Fluorescence Ellipsometry GD-OES Samples Preparation

Studying perovskite solar cells with HORIBA Scientific equipment

Ellipsometry: **Celine Eypert**, Fluorescence: **Alessia Quatela**, GD-OES: **Sofia Gaiaschi**, Samples: **Bernard Geffroy**, HORIBA Scientific, Palaiseau FRANCE.

With their ~20 % efficiency, hybrid perovskite solar cells are the new promising candidate for next generation photovoltaics. Thanks to the wide HORIBA Scientific portfolio, different techniques can be used to gain in depth knowledge on the optoelectronic properties and mechanisms of this class of materials. In this application note we decided to use spectroscopic ellipsometry, steady-state and time-resolved fluorescence and Glow Discharge Optical Emission Spectroscopy to investigate the properties of $CH_3NH_3PbI_3$ thin films deposited on a spin-coated PEDOT:PSS. The impact of the exposure to air was addressed.

Keywords: perovskites, solar cells, ellipsometry, fluorescence, GD-OES, aging, stability

Introduction

In the last few years hybrid organic-inorganic perovskite materials have emerged as a promising technology for 3rd generation thin film solar cells.

With its processing advantages (such as low fabrication cost and abundant raw materials) and efficiencies, which can reach around 20%, this new class of thin film absorbers has become a major investment for solar energy materials.

The general perovskite structural motif can be denoted ABX3, where X is an anion (usually oxygen), A is a large metal cation, and B is a smaller metal cation. This structure provides some interesting properties, and in material science has led to investigation of applications in microelectronics and telecommunication; principally because of their conductivity / resistance properties. The perovskite commonly used in this application is based on methylammonium lead triiodide ($CH_3NH_3PbI_3$). The efficiency relates to the large diffusion length that photoinduced electrons and holes have. This enables better current extraction, and also makes them suitable for use in a thin film form allowing more flexibility in device design.

Thanks to the large panel of characterization techniques developed within the HORIBA Scientific portfolio, a cross-technique analysis of perovskite materials has been conducted.

Spectroscopic Ellipsometry (SE) enables the ability to determine thickness and optical constants of thin films with a sensitivity at the atomic scale. As the knowledge of the optical constants and optical band gap of the absorber layer

is essential for designing the photovoltaic devices, SE proves to be a technique to get access to these parameters and to monitor the effect of air exposure on the optical properties of the material.

To monitor the efficiencies of perovskite material for photovoltaic applications, it is essential to have an accurate estimate of the carrier lifetime. The use of the time-resolved fluorescence with HORIBA Time Correlated Single Photon Counting (TCSPC) instrumentation can provide such information.

Finally, Glow Discharge Optical Emission Spectroscopy, which is a destructive technique, can be used to monitor the elemental distribution inside the perovskite device.

Samples and instruments

Perovskite samples were provided by the Physics of Interfaces and Thin Films Laboratory (LPICM) of the Ecole Polytechnique (France). $CH_3NH_3PbI_3$ thin films were deposited on a spin-coated PEDOT:PSS layer, on ITO on glass. As the $CH_3NH_3PbI_3$ films are sensitive to the air exposure, the samples were stored inside a glove box prior to the first analysis, in order to avoid any contact with the air. In this work, the perovskite solar cells were studied immediately after the exposure to air *(t=0)*, after 7 days of exposure *(t=7 days)* and after 14 days of exposure in air *(t=14 days)*. We decided to focus only on the air-exposure deterioration; therefore the samples were stored in the dark and protected using an Al foil.

The ellipsometric measurements were performed using the UVISEL+ spectroscopic ellipsometer (Figure 1), based on the phase modulated technology, with its double modulations and high frequency modulation for better signal to noise ratio. The measurements were performed over the spectral range 0.6-6.5eV (190-2100nm) at an angle of incidence of 70°. SE is a model dependent technique to get access to dielectric functions, film thickness, optical band gap taking into account all external parameters, such as sample structure, roughness, angle of incidence, etc.

Figure 1. Uvisel +

Steady state and Time-resolved measurements were performed using the hybrid spectrofluorometer FluoroMax4-Plus (Figure 2).
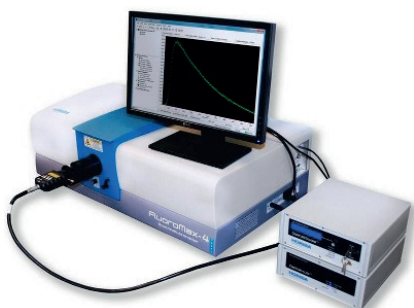

Figure 2. FluoroMax4-Plus

The excitation monochromator has an optical range of 220 – 600nm blazed at 330nm while the emission monochromator has an optical range of 290 – 850nm blazed at 500nm. The monochromators can be independently or synchronously scanned for mixtures. The slit widths may be continuously adjusted though the software from 0 - 30nm bandpass. The FluoroMax-4 is equipped with two detectors: one is a calibrated photodiode reference detector to correct for intensity and temporal fluctuations in the source during excitation scans. The other detector is an R928P red-sensitive PMT used in photon counting mode with signal linearity up to 2×10^6 CPS. With a photon-counting detector, only the signals originating from the sample are measured, noise from the detector is rejected.

A 150W Xenon, continuous output, ozone-free lamp was used as steady state excitation source and a 440nm emitting DeltaDiode laser (typical pulse width 60ps, 3mW average power at 100 MHz) as lifetime excitation source. The DeltaDiode pulse rate is automatically adjusted to suit the time range and its duration can be altered, which allows further control over the source intensity. All these parameters are set by the DataStation control software.

DAS6 software has been used for data analysis. It is designed to streamline the analysis of time-domain luminescence data, while still allowing for fine-tuning of parameters where necessary. Analysis modules include reconvolution analysis of multi-exponential models plus analysis of more specialized fluorescence decay processes (Multi-Exponential, Batch Exponential, Global Exponential, Distribution, Exponential Series, Förster Energy Transfer, Yokoto-Tanimoto Energy Transfer, Micellar quenching, Exciplex, Anisotropy analysis).

Solid-Sample Holder accessory (Figure 3) at a 30° or 60° angle was used for the thin films analysis.
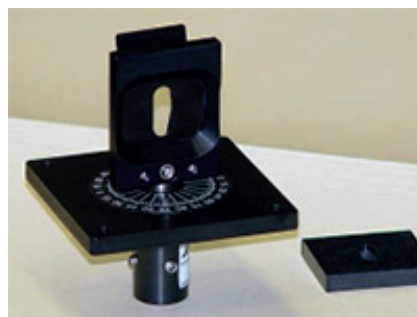

Figure 3. 1933 Solid-Sample Holder accessory with sample block

Finally, the elemental distribution of the perovskite solar cells was studied using Glow Discharge Optical Emission Spectrometry. The GD Profiler 2 (Figure 4) couples an advanced Radio Frequency (RF) GD source to a high resolution, wide spectral range Optical Emission Spectrometer. This technique relies on the precise and fast (typically µm/min) sputtering of a representative area of the investigated sample. All elements of interest are simultaneously measured, as a function of the sputtering time, using a spectrometer. Thanks to the use of the pulsed-RF as an excitation source, with the GD Profiler 2 it is possible to efficiently analyze conductive, insulating and hybrid materials.

Figure 4. GD Profiler 2

Results

In **Figure 5,** the raw ellipsometric data (Is and Ic) for a perovskite solar cell, are presented. It is noteworthy that the Is observable part of the $CH_3NH_3PbI_3$ presents several absorption peaks in the UV-Visible spectral region (black arrows). The presence of such absorption peaks allows the adjustment of the parameters of the dispersion formula used for modelling. Moreover, considering that perovskites are a direct transition semiconductor material, a N-Tauc Lorentz formula can be used to model the optical properties. In addition, **Figure 5** shows the difference of ellipsometric responses between the as-deposited sample (*t=0*) and the sample exposed to air during 14 days (*t=14 days*), and stored in the dark, protected using Al foil. This difference is significant on the Ic observable toward high energies, linked to the surface of the sample.
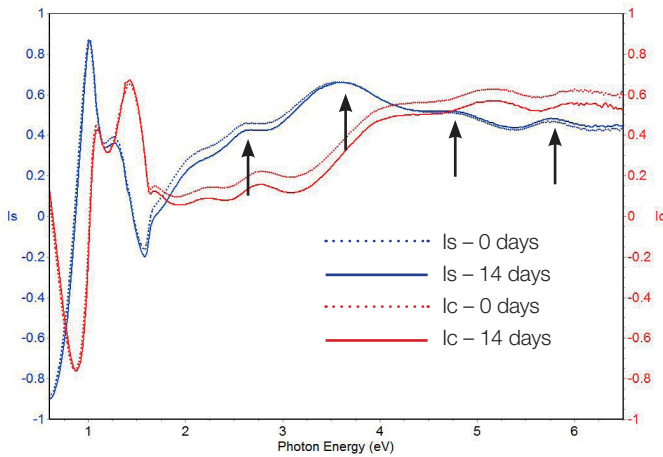

Figure 5. Experimental data of the structure $CH_3NH_3PbI_3$/Pedot/ITO/glass

The $CH_3NH_3PbI_3$ layer was modeled using a bulk layer with its roughness on the sub-structure previously studied (**Figure 6**) over the spectral range 0.6-4.6eV. The dielectric functions of $CH_3NH_3PbI_3$ were determined on the sample at *t=0* and are displayed in Figure 6. From the fit, the optical band gap was extracted and found at 1.57eV, and three optical electronic transitions occur at 1.61eV, 2.62eV and 3.5eV.
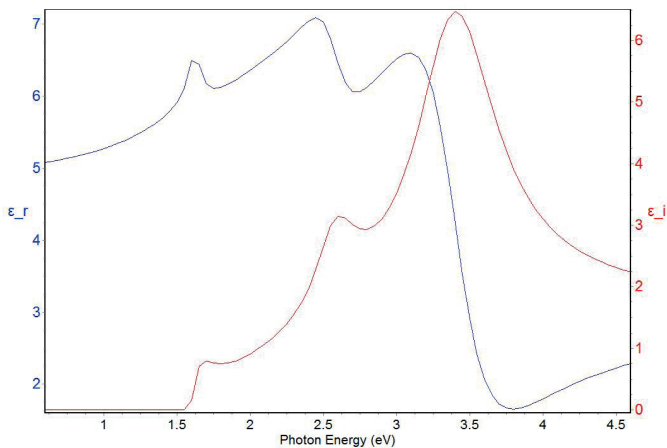

Figure 6. $CH_3NH_3PbI_3$ Dielectric function $(\varepsilon_r, \varepsilon_i)=f(E)$

For *t=14* days, the same model was used and only the thickness of the $CH_3NH_3PbI_3$ and its roughness were fitted. In Figure 7, the evolution of the modeled layers is presented.
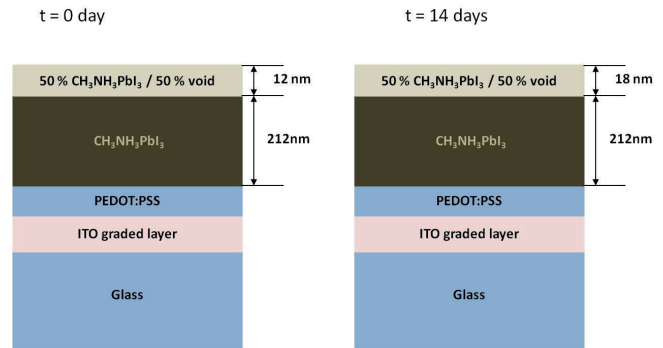

Figure 7. Ellipsometric Model for t=0 day and t=14 days

The result shows that when the perovskite is only exposed to air, but not exposed to direct light, the degradation that occurs is linked to an increase of the roughness. It has been shown that SE could be used to monitor the degradation of the perovskite exposed to air and light (Ref. 1)

Perovskite charge carrier mechanisms have been described elsewhere (Ref. 2). In Figure 8, the steady state performance of a perovskite solar cell is presented. The sample was measured as prepared, after 7 and 14 days. As pointed out previously, between each measurement the sample was stored in the dark, protected by an Al foil, and at room temperature.
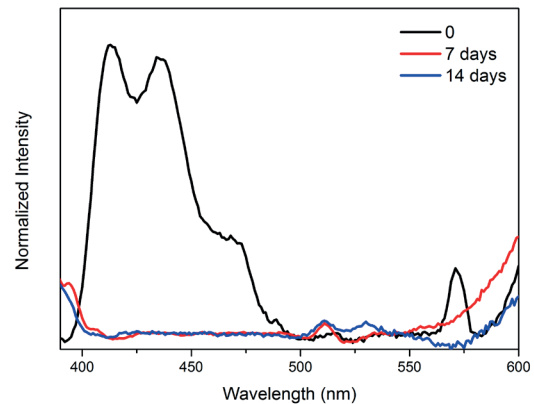

Figure 8. Normalized emission spectra of fresh, 7 and 14 days-old $CH_3NH_3PbI_3$/PEDOT/ITO samples (integration time = 0.1s, λ_{exc} = 350nm, slits = 5nm bandpass). Higher diffraction orders have been filtered by using long wave-pass filters

The emission spectrum of the as prepared sample shows three main bands at 413, 435 and 571nm, plus a shoulder at 469nm. These features completely disappear after 7 days of air exposure. After room temperature storage, three new bands at 394, 512 and 529nm appear; these two last are compatible with the formation of PbI_2.

As the chosen system, upon photoexcitation, contains several species, a simple steady state measurement is not sufficient to characterize the system and elucidate the dynamics involved. The use of a time-resolved technique, such as measuring the time-resolved emission spectrum (TRES), is useful in obtaining this information. Measurements involved incrementing the monochromator in 10nm steps from 470 to 600nm, with time resolved decays acquired to a predetermined time preset at each wavelength on an acquisition time range, chosen from the drop-down menu of 400ns (Figure 9).
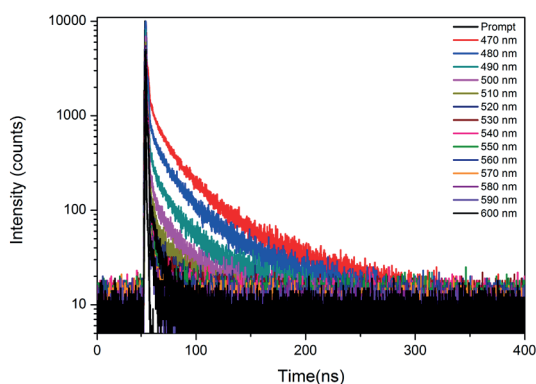

Figure 9. Time profiles of as prepared $CH_3NH_3PbI_3$ sample

Acquisition of the instrumental response (IRF or prompt) allowed further analysis using reconvolution. The decays were analyzed using DAS6 and found to be multiexponential (4 components in all the cases). After global analysis, this allowed the following plot of the average lifetimes associated spectra to be made with no significant intra-group difference (Figure 10).
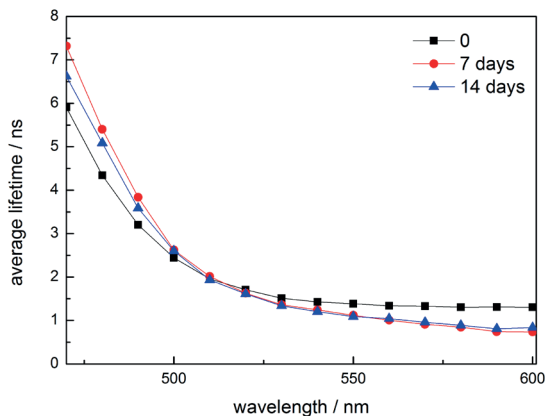

Figure 10. Average lifetime distribution

Finally, in Figure 11, the elemental depth profiles obtained for the *t=0* and the aged *t=14 days* samples are presented. It is shown that despite the exposure to air, which has a detrimental effect on the electrical properties of the material, no evident effect can be observed on the elemental distribution inside the perovskite material. However GDOES, thanks to its pulsed RF source, has been proved to be an efficient technique to study the impact of applied bias onto the ionic migration (Ref. 3).
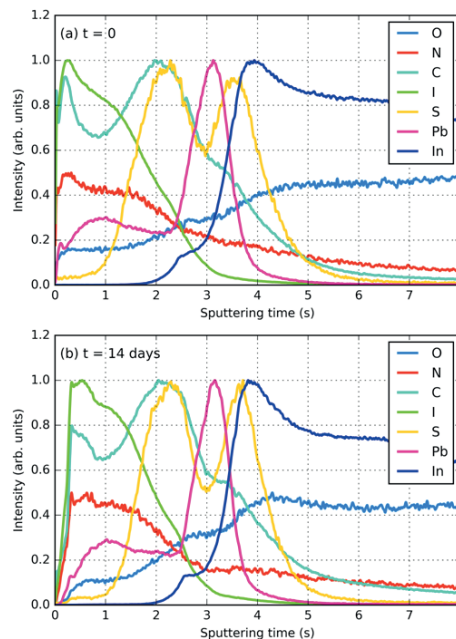

Figure 11. Qualitative elemental depth profile of (a) t=0 and (b) t=14 days

We decided to compare for some elements the profile before and after exposure. The results are presented in **Figure 12**.
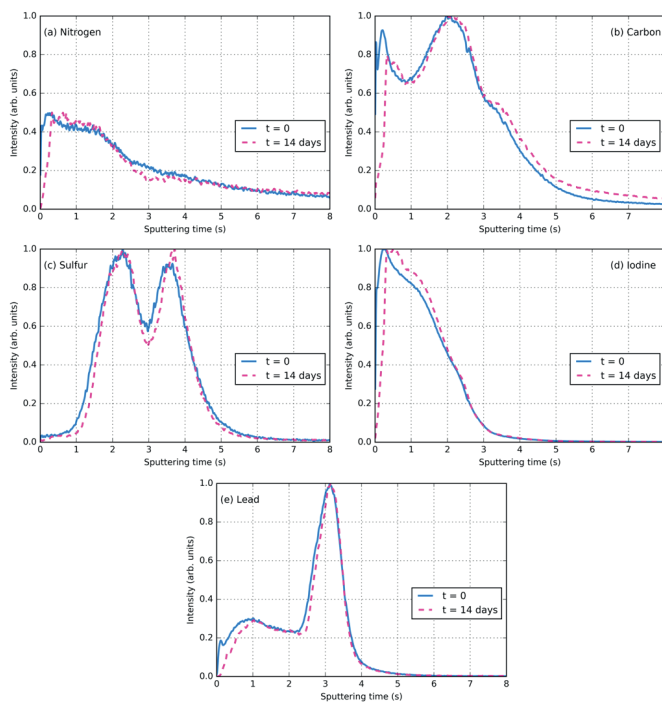

Figure 12. Direct comparison of the elemental distribution at first exposure to air (continuous blue curve) and after 14 days of exposure to air (hatched pink curve) for (a) nitrogen, (b) carbon, (c) sulfur, (d) iodine and (e) lead.

Slight variation in the elemental profile can be observed. However, the integrated area under the curves has been calculated and the results are presented in Table I proving that despite a slight displacement, no evolution in the total amount of composition can be observed.

Table I. Integrated areas for the elemental profiles presented in Figure 12.

Element	t = 0	t = 14 days
N	1.7	1.6
C	3.2	3.3
S	2.5	2.4
I	1.9	1.8
Pb	1.5	1.4

Conclusion

Air-exposed perovskite thin films were investigated using some techniques provided by HORIBA Scientific. Although the chosen techniques cannot be directly correlated, they can be used at different stages of the research process in order to understand the different mechanisms that impact the final performance of photovoltaic devices.

References

1. Solar Energy Materials and Solar Cells 178 (2018) 179-185
2. HORIBA Application note TRFA-17
3. ACS Energy Lett. 2017, 2, 943–949

HORIBA
Scientific

info.sci@horiba.com

www.horiba.com/scientific

200 YEARS
1819-2019
HORIBA JOBIN YVON

USA: +1 732 494 8660	**France:** +33 (0)1 69 74 72 00	**Germany:** +49 (0) 6251 8475 0
UK: +44 (0)1604 542 500	**Italy:** +39 06 51 59 22 1	**Japan:** +81(75)313-8121
China: +86 (0)21 6289 6060	**Taiwan:** +886 3 5600606	**Brazil:** +55 (0)11 2923 5400
Other: +33 (0)1 69 74 72 00		

Explore the future

Automotive Test Systems I Process & Environmental I Medical I Semiconductor I Scientific

HORIBA