Effect of LiF/metal electrodes on the performance of plastic solar cells

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The insertion of thin interlayers of LiF under the negative metal electrode (Al and Au) of bulk heterojunction solar cells significantly enhances the fill factor and stabilizes high open circuit voltages. Compared to devices without the LiF interfacial layer, the white light efficiencies increase by over 20% up to $\eta_{\mathrm{eff}} \sim 3.3\%$. Substitution of the LiF by another insulating interlayer SiO_x results in lower overall efficiencies. In the case of a LiF/Au electrode, substantial efficiency enhancement is observed compared to a pristine Au electrode and white light efficiencies up to $\eta_{\mathrm{eff}} \sim 2.3\%$ are reported. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1446988]

Recent progress on plastic solar cells with a power conversion efficiency of 2.5% under AM1.5 illumination.[1] included a strategy of incorporating a small amount of LiF at the interface between the photoactive layer and the aluminum cathode. This technique has previously been used to enhance the performance of organic light-emitting diodes (OLEDs) for devices fabricated either by thermal deposition of low-molecular-weight compounds[2-4] or by solution casting of polymers.[5,6] In the present work, we study the performance of the bulk-heterojunction, photovoltaic devices as a function of LiF thickness. We find that, insertion of thin layers of LiF (<15 Å) increases both the open circuit voltage and the fill factor of the device, yielding an increased power conversion efficiency.

Although LiF/Al electrodes are already widely used for enhancing the efficiency of OLEDs the underlying mechanisms are still under investigation. Several mechanisms have been suggested thus far, including

(i)   lowering of the effective work function of the aluminum;

(ii)   dissociation of the LiF and subsequent chemical reaction (doping) of the organic layer;

(iii)   formation of a dipole layer leading to a vacuum level offset between the organic layer and the Al; and

(iv)   protection of the organic layer from the hot Al atoms during thermal deposition.

In this letter, we study the underlying mechanisms of LiF/Al electrodes and discuss their positive implications on the operation of conjugated polymer/fullerene solar cells.

Photovoltaic devices were fabricated as reported earlier.[1] Thin layers of LiF or SiO_x were thermally deposited onto photoactive layer with a rate of 1–2 Å/min from a tungsten boat in a vacuum system with a base pressure of 10^{-4} Pa. We emphasize that for thickness values on the order of ~ 1 nm the LiF/SiO_x is not a continuous, fully covering

layer, but instead consists of island clusters on the surface of the photoactive layer. Characterization of the devices was performed under illumination by white light from a solar simulator with an incident intensity of 800 W/m^2. No corrections were performed to take into account the mismatch between the light of the solar simulator and the true air mass (AM) 1.5 spectrum.

A strong increase in the forward current and in the fill factor (FF) is observed for conjugated polymer/fullerene bulk heterojunction solar cells upon insertion of a thin layer of LiF between the organic layer and the Al electrode (negative electrode of the solar cell) as shown in Figs. 1(a) and
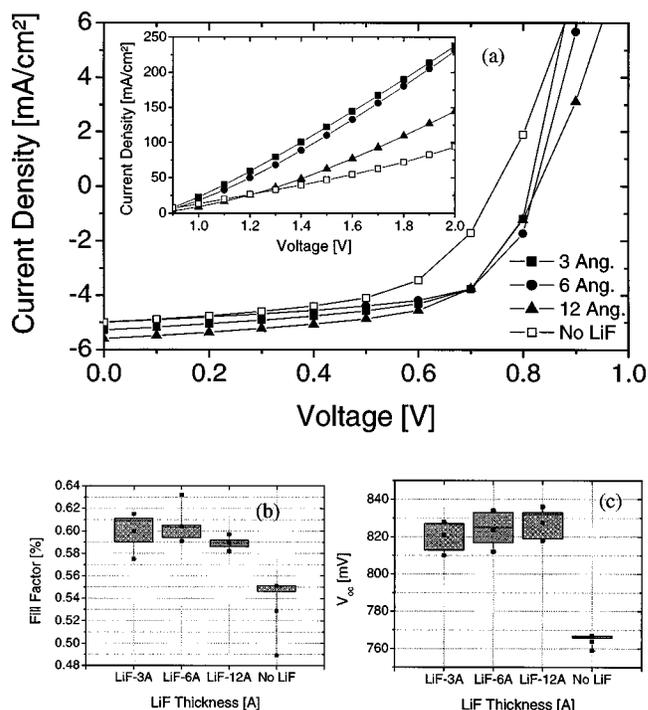

FIG. 1. (a) I/V characteristics of typical MDMO-PPV/PCBM solar cells with a LiF/Al electrode of various LiF thickness (■: 3 A, ●: 6 A, ▲: 12 A) compared to the performance of a MDMO-PPV/PCBM solar cell with a pristine Al electrode (□). (b) and (c) are box plots with the statistics of the FF and the V_{oc} from six separate solar cells.

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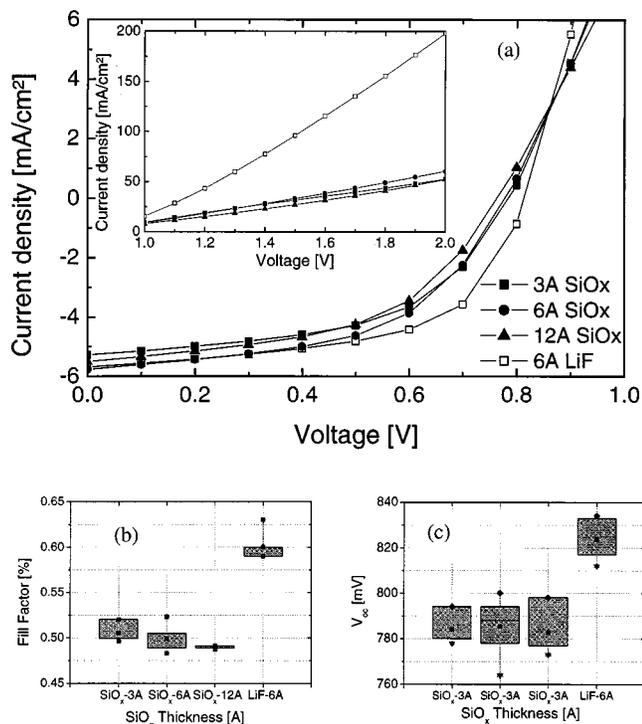
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FIG. 2. (a) I/V characteristics of typical MDMO-PPV/PCBM solar cells with SiO_x/Al electrodes of various SiO_x thickness (■: 3 A, ●: 6 A, ▲: 12 A) compared to the performance of a MDMO-PPV/PCBM solar cell with a LiF/Al electrode (□: 6 A LiF). (b) and (c) are box plots with the statistics of the FF and the V_{oc} from six separate solar cells.

1(b). A box plot diagram was chosen to present the results from current/voltage (I/V) measurements for the FF [Fig. 1(b)] and the V_{oc} [Fig. 1(c)]. The horizontal lines in the box denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The two symbols below and above the 5th/95th percentile error bar denote the highest and the lowest observed values, respectively. At least six different devices were evaluated for each LiF thickness which was varied between 0 and 15 Å. Upon insertion of only 3 Å of LiF, the FF already increased by ~20% compared to otherwise identical reference devices with a pristine Al electrode. Together with an I_{sc} of 5.25 mA/cm², an V_{oc} of 825 mV, the white light power conversion efficiency under 800 W/m² at 50 °C was calculated to be 3.3%.

Further increase of the layer thickness (up to 9 A) did not change the average value of the FF, but narrowed considerably the distribution of the FF of the single devices. At a LiF layer thickness of already 12 A a slight decrease of the FF is observed and at a layer thickness exceeding 20 A, the beneficial influence of the LiF layer on the FF was lost due to the high resistivity of the LiF layer.

Thin layers of SiO_x were evaporated as an inert reference interfacial layer between the organic layer and the Al electrode, in order to investigate the importance of the interfacial layer as a buffer preventing reactions between the hot, incoming Al atoms and the organic compounds during thermal deposition of the Al. Figures 2(a)–2(c) show the I/V behavior under illumination and the statistics on the FF and the V_{oc} for devices with SiO_x layers between 3 and 12 Å. As reference, results for the 6 Å LiF/Al electrode from Fig. 2 are compared. No enhancement of any of the power characteristics of the photodiode were observed upon insertion of a
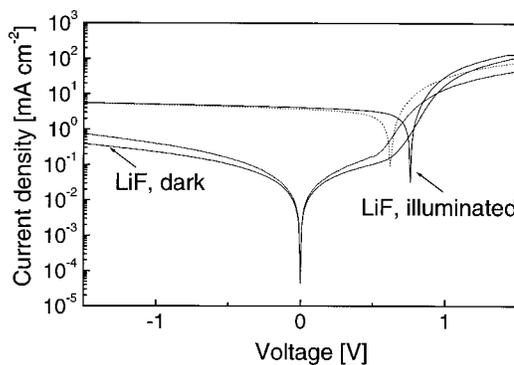

FIG. 3. I/V plot of a typical MDMO-PPV/PCBM bulk heterojunction solar cell with a Au electrode (dashed line) and a LiF/Au electrode (full line), respectively, in the dark and under illumination.

SiO_x layer as an inert buffer. From this, we conclude that the beneficial effects of LiF insertion can not be explained by an insulating buffer function.

The question arises as to whether Al is a necessary component in the enhancement of the photodiode properties upon insertion of a thin LiF layer. This was investigated by comparing devices where the LiF layer was covered by a Au electrode instead of a Al electrode. Typical I/V characteristics, shown in Fig. 3, reveal a clear difference upon insertion of a 6 Å thin LiF layer beneath the Au electrode. Most strikingly, the V_{oc} is found to increase to values as high as 770 mV, which is otherwise only obtained when using metals with a lower work function. The FF increases from ~50% up to >55%. Also, the short circuit current was observed to increase (4.1 mA/cm²), in good accordance with the expectations for a more selective diode contact, i.e., better ohmic to electrons [[6,6]-phenyl C61 butyric acid methyl ester (PCBM)] and better blocking to holes [poly[2-methoxy, 5-(3′,7′-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV)] as discussed recently.[7] The white light power efficiency of the MDMO-PPV/PCBM diodes with a LiF/Au electrode under 800 W/m² at 50 °C was calculated to be 2.3%. Table I summarizes the average FF and V_{oc} for the various diodes.

A numerical fitting analysis to the I/V curves was applied to evaluate the observations in terms of diode param-

TABLE I. Solar cell characteristics (FF and V_{oc}) for various interfacial layers (LiF and SiO_x) with different thickness compared to a solar cell with a pristine Al electrode as well as calculated diode characteristics (R_s, R_p) from Eq. (1) for the various interfacial layers.

	V_{oc} (mV)	FF (%)	R_s (kΩ)	R_p (kΩ)
No Spacer	759	53	1.0^{-2}	1.2
LiF [A]				
3	821	61.1	4.0×10^{-3}	1.1
6	834	63.2	3.8×10^{-3}	1.3
9	814	59.2	4.2×10^{-3}	1.2
12	832	58.8	5.1×10^{-3}	1.2
15	791	49	4.9×10^{-3}	1.2
SiO_x [A]				
3	794	52.2	1.7×10^{-2}	1.1
6	788	51.5	1.6×10^{-2}	0.9
12	796	49.8	1.7×10^{-2}	1.0
Au	620	51	8.0×10^{-3}	0.7
LiF (6 A)/Au	763	54	2.9×10^{-3}	0.9

eters. The current equation of an ideal Shottky diode:[8]

$$I(V) = I_0[\exp(q(V - IR_s)]/nkT) - 1)$$
$$+ (V - IR_s)/R_p + I_{sc}, \qquad (1)$$

where I_0, R_s, R_p, n, and q/kT are the saturation current density, the serial and parallel resistivity, the diode ideality factor, and the temperature potential (25 mV at room temperature), respectively, was fitted to measured I/V curves by a recursive algorithm. The essential diode parameters are summarized in Table I. While there is little or no change in the shunt resistivity for all of the diodes, the serial resistivity of the diodes is lowered by a factor of 3–4 upon insertion of a thin LiF layer, independent of the evaporated metal. This lowering of the serial resistivity is responsible for the increase of the FF due to formation of a better ohmic contact.

We propose a combined mechanism allowing to understand this behavior. Due to the strong dipole moment of LiF (6.3 D),[9] even a monomolecular layer of LiF can cause a significant vacuum level offset.[10] This shift of the vacuum level is well known in the field of surface science for the deposition and adsorption of molecules on metal surfaces.[10–12] This phenomenon results in a change in the work function (or surface potential) of the metal, as has been verified for LiF/Al electrodes by ultraviolet photon spectroscopy (UPS).[4] It is important to note that these techniques observed a lowering of the Al work function, i.e., a dipole moment directed from the metal, when LiF was evaporated on top of the Al under conditions in which a dissociation of the LiF is not expected (low evaporation rates, UHV). The improved electrode properties (i.e., lowering of the metal work function or shifting of the molecule levels towards higher energies) can thus be explained by an alignment of LiF resulting from the Li$^+$ adhering preferentially to the organic surface and the F$^-$ pointing towards the metal surface. Recent UPS studies observed such a mechanism for small molecule/LiF/Al interfaces.[13] Embedding of molecular dipoles in the form of organic monolayers at metal/inorganic semiconductor (like Ge, Si, or n-GaAs) interfaces shows qualitatively the same effect as insertion of LiF at the interface between a metal and an organic semiconductor.[14]

Additionally, we suggest that dissociation of LiF and subsequent doping of the underlying organic due to the formation of metallic Li[16] is not required to explain the enhancement seen in the present study for solar cells. Dissociation of LiF by way of chemical reactions that lead to charge transfer across the interface can produce an interface dipole much the same as intact LiF molecules. In the case of the LiF/Au cathode, the reaction pathways leading to the production of metallic Li are not clear, and it is possible that the observed enhancement is entirely due to the dipole moment of intact LiF molecules

In summary, we have shown that the white light efficiency of conjugated polymer/fullerene bulk heterojunction solar cells can be significantly enhanced up to 3.3% white light efficiency when using LiF/Al electrodes instead of pristine Al electrodes alone. A similar enhancement was observed for LiF/Au electrodes. The formation of a dipole moment across the junction, due to either orientation of the LiF or chemical reactions leading to charge transfer across the interface, is suggested as the mechanism for the enhancement.

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