High Efficiency Perovskite Solar Cells Fabricated under Ambient Conditions with Mesoporous TiO$_2$/In$_2$O$_3$ Scaffold

A. Apostolopoulou, D. Sygkridou, A. N. Kalarakis, E. Statthatos

Abstract—Mesoscopic perovskite solar cells (mp-PSCs) with mesoporous bilayer were fabricated under ambient conditions. The bilayer was formed by capping the mesoporous TiO$_2$ layer with a layer of In$_2$O$_3$. CH$_3$NH$_3$I$_{1-x}$Cl$_x$ mixed halide perovskite was prepared through the one-step method and was used as the light absorber. The mp-PSCs with the composite TiO$_2$/In$_2$O$_3$ mesoporous layer exhibited optimized electrical parameters, compared with the PSCs that employed only a TiO$_2$ mesoporous layer, with a current density of 23.86 mA/cm$^2$, open circuit voltage of 0.863 V, fill factor of 0.6 and a power conversion efficiency of 11.2%. These results indicate that the formation of a proper semiconductor capping layer over the basic TiO$_2$ mesoporous layer can facilitate the electron transfer, suppress the recombination and subsequently lead to higher charge collection efficiency.

Keywords—Ambient conditions, high efficiency solar cells, mesoscopic perovskite solar cells, TiO$_2$/In$_2$O$_3$ bilayer.

I. INTRODUCTION

In the past years a new class of third generation photovoltaics has emerged based on organometal halide perovskites. While results of the first efficient perovskite solar cells (PSCs) were published in 2012 [1], their efficiencies were rapidly lifted to 20% the very next year. Moreover, in early 2016 researchers managed to manufacture PSCs with cells (PSCs) were published in 2012 [1], their efficiencies were rapidly lifted to 20% the very next year. Moreover, in early 2016 researchers managed to manufacture PSCs with a power conversion efficiency of 21.1% [2]. Perovskite materials are direct bandgap semiconductors described by the general formula ABX$_3$, where X is an anion and A and B represent cations. The cation A is organic, typically methylammonium or formamidinium while cation B is lead (Pb) or tin (Sn) and the anion X is a halogen ion usually iodine, chlorine, bromine or a mixture of them [3]-[5].

For the fabrication of PSCs there are basically two different device architectures [6]. Planar or thin-film PSCs (Fig. 1 (a)) consist of a flat perovskite layer between n-type and p-type semiconductor. In this device structure, once the incident light is absorbed, the charge generation and the charge extraction are both occurring in the perovskite layer [7]-[9]. In the mesoscopic or sensitized PSCs (Fig. 1 (b)) the active layer consists of a mesoporous semiconductor which is sensitized with the perovskite. The perovskite absorber infiltrates the semiconductor’s layers creating a semiconductor-perovskite interface. Once the light is absorbed from the perovskite, the generated electrons are injected to the n-type semiconductor from where they are extracted and the holes are transferred to the p-type semiconductor [10], [11].

Andigoni Apostolopoulou and Dimitra Sygkridou are PhD candidates with the Physics Department, University of Patras, 26500, Greece (e-mail: andapolop@upatras.gr, dsygkridou@upatras.gr).
Alexander N. Kalarakis is with the Mechanical Engineering Department, Technological-Educational Institute of Western Greece, 26334 Patras, Greece; (e-mail: a_kalarakis@teiwest.gr).
Elias Statthatos is with the Electrical Engineering Department, Technological-Educational Institute of Western Greece, 26334 Patras, Greece (corresponding author to provide phone: 0030-2610-369242; e-mail: estathatos@teiwest.gr).
II. EXPERIMENTAL

A. Materials

Titanium disopropoxide bis(acetylacetonate) (75% in isopropanol, Aldrich), Titanium(IV) butoxide (97%, Aldrich), acetic acid, Pluronic P123 (5.800 MW, Aldrich), Indium(III) acetylacetone (Aldrich), Triton X-100 (646.86 MW, Fisher Scientific), Hexamethylenetetramine (HMT), Hydroiodic acid, Anhydrous dimethylformamide (DMF), Pb(II) chloride (Acrros organics), Chlorobenzene, Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, 95.5%, 94.000 MW, Ossila), Lithium Bis(trifluoromethanesulfonyl) imide and 76 mM 4-TBP as additives in order to improve the electrical characteristics. Two layers of P3HT were deposited on the films by spin coating at 1200 rpm for 10 s. After each layer the films were dried on a hot plate at 60 °C for 5 min in order to evaporate chlorobenzene [16]. Finally, all the samples were placed inside a high vacuum chamber (10⁻⁶ Torr) to sublime non-corrosive gold to form the back contacts.

B. PSCs Fabrication

All the fabrication processes were performed under ambient conditions. For fabricating the PSCs, fluorine-doped tin oxide (FTO) conductive substrates with a sheet resistance of 8 Ohm/square (Pilkington) were used, where a part of the conductive substrate was patterned by chemical etching with zinc powder and HCl aqueous solution. After the etching the conductive glasses were thoroughly cleaned with detergent solution and acetone in an ultrasonic bath and dried under nitrogen stream. A TiO₂ thin compact layer (c-TiO₂) was deposited on the FTO substrate by spin coating in 3000 rpm, which is obvious that the PSCs with the combined oxides TiO₂-In₂O₃ exhibit higher efficiencies than the cells with pure TiO₂ as photoanode in PSCs. The current density–voltage (J–V) characteristic curves are presented in Fig. 4. It is obvious that the PSCs with the combined oxides TiO₂-In₂O₃ exhibited large agglomerated clusters which can facilitate the perovskite solution infiltration.

Indium oxide was successfully combined with titanium dioxide and used as photoanode in PSCs. The current density–voltage (J–V) characteristic curves are presented in Fig. 4. It is obvious that the PSCs with the combined oxides TiO₂-In₂O₃ exhibited higher efficiencies than the cells with pure TiO₂ photoanode. Specifically, the highest efficiency (11.20%) is exhibited for the case of TiO₂-In₂O₃ photoanode where the In₂O₃ layer was deposited by spin coating at 3000 rpm, which corresponds to a 23% increase of the efficiency compared with

"Fig. 2 Band gaps and band positions of the n-type semiconductors used for the mesoporous bilayer"

III. RESULTS AND DISCUSSION

The top view images from the FE-SEM microscopy presented in Fig. 3 show no discrete morphology differences. Particularly, no apparent alterations were observed to the nanoparticles’ size or the film’s formation upon the deposition of the additional layer of In₂O₃. The films are highly porous, exhibiting large agglomerated clusters which can facilitate the perovskite solution infiltration.
pure TiO$_2$ photoanode. Generally, In$_2$O$_3$ layer acts as a barrier layer that suppresses the electron–hole pair recombination rate resulting mainly in an increase of the current density, whereas the voltage remains nearly constant. Thus the overall performance is improved. The measured and calculated values of the short circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), maximum power ($P_{MAX}$), fill factor (FF) and power conversion efficiency (n%) for all samples are summarized in Table I.

![Fig. 3 FE-SEM images (a) of mesoporous TiO$_2$ film and (b) of mesoporous TiO$_2$ and In$_2$O$_3$ bilayer](image)

**IV. CONCLUSION**

This work presents the fabrication and characterization of hybrid organic-inorganic mixed halide PSCs under ambient condition. mp-PSCs with plain TiO$_2$ mesoporous layer are compared against cells having a capping In$_2$O$_3$ layer over the mp-TiO$_2$ layer. Optimized electrical parameters were measured for the solar cells with the composite TiO$_2$-In$_2$O$_3$ mesoporous layer, which was ascribed to the fact that the top In$_2$O$_3$ layer facilitates the electron transfer and suppresses the recombination rate leading to higher power conversion efficiencies. The highest efficiency that was achieved was 11.2% which is a satisfactory performance for mp-PSCs with a simple structure fabricated without having controlled conditions or using expensive equipment, such as glove box.

![Fig. 4 Electrical characteristics of the PSCs with TiO$_2$ and TiO$_2$-In$_2$O$_3$ photoanodes, with different deposition speeds of the In$_2$O$_3$ layer](image)

**TABLE I**

<table>
<thead>
<tr>
<th>Cell</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$P_{MAX}$ (mW)</th>
<th>FF</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>21.59</td>
<td>0.853</td>
<td>0.794</td>
<td>0.55</td>
<td>9.13</td>
</tr>
<tr>
<td>TiO$_2$-In$_2$O$_3$ (3000rpm)</td>
<td>23.86</td>
<td>0.863</td>
<td>0.887</td>
<td>0.60</td>
<td>11.20</td>
</tr>
<tr>
<td>TiO$_2$-In$_2$O$_3$ (4000rpm)</td>
<td>21.85</td>
<td>0.843</td>
<td>0.876</td>
<td>0.61</td>
<td>10.21</td>
</tr>
<tr>
<td>TiO$_2$-In$_2$O$_3$ (5000rpm)</td>
<td>19.97</td>
<td>0.841</td>
<td>0.596</td>
<td>0.65</td>
<td>9.85</td>
</tr>
</tbody>
</table>

**ACKNOWLEDGMENT**

This research has been financed by the State Scholarships Foundation (IKY) through the Doctorate Fellowships RESEARCH PROJECTS FOR EXCELLENCE IKY/SIEMENS.

**REFERENCES**

Stathatos was a postdoctoral research fellow in University of Cincinnati, USA from Engineering Science Department also in University of Patras. Prof. Stathatos was born in 1968 in Patras, Greece. He obtained his first degree in Physics from University of Patras and then his Ph.D. degree from Engineering Science Department also in University of Patras. Prof. Stathatos is the head of the Nanotechnology and Advanced materials laboratory and he has more than 100 publications in peer review journals and five chapters in books which are recognized of more than 4200 citations (h-factor=33). He is an editorial board member for Journal of Advanced Oxidation Technologies, Materials science in semiconductor processing, Heliyon and International Journal of Photoenergy.

Andigoni Apostolopoulou received her Bachelor degree in Physics from University of Patras, Greece in 2010 and her M.Sc. degree in energy and environment from the same university in 2013. She is a PhD candidate at the Department of Physics, University of Patras since 2013. Andigoni Apostolopoulou has published her research in peer reviewed scientific journals and international conferences. Her field of research includes photocatalytic applications, third generation photovoltaics, materials science and building integration of photovoltaics.

Dimitra Sygkridou received her Bachelor degree in Electrical and Computer Engineering from the University of Patras, Greece in 2010 and her M.Sc in Environmental Sciences from the same university in 2013. She is a PhD candidate at the Department of Physics, University of Patras since 2013. Dimitra Sygkridou has published her research in peer reviewed scientific journals and international conferences. Her field of research focuses on third generation photovoltaics, materials science and building integration of photovoltaics. She is also a member of the Technical Chamber of Greece since 2010.

Alexandros N. Kalarakis is Lecturer of Mechanical Engineering Department at the T.E.I. of Western Greece. He obtained his Bachelor degree in Physics from the University of Patras and his M.Sc. and Ph.D. degrees from the Chemical Engineering Department also in the University of Patras. His research interests include transport phenomena modeling and experiments and in particular interfacial phenomena in physical processes, material modeling and material characterization. He has more than 25 publications in international scientific journals and conferences and one chapter in book which are recognized of more than 110 citations (h-index=6).

Professor Elias Stathatos was born in 1968 in Patras, Greece. He obtained his first degree in Physics from University of Patras and then his Ph.D. degree from Engineering Science Department also in University of Patras. Prof. Stathatos was a postdoctoral research fellow in University of Cincinnati, USA and now he is Lecturer of Mechanical Engineering Department at the T.E.I. of Western Greece. He obtained his Bachelor degree in Physics from the University of Patras and his M.Sc. and Ph.D. degrees from the Chemical Engineering Department also in the University of Patras. His research interests include transport phenomena modeling and experiments and in particular interfacial phenomena in physical processes, material modeling and material characterization. He has more than 110 publications in international scientific journals and conferences and one chapter in book which are recognized of more than 110 citations (h-index=6).

Professor Elias Stathatos was born in 1968 in Patras, Greece. He obtained his first degree in Physics from University of Patras and then his Ph.D. degree from Engineering Science Department also in University of Patras. Prof. Stathatos was a postdoctoral research fellow in University of Cincinnati, USA and now he is Lecturer of Mechanical Engineering Department at the T.E.I. of Western Greece. He obtained his Bachelor degree in Physics from the University of Patras and his M.Sc. and Ph.D. degrees from the Chemical Engineering Department also in the University of Patras. His research interests include transport phenomena modeling and experiments and in particular interfacial phenomena in physical processes, material modeling and material characterization. He has more than 110 publications in international scientific journals and conferences and one chapter in book which are recognized of more than 110 citations (h-index=6).