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Short Communication

A Comparative Study on Low-Temperature Sol-Gel Ga-Doped Zinc Oxide Inverted PSCs

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A low-temperature sol-gel Ga-doped ZnO (ZnO:Ga) thin film as the electron transport layer (ETL) for high efficiency inverted polymer solar cells (PSCs) has been realised. The ZnO:Ga precursor was prepared by dissolving zinc acetate and ethanolamine in the 2-methoxyethanol with $Ga(NO_3)_3$ at different concentration. Doped ZnO thin films were deposed on indium tin oxide (ITO)/glass substrates by spin-coating technique and the films annealed at 150°C for 5 minutes in air. To check performances of ZnO:Ga thin film were realized inverted polymer solar cells with the configuration ITO/ZnO:Ga/photoactive layer/MoO_3/Ag. The photoactive layer was a blend of poly[(4,8-bis-(2-ethylhexyloxy)-benzo(1,2-b:4,5-b′)dithiophene)-2,6-diyl-alt-(4-(2-octanoyl)-3-fluorothieno[3,4-b]thiophene-)-2-6-diyl)] (PBDTTT-CF) and [6,6]-phenyl C_{71} butyric acid methyl ester ([70]PCBM) (1:1.5 w/w). In this work was investigated the effect of gallium concentration on the photovoltaic behavior of PSCs. The best efficiency of 7.7% was reached by using a 6 at% ZnO:Ga film as ETL.

Keywords: polymer solar cells, gallium doped zinc oxide (ZnO:Ga), sol-gel.

1. INTRODUCTION

The polymer solar cell (PSC) is a layered structure with a transparent front electrode, an active layer by mixing semiconductive polymer materials with n-type material and a back electrode. PSCs are thin, light and highly flexible, cheap and environmentally friendly [1-7]. One of the most interesting areas of use is building of photovoltaic cells. The main device configuration is based on the bulk heterojunction (BHJ) concept where a semiconducting p-type polymer material is blended with a n-type fullerene molecule giving a phase separation at nanometer scale [8-12]. Different ways have been developed to enhance PSC-based devices performance. In comparison to conventional structure, inverted structure is relatively more stable in air [13-15]. In the inverted PSC [16, 17] the chargecollecting nature of the electrodes is reversed compared to the standard configuration. The ITO electrode, covered by n-type metal oxides (such as titanium oxide or zinc oxide) is used as the cathode and an air-stable high-work-function metal (e.g. Ag) is used as the anode, ZnO is a good interfacial material for inverted PSCs due to the high transparency in the visible range, high electron mobility, appropriate energy band structure and environmental stability [18-22]. The electrical conductivity of ZnO can be increased by using n-type metal dopants able to reduce the series resistance improving the device performance [23-25].

In this article we report the fabrication of inverted PSCs employing an ETL realized by low-temperature solution-processed doped ZnO film. The use of Ga as ZnO dopant permits to obtain more efficient ETL layers compared to undoped ZnO with an easily and low temperature process fully compatible with the latest printing technologies. The architecture of the devices is glass/ITO/ETL/blend/MoO_3/Ag. The photoactive layer is a blend of poly[(4,8-bis-(2-ethylhexyloxy)-benzo(1,2-b:4,5-b′)dithiophene)-2,6-diyl-alt-(4-(2-octanoyl)-3-fluorothieno[3,4-b]thiophene-)-2-6-diyl)] (PBDTTT-CF) and [6,6]-phenyl C_{71} butyric acid methyl ester ([70]PCBM). All the PSCs were characterized by external quantum efficiency (EQE) and current-voltage (I-V) measurements in dark and under AM1.5G illumination (100 mW/cm^2). We compared the electrical behavior of the devices to rationalise the influence of the doping on the performance of the solar cells.

2. EXPERIMENTAL

2.1. Characterizations and methods

The ITO coated Corning® Eagle XG glass substrates, were Delta Technologies products, LTD, with a sheet resistance of 10 Ω*square. PBDTTT-CF and [70]PCBM were respectively Solarmer and Solenne BV products. 1,2-dichlorobenzene (anhydrous, 99%, DCB), 1,8-diiodoctane (98%, DIO), zinc acetate dehydrate (99.9%), ethanolamine (99.5%), 2-methoxyethanol (99.8%) and gallium (III) nitrate hydrate (99.9%) were purchased from Sigma-Aldrich. MoO_3 (99.95%) and Ag (99.99%) were purchased from Materion and Umicore.

Sol-gel procedure is used to prepare both doped and undoped ZnO [16]. 0.75 g of zinc acetate dihydrate and 0.21 g of ethanolamine were dissolved in 8 mL of 2-methoxyethanol. The doping was obtained by adding the corresponding salt of Ga. Solutions containing different molar ratios of the metal with respect to the moles of Zn (2, 4, 6 and 8% for ZnO:Ga) were prepared. Also, undoped ZnO was prepared as a reference. The solutions were stirred for 20 h in air. The films were obtained by spin coating the corresponding solution at 4000 rpm for 60 s on the top of glass or glass/ITO substrates and annealed at 150 °C for 5 min.

The thickness of the doped and undoped ZnO films was about 40 nm and it was measured by KLA Tencor P-10 surface profiler. UV-VIS optical reflectance and transmittance of the layers deposited on glass substrates were analysed by a Perkin-Elmer Lambda 900 spectrophotometer.

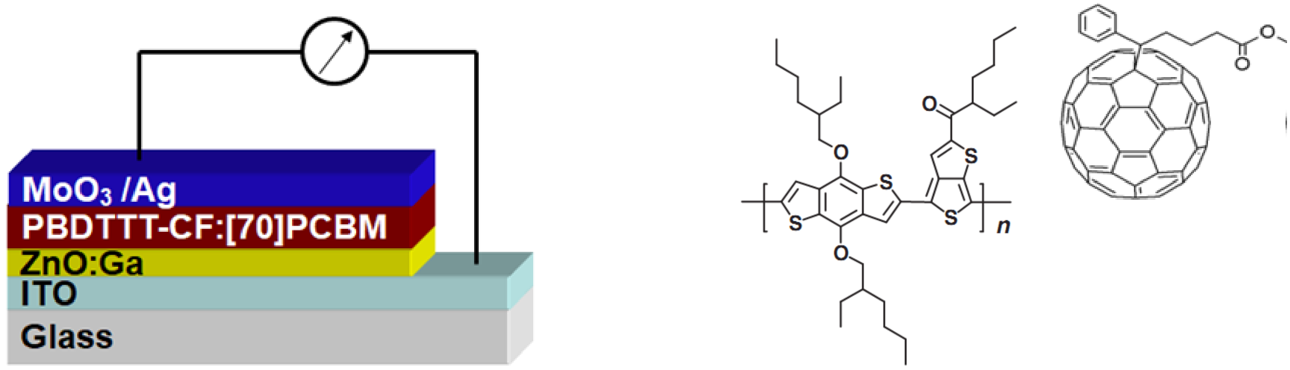

Figure 1. Device architecture of the investigated polymer solar cells and chemical structures of the materials used as photoactive layer.

2.2. Polymer solar cells realization and characterizations

Inverted PSCs with the configuration glass/ITO/ZnO:Ga/PBDTTT-CF:[70]PCBM/MoO_3/Ag were realized (see Figure 1). The ZnO:Ga was deposited on glass/ITO substrate as already described. The active layer (80 nm) was made by dissolving PBDTTT-CF (15 mg/mL) and [70]PCBM (22.5 mg/mL) in a mixture of solvents DCB:DIO (97:3% by volume) and spin coated on the ITO/ETL layer. A 5 nm MoO_3 layer and a 100 nm Ag layer were thermally evaporated through a shadow mask to form a top anode. The active area of the device is 22 mm^2.

The I-V light characteristics of PSCs were recorded in a nitrogen-filled glove box (O_2 and H_2O < 1 ppm) at 25 °C with a Keithley 2400 source measure unit (Keithley Instruments Inc., Cleveland, USA). Simulated AM 1.5G illumination was provided by a class "AAA" solar simulator (Photo Emission Tech, model CT100AAA, equipped with a 150W Xenon lamp); the intensity was standardized using a mono-Si reference cell with a KG5 filter for 1 sunlight intensity of 100 mW/cm^2. The EQE spectra were measured with a Bentham PVE300 apparatus calibrated with a Si detector. Measurements with different light intensity were performed using a set of neutral density filters with a light intensity calibrated by a Si solar cell of 90, 56, 36, 14 and 11 mW/cm^2.

3. RESULTS AND DISCUSSION

The ZnO:Ga mixtures prepared by sol-gel procedure were examined in transmittance and reflectance. The spectra of the ZnO:Ga films at various gallium content deposited on glass substrates are shown in Figure 2. Films show good transparency in the visible range (around 90% for wavelengths greater than 500 nm).

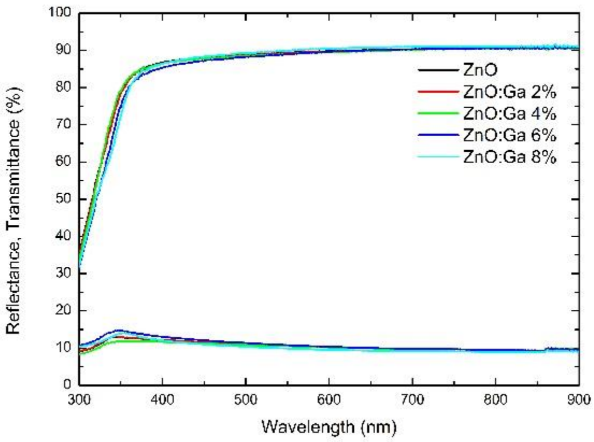

Figure 2. Reflectance and transmittance spectra of ZnO and ZnO:Ga films at various gallium content deposited on glass substrate.

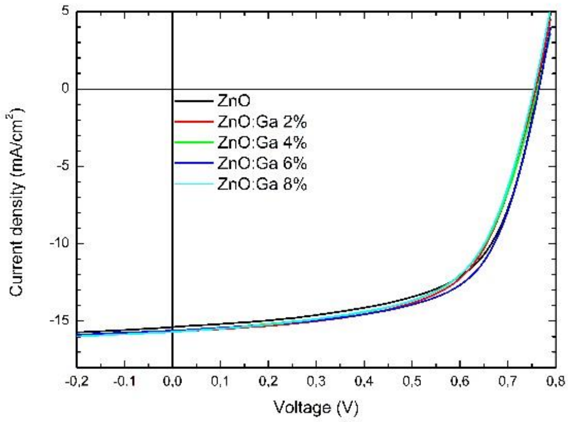

Figure 3. I-V light curves (AM 1.5G, 100 mW/cm^2) of inverted polymer solar cells using ZnO and ZnO:Ga films with various gallium contents, as electron transport layer.

To study the influence of the dopants on the performances of the ZnO films as ETLs in inverted PSCs, we realized devices having the following architecture: glass/ITO/ZnO:Ga/PBDTTT-CF:[70]PCBM/MoO_3/Ag. All the cells were prepared and characterized by EQE and I-V measurements performed under simulated AM 1.5G illumination (100 mW/cm^2) and in dark.

The I-V light characteristics of the devices realized at different Ga percent ([Ga]/[Zn]=0, 2, 4, 6, 8 %) are reported in Figure 3 and the corresponding PCE, open circuit voltage (Voc), short circuit current density (J_{sc}), fill factor (FF) are summarized in Table 1.

The PCE of the cell with undoped ZnO as ETL reaches the value of 7.27%. This value increases up to 7.74% for the sample doped with 6% of Ga. For greater percentages (8%) a drop in the PCE is observed. The cell based on ZnO doped with 8% of Ga shows a PCE of 7.31%. A value of 7.73% is reported in the literature for the same active layers used to made conventional PSC [22]. The best efficiency of 7.7% was reached by using a 6 at% ZnO:Ga film as ETL, comparable to that of a conventional PSC with the same active layer [26]. The J_{sc} remains almost constant (around 15.6 mA/cm^2) in agreement with the similar optical properties of the various ZnO layers. The V_{oc} remains almost the same between different devices (754-764 mV). The trend in the FF follows the one found in the PCE, with the best value (63.7%) for the 6% ZnO:Ga based device.

Table 1. Photovoltaic parameters extracted from the I-V light curves (Figure 3) of inverted polymer solar cells employing ZnO:Ga films with various gallium contents, as electron transport layer.

ZnO:Ga (% Ga)	PCE (%)	FF (%)	J_{sc} (mA/cm^2)	V_{oc} (mV)
0%	7.27	62.0	15.4	762
2%	7.43	62.2	15.8	757
4%	7.34	61.0	15.8	762
6%	7.74	63.7	15.9	764
8%	7.31	61.4	15.8	754

In Figure 4, we report the EQE of the inverted PSCs realized with undoped and Ga-doped ZnO as ETLs. All the devices show a broad response range from 300 to 850 nm with values up to 70%. The EQE of the cells are very similar each other indicating a similar current output, as found in the I-V light measurements.

To understand the improving in optical performance of the device realized with doped ZnO, the efficiency of different processes implicated during the photovoltaic conversion was analyzed. Absorption of a photon, exciton dissociation, charge transfer and charge collection [27, 28] were examined. Since the optical properties of the various ETL show only minor changes (Figure 2), the light absorption is almost the same in the investigated device. This is confirmed from the similar measured J_{sc} (Table 1).

By measuring the J_{sc} as a function of the light intensity (from 10 to 100 mW/cm^2) we had indications of the recombination processes. The dependence of the J_{sc} on the illumination conditions is similar for all the devices and follow the power law $J \sim I^{\alpha}$. The α values obtained from the best fit of the data are very similar for all the devices (close to the unity). This result show that the studied devices are affected by similar charge carrier recombination losses [29] so the electrical behaviour of the photoactive layer is not significantly influenced by the underlying ETLs.

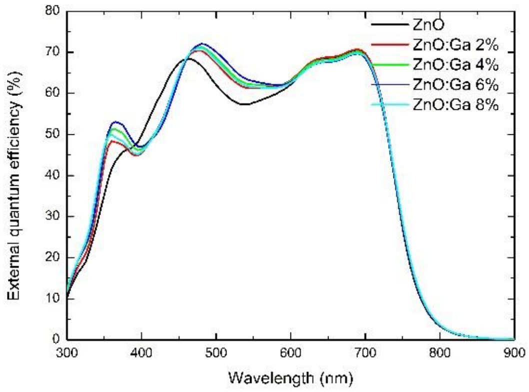

Figure 4. External quantum efficiency of inverted polymer solar cells employing ZnO and ZnO:Ga films with varying gallium content, reported as electron transport layer devices.

The efficiency of the charge collection process is related to the ratio between the photocurrent density (J_{Ph}) and the saturation current density (J_{SAT}). In Figure 5 is reported the ratio (J_{Ph}/J_{SAT}) as function of the applied voltage. The device with at 6% content of ZnO:Ga film shows better performance if compared with both the cell with undoped ZnO and the cells with a higher doping.

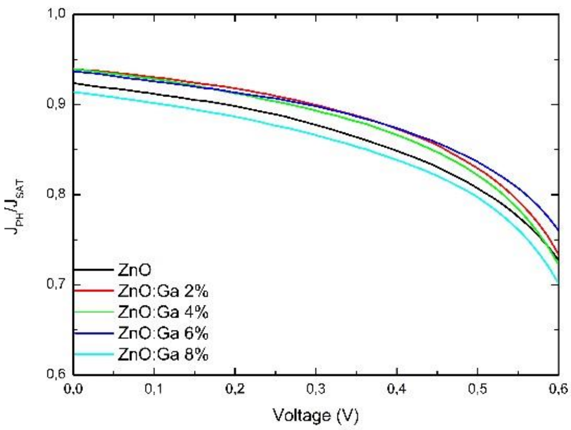

Figure 5. Photocurrent density (J_{PH}) and saturation current density (J_{STA}) ratio as function of the applied voltage of inverted polymer solar cells employing ZnO and ZnO:Ga films with various gallium contents.

4. CONCLUSIONS

In this work several low-temperature sol-gel Ga-doped ZnO thin films were prepared. Low-temperature process is an indispensable requirement for full compatibility with current printing processes over flexible substrates. These layers were tested as ETLs in high efficiency inverted PSCs based on a blend of PBDTTT-CF:[70]PCBM. A comparative study of the photovoltaic behavior of PSCs realized with different Ga concentration was carried out. The best efficiency of 7.7% was reached by using a 6 at% ZnO:Ga film as ETL. This result is comparable to that reported in the literature on a conventional PSC with the same active layer [26].

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