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Opportunities of Atomic Layer Deposition for Perovskite Solar Cells

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The fabrication of different functional layers by means of atomic layer deposition is proposed for the novel organo-lead halide perovskite solar cells. A plasma- assisted process at 150 °C was adopted to deposit an efficient TiO₂ compact blocking layer on ITO-polymer substrates. Efficient flexible devices were obtained already with layers as thin as 10 nm. A Thermal ALD Al₂O₃ process at 150 °C was successfully applied on a mesoscopic anatase TiO₂ structure: an improvement of the overall performance of the solar cell (+13%) was measured with only 1 ALD cycle compared to devices without over-layer. Interestingly, a drastic reduction of the performance was observed when increasing the number of the cycles.

Introduction

Atomic Layer Deposition (ALD) is nowadays extensively adopted in photovoltaics (PV) due to the accurate control in film thickness and composition, as well as the high deposition conformality and uniformity (1). Ultra-thin ALD Al₂O₃ layers have been successfully applied on the surface of crystalline silicon as excellent passivation layers (2). In copper indium gallium (di) selenide (CIGS) solar cells, ALD (Zn,Mg)O and Zn(O,S) have been deposited for the development of cadmium-free buffer layers for the window top contact (3). Recently, the outbreak of organo-lead (mixed) halide perovskite absorbers (CH₃NH₃PbI_{3-x}Y_x, Y = Br, Cl) has attracted a huge interest in the photovoltaic community due to the remarkable increase in the last 3 years of the device performance and the easy solution manufacturing steps. In addition to that, the wide and tunable band gap of this material makes it very promising for the fabrication of a top cell in a tandem junction configuration with crystalline silicon or CIGS as bottom devices (4). Although different structures have been proposed in literature, the most efficient and most stable perovskite solar cells consist of a complex 3D structure, generally a mesoporous TiO₂, to ensure an efficient light harvesting and an effective photo-generated carrier extraction and collection (5). The precise control on the large surface area and the several interfaces present in this architecture represents a fundamental strategy to reduce/suppress the charge carrier recombination processes which affect the final device performance (Figure 1). In general, two main recombination mechanisms can be identified: 1) a charge

transfer process at the interface between the transparent conductive oxide (TCO) and the perovskite (which acts also as hole conductor) or the hole transport layer (HTM) 2) the charge transfer process at the interface between the mesoporous TiO_2 film and the perovskite or the HTM (see Figure 1b).

Deposition of different metal oxide films via solution processed techniques appears in literature as the common method to achieve efficient devices (6-9). The high quality of the layers deposited via ALD and the precise control of the thicknesses also on structures with high aspect ratio such as in electronics and batteries applications (10), makes this technique a valid alternative for this new class of solar cells. Thus, in this work two different ALD layers were adopted to control the recombination mechanisms at the interfaces.

Figure 1: a) Schematic representation of the architecture of a mesostructured perovskite solar cell; b) Schematics of the two main recombination pathways in the device and the deposition of a compact blocking layer on the TCO and a passivation layer on the TiO_2 mesoporous structure.

Atomic Layer Deposition of Blocking Layers on Transparent Conductive Oxides

The conventional approach to control the interface between the TCO and the hole conductor layers (perovskite and HTM) consists in the deposition of a TiO_2 compact layer on top of the TCO surface. This layer should be extremely compact, without pinholes and exhibit rectification characteristics. Spray pyrolysis technique is a simple method typically reported in literature to deposit 50-100 nm of TiO_2 layer on FTO/glass substrates (6,11). The deposition occurs at high temperatures (450 °C) to allow the pyrolysis of the titanium precursor and the evaporation of the solvents (11). Recently, ALD process has been successfully adopted in glass-based perovskite solar cells, depositing 50 nm of titanium dioxide at 200 °C using tetrakis(dimethylamino) titanium (TDMAT) and H_2O precursors. The ALD layer exceeds the performance of devices with spray pyrolysis and sol-gel processes due to lower density of nanoscale defects and pinholes (12).

Plasma-assisted ALD can offer several advantages with respect to the conventional thermal approach (13). The fabrication of higher quality films in terms of density and materials properties in the range of processing temperatures compatible with conductive polymer substrates, is extremely attractive due to the potential development of high throughput, roll-to-roll manufacturing processes (14). In the first part of this contribution,

we show the effect of a plasma assisted ALD TiO_2 layer and the role of the thickness for an efficient compact blocking layer for flexible devices on ITO/PET substrates.

Atomic Layer Deposition for Passivation Layers on Mesoporous Structures

The strategy for the suppression/reduction of the recombination mechanisms at the interface between the mesoporous TiO_2 layer and the perovskite/HTM is the natural evolution of the approach followed in the dye-sensitized solar cell (DSC) technology. Here, solution processed TiO_2 (7), or thin wide band gap metal oxides such as Al_2O_3 , MgO , ZrO_2 (15, 16) were successfully adopted, with the main consequence of an enhancement of the overall performance. In the last 6 years also different ultra-thin ALD layers (Al_2O_3 , HfO_2 , Ga_2O_3) were tested in the DSC architectures (17-20). The choice of ALD was driven by the assumption that the precise control of the oxide film thickness plays a key role to provide an efficient passivation without any detrimental effect on the electron extraction from the dye molecules. Interestingly, while a passivation layer with a thickness in the nm-range is claimed to work for solution processed metal oxide coatings, a sub-nm thick ALD layer is sufficient to passivate the mesoscopic structure (15,18). For organo-lead halide solar cells, only sol-gel metal oxides have been applied (8,9). In the second part of this work we describe the effect of an Al_2O_3 passivation layer on the mesoporous TiO_2 structure.

Experimental details

The TiO_2 compact layers were deposited on conductive substrate (ITO-PET) at 150 °C in a thermal and remote plasma reactor (FlexALTM) using heteroleptic dimethylamido precursor with a methylcyclopentadienyl ligand ($\text{Ti}(\text{Cp}^{\text{Me}})(\text{NMe}_2)_3$) an O_2 inductively coupled plasma. Details and specifications of the ALD process have been extensively discussed in (22). A -plasma treatment (200W) of 3 min was performed prior to the ALD deposition. The Al_2O_3 passivation layer was deposited on the mesoporous TiO_2 film at 150 °C in a thermal and remote plasma reactor (OpAlTM) at 150 °C. Trimethylaluminum (TMA) precursor was dosed for 40 ms and H_2O vapour for 250 ms. Purges times between the precursors was kept at 20 s in order to suppress any CVD contribution to the growth.

The film thickness was determined using a J.A. Woollam, Inc. M2000U (0.75-5.0 eV) spectroscopic ellipsometer (SE). XPS (Thermo Scientific K-Alpha) depth profile measurements were acquired alternating narrow-scan measurements and sputtering with argon ions. TEM (FEI Tecnai 300 kV) in HAADF scanning mode was carried out to evaluate the conformity and the thickness of the Al_2O_3 layer on the TiO_2 nanoparticles.

Flexible perovskite solar cells were fabricated with the following architecture: PET / ITO / Compact-ALD TiO_2 / mesoporous- TiO_2 -scaffold / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ / Spiro OMeTAD / Au. Details on the fabrication of the several layers apart from the ALD TiO_2 were reported in (23). Glass perovskite solar cells were fabricated with the following structure: Glass / FTO / Compact- TiO_2 / mesoporous- TiO_2 -scaffold / (ALD- Al_2O_3) / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ / Spiro OMeTAD / Au. Details on the deposition of the several layers except for the ALD layers are given in (24). Class A solar simulator (ABET Sun 2000) at AM1.5 and 100 mW cm^{-2} illumination conditions calibrated with a reference silicon cell

was used to measure the current voltage curves and the photovoltaic parameters of the devices.

Results and Discussion

The efficiencies of the flexible perovskite solar cells as a function of the ALD number of cycles and the thickness are reported in Fig.2. TiO_2 thickness has been calculated by the growth per cycle measured on the silicon reference wafer, i.e. 0.055 nm/cycle. The absence of the compact layer leads to extremely poor performance of the cell ($\eta = 0.02\%$). The efficiencies start to increase already with a thin film of 5.5 nm (100 ALD cycles) achieving a maximum around 11 nm. After this value, a slight decrease (up to 42 nm) is observed. Higher performance devices (7-8%) with 11 nm of TiO_2 have been obtained using the same process in different experimental batches (23). Differently from the thick solution processed films reported in literature (50-100 nm), flexible perovskite devices work properly also with a thinner ALD compact TiO_2 layers.

Figure 2. Photovoltaic efficiencies for perovskite based solar cells as a function of TiO_2 ALD thickness.

The importance of the interface control in this technology emerges by the analysis of the current density-voltage (JV) dark curves as depicted in Fig.3a where the logarithmic representation (Tafel plot) has been used. When TiO_2 is not deposited on the ITO surface, the symmetric JV curve indicates no diode like behavior. The calculated exchange current density value, J_0 , at the interface ITO/perovskite is extremely high (3 mA cm^{-2}). The introduction of TiO_2 compact layer immediately has a significant impact on the JV dark current behavior, with the development of a rectifying behavior even for the thinnest TiO_2 . As a consequence of that, the value of J_0 is reduced of three order of magnitude, ($0.2\text{--}0.7 \text{ }\mu\text{A cm}^{-2}$) as well the reverse dark current (maximum value at 0.1 mA cm^{-2} for -1V). In the low positive voltage range where the forward dark current is governed by shunting mechanism (25), a drastic decrease is also detected. Interestingly, the reduction follows the number of the cycles. For voltages $> 0.5 \text{ V}$, JV curves show a steep increment which is ascribed to a diffusion-dominated current (25). As expected, no difference in slope is evident apart at higher voltages, where change in slope can appear due to the contribution of series resistance, likely related in this case to variations in the ITO sheet resistance.

Figure 3. J-V dark current curves for perovskite based solar cells with different ALD cycles (i.e. thickness) of the TiO_2 compact layer.

In order to control the second recombination interface between the mesoporous TiO_2 film and the hole conductors (the perovskite absorber and the hole transport material), the deposition of an ultrathin Al_2O_3 layer is adopted. In Fig.4, a high resolution-TEM micrograph shows a conformal amorphous Al_2O_3 layer on crystalline TiO_2 nanoparticles. TEM analysis shows a growth per cycle (GPC) of 0.1 nm/cycle at 150 °C which matches with the GPC values measured on the reference silicon wafer. This result points out the accurate control of the thickness for ALD processes also in complex 3D structures, such as mesoporous layers.

Figure 4: High resolution-TEM micrograph of thermal ALD Al_2O_3 on a nanocrystalline TiO_2 mesoporous film. The lines serve as a guide to the eye.

XPS depth profile measurement was used as efficient tool to investigate the distribution of Al within the mesoscopic TiO_2 film. This is a fundamental requirement to ensure the complete passivation of the complex TiO_2 surface. The result in Fig. 5 highlights the homogeneous content of [Al] in respect to [Ti].

Figure 5. Atomic concentration (%) as a function of sputtering time for 600 nm mesoporous TiO_2 layer on conventional FTO/glass substrate with 20 cycles of Al_2O_3 deposited via ALD.

The role of the overlayer thickness on the final performance of the perovskite solar cell was investigated, and the results are summarized in Table I.

The deposition of just one Al_2O_3 ALD cycle (estimated by GPC in 0.1 nm) leads to an improvement of the efficiency compared to the reference cells (+ 13%). In particular, a significant increase in open circuit voltage (V_{OC}) from 750 to 824 mV (+10%) is observed, as expected when the recombination rate is reduced (7-9,18-21). While the short circuit current (J_{SC}) remains constant, also the fill factor (FF) exhibits an improvement (+8%). Interestingly, increasing the number of the ALD cycles and consequently the thickness of the overlayer, a reduction on the short circuit current (J_{SC}) is observed, decreasing the overall efficiency although the increment in the V_{OC} . A similar behaviour has been reported in the case of DSC technology (18). The increase in photovoltage was related to the shift of the quasi-Fermi level toward vacuum as a consequence of the improvement in the electron lifetime into the mesoporous layer. On the other hand, the increase of the energy barrier height at the interface $\text{Al}_2\text{O}_3/\text{dye}$ molecule with the increment of the ALD cycles was considered responsible for the decrease of injection of photo-generated electrons and consequently the reduction of the J_{SC} (18).

TABLE I. Photovoltaic performance of perovskite solar cells as function of the ALD cycle numbers.

ALD cycles	Efficiency (%)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)
0	3.9 ± 0.4	-11.0 ± 1.0	749 ± 4	45.6 ± 1.2
1	4.4 ± 0.1	-10.8 ± 0.3	824 ± 13	49.6 ± 1.9
2	2.7 ± 0.1	-6.3 ± 0.3	884 ± 13	47.4 ± 1.3
5	1.00 ± 0.02	-2.8 ± 0.4	890 ± 5	37.4 ± 2.0
10	0.32 ± 0.01	-1.7 ± 0.2	852 ± 7	22.8 ± 0.4

Conclusion

Atomic layer deposition was successfully applied for the fabrication of efficient functional layers in organo-lead halide perovskite solar cells in order to control the recombination interfaces inside the device architecture. The deposition of thin compact TiO_2 layers via plasma-assisted ALD at 150 °C on ITO polymer surface enables the fabrication of efficient flexible devices over 5%. The reduction of the charge transfer processes at the interface ITO and perovskite/HTM is fulfilled already with a TiO_2 layer of 10 nm. An Al_2O_3 layer was deposited via thermal ALD process at 150 °C to control the recombination mechanism at the interface between the mesoporous TiO_2 and perovskite/HTM. The accurate control of the process in terms of growth per cycle (0.1 nm/cycle) was confirmed by TEM and the homogeneous distribution of the overlayer (in terms of Al content) was confirmed by XPS analysis. Preliminary investigation on the role of the Al_2O_3 thickness on the overall performance of perovskite devices highlights an improvement of the efficiencies (+13%) only with a single ALD cycle. Increasing the number of the cycles a reduction of the performance has been observed, becoming drastic already at 5 cycles. These results demonstrate how ALD is a successful strategy for the nanoscale control of interfaces in mesoscopic solar cell.

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