SCREEN PRINTING FOR PEROVSKITE SOLAR CELLS METALLIZATION

C. Quinto[1], A. Linares[2], E. Llarena[1], C. Montes[1], O. González[1], D. Molina[1], A. Pío[1], L. Ocaña[1], M. Friend[1] & M. Cendagorta[1].
[1]Instituto Tecnológico y de Energías Renovables, S. A. (ITER), Pol. Industrial de Granadilla, s/n, E 38600 S/C de Tenerife, España.
Tlf. +34 922 747 700, Fax +34 922 747 701, E-mail iter@iter.es
[2]Agencia Insular de Energía de Tenerife (AIET), Pol. Industrial de Granadilla, s/n, E 38600 Granadilla de Abona, España.
Tlf. +34 922 747 700, Fax +34 922 747 701, E-mail: agenergia@agenergia.org

ABSTRACT: In recent years, Perovskite solar cells have been experiencing a fast increase in their efficiency. Therefore, regardless of their stability problems, Perovskite devices are poised to reach the commercial stage in a near future. Thus, the inclusion of mature processing techniques could become essential in order to reduce manufacturing costs, from the standpoint of large-scale production. The present paper summarizes the methodology followed and first results obtained by using screen printing techniques in a clean room environment, for providing the deposition of metallic contacts, for manufacturing perovskite solar cells. Different pastes and inks were analyzed throughout the research, looking for the best possible performance behaviors, by taking into consideration substrate-friendly and low temperature depositions processes. Thus, silver pastes and inks commonly used for contact metallization in other technologies were tested. Drying processes were performed at low temperatures, in short-time periods, in order to avoid damaging the molecular nature of the deposited layers. Finally, the quality of the resulting contacts was evaluated to establish the electrical properties.
Keywords: Screen Printing, PV Materials, Metallization, Perovskite

1 INTRODUCTION

Nowadays, most of the Research and development in the field of PV cells based on perovskite structures employ the thermally evaporated under vacuum technique in order to form the metal contact formation by using either gold [1,2] silver [3,4,5] or aluminum [6] electrodes. Although such technique provides excellent result, its use on an industrial scale would involve an increase in the related costs due to its high energy and precious materials requirements. That is why it is reasonable to look into alternative processes, which would reduce the costs at the industry level.

Thus, the objective of this project is to evaluate the method of forming the metal contact by Screen Printing, a method which is commonly used in standard manufacturing process for crystalline silicon photovoltaic cells [7], which has contributed to help reducing the costs [8] and to introduce improvements [9,10] in the manufacturing processes. Also, this method has already been used by several research groups, in order to deposit carbon pastes as electrodes over perovskite structures, with Power Conversion Efficiencies (PCE) of 18.8% [11], 8.31% [12], 6.64 % [13] or 11.4% [14], demonstrating the feasibility of this kind of method.

To achieve this, we have study the use of different kinds of silver pastes and inks by screen printing them over planar structures based on methylammonium lead iodide perovskite (MAPI), and trying to obtain the right conditions to avoid damaging the molecular nature of the deposited layers, while correctly drying and curing [15] the electrodes without losing their conductive properties, thus following the manner in which manufacture processing could be like for this kind of solar cells [16].

Another objective of our study is to obtain process conditions to reduce or prevent the losses caused by the series resistance caused by metal contacts, thus preventing a decrease in the short circuit current (Isc) which affects the maximum power (Pmax) that the device is capable of generating.

2 METHODOLOGY

The study methodology was divided into 5 phases: The first one was devoted to the preliminary analysis of the design and geometry of the contacts which were to be printed. A second phase was devoted to the preparation of the substrate itself. The third one contemplated the study of the properties of the printed contacts, dried and cured at low temperatures. The fourth one was dedicated to the implementation of complete perovskite solar cell devices, being the fifth phase committed to their analysis.

Phase I: Analysis and design of the contact geometry

Having decided on the kind of methylammonium lead iodide perovskite (MAPI) solar cell we were going to produce, that is, a planar architecture made by sequentially depositing, over a glass coated with a transparent conducting layer (which consists of fluorine doped tin oxide or FTO), a compact layer (titanium dioxide), then a MAPI layer, and finally a Hole Transport Material (HTM) layer, with respect to the subject matter hereof, the starting point was to select the substrate size. Although most of the literature relies in using substrates of 10x10 mm, this was clearly too small an area for our 6" silicon wafer optimized screen printer. Therefore, a compromise was reached by adopting a substrate size of 2.5x2.5 mm.

To print the metal contacts, several geometric configurations were considered for the cathode, while maintaining the anode constant (see figure 1). After several trials, it was concluded that, in order to avoid traps due to possible structural imperfections derived from the device fabrication, it was better to use isolated low-surface contacts. However, finger-like contacts were ruled out due to probe incompatibility during the testing phases.

Although designs D6 and D7 met the above condition, design D7 was the one chosen, with designs

D10 and 11, as possible modifications, in order to allow utilizing n++ and p++ doped pastes for the anode and cathode respectively in the future.

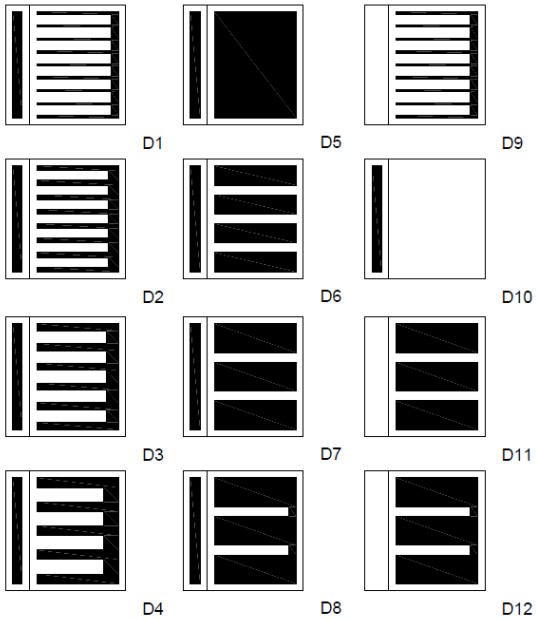

Figure 1: Screen designs.

Phase II: Preparation of the substrates

In order to avoid potential short circuits caused by an eventual overlapping of the titanium dioxide, the MAPI layer or the HTM layer over the FTO coated glass, a perimeter was isolated by using laser ablation in order to eliminate 400 nm off this layer (see figure 2). This was achieved by using a pulsed laser, with a fill spacing of 0.011 mm and a speed of 1.800 mm/s, a pulse of 100 ns with 100 kHz frequency and 20 W of power, obtaining a peak power of 80 J/S. Thus, with the screen printing design in mind, we were capable of preparing a flat architecture with an active region of over a substrate with an active area of approximately 9x22 mm (see figure 3).

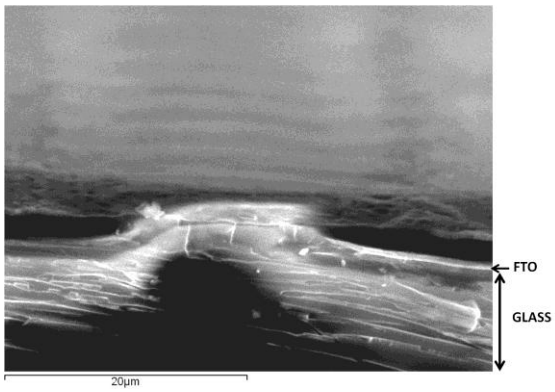

Figure 2: SEM image of a sample section, with an inclination of 7 degrees and an increase of 5000X, focusing on an area showing the FTO layer ablated.

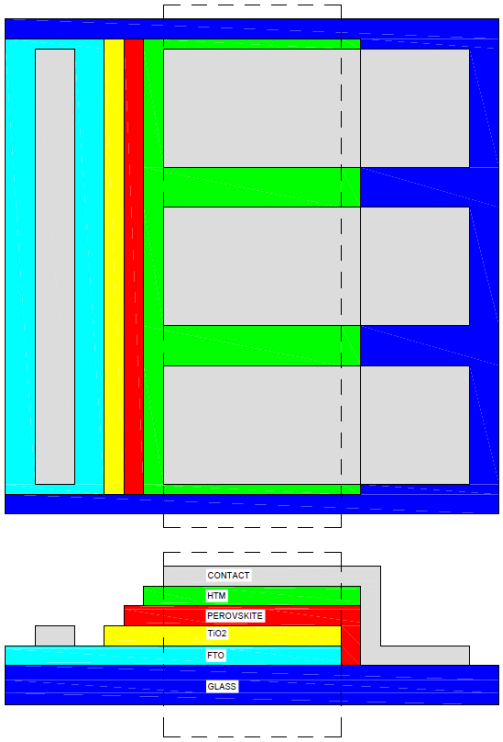

Figure 3: Schematic view of the device showing the different layers and highlighting the active area.

Phase III: Metal contact study over non conductive substrates

After selecting the design and geometry of the contacts, several preliminary screen printing were performed over non conductive glass substrates, in order to evaluate the properties of the metal contacts carried out at low temperatures. Thus, it was determined the behavior of the contacts without any possible effects that may be caused by their interaction with the rest of the deposited layers.

The pastes and inks used in this phase (see table 1) were classified in two groups, the pastes type A and B, normally used in the manufacturing of crystalline silicon cells, and a ink C used for Membrane Touch Switch (MTS).

Normally, the pastes used for crystal silicon manufacturing contain frites, requiring high curing temperatures (740-800ºC) in order to pass through SiN layers. However, since in this case it is not required, these temperatures can be reduced accordingly.

Table I: Pastes and inks under study.

ID	Usage	Thickness (fired)	Type	Material	% Silver
A	c-Si	15-25 µm	Paste	Silver	89.54
B	c-Si	4-8 µm	Paste	Silver	53.04
C	MTS	8-10 µm	Ink	Silver	54.00

Phase IV: Device implementation

Once the pastes and inks were studied over a non conductive substrate, we proceeded to deposit the contacts over actual planar structures based on methylammonium lead iodide perovskite (MAPI). In this way, it was possible to determine the interaction between the device and the screen printed metal contacts.

Phase V: Device characterization

In both, third and four phases, the samples were studied as follows:

In order to define conductivity characteristics for the printed contacts, 4 Probe resistivity test were performed with a semiconductor characterization system (Figure 6).

Measures were carried out by sweeping current values from -95 to 95 mA to obtain voltage in order to define resistance values for the contacts.

3 EQUIPMENT DESCRIPTION

The development of this methodological process was carried out inside a clean room type ISO 7 (Class 10,000), under stable conditions of temperature and relative humidity (21ºC and 65% RH).

The layer isolation performed by laser ablation was achieved in a pulsed laser of 1064 nm (± 10 nm) with a F-Theta lens of f= 103 nm,a pulse width of 4-200 ns and a guided by a galvanometric scanner.

The metal formation was performed with stainless steel fabric, 200 mesh, 0.040 D-Ø x 22.5 º high tension screens in a high precision screen printer, provided with 70 durometer squeegee blades and dial indicator for fine adjustment of screen and squeegee rods to the tool plate. This allows to control the thickness of the pastes deposited with an accuracy of micrometers, as well as to use spread speeds of 10 ips.

For curing the printed electrodes. at 5-250ºC with 2% homogeneity drying chamber was used

In order to undertake resistivity measures, samples were placed into a Faraday cage without illumination. Measures were performed using a 4 probe station connected to a semiconductor characterization system.

4 FABRICATION PROCESS

The following explains in detail the manufacturing process, with phases II and IV being the most critical ones, which consists of simultaneously depositing the pastes and inks over the FTO and HTM layers, in order to produce the anode and cathode for the device, respectively. Once the electrodes were printed (see figure 4), they were cured in a drying chamber during 10 minutes at 100ºC, leaving the device to cool down at room temperature for 20 minutes.

Figure 4: Image of the screen printer in operation.

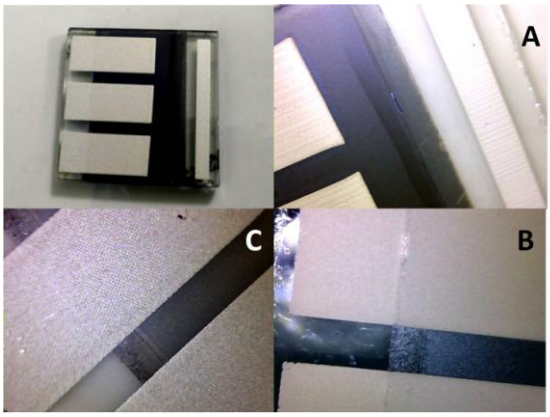

Figure 5: Close up view of finished devices, showing the different types of metal contacts.

5 FIRST RESULTS

Results are summarized in Table II for non conductive substrates, and table III for fully finished devices.

Volume resistivity values (ρ) were achieved following the calculation methodology developed by Smits [17]. For samples fabricated with material type C resistivity values match with manufacturer technical specification, which is ≤20 mΩ/sq/mils, confirming the values measured.

Results obtained with non conductive substrates exhibited a better conductivity for contacts implemented with material type A, rather close values for material type C, while considerably different ones in relation to material type B. This was found to be also true for fully finished devices.

For sample types A and C, a proportional increase on twice the resistivity values was found, which was a result compatible with the effect of device serial resistance produced by the deposited layers. However, and probably due to defects in the fabrication process, such value was considerably larger for sample type B.

Table II: Contacts resistivity values over non-conductive substrates.

ID	Contact	Resistance (mΩ)	ρs (mΩ/sq)	ρ (mΩ/sq/mil)
A	Anode	17.75	34.57	13.83
	Cathode	6.9	33.38	13.35
B	Anode	30	58.48	23.37
	Cathode	15	72.56	29.02
C	Anode	21	40.90	16.36
	Cathode	9	43.53	17.41

Table III: Contacts resistivity values over fully finished devices.

ID	Contact	Resistance (mΩ)	ρs (mΩ/sq)	ρ (mΩ/sq/mil)
A	Anode	16.76	81.05	32.42
	Cathode	30.98	60.33	24.13
B	Anode	478.74	2315.47	926.19
	Cathode	269.45	524.73	209.89
C	Anode	19.75	95.52	38.21
	Cathode	26.63	51.86	20.74

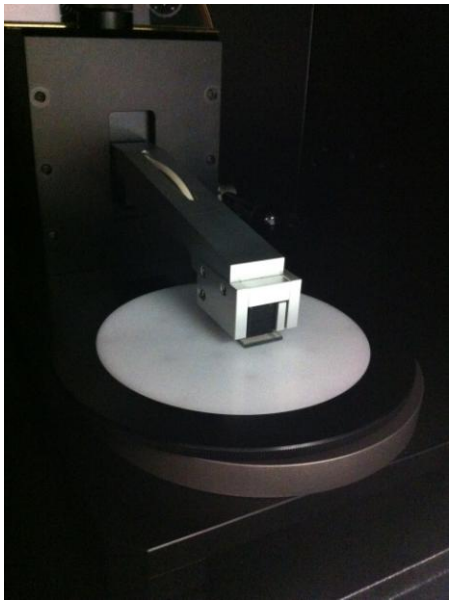

Figure 6: 4-Probe resistivity measurement for a cathode contact

6 CONCLUSION AND DISCUSSION

The present project demonstrates that it is possible to perform electrode deposition with enough reliability and adequate conductivity by using screen printing methods in conditions of low curing temperature. Also, after having used this technique to provide the metal contacts over perovskite planar structures, the differences were related to device serial resistance produced by the deposited layers. Therefore, it can be concluded that the contacts themselves were not appreciably affected by the sort of substrate they were deposited on.

However, since no fully functional perovskite cell could be used for performing the metallization process at the time when this paper was written, it is not clear whether the use of different pastes may improve their efficiency or even if the use of this kind of metallization is one of the principal reasons for the device to under operate.

Once this can be settled, a possible research result could lie on employing screen printing for studying the use of n++ and p++ doped pastes for the anode and cathode respectively, as well as carbon pastes to avoid the use of an HTM layer to simplify the device of the current device in the near future.

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