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On the use of Ga–In eutectic and halogen light source for testing P3HT–PCBM organic solar cells

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Abstract

In this paper, we report a simple and inexpensive method for testing the photovoltaic characteristics of organic devices. We report measurement data on P3HT–PCBM organic solar cells spin-coated from chloroform solutions, obtained using a Gallium–Indium eutectic top contact, and a halogen light source. We propose a method to correct the spectral mismatch of this light source with the solar spectrum. The effect of annealing and changing the P3HT:PCBM ratio are studied, and similar results as with evaporated aluminum are obtained. We conclude that Ga–In eutectic and halogen light source can conveniently be used instead of evaporated aluminum and a solar simulator for the study of polymer–fullerene bulk-heterojunction devices.

Keywords: P3HT; PCBM; Ga–In; Eutectic

1. Introduction

Organic photovoltaics [1–6] became more than a laboratory curiosity when the barrier of 1% conversion efficiency was approached by Tang in 1986 [7]. But still, the devices were made by methods very similar to the ones used for building inorganic solar cells, e.g. vacuum evaporation. The next breakthrough came with the development of soluble conjugated polymers such as modified poly (paraphenylene–vinylene) (PPV) [8] or poly (3-alkyl thiophene) (P3AT) [9], which opened the path to low-cost solution-based thin film

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deposition methods such as spin coating at the laboratory scale, screen printing or doctor-blade casting for mass production. Finally, the third breakthrough can be attributed to the discovery of the bulk-heterojunction, e.g. a blend of donor and acceptor materials, which considerably increased the area of contact between n- and p-type materials. This resulted in remarkable progress in conversion efficiency, the state-of-the art being now around 4–5% [10]. Yet, for organic solar cells to really have a commercial impact, values close to amorphous silicon, e.g. higher than 10% are sought. In this race for higher efficiencies, the research has taken considerable pace in the last few years, and many laboratories are aiming their expertise in nanotechnologies towards photovoltaics applications. For instance, materials such as nanorods [11], organic–inorganic hybrid particles, nanocolumn electrodes [12] or double-cable polymers [13] are of considerable interest for this field of research. However, the laboratories that possess the synthesis expertise may not always have the device fabrication and testing capabilities. In-house device making and testing capabilities are always desirable for evaluation of promising materials.

Organic photovoltaic films can be deposited from solutions by simple methods such as spin coating or drop casting, which can be easily implemented in any chemistry laboratory. However, in order to build and characterize organic photovoltaic devices, two items are required: a metal evaporator and a solar simulator, expensive pieces of equipment that require an investment on the order of several tens of thousands of dollars. In this work, we propose alternative solutions which can considerably reduce the cost of research, with little penalty on the performance and results. We illustrate the use of Gallium–Indium eutectic for making back contacts, and halogen light source for conversion efficiency measurement on the well-studied P3HT–PCBM organic solar cell [14].

Due to the use of very thin active layers in organic photovoltaics (~100 nm), and because organic semi-conductors have lower charge mobility than their inorganic counterparts, an electrical contact to the cell must cover the entire active surface without shorting the device and provide uniform contact to the organic film. Thus, metal evaporation is the preferred method for depositing contacts. Aluminum is most commonly used in organic PV because its work function of 4.3 eV is well suited for extracting electrons from fullerene derivatives. There are very few alternatives to metal evaporation, one of which is the use of mercury electrodes. Mercury is however very undesirable because of its high toxicity and its work function of 4.5 eV, very close to that of ITO. Similar work functions result in low built-in electric fields, causing low exciton separation and low cell output power. The second alternative is to test materials in liquid electrolyte, which can introduce other effects such as hysteresis due to double-layer capacitance and incorporation of ions in the conjugated polymers during *I–V* testing.

In this paper, we propose the use of Ga–In eutectic as a convenient substitute to evaporated aluminum. Pure gallium melts at 30 °C, and has a work function of 4.2 eV, very close to that of aluminum (4.3 eV). Even more convenient is Ga–In eutectic, which is liquid at room temperature. In the present work, we used a Ga–In eutectic which melts at 15.7 °C.

Also, proper solar simulation requires a costly Xenon Arc lamp, with high-voltage ignitor, stable power supply, and AM 1.5 filter. Xenon arc is the closest to natural sunlight, with a color temperature around 5800 K. On the other hand, natural sunlight is free, and has the desired spectral output.

Halogen light sources have many advantages over xenon light sources: they are inexpensive and readily available, their intensity output can be fully controlled with a variable power supply, and their small form factor makes them easy to use in a controlled atmosphere such as a glove-box. However, their color temperature of 3000 K is severely mismatched with the solar spectrum, and overestimated conversion efficiencies usually result from their use. Here, we propose to use them indoors to obtain *I–V* curves from which the fill factor can be measured. Then, a simple portable meter can be used outdoors to measure the short-circuit current and open-circuit voltage of the cell. A calibrated solar cell can be used to measure the sunlight intensity. Then, the fill factor measured indoors at similar current is used to calculate a very good approximation of the cell conversion efficiency

$$\eta = (\mathrm{FF}_{\mathrm{indoors}} \times I_{\mathrm{sc}_{\mathrm{outdoors}}} \times V_{\mathrm{oc}_{\mathrm{outdoors}}})/\mathrm{Light\ intensity}_{\mathrm{outdoors}}.$$

Finally, the output of the halogen light source can be recalibrated in sunlight equivalents to perform all measurements indoors.

We illustrate the use of these methods on the well-studied P3HT–PCBM plastic solar cells, and compare our results with results obtained using a metal evaporator and a solar simulator.

2. Experimental

Regioregular poly (3-hexyl thiophene) was donated by Plextronics, Inc. PCBM methanofullerene was purchased from American Dye Source. PEDOT:PSS Baytron P was purchased from H.C. Starck (A Bayer Division). ITO/Glass substrates with 25 Ω/square were purchased from Delta Technologies. Bulk-heterojunction solar cells were prepared from 8–10 g/L solutions of P3HT:PCBM in chloroform. A layer of PEDOT:PSS (Baytron P:MeOH 1:2) was spin-coated on the ITO/Glass substrates. Then, the P3HT:PCBM solution was spin coated on the PEDOT:PSS at 1000–2000 rpm. Ga–In eutectic (Aldrich 495425) was used for the contacts to the P3HT:PCBM layer. The photoactive area tested was 0.07 cm^2. A rubber o-ring of 3 mm diameter was used to contain the Ga–In droplet and control the back contact area. The *I–V* measurements were run in air at 25 °C, between −0.2 and +1 V at 100 mV/s, with an EG&G 273A potentiostat–galvanostat, using especially programmed Labview$^{\mathrm{TM}}$ software. The light source consisted of a 50 W MR16 halogen light bulb computer controlled by an HP6038A power supply. The light source intensity was calibrated in $\mathrm{W/m}^2$ as function of the power input with a reference Si solar cell (Daystar solar meter).

3. Results and discussion

3.1. *Light intensity and spectral mismatch correction*

When a light source other than the solar light is used to measure solar cells, two errors are introduced: first, the measurement of the integrated spectrum light intensity may be wrong if the sensor used has a responsivity curve that is not matched for the source used. Secondly, the spectral mismatch with the solar spectrum (Fig. 1) may cause the measured efficiency to differ from that in real sunlight, even if the integrated light intensity is the same. Thus, we have developed a method to recalibrate our light source and correct both errors at the same time.

The output of the halogen light source was initially measured with a calibrated Si solar cell. Since this solar cell is calibrated versus the solar spectrum, it gives a wrong value of the

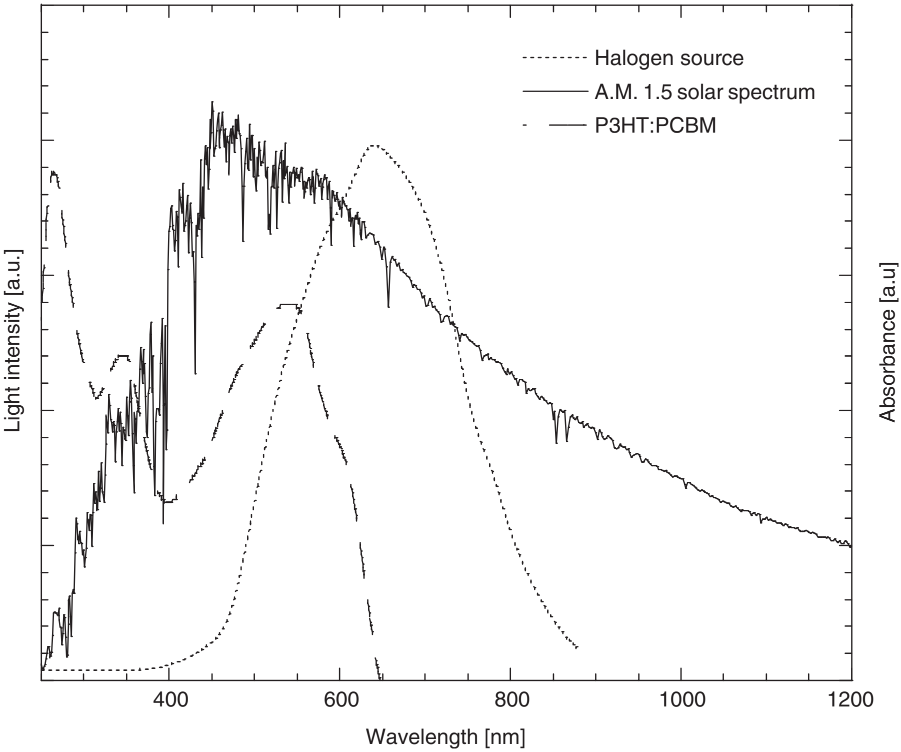


Fig. 1. Absorption spectrum of P3HT:PCBM 1:1 layer spin-coated on glass, spectral output of the halogen light source used to test them, and AM 1.5 solar spectrum.

illumination in W/m^2. However, it measures correctly the illumination changes, as they are proportional to its short-circuit current. A set of I–V curves was measured at various illuminations for a P3HT–PCBM solar cell. It yielded a curve of fill factor versus short-circuit current. The same solar cell was taken outdoors, and the short-circuit current and open-circuit voltage were measured with a portable meter. A sunlight illumination of $99\,mW/cm^2$ was also measured with the same calibrated Si solar cell.

By using the curve of fill factor versus short-circuit current measured indoors, the fill factor was estimated for the short-circuit current measured outdoors (Fig. 2). The only assumption here is that fill factor values are not sensitive to spectral output, but only to short-circuit current value. We will check the validity of this assumption with an AM 1.5 solar simulator.

Thus, the sunlight efficiency of the cell could be calculated as

$$\eta = (\mathrm{FF}_{\mathrm{indoors}} \times I_{\mathrm{sc}_{\mathrm{outdoors}}} \times V_{\mathrm{oc}_{\mathrm{outdoors}}})/\text{Light intensity}_{\mathrm{outdoors}}.$$

Then, Log(I_{sc}) versus Log(I_{hal}) curve was corrected by horizontal translation to intercept the experimental point in sunlight, while keeping the same slope (Fig. 3). This assumes that the variation of short-circuit current with light intensity is independent of wavelength.

Finally, the output of the halogen light source as function of its input power was recalibrated with the new Log(I_{sc}) versus Log(I_{sun}) curve. After this correction was done,

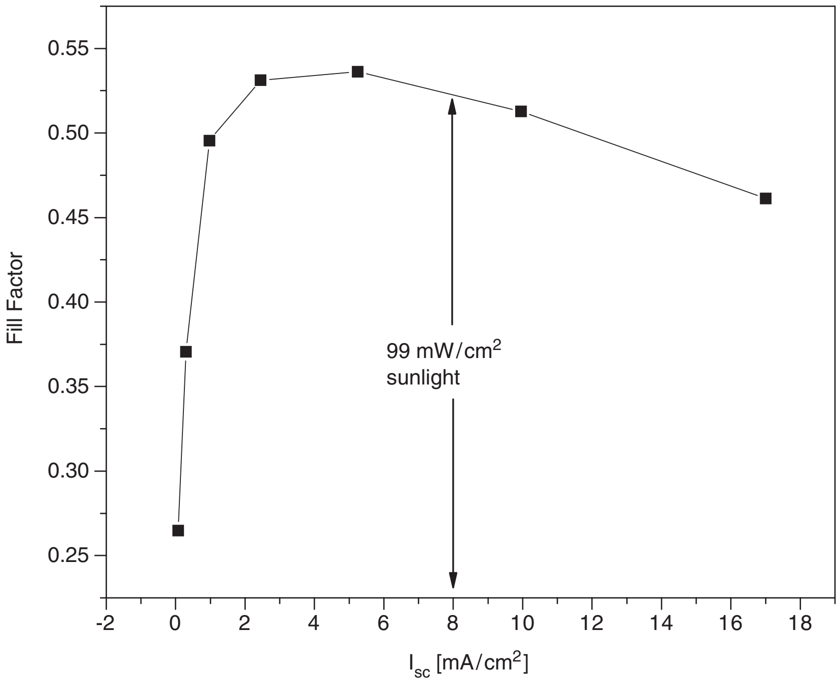


Fig. 2. Fill factor versus short-circuit current of a P3HT:PCBM 1:1 solar cell measured with halogen light source. The arrows indicates values of short-circuit current in sunlight and the corresponding fill factor.

same short-circuit currents were obtained at 100 mW/cm^2 simulated by the halogen light source, or 100 mW/cm^2 of real sunlight.

3.2. *In situ annealing and efficiency change monitoring*

Annealing has been reported by several authors to significantly and irreversibly increase the conversion efficiency of P3HT:PCBM solar cells. There are numerous annealing recipes, with optimal temperatures ranging from 50 °C [15] to 140 °C [16], and optimal times from 1–15 min. Some authors perform annealing in air, others in inert atmosphere, and some combine annealing with electrical polarization [17].

It has been our experience that optimal annealing conditions were dependent on layer thickness, film composition, solvent used and film deposition method. For instance, films coated from chlorobenzene or films with low PCBM contents anneal at lower temperature than films coated from chloroform and films with high PCBM contents (Table 1). In order to ensure optimal annealing conditions for each cell tested, we used the halogen light source set to ~2400 W/m^2 as the heat source, and monitored the efficiency evolution upon repeated *I–V* cycles (Fig. 4). We consistently observed an irreversible increase in efficiency after a few minutes, while the cells reached temperatures of ~80 °C. We stopped the light source when the efficiency reached a plateau, and let the cell cool down for further testing.

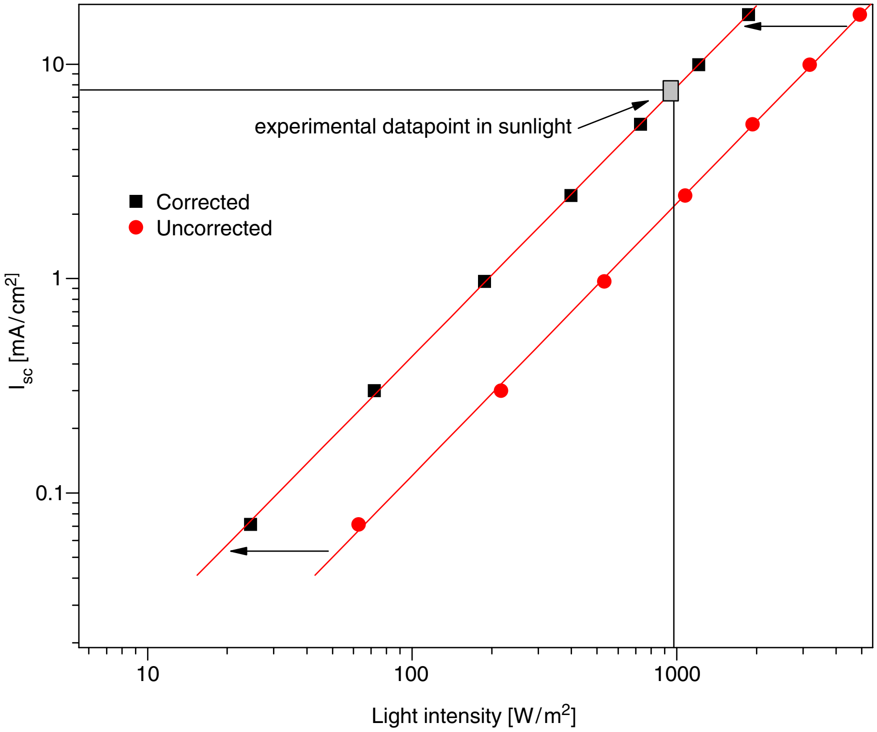


Fig. 3. Log–log plot of light intensity versus short-circuit current for P3HT:PCBM 1:1 solar cell measured with halogen light source. Uncorrected values of light intensity (dots) and corrected values (squares) intercepting datapoint in sunlight.

Table 1
Efficiencies before and after annealing and best annealing temperature as function of solvent, composition and spin coating speed for P3HT–PCBM photoactive layers

Solvent	Spin speed	1000 rpm	1500 rpm
	Composition	a/b (c)	a/b (c)
Chlorobenzene	1:1 (20 g/L)	0.05/0.33 (80)	0.12/0.55 (70)
Chlorobenzene	2:1 (20 g/L)	0.33/0.67 (60)	0.21/0.8 (55)
Chloroform	1:1 (10 g/L)	0.22/1.52 (75)	0.23/0.86 (75)
Chloroform	2:1 (10 g/L)	0.17/0.83 (60)	0.14/0.59 (70)

a. Efficiency before annealing (%);
b. Efficiency after annealing (%);
c. Best annealing temperature (°C).

3.3. Optimal P3HT:PCBM ratio

There are contradicting reports on the optimal P3HT:PCBM ratio, with optimal values proposed from 1:2 to 2:1. For instance, Inoue et al. [18] find the optimum P3HT:PCBM ratio at 2:1, using toluene as a solvent, and report 4% efficiency. Chirvase et al. [19] find an optimum P3HT:PCBM ratio between 1:1 and 1:0.9 using chloroform as solvent, and report

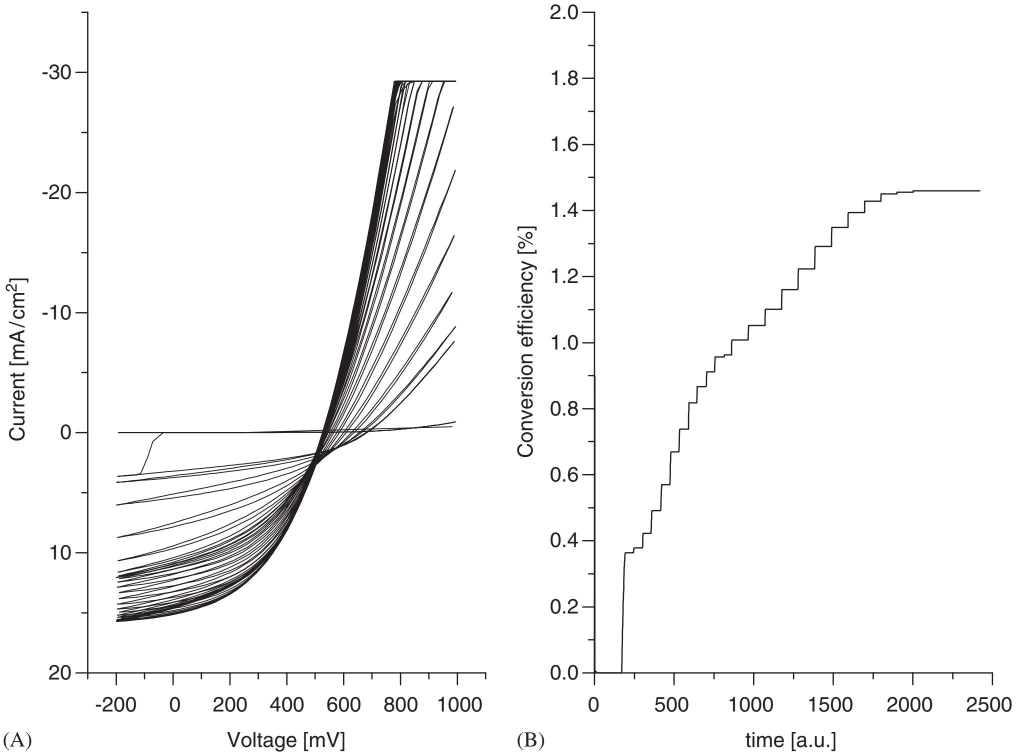


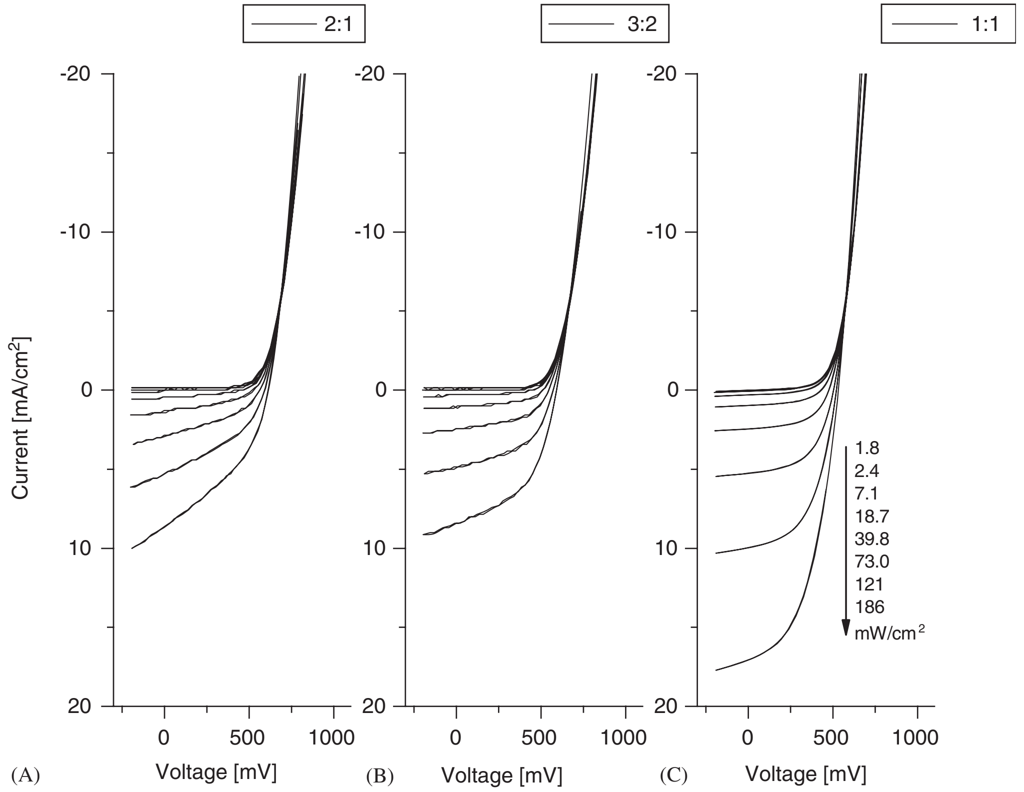
Fig. 4. Repeated *I–V* cycles under 2400 W/m^2 white light annealing (A) and evolution of conversion efficiency (B) for same P3HT:PCBM 1:1 cell spin coated from 10 g/L chloroform solution.

2.39% efficiency. As the morphology of the phases is strongly dependent on processing conditions such as solution concentration, solvent nature and annealing conditions, it is not surprising to find such discrepancies. The goal is to maximize electron and hole mobilities by forming two interpercolated phases of P3HT and PCBM. Also, the optimized P3HT:PCBM ratio can be determined by methods such as photoluminescence quenching [20] or measuring electron and holes mobilities [21], but the correlations with actual device performance are not always straightforward. While specific conditions vary from one laboratory to another, the only way to acquire certitude on the best composition was to perform a study on our own devices. The P3HT:PCBM compositions tested were 2:1, 3:2 and 1:1 (Fig. 5).

We used spin coating at about 1000 rpm from 8–10 g/L chloroform solutions, and the results presented are the best obtained for each composition. We find the best conversion efficiency of 2.1% at P3HT:PCBM ratio of 1:1 (Table 2). These results are in good agreement with those published by Chirvase et al.

3.4. Comparing the efficiencies measured with a halogen light source and with an AM 1.5 solar simulator

We used the optimal formulation and spin coating conditions previously determined to build more devices. They were first annealed and tested under the halogen light source at



(A) (B) (C)

Fig. 5. *I–V* curves at various light intensities of ITO–PEDOT:PSS/P3HT:PCBM/In–Ga solar cells with P3HT:PCBM ratio of 2:1 (A), 3:2 (B) and 1:1 (C).

Table 2
Photovoltaic parameters efficiency (η), fill factor (FF), short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of P3HT:PCBM solar cells at various P3HT:PCBM ratios, measured under 100 mW/cm^2 halogen white light, with Ga–In top contact

P3HT:PCBM ratio	η^*_{halogen} (%)	FF	I_{sc} (mA/cm^2)	V_{oc} (mV)
2:1	0.98	0.39	4.31	588
3:2	1.23	0.48	4.7	561
1:1	2.14	0.52	8.0	515

100 mW/cm^2, then taken the next day to an Oriel solar simulator and measured again under 100 mW/cm^2 (~1 sun). The *I–V* curves (Fig. 6) clearly show that similar photocurrents were measured at same light intensities. The lower photocurrents with the AM 1.5 solar simulator can be attributed to aging of the device (1day) between the two measurements, due to oxygen exposure. The solar cell parameters measured under the two light sources are summarized (Table 3). We observe a lower fill factor and lower I_{sc}, but

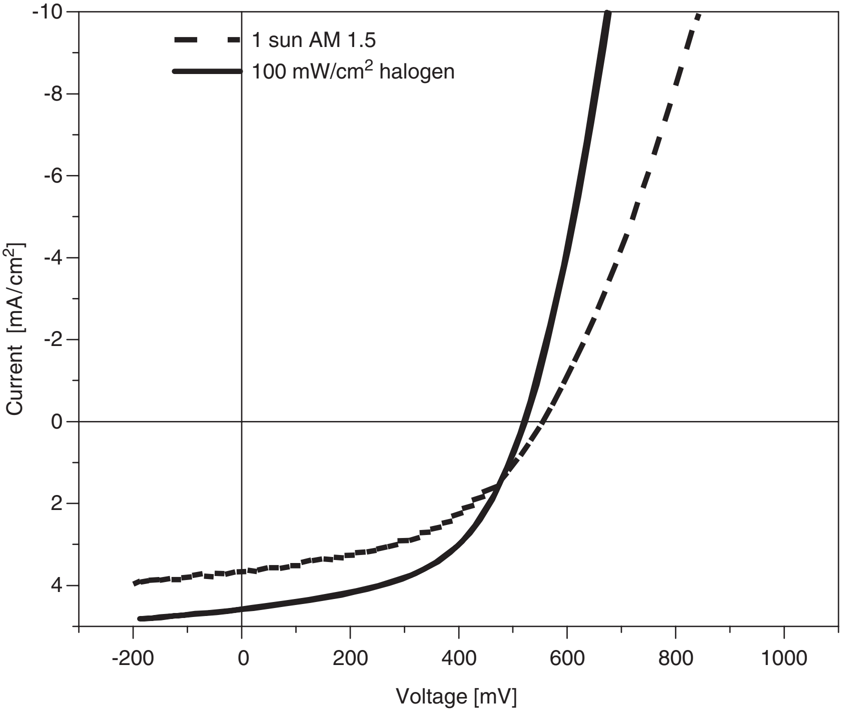


Fig. 6. *I–V* curves at 100 mW/cm^2 of simulated sunlight for the same ITO/PEDOT:PSS/P3HT–PCBM 1:1/Ga device measured with a halogen light source (—) or under AM 1.5 conditions (- - -).

Table 3

Photovoltaic parameters efficiency (η), fill factor (FF), short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of the same P3HT:PCBM solar cell, measured under 100 mW/cm^2 halogen white light or 100 mW/cm^2 AM 1.5 solar simulator

	η (%)	FF	I_{sc} (mA/cm^2)	V_{oc} (mV)
AM 1.5 1 sun	0.89	0.46	3.65	560
Halogen 1 sun	1.24	0.51	4.55	530

higher V_{oc} with the solar simulator. These parameters resulted in an efficiency of 0.89% vs 1.24% measured with the halogen light source. We conclude that our assumption that the fill factor did not change with wavelength was incorrect, and there is a spectral mismatch coefficient of ~0.71 to correct the efficiency measured with the halogen light source.

3.5. Comparison of the results with cells using evaporated aluminum versus In– Ga contacts

We applied the previously described conditions to spin-coat more films, on which two 0.24 cm^2 circular aluminum contacts where evaporated, under less than 10^{-6} mmHg vacuum. In order to have a fair comparison with the devices using In–Ga contact, no LiF

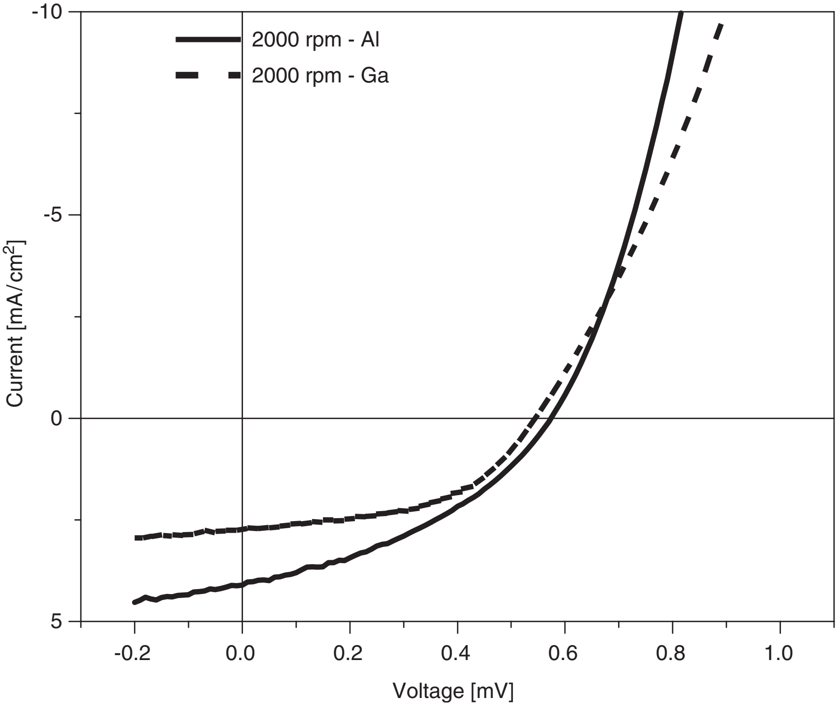


Fig. 7. *I–V* curves at 100 mW/cm^2 of AM 1.5 simulated sunlight for the same ITO/PEDOT:PSS/P3HT–PCBM 1:1/Ga device measured with aluminum top contact (__) or Ga–In top contact (- - -).

Table 4
Photovoltaic parameters efficiency (η), fill factor (FF), short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) of the same P3HT:PCBM solar cell, measured under 100 mW/cm^2 AM 1.5 solar simulator, using either an Al or Ga–In top contact

	Contact area (cm^2)	η (%)	FF	I_{sc} (mA/cm^2)	V_{oc} (mV)
Al contact	0.24	0.97	0.38	4.02	580
Ga–In contact	0.07	0.82	0.51	2.71	550

layer was deposited. About half of the P3HT–PCBM surface on each device was left undisturbed to be tested with Ga–In contact. Then, the cells were tested with an Oriel solar simulator under 100 mW/cm^2 light intensity, using either the aluminum or the Ga–In contact. We systematically observed higher short-circuit current and higher open-circuit voltage with the aluminum contacts, but lower fill factors (Fig. 7). The fill factor difference could be attributed to the device area difference (0.07 cm^2 for Ga–In vs 0.24 cm^2 for aluminum), where the series resistance decreases the fill factor in larger area devices. These differences resulted in overall higher efficiencies measured with the aluminum top contact (Table 4).

4. Conclusions

We have demonstrated the use of Ga–In eutectic as an efficient substitute to evaporated aluminum for P3HT–PCBM back contacts. We show that cells prepared in air using this type of cathode can reach conversion efficiencies close to state-of-the art with chloroform as the solvent. The only limitation of this setup is the absence of evaporated LiF layer between the P3HT–PCBM and the back contact, which is known to increase the value of fill factor [22].

We also show that cells can be tested with an inexpensive white halogen lamp, but this resulted in overestimated values of the conversion efficiency. We attribute this to the fact that the spectrum of halogen light source is a better match to the absorption of P3HT–PCBM than the AM 1.5 spectrum. We described a methodology to correct these values by using sunlight and a multimeter. On the other hand, we found that devices measured with an aluminum top contact yielded higher efficiencies than those measured with a Ga–In top contact. While finished devices cannot use in Ga–In top contact, its use at the research laboratory is extremely convenient for fast characterization of photovoltaic effect in bulk heterojunctions as is a halogen light source. This enables rapid evaluation of optimal device composition and deposition conditions. Then, aluminum evaporation can be used to generate finished prototypes and test them under AM 1.5 simulated solar conditions. We anticipate that these results will help other laboratories interested in testing organic photovoltaic devices.

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