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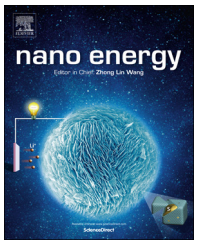

RAPID COMMUNICATION

Annealing-free efficient vacuum-deposited planar perovskite solar cells with evaporated fullerenes as electron-selective layers

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Abstract
We present efficient metal oxide-free and annealing-free planar perovskite solar cells with the regular cell structure using vacuum-deposited fullerenes C_{60} and C_{70} as the electron-selective layers and vacuum-processed perovskites as the light absorbers. The devices with an ultrathin C_{60} layer (5.5 nm) yielded an average power conversion efficiency of 14.3% and a maximum efficiency of 15.7%. The best-performing cell produced a steady-state efficiency of 14.6%. The high performance is attributed to the efficient blocking of holes and extraction of electrons by C_{60} due to a favorable energy level alignment between the C_{60} and the fluorine-doped tin oxide electrodes. With the realization of efficient cells, the annealing-free vacuum deposition of perovskite absorbers and C_{60} or C_{70} electron-selective layers and intermediate layers demonstrates its power for fabricating all-perovskite tandem solar cells.

Introduction

Organic–inorganic lead halide perovskite based solar cells have been extensively investigated over the past few years due to the excellent photovoltaic properties of perovskites such as high optical absorption coefficient, long charge

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carrier lifetime, high carrier mobility, and band gap tenability [1-5]. Moreover, perovskite solar cells can be made by low cost solution process at low temperature, enabling roll-to-roll manufacturing using flexible substrates. Perovskite-based solar cells have been considered recently as the most promising photovoltaic technology [6,7], with their power conversion efficiencies (PCEs) rapidly rising from 3.8% to a certified 20.1% [8-15].

The high efficiencies of perovskite solar cells are largely due to the high open circuit voltages (V_{oc}s), which are attributed to the long carrier lifetime [1,2]. It has been shown that the dominant defects do not create deep energy levels in the band gaps of perovskite absorbers [3,4], distinctively different from that seen in the common inorganic solar cell materials. The V_{oc} deficit, defined by $E_g/q - V_{oc}$, of the record perovskite solar cells, is as small as 0.42 V, approaching that of the best single crystal GaAs thin film solar cell [12]. Therefore, the V_{oc} of the high-efficiency perovskite solar cells has nearly reached its theoretical value. Unlike V_{oc}, the short-circuit current density (J_{sc}) of the high-performing perovskite solar cells still has considerable room for improvement. Typically, high-efficiency perovskite solar cells use approximately 350–450 nm thick absorbers, which are not sufficiently thick to fully absorb the incident light. Unfortunately, increasing the thickness of the perovskite absorbers could only lead to lower efficiencies, indicating that intrinsic electronic property issues exist for the low temperature processed polycrystalline perovskite thin films. Fabricating tandem cells is a legitimate option for further improving the overall device efficiency and has recently attracted great attention. So far, most perovskite tandem cells reported consist of perovskite solar cells as the top subcells and inorganic solar cells such as Si and Cu(In,Ga)Se_2 cells as the bottom subcells [16-18]. Efficient all-perovskite tandem cells, a preferred approach, have not been reported yet. Part of the challenge stems from depositing intermediate layers without damaging the existing underlying subcells.

The planar cell architecture is preferred for fabricating tandem cells. A typical planar cell consists of a solution-processed or vacuum-processed perovskite absorber layer sandwiched between an electron-selective layer (ESL) and a hole-selective layer (HSL). To avoid any damage to the existing subcell, the ESL or HSL and the perovskite absorber layer should be deposited preferably by vacuum processes and without additional annealing. Furthermore, compared to solution processes, vacuum processes are expected to result in thin films with better uniformity, smoother surfaces, complete coverage, and more accurately controlled thicknesses. However, to date efficient annealing-free vacuum-processed perovskite solar cells have not been reported. The current high-performing perovskite cells generally use either high-temperature processed metal oxide layers such as TiO_2 [19,20], solution-processed low temperature materials such as ZnO [21], SnO_2 [22], and Cs_2CO_3 [23], or organic materials such as [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{60}BM$) and C_{60} as the ESL [24]. The high temperature and/or solution processes could potentially either thermally decompose the existing perovskites or dissolve the underlying subcells and therefore would be incapable of producing high-efficiency tandem cells.

Vacuum-processed perovskite-based solar cells have been demonstrated by several groups, and the devices have exhibited promising efficiencies in both regular and inverted architectures [25-31]. The first successful vapor-deposited perovskite solar cells with 15% efficiency were presented in a regular structure and used high temperature processed compact TiO_2 as the ESL [25]. Most high-efficiency vacuum-processed perovskite based solar cells used the inverted structure [26,27,31], among which the best reported cells with the highest PCE of 16.5% employed solution-processed poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and various polymers as the HSLs [28]. Other groups have also reported efficient cells using vacuum-processed perovskite absorbers [26,27,30,31]. Likewise, these cells used either high temperature processed compact TiO_2 or solution-processed HSL/ESLs.

Here, we demonstrate efficient annealing-free vacuum-processed perovskite solar cells using thermal evaporation of both the fullerene C_{60} as the ESL and the perovskite as the light absorber. We used fullerene C_{60}, because it can function as an ESL [32] and can also be thermally evaporated [33,34]. Thermally evaporated C_{60} films exhibit good electronic properties without post-deposition annealing [35]. The devices with an ultrathin C_{60} layer (5.5 nm) showed an average PCE of 14.3% and a maximum PCE of 15.7%. The best-performing cell produced a steady-state efficiency of 14.6%. Our detailed device characterization revealed that the high performance of our annealing-free vacuum-processed perovskite cells resulted from the use of an ultrathin C_{60} layer which effectively transfers the electrons and blocks the holes due to the favorable energy level alignment between C_{60} and fluorine-doped tin oxide (FTO) electrodes. With the realization of efficient cells, the annealing-free vacuum deposition of perovskite absorbers and C_{60} or C_{70} electron-selective layers and intermediate layers demonstrates its power for fabricating all-perovskite tandem solar cells.

Experimental section

Perovskite synthesis

The deposition of the perovskite films was carried out using a thermal evaporator integrated with a glove box. CH_3NH_3I and PbI_2 were loaded into their individual crucibles. Two quartz crystal microbalances are placed close to each crucible, monitoring the rate of each evaporation source. In our approach, it is difficult to calibrate and monitor the CH_3NH_3I rate; therefore, it was preferable to monitor the CH_3NH_3I vapor phase pressure instead. After the crucibles are filled with CH_3NH_3I and PbI_2, the chamber is evacuated to a base pressure of 3×10^{-7} Torr. The PbI_2 crucible is heated until its deposition rate reaches our target value. Meanwhile, the CH_3NH_3I crucible is heated until the vacuum pressure is 5×10^{-5} Torr. For an optimal deposition condition of the perovskite film, the CH_3NH_3I vapor pressure is kept at 5×10^{-5} Torr by controlling the temperature of CH_3NH_3I crucible and the deposition rate of PbI_2 was kept at 0.75 Å/s, a procedure which achieves the best crystalline perovskite films. The samples for TRPL measurement were coated by poly(methyl methacrylate) (PMMA).

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