Supporting Information

Ag/Bi iodide Films Fabricated by Single-Source Thermal Ablation for lead-free perovskite-inspired solar cells

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Experimental details

Film preparation

SBI precursor solutions (0.25 M) were prepared by using commercially available AgI (Thermoscientific) and BiI_3 (Johnson Matthey) without further purification. To prepare precursor solutions with an Ag/Bi molar ratio of either 2.0, 1.0 or 0.5, mixtures of AgI and BiI_3 with the proper stoichiometric ratio were dissolved in dimethyl sulfoxide (Aldrich) by stirring for two hours at 60 ˚C and then naturally cooling down the solution, that appeared clear at room temperature.

Glass substrates were cleaned by sequential rinsing in 1% Hellmanex, de-ionized water, hot acetone, and isopropanol for 15 min. After drying in blowing nitrogen, up to four 25 mm x 25 mm substrates were placed on a sample holder that was mounted into the evaporation chamber at a fixed vertical distance from the evaporation source. The evaporation system is tailor made [1,2] and allows power to be increased from 0 to the preset value with a rate of approximately 600 W/s, the maximum power being 1000 W. The precursor layer for evaporation was created by spreading the precursor solution onto a tantalum boat that was then placed on a hotplate at 100 ˚C, while maintaining the precursor distribution as even as possible. The temperature finally increased up to 150 ˚C to complete solvent evaporation. The boat was then clamped between two electrodes in the evaporation chamber that was immediately pumped to vacuum. When the pressure in the chamber was below $5\ 10^{-6}$ mbar, electrical current was passed through the boat to promote the precursor evaporation. Unless otherwise stated, a preset power of 950 W was

applied for about 4 s, which prevents precursor residues from remaining on the boat and avoids uncontrolled heating of the film due to exposure to the incandescent heater. After waiting 5 min in vacuum, nitrogen was finally inlet and samples removed from the chamber with the ambient humidity maintained around 30%. Unless otherwise stated, immediately after their extraction from the deposition chamber, films were hot-plate annealed at 150˚C for 30 min and then stored into a desiccator in the dark. Under these conditions, when using 200 µl of Ag/Bi = 2.0 precursor solution, for a vertical distance of 12 cm between the crucible and the substrate, a film thickness of 250 nm was measured using a stylus profiler.

BiI_3 films were deposited by directly placing the powder on the boat. After pumping to vacuum, evaporation was achieved by applying 100 W for 20 s and then 200 W for 20 s.

Device fabrication

Figure S1 depicts the preparation steps followed in the preparation of the devices used ion this work. Solar cells have been fabricated (Figure S1) using FTO substrates (2.2 mm-thick TEC15 Pilkington, 15 Ω/square) on 25x25 mm^2 substrate area patterned by using nanosecond UV as detailed in Ref.[3]. The patterned substrates were cleaned in an ultrasonic bath, using de-ionized water and soap and finally IPA (10 min for each cleaning step). Screen-printed silver contacts (DuPont 7713) are deposited over FTO photoanodes.

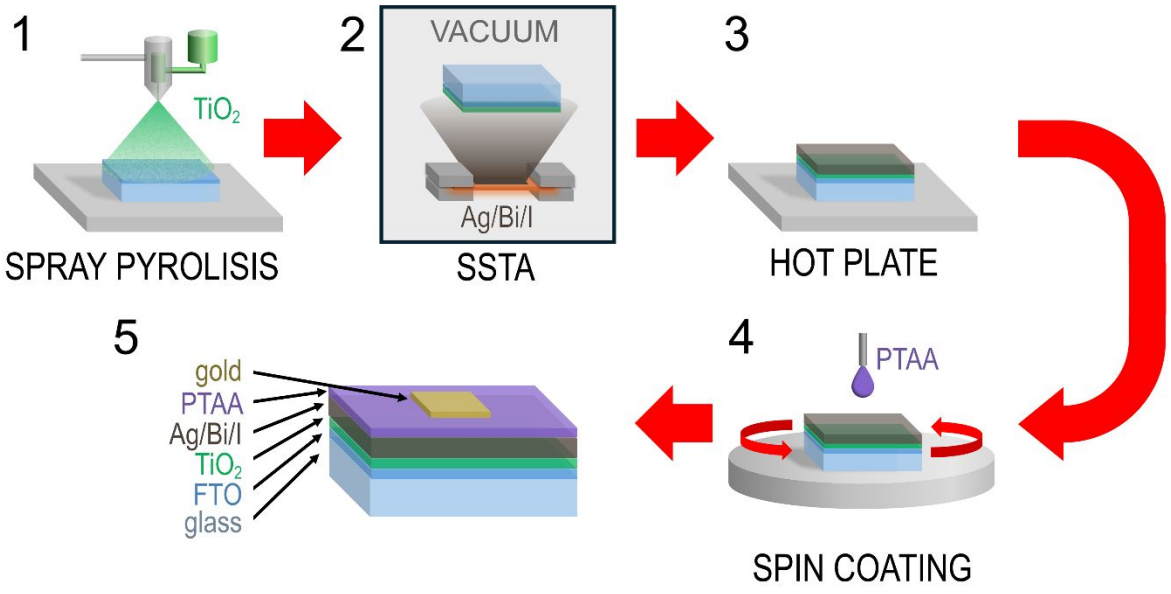

Figure S1 Schematic illustration of the solar cell fabrication procedure.

A 40 nm-thick TiO_2 compact layer (c-TiO_2) was deposited by spray pyrolysis at 465˚C starting from a precursor solution made up of titanium diisopropoxide bis(acetylacetonate), acetylacetone and ethanol in a 3:2:45 volume ratio. With air as gas carrier at a pressure of 1.6 bar and the nozzle angle of about 45˚, 10 spray cycles (one every 10 seconds) have been deposited. The substrates were left 10 minutes at 460 ˚C before cooling down the temperature.

The TiO_2 substrates were then treated in an Ar/O_2 plasma for 8 min at 60W by a Diener Femto SRS and loaded in the SSTA system for the deposition of 240 nm thick SBI films.

The hole transporting layers were deposited by spin coating at 4000 rpm for 60 seconds a solution obtained by dissolving 10 mg of the PTAA powder in 1 ml of toluene solvent. Pristine PTAA was used for the preparation of the HTL because the addition of TBP was found to bleach silver bismuth iodides in a way similar to what was reported for spiro-OMETAD[4].

Finally, 100 nm thick gold contacts were deposited through a shadow mask to achieve 4x4 mm^2 cells.

Characterization

All the film characterizations were carried out in low humidity atmosphere (RH ≤ 30%). In particular, the structural quality of the films was studied by X-ray diffraction (XRD) measurements in a Siemens (D500) powder diffractometer, with CuKα radiation, while polycrystalline powders obtained by mechanically scratching the films from the glass substrate were investigated in a Rigaku Smartlab XE diffractometer.

Film absorbance spectra were measured by a Jasco UV–vis V-770 spectrometer. Morphological characterization was performed by atomic force microscopy (AFM) in tapping mode using a Veeco Dimensions 3100 SPM and by scanning electron microscopy (SEM) using a Zeiss Auriga field emission microscope (FESEM) operated at 5 kV. High Resolution Transmission Electron microscopy (HRTEM), Selected Area Electron Diffraction (SAED), High Angle Annular Dark Field (HAADF) imaging in scanning mode and Energy Dispersive X-ray Spectroscopy (EDS) were performed in a Jeol 2200FS microscope.

Confocal Raman measurements were carried out using a Horiba LabRAM HR Evolution confocal spectrometer (focal 800 mm), using a backscattering configuration with a 600 lines/mm grating, a set of Bragg ultra-low frequency filters for the rejection of the Rayleigh scattering and a liquid nitrogen-cooled CCD detector. The 633 nm laser line were used for excitation applying a 0.01% density filter. An optical 100x objective was used to obtain a spatial resolution of about 1 μm, with 0.5 cm^{-1} resolution. Typical

collection time for the confocal configuration was 5 s for each acquisition. Before each set of measurements, a calibration was performed using the 520.6 cm^{-1} main silicon peak.

The current–voltage (I–V) characteristics of the solar cells were measured at 25 ˚C under a solar simulator (ABET SUN 2000) at 1 sun.

Table S1. Performance parameters for the-solar cells obtained by the different precursors.

precursor	Scan direction	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
Ag/Bi=2	Forward	0.71	3.09	0.46	1.02
Ag/Bi=2	Reverse	0.70	2.98	0.25	0.51
Ag/Bi=1	Forward	0.69	1.64	0.38	0.43
Ag/Bi=1	Reverse	0.68	1.54	0.31	0.32
Ag/Bi=0.5	Forward	0.39	0.51	0.31	0.06
Ag/Bi=0.5	Reverse	0.36	0.48	0.23	0.04
BiI_3	Forward	0.29	0.29	0.31	0.03
BiI_3	Reverse	0.29	0.29	0.30	0.03

References

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