Video Article

Ambient Method for the Production of an Ionically Gated Carbon Nanotube Common Cathode in Tandem Organic Solar Cells

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URL: http://www.jove.com/video/52380
DOI: doi:10.3791/52380

Keywords: Physics, Issue 93, Organic Photovoltaic, Carbon Nanotubes, Ionic Liquid, Tandem Photovoltaic, Conjugated Polymers, Ambient Processing

Date Published: 11/5/2014

Citation: Cook, A.B., Yuen, J.D., Micheli, J.W., Nasibulin, A.G., Zakhidov, A. Ambient Method for the Production of an Ionically Gated Carbon Nanotube Common Cathode in Tandem Organic Solar Cells. *J. Vis. Exp.* (93), e52380, doi:10.3791/52380 (2014).

Abstract

A method of fabricating organic photovoltaic (OPV) tandems that requires no vacuum processing is presented. These devices are comprised of two solution-processed polymeric cells connected in parallel by a transparent carbon nanotubes (CNT) interlayer. This structure includes improvements in fabrication techniques for tandem OPV devices. First the need for ambient-processed cathodes is considered. The CNT anode in the tandem device is tuned via ionic gating to become a common cathode. Ionic gating employs electric double layer charging to lower the work function of the CNT electrode. Secondly, the difficulty of sequentially stacking tandem layers by solution-processing is addressed. The devices are fabricated via solution and dry-lamination in ambient conditions with parallel processing steps. The method of fabricating the individual polymeric cells, the steps needed to laminate them together with a common CNT cathode, and then provide some representative results are described. These results demonstrate ionic gating of the CNT electrode to create a common cathode and addition of current and efficiency as a result of the lamination procedure.

Video Link

The video component of this article can be found at http://www.jove.com/video/52380/

Introduction

Polymer semiconductors are the leading organic photovoltaic (OPV) materials due to high absorptivity, good transport properties, flexibility, and compatibility with temperature sensitive substrates. OPV device power conversion efficiencies, η, have jumped significantly in the past years, with single cell efficiencies as high as 9.1%[1], making them an increasingly viable energy technology.

Despite the improvements in η, the thin optimal active layer thicknesses of the devices limit light absorption and hinder reliable fabrication. Additionally, the spectral width of light absorption of each polymer is limited compared to inorganic materials. Pairing polymers of differing spectral sensitivity bypasses these difficulties, making tandem architectures[2] a necessary innovation.

Series tandem devices are the most common tandem architecture. In this design, an electron transport material, an optional metallic recombination layer, and a hole transport layer connect two independent photoactive layers called sub-cells. Linking sub-cells in a series configuration increases the open circuit voltage of the combination device. Some groups have had success with degenerately doped transport layers[3–5], but more groups have used particles of gold or silver to aid recombination of holes and electrons in the interlayer[6,7].

In contrast, parallel tandems require a high conductivity electrode, either anode or cathode, joining the two active layers. The interlayer must be highly transparent, which limits series tandem interlayers containing metallic particles, and even more so for the parallel tandem interlayers composed of thin, continuous metal electrodes. Carbon nanotubes (CNT) sheets show higher transparency than metal layers. So the NanoTech Institute, in collaboration with Shimane University, has introduced the concept of using as the interlayer electrode in monolithic, parallel tandem devices[8].

Previous efforts featured monolithic, parallel, tandem OPV devices with CNT sheets functioning as interlayer anodes[8,9]. These methods require special care to avoid shorting of one or both cells or damaging preceding layers when depositing later layers. The new method described in this paper eases fabrication by placing the CNT electrode on top of the polymeric active layers of two single cells, then laminating the two separate devices together as shown in **Figure 1**. This method is remarkable as the device, including an air-stable CNT cathode, can be fabricated entirely in ambient conditions employing only dry and solution processing.

CNT sheets are not intrinsically good cathodes, as they require n-type doping to decrease the work function in order to collect electrons from the photoactive region of a solar cell[10]. Electric double layer charging in an electrolyte, such as an ionic liquid, can be used to shift the work function of CNT electrodes[11–14].

As described in a preceding paper[15] and depicted in **Figure 2**, when the gate voltage (V_{Gate}) is increases, the work function of the CNT common electrode is decreased, creating electrode asymmetry. This prevents hole collection from the OPV's donor in favor of collecting electrons from the OPV's acceptor, and the devices turn ON, changing from inefficient photoresistor into photodiode[15] behavior. It should also be noted that the energy used to charge the device and the power lost due to gate leakage currents is trivial compared to the power generated by the solar cell[15]. Ionic gating of CNT electrodes has a large effect on the work function due to the low density of states and the high surface area to volume ratio in CNT electrodes. Similar methods have been used to enhance a Schottky barrier at the interface of CNT with n-Si[16].

Protocol

1. Indium Tin Oxide (ITO) Patterning and Cleaning

NOTE: Use 15Ω/□ ITO glass, and purchase or cut the ITO glass into sizes suitable for spin coating and photolithography. It is most efficient to perform steps 1.1-1.7 on a piece of glass as large as possible, and then cut it into smaller devices. Also note that steps 1.1-1.7 require the ITO glass to be oriented with the ITO-side up. This can be checked easily with a multimeter's resistance setting.

1. Spin coat 1 ml of S1813 positive photoresist onto the ITO-side of the ITO glass at a rate of 3,000 rpm for 1 min. Use more resist for larger pieces of glass, make sure the entire glass is coated, and remove any bubbles before starting the spin coater.
2. Anneal the resist coated glass, on a hot plate, at 115 °C for 1 min.
3. Load the sample and the photomask onto the contact aligner.
4. Expose the photoresist coated ITO glass for an appropriate time. The exposure time is around 10 sec, but vary this time based on the UV lamp intensity, photoresist type, and thickness.
5. Develop the UV-exposed substrates in MF311 developer. A spin processor's automated process produces the best and most repeatable results, but development can be done manually as followed.
    1. Submerge the UV-exposed substrates for 1 min in the developer, followed by rinsing in deionized (DI) water and drying with a nitrogen gun. Because the developer loses strength quickly, replace the developer between samples, or alternatively increase the development time when reusing developer.

6. Etch the ITO substrates in concentrated hydrochloric acid (HCl). This takes between 5-10 min depending on the concentration of the HCl. Rinse in DI water, dry, and test the resistivity of the etched portions with a multimeter. If any conductivity remains, etch for a longer time.
7. Once the etching is complete, remove the photoresist with acetone. Note that prompt removal of the photoresist prevents residual HCl from over-etching the patterned ITO.
8. If needed, cut the etched ITO glass substrates into device sizes.
9. Clean the ITO substrates in a bath ultrasonicator in a sequence of solvents - DI water, acetone, toluene, methanol, and finally isopropyl alcohol.

2. OPV Sub-cell Fabrication

1. Prepare P3HT:$PC_{61}BM$ solution.
   NOTE: For the most consistent results, prepare the solutions in a nitrogen environment. It is possible to follow this procedure in ambient conditions.
    1. Find and write down the mass of two clean, ~4 ml glass vial and their caps, and mark them with a permanent marker to distinguish them from another.
    2. In a nitrogen or argon glove box, transfer approximately 10 mg of poly(3-hexylthiophene-2,5-diyl) (P3HT) to one vial and approximately 10 mg of phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) to the other.
    3. Weigh the vials again to find the mass of the P3HT and $PC_{61}BM$.
    4. Transfer the vials with P3HT and $PC_{61}BM$ into a glovebox for the rest of the solution making process.
    5. Add a magnetic stir bar into each vial and then add enough chlorobenzene to each to create 45 mg/ml solutions.
    6. Place the solutions on a magnetic stirring hot plate at 55 °C for approximately 2 hr or until the solutes have completely dissolved.
    7. Mix equal volumes of the P3HT and $PC_{61}BM$ solutions together, and let the mixed solution stir for another hour prior to use.

2. Prepare PTB7:$PC_{71}BM$ solution.
    1. Repeat steps 2.1.1 to 2.1.4 with poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) and phenyl-7,1-butyric acid methyl ester ($PC_{71}BM$) instead of P3HT and $PC_{61}BM$.
    2. Make a mixture of 3% by volume 1,8-diiodooctane (DIO) in chlorobenzene. This mix is called DIO-CB.
    3. Add a magnetic stir bar into each vial and then add enough DIO-CB to the PTB7 vial to have a 12 mg/ml solution and enough DIO-CB to the $PC_{71}BM$ vial to have a 40 mg/ml solution.
    4. Let these solutions stir on a hot plate at 70 °C for two days.
    5. Mix the solutions in a weight ratio of PTB7 to $PC_{71}BM$ of 1 to 1.5.
    6. Let the mixed solution stir for another hour at 70 °C prior to use.

3. Filter poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) through a 0.45 µm pore size nylon filter. Note this procedure uses P VP AI4083.
4. Spin Coat Active layers.

1. Place cleaned ITO substrates, ITO-side up, into a UV-Ozone cleaner for 5 min.
2. Spin-coat 120 µl of the filtered PEDOT:PSS onto UV-ozone treated, patterned ITO- glass substrates at 3,000 rpm for 1 min. This should yield a 30 nm thick layer.
3. Anneal the PEDOT:PSS coated ITO substrates for 5 min at 180 °C.
4. Spin-coat 70 µl of the mixed P3HT:$PC_{61}BM$ solution onto PEDOT:PSS coated ITO substrates at approximately 1,000 rpm for 1 min. Vary the rate as needed to deposit a 200 nm thick active layer.
5. Anneal the P3HT:$PC_{61}BM$ coated substrates at 170 °C for 5 min. The results may vary on optimal annealing temperature.
6. Spin-coat 70 µl of the mixed PTB7:$PC_{71}BM$ solution onto PEDOT:PSS coated ITO substrates at approximately 700 rpm for 1 min. Vary the rate as needed to deposit a 100 nm thick active layer.
7. Load the PTB7:$PC_{71}BM$ coated substrates into a high vacuum ($< 2 \times 10^{-6}$ Torr) chamber to remove the residual DIO. Typically, leave the samples in the chamber O/N.

3. Fabricate the Tandem Device

1. Laminate CNT electrodes.
    1. Cut the PTB7 and P3HT substrates in half to make a tandem device. A specialized ITO pattern would not require this step. The ITO pattern should have at least two parallel ITO electrodes extending from one edge to one mm away from the other.
    2. First prepare the PTB7 and P3HT coated substrates by wiping away polymer and PEDOT from the edges of the glass, and expose the ITO strip which will be used as the common electrode as seen in the first panel of **Figure 1**.
    3. Laminate the CNT common electrode on top of the PTB7 and P3HT electrodes. Apply a SWCNT film by placing the CNT side of the filter paper on the device, pressing gently, and then peeling the filter paper away. This is shown in the second panel of **Figure 1**.
    4. Densify the CNT electrode onto the surface by applying methoxy-nonafluorobutane ($C_4F_9OCH_3$) (HFE) and by coating the CNT with a small amount of the liquid and then letting it dry off.
    5. Wipe away the polymer and CNT on top of the ITO and glass which will have the gate electrode as shown in the third panel of **Figure 1**. Remove all the polymer from the glass to prevent gate leakage with a razor blade.
    6. Laminate the CNT gate electrode onto the cleaned area of the PTB7 and P3HT coated substrates. Laminate the MWCNT by pulling from the edge of the MWCNT forest with a razor blade and let the sheet stand freely between some capillary tubes. Pass the device through the freestanding sheet to laminate the CNT onto the device. The gate electrode should have 2-3 times the number of layers as laid onto the common electrode.
    7. Densify the gate electrode with HFE.

2. Place a small drop (≈10 µl) of ionic liquid, *N,N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium tetrafluoroborate, DEME-BF_4, on top of both CNT electrodes of one of the substrates.
3. Carefully place the substrate without ionic liquid on top of the substrate with ionic liquid with the common and gate electrodes on top of each-other. This is shown in the last panel of **Figure 1**.
4. Place a photomask with an aperture size smaller than the electrode size over the active area. Use small clips to hold the photomask in place as well as to hold the device together during testing.

4. Measure the Device

1. Transfer the device into the measurement glovebox.
2. Make the electrical connections.
    1. Connect the gate power supply between the common electrode and the gate electrode with the common as ground.
    2. Connect the two ITO anodes to wires which are connected to a switch which allows selection of either anode or both anodes.
    3. Connect the output of the switch to the input of the source measure unit.
    4. Connect the ground of the source measure unit to the common electrode.

3. Measure the device's IV characteristics by repeating the following steps for ascending V_{Gate}.
    1. Set V_{Gate} to the next value, starting from V_{Gate} = 0 V to V_{Gate} = 2 V in increments of 0.25 V.
    2. Wait 5 min or until the gate current is stabilized. Ideally, the gate current should stabilize around 10s of nanoamperes.
    3. Set the switch to both sub-cells.
    4. Open the lamp shutter.
    5. Run a voltage sweep on the source measure unit from -1 volt to +1 volt at about 100 increments or more.
    6. Run a voltage sweep from +1 volt to -1 volt.
    7. Close the lamp shutter.
    8. Run the voltage sweeps again.
    9. Set the switch to the front sub-cell.
    10. Repeat steps 4.3.4 to 4.3.8.
    11. Set the switch to the back sub-cell.
    12. Repeat steps 4.3.4 to 4.3.8.

4. Calculate device parameters.
    1. Find the short circuit current (J_{SC}) of each sub-cell at each V_{Gate} by finding the current produced by the device when the voltage across the sub-cell is 0 V.
    2. Find the open circuit voltage (V_{OC}) of each sub-cell at each V_{Gate} by finding the voltage produced by the device when the current through the sub-cell is 0 A.
    3. Find the maximum power output from the solar cell by multiplying each voltage value with each current value and selecting the maximum (most negative) value. This assumes that one measures photo-generated current as negative current.

4. Find the power conversion efficiency (η) by dividing the maximum power by the input light power.
5. Find the filling factor (FF) by dividing the maximum power by the product of J_{SC} and V_{OC}.

Representative Results

A tandem device formed from differing polymers, particularly polymers of significantly differing band gaps, is of practical interest as these devices can absorb the largest spectral range of light. In this device structure, the PTB7 sub-cell is the back cell and P3HT is the front sub-cell. This is intended to absorb the greatest amount of light as the P3HT sub-cell is largely transparent to the longer wavelength light absorbed by the PTB7 sub-cell. For the sake of clarity, the solar cell parameters, V_{OC}, J_{SC}, FF, and η will be decorated with a superscript ^{T}, ^{F}, or ^{B} when referring to the tandem, front or back cell respectively. **Table 1** shows these abbreviations.

A selection of current voltage curves for the device are depicted in **Figure 3**, and extracted solar cell parameters in **Figure 4**. It is observed that the PTB7 sub-cell (back) turned ON at a much lower V_{Gate} than the P3HT sub-cell (front). **Figure 4** shows that the PTB7 cell begins to turn ON at V_{Gate} = 0.5 V and peaks around V_{Gate} = 1.5 V. The front sub-cell shows signs of turning ON around V_{Gate} = 1.0 V, but does not fully turn ON below V_{Gate} = 2.0 V. V^{T}_{OC} and FF^{T} mimic the behavior of the worse sub-cell, being slightly higher than the front sub-cell for V_{Gate} < 2.0 V and slightly higher than the back cell for V_{Gate} > 2.0 V. J^{T}_{SC} is far less than the sum of J^{F}_{SC} and J^{B}_{SC} for V_{Gate} < 1.5 V, after which point the current addition is quite good. η^{T} is less than the greater of η^{F} or η^{B} for all V_{Gate} except at 1.5 V.

The poor addition of current and efficiency for low V_{Gate} appears to be due to the front sub-cell acting as a shunt in its OFF state. This is seen from the highly linear curves of the front cell and the tandem at V_{Gate} = 1.5 V in **Figure 3**. Conversely, after the PTB7 back cell has degraded, (at V_{Gate} = 2.25 V), it still maintains a diode characteristics, as shown by the curve in **Figure 3**, and thus does not act as a shunt. This results in addition of J_{SC}, but V^{T}_{OC}, FF^{T} and η^{T} are reduced due to the low V^{B}_{OC}. While the process draws robustness from its simplicity, there are variations due to the manual processing and batch-to-batch variations in materials. This can result in shifts in turn on voltage of ±0.25 V and peak efficiency by ±0.5%. This variation can be decreased with a more automated process.

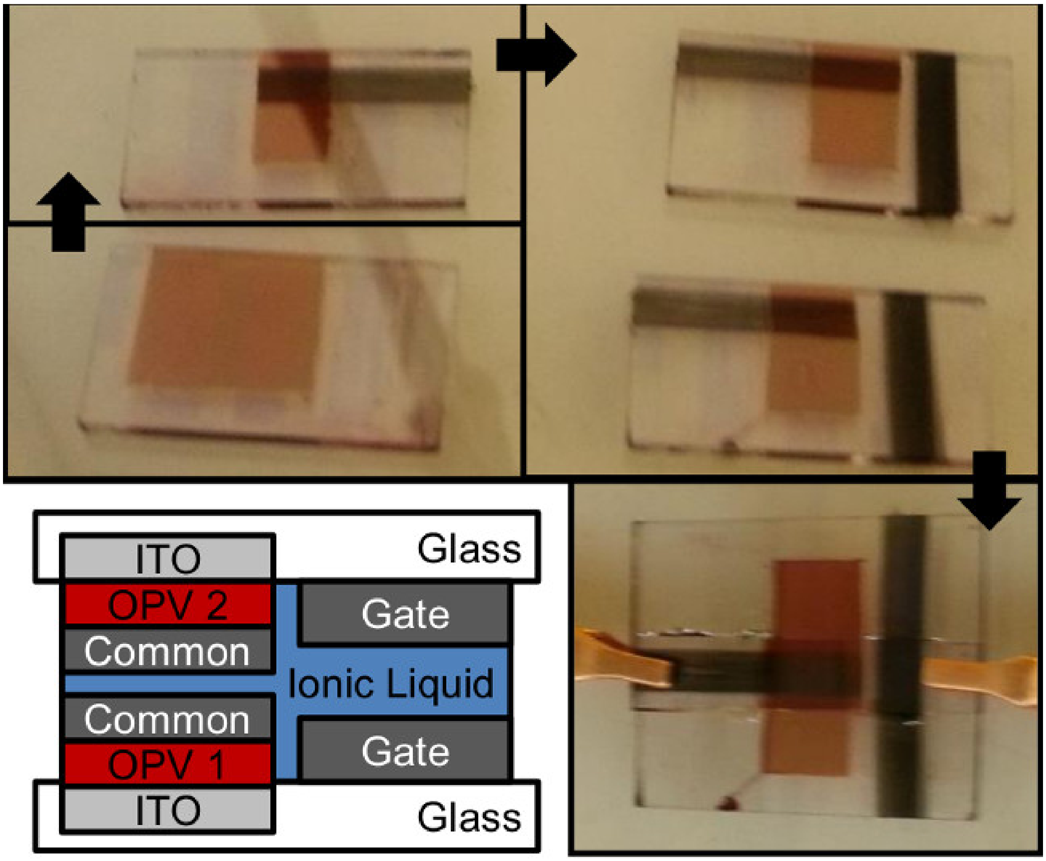

Figure 1. Tandem device design process. The fabrication and lamination process used in building the ionically-gated tandem OPV, with arrows depicting the sequence. A diagram of the final device structure is shown on the bottom left corner. Please click here to view a larger version of this figure.

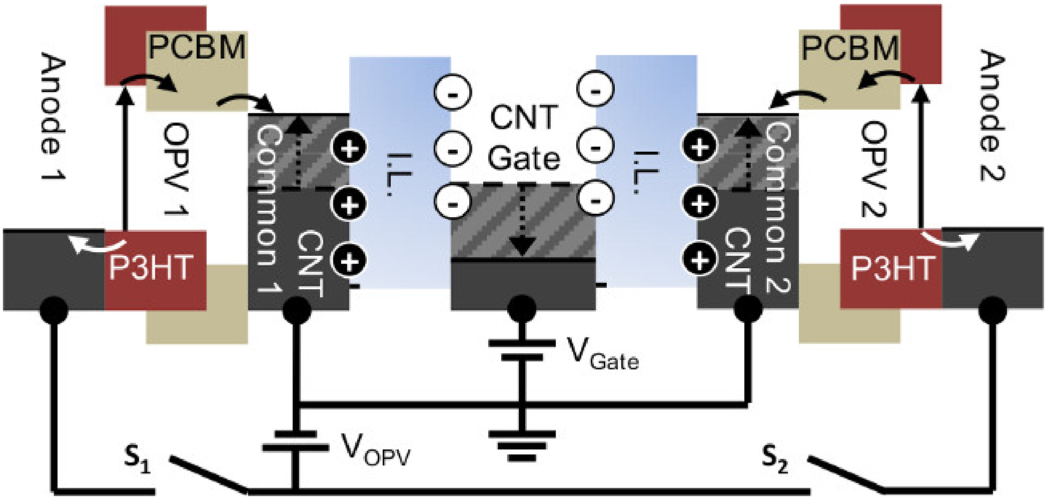

Figure 2. Tandem device band and electrical diagram. The approximate band diagram of the tandem device is shown along-side the electrical diagram of the device. The shaded regions with arrows on the CNT electrodes show the shift in work function. The solid lines and circuit elements below show the electrical connections. Please click here to view a larger version of this figure.

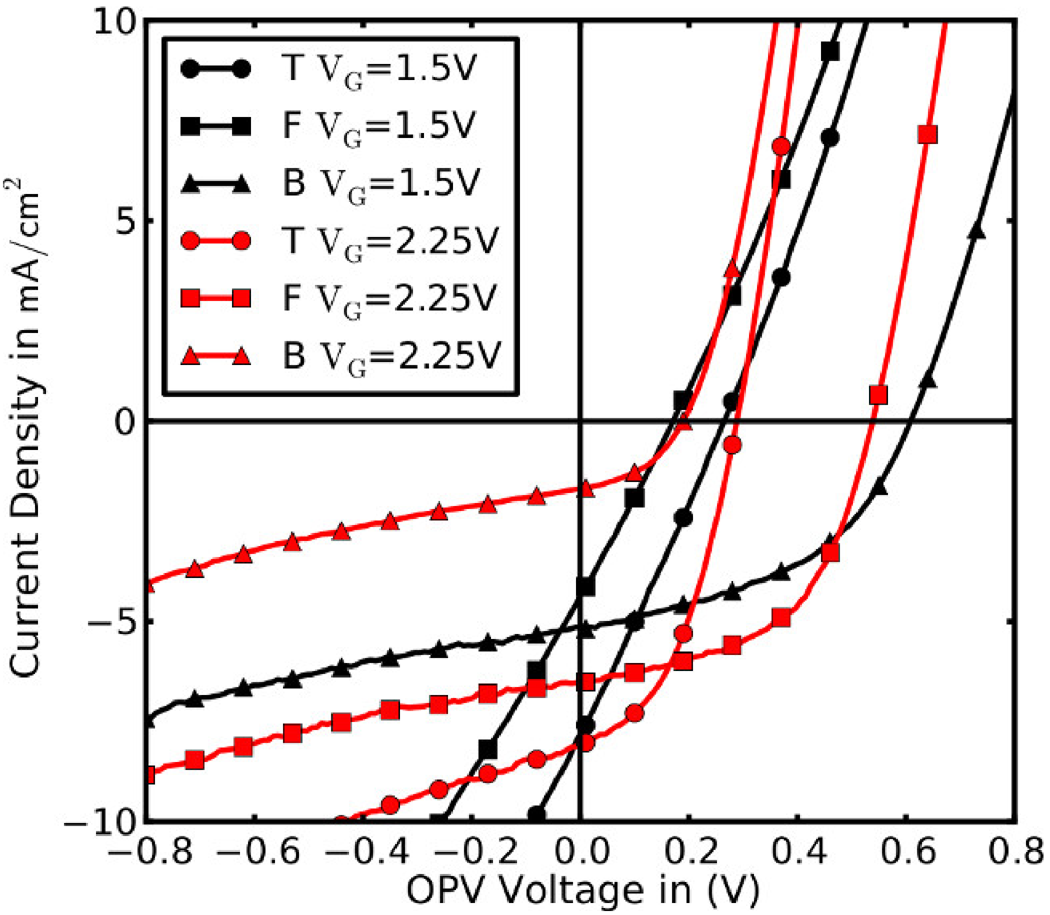

Figure 3. Selected IV curves. IV curves for a V_{Gate} (1.5 V) in which the back (PTB7) cell shows its best performance and a higher V_{Gate} (2.25 V) in which the front (P3HT) cell shows its best performance. 'T' and circles denote the tandem curve, 'F' and squares the front, and 'B' and triangles the back.

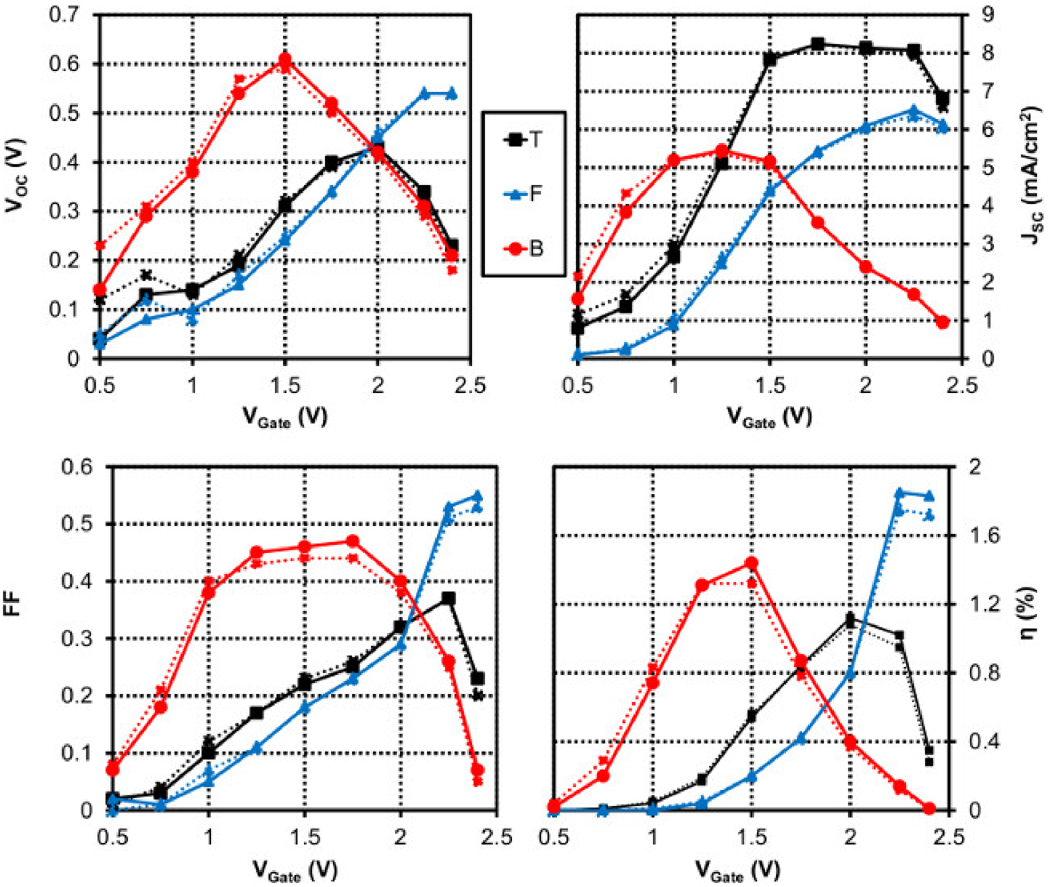

Figure 4. Device parameters. Solar cell parameters extracted from IV measurements from V_{Gate} = 0.5 V to V_{Gate} = 2.25 V. 'T' and black squares denote the tandem curve, 'F' and blue triangles the front, and 'B' and red circles the back. The dotted lines show results for descending voltages sweeps of the OPV device while the solid lines show the ascending results.

OPV Parameter	**Sub-cell measured**			
		Tandem	**Front**	**Back**
	V_{OC}	V^T_{OC}	V^F_{OC}	V^B_{OC}
	J_{SC}	J^T_{SC}	J^F_{SC}	J^B_{SC}
	FF	FF^T	FF^F	FF^B
	η	η^T	η^F	η^B

Table 1. Parameter abbreviations. Summarized solar cell parameter abbreviations. Superscripts, ^{T}, ^{F}, and ^{B} denote tandem, front and back respectively.

Discussion

The results highlight a few considerations when designing parallel tandem solar cells. Notably, if one of the sub-cells is performing poorly, tandem performance in negatively affected. The results show that there are two main effects. If one sub-cell is shorted, *e.g.*, shows ohmic behavior, the FF^T will be no higher than the FF of the bad sub-cell. J^T_{SC} and V^T_{OC} will be similarly affected. This is the case when V_{Gate} is low and the P3HT sub-cell has not turned ON.

Conversely, if one sub-cell has good diode properties, but low V_{OC} or J_{SC}, then J^T_{SC} is nearly the sum of J^F_{SC} and J^B_{SC}. However, if there is a large difference between each sub-cell V_{OC}, then V^T_{OC} is nearly equivalent to the lesser V_{OC}. This performance is demonstrated when V_{Gate} is high and the PTB7 cell has turned off. The η^T can be somewhat higher in the case, but is still likely to be less than that of the better sub-cell alone.

The back sub-cell turning on earlier than the front sub-cell was unexpected as the sub-cells share gate and common electrodes. The work function of their cathode, and therefore the degree of electrode asymmetry between the ITO and cathode, should be identical. Furthermore, the back sub-cell shows a higher V_{OC} than the front sub-cell and should require greater electrode asymmetry with respect to work function than the front sub-cell, and thus a larger V_{Gate} before turning on.

Given the lower HOMO level of the PTB7 polymer, it is possible that suppression of hole injection/extraction occurs more rapidly in PTB7, and thus the device turns on at a lower V_{Gate}. Other effects to consider are the fact that PTB7 is a copolymer, which is a polymer composed of alternating donor and acceptor units. This might have an impact on the interface dipoles generated between the polymer and the CNT common electrode.

The procedure described in this text is applicable to applications which adhere to the following constraints. The semiconducting active material must not be soluble or adversely affected by the ionic materials. In the case of light emitting or photovoltaic devices, the anode and semiconducting layers should not be opaque in the same spectral regions. Given these constraints, it is possible to apply these techniques to organic light emitting diodes, organic field effect transistors, and similar inorganic devices.

In conclusion, a parallel tandem device fabrication method that possesses benefits over conventional processing methodologies is described. The method requires no vacuum processing, is scalable, can be performed in ambient conditions, and each active layer is fabricated in an optimal manner, reducing the incidence of shorts and simplifying processing. Salient features are identified in the operation of parallel OPV tandems. While the overall efficiencies are somewhat low, further improvements can be made by optimizing photoactive layers and CNT electrodes. Additionally, if sub-cell turned on at the same time, an η^T over 3% would be observed.

Disclosures

The authors have nothing to disclose.

Acknowledgements

Support for this work was provided by DOE STTR grant DE-SC0003664 on Parallel Tandem Organic Solar Cells with Carbon Nanotube Sheet Interlayers and Welch Foundation grant AT-1617. The authors thank J. Bykova for providing CNT forests and A. R. Howard, K. Meilczarek, and J. Velten for technical assistance and useful discussions.

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