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A Simple Interconnection Layer for Tandem Organic Solar Cells with Improved Efficiency and Fill Factor *

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We demonstrate a simple interconnection layer (ICL) that can be employed in tandem organic solar cells. An ICL with an optimized structure of Ca/Au/MoO_3 is used between two sub cells composed of identical regioregularpoly(3-hexylthiophen) (P3HT):[6,6]-phenyl C_{61}-butyric acid methylester (PCBM) photoactive layers. Power conversion efficiency (PCE) of 3.24% and fill factor (FF) of 68.0% are achieved with such an ICL under simulated sunlight (100 mW·cm^{-2}). Compared with the best values of devices with ICLs of Ca/Al/MoO_3, PCE is improved by 68.9% and FF is improved by 15.5%. The improved performances are attributed to the optical and electrical balances in both sub cells. The presented ICL extracts free charges efficiently from both sub cells thereby suppressing the exaction recombination in each sub cell.

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In the past decades, organic solar cells (OSCs) have attracted considerable interest due to their potential for low cost, light-weight, flexibility and suitability for large-area fabrication.[1,2] The current research interest of OSCs includes high power conversion efficiency (PCE), roll-to-roll feasibility and high stability.[3] High PCE can be achieved by using low band-gap materials,[4–6] optimized morphology,[7,8] modified interfaces,[9,10] and tandem structures.[1,11–15] A tandem structure consists of at least two sub cells with complementary absorption spectra connected by interconnection layers (ICLs).[11,14,16,17]

A large challenge in successfully fabricating tandem OSCs is to choose a proper ICL. The ICL electronically connects each sub cell by recombining opposite charge carriers from adjacent sub cells. Another important function of the ICL is to protect fabricated bottom sub cells from dissolving away during the spin coating of top sub cells. Two fundamental requirements for a proper ICL are optical transparency and energy level matching. The former makes it possible for the light-energy dissipation in sub cells to be balanced, while the latter ensures that the transport of opposite charges is balanced in adjacent sub cells. Molybdenum oxides are appropriate intermediate materials due to their high optical transparency, appropriate hole mobility and excellent exciton blocking property. On the other hand, calcium is a suitable material for collecting electrons and preventing exciton quenching at the cathode side, as Ca forms an ohmic contact with PCBM by pinning their work functions, while it forms a rectifying contact with P3HT.[13,18]

To achieve an optimal ICL structure, two identical P3HT:PCBM layers are usually used to constitute photoactive layers. Hereinafter, we call such a structure with identical sub cells an identical-tandem (id-tandem) structure. The device efficiency of such an id-tandem structure was usually very low, due to a largely reduced current density.[19,20] Krebs *et al*[19] used V_2O_5/ZnO as ICLs to fabricate id-tandem OSCs, which generate PCE of 1.4% and FF of 34%. Shim *et al*[21] fabricated id-tandem OSCs using MoO_x/Ag/PEIE as ICLs and achieved PCE of 2.1% and FF of 62%. Zhao *et al*[22] employed MoO_3/Ag/Al/Ca as ICLs, with which the device PCE reaches 2.89% and FF of 59%. Graphene-oxide (GO) based ICLs, such as GO:PEDOT:PSS[23] and GO/GO-Cs (cesium neutralized GO)/Al/MoO_3,[24] have also been reported. Huang *et al*[25] employed ZnO/GO:SWCNTs as ICL, and achieved PCE of 4.10% and FF of 58%.

In this Letter, we demonstrate for the first time the use of an ICL of Ca/Au/MoO_3, which satisfies all the requirements for proper ICLs. Using such an ICL, PCE of 3.24% and FF of 68.0% are achieved for an id-tandem P3HT:PCBM device. The performance improvements are attributed to two important balances in sub cells as discussed in the following.

Devices with structures of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al (or Au)/MoO_3/P3HT:PCBM

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/Ca/Al were fabricated on cleaned indium tin oxide (ITO) glass substrates (10 Ω/sq). A 50-nm-thick poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS, Baytron P4083) layer was spin-coated and baked at 140℃ for 20 min. A blend solution of P3HT (Rieke Metals Inc.) and PCBM (American Dye Sources Inc.) with a weight ratio of 1:1 in dichlorobenzene (20 mg·mL^{-1}) was then spin-coated to form the bottom active layer (100 nm) in a glove box filled with Ar(H_2O<0.1 ppm and O_2 < 10 ppm). The photoactive layer was then annealed at 120℃ for 10 min. Ca, Al or Au, and MoO_3 of various thicknesses were evaporated in sequence to form the ICL under a vacuum of 10^{-6} Torr. Then a second P3HT:PCBM film (120 nm) was spin-coated onto the ICL before a Ca (20 nm) and Al (100 nm) cathode was finally deposited. The active area defined by overlapped electrodes was 0.126 cm^2. The thicknesses of films were monitored with quartz oscillators calibrated with a Dektak 3030 profiler.

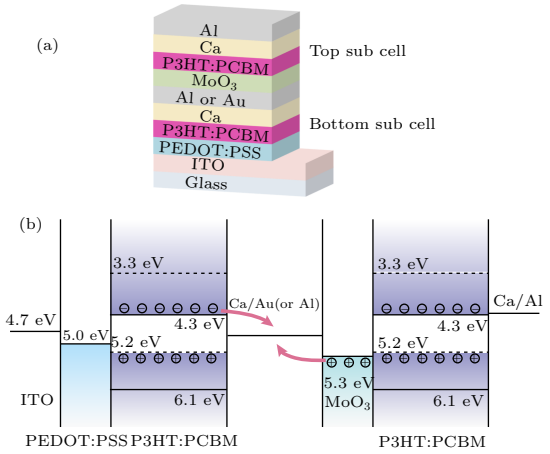


Fig. 1. (a) Device structure of the tandem OSCs, and (b) energy-level diagram showing the HOMO and LUMO energies of each of the component materials before contact.

The device structure is shown in Fig. 1(a). Current density-voltage (J–V) curves were measured with a Keithley 2400 sourcemeter under illumination of a Newport Oriel 150 W solar simulator (AM 1.5 G, 100 mW·cm^{-2}). All devices were tested in air. Absorbance and transmittance spectra were measured with an HP 8453 UV-vis spectrometer. The work functions were measured under the KP020 Kelvin Probe in ambient conditions at room temperature.

We first optimized the thickness of Ca by comparing the efficiencies of devices with ICLs of Ca of different thicknesses, with the results listed in Table 1. The Ca layer thickness was optimized to be 5 nm, with a V_{OC} of 0.94 V. This means that the Ca layer could collect opposite charges from both sub cells, in spite of a Schottky barrier indicated by the relatively lower V_{OC} compared to the sum of both sub cells (0.58 V). On the other hand, when the thickness was 2 nm, V_{OC} was very low, perhaps due to the fact that such a Ca layer was too thin to effectively separate both sub cells. However, increasing the Ca thickness to 10 nm led to significant decrease in the device performance, especially FF. Similar phenomena were observed previously.[26] One possible explanation is that the Ca layer was oxidized to CaO, which was thick enough to block the electron attraction from the bottom sub cell, and resulted in a very low FF.

Table 1. Key parameters of tandem solar cells with ICLs of x nm thick Ca.

x	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	PCE (%)
2	0.40	2.62	33.93	0.36
5	0.94	3.14	44.49	1.32
10	0.84	2.29	10.33	0.20

We then optimized the thickness of MoO_3 to be 12 nm similarly. However, device performance was reduced (magenta dashed curve in Fig. 2), which can be well understood since Ca forms a Schottky connection with MoO_3.[22] An aluminum layer was inserted between Ca and MoO_3 to reduce the Schottky barrier between Ca and MoO_3. Table 2 shows the results of id-tandem solar cells with ICLs of Ca (5 nm)/Al (y nm)/MoO_3 (12 nm).

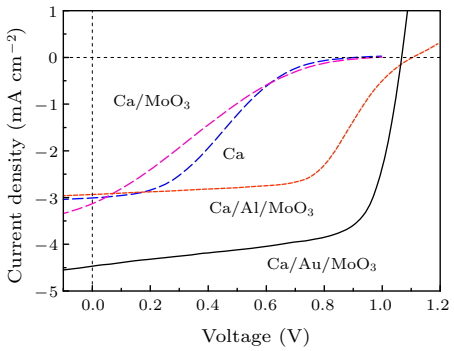


Fig. 2. Current density-voltage curves of tandem devices with different interconnection layers under simulated solar irradiation.

Table 2. Key parameters of tandem solar cell with ICLs of Ca (5 nm)/Al (y nm)/MoO_3 (12 nm).

y	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF (%)	PCE (%)
5	1.13	3.64	21.91	0.91
10	1.11	2.93	58.93	1.92
12	1.15	2.57	46.97	1.39

The values of V_{OC} of the devices with ICLs of Ca/Al/MoO_3 equal the sum of V_{OC} of both sub cells. This indicates the formation of all ohmic contacts between sub cells. Nevertheless, appearance of S-shaped J–V curves limited the efficiency of the devices (red curve in Fig. 2). Similar phenomena were observed previously.[22,27] The S-shaped J–V curves are normally attributed to imbalanced transport rates of electrons and holes. We speculate that such an imbalance was due to the formation of aluminum oxides nearby the Al/MoO_3 interface, which hindered the extraction

of holes from the top sub cell.

To overcome this problem, we replaced Al with Au, which has a work function (5.1 eV) matching with MoO_3 (5.4 eV). The thickness of Au was chosen to be 6 nm, as it has been reported that an Au film with thickness less than 5 nm usually leads to a very high resistance and a poor device performance.[12,28] The J–V curve of an id-tandem cell with an ICL of Ca (5 nm)/Au (6 nm)/MoO_3 (12 nm) was shown in Fig. 2 (black curve). The device showed V_{OC} of 1.06 V, J_{SC} of 4.47 mA·cm^{-2}, FF of 68.0%, and PCE of 3.24%. Compared with the best device with an ICL of Ca/Al/MoO_3, PCE was improved by 68.9% and FF was improved by 15.5%. Series resistance (R_sA), shunt resistance (R_{sh}A), ideality factor (n), reverse saturated current density (J_0) and light-induced current density (J_{ph}) of the device are 9.50 Ωcm^2, 1355 Ωcm^2, 1.89, 1.77×10^{-8} mA·cm^{-2}, and 4.50 mA·cm^{-2}, respectively. The relatively low n value, compared to the n values in previous reports,[29] suggests a low exciton recombination rate in the device.[30] In other words, the Ca/Au/MoO_3 ICL efficiently extracts free charges from the photoactive layers prior to the exaction recombination (Fig. 1(b)).

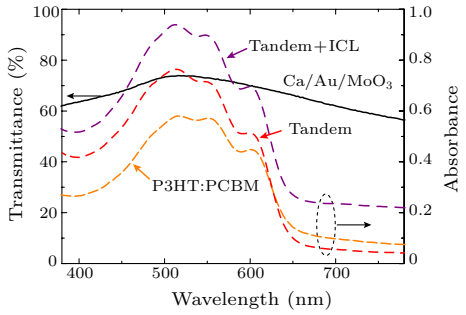


Fig. 3. Transmittance spectra of a Ca (5 nm)/Au (6 nm)/MoO_3 (12 nm) film, and absorbance spectra of a P3HT:PCBM film (100 nm), a tandem cell without either ICL or the cathode (Tandem), and a tandem cell with an ICL of Ca/Au/MoO_3 without the cathode (Tandem+ICL).

Figure 3 shows the transmittance spectra of a Ca/Au/MoO_3 ICL, and absorbance spectra of a P3HT:PCBM film (orange dashed curve), a tandem cell without either ICL or the cathode (red dashed curve), and a tandem cell with a Ca/Au/MoO_3 ICL without the cathode (purple dashed curve). The transmittance of the Ca/Au/MoO_3 ICL was about 70% in the absorption region of P3HT:PCBM. The P3HT:PCBM film, the tandem cell without ICL, and the tandem cell with ICL absorb about 58%, 76%, and 93% of incident light around 520 nm, respectively. The absorbance of the tandem cell in the range of 450–600 nm was enhanced by the ICL, which is attributable to the absorption of the ICL.

We further calculated optical field distributions (optical electric field energy dissipation) in tandem cells with different ICLs using the matrix transfer method.[31] Photons dissipated in each layer are directly related to excitons that probably contribute to the photocurrent. Three wavelengths were chosen at 450, 520 and 600 nm, representing the cutting edges and peak of the P3HT:PCBM absorbance. All films were considered isotropic and separated with parallel interfaces. Figure 4 shows that the optical field distributions in both active layers are much imbalanced between top and bottom active layers when Ca/Al/MoO_3 is used as the ICL. The ratio of integrated dissipated light energy at 520 nm (2.38 eV) in the top cell and in the bottom cell is about 1/11. This is mainly due to the large reflection coefficient of aluminum. Such an imbalance limited J_{SC}, which is determined by the smaller value between sub cells. On the contrary, the optical field distribution in the Ca/Au/MoO_3 device is relatively balanced. The top/bottom ratio is 1/2 at 520 nm. As a consequence, J_{SC} is relatively higher in the device with an ICL of Ca/Au/MoO_3. Note that such a divergence is a consequence of the optical property difference between Al and Au films, instead of the thickness difference. Further optimization of the thicknesses of photoactive layers or application of an optical space layer near the top electrode will overcome the problem and yield higher efficiency.[32]

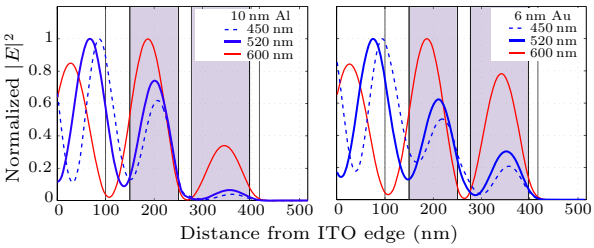


Fig. 4. Calculated optical field distributions in tandem cells with different intermediate layers: Ca/Al/MoO_3 (left) or Ca/Au/MoO_3 (right). The light purple patches are P3HT:PCBM layers.

In conclusion, we have demonstrated a simple interconnection layer with a structure of Ca/Au/MoO_3 that can be used in tandem organic solar cells. Power conversion efficiency of 3.24% and fill factor of 68.0% are achieved for a tandem cell with sub cells made of identical P3HT:PCBM photoactive layers. Compared with the best device with an ICL of Ca/Al/MoO_3, PCE is improved by 68.9% and FF is improved by 15.5%. The interconnection layer generates such a high performance, mainly resulting from the realization of optical and electrical balances in both sub cells. The presented interconnection layer could provide an efficient approach to attain improved performances in tandem organic solar cells composed of solution-processed complementary absorbing photoactive layers.

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