A ONE-STEP DEPOSITION METHOD ASSISTED WITH NON POLAR WASHING SOLVENT TREATMENT TO PRODUCE UNIFORM THIN LAYERS OF PEROVSKITE VALIDATED THROUGH ELLIPSOMETRY

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ABSTRACT: The present work summarizes the methodology developed by the laboratory of solar cells (SiCelLab) from the Instituto Tecnológico y de Energías Renovables (Canary Islands, Spain), which has been validated by the use of spectral ellipsometry characterization, in order to evaluate the optical properties and the thickness of thin films of methylammonium lead iodide ($CH_3NH_3PBI_3$), deposited from solutions of their chemical precursors, via spin coating over glass substrates by the one-step method, assisted with non polar washing solvent treatment. The application of this methodology has lead to produce samples with a high degree of uniformity and repetitiveness.
Keywords: Characterization, deposition, optical properties, thin film, perovskite.

1 INTRODUCTION

The use of thin film organometal halide perovskites as the light-harvesting layer on solar cell devices, has led to the development of technologies to achieve unprecedented increases on their power conversion efficiencies (PCE) in a very short period of time [1,2].

In the literature have been reported different methods for producing perovskite layers [3-5]. One of the most extended procedures is based on the use of wet chemical formulations of its precursors by dissolving them in polar organic solvents, which then can be deposited by spin coating techniques [6,7].

The laboratory of solar cells (SiCelLab) from the Instituto Tecnológico y de Energías Renovables (ITER), with the support of the University of La Laguna (ULL), has been researching extensively on the one-step deposition method, assisted with non polar washing treatment, in order to produce thin films of perovskite [8,9] and, since the optoelectronic properties of these films strongly depend on their corresponding processing parameters [10,11], a spectral ellipsometer has been used to elucidate and to establish the correspondence between the fabrication parameters and the optoelectronic properties of the resulting devices.

2 EXPERIMENTAL

2.1 Fabrication methodology

The actual sample fabrication required two days and was divided into four subprocesses. All of them were carried out inside an ISO 7 cleanroom, operating at a set temperature of 21 °C and, although our current facilities do not have the means for controlling the ambient relative humidity (RH), this parameter were monitored to guarantee that the fabrication process was carried out at values below 50% RH.

During the first day, the substrates were cleaned and the perovskite precursor solution was prepared. The deposition of the layer to be studied and the curing of the sample were undertaken during the second day.

The substrates, with a size of 25mm x 25 mm x 2 mm, were cleaned in a 4 stages sonication process with temperature during 10 minutes each. In this sense, the substrates were immersed sequentially in a 2% soap solution, in ultra pure water, in acetone and finally in 2-propanol [6]. The rinsing of the substrates between stages was carried out with ultrapure water at a temperature close to the boiling point. This allowed erasing all the active agents that may remain after each cleaning step [12]. Finally, the substrates were dried with nitrogen and stored individually.

The synthesis of the perovskite precursor was performed by stirring PbI_2 and CH_3NH_3I at a molar ratio of 1:1 (0.723 g: 0.25 g) in dimethylformamide (DMF) solvent (1260 µL) at 75 °C [6,7]. After 50 minutes stirring, the velocity was increased (~ 1000 rpm). Finally, the solution was further stirred overnight, this time at room temperature. This allowed for the molecules of the precursors to be adequately suspended and to avoid undesired sedimentation effects.

The perovskite precursor solutions were spin-coated in a one-step deposition method. During this process the relative humidity inside the chamber of the spin-coater was controlled so that the depositions were carried out only when values below 10% RH were reached. The perovskite precursor solutions (100 µL) were statically dispensed on top of a glass substrates, and then the samples were subjected at a spin rate of 5000 rpm for 30 seconds. At the 6th second along the spinning, a non-polar solvent, in this case chlorobenzene, was dispensed in a 3:1 volume ratio with respect to the precursor [6]. This washing treatment helped evacuate the DMF from

the precursor solution, accelerating and improving the crystallization of the perovskite [7].

After the deposition process, the samples were cured for 10 minutes inside a stove at a temperature of 100 °C [6]. Finally, the samples were stored in a vacuum desiccator to avoid the degradation of the deposited layers due to the ambient humidity [13].

2.2 Characterization methodology

To get started, all the samples were examined by using a digital microscope [14] just after their deposition, evaluating their macroscopic appearance before proceeding with any further characterization.

Also, in order to elucidate whether the initial deposited layers effectively were of methylammonium lead iodide, X-ray crystallography techniques [15] were applied.

However, the main characterization method applied throughout the project relied on the use of a spectroscopic ellipsometer in order to derive the optical properties of the deposited layers and compare them with those published in the literature [16,17].

With such an equipment, it was possible to obtain the ϕ (PSI) and δ (DELTA) as experimental values for the glass substrate and the deposited thin film considered as a whole and then to develop a fit model from which to derive the optical properties of the studied material [9]. Thus, once set the experimental data to the model, the optical properties of the samples, the refractive index (n) and the extinction coefficient (κ) could be obtained. The absorption coefficient (α) was estimated from the extinction coefficient by the following equation:

$$\alpha = (4 \cdot \pi \cdot \kappa) / \lambda \qquad [18]$$

The values of the deposited thickness derived from the fit model were validated by comparing them with the ones measured by an atomic force microscope (AFM) [9, 19].

The ellipsometer also allowed obtaining experimentally the values of transmittance and optical reflectance of the studied samples, so it was possible to cross-reference them with the values published in the literature [16,20,21] and, in addition, to derive the values of the bandgap of the samples from their optical transmittance [22].

Finally, in order to gain data with a spatial resolution over the surface of the deposited samples, the ellipsometry measurements were performed in a five-point pattern, which will be explained in the following section.

3 RESULTS AND DISCUSSION.

As it can be observed in figure 1, the appearance of a typical sample deposited with the fabrication methodology described in this paper was of a smooth brownish layer that uniformly covers the entire surface of the substrate. Neither discoloration nor defects were appreciable.

Figure 1: Image taken with a digital microscope, depicting a typical perovskite layer deposited on a 25mm x 25 mm x 2 mm substrate with the current fabrication methodology.

The studies conducted by exposing the deposited layers to X-ray diffraction (XRD) showed [8] significant peaks at 14.08°, 28.41°, 31.85°, and 43.19°, which had been assigned to (110), (220), (310), and (330) of pure CH3NH3PbI3 crystals, respectively [23, 24].

As it can be seen in figure 2, the refractive index and extinction coefficient corresponding to the best sample produced (ID number 17027), when plotted together with the ones published by Löper et al [15], Leguy et al [17] and a previous results published by our laboratory [9], adjusted better with the ones from Löper et al [16] (although the obtained values are rather closer to the ones from Leguy et al[17] for the peaks at the refractive index values at 400 and 500 nm and at the extinction coefficient peak values at 350 and 450 nm).

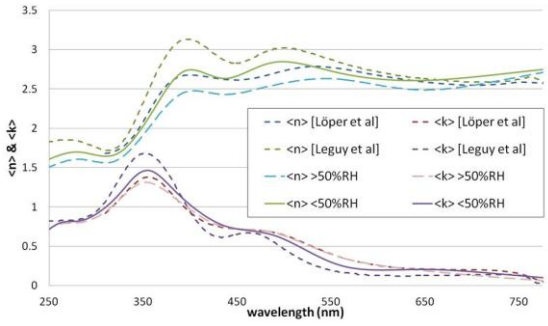

Figure 2: Comparison of the refractive index and the extinction coefficients.

Figure 3 shows a similar adjustment, this time considering the absorption coefficient. Notice that, taking into account our previously published results, the ones communicated in the present paper were a noticeable improvement on the measured absorption in the range of the visible spectrum.

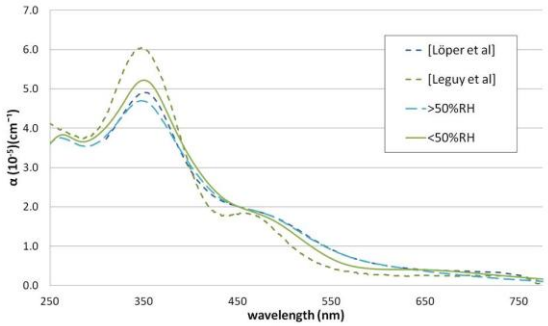

Figure 3: Comparison of the absorption coefficients.

The values obtained for the reflectance and the transmittance were cross-referenced with the literature [16, 25, 26]. Thus, figure 4 shows that the obtained reflectance values are located between 0.2 and 0.4, while the transmittance ones begin from 500 nm on. Also, for the transmittance, it can be observed that there is an inflection point around the 760 nm, which matches with the band gap value.

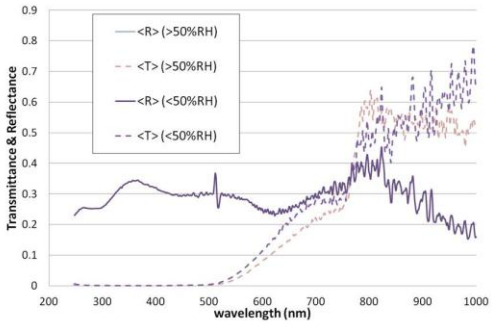

Figure 4: Comparison of the reflectance and the transmittance.

Finally, by using the fit model, the thickness of the deposited layers was obtained and cross-referenced with AFM measurements [9]. Also, by taking measurements distributed over the samples in five locations, the uniformity of such layers was estimated. As it can be seen in figure 5 and Table I, the average thickness of the best sample produced with the current fabrication methodology was around 370 nm, which was a value similar to the one published by Manda Xiao et al [6], improving our previously published results [9].

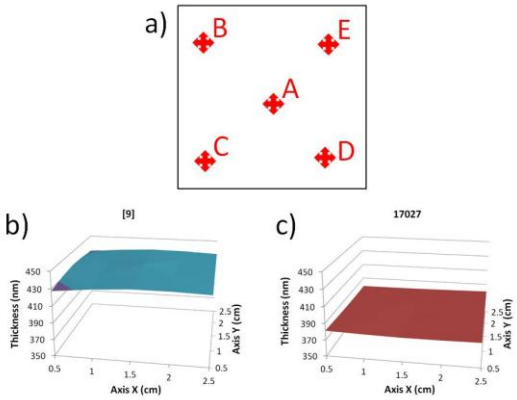

Figure 5: Measurement points (a), perovskite thickness distribution of samples from previously published results (b) and fabricated by current methodology (c).

Table I: Values obtained for the bandgap, thickness, average thickness and standard deviation of the best sample deposited by the current fabrication methodology (17027) and in previously published results (16035).

Sample ID	Band Gap (eV)	Thickness (nm)	Average Thickness (nm)	Standard deviation (nm)
16035_A	1.60	438.78		
16035_B	1.60	428.92		
16035_C	1.60	427.58	432.15	4.37
16035_D	1.60	433.24		
16035_E	1.60	432.25		
17027_A	1.60	377.85		
17027_B	1.60	377.91		
17027_C	1.60	381.26	379.35	1.46
17027_D	1.60	379.95		
17027_E	1.60	379.80		

Thus, in order to conclude, the measurements performed in the samples obtained by the applied fabrication methodology, which has been refined by making use of a characterization methodology that is mainly supported by spectroscopic ellipsometry, seem to lead to a consistent improvement on the quality of the deposited layers.

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