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Improved light harvesting in tin-doped indum oxide (ITO)-free inverted bulk-heterojunction organic solar cells using capping layers

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We show that ultrathin metal layers (Ag or Al/Ag) are feasible as transparent top contacts for zinc phthalocyanine: C_{60} bulk-heterojunction inverted organic solar cells thermally evaporated on glass substrates. Furthermore, it is demonstrated that the introduction of an organic capping layer drastically increases light incoupling and photon harvesting, in accordance with optical simulations. Proof of principle tin-doped indium oxide (ITO)-free solar cells employing a transparent metal contact and a capping layer reach efficiencies of 1.06%, compared to 0.69% without addition of the capping layer. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2981525]

In the past years, organic solar cells have attracted considerable interest as a potential cost-efficient alternative to current silicon solar cells. Since the first breakthrough with a copper phthalocyanine/perylene derivative heterojunction by Tang,[1] new materials and concepts have resulted in efficiencies of up to 5%.[2]

Due to the scarcity of indium and increasing prices of tin-doped indium oxide (ITO), the standard transparent electrode material, an increasing effort is made to find alternatives, e.g., carbon nanotubes for polymer-based solar cells,[3] conductive polymers,[4,5] metals,[6] or aluminum-doped zinc oxide.[7] Another important issue for organic solar cells is the incoupling of light. It is possible to tune and influence the optical properties of a device by using capping layers on top of a transparent contact, as has been found for organic light-emitting diodes,[8] and has been proposed for solar cells.[9]

In this letter, these issues are addressed by investigating inverted solar cells with transparent metal contacts and tris(8-hydroxy-quinolinato)-aluminum (Alq_3) capping layers. It is shown that ITO-free organic solar cells with transparent metal contacts are a feasible, cost-efficient alternative with good processibility. Furthermore, organic capping layers are shown to lead to considerable improvements in the solar cell efficiency, paving a way for further optimization toward efficient devices.

The solar cells are fabricated in a custom-made vacuum system (K.J. Lesker, U.K.) at a base pressure of 10^{-6} mbar, using shadow masks. Float glass precleaned with acetone and ethanol is used as substrate.

A metal back contact of 100 nm Al is deposited, followed by 1 nm of a proprietary *p*-type dopant (Novaled AG, Dresden, Germany).[10] As hole transporting material, 30 nm of 10 wt % *p*-doped $4,4',4''$-tris(1-naphthylphenylamino)-triphenylamine is used. For light absorption, a layer of zinc phthalocyanine (ZnPc) (10 nm) followed by a layer of co-evaporated $ZnPc:C_{60}$ (25 nm, ratio 1:1) are deposited. After an additional absorber and transport layer of C_{60} (40 nm), 7 nm of 4,7-diphenyl-1,10-phenanthroline (BPhen) is used as exciton blocker. All materials had been purified by vacuum gradient sublimation. Different thicknesses and combinations of Al/Ag (11–15 nm total thickness) are used as transparent top contact, as well as different thicknesses (0–100 nm) of Alq_3 as capping layer.

The 16 samples are made on the same substrate in one run. This way, the only variations are for the top contact and capping layer while keeping the conditions for all other layers (hole transport layer, absorber, and electron transport layer) constant. Typical solar cell areas are around 6.7 mm^2 (measured using a light microscope).

The finished solar cells are encapsulated in a nitrogen glovebox attached to the vacuum deposition chamber, then stored at ambient conditions. $J(V)$-characteristics are recorded using a source measurement unit 236 SMU (Keithley) under an AM 1.5 g sun simulator (Hoenle AG), monitored with a silicon photodiode with respect to which intensities are given. External quantum efficiency (EQE) is measured employing the lock-in technique in a custom-made setup with Xe illumination and a Cornerstone 260 monochromator.

Reflection and transmission measurements are performed on an UV-3100/MPC-3100 spectrometer (Shimadzu); the morphology of deposited Ag layers is analyzed using atomic force microscopy (Digital Instruments) and scanning electron microscopy (Zeiss DSM 982 Gemini) (not shown).

Optical simulations are performed using a numerical code based on the transfer matrix approach, using refractive index n, extinction index k (obtained from reflection and transmission measurements), and layer thickness to calculate, e.g., photon absorption and distribution of the optical field within the solar cell.

The obtained solar cell characteristics for different metal contacts and Alq_3 layers are summarized in Table I. It can be seen that the composition of cathode and layer thickness of

TABLE I. Solar cell characteristics.

Metal contact	Alq_3 capping (nm)	J_{SC} (mA/c^2)	V_{OC} (V)	FF (%)	η (%)
5 nm Al, 10 nm Ag	0	3.37	0.41	48.42	0.69
5 nm Al, 10 nm Ag	10	3.26	0.41	52.14	0.69
5 nm Al, 10 nm Ag	50	4.92	0.42	52.64	1.06
5 nm Al, 10 nm Ag	100	3.99	0.42	52.52	0.87
15 nm Ag, 0 nm Al	50	0.34	0.44	39.20	0.06
3 nm Al, 8 nm Ag	50	5.67	0.44	43.42	1.01

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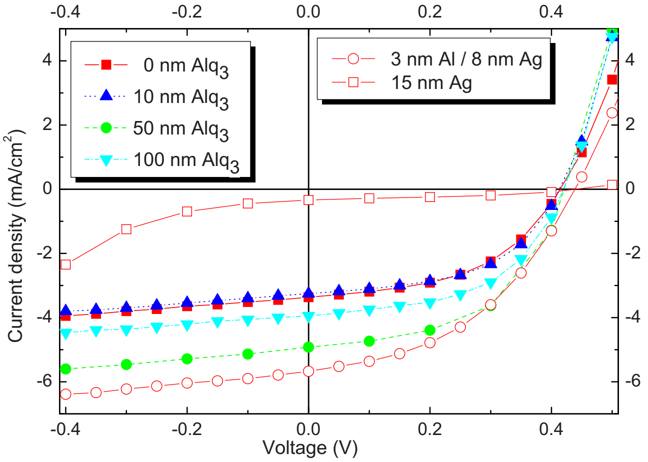

FIG. 1. (Color online) Current voltage curves. Solar cells with metal top contact of 5 nm Al and 10 nm Ag, with 0 nm (filled squares), 10 nm (filled triangles), 50 nm (filled circles), and 100 nm (filled upside-down triangles) Alq_3 capping. Open symbols: Solar cells with 50 nm Alq_3 and 15 nm Ag (open squares) and 3 nm Al / 8 nm Ag (open circles) top contact.

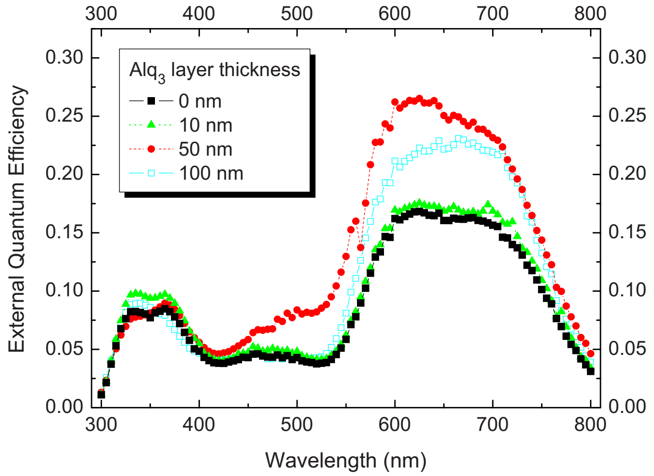

FIG. 2. (Color online) EQE of solar cells having 5 nm Al / 10 nm Ag as metal contact and different Alq_3 capping layer thicknesses.

the transparent top contact have a significant influence on the overall device performance, as summarized below.

(i) With 11 nm Ag as top contact, no devices, independent of any other layers, have electrical contact. We attribute this to the morphology: below a certain thickness threshold, Ag grows as islands or as disjunctive two-dimensional networks instead of forming continuous films, lacking conductive pathways. It was reported that uniform films are found at thicknesses above 10 nm.[11] In the current work, however, a more sensitive dependence of the morphology on the deposition parameters is noted.

(ii) 15 nm Ag: devices are successfully fabricated; despite an open circuit voltage V_{OC} similar to the Al/Ag cells (0.44 V), they suffer from extremely low short-circuit currents with $J_{SC} < 0.5\ mA/cm^2$ and lower fill factor (FF). Even though pure Ag layers are optically more favorable than Al/Ag layers, a bad electrical contact (high series resistance R_S) is observed, attributed to morphological issues. The clear "S-kink" visible in the $J(V)$-curves also suggests a high barrier for charge extraction, which may hint at diffusion of Ag into adjacent organic layers.[12]

(iii) 3 nm Al/8 nm Ag: these samples have the highest currents, up to $J_{SC} = 5.67\ mA/cm^2$ at $106\ mW/cm^2$ simulated sunlight. Nonetheless, the series resistance of this relatively thin layer limits FF to $<43\%$. It is noteworthy that the total metal layer thickness is small with only 11 nm, but working solar cells with efficiencies $\eta > 1\%$ were obtained. We attribute this to the Al acting as smooth mediating layer between BPhen and Ag, promoting a closed film and thus better conductivity, combined with lower absorption compared to 15 nm thick metal films.

(iv) 5 nm Al/10 nm Ag: this combination leads to solar cells having $FF > 52\%$ and high currents of $J_{SC} = 4.9\ mA/cm^2$. This combination of material and layer thickness seems the best compromise between morphology, electrical, and optical properties.

In order to study the influence of a variation on the Alq_3 capping layer, four solar cells are made with Alq_3 layer thicknesses of 0, 10, 50, and 100 nm, respectively. Comparing samples with different Alq_3 layers and the best metal contact (5 nm Al/10 nm Ag), it is observed that V_{OC} remains almost constant, while J_{SC} and FF (and thus η) profit greatly from the capping layer (Table I).

A comparison of the resulting $J(V)$-curves can be seen in Fig. 1, with the best efficiencies obtained with a 50 nm layer of Alq_3. Figure 2 shows the EQE. The influence of the Alq_3 layer thickness on the absorption in the ZnPc is obvious, with the EQE from 600–700 nm increasing from 15% (0 nm Alq_3) to around 25% (50 nm Alq_3).

Simulations confirm that a capping layer of Alq_3 drastically improves light absorption within the active layers of the solar cell. At the same time, it influences the light reflection. Both effects can be explained by considering a microcavity effect between the semitransparent top contact and the reflecting back contact. The Alq_3 capping layer can be used to tune the optical field in the solar cell stack in such a way that field maxima correspond to the position of the absorber materials, increasing the absorption probability of a photon entering the solar cell. This is illustrated in Figs. 3 and 4, where the calculated absorption (Fig. 3) and reflection (Fig. 4)

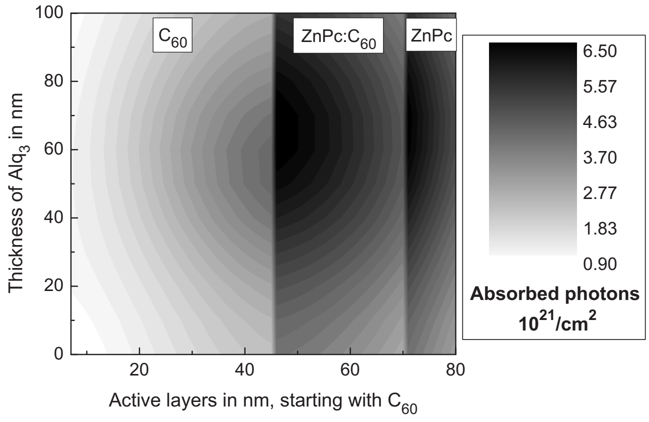

FIG. 3. Simulated photon absorption in the ZnPc and C_{60} absorber layers depending on Alq_3, calculated in $photons/cm^2$. A light intensity of AM 1.5 g is assumed.

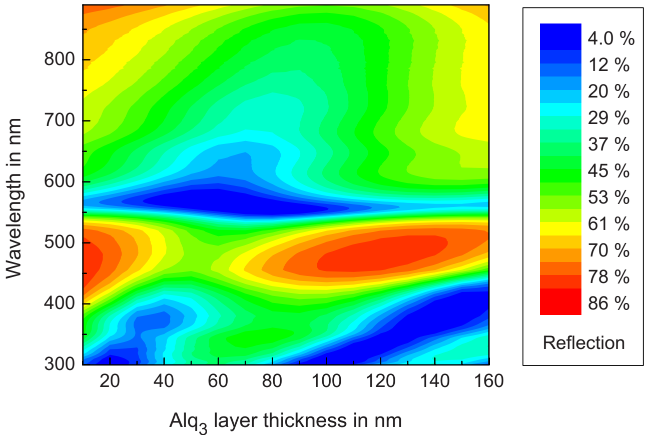

FIG. 4. (Color online) Simulated external reflection depending on Alq$_3$ thickness.

within the solar cell stack are plotted together with the Alq$_3$ layer thickness. The highest absorption occurs, as expected, in the ZnPc and ZnPc:C$_{60}$, with optimized Alq$_3$ layers being 50–75 nm thick, while the effect in the pure C$_{60}$ electron transport/absorber layer is smaller, as shown experimentally in the EQE spectra. Similarly, lower reflection values are obtained for this thickness range of 50–75 nm, compared to 0 nm of Alq$_3$. Even at the optimized Alq$_3$ layer thickness, one observes significant reflection, especially in the wavelength range of 450–550 nm and above 700 nm. It is expected that this total external reflection can be reduced by using different absorber materials.

In summary, ITO-free inverted organic bulk-heterojunction solar cells were presented. The effect of morphology on metal contact efficiency was discussed. It was shown that a capping layer of Alq$_3$ significantly improved solar cell performance by decreasing external reflection and increasing absorption within the active layers, a behavior confirmed by optical simulations.

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