engineering proceedings

Proceeding Paper

Process Engineering for Low-temperature Carbon-based Perovskite Solar Modules †

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† Presented at 2nd International Electronic Conference on Processes, 17—31 May 2023; Available online: https://ecp2023.sciforum.net/.

Abstract: In less than a decade, Perovskite solar cell (PSC) technology gained high efficiency and the broad attention because of key enabling physical and morphological features. One of the main obstacles to the PSC industrialization and commercialization deals with the demonstration of stable devices by adopting low-cost and reliable materials and fabrication process methods. Here, we report a Perovskite solar module based on a low-temperature carbon electrode. The full process is in ambient air and engineered by printing techniques.

Keywords: perovskite solar cell; carbon; nanomaterial; low cost; hole transporting layer; stability; printing technique; upscaling; module; processes

Citation: Vesce, L.; Stefanelli, M.; Nikbakht, H.; Carlo, A.D. Process Engineering for Low-temperature Carbon-based Perovskite Solar Modules. **2023**, *5*, x. https://doi.org/10.3390/xxxxx

Published: 5 May 2023

1. Introduction

The photovoltaic (PV) sector has the fundamental role to cover the energy demand caused by the constant and never-ending technology progress [1]. To date, the PV market is based mainly on the "first generation" technology, i.e. monocrystalline and polycrystalline silicon. Despite that, the expensive manufacturing processes of silicon and its decreasing availability in nature have accelerated the "second generation" thin-film technologies exploitation based on materials such as cadmium telluride (CdTe) and amorphous silicon (a-Si) [2]. The "third generation" PV based on hybrid-organic materials was born to keep high efficiency by reducing process fabrication costs [3–6]. Natural dyes such as anthocyanins [7], polymers [8] or fullerenes [9] are just a few examples of molecules used for this purpose. The main issues concerning these new technologies are the stability and the upscaling from lab scale cells (area <1 cm^2) to modules (interconnection of cells) [10].

In the recent years, Perovskite (PVSK) gained attention from scientists and investors because of its optical and electronic properties allowing a continuous development reaching record efficiencies (close to 26%)[11–14]. PVSK is a chemical compound with ABX_3 formula, where A and B are cations with different atomic radii and X represents an anion. PVSK-based materials organometallic compounds of halogens have gathered particular interest in PV field thanks to the easy processability by solution-based methods [15].

Each layer forming a PVSK solar cell (PSC) has a well-defined function affecting the performance and the stability of the device. The PVSK is sandwiched between one electron transport layer (ETL) and a hole transport layer (HTL). ETL and HTL are both connected to an external circuit by gold or silver contacts. In case of the n-i-p architecture, ETL is generally composed by c-TiO_2 (compact TiO_2) and mp-TiO_2 (mesoporous TiO_2) or

SnO_2 and guarantee good conduction, low charge recombination and high transparency. The most widespread HTM (hole transporting material) is the 2,2′,7,7′-Tetrakis(N,Ndi-p-methoxyphenylamine)-9,9′- spirobifluorene. Spiro-MeOTAD ensures good energy levels of band gap, quick charge transfer and low recombination, however it has low stability, high cost (about 200 euro/g), complex synthesis and low yield [16]. Moreover, spiro-OMeTAD is doped to increase the mobility of the holes with highly hygroscopic salts (lithiumbis(trifluoromethylsulfonyl)imide (Li-TFSI) or 4-tert-butylpyridine (t-BP)) leading to PSC degradation deterioration. About the metal counter-electrode, gold diffuses into the structure of the device when exposed to continuous lighting, causing huge PVSK degradation. Both the organic HTL and the metal electrode can be replaced with one low temperature conductive carbon layer. Carbon materials are cheap if compared to HTMs and gold, resulting in a reduction of cells cost and an increase in stability. Carbon is a key material widely used in the PV field due to its abundance, low cost, and appropriate energy level. In the PVSK field, low temperature carbon pastes, unlike the porous high temperature inks [17,18], can be processed at temperatures below 130 °C exhibiting features of high conductivity, low cost, good stability and high throughput process [18–23].

In this paper, we demonstrate a simple process based on scalable printing techniques out of glove-box to fabricate a gold-free perovskite solar module (PSM) based on low temperature carbon counter-electrode.

2. Materials and Methods

The 31.36 cm^2 module (active area 6.25 cm^2) is fabricated by interconnecting in series four n-i-p cells. The stack of each cell and the device process fabrication steps are depicted in Figure 1a and Figure 1b, respectively.

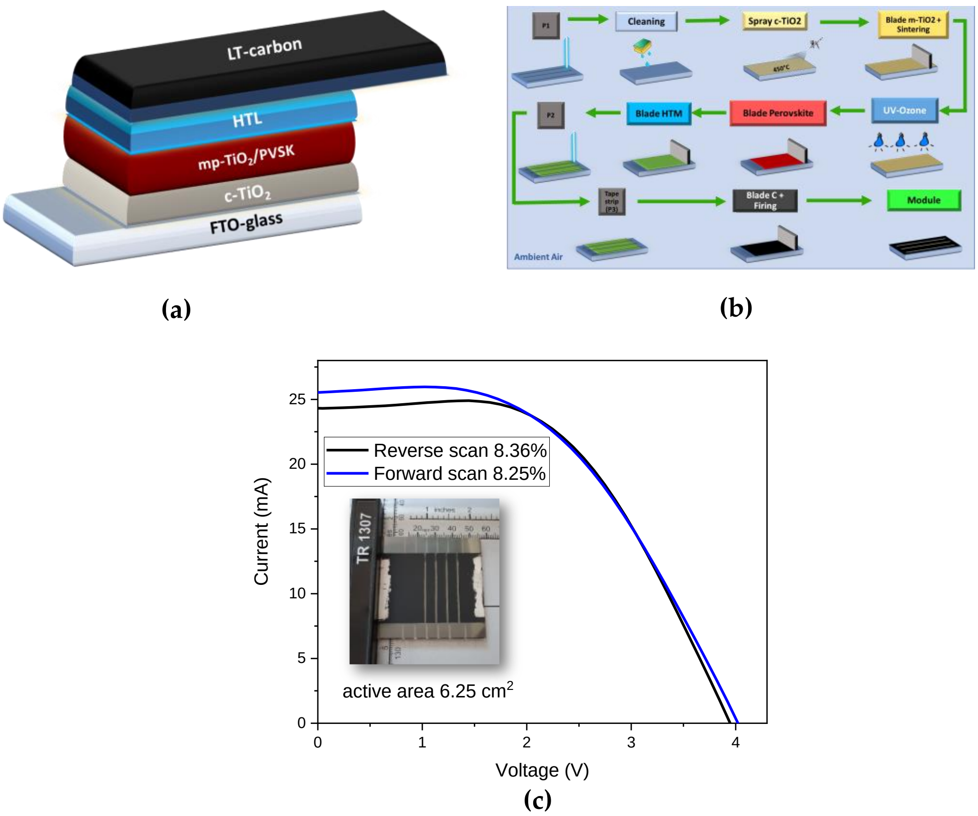

Figure 1. (**a**) PSC layers; (**b**) Module fabrication process steps; (**c**) Module IV curves in reverse and forward scan.

A nanosecond raster Nd:YVO_4 pulsed scanning laser patterned (P1, fluence=10.5 J/cm^2) the FTO (fluorinated tin oxide) glasses (NSG, 7 Ω/sq) to form 4 series connected cells. Then, we cleaned the substrates in an ultrasonic system by using subsequent solvents (soap/water, acetone, ethanol and isopropanol) for 5 min each. We deposited 40 nm thick c-TiO_2 as reported in [24] and 250 nm thick mp-TiO_2 paste (Great Cell Solar 18 nrt, diluted with ethanol 1:4 *w*/*w*) by blade coating method followed by 30 min@500 °C sintering in oven. The substrates are exposed to an UV lamp and then we deposited the triple cation PVSK ($Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ in DMF/DMSO) (PbI_2 from TCI Co. Ltd.; CsI, FAI and MABr from Great Cell Solar) by a double step blade-coating method in ambient air according to Vesce et al. [24]. We reduced the recombination by depositing PEAI (phenethyl ammonium iodide) passivating agent [25,26]. A stable HTM suitable for carbon was deposited by blade-coating technique. Then, the ETL/PVSK/PEAI/HTL stack is removed from the vertical connection areas by laser (P2, fluence=200 J/cm^2) to series connect two adjacent cells by the counter-electrode. Following this, the carbon counter-electrode (Dyenamo) is blade-coated on the cells composing the module and annealed at 120 °C in air for 15 min. The IV curves are reported by a Keithley source meter/LabVIEW under a class A sun simulator (Sun 2000, Abet) at AM 1.5 1000 W/m^2 calibrated by a Skye Instruments sensor Ltd.

3. Results and Discussion

In the upscaling process from lab-scale cell to module there are different issues to be considered: the high front contact sheet resistance, the interconnection dead area and resistance, the layer inhomogeneity. In this work, we apply reliable mitigation action to reduce the losses. The sheet resistance is faced by using low sheet resistance substrate, by adopting the series interconnection strategy and by optimizing the cell width (i.e. reducing the recombination path). The interconnection dead area is reduced by narrowing the interconnection and separation areas. The laser process optimization is useful to limit the interconnection resistance. The layer homogeneity is achieved by combining the right coating technique and the material composition according to the deposition environment. Moreover, we worked in ambient air to simulate a real plant condition.

In Figure 1c, the fabricated PVSK carbon-based module exhibit 8.36% and 8.25% efficiency in reverse and forward scan, respectively. The Voc is about 4 V meaning about 1 V per cell, because the cells are series connected in Z configuration.

4. Conclusion

The PV exploitation should avoid high-cost and high-CO_2 footprint materials and fabrication processes. The adoption of low-temperature carbon-based counter-electrodes permits to avoid expensive and unstable organic HTM and metal counter-electrodes, such as gold or silver. Besides this, the full fabrication process must be based on scalable printing techniques out of glove box to be transferred to industry. In this direction, the carbon inks can be deposited by large area printing techniques, such as screen-printing and blade-coating. Since the carbon layer can be annealed at temperature less than 120 °C, the impact from the LCA (life cycle assessment) point of view is low. Here, we demonstrated a printed PSM based on low temperature carbon counter-electrode.

Author Contributions: Conceptualization, L.V. and A.D.C; methodology, L.V.; validation, L.V. and A.D.C.; formal analysis, L.V., M.S. and H.N.; investigation, M.S., L.V. and H.N.; resources, A.D.C.; data curation, L.V. and M.S.; writing—original draft preparation, L.V.; writing—review and editing, L.V.; visualization, L.V.; supervision, A.D.C. and L.V.; project administration, A.D.C. and L.V.; funding acquisition, A.D.C. and L.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union's Horizon Europe programme, through an FET Proactive research and innovation action under grant agreement No. 101084124 (DIAMOND) and No. 881603 (Graphene Flagship Core 3). The authors acknowledge the project UNIQUE, supported under the umbrella of SOLARERA. NET_cofund by ANR, PtJ, MUR (GA

775970), MINECOAEI, SWEA, within the European Union Framework Program for Research and Innovation Horizon 2020 (Cofund ERANET Action, No. 691664).

Data Availability Statement: Data supporting reported results are available in repository.

Conflicts of Interest: The authors declare no conflict of interest.

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