CONDUCTIVE INKS WITH EPOXY RESIN BASED VEHICLES FOR PEROVSKITE SCREEN PRINTING METALLIZATION AS A VIABLE AND LOW-COST ALTERNATIVE TO THERMAL EVAPORATION

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ABSTRACT: In this work, new advances in the research conducted by the solar cells laboratory (SiCelLab) from the Instituto Tecnológico y de Energías Renovables (Canary Islands, Spain) in order to develop inks for screen printing metallization, based on the use of epoxy resin and anhydrous solvent vehicles are presented. This approach has been designed to be applied on thin film perovskite substrates. The methodology applied makes use of an overhead stirrer for mixing and a three roll mill for homogenizing the ink components. From the developed inks, samples have been printed with average volume resistivities measured as low as 3.31 Ω·cm. Preliminary results suggest that a further reduction on these values is possible by way of including a co-binder species that allows reducing the amount of epoxy resin within the mix.
Keywords: Contact, Characterization, Metallization, Screen Printing, Perovskites.

1 INTRODUCTION

Screen printing is a mature, cost-effective and easily scalable metallization technique, widely used nowadays for photovoltaic (PV) cell manufacturing purposes. Thus, from the point of view of its industrial application, due to its relative simplicity and low energy consumption, this technique could become a better alternative to the thermal evaporation processes that are actually being in use for the metallization of perovskite solar cells fabricated on laboratory scale. With this purpose in mind, the Instituto Tecnológico y de Energías Renovables (ITER), has been working on screen printing solutions for perovskite solar cell metallization since 2015, by initially using different commercial pastes and inks. Although these tests were carried out with perovskite-friendly fabrication methods, the aqueous nature of the vehicles used in their formulation, produced a strong degradation in the finished devices [1].

In order to overcome this problem, the laboratory started developing several conductive ink formulas composed by epoxy resins and anhydrous solvents, as vehicles, and different kinds of graphite powders, as the conductive material. Optimal proportions of these three components have been largely studied in order to obtain inks suitable for printing purposes. Different solvents were also analyzed with the aim to increase the quantity of graphite to the mixture and, subsequently, improve the conductivity of the printed contacts [2].

The present paper summarizes the more recent results obtained in this ongoing research, which has been focused on preventing the degradation of perovskite substrates by using non-polar solvents, as well as in extending the kind of conductive powders used, in order to include metallic ones.

2 CONDUCTIVE INK PREPARATION

All the experiments were carried out in an ISO 7 clean room environment. The inks were prepared in three mixing stages: In the first stage, different kinds of conductive powders [3-6] were mixed with the epoxy resin [7] by using an overhead stirrer [8] equipped with a kneading stainless steel beater, until obtaining a conveniently distributed mixture. In the second stage, a three roll mill [9] was used by giving as many passes as it was deemed necessary in order to homogenize the mixture. Finally, in the third stage, the overhead stirrer was used again, albeit this time with a steel beater for lower density blends, in order to add to the mix the hardener [7] and the toluene anhydrous [10].

Table I: Conductive powders used for the performed ink trials.

Conductive powder	Particle maximum size (µm)	Purity (%)
Graphite 1 [11]	<20	n/a
Graphite 2 [12]	<50	99.9
Graphite 3 [13]	<60	99
Graphite 3 [13]/ Ferrocene [14]	<60 / n/a	99 / 98
Graphite 4 [15]	<75	99.95
Aluminium 1 [16]	<75	99

Aluminium 2 [17]	n/a	93
Nickel [18]	<50	99.7
Copper [19]	<45	99.7

Figure 1: Ink being mixed in the overhead stirrer (left) and homogenized at the three roll mill (right).

3 CONTACT PRINTING AND CURING

It is important to indicate that, because of the nature of the vehicle chosen for producing these inks, as soon as the hardener was added to the mixtures, the polymerization reaction was started. Therefore, the inks so prepared had to be not only kept under continuous stirring but also had to be printed at the same time, in order to determine their optimum application moment. Thus, the elapsed time between each impression chosen in an ink trial was set to be of approximately 10 minutes, being the first print performed 10 minutes after adding the hardener, and the last one about 60 minutes later.

The printing itself were performed using screens [20] capable to handle inks with up to 67 micron particle sizes. The screens were mounted on a screen printer [21], provided with a 70 durometer squeegee blade and a dial indicator for fine adjustment of the screen and the squeegee rod to the tool plate, to finely control the pressure exerted and the thickness of the inks and pastes deposited with an accuracy of micrometers.

The contacts were printed over glass substrates of 175mm x 175mm x 2mm, in order to carry out their electrical characterization. In addition, the contacts were also printed on glass substrates of 25mm x 25mm x 2mm with perovskite layer pre-deposited on them, in order to evaluate their effects on these layers.

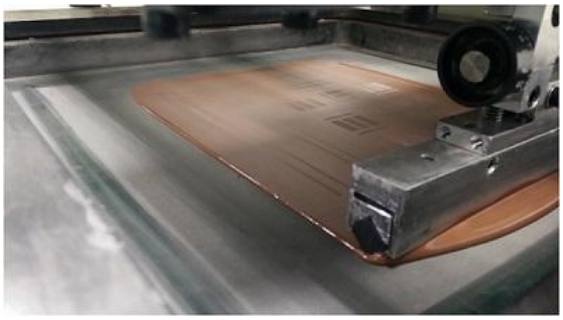

Figure 2: Contacts being deposited by screen printing.

Finally, the curing process was carried out during 24 hours and at room temperature in the air for the contacts printed on the bigger substrates, and in a vacuum desiccator [22] for the ones printed over the perovskite layered ones, in order to preserve their integrity [23].

4 CHARACTERIZATION

The printed contacts were characterized following the Standard F 1896 Test Method for Determining the Electrical Resistivity of a Printed Conductive Material [24], according to which, the sheet resistance (R_s) can be derived from printed contacts that comply with a length (L) to width (W) geometric ratio of at least 50:1.

$$\mathbf{R_s = R \cdot W/L} \qquad (\Omega / \square)$$

Also, when the thickness (t) of the contact is known, it is possible to obtain its volume resistivity (ρ) by the following formula:

$$\boldsymbol{\rho = R_s \cdot t} \qquad (\Omega \cdot \mathrm{cm})$$

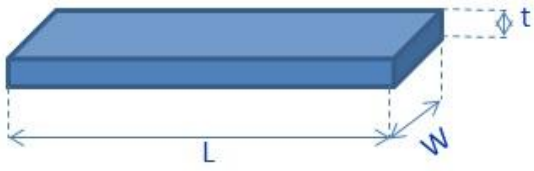

Figure 3: Geometry of a printed contact.

Therefore, screens were designed and produced so as to provide printing patterns that comply with the aforementioned Standard, while being conveniently distributed over the printing area in order to also allow uniformity studies.

The actual measurements were carried out using a semiconductor characterization system [25], configured to operate as an ohmmeter.

Finally, visual inspections of the all the printed samples were carried out by using a digital microscope [26], which allowed us to evaluate the morphology, adhesion level and, for the ones printed over perovskite layers, the degree of interaction between contact and perovskite.

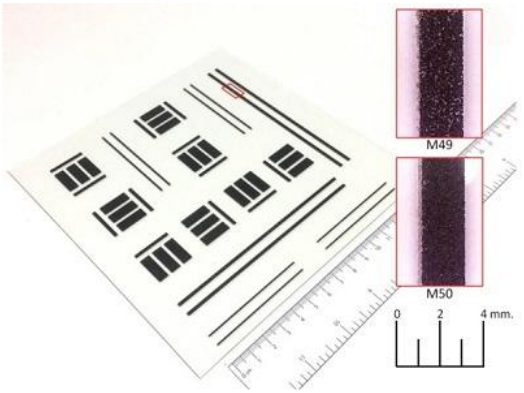

Figure 4: Contacts printed on a 175mm x 175mm x 2mm glass (left), detail of microscopic images of the contact area for different inks (right).

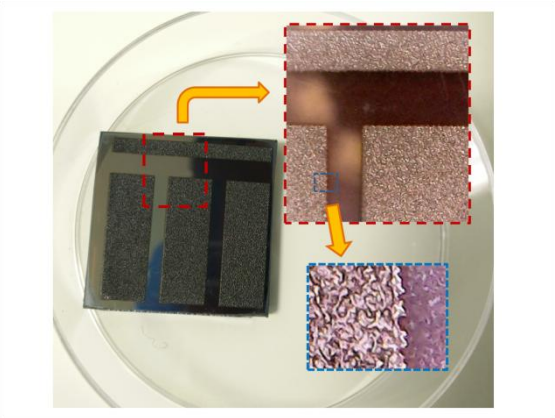

Figure 5: Contacts printed on a 25mm x 25mm x 2mm perovskite covered glass (left), detail of microscopic images with different zoom degrees (right).

5 RESULTS AND DISCUSSION

The methodology followed for producing the ink recipes was as follows: For each of the conductive powders used, a preliminary recipe of ink was sought by way of trial and error until it allowed producing printed contacts with a good appearance and level of adhesion (to the substrate). The ink that complied with both guidelines usually resulted in contacts that had such a high resistance as to be virtually indeterminate. Then, while keeping the proportions of the vehicle used constant, larger amounts of conductive powders were added iteratively, looking for a reduction on the resistances measured in the printed contacts. This process was continued up to reach a state of saturation of powders in the ink, from which it was virtually impossible to obtain a proper impression.

Taking into account that, as explained before, for each ink 6 prints were made, separated by 10 minute intervals, and considering that, in order to impress a proper pattern over the substrates, for many of these prints it was required a fine adjustment on the printing parameters, and that, finally, for each impression, the used screens allowed to produce a set of 12 contacts in total, it was decided to pursue the aforementioned state of saturation by means of looking for the minimum average volume resistivity obtained of all the contacts deposited by each print for any given ink.

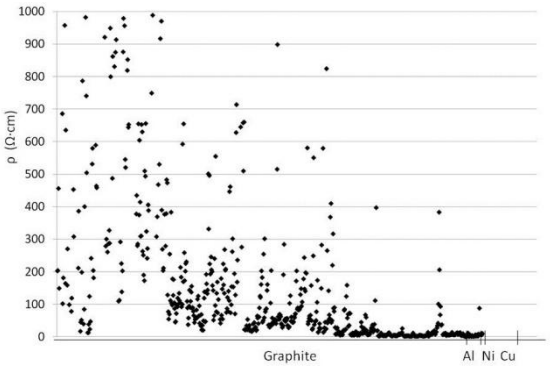

Figure 6: Volume resistivity of all the printed contacts, arranged chronologically and grouped by type of conductive powder.

However, as it can be seen in Figure 6, the volume resistivity values obtained for the printed contacts had a high degree of dispersion, so much so that it became difficult to elucidate whether a variation in a given ink formulation resulted or not in an improvement for said ink. Therefore, the following method was devised as a way of filtering these values and to reduce their dispersion:

Let x1, x2, x3, …, x12 be the set of volume resistivity values measured for the contacts 1, 2, 3, …, 12 in a given print. By arranging all the values from the smallest to greatest, it is possible to obtain their median value, $\mathbf{x_m}$.

Let $\mathbf{x_{fi}}$ be defined as:

$$\mathbf{x_{fi} = x_i / x_m}$$

Where i=1, 2, 3, …, 12 (the number of contacts per print).

A filter for the set of data can be established so as to, from all the possible values, only accept the ones with an x_{fi} below any arbitrary number. If the chosen value for x_{fi} is 10, this is equivalent to filter out all the measured volume resistivity values which resulted to be bigger than an order of magnitude from the set's median value (x_m).

Finally, in order not to lose how objectively representative were the filtered average volume resistivity values ($\bar{\mathbf{x}}$), yet another parameter was required: For any given print, let $\mathbf{C_{xf}}$ be defined as the amount of values which were not filtered (that is, which have an $\mathbf{x_{fi}}$ less than or equal to 10). Then, the representativeness or R, of the calculated average volume resistivity ($\bar{\mathbf{x}}$) can be defined as:

$$\mathbf{R = C_{xf} / 12}$$

This parameter can be expressed as a percentage (%).

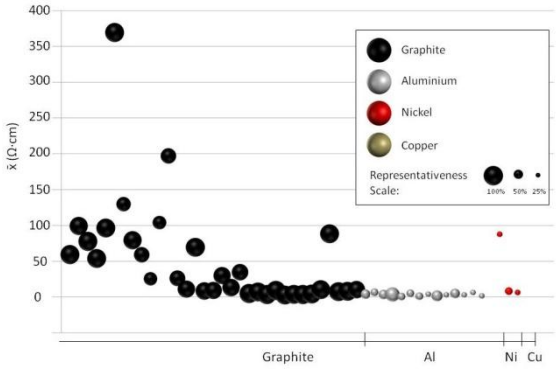

Figure 7: Filtered average volume resistivity ($\bar{x}$) of each print, the size of the balls indicates the representativeness (R) of the plotted value.

Table II shows the best filtered average volume resistivities values obtained from the contacts printed for each conductive powder, together with their representativeness and their corresponding ink recipe expressed in their mass fraction.

Table II: Summary with the best results obtained with their corresponding ink recipes. There is no value of $\bar{x}$ for copper because the obtained one was so high as to be considered off-scale.

Powder	Print time (min.)	$\bar{x}$ (Ω·cm)	R (%)	Recipe (wt%)		
				Conductor	Resin	Solvent
Graphite 2 [12]	50	3.31	100	36.2	54.1	9.7
Aluminium 1[16]	50	3.40	58.3	70.4	25.6	4.0
Nickel [18]	50	6.26	8.3	68.4	26.9	4.7
Copper [19]	30	-	-	78.7	17.8	3.5

Looking at the results summarized in Table II, it is clear that more effort is required in order to improve the quality of the contacts printed with the ink recipes made with aluminium, nickel and copper (particularly for the latter case). However, the results obtained seem to indicate that, contrary to expectations, by simply replacing graphite powders with metallic ones in the ink recipes, the resulting printed contacts do not have lower volume resistivity, despite of having used powders from materials with considerably higher bulk conductivities and densities.

We believe that this is due to an excess of epoxy resin in the formulation of the inks. In order to test such hypothesis, the printed substrates produced with inks that have the heavier conductive powders in their formulations, that is, the ones of nickel and copper, were annealed at 300 ° C for 30 minutes, and the resistivity values of the contacts were obtained again. The results shown in Table III seem to confirm that, possibly due to the evaporation of part of the existing epoxy resin in said contacts, not only did their volume resistivity decreased, but also the representativeness of the obtained values increased.

Table III: Results obtained after annealing the contacts at 300 ºC for 30 minutes.

Powder	Print time (min.)	$\bar{x}$ (Ω·cm)	R (%)	Recipe (wt%)		
				Conductor	Resin	Solvent
Nickel [18]	50	0.02	100	68.4	26.9	4.7
Copper [19]	30	1.02×10^{-3}	91.7	78.70	17.8	3.5

Unfortunately, annealing substrates with perovskite thin films at 300 ºC will result in the loss of its properties as a light-harvesting material [27]. Therefore, it is necessary to look for alternative strategies, in order to reduce the amount of epoxy resin required in the ink formulations by adding some kind of material that acts as a co-binder in the vehicle. Candidates for this purpose could be mineral paraffins such as Nujol and Uvasol [28] or solidifying substances such as phenanthrene or paraffin wax, which become liquid when heated up, so they can be properly homogenized with the conductive powders, and act as solid binders when cooled down [29].

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[5] Graphite powder SC 20 OS from Graphite Kropfmühl GmbH Langheinrichstraße 1, 94051 Hauzenberg Germany.

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[9] ESSG65 Laboratory Three roll mill, made by Shanghai Espread Industry Co. Ltd.

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