



Improved performance of sol–gel ZnO-based perovskite solar cells via TiCl₄ interfacial modification

Yohan Ko^a, Yechan Kim^a, Seong Young Kong^b, Sakeerali Cheeran Kunnan^{a,b}, Yongseok Jun^{a,*}

^a Dept. of Energy Engineering, & Dept. of Materials Chemistry and Engineering, Konkuk University, 120 Neungdongro Gwangjingu, Seoul 05029, Republic of Korea

^b Seoul center, Korea Basic Science Institute, Anam-dong 5-ga, Seongbuk-gu, Seoul 136-713, Republic of Korea

ARTICLE INFO

Keywords:

Sol–gel ZnO
Perovskite solar cell
TiCl₄
Interfacial modification

ABSTRACT

CH₃NH₃PbI₃ perovskite materials deposited on ZnO electron transport layers (ETLs) undergo decomposition during annealing in N₂ atmosphere. We found that this decomposition can be retarded by restricting sublimation. Moreover, the decomposition upon thermal annealing is highly suppressed by TiCl₄ treatment of the ZnO ETLs. Finally, we present a facile method for prolonged annealing in sol–gel ZnO-based perovskite solar cells, which exhibit a power conversion efficiency of 16.5% at a small area of 0.098 cm² and 15.1% at a large area of 1 cm² (active area) under AM 1.5 simulated sunlight illumination. This study shows that TiCl₄ hydrolysis is an effective surface treatment for ZnO ETLs to be used in low-temperature and efficient sol–gel ZnO-based perovskite solar cells.

1. Introduction

Hybrid organic–inorganic perovskite solar cells (PSCs) have drawn tremendous interest because of their great potential as a game changer in the photovoltaic market. The power conversion efficiencies (PCEs) of PSCs have exceeded 20% within six years after their first report [1–3]. The superior performance of PSCs over other solar cell technologies is due to their outstanding photoelectric properties, such as remarkable electron-hole diffusion length, low exciton binding energy, and high absorption coefficient [4–8].

The original concept of regular PSCs (n-i-p) evolved from solid-state dye sensitized solar cells (ss-DSSCs), in which n-type metal oxides were used as the photoanode and solid organic charge transport materials were used as the hole transport layer [2]. Manipulation of the mesoporous TiO₂ layers in PSCs affords effective thin photoactive layers. PSCs with a mesoporous TiO₂ layer exhibit outstanding efficiency. However, the high temperature required for sintering the mesoporous layer hinders low-temperature processes [9,10]. Finding ambipolar characteristics in perovskite materials has facilitated the development of a simple planar heterojunction configuration with the obliterated nanostructure [11,12]. Exploiting a planar structure for PSCs has the advantages of reducing production costs, forming polycrystalline perovskite via vacuuming or spray process for large dimensions, and feasibility of utilizing various n-type organic or inorganic materials for electron transport layers (ETLs) [13–16]. In addition, the planar structure can be applied in an inverted device configuration (p-i-n), in

which ETLs are used on the top [17–19]. The p-i-n structure originated from organic photovoltaics (OPVs); thus, the charge selective materials used in the OPVs are extensively inherited in planar heterojunction PSCs [19]. The planar heterojunction device configuration that allows for low-temperature processing of PSCs has promoted the investigation of various metal oxides as ETLs, such as ZnO, SnO₂, WO_x, TiO_x, and Zn₂SO₄ [20–23]. Among these, the ZnO semiconductor is particularly advantageous for solar cell applications because of its direct wide band gap, high transparency, and considerably higher electron mobility than TiO₂. Moreover, the synthetic route to ZnO is a simple process with a significantly low annealing temperature and a short annealing time. These factors facilitate the widespread application of ZnO to thermally unstable flexible substrates and scalable processing [21,24,25].

In the inverted structure (p-i-n), the use of ZnO as the top ETL has been proven to significantly improve device performance and stability [19]. However, using ZnO as an ETL in regular PSCs (n-i-p) has limitations because the CH₃NH₃PbI₃ materials deposited on ZnO easily undergo decomposition during the thermal-annealing treatment for the perovskite film formation [25–28]. Accordingly, the PSCs employing ZnO as an ETL are exploited for either a short annealing time or a non-thermal annealing treatment. Such periphrastic heat treatment has a negative effect on the perovskite crystal quality, morphologies, and sizes, which play a pivotal role not only in determining the PCEs but also in sustaining device stability [21,29,30]. Previous investigations demonstrated that doping and/or alteration of ZnO ETLs can mitigate the thermal decomposition of CH₃NH₃PbI₃ on ZnO, thereby leading to

* Corresponding author.

E-mail address: yjun@konkuk.ac.kr (Y. Jun).

better device performance than that in the case of pure ZnO ETL-based PSCs. Even so, the fundamental issue of the thermal instability of perovskite films on ZnO during the annealing process still remains challenging [31–34]. The decomposition is the result of deprotonation at the ZnO/perovskite interface accompanying sublimation accelerated by the presence of hydroxyl and carboxyl groups at the interfaces [27,28,35].

The present study investigates the decomposition of perovskite films deposited on ZnO ETLs and demonstrates that the decomposition mechanism is affected by sublimation of the perovskite materials (removal of organic species). We further represent a reliable method for suppressing the thermal decomposition of the perovskite materials on ZnO. The surfaces of the ZnO ETLs were treated by TiCl_4 hydrolysis under mild condition which is suitable for low-temperature processing. Consequently, this simple treatment prevents the perovskite materials from decomposing even during prolonged thermal annealing (105 °C for 75 min). The sol–gel ZnO-based perovskite solar cell showed a PCE of 16.5%, and the results pave the way for surface treatment to maximize the use of ZnO in PSCs.

2. Experimental section

2.1. ETL preparation

The ZnO sol–gel precursors comprised 1.64 g zinc acetate dehydrate, 10 mL 2-methoxyethanol, and 0.5 mL ethanolamine, and stirred at 60 °C overnight before use. For the ZnO ETL fabrication, the ZnO sol–gel precursors were spin-coated onto O_2 plasma-treated substrates at 3500 rpm for 30 s, followed by annealing at 150 °C for 10 min. The TiCl_4 treatment was performed by immersing the ZnO ETLs into a 40 mM TiCl_4 solution at 70 °C for 30 min and drying them at 130 °C in air for 30 min. Subsequently, PC₆₁BM ([6,6]-phenyl-c61-butyric acid methyl ester) solutions (10 mg/mL in chlorobenzene) were spin-coated on ZnO ETLs at 2500 rpm for 30 s and dried at 90 °C for 10 min.

2.2. Film formation

The sequential deposition method was applied to fabricate a $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film onto the substrates. After this, 462 mg of PbI_2 was dissolved in 1 mL DMF (1 M) and stirred at 60 °C overnight. The PbI_2 solution was spin-coated at 3500 rpm for 30 s and dried at 70 °C. After drying, the PbI_2 -deposited ZnO films were immersed in MAI ($\text{CH}_3\text{NH}_3\text{I}$) solution (10 mg/mL in isopropanol) for 6 min. After the perovskite film formation, all the samples were heated at 100 °C in a glove box for different times for experimental purpose.

2.3. Device fabrication

The ETLs fabricated onto FTO (TEC 8) were used to fabricate the perovskite solar cells. As previously reported, the perovskite layer was processed via a $\text{PbI}_{2-x}\text{Cl}_x$ seed layer. PbI_2 (99.999%, Alfa Aesar) and PbCl_2 (99.999%, Alfa Aesar) were dissolved in *N,N*-dimethylformamide (DMF) and stirred at 60 °C. The molar ratio of the precursor solution ($\text{PbI}_2:\text{PbCl}_2$) was 1:0.5 (1 M). The PbI_2 and PbCl_2 mixture was spin-coated at 5000 rpm for 30 s in a glove box, followed by drying on a hotplate at 70 °C. For the perovskite material conversion, 120 μL of MAI solution (40 mg/mL) was loaded at 0 rpm for 35 s, spin-coated at 3500 rpm for 20 s, and isothermally annealed at 105 °C for 75 min under ambient conditions. The films were transferred into the glove box in a N_2 atmosphere after annealing. The hole transporting material (HTM) was then spin-coated on the $\text{MAPbI}_{3-x}\text{Cl}_x/\text{ETL}/\text{FTO}$ film at 4000 rpm for 30 s. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (MS solutions) (PTAA) solution (20 mg/mL in toluene) was used as the HTM, including 15 μL Li-TFSI (Li-bis(trifluoro-2-methanesulfonyl)imide)/acetonitrile (170 mg/mL) and 15 μL tBP (*tert*-butylpyridine). Finally, Au (70 nm) was deposited via thermal evaporation.

2.4. Characterization

The absorption spectrum of each sample was obtained using a Cary 5000 (Agilent) instrument. The crystalline structure of the samples was characterized by X-ray diffraction (XRD, Rigaku, d_{max} 2500 V, Cu $\text{K}\alpha$). The sample morphologies were observed by a field-emission scanning electron microscope (FE-SEM, FEI Quanta 250 FEG). Fourier transform infrared spectroscopy (FTIR, JASCO) analysis was performed by preparing a KBr pellet with the ZnO particles (100:1 wt) scraped from the corresponding films. Thermogravimetry analysis was conducted using Q600 (TA instruments) at a heating rate of 5 °C/min under a constant N_2 flow (100 mL/min). The *J*–*V* curves of the perovskite solar cells were obtained using an electrochemical station (VSP 200, Bio-Logic) under 100 mW/cm² AM 1.5 G light (Sun 3000 class AAA, ABET Technology) with a metal mask of area (active area) 0.098 and 1 cm². The external quantum efficiency (EQE) was measured by a combination of an IVIUM potentiostat (IVIUM) and a monochromator (DONGWOO OPTRON co., Ltd.) under illumination by an ABET 150 W Xenon lamp (ABET Technology). Electrochemical impedance spectroscopy was performed with the IVIUM. The obtained Nyquist plots were fitted using Zview software. EQE data acquisition was performed in DC mode.

3. Results and discussion

3.1. Perovskite decomposition on a ZnO layer

We fabricated ZnO ETLs via a sol–gel process using zinc acetate, 2-methoxyethanol, and ethanolamine, as explained in the experimental section [36]. This is a highly cost-effective method of manufacturing ETLs for commercialization and allowing versatile application to flexible substrates that need low-temperature processing [21]. We evaluated the UV spectra for the thermal stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) deposited on ZnO by comparing the perovskite films prepared on a ZnO layer with those prepared on a glass substrate. The degradation of the perovskite films on ZnO was easily confirmed by the changes in their absorption spectra (Fig. 1a). The absorption edge (760 nm) of the perovskite film disappeared, and a shoulder peak appeared at 520 nm. The peak at 520 nm was closely related to the PbI_2 phase, which indicated degradation of the perovskite films. In contrast, the perovskite film deposited on glass preserved its onset point. The UV spectra implied that perovskite decomposition was facilitated on the ZnO films, as reported in a previous study [27,28]. X-ray diffraction (XRD) analysis was conducted on the samples to confirm the structure of the perovskite films after annealing. Fig. 1b shows that the perovskite films prepared on glass exhibited a strong (110) diffraction peak of the MAPbI_3 , regardless of the annealing time. Another set of perovskite films on the ZnO layer exhibited changes in the (110) diffraction peak depending on the thermal treatment. The peak for the (110) diffraction of the MAPbI_3 disappeared and a strong PbI_2 peak was seen after the heating treatment [37]. The XRD data well corroborated the absorption change in the UV spectra.

Comparative studies were performed to further investigate the origin of the MAPbI_3 film decomposition on ZnO. First, we prepared perovskite films with different layers. One was a pristine MAPbI_3 film on ZnO, whereas the other was covered with polymethylmethacrylate (PMMA). Upon heat treatment at 100 °C for 20 min, the sample covered with PMMA preserved its dark brown color, whereas the other showed a color change from dark brown to yellow. We then conducted energy-dispersive X-ray (EDX) analyses on the samples to observe the elemental composition of the perovskite films on ZnO. Fig. 2c presents the atomic percentage determined from the EDX profiles. The sample without the PMMA blocking layer exhibited a significantly reduced atomic ratio of 1:2.20 (Pb:I) as compared to the others. This result clearly suggested that the release of chemical species from the perovskite film is closely linked to the decomposition mechanism on a ZnO layer. That is, by adopting a closed annealing system, the perovskite

Download English Version:

<https://daneshyari.com/en/article/6534089>

Download Persian Version:

<https://daneshyari.com/article/6534089>

[Daneshyari.com](https://daneshyari.com)