ADAPTATION OF A CRYSTALLINE SILICON SOLAR CELL LABORATORY TO PRODUCE PEROVSKITE SOLAR DEVICES

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ABSTRACT: Instituto Tecnológico y de Energías Renovables, S.A. (ITER) continues to research on ways to optimize standard manufacturing processes for photovoltaic devices, taking the advantage of the acquired core competences, as well as the available facilities such as the solar cell laboratory, in order to extend its capabilities over solar cells based on perovskite structures, due to its growing trend in photo conversion efficiency in the last five years. Thus, efforts were focused on extending the know-how on hot and emerging topics such as perovskite solar devices, so as to reduce the inherent costs by using the in house equipment as much as possible. A perovskite state of art assessment, as well as a market study, was performed in order to estimate the cost for adopting a device architecture type, together with its fabrication ones, by taking into account the modification of the already available equipment, the acquisition of essential ones, as well as the required fungible. Experimental procedures were performed aiming to evaluate the degree of adaptation of the laboratory from the fabrication to the characterization of the fully finished devices.

Keywords: Perovskite, Design, Economic Analysis, Fabrication, Characterization

1 INTRODUCTION

Since its foundation in 2009, the solar cell laboratory from Instituto Tecnológico y de Energías Renovables, S.A. (ITER) has been devoted to the Research and Development (R&D) of photovoltaic cells based on crystalline silicon technologies, focusing on ways to optimize standard manufacturing processes [1]. Although nowadays ITER continues to research on this topic, it has taken the advantage of the acquired core competences, as well as the available infrastructures, to extend its capabilities also to research on solar cells based on perovskite structure as the main absorber layer, fulfilling three clearly defined purposes: to diversify the R&D efforts by focusing also on hot and emerging topics such as perovskite solar devices, to reduce substantially the inherent costs by using the available equipment and procedures as much as possible, and to assess the feasibility of converging this kind of technologies with the standard fabrication of crystalline solar cells.

The present paper will summarize the work done to start such a new R&D line, addressing the inherent cost, first results obtained so far and will conclude with a discussion for possible improvements on those results.

2 METHODOLOGY

First of all, a comprehensive effort was devoted to study the state of the art of perovskite solar cell technologies as well as fabrication processes [2-4]. An analysis of the market costs and availability for all the required equipment has also been performed in order to asses cost effectiveness. From this study, a device architecture type and a fabrication process were undertaken in order to characterize a reliable and suitable perovskite device according to the availability of the equipment.

3 PEROVSKITE SOLAR CELLS TECHNOLOGIES

Perovskite solar cells emerged as solid-state dye-sensitized devices in which both the liquid electrolyte and the molecular dye were replaced by a solid hole transport material (e.g. Spiro-MeOTAD, P3HT) and a methylammonium lead halide perovskite structure ($MAPbX_3$) as the light-harvester. Furthermore the mesoporous film based on metal oxides (TiO_2, Al_2O_3) was still present as the electron injecting layer [5,6]. Due to the difficulty in pore filling of such irregular structures, scaffolds based on nano-structures were developed in order to improve the charge transport and decrease the electron recombination in devices [7]. Moreover, several studies demonstrated that the perovskite layer works efficiently for light harvesting, as well as charge generation and transport of both electrons and holes. For this reason, perovskite solar cells could operate in a planar heterojunction architecture (p-i-n), reaching extremely high photo conversion efficiencies over 15% [8,9].

Since the approach for this project was in the line of making the most of the available equipment, while purchasing only what was considered essential in order to extend their capabilities for accomplishing the required tasks, the approach chosen was to fabricate planar structures due to the reported considerable high cell efficiencies [8-11], as well as their apparent manufacture simplicity which might enable the industrial breakthrough.

Therefore, the chosen fabrication procedure was focused on obtaining a planar structure solar cell based on methylammonium lead iodide ($MAPbI_3$) as the photon absorbing layer, which was placed over a transparent conductive substrate (TCO), aided by a hole-blocking supporting film layer at the bottom side and a hole-transport layer at the upper one (Figure 1).

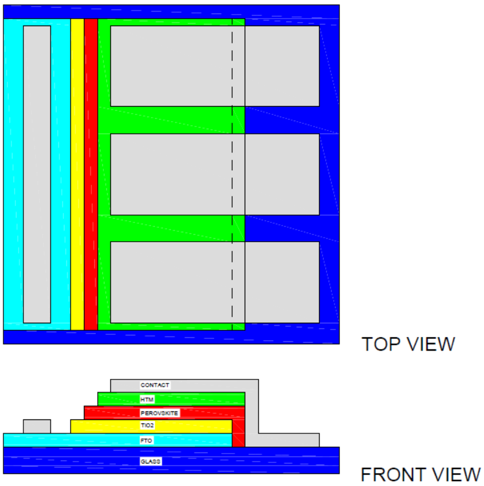

Figure 1. Planar heterojunction architecture of the perovskite device.

4 FACILITIES AND FUNGIBLE

As an alternative to a glovebox controlled environment [8-10], the different fabrication process stages were performed in an ISO 7 (Class 10,000) clean room [1]. Different stages in the fabrication process were the substrate preparation, the synthesis of solutions in order to be deposited as layers over the substrate and the contact metallization. Following this steps a characterization stage was performed in order to evaluate the fabricated devices.

4.1 Substrate preparation

The most available substrates are transparent conducting ones such as fluorine-doped tin oxide (FTO) coated glass. These substrates can be found in different sizes and qualities. Therefore, the use of a cutting tool provides the capability of working with substrates of any dimension, allowing an eventual substrate scaling as well as a significant reduction on the purchasing costs.

To prevent short-circuit phenomena due to possible overlapping of the deposited layers, the technique of laser ablation was chosen in order to remove selective areas from the FTO coating [10], instead of patterns based on the use of Zn powder and HCl for the chemical etching [8,9].

Several procedures for substrate cleaning include oxygen plasma or ozone/ultraviolet treatments as final steps [6,8,9,11]. However, since ultrasonic cleaning establishes the basis for such procedures, its stand alone use [10] is a suitable option and a better adjust to our available resources by using an alkaline aqueous washing solution, de-ionized water (DIW), acetone and 2-propanol in several steps.

4.2 Solutions synthesis

In order to provide a safe environment for the synthesis of all the necessary solutions a fume hood was required as well as the essential laboratory equipment for measuring reactants, such as precision weighing scales and pipettes for different volumes (Figure 2).

Each layer that is going to be deposited requires the preparation of its corresponding solution. Therefore, to perform such solutions, a combined hot-plate magnetic-stirrer was essential for both, hot and room temperature processes, depending upon the characteristics of each chemical reaction.

Figure 2. View of the fume hood in which synthesis of solutions is undertaken.

4.3 Layer depositions

Literature reflects several deposition methods regarding the composition of the layer such as drop casting, vapor deposition or spin coating among others [2-4, 12]. The spin coating technique provides high quality and uniformity results [10-11]. Moreover, such approach allows using equipment already available in the laboratory [1]. One step spin coating and sequential spin coating procedures were tried. Obviously, for the spin coater to be useful, the chuck was redesigned and modified allowing substrates of different sizes.

Finally, since the deposited layers require different curing periods, controlled temperatures and environments were necessary by the use of diverse drying chambers and furnaces.

4.4 Metallization

For reducing the metallization costs and to assess its feasibility for its inclusion in an industrial scale, a screen printing method (Figure 3), which is commonly used for crystal silicon processing [13,14], was employed as an alternative to thermal evaporation [8-11]. However, we had to perform several adaptations for printing contacts with substrates of different sizes and geometries [19].

Considering that perovskite layers cannot withstand temperatures over 100 ºC [10], it was required the use of low curing conductive inks, as well as a drying chamber with fine tuning in the range of 50 to 200 ºC of heating temperatures.

Figure 3. Screen printing process for a contact metallization.

4.5 Characterization

For acquiring the necessary knowledge over the correct execution throughout the fabrication process, several characterization equipments were essential. Thus, in order to verify the chemical nature, quality and uniformity of the deposited layers, external services of X-ray Crystallography and Scanning Electron Microscope imaging were used. The obtained information also helped to optimize the parameterization of our laboratory's Spectroscopic ellipsometer, which became indispensable from then on for providing quick tests capabilities on the fly.

Photo conversion efficiency test according to perovskite technologies [15,16] were performed with a semiconductor characterization system, using a Xenon light source from a spectral response equipment in order to obtain operation values for the fabricated devices.

5 COSTS

In order to undertake the laboratory adaptation to produce perovskite solar devices, an assessment of equipment costs as well as needed fungible is required. This data is summarized in Table 1.

The modification of the already available equipment as well as the acquisition of new ones resulted on an expenditure of 14,655.42 €.

In order to evaluate the new research line it was considered necessary to produce a significant number of fully-finished devices. This was achieved by ensuring enough fungible to perform 90 trials. The costs to execute all the fabrication process was 9,143.77 €, with an estimated cost of 101.60 € per device fabricated.

External services of X-ray Diffraction and Scanning Electron Microscope Imaging were required in order to confirm the correct carrying out of the device, adding 2,080.50 € to the expected costs.

In conclusion the total amount to upgrade the laboratory to start the new research on perovskite solar cell was estimated to be 25,879.69 €.

Table 1. Cost of the crystalline silicon solar cell laboratory adaptation to produce perovskite solar devices.

Process stages	Facilities	Fungible	External service
Substrate preparation	1,172.13 €	174.50 €	-
Solutions synthesis	870.81 €	7,241.21 €	-
Layer depositions	3,183.00 €	550.35 €	-
Metallization	1,663.48 €	1,177.71 €	-
Characterization	7,766.00 €	-	2,080.50 €
Sub-Total	14,655.42 €	9,143.77 €	2,080.50 €
Total			**25,879.69 €**

Finally, a technological leap has been evaluated by considering the equipment referenced in section 4, such as ozone/ultraviolet cleaning treatments, environment controlled glovebox and electrode deposition by thermal evaporation systems. These improvements extend the range of research but increase the cost in 65,329.64 €.

6 EXPERIMENTAL PROCESS

As explained in section 4, the fabrication process consists of several stages which culminate with a finished device that can be tested.

6.1 Substrate preparation

Selected substrate was a FTO coated glass, purchased as a 300x300x2 mm slide with surface resistivity ~7 Ω/sq, which was cut in order to obtain a process substrate size of 25x25mm.

A 1064nm pulsed laser was used in order to remove FTO coating selective areas (Figure 4). The laser was set for a pulse of 100 ns, a frequency 100 kHz and 8 Watts power.

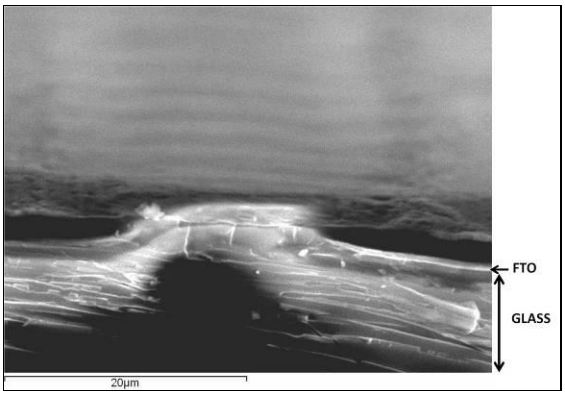

Figure 4. SEM image of a sample section, with an inclination of 7 degrees and an increase of 5000X, focusing on an area showing the FTO layer ablated.

Ultrasonic cleaning processes were applied in four steps of 10 minutes each at 40ºC: At first a 2% Hellmanex solution was used, the second by using DI-water, the third by using acetone and the fourth by using isopropyl alcohol. Finally, the substrates were dried with nitrogen at 2 bar of pressure.

6.2 Device Fabrication

Deposition of the compact pinhole-free blocking-layer of titanium dioxide (Ti-Nanoxide BL/SC from Solaronix) was performed by spin coating of 150 µl at 5000 rpm during 30 seconds, with an acceleration of 2000 rpm/s. The drying process was performed in a controlled temperature furnace, with an initial stage of 10 minutes at 125 ºC and a second stage of 70 minutes at 550 ºC

The perovskite layer was prepared by mixing 557 µl of Anhydrous N,N-dimethylformamide and 0.338 g of Lead(II) iodine in a hot-plate magnetic-stirrer during 30 minutes at 300 rpm and 75 ºC. Then, to such solution, 0.119 g of Methanamine hydriodide was added and the mixing was continued with the same conditions during 20 minutes. The finished solution was left to rest at room temperature overnight. The layer of perovskite was deposited over the substrate made by glass/FTO/TiO_2 by means of the sequential spin coating method. The first step used 313.5 µl of the solution at 5000 rpm during 66 seconds with an acceleration of 2000 rpm/s. At the 6th second 940 µl of Chlorobenzene anhydrous was poured. The device was placed in a drying chamber at 100 ºC during 10 minutes.

The Hole Transport Material (HTM) recipe was prepared by mixing 20 µl of a stock solution made by 1000 µl of Acetonitrile anhydrous and 0.522 g of Bis(trifluoromethane) sulfonamide lithium salt, with 0.082 g of Spiro OMeTAD, 1140 µl of Chlorobenzene anhydrous and 32.9 µl of 4-tert-Butylpyridene during 30 minutes at 300 rpm. The deposition of the HTM layer was performed by spin coating of 212.05 µl of this solution at 4000 rpm during 30 seconds with an acceleration of 1000 rpm/s. The device was left to rest at room temperature overnight in a low humidity environment chamber.

The metallization was performed by screen printing low temperature curing silver ink (EnTouch S-190A by Metalor) over a stainless steel fabric, 200 mesh inox 0.040 D-Ø x 22.5 º high tension. The ink was cured on a drying chamber at 100 ºC during 10 minutes.

In Figure 5 it is shown an example of a complete processed device.

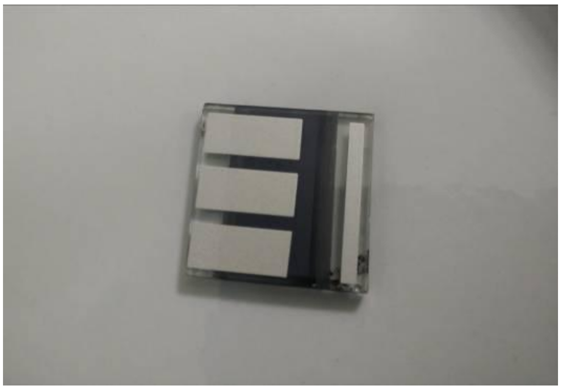

Figure 5. Sample of perovskite solar cell.

7 FIRST RESULTS

Following the fabrication process explained above, several samples were prepared by depositing the layers of TiO_2 and perovskite over FTO/glass substrates, so they could be analyzed by the X-ray Crystallography laboratory at the Research Support General Service from the University of La Laguna (Canary Islands, Spain). Results obtained from an the X-ray diffractometer (Figure 6) demonstrate that perovskite has been successfully synthesized, obtaining the main significant diffraction peaks at 14.08°, 28.41°, 31.85°, and 43.19°, assigned to (110), (220), (310), and (330) respectively [8,17], the FTO layer as well as TiO_2 compact layer were also identified.

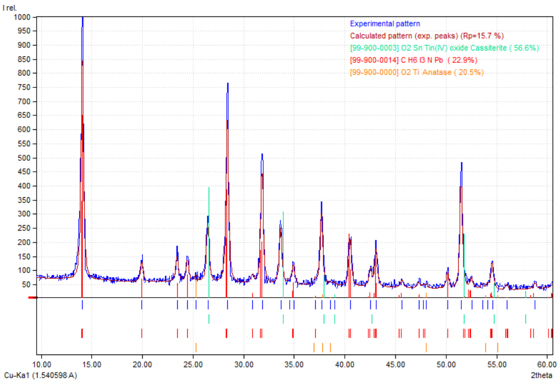

Figure 6. Difractrometer for a sample were TiO_2 compact layer and perovskite have been deposited over FTO.

In order to assess the quality and uniformity of the deposited layer, these samples were studied in our laboratory's Spectroscopic ellipsometer by taking into account a substrate with a thickness of 2 mm and a refractive index of 1.52 [18]. Also, the Scanning Electron Microscope (SEM) facilities at the Research Support General Service from the University of La Laguna (Canary Islands, Spain) was used.

From the performed studies, the uniformity of the deposited layers was obtained from the optical constants (refractive index and thickness). The Spectroscopic ellipsometer established that the fluorine doped tin oxide thickness was 400 nm and that the compact layer one was in between 70 and 114 nm (See figure 7).

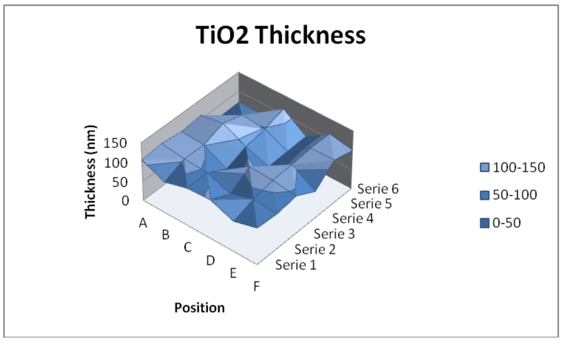

Figure 7. Graph depicting the uniformity thickness of the deposited TiO_2 layer with a 0.42 mm resolution.

In addition, the derived thicknesses were cross-checked with the SEM and the absorber layer thickness was determined (Figure 8).

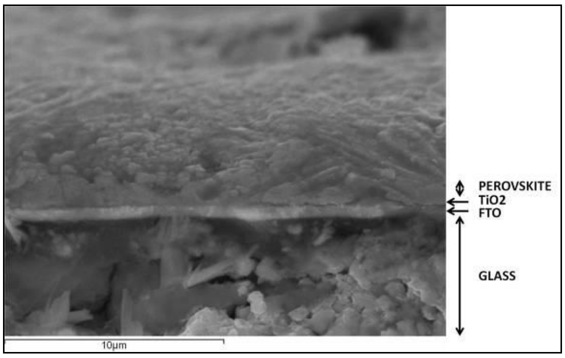

Figure 8. Section view of the left corner of the sample, with an inclination on 7 degree and 600X rise. This image shows a FTO layer of 400 nm, a TiO_2 layer of 70 nm and a perovskite layer of 1000 nm.

The complete device was characterized measuring the photoconductive efficiency including open circuit voltage (V_{oc}) and short-circuit current (I_{sc}) using a semiconductor characterization system and a Xe light source set to 1000 W/m^2. The device was measured by forward biased voltage from -0.05 to 1.2 V, keeping during 1 minute the voltage value fixed in order to reach a steady-state.

Results reflect V_{oc} values under 80 mV and 200 nA for I_{sc} and negligible values for the photo conversion efficiency.

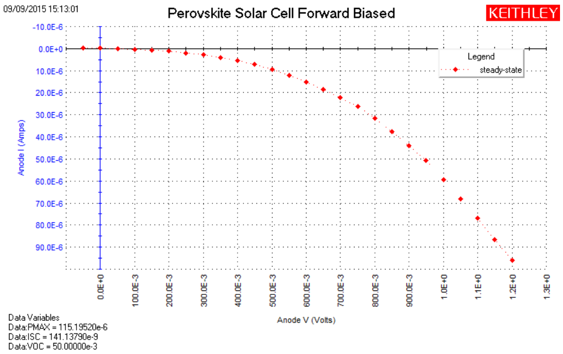

Figure 9. IV Curve for a complete processed device.

8 CONCLUSION AND DISCUSSION

As it can be seen in section 4, the achieved results were not as expected. However, since the obtained IV curve follows the projected shape of a device of this kind of perovskite typology and, although the obtained electric parameters were substantially low, in relation to the ones mentioned in the available bibliography, we believe that the fabrication methodology is rather correct but lacking essential improvements. These improvements could be achieved by providing strict environment control throughout the whole process, by pushing on the quality and uniformity of the layer deposition techniques and by guaranteeing the lack of electric traps.

Nevertheless, the purpose of adapting a silicon cell laboratory to include a perovskite research line, in relation to costs effectiveness as well as fabrication capabilities, has been mostly achieved. Future research is forecasted in order to settle whether introducing the above mentioned improvements may lead to producing fully-functional high efficiency devices.

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