Low temperature, solution-processed perovskite solar cells and modules with an aperture area efficiency of 11%

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ABSTRACT

Planar perovskite solar cells and modules were realized by using low temperature solution-process fabrication procedures. The photovoltaic performance was improved by optimizing a SnO$_2$ electron transport layer and its interface with the perovskite layer. We achieved a power conversion efficiency (PCE) of 17.3% on small area cell (0.09 cm^2) with negligible hysteresis and a steady-state PCE equal to 17.4%. Furthermore, shelf life tests showed a relative decrease of only 5% in PCE from its initial value after 1000 h of storage in dark conditions in air (RH 20%). Up-scaling of the technology was implemented entirely in air with fabrication of modules with a high aperture ratio of 91%. The modules delivered a maximum PCE of 13.1% obtained on an active area of 13.8 cm^2 and of 11.9% on an aperture area of 15.2 cm^2 representing state of art performance for fully low temperature solution processed planar perovskite solar modules.

1. Introduction

Lead halide perovskite solar cells (PSCs) are emerging as one of the most promising third-generation photovoltaic (PV) technology that compare well with other thin films PVs, such as CdTe and CIGS [1], and also well suited for tandem application with Silicon solar cells. In just a few years, the conversion efficiency of PSC remarkably increased from 3.9% to 22.7% thanks to the intensive research on material synthesis, interfaces and device architectures [2–4]. Perovskite compounds show general ABX$_3$ structure where A is a cation such as Methylammonium, Formamidinium or Cesium, B is a metal like Pb or Sn and X is an halogen generally iodine or bromine [5,6]. Lead halide perovskites show excellent optical/electrical properties in terms of high absorption coefficient in the visible spectrum, long electron and hole diffusion lengths and high carrier mobility [7,8]. These peculiar properties have been exploited in several optoelectronic devices applications such as solar cells, photodetectors, light emitting diodes and lasers [9–11]. Moreover, hybrid perovskites can be solution processed thus permitting an easy scaling up of PSCs to the module level [12]. Concerning PSCs,

both *n-i-p* or *p-i-n* architectures have been proposed, where the non-intentionally doped perovskite layer (i) is placed between the electron (n) and the hole (p) transport materials. Regarding the *n-i-p* architecture, PSCs can be classified as planar or mesoscopic where the main difference is the presence of a scaffold layer used as Electron Transport Layer (ETL). Although, the mesoporous scaffold (generally TiO$_2$) can be useful to control the perovskite growth thus leading to highly performant devices, its fabrication procedure typically requires a high temperature process for the sintering steps [13]. From the best of our knowledge, finding alternative low-temperature (LT) solution-processed ETLs is a critical issue that limits the use of PSCs in a wide variety of applications, where a processing temperature below 200 °C is required, for example flexible PV or monolithic tandem Si/Perovskite devices [14]. One of the most promising LT ETLs for n-i-p structured devices is tin oxide (SnO$_2$), because it guarantees high transparency [15], high electron mobility (100–200 cm^2 V^{-1} s^{-1}), a lower conduction band respect to TiO$_2$ [16], and a pinhole-free deposition [17]. SnO$_2$ can be uniformly deposited by solution process techniques from a solution containing its chemical precursors using nonhazardous solvents

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like alcohols [18]. The resulting layer can be sintered at low-temperature in order to fabricate highly efficient planar MAPbI$_3$ based solar cell. The best efficiency obtained on small area PSCs using the device stack FTO/SnO$_2$/MAPbI$_3$/Spiro-OMeTAD was reported by Ke et al. showing 17.2% on 0.09 cm^2 [19]. Further improvements were obtained by using Li-doped SnO$_2$ or by passivating the SnO$_2$ surface passivation with PCBM showing PCEs as high as 18.2% and 19.1% on small area devices, respectively [20,21]. By varying the perovskite composition and using mixed cation perovskite, it was possible to push the PCE up to 20.8% and 21.1%, which represent the state of art for PSCs based on SnO$_2$ ETL [22,23]. However, by increasing the geometrical active area, further issues related to the deposition have to be solved. In particular, the main issue is related to the pin-hole free ETL deposition, which is essential in order to block the carrier recombination at FTO/perovskite interface, and for this reason only few results have been up to now reported on large area devices (close to 1 cm^2). By using MAPbI$_3$ perovskite, a maximum PCE equal to 15.4% was demonstrated [24], while an enhanced PCE of 20.1% was obtained replacing MAPbI$_3$ with mixed cation perovskite based on a mixture of formamidinium (FA) and methylammonium (MA) cations [23]. Further efforts in the scaling up of PSCs led to the realization of perovskite solar modules (PSMs), where the deposition uniformity and the interconnection design were found to be of paramount importance in influencing the photovoltaic parameters of the devices [25,26]. In particular, the use of laser patterning reduces the interconnection ohmic losses with a consequent improvement of the PSM's Fill-Factor (FF) [26], and increases the aspect ratio (AR) between active area and aperture area of the module [27,28]. Concerning planar PSMs, the n-i-p module architecture was considered by Qiu et al. using a TiO$_2$ based LT ETL deposited by Electron Beam Evaporation. The 4 cm^2 size mini-module, showed an active area PCE of 14.9% and an aperture area PCE of 13.6% (AR = 91%) [29]. On the other hand, a planar p-i-n architecture was used by Liao et al. showing a PCE of 12% on active area and a PCE of 7.2% on aperture area [30]. Recently also Troughton et al. fabricated a planar p-i-n PSM showing a best PCE on active area (13.5 cm^2) of 11.8% and a geometrical fill factor of 54%, with the HTL layer deposited in air at high RH and sintered at 500 °C [31]. In this work we study and develop a fully printable SnO$_2$ layer for LT planar PSCs which is also suitable for large area modules in an industrial relevant environment. The first part focuses on the study of the SnO$_2$ layer deposition by optimizing the annealing procedure and UV treatment during the sol-gel formation and how the properties of the film influence the photovoltaic performance of planar PSC devices. XPS measurements were carried out to explain the role of the UV treatment after the annealing procedure on the two-step assisted sol-gel mechanism forming the final SnO$_2$ layer. The second part is focused on valuating the role of the manufacturing environment on the MAPbI$_3$ perovskite formation. In fact, we found that the morphology of the perovskite film (in terms of compactness, grain size and grain boundaries) obtained in air under 40% RH is better than the one obtained in a glove box environment, thus leading to higher photovoltaic performance. The best small area cell shows a steady-state efficiency of 17.4% under 1 Sun AM 1.5 G illumination conditions, and it retains 95% of initial efficiency after 1000 h of shelf life test under dark condition in air with 20% RH. The third part of this work deals with the optimization of a reproducible up-scaling process for planar perovskite solar modules (active area ≈ 14 cm^2), performed in air to fabricate devices with a high aspect ratio (AR = 91%) by using laser assisted ablation. Thanks to the uniformity of the layers deposition and an optimized laser scribing process, we demonstrate a reproducible fabrication process for high efficiency modules which allowed us to achieve a maximum PCE of 13.1% on active area and 11.9% on aperture area.

2. Experimental section

2.1. Materials

Anhydrous dimethylformamide (DMF) (99.8%), anhydrous dimethylsulfoxide (DMSO) (99.9%), ethanol (EtOH) (98%), 2-propanol (IPA) (99%), anhydrous diethyl ether (99.9%), tin chloride dihydrate (SnCl$_2$·2H$_2$O, 98%), bis(trifluoromethanesulfonyl)imide (Li-TFSI) (99.95%), 4-tert-butyl pyridine (tBP, 96%) were purchased from Sigma Aldrich. PbI$_2$ (99.99%) was purchased by TCI. Methylammonium iodide (MAI, 99.98%) and FK209 cobalt salt (98%) was purchased from Dyesol. Spiro-OMeTAD was purchased from Borun.

2.2. Devices fabrication

Small area cells and modules were realized over patterned FTO substrates. A raster scanning laser (Nd:YVO$_4$, λ = 1064 nm, 15 ns, pulsed at 30 kHz with a fluence of 11.54 J cm^{-2}) was used to etch the FTO/glass substrates (Pilkington, 8 Ω cm^{-1}, 25 × 25 mm^2 for the small and large area cells, 50 × 50 mm^2 for 13 cm^2 modules) to obtain the desired layouts for both cells and modules (P1 process). The patterned substrates were cleaned in an ultrasonic bath, using de-ionized water and soap, acetone, EtOH and IPA (10 min for each cleaning step). Before the deposition of the ETL and perovskite, the substrates were treated under UV lamp for 30 min to ensure good wettability of the substrates (and to remove organic residues). The 0.1 M SnO$_2$ solution in EtOH was spin coated onto Glass/FTO substrates at 500 rpm for 4 s, followed by 2500 rpm for 30 s [19]. The substrates were annealed on an hot plate in ambient air at 100 °C for 5 min and then 180 °C for 3 h. The perovskite films were deposited by solvent-engineering method, as reported elsewhere [32]. To obtain the perovskite solution, PbI$_2$ and CH$_3$NH$_3$I were dissolved in DMF:DMSO 9:1 (v/v) to obtain a 1.41 M concentration for each precursor, and stirred overnight at room temperature. For the deposition in a N$_2$ filled glove box 100 µL of solution were spin coated on the ETL at 6000 rpm for 20 s, and 0.7 mL of chlorobenzene dropped at 15 s remaining before the end of the spinning process. For the deposition in air, 70 µL of the same solution were spin coated on the SnO$_2$ layer at 1000 rpm for 10 s and then 5000 rpm for 45 s. Then 0.7 mL of diethyl ether were dropped on the substrates when 35 s were remaining before the second step of the spin coating process. To obtain an homogeneous and mirror-like dark film, in both environments the perovskite layer was treated with a double-step annealing process, performed at 50 °C for 2 min and then at 100 °C for 10 min [32]. The ETL and perovskite depositions in air were conducted at relative humidity (RH) ≤ 40% and a temperature of 20 °C. After the annealing steps, the substrates were transferred in a glove box for the deposition of HTL in N$_2$ environment. Spiro-OMeTAD solution in chlorobenzene (74 mg mL^{-1}) was spin coated at 2000 rpm for 20 s. The solution was doped by addition of 27 µL of TBP, 16 µL of Li-TFSI solution (520 mg mL^{-1} in acetonitrile solvent) and 7 µL of cobalt additive (FK209, 0.25 M in acetonitrile). For the deposition of Spiro-OMeTAD in ambient atmosphere, 90 µL of doped solution were deposited via blade coating on a hot substrate (70 °C) with blade speed of 20 mm s^{-1} and distance from the surface of 110 µm. We employed a raster scanning Nd:YVO$_4$ laser, emitting at λ = 532 nm, 15 ns, pulsed at 30 kHz to realize the P2 step over the modules, removing the SnO$_2$/perovskite/ Spiro-OMeTAD stack from the interconnection areas. Finally the substrates were transferred into a high vacuum chamber (10^{-6} mbar) to thermally evaporate 80 nm-thick Au back contacts. The thickness of the constituent layers was measured by using a profilometer (Dektak Veeco150) and confirmed by Cross-Section Scanning Electron Microscopy. The full stack of the planar PSC is around 700 nm thick (SnO$_2$ = 30 nm; MAPbI$_3$ = 500 nm; Spiro-OMeTAD = 150 nm; Au = 80 nm). We used a raster scanning Nd:YVO$_4$ laser, emitting at λ = 532 nm, 15 ns, pulsed at 30 kHz with a fluence of 157 mJ cm^{-2} to realize the P3 step to insulate the counter electrodes of subsequent cells in the