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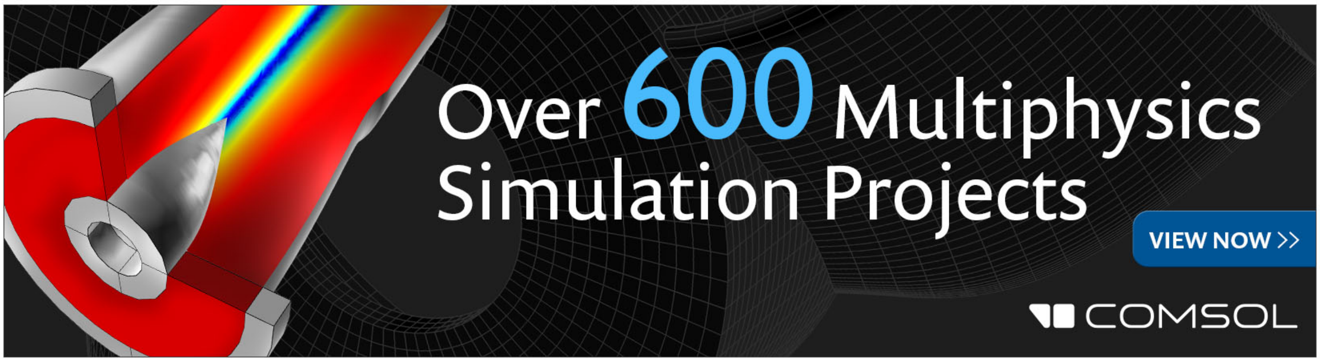

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The role of a LiF layer on the performance of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/Si organic-inorganic hybrid solar cells

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We report an ultra-thin layer of lithium fluoride (LiF) between silicon (Si) and aluminum (Al) in a Si/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hybrid solar cell which resulted in a power conversion efficiency (PCE) of 11.09%. The insertion of a thin layer of LiF improved the contact between Si and Al, which decreased the contact resistance from 5.4×10^{-1} Ω cm^2 to 2.6×10^{-2} Ω cm^2. Also, the electron transport from Si to Al was improved and charge carrier recombination was suppressed. As a result, the short circuit current density, the open circuit voltage, and the fill factor were all improved with the presence of the LiF layer. The solar cell with the LiF/Al bilayer as a cathode displayed a 14.45% enhancement on PCE when compared with the device using pristine Al as a cathode. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4866968]

Organic-inorganic hybrid solar cells based on silicon (Si) and conjugated polymers have attracted considerable research interests because they combine the advantageous properties of Si and the solution processability of organic materials at low temperatures.[1–12] Up to now, power conversion efficiency (PCE) of approximately 10% has been reported for solar cells based on Si/poly(3-hexylthiophene), 2,2,7′,7′-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9′-spirobifluorene.[5,9,13] And PCE of ∼11% has been achieved for Si/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) based solar cells.[7,8,10] Due to its high transparency, conductivity, excellent thermal stability, and mechanical flexibility, PEDOT:PSS is one of the most widely used transparent conducting materials for organic electronics.[14] In recent years, enormous efforts have been made to improve the performance of hybrid solar cells based on Si/PEDOT:PSS.[6–8]

An ultra-thin layer of lithium fluoride (LiF) was widely used to improve the efficiency of organic photovoltaics (OPVs)[15–17] and organic light-emitting diodes (OLEDs).[18–20] The fill factor (FF) and open circuit voltage (V_{oc}) for OPVs were enhanced by inserting the LiF layer.[16] In OLED devices, the enhanced electron injection properties resulted in a decreased operating voltage, which led to the improvement of device performance and color purity of emission. With LiF/Al as a back electrode, the device performance of the heterojunction with intrinsically thin (HIT) layer solar cell was enhanced due to the improved back contact.[21]

In this work, we inserted an ultra-thin layer of LiF between aluminum (Al) and Si to improve the electron collection efficiency in the Si/PEDOT:PSS hybrid solar cell. It was found that the contact resistance decreased from the original $5.4 \times 10^{-1}\,\Omega\,\mathrm{cm}^2$ to $2.6 \times 10^{-2}\,\Omega\,\mathrm{cm}^2$. The decreased contact resistance resulted in improved electron collection between Si and Al. The insertion of a LiF layer led to a 14.45% enhancement of the PCE when compared to the device with pristine Al as a cathode. The PCE of the device reached ∼11% due to the improvement of the back contact of the hybrid solar cells.

The schematic of the solar cell is depicted in Figure 1. Before device fabrication, n-type single-crystalline Si substrates with resistivity of 1–3 Ω cm, thickness of 450 μm, and (100) orientation were treated by a two-step chlorination/alkylation process.[22,23] Then the highly conductive PEDOT:PSS (CLEVIOS PH 1000) mixed with 5 wt. % dimethyl sulfoxide (DMSO) and 1 wt. % Triton was spin-coated onto the Si substrate and then annealed at 125 °C for 30 min in nitrogen atmosphere. Silver grid electrodes defining an active area of 1×0.8 cm^2 were deposited onto the PEDOT:PSS layer by vacuum thermal evaporation through a shadow mask. Subsequently, a 0.5-nm-thick LiF layer and a 150-nm-thick Al layer were successively thermally deposited onto the back side of the silicon substrate as the rear electrode to complete the device. The reference device was also fabricated by the same process, only without the LiF layer.

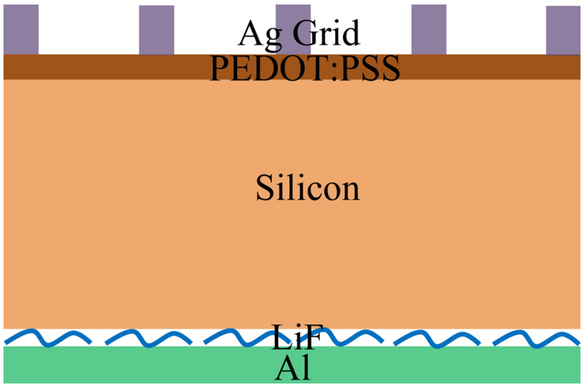

FIG. 1. Schematic of the Si/PEDOT:PSS hybrid solar cells. The layer thickness in the scheme does not represent the real thickness of the devices. In the actual devices, the silicon layer was much thicker than any of the other layers.

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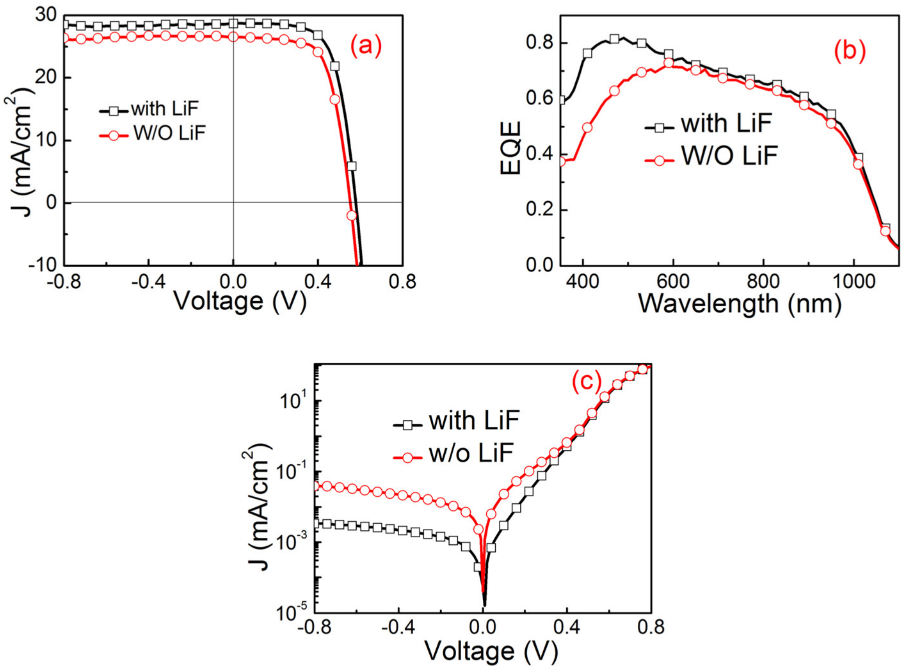

FIG. 2. (a) Current density-voltage (J-V) characteristics of the hybrid solar cells with and W/O LiF fabricated under the same conditions and measured under AM 1.5 light illumination at 100 mW/cm^2; (b) EQE spectra of the devices with and W/O the LiF layer; and (c) J-V characteristics of hybrid solar cells with and W/O LiF under dark conditions.

Figure 2(a) displays the current density-voltage (J-V) characteristics of the hybrid solar cells based on different rear electrodes, with and without (W/O) the LiF layer under simulated air mass (AM) 1.5G illumination at 100 mW/cm^2. The extracted photovoltaic parameters of the short circuit current density (J_{sc}), V_{oc}, FF, and PCE for each condition and their statistics (of five cells for each type) are summarized in Table I. Compared to the reference device, the PCE of the device with LiF layer increased from 9.69% to 11.09%, as a result of the improved J_{sc}, from 26.56 mA/cm^2 to 28.71 mA/cm^2, V_{oc}, from 0.55 V to 0.57 V, and FF, from 66% to 68%. The external quantum efficiency (EQE) spectra of the Si/PEDOT:PSS hybrid solar cells with and W/O the LiF layer were measured, and the results were shown in Figure 2(b). The device with the LiF layer displayed a higher EQE value than the reference device. The thin LiF layer led to an 8.09% increase in J_{sc} which was consistent with the improved EQE of these devices. However, the EQE was only enhanced at short wavelengths, instead of longer wavelengths, which was different from the HIT device.[21] The exact mechanism for this is still unclear at the present. Further investigation is under way.

The increased device performance was ascribed to the improved junction quality between Si and Al. The dark current density *versus* voltage characteristics of the hybrid solar cells with and W/O LiF were measured and shown in Figure 2(c). The reverse saturation current density (J_0) and ideality factor (n) of the device with and W/O the LiF layer were extracted.[24] The J_0 was almost an order of magnitude lower than the reference device. The J_0 for device with the thin layer of LiF was 4.58×10^{-8} A/cm^2, while the reference device was 1.15×10^{-7} A/cm^2. The n for the device with and W/O the LiF layer was 1.78 and 1.92, respectively. The J_0 and n in this Schottky diode is related with the contact between Si and Al. The decrease of J_0 and n was obvious evidence that electrons were efficiently collected by the cathode due to the improved contact between Si and Al. It implied that the junction property was improved when the thin layer of LiF was inserted between Si and Al. The improved contact resulted in enhanced electron extraction to Al, leading to a reduced recombination loss and an increased J_{sc} and V_{oc}. Besides the J_{sc} and V_{oc}, the FF was improved up to 68% with the insertion of the LiF layer, which also confirmed the improved junction property. With the improvement of the J_{sc}, V_{oc}, and FF, a PCE of 11.09% was achieved from the planar Si/PEDOT:PSS hybrid solar cell with LiF/Al as the cathode.

In order to further confirm that the junction property was improved, after a thin layer of LiF was inserted, the contact resistance between Si and Al was explored. Al pads were deposited by thermal evaporation at the rear side of the Si substrate (shown in the inset of Figure 3(a)) and the current-voltage characteristics between the Al pads were measured and the results were shown in Figure 3(a). It was obviously that an ohmic contact could not form if Al was directly deposited on Si. When a thin layer of LiF was inserted between Si and Al, the contact was dramatically improved. The contact resistance was measured by the transmission line measurement (TLM) method.[25] The current-voltage (IV) curves between any two contacts (of length d and width W) were measured by the probe station as shown in Figure 3(b). The value of "W," "d," and "ℓ" were determined by an optical microscope. The contact resistance was

TABLE I. Summary of photovoltaic parameters of the hybrid solar cells with and W/O LiF fabricated under the same conditions.

Rear electrode[a]	V_{oc}[b] (V)	J_{sc}[b] (mA/cm^2)	FF[b] (%)	PCE[b] (%)
Al	**0.55**	**26.56**	**66**	**9.69**
	0.55	27.00	64	9.45
	(0)	(±0.45)	(±0.023)	(±0.220)
LiF/Al	**0.57**	**28.71**	**68**	**11.09**
	0.57	27.72	69	10.86
	(±0.007)	(±0.63)	(±0.008)	(±0.227)

[a] Data and statistics based on five cells in each condition.

[b] Numbers in bold are the maximum recorded values.

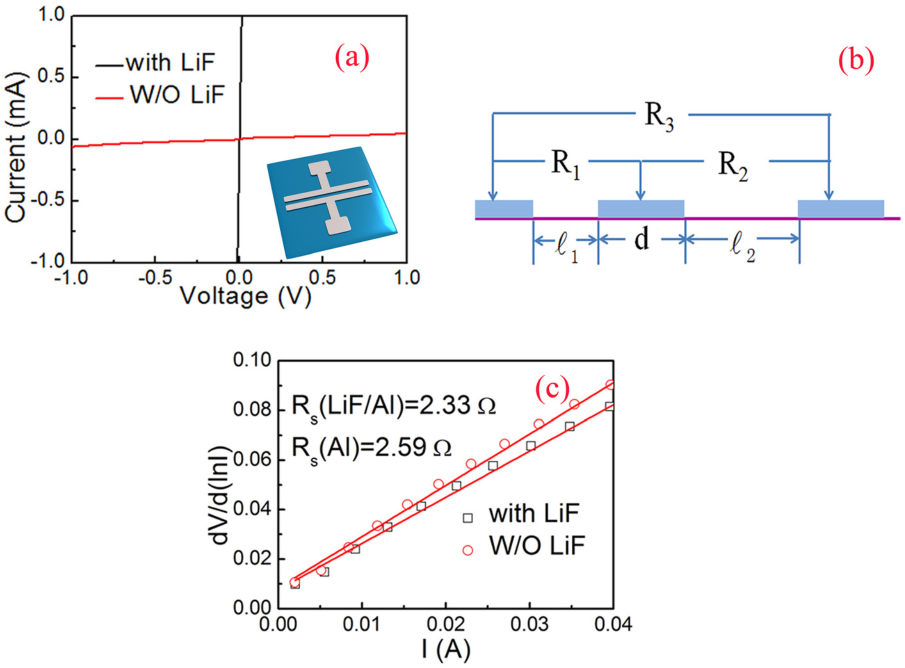

FIG. 3. (a) Current-voltage measurements between T-shaped Al pads at the rear side of the Si with and W/O the thin layer of LiF. Inset: The schematic diagram of T-shaped pads on a silicon substrate. The channel length and width are 3 mm and 110 μm, respectively. The Al pad thickness is 150 nm. (b) The schematic diagram for measuring the contact resistance value. The contact length and width are 140 μm and 200 μm, respectively. The value of ℓ_1 and ℓ_2 are 135 μm and 266 μm, respectively; (c) The series resistance R_s values extrapolated from dV/dlnI versus I curves of the hybrid solar cells with and W/O LiF.

5.4×10^{-1} Ω cm^2 for Al directly contacting with Si. When the layer of LiF was inserted, the contact resistance decreased to 2.6×10^{-2} Ω cm^2. This indicates that the presence of LiF dramatically decreases the contact resistance. The reduced contact resistance can be ascribed to the lowering of the effective work function of Al, which was widely observed in the organic electronic devices.[18,19,26–29] Furthermore, the presence of LiF could form a dipole layer leading to a vacuum level offset between Si and Al to sweep electrons to Al, this also decreased contact resistance. In addition, the LiF layer could partly protect Si from damaging by hot Al atoms during thermal deposition, and mitigate silicide formation. Series resistance (R_s) was also extracted from dV/dlnI versus I curves.[30] From Figure 3(c), the R_s value of device with and W/O LiF layer corresponding to the slope was 2.33 Ω and 2.59 Ω, respectively. The R_s was slightly reduced, which could lead to improved FF. All of the above proved that the thin layer of LiF improved the contact between Si and Al.

In summary, we have demonstrated that the performance of Si/PEDOT:PSS hybrid solar cells can be improved by inserting a thin layer of LiF between Si and Al. A PCE of 11.09% was achieved with reduced saturation current density. The improved device performance was ascribed to the decrease of contact resistance from 5.4×10^{-1} Ω cm^2 to 2.6×10^{-2} Ω cm^2 between Si and Al, which was determined by the TLM method. This method avoids high-temperature doping to improve the contact between Si and Al, which can also be applied to other contact between semiconductors and metals.

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