Study of gas diffusion mechanisms within ALD and SALD (Spatial ALD) thin films for the encapsulation of perovskite-based photovoltaic cells.

Aubin Parmentier[1,2], Damien Coutancier[1], Marion Provost[3], Anyssa Derj[3], Karim Medjoubi[3], Stéphane Cros[4], Timéa Bejat[4], Marc Fivel[5], David Muñoz-Rojas[2], Nathanaelle Schneider[1]

[1]Institut Photovoltaïque d'Île de France (IPVF), UMR CNRS 9006, 91120 Palaiseau, France
[2]Université Grenoble Alpes, CNRS, Grenoble INP, LMGP, 38000 Grenoble, France
[3]Institut Photovoltaïque d'Île de France (IPVF), 91120 Palaiseau, France
[4]Univ. Grenoble Alpes, CEA, Liten, INES, 73375 Le Bourget du Lac, France
[5]Univ. Grenoble Alpes, CNRS, Grenoble INP, SIMAP, 38000 Grenoble, France.
E-mail: aubin.parmentier@cnrs.fr

In the context of decarbonization of energy production, new types of photovoltaic solar cells are elaborated to achieve higher power conversion efficiencies at lower manufacturing costs. Tandem silicon-perovskite cells are currently promising technologies, that have reached 34.9 % efficiency, far beyond current standard silicon-based cells at 27.8 % [1]. However, those new architectures come with new challenges: for example, perovskite materials are highly sensitive to humidity permeation, which severely limits their long-term stability. One possible solution to protect them from that extrinsic degradation is the use of efficient encapsulation layers [2].

Thin Film Encapsulation (TFE) is a powerful approach to meet the encapsulation needs of perovskite-based cells, namely, *i)* to achieve WVTRs (physical quantity, Water Vapor Transmission Rate, used to quantify barrier properties of thin polymer films [3]) values between 10^{-4} and 10^{-6} $g.m^{-2}.d^{-1}$ [4]; *ii)* to offer laminated films with high flexibility (Young's modulus ≤ 20 MPa at 25 °C [4]); and *iii)* to ensure good light transmission between 400 and 1100 nm (> 80 % [4]). In addition, due to the sensitivity of perovskite materials (PSC), encapsulation solutions must be elaborated under mild conditions (deposition temperature ≤ 100 °C) and compatible with high-throughput mass production. Among the various thin film deposition methods available, Atomic Layer Deposition (ALD) is an attractive technique since it enables the deposition of uniform and dense [5] thin films of controlled thickness (nm-scale), with low pinhole defect densities and at low temperature (≤ 100 °C) thus avoiding damage to the perovskite materials [6]. In addition, the recent Spatial ALD (SALD) approach enables scalable, high-throughput ALD [7].

In fact, one of the most important factors in guaranteeing optimum resistance to gas permeation is a low density of void defects, which are preferential permeation paths. Void defects within thin films can be linked to the detachment of particles initially present on the substrate, or to pinholes inherent to the morphology of the layer, this latter resulting from the growth mechanism.

These explain the large efforts, from both academia and industry to produce nanolaminated films composed of multilayers that allow pinholes to be misaligned, thereby lengthening the diffusion paths of gaseous species within the films [8].

Thus, inorganic or organic-inorganic hybrid nanolaminate structures synthesized by ALD have been made, with WVTRs reaching values close to 10^{-6} $g.m^{-2}.d^{-1}$ [6]. Concerning the nature of the nanolaminates, there are many candidate materials, most of which are metal oxides (e.g. Al_2O_3, TiO_2). They are often combined in nanolaminate structures with their "metalcones" counterparts, which are organic-inorganic hybrid materials typically synthesized by ALD-MLD (ALD-Molecular Layer Deposition) using metal precursors and various organic coreactants that yield metal alkoxide films [9]. For this reason, ALD is the method of choice for nanolaminates: thanks to the precise thickness control it provides, any multilayer structure can be envisaged. This makes the determination of an optimal structure achievable at the cost of an almost infinite number of possibilities.

In this study, we first screened metal oxides and hybrid materials - such as alucones deposited by ALD from trimethylaluminium (TMA) and ethane-1,2-diol (EG) - gas permeation resistance properties using helium permeation measurements which are less time-consuming than water permeation measurements. Establishing the Barrier Improvement Factor (BIF) - described as the ratio between the Helium Transmission Rates (HeTRs) of the substrate and the thin film, makes it possible to select the best candidates for integration into nanolaminated multilayers effective against gas permeation (classification shown in *Figure 1*).

Then, we propose to study the role of void defects existing within encapsulating films by identifying and magnifying them with an electroplating method and optical microscopy techniques; coupled to 1D and 3D modelisation of gas permeation through nanolaminates thin films (example of modelling results in *Figure 2*).

Finally, the ALD encapsulation layers were tested on perovskite cells and subjected to accelerated damp heat ageing conditions (85 °C / 85 % HR) to assess the electrical characteristics of the cells over time.

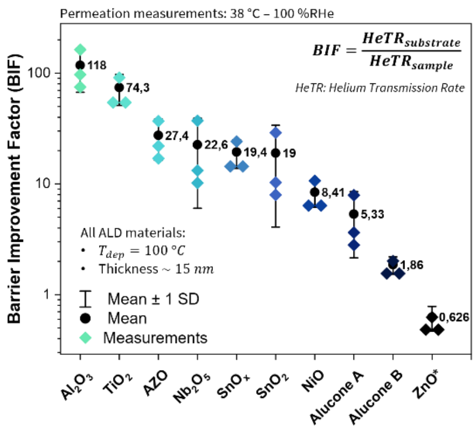

Figure 1. HeTR of different ALD thin films with a thickness of around 15 nm deposited at 100 °C.

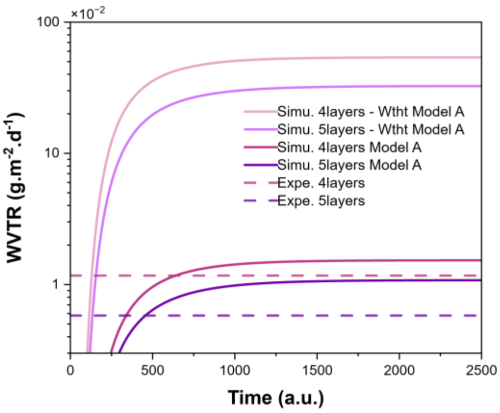

Figure 2. Comparison of WVTR of simulated ALD multilayers using or not a 1D numerical tool.

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