

Copyright © 2008. Reprinted from APPLIED PHYSICS LETTERS 93, 083305 .2008. Such permission of the American Institute of Physics does not in any way imply the American Institute of Physics endorsement of any of Institute of Microelectronics' products or services. Internal or personal use of this material is permitted. However, permission to reprint/republish this material for advertising or promotional purposes or for creating new collective works for resale or redistribution must be obtained from the American Institute of Physics by writing to [Rights@aip.org](mailto:Rights@aip.org).

## Efficient tandem organic solar cells with an Al/MoO<sub>3</sub> intermediate layer

D. W. Zhao,<sup>1,2</sup> X. W. Sun,<sup>1,2,a)</sup> C. Y. Jiang,<sup>1,b)</sup> A. K. K. Kyaw,<sup>1</sup> G. Q. Lo,<sup>1</sup> and D. L. Kwong<sup>1</sup>

<sup>1</sup>Institute of Microelectronics, A\*STAR (Agency for Science, Technology and Research), 11 Science Park Road, Science Park II, Singapore 117685, Singapore

<sup>2</sup>School of Electrical and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

(Received 13 June 2008; accepted 28 July 2008; published online 26 August 2008)

We report efficient tandem organic solar cells with an Al and MoO<sub>3</sub> intermediate layer. Such an intermediate layer with optimized thickness (1 nm Al and 15 nm MoO<sub>3</sub>) has high transparency (~98% in the range from 350 to 900 nm) and efficient charge collections to realize electric connection in series. For polymer-small molecule tandem cell, due to the summation (1.01 V) of the open-circuit voltages of individual cells and a short-circuit current density of 6.05 mA/cm<sup>2</sup>, a power conversion efficiency (PCE) of 2.82% was obtained under 100 mW/cm<sup>2</sup> illumination, which is larger than either of the individual cells. The PCE reached 3.88% when the tandem cell was illuminated under 300 mW/cm<sup>2</sup>. Additionally, we applied Al/MoO<sub>3</sub> intermediate layer to realize a solution-processed polymer tandem cell with a high PCE (2.23%). The thick MoO<sub>3</sub> (15 nm) provides a complete protection of the prior-deposited polymer layer from dissolving during the top cell polymer coating. © 2008 American Institute of Physics. [DOI: 10.1063/1.2976126]

Organic solar cells (OSCs) have attracted much attention in the past few years with their potential as a low-cost, easy-fabrication, and flexible alternative to traditional inorganic solar cells. The power conversion efficiency (PCE) of OSCs based on small molecules and polymers has reached 5%.<sup>1-4</sup> The tandem or stacked structure,<sup>5-10</sup> which consists of two or more cells with complementary absorption spectra, is believed to be an effective approach to improve the efficiency. In tandem OSCs, the intermediate layer is crucial and should possess the following properties: (1) low electrical resistance, (2) high optical transparency in the visible and infrared range, (3) low barriers for both electron and hole extractions, (4) easy-fabrication process, and (5) the protection for the prior-deposited active layer in solution-processed tandem OSCs. Generally, metal thin films can be used as the semi-transparent intermediate layer for tandem OSCs, such as Ag (Ref. 5) and Al/Au.<sup>6</sup> However, such intermediate layer alone is not suitable for solution-processed tandem cells (thickness is not enough for protecting the prior-deposited polymer layer) and light loss is usually high. Recently, the combination of *n*-type metal oxides [e.g., TiO<sub>x</sub> (Ref. 10) and ZnO (Ref. 11)] and poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) has been applied as the intermediate layer for solution-processed tandem OSCs, where the *n*-type metal oxide and PEDOT serve as the electron and hole transporting layer, respectively, and the recombination of charges occurs at the interface between *n*-type oxide and PEDOT. However, such intermediate layers need to be fabricated in an oxygen and moisture environment (outside the glovebox) with baking, which is harmful to the organic/polymer layer of the bottom cell.<sup>12</sup> For ZnO/PEDOT intermediate layer, it is more troublesome, as PEDOT is a water-based acidic solution, which could dissolve ZnO. So, PEDOT solution needs to be modified to neutral.<sup>11</sup>

There are other *p*-type-like metal oxides, such as NiO, MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and WO<sub>3</sub>, with high work function and good hole conductivity, which have been used previously for hole injection in organic light-emitting diodes (OLEDs) (Refs. 13-16) and anode buffer layer in single OSCs.<sup>17-19</sup> These oxide films can be generally deposited by thermal evaporation, which does not do harm to the prior-deposited organic layers. However, there is a lack of study of tandem OSCs using the combination of *p*-type-like oxide layer and metal as the intermediate layer,<sup>8</sup> especially for solution-processed tandem cells.

In this letter, we shall report an intermediate layer consisting of Al (1 nm) and MoO<sub>3</sub> (15 nm) for efficient tandem OSCs. This intermediate layer fulfills the requirements for tandem OSCs as outlined above; especially it features a high transparency and a good protection of the bottom cell polymer in solution-processed tandem cells.

All cells were fabricated on indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω/□. PEDOT:PSS (Baytron P 4083) was first spin-coated onto pre-cleaned ITO-glass with a thickness of 40 nm, and baked at 120 °C for 20 min. For the bottom cell, the active layer was fabricated by spin coating the blend solution, made of poly(3-hexylthiophene) (P3HT) (Rieke Metals, Inc.) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C<sub>61</sub> (PCBM) (Nano-C) with a weight ratio of 1:0.8 in chlorobenzene (18 mg/mL), onto PEDOT coated substrates. For the top small molecule cell, the MoO<sub>3</sub> layer and copper phthalocyanine (CuPc), fullerene (C<sub>60</sub>), bathophenanthroline (BPhen) were deposited sequentially by thermal evaporation in organic deposition chamber (5.0 × 10<sup>-5</sup> Pa). Al and Ag were deposited by e-beam and thermal evaporations under 2.0 × 10<sup>-4</sup> Pa, respectively. The active area was 0.1 cm<sup>2</sup>.

The current-voltage (*I*-*V*) characteristics were measured with a Keithley 2400 Sourcemeter in dark and under illumination of a solar simulator (Solar Light Co., Inc.) operating at various light intensities ranging from 50, 100 (AM1.5G),

<sup>a)</sup> Author to whom correspondence should be addressed. Electronic mail: exwsun@ntu.edu.sg.

<sup>b)</sup> Electronic mail: jiangcy@ime.a-star.edu.sg.

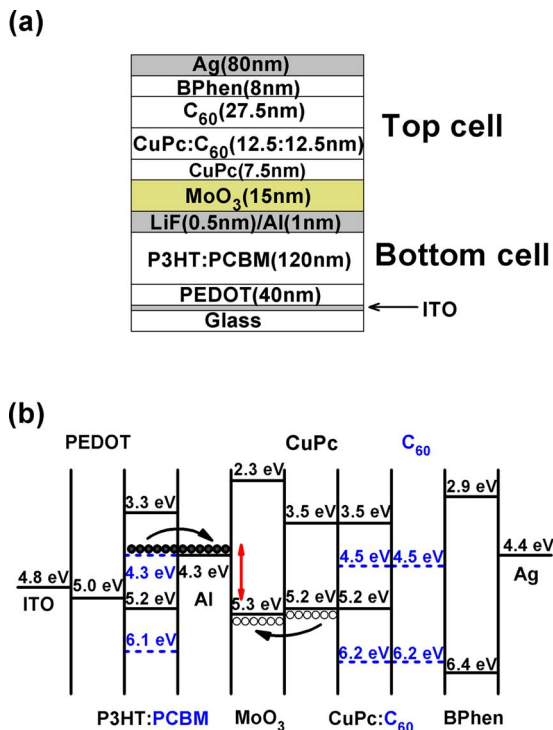


FIG. 1. (Color online) (a) Structure of the polymer-small molecule tandem OSC with an optimized intermediate layer of 1 nm Al and 15 nm MoO<sub>3</sub>. (b) The energy level diagram of the polymer-small molecule tandem OSC.

150, 200, to 300 mW/cm<sup>2</sup>. The absorption and transmittance spectra of these films were characterized by a HP 8453 UV-VIS Spectrometer. The resulting structure of the polymer-small molecule tandem cell is shown in Fig. 1(a), with a structure of ITO/PEDOT(40 nm)/P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(1 nm)/MoO<sub>3</sub>(15 nm)/CuPc(7.5 nm)/CuPc:C<sub>60</sub>(12.5:12.5 nm)/C<sub>60</sub>(27.5 nm)/BPhen(8 nm)/Ag(80 nm). For comparison, the bottom and top single cells were fabricated in the same run as the tandem cell, with the structures of ITO/PEDOT(40 nm)/P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(100 nm) and ITO/MoO<sub>3</sub>(15 nm)/CuPc(7.5 nm)/CuPc:C<sub>60</sub>(12.5:12.5 nm)/C<sub>60</sub>(27.5 nm)/BPhen(8 nm)/Ag(80 nm), respectively. The energy level diagram of the polymer-small molecule tandem cell is shown in Fig. 1(b).

Figure 2 shows the absorption spectra of P3HT:PCBM, CuPc/CuPc:C<sub>60</sub>/C<sub>60</sub>, and P3HT:PCBM/LiF/Al/MoO<sub>3</sub>/CuPc/CuPc:C<sub>60</sub>/C<sub>60</sub> films used in the bottom single, top single, and tandem cells, respectively. It is obvious that the bottom film mainly covers the visible range from 400 to 650 nm, while the top film absorbs complementarily from 650 to 750 nm. By stacking these two films together, the absorption spectrum is broadened (see the tandem film curve in Fig. 2). In addition, the transmittance spectrum of Al(1 nm)/MoO<sub>3</sub>(15 nm) intermediate layer is also shown in Fig. 2. Compared to the commonly used Al/Au intermediate layer with only 80% of transmittance in the visible range,<sup>8,20</sup> it can be seen that the transmittance is almost 98% in the range from 350 to 900 nm, ensuring enough light to be absorbed by the top cell. Hence, this intermediate layer with high transparency satisfies the optical requirement as outlined in the beginning.

The *I-V* characteristics of bottom single, top single, and tandem cells in polymer-small molecule tandem structure are

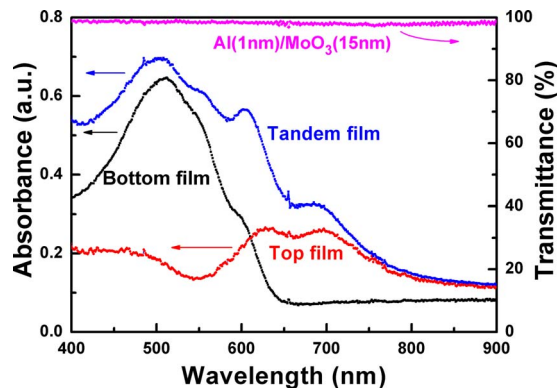


FIG. 2. (Color online) The absorption spectra of the bottom film P3HT:PCBM (120 nm), top film CuPc(7.5 nm)/CuPc:C<sub>60</sub>(12.5:12.5 nm)/C<sub>60</sub>(27.5 nm) and tandem film P3HT:PCBM(120 nm)/LiF(0.5 nm)/Al(1 nm)/MoO<sub>3</sub>(15 nm)/CuPc(7.5 nm)/CuPc:C<sub>60</sub>(12.5:12.5 nm)/C<sub>60</sub>(27.5 nm) films. The transmittance spectrum of the Al(1 nm)/MoO<sub>3</sub>(15 nm) intermediate layer. All films were fabricated on quartz substrates and postannealed at 140 °C for 5 min.

shown in Fig. 3(a) with their corresponding fill factors (FFs) and PCEs under 100 mW/cm<sup>2</sup> illuminations. The PCEs of the bottom and top single cells are 2.11% and 1.68%, respectively. With the Al (1 nm)/MoO<sub>3</sub> (15 nm) intermediate layer, the tandem cell has a PCE of 2.82% open-circuit voltage  $V_{oc}=1.01$  V, short-circuit current density  $J_{sc}=6.05$  mA/cm<sup>2</sup>, and FF=46.2%. The  $V_{oc}$  (1.01 V) of the tandem cell is the summation of the  $V_{oc}$  of the bottom single cell (0.63 V) and top single cell (0.45 V), which demonstrates that the tandem cell is connected electrically by this Al/MoO<sub>3</sub> intermediate layer. It is known that matched  $J_{sc}$  of bottom and top single cells is important for the tandem cells in series. It can be found in Fig. 3(a) that the  $J_{sc}$  (7.83 mA/cm<sup>2</sup>) of top single cell is slightly higher than that (6.54 mA/cm<sup>2</sup>) of bottom one, demonstrating that the nearly matched photocurrent density between the bottom and top cells was obtained in such tandem cell. Overall, the PCE of the tandem cell is higher than either of the individual single cells due to the increase in  $V_{oc}$ .

It should be pointed out that although the  $V_{oc}$  in the bottom P3HT:PCBM single cell is comparable to literature,<sup>3</sup> the  $J_{sc}$  and FF are lower, which might be due to low annealing temperature (this low annealing temperature is preferred for the top small molecule OSC).<sup>2</sup> Figure 3(b) shows the *I-V* characteristics of the polymer-small molecule tandem cell under different illuminations. It is seen clearly that its  $V_{oc}$  increases with the intensity of illumination because of the increase in the  $V_{oc}$  of both bottom and top single cells (data not shown here). Despite the FF reducing from 47.20% (at 50 mW/cm<sup>2</sup>) to 43.3% (at 300 mA/cm<sup>2</sup>) monotonically, the maximum PCE reached 3.88% at 300 mW/cm<sup>2</sup> primarily due to the enhanced  $V_{oc}$ .

In the polymer-small molecule tandem cell, MoO<sub>3</sub> has dual functions of (1) hole transporting, and (2) exciton blocking. The holes collected/transported by MoO<sub>3</sub> and electrons generated from the bottom cell are recombined in the Al layer (1 nm, most likely in nanocluster form). MoO<sub>3</sub> has been previously used as a hole-injection layer for OLEDs,<sup>15,16</sup> and a replacement of PEDOT:PSS in polymer OSCs.<sup>17</sup> So MoO<sub>3</sub> has very good hole transporting property. Moreover, the valence band of MoO<sub>3</sub> is 5.3 eV,<sup>17</sup> close to the highest occupied molecular orbital of CuPc [5.2 eV (Ref. 4)]

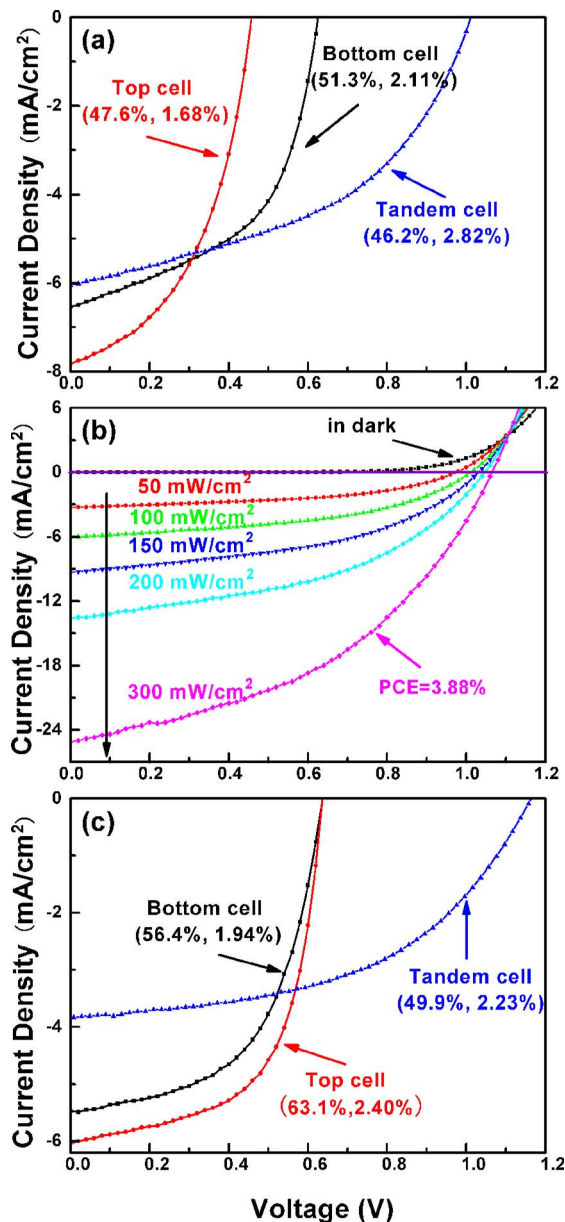


FIG. 3. (Color online) (a) The  $I$ - $V$  characteristics of bottom single, top single cells, and polymer-small molecule tandem cell under  $100 \text{ mW/cm}^2$ . (b) The  $I$ - $V$  characteristics of polymer-small molecule tandem cell under different illuminations. The cells for the polymer-small molecule tandem cell were postannealed at  $140^\circ\text{C}$  for 5 min. (c) The  $I$ - $V$  characteristics of the solution-processed polymer tandem cell, and the corresponding bottom and top single cells under  $100 \text{ mW/cm}^2$ . The corresponding FF and PCE are shown in the format of (FF, PCE).

and P3HT [5.2 eV (Ref. 21)]. Thus thicker  $\text{MoO}_3$  layer (15 nm in our case) will not result in significant degradation in the tandem cell. Meanwhile,  $\text{MoO}_3$  has the other function of exciton blocking. The conduction band of  $\text{MoO}_3$  [2.3 eV (Ref. 17)] is well above the lowest unoccupied molecular orbital of CuPc [3.5 eV (Ref. 4)] or P3HT (3.3 eV [Ref. 21]) [Fig. 1(b)]. Excitons formed in the top cell will be blocked by  $\text{MoO}_3$ . Only after exciton dissociation (at the CuPc/ $\text{C}_{60}$  interfaces), holes can be collected by  $\text{MoO}_3$  layer contributing to photocurrent.

We further applied this intermediate layer in a solution-processed polymer tandem cell with a structure

of ITO/PEDOT(40nm)/P3HT:PCBM(70 nm)/Al(1 nm)/ $\text{MoO}_3$ (15 nm)/P3HT:PCBM(70 nm)/Al(100 nm). With a 15 nm thick  $\text{MoO}_3$  layer, dissolving of the prior-deposited polymer (bottom cell) is avoided during spin coating of the top cell polymer, i.e., a complete coverage of the bottom cell is realized. The  $I$ - $V$  characteristics of the solution-processed polymer tandem OSC under  $100 \text{ mW/cm}^2$  are shown in Fig. 3(c). For comparison, the  $I$ - $V$  characteristics of the bottom and top single cells are also presented. We can see that reasonable performance is obtained ( $V_{\text{oc}}=1.17 \text{ V}$  and  $\text{PCE}=2.23\%$ ) for this solution-processed polymer tandem OSC. Therefore, the intermediate layer is a potential candidate for the solution-processed multitandem solar cells (and OLEDs) with complementary absorptions.

In conclusion, we have demonstrated an effective intermediate layer made of 1 nm Al and 15 nm  $\text{MoO}_3$  for tandem OSCs. Such an intermediate layer, which can be easily fabricated, is highly transparent in the entire solar spectrum, and provides good protection of prior-deposited polymer layer in solution-processed polymer tandem cell. We applied this intermediate layer in both polymer-small molecule and solution-processed polymer tandem OSCs with good and repeatable results. The PCE of the polymer-small molecule tandem cell was 2.82% at  $100 \text{ mW/cm}^2$  (3.88% at  $300 \text{ mW/cm}^2$ ), higher than either of the individual ones.

- <sup>1</sup>K. Kim, J. Liu, M. A. G. Namboothiry, and D. L. Carroll, *Appl. Phys. Lett.* **90**, 163511 (2007).
- <sup>2</sup>W. L. Ma, C. Y. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.* **15**, 1617 (2005).
- <sup>3</sup>M. Reyes-Reyes, K. Kim, and D. L. Carroll, *Appl. Phys. Lett.* **87**, 083506 (2005).
- <sup>4</sup>M. Y. Chan, S. L. Lai, M. K. Fung, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.* **90**, 023504 (2007).
- <sup>5</sup>J. G. Xue, S. Uchida, B. P. Rand, and S. R. Forrest, *Appl. Phys. Lett.* **85**, 5757 (2004).
- <sup>6</sup>A. Hadipour, B. de Boer, J. Wildeman, F. B. Kooistra, J. C. Hummelen, M. G. R. Turbiez, M. M. Wienk, R. A. J. Janssen, and P. W. M. Blom, *Adv. Funct. Mater.* **16**, 1897 (2006).
- <sup>7</sup>A. Colsmann, J. Junge, C. Kayser, and U. Lemmer, *Appl. Phys. Lett.* **89**, 203506 (2006).
- <sup>8</sup>A. G. F. Janssen, T. Riedl, S. Hamwi, H. H. Johannes, and W. Kowalsky, *Appl. Phys. Lett.* **91**, 073519 (2007).
- <sup>9</sup>G. Dennler, H. J. Prall, R. Koeppel, M. Egginger, R. Autengruber, and N. S. Sariciftci, *Appl. Phys. Lett.* **89**, 073502 (2006).
- <sup>10</sup>J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, *Science* **317**, 222 (2007).
- <sup>11</sup>J. Gilot, M. M. Wienk, and R. A. J. Janssen, *Appl. Phys. Lett.* **90**, 143512 (2007).
- <sup>12</sup>A. Moliton and J. M. Nunzi, *Polym. Int.* **55**, 583 (2006).
- <sup>13</sup>H. C. Im, D. C. Choo, T. W. Kim, J. H. Kim, J. H. Seo, and Y. K. Kim, *Thin Solid Films* **515**, 5099 (2007).
- <sup>14</sup>C. C. Chang, J. F. Chen, S. W. Hwang, and C. H. Chen, *Appl. Phys. Lett.* **87**, 253501 (2005).
- <sup>15</sup>S. Tokito, K. Noda, and Y. Taga, *J. Phys. D* **29**, 2750 (1996).
- <sup>16</sup>H. You, Y. F. Dai, Z. Q. Zhang, and D. G. Ma, *J. Appl. Phys.* **101**, 026105 (2007).
- <sup>17</sup>V. Shrotriya, G. Li, Y. Yao, C. W. Chu, and Y. Yang, *Appl. Phys. Lett.* **88**, 073508 (2006).
- <sup>18</sup>M. Y. Chan, C. S. Lee, S. L. Lai, M. K. Fung, F. L. Wong, H. Y. Sun, K. M. Lau, and S. T. Lee, *J. Appl. Phys.* **100**, 094506 (2006).
- <sup>19</sup>M. D. Irwin, B. Buchholz, A. W. Hains, R. P. H. Chang, and T. J. Marks, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 2783 (2008).
- <sup>20</sup>V. Shrotriya, E. H. E. Wu, G. Li, Y. Yao, and Y. Yang, *Appl. Phys. Lett.* **88**, 064104 (2006).
- <sup>21</sup>J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. L. Ma, X. Gong, and A. J. Heeger, *Adv. Mater. (Weinheim, Ger.)* **18**, 572 (2006).