All solution processing of ITO-free organic solar cell modules directly on barrier foil

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In this study, we demonstrate fully solution processed semi-transparent silver electrodes on flexible substrates having a sheet resistance as low as $\Omega/\square$ and transmittance of $\sim30\%$ at 550 nm. We demonstrate the use of this electrode as a substitute for ITO in an inverted organic solar cell (OSC) with the layer sequence, PET/Ag/ZnO/P3HT:PCBM/PEDOT:PSS/Ag where illumination is achieved through the first Ag layer. Power conversion efficiency of up to 1.6% under 1 sun illumination (100 mW cm$^{-2}$ and AM1.5G) is achieved for small area (1 cm$^2$) test devices. We further demonstrate scalability of the semi-transparent Ag electrode fabrication in a roll-to-roll (R2R) process using slot-die coating. This electrode is further utilized in R2R processing of large area modules (active area 35.5 cm$^2$) where all layers in the modules are R2R processed with solution-based materials in ambient conditions without any use of vacuum steps. We further demonstrate the possibility of using barrier foil as the substrate in the R2R processing of modules. Module performance is evaluated by current–voltage characterization and Light Beam Induced Current (LBIC imaging). Such a semi-transparent Ag electrode incurs very little material and processing cost and is a cost-effective alternative to ITO for low-cost organic solar cells.

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1. Introduction

Photovoltaic cells contribute less than 0.1% of current world’s electricity demand [1]. This is in spite of the fact that inorganic solar cells with high efficiency and lifetime have been commercialized more than half a century ago. High cost of raw materials and processing are the major impeding factors for market penetration of such inorganic devices. In contrary, organic solar cells (OSCs) have the potential to deliver cost-competitiveness on par with conventional energy means such as fossil fuels. This cost-competitiveness of OSC rests in its virtue of low cost of raw materials and their processing.

Indium tin oxide (ITO), the commonly used transparent conductor, represents a major impediment to lowering material and processing cost of OSC. ITO requires highly energy intensive processing bearing more than 70% of net embedded energy in the production of an OSC module [2]. Besides, the limited abundance of indium resources and the associated cost volatility may create a bottleneck for upscaling of OSC [3]. As such, finding a replacement for ITO is crucial if OSC is to foray into a large market.

A number of studies delving into finding replacement to ITO are present; however, only few are applicable to low cost production of OSC. Low-cost production of OSC is envisaged through roll-to-roll (R2R) printing and coating methods employing no vacuum steps. Vacuum processing are throughput-limiting steps in a R2R line. Unfortunately, many of the ITO-free alternatives employ vacuum-steps and in some cases require higher energy intensive processing than that required in the processing of ITO electrodes as shown in life-cycle analysis studies [2,4–6]. Such alternatives offer no cost advantages to ITO while efficiency is sacrificed. As such, the ideal alternative for ITO electrodes for OSC should be free of vacuum processing steps; the associated materials should be abundant; and the cost of the raw materials should be low or very little materials should be used to balance cost. Working under such a boundary condition is a difficult challenge and very few potential solutions have been proposed.

The potential low cost solution to ITO could be classified into four groups of materials: (1) conducting polymers (2) nanowires and nanoparticles of metals; (3) carbon nanotubes; and (4) inorganic TCOs. PEDOT:PSS is the most commonly used conducting transparent polymer electrode. PEDOT:PSS is easily solution processed, however, a trade-off between transparency and conductivity is often observed. Overlaying PEDOT:PSS with a thin metal grid has been utilized to maximize transparency and conductivity [7]. In devices where PEDOT:PSS serves as transparent conductor, the counter electrode is typically a non transparent...
layer such as Ag nanoparticles [8], Al/Cr/Al [9], Cu sheets [10], LiF/Al [7]. Nanowires and carbon nanotubes are potentially low cost alternatives to ITO that can display excellent transmission and conductivity but they still have challenges to overcome in controlling topology and junction resistance [11–13]. Other TCOs such as ZnO have been studied [14] but their use as standalone electrodes in OSC are unlikely because of challenges in solution processing as well as their brittleness which is undesirable for a R2R process.

In this study, we demonstrate a highly conductive semi-transparent silver electrode that is easily solution processed as a replacement of ITO. We accomplish this by modifying a commercially available Ag ink. We then compare OSC devices built on this semitransparent silver electrode (referred as ProcessH) with optimized devices built on solution-processed silver nanoparticles where PEDOT:PSS/metal grid serves as the transparent conductor (referred to as ProcessTwo [8]). Because of the similar device architecture with the same material profile, ProcessTwo and ProcessH devices will allow a more realistic comparison between functionality of PEDOT:PSS/metal grid and semi-transparent silver as transparent conductors. Fig. 1 demonstrates the device architecture for ProcessH and ProcessTwo. Furthermore, we demonstrate an upsampling compatibility of ProcessH devices by processing large-area modules in complete R2R printing and coating line where all layers including the electrodes are solution-processed without any vacuum steps.

2. Materials and instrumentation

2.1. Materials

Silver for the semi-transparent back-electrode is a non-particle based conductive ink purchased from Kunshan Hisense Electronic (SC-100). Silver content of the pristine ink was 18 wt%. The aqueous zinc oxide solution was precursor-based prepared as described earlier [15]. The active layer was a mixture of poly (3-hexylthiophene) (P3HT) (Sepiolid P200, BASF or OS2100, Plextronics) and phenyl-C61-butyric acid methylester (PCBM) (99%, Solenne B.V.). The active ink was prepared by dissolving P3HT:PCBM (1:1; wt/wt) with a total solid concentration of 60 mg in 1 ml of solvent comprising a mixture of 1-chloronaphthalene (5 vol%) and (95 vol%) chlorobenzene. Prior to coating, ZnO and the active ink were filtered through a 0.45 μm filter.

Poly[3,4-ethylenedioxythiophene]:poly(styrenesulfonate) PEDOT:PSS was purchased from Agfa (Orgacon EL-P 5010) and diluted with isopropanol in a ratio of 2:1 by weight. A UV curable silver paste from Toyo (Rexalp Porta RA FS FD 018) was used for screen printing the top metal electrode to serially connect the cells to a module. The substrate for ProcessTwo test cells was glass, for ProcessH test cells it was polyethylene terephthalate (PET), and finally for the R2R produced modules it was barrier foil from Amcor. Amcor barrier foil was also used for encapsulation of the modules. The barrier had a thickness of 55 μm and a UV filter (cut-off at 390 nm). The barrier performance was $0.01 \text{ cm}^2 \text{ m}^{-2} \text{ bar}^{-1} \text{ day}^{-1}$ with respect to oxygen (measured according to ASTM D 3985-81) and $0.04 \text{ g} \text{ m}^{-2} \text{ day}^{-1}$ with respect to water vapor (measured according to ASTM F 372-78). For the module encapsulation the barrier foil was pre-laminated with a pressure sensitive adhesive (467MPF) from 3 M.

2.2. Characterization instrumentation

JV characteristics were measured in ambient atmosphere and humidity with a Keithley Series 2400 sourcemeter, controlled by custom made software. Illumination was provided by a KHS SolarConstant 575 sun simulator (Steuerag Lichttechnik) at an intensity of 1000 W m$^{-2}$ (AM 1.5 G). The temperature was not actively controlled and was $85 \pm 5 \, ^\circ \text{C}$.

Transmittance was measured in the range of 350–800 nm with a UV–vis spectrophotometer (Shimadzu UV-1700). A Jandel RM3 4-point probe station was used to measure the sheet resistance. Field emission scanning electron microscopy (FESEM, FEI Nova NanoSEM 600), 3D white light interferometry (Veeco Wyko NT9100) and stylus profiler (Veeco Dektak) was used for surface characterization.

2.3. Roll-to-roll processing equipment

All layers except the silver back-electrode were slot-die coated on an inline R2R printing and coating machine. The silver back-electrode was screen printed on a flat-bed R2R screen printer and the encapsulation was done in a R2R laminator. Further details on the equipment were already reported in [16,17].

3. Processing

3.1. Semi-transparent silver electrode

The as-received Hisense Ag ink was semitransparent in appearance with a brown tint. Spin coating of as-received ink and subsequent annealing on a hot plate for 30 s gave a near perfect mirror. Transparency was noticed when the ink was diluted with solvents. The pristine Ag ink was diluted in 1:5, 1:6 and 1:7 volume ratios with isopropanol and 1-butanol respectively. Ag films were spin coated at 1500 rpm and annealed at 140 °C for 2 min. During this short annealing period, an immediate color change from a clear mirror. Transparency was noticed when the ink was diluted with solvents. The pristine Ag ink was diluted in 1:5, 1:6 and 1:7 volume ratios with isopropanol and 1-butanol respectively. Ag films were spin coated at 1500 rpm and annealed at 140 °C for 2 min. During this short annealing period, an immediate color change from a clear film to a semi-transparent highly reflective silver film occurred. Dilution was optimized with respect to transparency and sheet resistance of the corresponding films.

3.2. Test (model) cells

ProcessTwo: In house prepared Ag nano-particle ink was spin coated at 1000 rpm and annealed at 140 °C for 10 min. Two layers of ZnO were spin coated at 1000 rpm and dried subsequently after deposition of each layer at 140 °C for 5 min and 10 min respectively. P3HT:PCBM was spin coated at 800 rpm and left in ambient air for 2 min to dry. PEDOT:PSS was spin coated at 1000 rpm and dried at
140 °C for 5 min. The Ag grid was screen printed and subsequently dried at 140 °C for 3 min. The active area of the device was 3 cm².

ProcessH: The optimized diluted ink of non-particle Ag ink with isopropanol was spin coated at 1000 rpm and dried at 140 °C for 5 min. Processing of the remaining stack except the last Ag layer was similar ProcessTwo; the last layer was evaporated. The active area of the device was 1 cm².

3.3. Roll-to-roll processing of modules

Modules were built directly on barrier foil as a cost saving measure and the need for a separate PET substrate was eliminated. The barrier foil (web width of 305 mm) was heat stabilized and pre-shrunk to minimize registration problems in subsequent coating and printing steps due to heat shrinkage. The foil was run through two ovens with a combined length of 4 m at 140 °C with a web speed of 1 m min⁻¹. The cross-directional shrinkage was ca. 0.6%.

The module architecture and processing is similar to a previous report for ITO-based inverted devices, ProcessOne, as described in [16,18]. Briefly, each module had 16 serially interconnected stripes (or cells) with a total module active area of 35.5 cm². All layers were slot-die coated under ambient conditions and consecutively dried by passing through an oven set at 140 °C. Coating web speeds of 2 m min⁻¹ for semi-transparent silver electrode and aqueous ZnO ink, 1.4 m min⁻¹ for P3HT:PCBM and 0.5 m min⁻¹ for PEDOT:PSS were used. The top metal electrode was screen-printed at a web speed of 2 m min⁻¹ under ambient conditions with a UV dose of 420 mJ cm⁻². A second run with an equal dose was done to achieve a complete curing.

The ink of semitransparent Ag electrode was 1:5 (v/v) solutions of Hisense Ag ink and 1-butanol as optimized for transmittance, sheet resistance and processability. Note that isopropanol diluted Ag could not be used for R2R coating as described in results and discussion section. The modules were finally laminated in a R2R laminator at 20 m min⁻¹ using 85 mm wide barrier foil with pre-laminated adhesive to cover the active area of the solar cell modules. R2R processing of all layers is shown in Fig. 2. The transparency of the slot-die coated foil is displayed in Fig. 3.

4. Results and discussions

In this study, we demonstrate the possibility of solution processing of semitransparent silver electrode as a replacement to ITO in OSCs. We show the feasibility of incorporating such an electrode in an OSC with the layer sequence semitransparent Ag/ZnO/P3HT:PCBM/PEDOT:PSS/Ag (ProcessH). We compare the effectiveness of this electrode against the commonly employed R2R compatible semi-transparent electrode in ITO-free OSCs, PEDOT:PSS/Ag grid, in a ProcessTwo device having similar materials stacking as ProcessH. We finally show all-solution processing of complete OSC modules through R2R coating and printing in ambient conditions.
4.1. Semi-transparent silver electrode for ProcessH devices

Table 1 lists transmittance and sheet resistance of the Ag films when as-received Hisense Ag was diluted with isopropanol and 1-butanol respectively at different volume ratios. These results are on spin coated samples. All Ag dilutions with 1-butanol show much higher transmittance (ca. 20%) than Ag dilutions with isopropanol. However, the sheet resistance of Ag/1-butanol films is significantly higher at all dilution levels than Ag/isopropanol-based films. The sheet resistance of Ag/isopropanol at 1:7 (v/v) is 10 Ω□⁻¹ while the sheet resistance of Ag/1-butanol at the same dilution level is 100 times higher at 1 kΩ □⁻¹. Ag/isopropanol with 1:5 v/v was used in the subsequent processing of semitransparent Ag electrode primarily on account of its lower sheet resistance at a relatively lower expense of transmission. Table 2 also shows the results of transmittance and conductivity from a roll-to-roll R2R gradient experiment. This is described in Section 4.3.1.

### Table 1

| Ag:solvent (v:v) |  |  |  |
|------------------|------------------|------------------|------------------|------------------|
|                   | Ag:1-butanol (spin coated) |
|                   | Ag: isopropanol (spin coated) |
|                   | Ag:1-butanol (R2R gradient test) |
|                   | Sheet resistance (Ω □⁻¹) | Transmittance at 550 nm (%) | Sheet resistance (Ω □⁻¹) | Transmittance at 550 nm (%) | Sheet resistance (Ω □⁻¹) | Transmittance at 550 nm (%) |
| 1:5 | 29 | 43 | 5 | 28 | 1 | 25 |
| 1:6 | 46 | 51 | 9 | 38 | 34 | 30 |
| 1:7 | 1000 | 53 | 10 | 38 | 103 | 39 |

Fig. 4. JV curve of ProcessTwo and ProcessH devices (best performing devices).

Fig. 5. Transmittance comparison of light transmitting layers to the photoactive region in ProcessTwo devices (PEDOT:PSS) and ProcessH (Hisense Ag). Absorbance of P3HT is also shown.

4.2. Test devices: JV characteristics

Table 2 lists photovoltaic parameters for ProcessTwo and ProcessH devices.

### Table 2

<table>
<thead>
<tr>
<th>Device</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA cm⁻²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ProcessTwo</td>
<td>0.50</td>
<td>7.60</td>
<td>39.0</td>
<td>1.47</td>
</tr>
<tr>
<td>ProcessH</td>
<td>0.51</td>
<td>5.34</td>
<td>58.3</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Fig. 4 shows the JV curves of ProcessTwo and ProcessH devices and Table 2 lists their key photovoltaic parameters. In ProcessTwo devices, the AgNP film had spikes of > 150 nm in height. The possibility of shunting of the device due to these spikes was avoided by using thicker ZnO and active layers. The thickness of the ZnO and photoactive layer was optimized for maximum efficiency.

ProcessTwo cells have lower efficiency than ProcessH cells mainly due to their lower FF. The lower FF of ProcessTwo cell is reminiscent of all devices employing PEDOT:PSS/screen printed Ag grid [6,16] and is due to their high sheet- and contact resistance. The lower FF for ProcessTwo devices is also caused by the presence of unavoidable shunt paths presented by occasional spikes in the Ag film.

In contrast, semitransparent Ag films on PET for ProcessH devices were extremely smooth (line roughness 2 nm, length=500 nm) and no spikes were observed. Furthermore, illumination in ProcessH cells is achieved through the semi-transparent Ag film and therefore the top PEDOT:PSS can be covered with a full layer of silver. This results in higher conductivity of this electrode than the Ag grid employed in ProcessTwo cells. These facts explain the increased FF in ProcessH in comparison to ProcessTwo cells.

V<sub>oc</sub> for ProcessH and ProcessTwo devices are similar indicating that the electric potential across the photoactive layer is similar as can be expected with the same layer structure in both types of devices and is very similar to ProcessOne. ProcessOne is an ITO-based inverted device having all other layers similar to ProcessH and ProcessTwo [18]. Fig. 5 shows a UV–vis transmittance comparison between the semi-transparent layers of ProcessTwo and ProcessH device (namely PEDOT:PSS and Hisense Ag) through which light travels to reach the photoactive layers in the respective devices. The transmittance of the Hisense Ag film is attributed to the diffraction of light through the pores in the film as seen in the SEM image (Fig. 6). Although transmittance through the Hisense Ag film is poorer relative to the PEDOT:PSS film, the addition of a ZnO layer on the Ag electrode causes an enhancement in transmittance. In fact, when transmittance is integrated between 350 and 650 nm that corresponds to the maximum absorbance region of P3HT, the net transmittance of Ag/ZnO is
16% higher than of the PEDOT:PSS film not including the 20% shadowing loss due to the Ag grid employed in ProcessTwo. Note that higher transmission through PEDOT:PSS can be achieved with lower thickness at an expense of conductivity. Here, we used a large PEDOT:PSS thickness to prevent solvent from the screen printed Ag layer seeping into the photo active layer (PAL). The enhancement in transmittance upon addition of ZnO to the Ag film is most likely caused by surface plasmon resonance (SPR) effects at the Ag/ZnO interface [19]. SPR effects in multilayer structures of ZnO with noble metals can improve both transmittance and conductivity of ZnO and is a widely studied material for its potential as an ITO replacement [20]. SPR relies on surface plasmons of metal nanoparticles and is sensitive to size and shape of the nanoparticles. The effect of SPR diminishes with larger size of Ag islands/particles as studied by Zhang et al. [19]. We suspect that the uncoalesced Ag islands of < 10 nm size within the large pores as present in the morphology of the Hisense Ag substrates are mostly responsible for transmittance enhancement due to SPR (Fig. 6).

Despite the similar $V_{oc}$ and layer thicknesses, and higher illumination to PAL, $J_{sc}$ in ProcessH devices is lower than ProcessTwo devices. This is due to higher series resistance in ProcessH devices due to the higher sheet resistance of semi-transparent Ag film (5 $\Omega \square^{-1}$). On the other hand, the AgNP electrode as used in ProcessTwo had a much lower sheet resistance (0.6 $\Omega \square^{-1}$). The calculated series resistance from the J-V graph for ProcessH and ProcessTwo devices are 79.4 and 8.75 $\Omega$ respectively. Furthermore, lower $J_{sc}$ and higher sheet resistance can be explained by the presence of large number of holes and grain boundaries in semi-transparent Ag films that represents recombination centers for charge carriers. Some enhancement in $J_{sc}$ of ProcessTwo devices could be caused by light trapping and scattering due to the higher surface roughness of the Ag bottom electrode.

4.3. Roll-to-roll module fabrication (ProcessH)

Below we describe results from R2R processing of large area modules based on ProcessH. ProcessTwo has already been demonstrated in R2R processing of modules and the results are published elsewhere [8].

4.3.1. Slot-die coated large area semitransparent Ag substrate

For a finer and more accurate optimization of sheet resistance and transmittance, gradient dilutions of the Hisense Ag ink with 1-butanol were performed using differentially pumped slot-die coating method on a R2R set-up as described elsewhere [21]. Such a screening method enables the probing of a wide parameter space and allows accurate reproducibility of processing conditions as the gradient test was done on the same R2R equipment on which the final modules were produced. In brief, as-received Hisense Ag ink was diluted with 1-butanol (1:5 v/v) was used as a start solution and then linearly diluted with 1-butanol while slot-die coating on PET substrate at a web speed of 2 m min$^{-1}$. The ink was dried at 140 $^\circ$C for 2 min as found optimum on test devices. The films were studied for transmittance and sheet resistance.

Transmittance and sheet resistance of selected dilution levels are listed in Table 1. It was found that beyond a dilution of 1:7 v/v (Ag:1-butanol), the film was largely non-conductive. This corresponded well with our arbitrary selection of dilution factors for our preliminary study on spin-coated films. Compared to spin coated films, the slot-die coated films showed lower sheet resistance and lower transmittance for the 1-butanol diluted
Hisense Ag ink pointing to higher thickness films in slot-coated films than spin coated (Table 1). We proceeded with the R2R module preparation with the semi-transparent Ag electrode fabricated with Ag:1-butanol (1:5 v/v) ink as this dilution gave a thickness of approx. 20 nm. The standard deviation of sheet resistance across the film was the lowest and transmittance was similar to that obtained for the spin-coated Hisense Ag films, with reasonably low sheet resistance. Isopropanol could not be used for dilution of Hisense Ag ink on our current R2R set-up although it was found better in our preliminary optimization study with test devices described earlier.

4.3.2. LBIC mapping to investigate damage due to processing and mechanical handling

**Defects due to processing:** Light beam induced current (LBIC) imaging was used to ascertain the active area of the module (35.5 cm²) and to observe the differences in current generation when the same module was illuminated from the semi-transparent Ag electrode or the semi-transparent PEDOT:PSS electrode (Fig. 7). Note that both electrodes of the modules are semi-transparent and either side can be illuminated. Illumination from the semi-transparent Ag electrode resulted in a more homogeneous current density than when the same module was illuminated through the PEDOT:PSS electrode. When illuminated from PEDOT:PSS, the imaged surface revealed that that solvent from the Ag paste used for serial interconnection of the stripes on top of PEDOT:PSS had diffused through the PEDOT:PSS layer to reach parts of the PEDOT:PSS/PAL (photoactive layer, P3HT:PCBM) interface in all the stripes (cells), thus rendering lower current generation in these parts (Fig. 7b). When LBIC imaging is carried out with module illuminated from the semi-transparent Ag bottom electrode, damage of the PAL due to solvent diffusion from the Ag paste was not observed over the imaged surface (PAL/ZnO interface). To reach this surface, the solvent must transverse through PEDOT:PSS and PAL, which did not occur due to the large thickness of the PAL layer. The surface of the PAL is the most active region when illuminated through the semi-transparent Ag electrode as light first reaches this surface and electrons thus produced are immediately collected by the negative electrode. Partial contribution to current generation may also have come from the pn-junction that P3HT forms with ZnO [22]. On the other hand, the PAL/PEDOT:PSS interface is the most photoactive region when the modules are illuminated through PEDOT:PSS electrode is compromised due to solvent diffusion from the Ag paste. All modules characterized thus had higher performance when illuminated from the semi-transparent Ag side than when the modules were illuminated from the PEDOT:PSS side.

**Damage/defects due to bending and creasing:** LBIC is a great imaging tool for fast and easy scanning of modules in order to investigate damage due to mechanical handling such as bending and creasing, and to pin point defective areas. Fig. 8 shows an extreme example where a crumpled module is scanned with LBIC. Here, one can differentiate the severity of the damage as some creases have led to delamination of the materials inside while others have not induced any noticeable change in current density. LBIC is hence a great tool for both inline inspections during R2R processing as well as for post-processing inspections for quality assurance.

4.4. Module performance

All modules were illuminated from the semi-transparent Ag side. Dynamic photovoltaic behavior was observed upon IV characterization whereby freshly prepared encapsulated modules showed no or very poor photovoltaic behavior. These modules upon prolonged exposure to illumination evolved to functional devices. A representative IV characteristic of a module and its evolution upon constant exposure to illumination are shown in Fig. 9.

The dynamic photovoltaic performance of the modules is caused by metastable photoconductivity of ZnO [23–25]. Conductivity of ZnO improves upon photo illumination as a result of elimination of adsorbed oxygen on the surface of ZnO. UV exposure induces photo excitation in ZnO (band gap of 3.2 eV) and the resulting hole generation leads to oxygen desorption, consequently increasing conductivity of ZnO. Directly injecting holes by increasing reverse bias also results in oxygen desorption and ultimate increase in ZnO conductivity.

The UV filter in the encapsulation foil (cut off at 390 nm) also slows down the mechanism of oxygen desorption from the ZnO surface as less than 2% of the light wavelength that could induce photo-excitation in ZnO (363 nm) is transmitted to the ZnO layer.
The UV filter in the barrier foil is essential for longer lifetime of the device as UV causes chain scission in the polymer components, PAL and PEDOT:PSS, of the organic solar cell. While conductivity improvement of ZnO upon UV exposure is a gradual process and even more so for our modules receiving limited amount of UV light, increasing reverse bias sweep can result in much faster increase in ZnO conductivity consequently shortening the duration to peak efficiency. Table 3 shows that the time to reach the peak efficiency was smaller for modules subjected to higher negative biases. Hence, the use of a negative bias sweep reduces the characterization time of devices having ZnO components.

The negative bias also burns shunts. The presence of shunting was not expected, as it was not observed in our test devices. Surface analysis of the barrier foil employed in the R2R processing showed that it was rough and responsible for creating shunt paths in the modules. Fig. 10 shows surface roughness of Amcor barrier foil and Melinex PET used in processing of modules and test devices, respectively. Numerous spikes reaching 2 μm in height were observed in the topography of the Amcor barrier foil whereas such spikes were not present in Melinex PET foil. When Hisense Ag ink was deposited on these substrates, the topology of the Ag film mirrored that of the substrate foil.

Nonetheless, all devices evolved to functional devices with the best module exhibiting a PCE: ~0.44%, $I_{sc}$: ~5.8 mA cm$^{-2}$, FF: ~40%, and $V_{oc}$: ~6.8 V. The module should ideally give a $V_{oc}$ of 8 V for 16 serially connected stripes (cells) module based on $V_{oc}$ of ~0.5 V of single cell test device. The lower FF in comparison to the test device is a result of higher sheet resistance of the electrode reached through R2R processing of modules where we employed 1-butanol diluted Hisense ink. The sheet resistance of the R2R processed electrodes was 17 Ω $\square^{-1}$ which is significantly higher than the test devices that had a sheet resistance of 5 Ω $\square^{-1}$ with similar transparency. Furthermore, the lower FF could also be caused by absence of a full layer of Ag on top of PEDOT:PSS as employed in test devices. Ideally, overlaying PEDOT:PSS with a complete layer of Ag would improve FF; however this was avoided in fabricating our module due to the problem of solvents from the Ag ink leaking into the photoactive layer as noticed in the LBIC imaging.

### Table 3

<table>
<thead>
<tr>
<th>Applied bias (V)</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Time to peak efficiency during photoannealing (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Module 1</td>
<td>-20</td>
<td>6.8</td>
<td>5.8</td>
<td>40.3</td>
<td>0.44</td>
</tr>
<tr>
<td>Module 2</td>
<td>-30</td>
<td>6.8</td>
<td>2.9</td>
<td>41.9</td>
<td>0.23</td>
</tr>
<tr>
<td>Module 3</td>
<td>-40</td>
<td>5.7</td>
<td>2.8</td>
<td>41.8</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Fig. 9. Evolution of IV curve of a freshly prepared encapsulated module to its peak efficiency at 475 min. were characterized under 1 sun illumination (1000 Wm$^{-2}$; AM1.5). Efficiency improved from 0.01% to 0.26% in 475 min.

Fig. 10. Optical profilometry (white light interferometry) images showing the surface roughness of (a) Amcor barrier foil and (b) Melinex PET.

5. Conclusion

In this work, we have successfully demonstrated solution processing of semi-transparent silver electrodes with a transmission of 30% at 550 nm and a sheet resistance of 5 Ω $\square^{-1}$. Such a film on flexible PET substrates has a line roughness of 2 nm and displays strong adhesion. Addition of a ZnO layer improves optical transmission. We then demonstrated the feasibility of using this electrode as an ITO-replacement in laboratory scale test devices having the layer sequence Ag/ZnO/P3HT:PCBM/PEDOT:PSS/Ag where the first silver layer was semi-transparent Ag (ProcessH). Power conversion efficiencies of up to 1.6% was achieved. ProcessH was then adopted for R2R processing of large area modules where all layers were solution-processed in ambient air without the use of vacuum. Given the available R2R setup, the optimized dilution for best transparency and conductivity of the Ag electrode could not be directly adapted to R2R processing and had to be modified. We demonstrated working modules with a power conversion efficiency of 0.25% with semitransparent Ag electrodes having a sheet resistance of ~20 Ω $\square^{-1}$ and a transmittance of...
Further improvement in the devices may be achieved by overlaying the PEDOT:PSS layer with a complete Ag layer such as that adapted in the test devices. This was not possible with the available screen printable Ag formulations as the solvent in the Ag ink penetrates to the PAL destroying it. With alternative printing techniques such as flexographic or inkjet printing, we expect that this problem could be resolved. Lastly, we demonstrated an important cost saving measure in R2R processing of OSC modules by eliminating the need for a separate PEN substrate and utilizing barrier foil directly as a substrate. With improvement in physical properties of the barrier foil such as roughness and shrinkage, there should be no reason why barrier foil cannot be used generally as a substrate for flexible OPV.

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