

Supporting Information

Atomic Layer Deposition of SnO₂ Electron-Transporting Layer for Planar Perovskite Solar Cells with a Power Conversion Efficiency of 18.3 %

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Experimental

Materials

Methylammonium iodide (CH₃NH₃I) was purchased from Dyesol Ltd. (Queanbeyan, Australia). Tetrakis(dimethylamino) tin(IV) (TDMASn) was purchased from iChems Co., Ltd. (Gyeonggi-do, Korea). Tetrakis(dimethylamino) titanium(IV) (TDMAT) and trimethylaluminum (TMA) were purchased from EGChem Co., Ltd. (Daejeon, Korea). Lead(II) iodide (PbI₂, 99.99%) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI), 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) was purchased from Ossila Ltd. (Sheffield, UK). Hellmanex III, anhydrous dimethyl formamide (DMF, 99.9%), anhydrous dimethyl sulfoxide (DMSO, 99.9%), toluene (99.8%), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, 99.95%) and 4-tert-butylpyridine (tBP, 96%) were purchased from Sigma-Aldrich Co., Ltd. (St. Louis, MO, USA). All other chemicals were purchased from Sigma-Aldrich or Alfa Aesar unless otherwise specified.

Electron transporting layer preparation

Fluorine-doped tin oxide (FTO) glasses (Pilkington, TEC 8) with dimensions of 22 × 21 mm were patterned (etched area: 4 × 22 mm) by wet etching with 4 M HCl. Substrates were rinsed by ultrasonication in detergent (5 wt% of Hellmanex III in deionized (DI) water), deionized water, acetone and ethanol in sequence for 10 min, respectively. After drying in N₂ blow gas, they were treated in a UV/Ozone cleaner for a 10 min.

The TDMASn precursor which was kept at 45 °C and O₃ as the oxidizer were used for deposition of SnO₂ by the hand-made ALD system at the temperature of 100 °C. The base pressure was maintained at 3 × 10⁻² torr with an additional flow of Ar 20 sccm under working conditions. The growth rate for the SnO₂ were 0.12 nm per cycle. ALD-SnO₂ films deposited onto FTO were heated further in the furnace at ambient condition at different temperatures of 180 °C and 300 °C for 1h.

The TDMAT precursor, which was kept at 50 °C, and H₂O as the oxidizer were used for deposition of TiO₂ by the ALD system (NCD Lucida, Daejeon, Korea, flow-type reactor) at the temperature of 165 °C. The base pressure was maintained at 5 × 10⁻² torr with an additional flow of Ar 50 sccm under working conditions. The growth rate for TiO₂ was 0.05 nm per cycle. ALD-TiO₂ films deposited onto FTO were heated further in the furnace at ambient condition at 400 °C for 1 h.

The TMA precursor, which was kept at room temperature, and H₂O as the oxidizer were used for deposition of Al₂O₃ by the ALD system (NCD Lucida, Daejeon, Korea, flow-type reactor) at the temperature of 200 °C. The base pressure was maintained at 5 × 10⁻² torr with an additional flow of Ar 50 sccm under working conditions. The growth rate for Al₂O₃ was 0.1nm per cycle.

Devices fabrication

SnO₂ and TiO₂ deposited FTO glasses were transferred into an argon-filled glove box (H₂O and O₂ concentrations < 1 ppm). 1.45 M stoichiometric MAPbI₃ solution was prepared in a mixture of DMF and DMSO (4:1 v/v) and then was stirred at room temperature for 12 h to prepare fully dissolved solution. The solution was dropped onto the substrate and then coated by spin coating at 1000 rpm for 5 s and then at 5000 rpm for 25 s. During the second step, toluene (300 μL) was also added to perform solvent engineering, and the substrates were subsequently transferred to a hot plate at 100 °C for 10 min. Next, 25 μL of spiro-OMeTAD solution, which consisted of 50.5 mg spiro-OMeTAD, 20.16 μL of tBP and 12.25 μL of Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile) in 0.7 mL of chlorobenzene, was coated by spin coating at 3000 rpm for 30 s. Finally, a 100 nm thick Ag layer was thermally evaporated on top of the active area (0.24 cm²) with a shadow mask under

high vacuum ($<3.0 \times 10^{-6}$ torr).

Device characterization

J-V curves were measured using a solar simulator (Peccell Technologies) with a potentiostat (CHI 608C, CH instruments) under AM 1.5 illumination ($100 \text{ mW}\cdot\text{cm}^{-2}$) and calibrated using a reference cell (PV measurements). The illuminated active area was fixed by a metal shadow mask (0.1 cm^2) during the measurement. PL intensity spectra was recorded with fluorescence lifetime spectrometer (C11367, Hamamatsu Photonics K.K.). The cross-sectional structure and morphology of device and ALD films and perovskite films were taken by field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL). X-ray diffraction (XRD, SmartLab, Rigaku) was used to confirm crystalline structure of films. Transmittance and absorption spectra of films were recorded by using a UV/Vis spectrophotometer (OPTIZEN POP, Mecasys and V-670, JASCO). Ultraviolet photoelectron spectroscopy (UPS, Axis Nova and Ultra DLD, Kratos analytical Ltd) was used to obtain work function and valence band maximum. Topography and local conductance of films were measured by atomic force microscopy (AFM) and conductive-AFM (C-AFM, Nanonavi II, SII Nanotechnology). Cyclic voltammetry (CV) analysis was produced by potentiostat system (VMP3, Bio-logic science instruments). The electrical resistance of various metal-insulator-metal (MIM) devices was measured by a Keithley 2400 source meter. The elemental composition was measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Scientific Inc.)

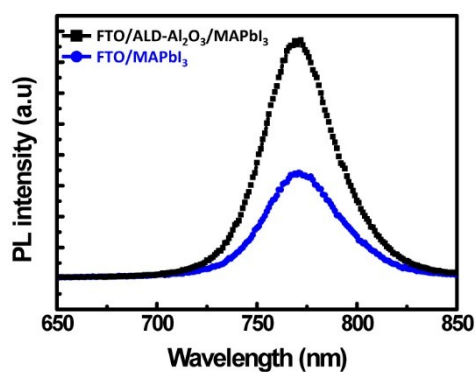


Figure S1. PL Intensity of FTO/MAPbI₃ decreased more than 50% compared to FTO/Al₂O₃/MAPbI₃ sample, resulting from extraction of photoexcited electron through FTO.

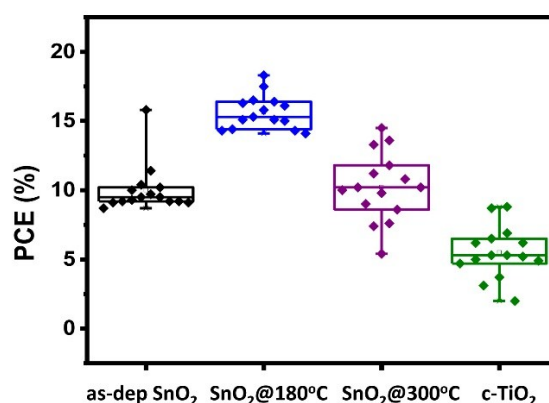


Figure S2. PCE statistics measured for 15 PSCs based on each ETL.

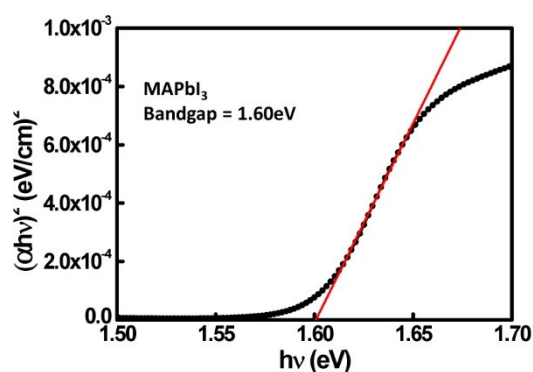


Figure S3. Optical band gap of MAPbI₃ calculated from Tauc plot of absorption coefficient (α^2) vs. photon energy ($h\nu$).

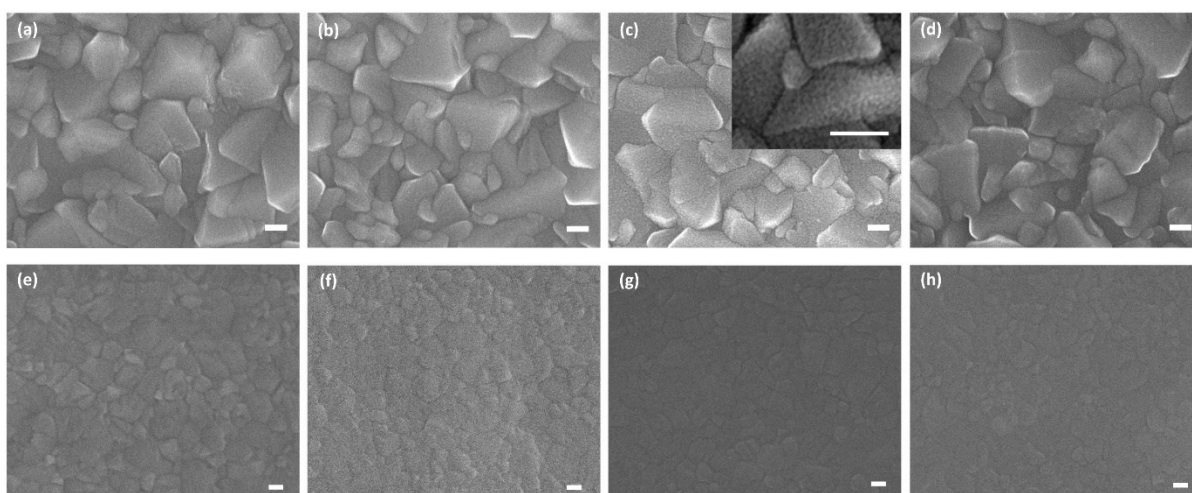


Figure S4. Field emission scanning electron microscopy (FESEM) image of ALD films deposited onto FTO and MAPbI₃ coated onto FTO/ETL, top view images of as-dep SnO₂, SnO₂@180°C, SnO₂@300°C and c-TiO₂ are (a), (b), (c) and (d). The inset of (c) is the enlarged view of nanocrystalline SnO₂. In addition, (e), (f), (g) and (h) represents top view image of MAPbI₃ coated onto FTO/ETL of as-dep SnO₂, SnO₂@180°C, SnO₂@300°C and c-TiO₂, respectively. All scale bar in each image represents 100 nm. Rough FTO morphology was observed in images shown in Figs. S3(a), (b) and (d), when thin film (~ 12 nm) was deposited onto FTO, since the ALD processes layer by layer deposition sequence along the surface of the FTO resulting the complete conformal coating. Whereas, as shown in Fig. S3(c), the SnO₂@300°C was crystallized with nanocrystallites, corresponding to the result of XRD patterns with broader peak width confirmed in Fig. 2(a). Also, the compact and pinhole-free perovskite layer deposited on each ETL with a grain size of around 100 nm or more is formed and has a similar morphology despite the difference in ETL as shown in Figs. S3(e), (f), (g) and (h). All scale bar in each image represents 100 nm.

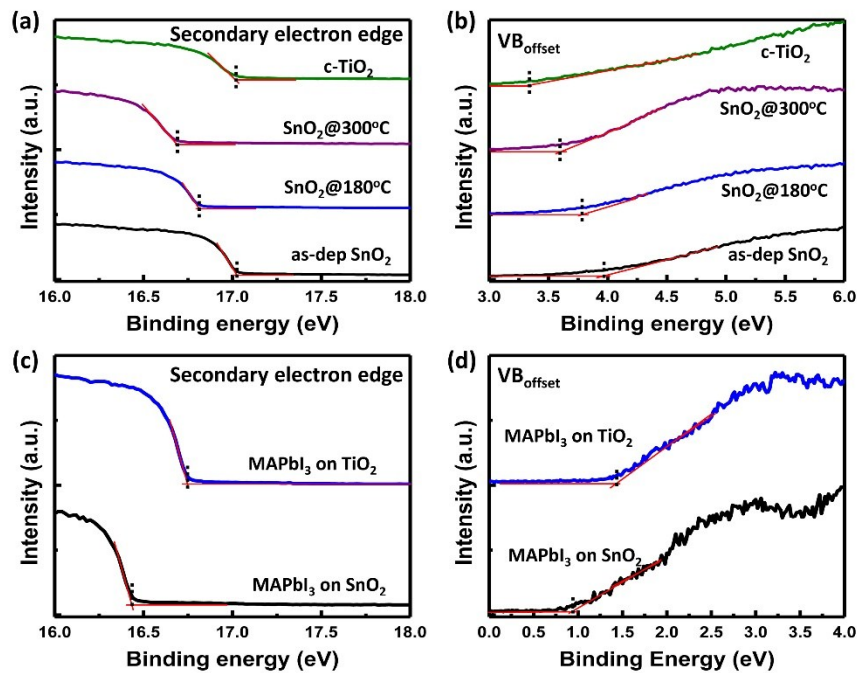


Figure S5. UPS spectra and energy band level of different ETL and perovskite. Cut-off binding energy of secondary electron edge measured by UPS using He(I) source (21.22 eV). (a) Each value of as-dep SnO₂, SnO₂@180°C, SnO₂@300°C and c-TiO₂ is 17.02, 16.80, 16.70 and 17.02 eV, and MAPbI₃ coated on SnO₂ and TiO₂ film with a value of 16.44 and 16.75 eV (c). Valence band maximum spectra measured by UPS. (b) Each value of as-dep SnO₂, SnO₂@180°C, SnO₂@300°C and c-TiO₂ is 3.96, 3.76, 3.65 and 3.27 eV, and MAPbI₃ coated on SnO₂ and TiO₂ film with a value of 0.89 and 1.38 eV (d). The fermi level (E_F) was extracted by subtracting the value extrapolated from secondary electron edge shown in (a) and (c) from He(I) source energy (21.22 eV). In addition, valence band was extracted by subtracting the value valence band offset shown in (b) and (d) from E_F . Conduction band was calculated by adding valence band and optical bandgap shown in Fig. 2(c).

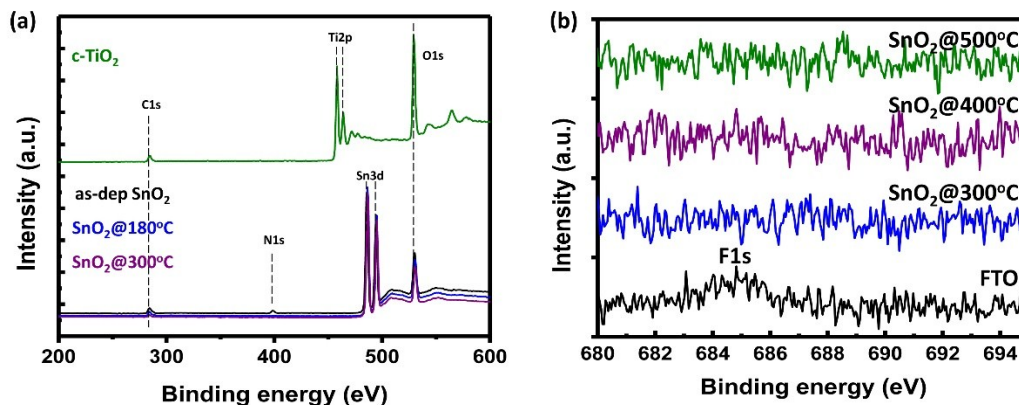


Figure S6 (a) XPS spectra of ETLs deposited on Si. The XPS spectra decided based on C1s binding energy (284.4 eV). The Sn3d signal and Ti2p signal were detected in SnO₂ and TiO₂ samples, respectively. Also, O1s peak was detected in both samples. In addition, N1s signal issued residual of Sn precursor was detected in as-dep SnO₂ and SnO₂@180°C samples (b) XPS spectra of F1s signal of SnO₂ deposited onto FTO according to different annealing temperature. F1s signal of FTO samples was weak and amount of detected signal was 1.27 atomic percent.