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Dual-step thermal engineering technique: A new approach for fabrication of efficient $CH_3NH_3PbI_3$-based perovskite solar cell in open air condition

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ABSTRACT

Fabrication of most-promising $CH_3NH_3PbI_3$ based perovskite solar cell in ambient condition is excessively essential to industrialize this revolutionary development. In this research work, an efficient, facile and economical technique has been developed to fabricate $CH_3NH_3PbI_3$ perovskite solar cell in ambient condition which is termed as dual-step thermal engineering technique. In this dual-step thermal engineering technique, the perovskite precursor solution has been spin coated over a mildly hot substrate which was heated at 60 ^{0}C for 10 min and followed by annealing at 80 °C for 30 min immediately after spin coating and compared with the perovskite film fabricated by conventional annealing in which the film was heated once at 120 °C for 60 min after spin coating. The comparative study shows that the newly developed dual-step thermal engineering technique is highly efficient and forms smooth, dense, well-crystallize, almost pinhole free perovskite solar cell at open air condition and exhibit remarkable enhanced efficiency over conventional annealing. This is because the precursor solution spontaneously started to develop a perovskite layer over the substrate during spin coating similarly as epitaxial-growth by utilizing the kinetic energy of the hot substrate and it serves as foundation layer for the high quality device.

1. Introduction

Emerging $CH_3NH_3PbI_3$-based perovskite renewable energy harvesting technology has snatched attention due to its capability to encounter the rapidly growing global energy demand. Due to raw materials availability, ease manufacturing process, attractive semiconducting and optoelectronic properties [1–6], long-range ambipolar transport characteristics [7], high dielectric constants, low exciton binding energies [8,9], intrinsic ferroelectric polarizations [10,11] and spin-dependent responses [12,13], the perovskite solar cell has strengthened the aspect as future energy harvesting technology. Numerous researches are dedicatedly going on globally to find out a suitable manufacturing method to commercialize the perovskite photovoltaic device. As outcomes, dozens of fabrications method has already been developed like one-step spin-coating technique [14], vapor-assisted solution procedure [15], two-step spin-coating method [16], different annealing treatments [17,18], solvent-solvent extraction mechanism [19] and sequential deposition method [20]. Majority of research groups have followed different fabrication techniques but, in most cases, the basic similarities, i.e., uses of nitrogen environment, in device fabrication is present to fend off air-moisture and simultaneously very few have reported device formulation techniques at ambient condition [18,21]. Recent literature shows that an attractive, efficient and effective fabrication procedure is necessary to accelerate the industrialization of perovskite solar cell and hence the simple heterojunction structure and annealing at open air atmosphere are the best combination to promote bulk production of perovskite photovoltaic device. But factor like the instability of perovskite material ($CH_3NH_3PbI_3$), due to air moisture affects can damage the device quality. Fabrication of perovskite solar cell with appropriate annealing or thermal energy treatment could be an effective way to suppress the obstructing parameter behind perovskite solar cell fabrication at open air condition. Few attractive planar heterojunction perovskite solar cell and its rebuilding improvement mechanism has already been reported [22–24]. Highly hygroscopic methylammonium cation $[(CH_3NH_2)^+]$ can enhances the device efficiency by enlarging $CH_3NH_3PbI_3$ crystal besides its detrimental and degradation tendency to $CH_3NH_3PbI_3$ perovskite solar cell by absorbing moisture during air-annealing [22]. So, the fabrication of $CH_3NH_3PbI_3$ perovskite solar cells in presence of air could be beneficial besides its degradation hindrance. Therefore, an effective and efficient fabrication technique is urgently essential to fabricate the $CH_3NH_3PbI_3$ perovskite solar cell in open atmosphere which can control the performance, film's morphology, proper phase formation. Besides the pure perovskite materials, the application of the

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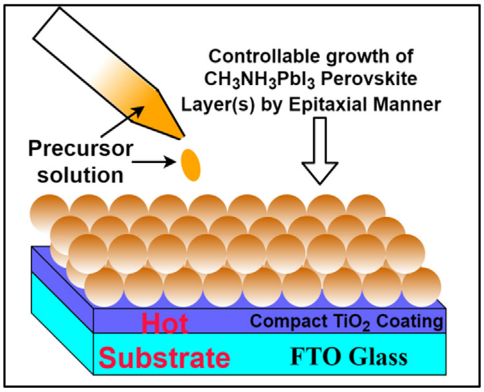

Fig. 1. Epitaxial growth of $CH_3NH_3PbI_3$ perovskite thin layer over hot substrate during spin coating.

recent advancement of the low dimensional photoelectronic materials could boost the commercialization of perovskite solar cells in near future [25–35].

In this research work, a high efficient, dense, well-crystallize, almost pin-hole free, smooth perovskite solar cell ($CH_3NH_3PbI_3$) has been fabricated using one-step spin-coating approach with adopting a newly derived dual-step thermal engineering technique at ambient condition unlike at nitrogen (N_2) atmosphere. The $CH_3NH_3PbI_3$ thin film spun up on the hot substrate and a subsequent heat treatment has been performed after spin coating in this newly developed dual-step thermal engineering approach. This attractive and beneficial technique works efficiently and converts perovskite precursor solution into $CH_3NH_3PbI_3$ thin film utilizing kinetic energy used during spin coating. Epitaxial growth starts instantly during spin coating and few foundation layers of perovskite materials ($CH_3NH_3PbI_3$) developed which drives the high-quality, smooth and dense perovskite thin film ultimately. The epitaxial growth and the formation of baseline $CH_3NH_3PbI_3$ perovskite materials are portrayed in Fig. 1. The figure is describing the formation of epitaxial growth of $CH_3NH_3PbI_3$ film over hot substrate during spin coating which is the most fundamental and powerful intrinsic features of this dual-step thermal engineering technique that builds the foundation of a high efficient solar device at air atmosphere.

2. Experimental section

2.1. Preparation of $CH_3NH_3PbI_3$ precursor solution

0.3 mol (40 mL) hydroiodic acid (57 wt% in water, 99.95% pure, Sigma Aldrich) and equimolar methylamine (38 mL) (33 wt% in absolute ethanol, ≥ 99.0% pure, Sigma Aldrich) were mixed in 100 mL ethanol (99.9% pure, Changshu Hongsheng Fine Chemical) with continuous stirring at 1200 rpm in an ice bath for 2 h followed by evaporated at 60 °C with continuous stirring at 1200 rpm until it completely forms white precipitation of CH_3NH_3I. The crystallite CH_3NH_3I was washed properly using diethyl ether [(C_2H_5)O] (≥ 99.7% pure, Merck Specialities Pvt. Ltd.) with continuous stirring at 1200 rpm for 45 min and repeated same the step for three times and finally dried at 70 °C in an hot air oven (Laboratory Hot Air Oven, B.C Chatterjee & Co.) for overnight. An equimolar amount (1:1 mol ratio) of methylammonium iodide (CH_3NH_3I) and commercially bought lead (II) iodide powder, PbI_2 (99% pure, Sigma Aldrich) were mixed in organic dimethylformamide (DMF) solvent (99.8% pure, Merck Specialities Pvt. Ltd.) and stirred for 10 h at room temperature to obtain reddish-brown methylamine lead iodide ($CH_3NH_3PbI_3$) precursor solution followed by filtered with Whatman filter paper (0.45 µm pore PVDF syringe filter).

2.2. Device fabrication

Fabrication of a complete $CH_3NH_3PbI_3$ based solar cell device involves combination of several steps together. Concentrate HCl (≥ 98% pure, Merck Specialities Pvt. Ltd.) and Zn powder (≥ 93% pure, Merck Specialities Pvt. Ltd.) were used to etched fluorine doped tin oxide (FTO) glasses (Pilkington, 7 Ω per sq) followed by cleaning with ultrasonication using normal water, deionized water, detergent (2% Hellmanex) in water, acetone (99.5% pure, Sigma Aldrich) and ethanol (99.5% pure, Merck Specialities Pvt. Ltd.) for 10 min each. The patterned FTO glasses were dried in oven drier for 30 min. Titanium isopropoxide (TTIP) (98% purity, Sigma Aldrich) was diluted in ethanol and spun up at 3000 rpm for 30 s to deposit a thin, compact, transparent, electron transporting layer (ETL) of TiO_2 on FTO glasses. This TiO_2 layer was sintered for 30 min at 110 °C and a subsequently heated at 450 °C for 45 min in a muffle furnace. After that TiO_2 coated FTO glasses were kept overnight to cool down to normal room temperature (27 °C) to use it further. In our newly developed dual-step annealing engineering approach, a TiO_2 coated FTO glass substrate was heated at 60 °C for 10 min on oven and the reddish-brown $CH_3NH_3PbI_3$ precursor solution was spin coated immediately on top of that hot substrate for 30 s at 3000 rpm followed by annealing at 80 °C for 30 min under normal atmospheric condition. The use of heat energy before spin coating is the best innovative part in our newly developed dual-step annealing engineering technique. Again $CH_3NH_3PbI_3$ film was spin coated using reddish-brown $CH_3NH_3PbI_3$ precursor solution at 3000 rpm for 45 s on top of normal TiO_2 coated FTO substrate followed by annealed at 120 °C for 60 min under normal atmospheric condition. Finally, copper thiocyanate (CuSCN) (99% pure, Sigma Aldrich) layer was deposited as hole transporting material (HTM) on top of both $CH_3NH_3PbI_3$ perovskite devices accordingly followed by recent literature [21,36]. Fig. 2 represents the fabricated devices structure with electrical and photo response properties of FTO/TiO_2/$CH_3NH_3PbI_3$/CuSCN/Ag based solar cells using dual step annealing and conventional annealing engineering.

2.3. Characterization

Field Emission Scanning Electron Microscopy (JEOL JSM-7600F) and Scanning Electron Microscopy (Zeiss EVO MA10) were performed to evaluate the morphologies of the $CH_3NH_3PbI_3$ perovskite films. To understand the presence of defect densities and disorder, UV/Vis Spectrophotometer (Hitachi spectrophotometer U-4100, range: 240–2600 nm) was used to execute the UV–vis absorption spectroscopies, light absorption tendency and investigate the Urbach energy (E_U). The crystallinity and phase formation of the perovskite films were recognized by an X-ray diffraction (XRD) characterizing tool (Philips Analytical PW 3050/60X'Pert Pro) equipped with Cu Kα X-ray (1.540 Å) source. Finally the photovoltaic performances of the $CH_3NH_3PbI_3$ based photovoltaic devices were carried out by means of current-voltage characterization and incident photon-to-current conversion efficiency (IPCE). The current-voltage characterization was carried out through 2450 Keithley programmable source meter and Zolix (HPS-300XA) solar simulator under AM 1.5 G condition (1 Sun illumination, 100 mW cm^{-2}) and the IPCE was measured under a commercial setup (IPCE measurement system, PEC- S20, Peccell Technologies, Japan).

3. Result and discussion

3.1. X-ray diffraction (XRD) studies

XRD pattern of the $CH_3NH_3PbI_3$ perovskite film, Fig. 3**(a-c)**, fabricated by different annealing techniques ensure the desire $CH_3NH_3PbI_3$ perovskite formation by diffraction peaks originate at 14.1°, 28.4°, 43.2°, and 58.9° which are refers to the (110), (220), (330), and (440)