Linking Vertical Bulk-Heterojunction Composition and Transient Photocurrent Dynamics in Organic Solar Cells with Solution-Processed MoO$_x$ Contact Layers

Bertrand J. Tremolet de Villers,* Roderick C. I. MacKenzie, Jacek J. Jasieniak, Neil D. Treat, and Michael L. Chabinyc*

1. Introduction

Organic photovoltaics (OPVs) now have power conversion efficiencies around 10% and continue to evolve towards being a viable low-cost energy technology. [1] Of these, bulk heterojunction solar cells (BHJs) with nanoscale phase-separated domains of electron donors and acceptors have the highest efficiency. However, controlling the nanoscale mixing still presents a significant challenge. Interfacial interactions between the BHJ and the electrodes also have a key role in defining the organization of the BHJ. Transition-metal oxides are now widely used as contact layers in BHJs and recombination layers in multijunction solar cells. [2,3] When used as contact layers, metal oxides can modify the work-function of the electrodes, providing charge-selective blocking properties, [3–7] and they increase the operational lifetime of the device. [8–10] However, the variability of their surface chemistries and electronic structure make it difficult to predict their interactions with organic semiconductors and the impact on power conversion efficiency. [11]

Here, we look at an idealized system to consolidate the relationships between the processing conditions of a metal oxide interlayer, molybdenum oxide (s-MoO$_x$), the morphology of the bulk-heterojunction. By selecting either a low- or high-temperature annealing (70 °C or 150 °C) for the s-MoO$_x$ layer, a well-performing device is fabricated with an ideally interconnected, high-efficiency morphology, or a device is fabricated in which the fullerene phase segregates near the hole extracting contact preventing efficient charge extraction. By probing the photocurrent dynamics of these two contrasting model systems as a function of excitation voltage and light intensity, the optoelectronic responses of the solar cells are correlated with the vertical phase composition of the polymer:fullerene active layer, which is known from dynamic secondary-ion mass spectroscopy (DSIMS). Numerical simulations are used to verify and understand the experimental results. The result is a method to detect poor morphologies in operating organic solar cells.

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Dr. B. J. Tremolet de Villers,[+] N. D. Treat, Prof. M. L. Chabinyc
Materials Department
University of California
Santa Barbara, CA 93106–5050, USA
E-mail: bertrand@mrl.ucsb.edu; mchabinyc@engineering.ucsb.edu
Dr. R. C. I. MacKenzie
Department of Mechanical, Materials and Manufacturing Engineering
Room B86, Coats Building
University Park
Nottingham, NG7 2RD, UK
Dr. J. J. Jasieniak,[++] Center for Polymer and Organic Solids
Physics Department
University of California
Santa Barbara, CA 93106, USA
[+]Present address: National Renewable Energy Laboratory, Golden, CO 80401, USA
[++]Present address: CSIRO Material Science and Engineering, Bayview Ave, Clayton, VIC 3168, Australia
solution precursors and cured at relatively low temperatures, compatible with roll-to-roll fabrication techniques. However, these processes result in morphologically and electronically disordered layers with uncertain optoelectronic properties.[16] Despite these difficulties, solution-processed metal oxides have proven to form high-performance BHJs. In some cases, non-ideal (s-shaped) current–voltage characteristics are observed in BHJ solar cells and the origin is difficult to uncover using steady-state measurements.[17–19]

Information about the underlying physical processes defining cell operation can be gained from studying dark and light steady-state current–voltage (J–V) measurements.[20,21] Dark J–V measurements provide information about the ideality factor, which is defined by the distribution of trap states through which recombination occurs within a device.[22–25] Similarly, light J–V curve measurements provide insight into the underlying photophysical processes such as charge generation. However, more detailed information about transport and recombination processes can only be obtained through transient measurements.[26–29] In recent years, several transient photocurrent techniques have been developed to investigate charge transport and recombination in OPV devices. Both photogenerated charge extraction with a linearly increasing voltage pulse (photo-CELIV) and transient photocurrent techniques have been used to study recombination in OPV devices.[17,29–31] Charge extraction (CE) and transient photocurrent measurements have been used to study the role of energetic disorder, particularly in the low-energy tail of the density-of-states (DoS) of polymer:fullerene OPVs.[32,33] Pulsed light transient photocurrent measurements have been used to investigate charge trapping and recombination in a variety of organic and hybrid solar cells.[34–37] To quantitatively understand the results from such transient experiments, it is important to know the structure of the BHJ layer and thereby gain information about the charge transport pathways. Until now, the link between device structure and transient photocurrent experiments of solution-processed OPVs has not been established.

Model systems with controlled morphology and common electrode layers can help untangle the origin of non-ideal current–voltage characteristics in BHJs. It is known that device performance can depend on the distribution of the electron-donor and acceptor molecules within a BHJ organic solar cell.[38–40] There has been work to form intentionally stratified structures by physical transfer to test hypotheses about charge extraction,[41] but here we study structures formed spontaneously during solution casting. In a previous study, we found the shape of the steady-state J–V curve of a P3HT:PCBM BHJ solar cell utilizing an s-MoO₃ hole-contact layer depends on the temperature used to treat the s-MoO₃.[41] We found that the vertical composition of the BHJ is affected by the heat treatment of the s-MoO₃ before spin-casting of the active layer. Surprisingly, the electronic structure of the s-MoO₃ layer determined by ultraviolet photoemission spectroscopy (UPS) is not significantly changed by varying the s-MoO₃ annealing temperature. Thus, the system here provides an important model system of a vertically segregated BHJ that can be used to understand the impact of vertical composition of the BHJ on the optoelectronic response of the solar cell.

Our approach here is to use solution-processed molybdenum oxide (s-MoO₃) interlayers to control the vertical morphology of P3HT:PCBM BHJ solar cells. We fabricated two model devices, one with the MoOₓ interlayer annealed at 70 °C [s-MoOₓ(70 °C)] and one with the interlayer annealed at 150 °C [s-MoOₓ(150 °C)]. Using DSIMS, we have demonstrated that when the s-MoOₓ layer is annealed at 150 °C, a PCBM layer builds up at the hole-extracting contact.[42] Comparing experimental measurements and simulations of both the steady-state and transient photocurrent responses of devices with ideal and non-ideal morphologies, we observe characteristic photocurrent features of a device with charge-carrier extraction problems. Thus, we demonstrate that photocurrent transients can be used as a signature of the vertical composition of the BHJ in functioning devices.

2. Results and Discussion

2.1. Vertical Phase Composition of Model BHJ Solar Cells

To form BHJs with different vertical compositional profiles, we fabricated BHJs with an s-MoOₓ contact layer. An s-MoOₓ layer was deposited by spin-casting MoOₓ precursor solution onto clean indium tin oxide (ITO) substrates. The s-MoOₓ layer was then annealed at a temperature, T = Δt. In this work, we used two different s-MoOₓ annealing temperatures, T = 70 °C and Δt = 150 °C. A P3HT:PCBM photoactive layer was then spin-cast onto the annealed s-MoOₓ layer. An aluminum cathode was thermally deposited on top of the P3HT:PCBM and the device was subsequently annealed at Δt = 150 °C. More details on device fabrication can be found in ref. [13] and in the Supporting Information; more details about the electronic structure of solution-processed MoOₓ are described elsewhere.[13]

The vertical composition of these two devices was determined by dynamic secondary ion mass spectrometry (DSIMS) in a separate study investigating how the surface of the solution-processed MoOₓ affects the BHJ vertical phase composition.[42] The outcome of that work that is relevant here is depicted in Figure 1. It shows the volume fractions of P3HT and deuterated-PCBM in the blend film as a function of depth from the surface of the film down to the organic/MoOₓ interface as measured by DSIMS. When the s-MoOₓ is treated at 70 °C [s-MoOₓ(70 °C)], the P3HT:PCBM adopts a favorable blend composition for operation (red traces). At the cathode/active layer interface, the DSIMS profile shows a very thin (<5 nm) layer of P3HT and just below that there is fullerene enrichment. Further into the film, the volume fraction of PCBM decreases until the distribution of P3HT and PCBM becomes homogeneous, as represented by the flat part of the trace showing a constant fullerene volume fraction. This composition profile has been observed previously and will not impede extraction (or injection) of electrons.[43]

When the s-MoOₓ is treated at 150 °C [s-MoOₓ(150 °C)], the DSIMS profile (black traces in Figure 1) reveals a different vertical compositional profile compared to the devices with s-MoOₓ(70 °C), particularly at the active layer/MoOₓ interface. While accumulation of fullerene takes place at the top of the film near the cathode interface and the center of the
film contains a constant volume fraction of each component, the composition of the film near the organic/anode interface is greatly enriched in fullerene. We found that within approximately 10 nm of the s-MoO$_x$(150 °C)/ITO substrate, the polymer:fullerene active layer is composed of up to 75% PCBM, by volume fraction.

2.2. Vertically Phase Separated Structures Lead to S-Shape J–V Characteristics

Solar cells with significant enrichment of PCBM at the s-MoO$_x$ anode show drastically different current–voltage characteristics upon illumination than those without (Figure 2). While the device using s-MoO$_x$(70 °C) (red curves) exhibits relatively ideal characteristics, a device with s-MoO$_x$(150 °C) (black curves) shows s-shaped J–V curves resulting in a low fill factor (Figure 2a). Figure 2b,c show how the short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$), respectively, change as the light intensity is varied. In an ideal solar cell, $J_{sc}$ should scale linearly with the light intensity at moderate illumination (1 sun and below). While both types of cells show nearly linear behavior at low intensity illumination, at higher light intensities, e.g., $I > 10\%$ of one sun, significant deviation from linearity occurs for the device with s-MoO$_x$(150 °C). See Table S1 in the Supporting Information for tabulated $J_{sc}$, $V_{oc}$, FF, and $\eta_{max}$ values under varying light intensities.

The steady-state J–V characteristics of the s-MoO$_x$(70 °C) and s-MoO$_x$(150 °C) show strikingly different behavior due to the vertical composition. Having mostly fullerene at the anode interface represents a significant barrier to the hole extraction (and injection), as holes are primarily transported through the P3HT phase. This profile provides an explanation for why the steady-state J–V curves of s-MoO$_x$(150 °C) devices show a pronounced kink (see Figure 2). Holes cannot be extracted from the device as easily as electrons can and therefore a significant space-charge develops within the active layer. This result is larger than previous observations of the J–V characteristics with intentionally placed layers, e.g., a thin layer of P3HT at the cathode.$^{[41]}$

S-shape J–V curves have been described in several other organic and hybrid organic-inorganic solar cells, including ones with P3HT:PCBM active layers.$^{[17–19,44–46]}$ However, there is no single cause for the appearance of solar cells with non-ideal J–V characteristics and low-fill-factors. Bulk effects, such as an imbalance of the electron and hole mobilities, have been suggested as well as energetic offsets at electrode interfaces that are intrinsic to the materials or caused by degradation. The vertical distribution of phases in the blend-film active layer has been shown to matter in some cases, but not have significant effects in others, depending on whether the donor or acceptor accumulates at an interface.

Here, we show that excess fullerene at the cathode is the dominant cause of the distorted J–V response. Despite the differences in steady-state behavior near the open-circuit voltage, the internal microstructure of the bulk in devices with low and high temperature s-MoO$_x$ allows essentially the same charge generation efficiency in both cases. The current density for both sets of curves is roughly identical at a large negative bias, e.g., when $V_{app} < -1.0$ V, but differs significantly as the applied voltage increases toward open-circuit conditions. P3HT:PCBM BHJs have not been reported to exhibit field-dependent charge generation.$^{[47,48]}$ This result therefore implies a field-dependent barrier to charge extraction exists in our “s-curve” device while the bulk of the BHJ is similar in both cases. In other words, holes and/or electrons cannot be collected easily at the electrodes without a large enough internal field to extract the carriers. Furthermore, the onset of the J–V curve “kink” shifts with light-intensity as the voltage is swept from negative to positive bias. This indicates the kink is a function of the photogenerated charge density. Both the electric-field dependence and carrier concentration effects can be explained by the presence of a charge extraction barrier. During device operation, this barrier results in the buildup of one type of charge carrier in the film (holes in our case) that then creates a space-charge inhibiting current flow. To better understand these results, we have performed transient photocurrent measurements and modeled the device behavior with a numerical drift-diffusion simulator.

2.3. Transient Photocurrent Response

2.3.1. Light-intensity Dependence of the Transient Photocurrent

The transient response of BHJs to illumination can reveal the dynamics of how the steady-state characteristics are reached. The transient current responses of the devices to 500-μs pulses of light from an array of red light-emitting diodes (LEDs), whose output is centered around 625 nm, are shown in Figure 3. The light intensity is varied from one sun equivalent down to 10% of one sun, which varies the charge carrier concentration in the devices. See the Experimental Section and Figure S4 (Supporting Information) for more details of one-sun equivalence. In both solar cells the BHJ active layer
is the same thickness so the geometric capacitance is equal for both devices.

First, we examine the transient response of the device that produces $J-V$ curves without the s-shape. For the device made with s-MoO$_x$ (70 °C), the photocurrent dynamics are mostly independent of the light intensity, as shown in Figure 3a. Upon turn-on of the light, the photocurrent increases quickly, reaching a steady-state value within the first 25 μs. The rise and fall of the photocurrent following turn-on/turn-off of the LEDs are shown in the insets of Figure 3a, in which the photocurrent has been normalized to the mean value of the current from 450–500 μs when steady-state has been established. In the s-MoO$_x$ (70 °C) device, the photocurrent rise slows slightly as the light is decreased indicating a dependence of the rise on the photo-generated charge concentration. This is evidence of trap-filling. When the light is turned off, the photocurrent decays quickly to zero. As is the case for the rise, the decay slows down at the lowest light intensity (10% of one sun), possibly due to less recombination in the device at low light intensity. This is supported by the higher fill factor of the steady-state $J-V$ curve at this light intensity (Table S1, Supporting Information). That the s-MoO$_x$(150 °C) device exhibits a significant s-shape indicating charge extraction problems. In Figure 2b, the photocurrent at one sun does not rise monotonically to its steady-state value within the first 25 μs. Instead, the current quickly overshoots steady-state by $\approx 3$ times at its peak, before settling down to a constant value after $\approx 80$ μs. When the excitation light intensity is reduced to 40% of one sun, an overshoot peak is also observed, albeit with a lower peak height, approximately 1.8 times the...
that opposes the photocurrent and brings the devices towards open-circuit conditions (around +0.5 V). Comparing the shapes of the transients for s-MoO$_x$(70 °C) and s-MoO$_x$(150 °C) devices, Figure 4 a,b, respectively, one sees the former is relatively independent of bias while the latter is greatly affected by the applied electrical bias.

The early-time dynamics after turn-on and the photocurrent decay after turn-off of the excitation light are rich in information. As shown in the insets of Figure 4 a, we found that for the s-MoO$_x$(70 °C) device, the current always rises monotonically to its steady-state value, independent of the applied bias. Sweeping the applied bias towards a larger positive value reduces the internal electric field and causes the photocurrent rise to slow down. Similarly, the decay of the photocurrent after light turn-off retains a constant shape at all negative voltages and only changes shape when the polarity of the applied bias is switched to positive. Retarding of the rise/fall time of the current indicates that the device requires a longer time to reach equilibrium. A possible explanation for this could be the higher recombination rate in forward bias annihilating many of the photogenerated carriers and slowing down the trap filling process.

As was the case with varying the light intensity, changing the applied bias (while maintaining a constant one-sun illumination intensity) has a greater effect on the s-MoO$_x$(70 °C) device than the one with MoO$_x$(70 °C). Figure 4b shows that at very negative voltages, $V_{app} \leq -0.7$ V, the photocurrent behaves similar to that of the s-MoO$_x$(70 °C) device in that it exhibits a smooth rise to steady-state and only changes shape when the polarity of the applied bias is switched to positive. The early-time dynamics after turn-on and the photocurrent decay after turn-off of the excitation light are rich in information.

Interpretation of the origin of the shape of photocurrent transients is challenging. Similar transient peaks have been observed previously in a P3HT:polyfluorene polymer blend solar cell.\[49\] In that case, the transient peak was attributed to a build-up of trapped electrons near the anode due to a slower electron trapping/de-trapping process. This resulted in a lower internal electric field near that interface; thus enhancing recombination and reducing exciton dissociation. Here we know from morphological measurements that excess PCBM exists at the anode and this supports the claim that the peak corresponds to poor extraction of holes caused by the energetic barrier at the s-MoO$_x$(150 °C)/ITO interface.

2.3.2. Voltage Dependence of the Transient Photocurrent

In addition to the light intensity dependence of the photocurrent with pulsed illumination, we have also investigated the effects of an applied voltage on the transient current. Figure 4 describes the photocurrent transient response of the devices under the influence of an external voltage bias, illuminated with a light intensity equal to one sun. As before, the rise and fall of the transients are shown in absolute scale and normalized to the mean value of the current from 450–500 μs, when steady-state has been established. The applied bias was varied from $-1.5$ to $+0.5$ V, thus manipulating the internal electric field within the device from one that facilitates drift of the charge carriers to their respective electrodes (at negative bias) to a field that opposes the photocurrent and brings the devices towards open-circuit conditions (around +0.5 V). Comparing the shapes of the transients for s-MoO$_x$(70 °C) and s-MoO$_x$(150 °C) devices, Figure 4a,b, respectively, one sees the former is relatively independent of bias while the latter is greatly affected by the applied electrical bias.

The early-time dynamics after turn-on and the photocurrent decay after turn-off of the excitation light are rich in information. As shown in the insets of Figure 4a, we found that for the s-MoO$_x$(70 °C) device, the current always rises monotonically to its steady-state value, independent of the applied bias. Sweeping the applied bias towards a larger positive value reduces the internal electric field and causes the photocurrent rise to slow down. Similarly, the decay of the photocurrent after light turn-off retains a constant shape at all negative voltages and only changes shape when the polarity of the applied bias is switched to positive. The early-time dynamics after turn-on and the photocurrent decay after turn-off of the excitation light are rich in information.

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Figure 4. Photocurrent transients as a function of applied voltage bias at illumination intensity equivalent to one sun. Transients are shown for a) 70 °C- and b) 150 °C-MoO$_x$ devices. The rise and decay of the photocurrent following turn-on and turn-off, respectively, of the light pulse are shown in the insets above the full photocurrent traces. In the insets, the traces have been normalized to the mean value of the current from 450–500 μs when steady-state has been established. Samples were illuminated with an array of fast-switching LEDs centered at 625 nm. Time = 0 is set to the onset of the 500-μs light pulse.

The photocurrent decay of the s-MoO$_x$(150 °C) device reveals an interesting phenomenon. As shown in the right inset of Figure 4b, initially the decay slows down as the magnitude of the negative voltage bias is reduced from −1.5 V to −0.3 V. This is the slowing of the decay due to the reduction of the electric field. The collected charge (time-integrated current) after turn-off of the light pulse is shown in Figure S5 (Supporting Information). However, at $V_{app} \geq −0.2$ V, the current initially decays quickly (and switches signs at more positive voltages) before slowly returning to zero. Due to the long lifetime of charge carriers in a P3HT:PCBM blend, the current can take 100 μs or longer to decay.\[26\] Numerical modeling shows that when the light is turned off, the electrons can leave the device very quickly, which accounts for the sudden drop in current. However, there remains a large reservoir of holes within the device that cannot escape due to the PCBM-rich blocking layer. Electrons are then drawn into the device to bring the device back to equilibrium by annihilating the holes. The height of the barrier dictates how large the reservoir of holes within the device is; the higher the barrier, the more holes are trapped in the device. Figure S6 (Supporting Information) shows the influence of barrier height on the magnitude of the spike.

3. The Physical Meaning of the Photocurrent Transients

To further interpret the physical origins of the changes in photocurrent signals between devices with varying vertical blend composition as described above, we performed a series of device simulations with and without a layer of PCBM close to the hole collecting contact. To simulate the device without the PCBM accumulation layer, an effective medium approximation was used where the LUMO and HOMO mobility edges were taken as −3.8 eV and −4.9 eV, respectively. Between the HOMO and LUMO, electron and hole traps were introduced as an exponential distribution decaying away from the band edge.\[48,50\] Poisson’s equation and the bipolar drift and diffusion equations were solved using a finite difference approach to describe electrostatic effects and carrier transport between the contacts. Carrier trapping and recombination within the device were described using the Shockley-Read-Hall recombination mechanism.\[52,51–54\] Both the electrical and optical models have been described in detail elsewhere.\[48,55,56\] To calibrate the model, it was fit to the experimental one-sun $J$–$V$ curve and short-circuit pulsed data at 0.4 and 1.0 sun of the device without the PCBM-rich layer, s-MoO$_x$(70 °C). The resulting simulated and experimental steady-state $J$–$V$ curves are plotted together in Figure 5 and the simulated transient data is plotted in Figure 6. The model parameters are listed in Table S2 (Supporting Information).
To understand the influence of the PCBM buildup near the s-MoO$_3$(150 °C) interface, a 10-nm thick layer of PCBM was inserted into the simulation 5 nm away from the anode. To simplify interpretation of the results, all material parameters of the pure PCBM layer (dielectric constant, electron and hole mobilities, etc.) were kept identical to that of the calibrated BHJ layer except for the HOMO level. The HOMO level was lowered until the simulated $J$–$V$ curves in Figure 5 resembled those from the s-MoO$_3$(150 °C) device at varying light intensities. The distribution of carrier-trapped states is plotted in Figure 6 a,b for the devices with and without the hole-blocking PCBM layer, respectively. The PCBM layer can be seen in Figure 6 b as a small energetic step. Although the difference between the HOMO of P3HT and that of PCBM is around 1.5 eV, it was found that we only needed an energetic step of 0.4 eV to reproduce the experimentally observed s-shaped $J$–$V$ curves. This suggests there is some percolation of charge through the barrier due to remaining domains of P3HT, consistent with the DSIMS profile that revealed ≈25% P3HT volume fraction in this region. In Figure S3 (Supporting Information) we show the effect of the energetic barrier height on the simulated $J$–$V$ curves. It was...
found that when this energetic step was increased, the voltage at which the short-circuit current resembled that of a device without a blocking layer moved to more negative voltages. This is because a device with a larger barrier requires a larger negative potential to efficiently extract the carriers from it. Figure 6d shows the simulated photocurrent response of the device with the PCBM layer. It can be seen that the addition of this layer also generates photocurrent transients very close to the experimentally-observed curves. This again suggests that the blocking layer is indeed the cause for the sharp spike at the beginning of the experimental transients and reduced steady-state current.

The transient data provides a measure of the recombination loss due to the presence of an effective barrier to extraction. Figure 7 plots the simulated charge density and recombination rate from a device with and without the hole-blocking layer in Figure 7a,b, respectively. It can be seen that in the device without the blocking layer, the transient oscillations die down after a few microseconds, as observed experimentally, and the charge density levels off at around 4 × 10^{20} m^{-3}. In the device with the PCBM-rich layer, the charge density steadily climbs more than an order of magnitude higher to a value of 2 × 10^{22} m^{-3} within 200 μs, and during this time the recombination rate also steadily increases. We now have enough information to explain the shape of the photocurrent transient from the device with the blocking layer. In a device with the PCBM layer, just after photoexcitation there is a high current spike because photogenerated electrons are initially free to produce current as the PCBM layer only blocks holes. Furthermore around 50% of the holes generated are able to surmount the PCBM barrier to produce current. Thus, the maximum observed photocurrent is around 75% of that one would expect from a device without a hole-blocking layer. As time passes, the hole population between the blocking layer and n-contact steadily builds due to the presence of the barrier. This increasing excess hole population causes increasing recombination within the device and a reduction in electron photocurrent. As the carrier population within the device becomes stable, the photocurrent levels off. Thus, the difference between the peak of the photocurrent transient and the stable current can be thought of as an estimate of the recombination losses due to the blocking layer.

The experimental data for the device with the hole-blocking morphology (Figure 7b) shows that the photocurrent spike broadens when the light intensity is reduced. We also observe this in the simulations (Figure 6d). This effect can be explained by the fact that at a low light intensity there are fewer photogenerated carriers so it takes longer for the device to reach a stable carrier density, hence the broader peak observed at low light intensity. This is shown in detail in Figure S1 (Supporting Information). As shown in Figure S2 (Supporting Information), simulations also confirm that a slow-down of the rise and fall in the photocurrent transients corresponds to either a low free-carrier mobility or a high number of trap states.

4. Conclusions

Model systems are valuable for understanding the impact of morphology on the current-voltage behavior of BHJs. We have studied the steady-state and transient J–V behavior of BHJs with spontaneously formed, stratified BHJs. Solution-processed MoO₃ provided a means to form BHJs with either ideal J–V characteristics or non-ideal characteristics due to accumulation of fullerene near the anode. Importantly, the vertical composition was verified and the electrode layers had identical electronic structure. This allowed changes in performance to be isolated to interfacial effects, revealing the behavior of BHJs that have barriers to extraction of holes at the anode solely due to processing methods. Experimentally measured and simulated microsecond photocurrent transients showed the device with PCBM accumulation at the s-MoO₃ hole-collecting interface displays a characteristic initial peak and subsequent reduction in photocurrent signal before reaching steady-state. This reduction in photocurrent enables an estimation of recombination losses due to the charge extraction barrier. Upon turn-off of the light, this device also showed unique decay dynamics in which the current dropped rapidly at first, then very slowly returned to zero. These signatures can be used to understand the J–V behavior of BHJs where
morphological characterization may be difficult, e.g., long-term studies of lifetime.

Our results underscore the importance of understanding how the composition at solution-processed recombination layers may differ from the bulk due to processing conditions. The heat treatment of the metal oxide, necessary for its electronic behavior, can have indirect effects on the morphological behavior of organic blends films deposited onto it, independent of how the organic layer is subsequently treated. This result may be of particular importance in multilayer tandem solar cells in which metal oxides are now frequently used as recombination layers. In a tandem cell, the rates of hole and electron extraction at the front and back cells must be balanced by the recombination of charges in the interlayer(s) between the cells. It is therefore critical to avoid charge extraction barriers in either of the individual photoactive cells. Thus, if metal oxides are to be used as the recombination layer materials, care must be taken to ensure they are not an indirect cause of an undesirable distribution in the active-layer phase composition.

Because fullerenes are known to nucleate and grow crystals at interfaces, the accumulation of fullerene at the anode of a BHJ is likely a long-term degradation mechanism.\[39,57\]. Our results here suggest that even if electrode layers do not undergo degradation, a morphological instability can lead to reduced fill-factors if extraction of carriers is impeded. We have presented a straightforward method that may be helpful for relating the photovoltaic response of the cell with such changes in vertical composition.

5. Experimental Section

**MoO\textsubscript{x}, Recipe and Device Fabrication:** Preparation of the MoO\textsubscript{x} precursor solutions and fabrication of the solar cell devices were carried out using the methods described in ref. [13] and details are included the Supporting Information.

**Dynamic Secondary-Ion Mass Spectroscopy (DSIMS):** In a companion paper, a detailed DSIMS study of the solar cells used here was performed.\[42\] Experimental details of the DSIMS measurements are described there and summarized in the Supporting Information.

**Pulsed LED Transient:** Pulsed LED illumination was used to study the transient photocurrent response of polymer:fullerene photovoltaics in a manner similar to previous work.\[53\] The solar cells were subjected to a square-pulse optical excitation provided by an array of fast-switching LEDs with an output wavelength centered around 625 nm. A pulse duration of 500 \(\mu\)s was chosen in order to ensure the photocurrent attained steady-state. The “off-time” between pulses was 1 s so that all photogenerated carriers had ample time to exit the device before the next excitation pulse. Photocurrent transients were measured as a function of excitation light intensity and applied voltage bias.

To set the light intensity of the LED array to “1 sun equivalent”, \(J_{sc}\) of the solar cells was first measured using a calibrated AM1.5 solar simulator. Next, the power supply controlling the LEDs was adjusted until the \(J_{sc}\), under illumination from the LEDs matched the \(J_{sc}\) measured with the solar simulator.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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