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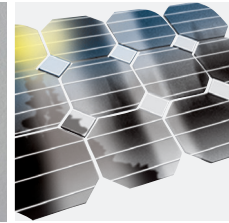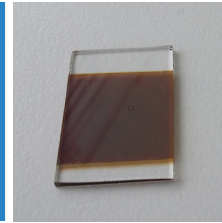**Spectroscopic Ellipsometry**

Determination of Perovskite Optical Constants by Spectroscopic Ellipsometry

Application Note

Photovoltaic SE38

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Abstract

Hybrid organic-inorganic perovskite materials have emerged over the past five years as promising absorber layers for new high-efficiency and low-cost solar cells that combine the advantages of organic and inorganic semiconductors. The increasing interest in this technology is pushing research laboratories to find the optimal techniques for the accurate characterization of opto-electronic properties of these materials.

Spectroscopic ellipsometry (SE) turns out to be an efficient technique to study the optical response of this new class of materials. Indeed, properties like optical absorption and energy band gap are crucial for the efficient design of photovoltaic devices. In this note, a SE study of the most common perovskite methylammonium lead iodide ($CH_3NH_3PbI_3$) thin film is presented. We show the performance of SE for the characterization of layers deposited using different techniques, revealing the impact of the deposition onto the structural properties of the material, and also the key role of this characterization technique for studying the degradation of perovskite layers after exposure to air.

Introduction

Perovskite is an emerging 3rd generation thin-film PV technology with cell efficiencies that have drastically risen from 4% in 2010 to 20.1% in 2014, approaching the commercial second-generation thin films. As perovskites raw materials are abundant, this is a promising technique for large-scale deployment. However, such potential demands a precise characterization of all those material properties which are fundamental for the final device performance. In order to be able to predict the behaviour of a material when applied into a working device, it is necessary to extensively study both structural and opto-electronical properties, especially in the aim of establishing a correlation between the fabrication process and the cell characteristics. Indeed, in an ideal solar cell, the parameters that define the quality of the device are the short-circuit current (Jsc), the open-circuit voltage (Voc), the fill factor (FF) and the efficiency. Assuming low levels of bulk and interface recombination, Jsc and Voc are ultimately controlled by the optical absorption and the energy band gap of the solar-cell absorber layer. For this reason, in order to develop the perovskite technology, an accurate study of the optical properties through spectroscopic ellipsometry (SE) has been implemented.

Instrument and samples

The analyses were carried out using a UVISEL2 in the 0.6-4.6 eV spectral range, with an incidence angle of 60°.

As the $CH_3NH_3PbI_3$ films are sensitive to the air, a sealed cell was used to keep them under N_2 atmosphere.

Air exposure was avoided by directly transferring the samples from the glove-box into the sealed cell (Figure 1(a) and 1(b)).
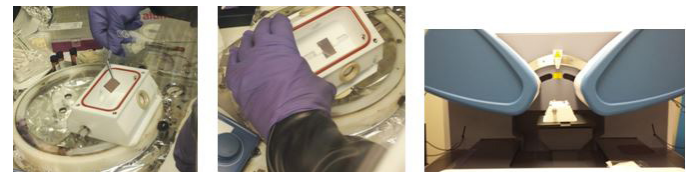

Figure 1: a,b : Transfer of the sample into the sealed cell – c: Sealed cell on UVISEL2

No additional sample preparation is needed. Moreover, the backside reflection of the glass has been collected and modelled; the analysis of the enclosed sample becomes straightforward.

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Two different $CH_3NH_3PbI_3$ thin films were studied, the first one was deposited by spin coating and the second one by co-evaporation of methylammonium iodide (CH_3NH_3I) and PbI_2. In both cases the perovskite thin film is deposited on a spin-coated PEDOT:PSS layer, on ITO on glass. For this reason, the first step has been to characterize separately the 80 nm thick ITO on glass and the PEDOT:PSS/ITO/glass stack in order to be able to focus the ellipsometry analysis only on the perovskite layer.
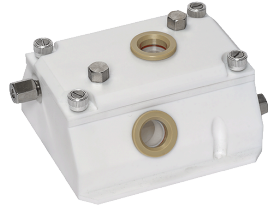
Results

From the raw ellipsometric data (Is and Ic) presented in Figure 2, it can be seen that the $CH_3NH_3PbI_3$ presents several absorption peaks in UV spectral region. Such absorption peaks (black arrows in Figure 2) allow the adjustment of the parameters of the dispersion formula used for modelling. Considering that perovskites are a direct transition semiconductor material, a N-Tauc Lorentz formula can be used to model the optical properties . Moreover, Is and Ic show several oscillations in the near infrared spectral region, which are linked to the transparency of the film and give information about the thickness of the analysed layer.
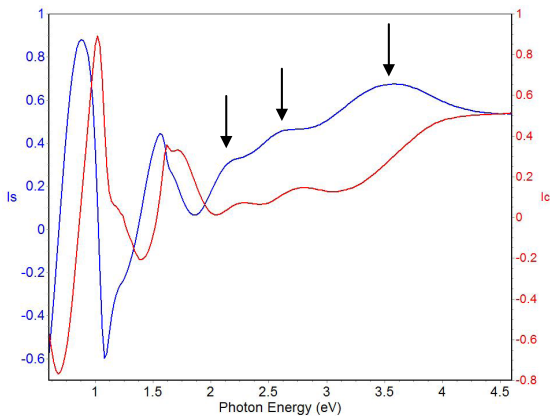
Figure 2 : Ellipsometric raw data (Is,Ic)=f(E) for $CH_3NH_3PbI_3$/PEDOT:PSS/ITO/Glass

Using the DeltaPsi 2 software, the two samples were modelled in order to infer the optical properties of the photovoltaic material.

For the first sample (spin-coating), the $CH_3NH_3PbI_3$ film had to be modelled using a 3 layer stack to account for in-depth variation of index. Using the Bruggeman Effective Medium Approximation, the surface layer and the interface
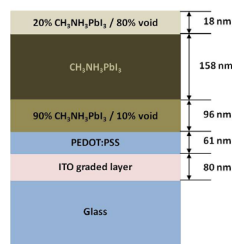
layer were described as a mixture of perovskite material and void (percentages are given in Figure 3(a)). A 4-Tauc Lorentz dispersion formula was used to model the optical properties.

From this fit, the optical band gap was extracted and found at 1.57 eV and three optical electronic transitions occur at 1.60 eV, 2.4 eV and 3.4 eV.
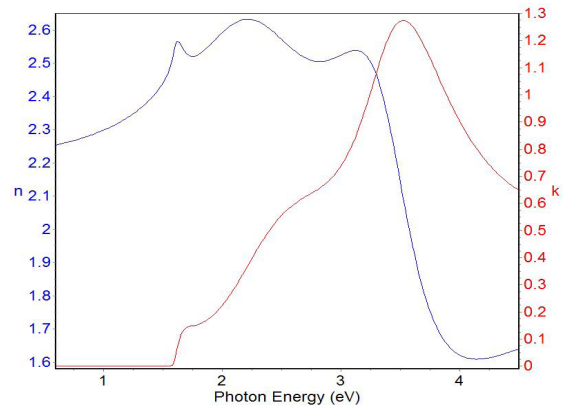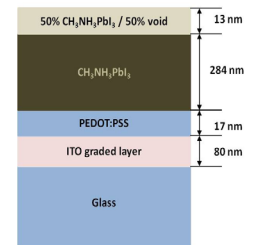
Figure 3: ($CH_3NH_3PbI_3$) solution optical constants (n,k)=f(E)

For the second sample (co-evaporation), a single film with surface roughness (described as a mixture of 50% material and 50% void) was used.

Even for this sample, a 4-Tauc Lorentz dispersion formula was used to model the optical properties of the perovskite layer. An optical band gap of 1.57 eV was found and three optical transitions are observed at 1.6 eV, 2.6 eV, 3.38 eV, corresponding to the interband transitions.
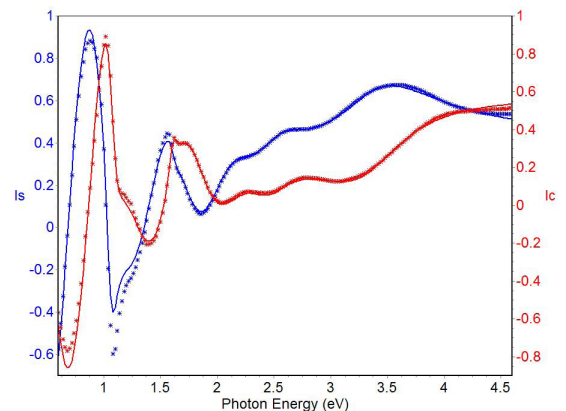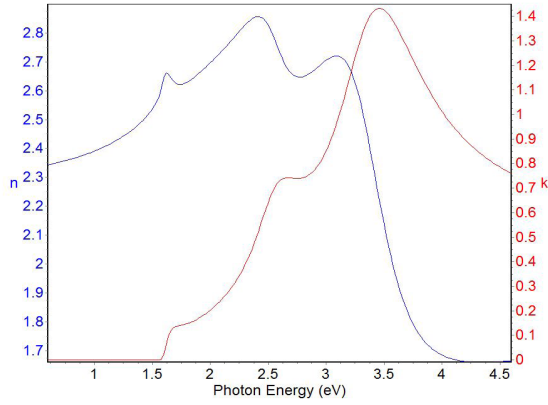
Figure 4: Fit results

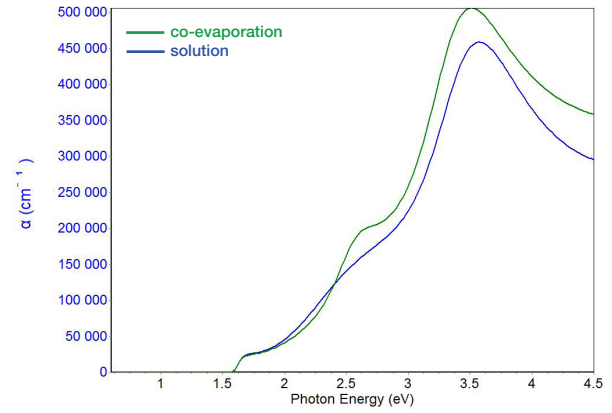Figure 5 : CH$_3$NH$_3$PbI$_3$ optical constants (n,k)=f(E)

Figure 7 : absorption coefficient for both perovskite

The difference in the two samples may be ascribed to the impact of the deposition technique on the structural properties of the layers. For instance, not only the deposition method seems to induce variations in surface roughness, which is represented by a difference in the void percentage, but also on the interface between the perovskite and the ITO. For a correct modelling of the spin-coated sample, an interface layer, with a different porosity, had to be considered.

Nevertheless, a comparison of the obtained dielectric constants (Figure 6) shows a good agreement between both samples, with the absorption peak at ~2.4-2.6 eV which is more enhanced for the co-evaporated perovskite.
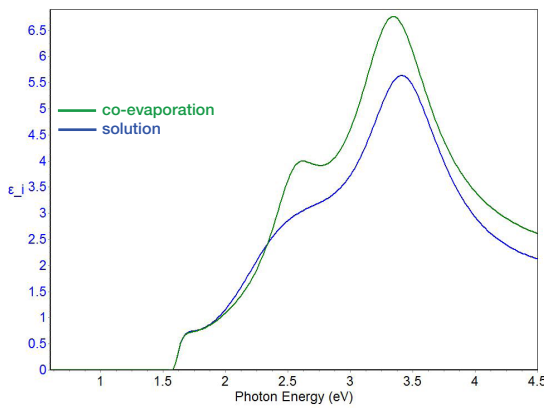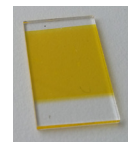
Finally, the degradation of the CH$_3$NH$_3$PbI$_3$ material was studied by SE at room temperature. Ellipsometry measurements were performed over 18 days. The results are presented in Figure 8(a,b), and show an evolution of the raw ellipsometric observables (Is,Ic). More specifically, from the 6th day the appearance of an additional signature at ˜2.4 eV can be observed. Such signature can be ascribed to the presence of a PbI2 phase which stabilizes from the 10th day.
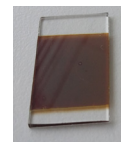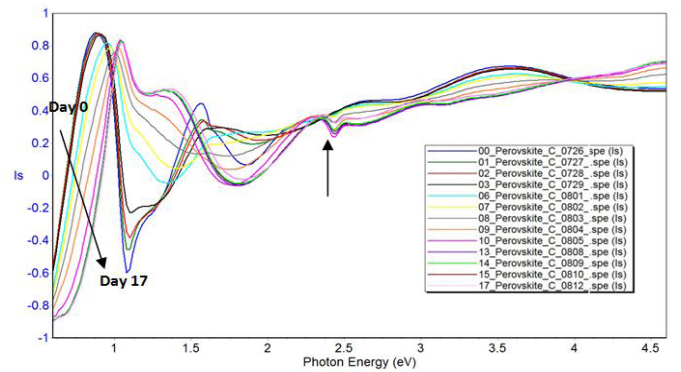
CH$_3$NH$_3$PbI$_3$ before degradation day 0   *CH$_3$NH$_3$PbI$_3$ after degradation day 17*

Figure 6 : Imaginary part of dielectric function (ε_i)=f(E)

A crucial parameter for the efficiency of a solar cell is the light penetration through the absorber and the resulting carrier generation, which depend on the absorption coefficient α. In Figure 7, we present the evolution of the absorption coefficient α, which can be directly obtained from the extinction coefficient k through the relation $4\pi\kappa/\lambda$. At 2 eV, we find α~4.1.10^4 cm^{-1} for co-evaporation and α~4.5.10^4 cm^{-1}.
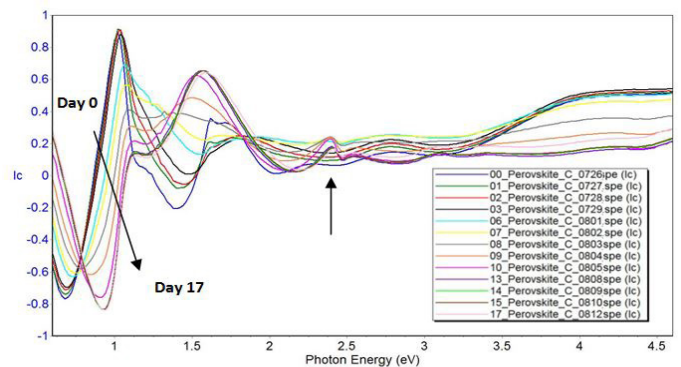
Figure 8 : Raw SE spectrum of the perovskite degradation in air.
(a: Is=f(E); b: Ic=f(E))

Conclusion

Spectroscopic ellipsometry (SE) proved to be an efficient technique for the analysis of optical properties of perovskite solar cells. Thanks to the use of the sealed cell in N_2 atmosphere, even the air-sensitive materials can be easily analyzed and the determination of the optical constants and the energy band gap can be efficiently obtained. We proved the efficiency of this technique by characterizing the most common perovskite ($CH_3NH_3PbI_3$) material, however this can be easily transferred to other perovskite structures, such as $CH_3NH_3PbX_3$ (X=I, Br, Cl). Moreover, SE allows to monitor the tuning of the energy band gap depending on the halide content. Finally, we proved that SE allows to characterize each layer of a multistack.

Acknowledgment

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References

P.Löper; J.Phys.Chem. Lett., 2014

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