) The surface composition of the delaminated Ag side represented as the atomic fraction of each compound, measured by NEXAFS TEY, as a function of the annealing time. (b) XPS scans around the S_{2p} core level on the delaminated surface of the intermixed layer. (c) UV-VIS absorption spectra through the OPV before delamination. The TEY in the range of 282 – 290 eV for (d) non-annealed OPV (e) 1h/130°C annealed OPV and (f) 24h/130°C annealed OPV

References

- [1] C.J. Brabec, S. Gowrisanker, J.J.M. Halls, D. Laird, S.J. Jia, S.P. Williams, Polymer-Fullerene Bulk-Heterojunction Solar Cells, *Adv Mater*, 22 (2010) 3839-3856.
- [2] G. Dennler, M.C. Scharber, C.J. Brabec, Polymer-Fullerene Bulk-Heterojunction Solar Cells, *Adv Mater*, 21 (2009) 1323-1338.
- [3] F.C. Krebs, Fabrication and processing of polymer solar cells: A review of printing and coating techniques, *Sol Energ Mat Sol C*, 93 (2009) 394-412.
- [4] K.E. M. A. Green, Y. Hishikawa, W. Warta, E. D. Dunlop, Solar cell efficiency tables (version 39), *Progress in Photovoltaics: Research and applications* 20 (2012) 12-20.
- [5] S.R. Dupont, M. Oliver, F.C. Krebs, R.H. Dauskardt Interlayer adhesion in roll-to-roll processed flexible inverted polymer solar cells *Sol Energ Mat Sol C*, 97 (2012) 171-175.
- [6] S.R. Dupont, E. Voroshazi, P. Heremans, R.H. Dauskardt, Adhesion properties of inverted polymer solarcells: Processing and film structure parameters, *Org Electron*, 14 (2013) 1262-1270.
- [7] V. Brand, C. Bruner, R.H. Dauskardt, Cohesion and device reliability in organic bulk heterojunction photovoltaic cells, *Sol Energ Mat Sol C*, 99 (2012) 182-189.
- [8] S.R. Dupont, Eszter Voroshazi, Dennis Nordlund, Koen Vandewal, Reinhold H. Dauskardt, Controlling Interdiffusion, Interfacial Composition and Adhesion in Polymer Solar Cells *Advanced Materials Interfaces*, in press, (2014).
- [9] C. Bruner, Reinhold. H. Dauskardt, Role of Molecular Weight on the Mechanical Device Properties of Organic Polymer Solar Cells, *Macromolecules*, (2014).
- [10] C. Bruner, N.C. Miller, M.D. McGehee, R.H. Dauskardt, Molecular Intercalation and Cohesion of Organic Bulk Heterojunction Photovoltaic Devices, *Adv Funct Mater*, 23 (2013) 2863-2871.

- 1
2
3
4 [11] E. Verploegen, R. Mondal, C.J. Bettinger, S. Sok, M.F. Toney, Z.A. Bao, Effects of
5 Thermal Annealing Upon the Morphology of Polymer-Fullerene Blends, *Adv Funct Mater*, 20
6 (2010) 3519-3529.
7
8
9
10
11 [12] J. Zhao, A. Swinnen, G. Van Assche, J. Manca, D. Vanderzande, B. Van Mele, Phase
12 Diagram of P3HT/PCBM Blends and Its Implication for the Stability of Morphology, *J Phys*
13 *Chem B*, 113 (2009) 1587-1591.
14
15
16
17
18 [13] E. Voroshazi, B. Verreet, A. Buri, R. Muller, D. Di Nuzzo, P. Heremans, Influence of
19 cathode oxidation via the hole extraction layer in polymer:fullerene solar cells, *Org Electron*, 12
20 (2011) 736-744.
21
22
23
24
25
26 [14] M.F. Kanninen, Augmented Double Cantilever Beam Model for Studying Crack-
27 Propagation and Arrest, *Int J Fracture*, 9 (1973) 83-92.
28
29
30
31 [15] J. Sto\hr, NEXAFS spectroscopy, Springer-Verlag, Berlin ; London, 1992.
32
33
34 [16] K.G. Tirsell, V.P. Karpenko, A General-Purpose Sub-Kev X-Ray Facility at the Stanford-
35 Synchrotron-Radiation-Laboratory, *Nucl Instrum Meth A*, 291 (1990) 511-517.
36
37
38 [17] A.F. Tillack, K.M. Noone, B.A. MacLeod, D. Nordlund, K.P. Nagle, J.A. Bradley, S.K.
39 Hau, H.L. Yip, A.K.Y. Jen, G.T. Seidler, D.S. Ginger, Surface Characterization of
40 Polythiophene:Fullerene Blends on Different Electrodes Using Near Edge X-ray Absorption Fine
41 Structure, *Acs Appl Mater Inter*, 3 (2011) 726-732.
42
43
44
45
46
47
48 [18] G. Greczynski, T. Kugler, W.R. Salaneck, Characterization of the PEDOT-PSS system by
49 means of X-ray and ultraviolet photoelectron spectroscopy, *Thin Solid Films*, 354 (1999) 129-
50 135.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4 [19] V. Turkovic, S. Engmann, G. Gobsch, H. Hoppe, Methods in determination of
5 morphological degradation of polymer:fullerene solar cells, *Synthetic Met*, 161 (2012) 2534-
6 2539.
7
8
9
10
11 [20] X.N. Yang, A. Alexeev, M.A.J. Michels, J. Loos, Effect of spatial confinement on the
12 morphology evolution of thin poly(p-phenylenevinylene)/methanofullerene composite films,
13 *Macromolecules*, 38 (2005) 4289-4295.
14
15
16
17
18 [21] B. Watts, W.J. Belcher, L. Thomsen, H. Ade, P.C. Dastoor, A Quantitative Study of PCBM
19 Diffusion during Annealing of P3HT: PCBM Blend Films, *Macromolecules*, 42 (2009) 8392-
20 8397.
21
22
23
24
25
26 [22] C. He, D.S. Germack, R.J. Kline, D.M. DeLongchamp, D.A. Fischer, C.R. Snyder, M.F.
27 Toney, J.G. Kushmerick, L.J. Richter, Influence of substrate on crystallization in
28 polythiophene/fullerene blends, *Sol Energ Mat Sol C*, 95 (2011) 1375-1381.
29
30
31
32
33 [23] B.A. Collins, J.R. Tumbleston, H. Ade, Miscibility, Crystallinity, and Phase Development in
34 P3HT/PCBM Solar Cells: Toward an Enlightened Understanding of Device Morphology and
35 Stability, *J Phys Chem Lett*, 2 (2011) 3135-3145.
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40
41 [24] G. Bao, Z. Suo Remarks on crack-bridging concepts, *Appl. Mech. Rev.*, 45 (1992) 355-366.
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Figure Captions

Figure 1: Adhesion Energy and Efficiency.

The measured adhesion energy, G_c (J/m^2) and efficiency, PCE (%) as a function of the 10 min annealing temperature. Insets are illustrations of the OPV device structure with either adhesive or cohesive failure.

Figure 2: Interfacial Composition.

The surface composition of the delaminated (a) Ag and (b) ZnO side represented as the atomic fraction of each compound, measured by NEXAFS TEY, as a function of the annealing temperature. (c) XPS scans around the S_{2p} core level on the delaminated surface of the intermixed layer. (d) UV-VIS absorption spectra through the OPV before delamination.

Figure 3: PCBM clusters.

Microscopy and AFM images of the PCBM crystallites in the OPVs annealed at 130C for various annealing time. (a) before delamination illustrating increased fraction and size (b) after delamination on the debonded surfaces indication clusters and holes (c) AFM illustrates clearly holes on the Ag side and PCBM clusters sticking out of the sample surface on the ZnO side with increasing height.

Figure 4: Adhesion Energy, Efficiency and Bridging Model.

(a) G_c (squares) and PCE (circles) as a function of annealing time for pre-electrode deposition annealed OPVs. Comparison of the G_c values for post-electrode deposition annealing is included

(triangles and dashed line). (b) Fit of the bridging toughening model to the experimental data calculated using equation 5.

Figure 5: Surface and bulk characterization

(a) The surface composition of the delaminated Ag side represented as the atomic fraction of each compound, measured by NEXAFS TEY, as a function of the annealing time. (b) XPS scans around the S_{2p} core level on the delaminated surface of the intermixed layer. (c) UV-VIS absorption spectra through the OPV before delamination. The TEY in the range of 282 – 290 eV for (d) non-annealed OPV (e) 1h/130°C annealed OPV and (f) 24h/130°C annealed OPV