Solar Energy Materials & Solar Cells 159 (2017) 251–264

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

# Low temperature processed ZnO thin film as electron transport layer for efficient perovskite solar cells

Md Arafat Mahmud, Naveen Kumar Elumalai *, Mushfika Baishakhi Upama, Dian Wang, Kah Howe Chan, Matthew Wright, Cheng Xu, Faiazul Haque, Ashraf Uddin *

*School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, 2052 Sydney, Australia*

ARTICLE INFO

*Article history:*
Received 10 March 2016
Received in revised form
8 September 2016
Accepted 11 September 2016
Available online 23 September 2016

*Keywords:*
ZnO thin film
Low temperature
Deep trap states
Electronic properties
Mott-Schottky analysis
Charge transport

ABSTRACT

Organic inorganic lead halide Perovskite photovoltaic devices are promising candidates for commercial application because of their high efficiency and low production cost. One integral part of these high efficiency solar cells is electron transport layer that provides the electron contact selectivity and mitigates recombination phenomena for enhanced device performance. However, high temperature sintering process of most widely used Titanium oxide electron transport layer or the sophisticated, time consuming processing with nanostructured electron extraction material is a fundamental barrier to mass production of Perovskite solar cell with roll-to-roll process. In this work, we have reported the application of simple, low temperature processed ( $< 150$ °C) sol-gel ZnO thin film as electron transport layer with efficient (PCE: 8.77%), highly reproducible Perovskite solar cell. Consecutive spin coating process has been implemented to find a multi-layer ZnO film that ensures high optical absorption in photoactive Perovskite layer by acting as a highly transmitting, less reflective, transparent layer. The optimized ZnO film also provides coherent surface morphology for the proper crystalline growth of overlying Perovskite layer and suppresses the deep trap states existing at the ZnO/perovskite interface. A systematic impedance spectroscopy study has been presented in this work to comprehend the improved device performance with the optimized multilayer electron transport material. The electronic properties like contact resistance, recombination resistance, flat-band potential and depletion width of the best performing device have been investigated. The interfacial charge transfer characteristics between methyl ammonium lead triiodide perovskite and low temperature solgel ZnO have also been elaborated based on the interface electronic properties.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Highly efficient methyl ammonium lead halide perovskite solar devices have agitated the photovoltaic research arena in the recent years due to their high power conversion efficiency and nominal fabrication cost compared to silicon solar cells [1,2]. Methyl ammonium lead halide Perovskite is a class of hybrid organic-inorganic material families whose general formula can be given as $ABX_3$, where A, B and X stand for organic cation (methyl ammonium [2] or formamidinium cation [3]), divalent metal ion (Pb or Sn [4]) and an individual halogen element (Iodine, Chlorine, and Bromine) or a composition of them with a fixed molar ratio respectively. With efficiency already reported over 20% [3], Perovskite material has a unique set of semiconductor properties that makes it compatible with high performance photovoltaic device fabrication. Methyl ammonium lead triiodide perovskite has a direct band gap of 1.57 eV [5] which only demands a photon with identical energy as the material bandgap for creating electron hole-pair without significant change in electron momentum. It is also blessed with high carrier mobility being as high as 10 $cm^2 V^{-1} s^{-1}$ [6]. Additionally, a considerably large exciton diffusion length of $\sim$100 nm [7,8] for pure tri-iodide perovskite material and more than 1 μm [9] for mixed halide perovskite has already been reported. The exciton binding energy for tri-iodide perovskite has been found to be $16 \pm 2$ meV in a recent study [10] which explains its exciton dissociation even at room temperature [11]. This contributes to a significant boost in the short circuit current density and fill factor of the perovskite device structure [12]. Furthermore, the procedure of perovskite layer formation can be greatly simplified by virtue of its compatibility with solution-processing [9,13]. All these traits reflect the unprecedented potential of perovskite material in solar industry.

Although perovskite solar cells do not require any

* Corresponding authors.
*E-mail addresses:* n.elumalai@unsw.edu.au (N.K. Elumalai), a.uddin@unsw.edu.au (A. Uddin).

http://dx.doi.org/10.1016/j.solmat.2016.09.014
0927-0248/© 2016 Elsevier B.V. All rights reserved.

heterojunction for the dissociation of the excitons [11] like organic photovoltaic cells (OPV), Electron transport layer (ETL) plays a vital role in perovskite solar cells for contact selectivity [14] and in optimizing device performance [15,16]. ETL works as electron selective contact that preferentially extracts electrons to one side of the device and blocks the direct contact between transparent conductive oxide and hole transporting layer [14]. Besides working as a HBL (Hole Blocking Layer), ETL enhances the fill factor [15] and the open circuit voltage [16] of a perovskite solar cell as the recombination rate is mitigated by electron selective contact between perovskite and ETL [15]. Additionally, ETL influences the perovskite layer morphology and its loading and controls the quality of perovskite/ETL interface and perovskite layer itself since ETL provides the intervention in the full perovskite transformation from the precursor [17]. For this reason, although some ETL free perovskite device structures have already been reported [18,19], none of them was as efficient as those with ETL. However, most of the highly efficient Perovskite devices with normal device structure need a high temperature sintering process of ~500 °C [2,20–23] for the compact $TiO_2$ (titanium oxide) layer as electron transport layer (ETL). This high temperature is one of the fundamental barriers to mass production of perovskite solar cell since it does not satisfy the requirement of 100–150 °C [24] temperature range for flexible substrates with roll-to-roll process [25]. Although the inverted device structure having PEDOT: PSS [Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)] HTL underlying the perovskite layer is completely low temperature processed [26,27], due to the hygroscopic nature of PEDOT: PSS [28], the ambient device stability is expected to be lower with such device structure. Besides, the inverted structure includes PCBM ([6,6]-Phenyl $C_{61}$ butyric acid methyl ester) ETL on top of perovskite layer and in a recent study [29], it has been found that inverted structure has lower stability due to chemisorption of water and oxygen in PCBM layer. As such, replacing the high temperature process of $TiO_2$ ETL with a low temperature alternative in a normal device structure can pave the way for large scale production of stable perovskite solar cells. As such, a number of research works have already been carried out to find the suitable substitute for Titania ETL. The studies used either ZnO nanorod [30–32] or ZnO nanocrystal [33] as alternative ETL to Titania. ZnO is a wide band gap semiconductor that can achieve high structural quality even at low temperature [34,35]. Along with the large bandgap, ZnO has a high exciton binding energy of 60 meV that contributes to its excellent chemical and thermal stability [36]. ZnO has a favorable conduction band energy level of 4.4 eV [37] which facilitates electron extraction from LUMO level (3.9 eV) [38] of methyl ammonium iodide perovskite. Similarly, the valence band energy level (7.6 eV) [37] of ZnO is at a conforming level to block holes from HOMO (highest occupied molecular orbital level) (5.4 eV) of perovskite [38]. Thus, ZnO can simultaneously play the role of ETL and HBL in a perovskite solar cell that makes it a befitting n-type conducting layer. The outstanding optical transparency of ZnO in the visible light spectrum [39] also makes it a worthy contender to be ETL in a normal device structured Perovskite solar cell. ZnO has nearly identical electrical affinity (4.2 eV) as $TiO_2$ [17], but has higher conductivity (~0.85 mS/cm) compared to Titania (~0.4mS/cm) [40,41]. Besides, the electron mobility in ZnO (~200–300 $cm^2 V^{-1} s^{-1}$) is several orders of higher than $TiO_2$ (~0.1–4 $cm^2 V^{-1} s^{-1}$) [42]. All these optoelectronic properties of ZnO make them preferable alternative to $TiO_2$ as ETL in Perovskite solar devices. But most of the reported ZnO ETL perovskite devices [30–33] involve around ~400 $^0$C annealing temperature for ZnO nanostructures. As a result, although the titania layer was replaced with ZnO nanostructures, the high temperature processing is still a concern. Of late, Timothy et al. [16] have reported ZnO nanoparticle processing which involves temperature lower than 70 °C. Pauport'e et al. [17,43] have used electrodeposition of ZnO ETL at around 60 °C for perovskite devices. Seok et al. [44] have implemented highly dispersed Zinc stannate ($Zn_2SnO_4$) nanoparticles as ETL in a perovskite photovoltaic device at less than 100 °C temperature. Despite being promising endeavors in terms of low temperature processing, these processes [16,17,43,45] comprise of time consuming precipitation, dilution and washing processes coupled with a long reaction time or the need for sophisticated handling and delicate electrochemical machinery. A simple, low temperature processing technique devoid of these nanoparticle synthesis complexities, thus, can be a potential candidate for ETL in mass production of perovskite solar devices. Likewise, low temperature, easily processable sol-gel processed ZnO bids fair to be a promising contender for its nanoparticle counterparts. There has been only one study [46] on sol-gel ZnO as ETL for perovskite device. Sol-gel ZnO process enabled them to drop down the ETL processing temperature to 290 °C [46] from a higher temperature of 500 °C normally used with $TiO_2$ compact layer or scaffolding structure. However, the process temperature (290 °C) in this work [46] still does not satisfy the constraint of 100–150 °C [24] temperature range for flexible substrates with roll-to-roll process.

In this work, we have reported a simple, low temperature ( < 150 °C) processed sol-gel ZnO thin film as ETL for methyl ammonium lead triiodide perovskite solar device. An optimized thickness has been found out for the sol-gel ZnO ETL to be applied in highly reproducible perovskite photovoltaic devices. Two step dipping technique [22] has been chosen to form the perovskite layer over the sol-gel ZnO ETL in a normal device structure on ITO/glass substrate. Two step dipping technique has been successfully implemented previously for perovskite formation on flexible PET (Polyethylene terephthalate) substrates as well [16,24]. Thus the two step dip-coating technique in our work can be easily scalable to roll-to-roll process [47] for mass production of perovskite solar devices. In our work, we have also ensured the complete conversion of $PbI_2$ to $CH_3NH_3PbI_3$ in the dipping process by the incorporation [48] of 4-*tert*-Butylpyridine (4-TBP) which improves the device performance by enhancing the Fill Factor of the device. Doped P3HT [49] has been implemented as a cheap and readily available hole transport layer (HTL) instead of commonly used Spiro-OMeTAD which is quite expensive. Combining all these thin film layers, we have reported a low temperature processed device structure, which, to the best of our knowledge, has never been reported so far with a $CH_3NH_3PbI_3$ Perovskite device. Another special feature of our work lies in the in-depth study conducted by means of Electrochemical Impedance Spectroscopy (EIS) that enables us to dig into the physical phenomena like charge transport, carrier recombination, interfacial charge transfer etc. taking place inside the device those directly affect the device performance. A number of research studies have already been conducted for perovskite solar cell with EIS, focusing on mesoscopic [50] or thin-film structure with $TiO_2$ compact layer [45,51,52] or $TiO_2$ and ZnO nanostructures [18,52]. In this work, we have used EIS study to extract the perovskite/solgel ZnO interface contact resistance, device recombination resistance, carrier density, flat-band potential and depletion width at zero bias using the fitted data from Nyquist plot and Mott-Schottky curve. Interpreting these basic device parameters, we have explored how the trap states present in the low temperature processed sol-gel ZnO ETL affect charge extraction and thus the overall device performance in a perovskite device. Using the EIS study, we have also explained how the optimized sol-gel ZnO ETL in our work suppresses the trap states for enhanced device performance. Thus the optimization process of low temperature sol-gel ZnO presented in our work can be very useful for the future endeavors regarding low temperature ETL processed perovskite solar cells.

Download English Version:

https://daneshyari.com/en/article/6457493

Download Persian Version:

https://daneshyari.com/article/6457493

Daneshyari.com