

During the first 6 months of project we have explored various deposition and processing methods (chemical and / or physical) for all the layers contained in a solar cell (the perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer, the TiO_2 layer, the spiro OMeTAD layer) including the AZO layers designed to replace the classical FTO electrodes.

Regarding the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer we approached several deposition methods, namely:

- a) synthesis in a single step of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite layer and trying to make a thin film by spin coating on a platinum support
- b) $\text{CH}_3\text{NH}_3\text{PbI}_3$ two-steps synthesis
- c) synthesis in a single stage, but with the addition of a non-solvent during the process of forming the perovskite layer
- d) deposition by evaporation

Among these methods the two-step synthesis of layers proved to be the most effective in terms of solar cell efficiency. The TiO_2 layers and OMeTAD were deposited only by chemical methods (spin coating).

In all sets of films deposited by different methods structural and compositional characterization has been performed. In addition, finding during experiments that the films degrades in atmosphere environment due to the hygroscopicity, a plastic glove-box with controlled inert atmosphere during the process was built by own efforts in order to ensure a humidity below 10%.

In order to obtain AZO films with conductivity and transparency large enough to replace FTO electrodes experiments were made using two deposition techniques, namely: (i) deposition by PLD at ambient temperature or on a heated substrate at 300 and 500⁰C, and (ii) by RF magnetron sputtering / DC at room temperature. The best layers obtained so far, superior to the commercial FTO films, were deposited by PLD at 300⁰ C. However, also the layers deposited at room temperature (both by PLD and by sputtering) have shown good conductivity ($10^3/\Omega\text{cm}$).

Some atomistic simulations, with Siesta and Quantum Espresso programs, have been made. Bulk configurations were simulated for the halide-perovskite and for crystalline structure of oxides with which the perovskite-halide is placed in contact, primarily TiO_2 . A structural optimization was achieved with complete relaxation of atomic positions. Several compounds have been studied, on the one hand $\text{CH}_3\text{NH}_3\text{PbX}_3$ halide-type perovskites, where $\text{X} = \text{Br}, \text{Cl}$ and I , and on the other hand different type of oxides. After obtaining the

convergence conditions for halide-perovskite and oxide bulk structures the simulations have been extended for the case of thin films with thicknesses of one or two atomic layers for each of these materials. These simulations were followed by others regarding the junction between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and TiO_2 , with periodical conditions for the direction parallel with the interface. These data will be used for estimating the junction electrical field and further for calculating the I-V characteristics, in dark and under illumination, based on drift-diffusion equations.

Another important task in simulations of the halide-perovskite bulk configurations is observe the orientation of the CH_3NH_3 molecules in the crystalline structure. The simulations results indicate that the dipoles having the same orientation have correlation and so a larger stability than those of oposite orientations. These results suggests that the CH_3NH_3 molecules are interacting favouring the paralel orientation.

During this phase an evaluation of existing low-cost techniques for depositing thin films in order to adapt solutions to technology developed in the laboratory submission "screen printing", including the possibility of replacing the auxiliary electrode (counter electrode) has been carried out. It resulted that the "screen printing" technique is the most suitable for the manufacture of hybrid organic and inorganic layers include metal nano networks. At this stage of the project, a preliminary scheme of the equipment proposed to be built by the industrial partner was developed.

In addition to what was foreseen to achieve for this stage of the project, we began the electrical and photoelectrical measurements on structures grown in a solar cell configuration. The results on 4 sets of samples, shown in the table below, reveal the progress achieved so far, with a maximum PCE of 7%.

Set of samples	V_{OC} (V)	I_{SC} (A)	J_{sc} (mA/cm ²)	% FF	% η	Counter electrod
1	0.15	9.7e-4	6.1	23	0.21	Au
2	0.17	9.4e-4	5.9	43	0.43	Ag
3	0.77	1.1e-3	6.9	48	2.55	Mo/Ag
4	0.745	3.93	19.65	48	7	Mo/Ag