

Flexible high efficiency perovskite solar cells

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Supporting Information

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Cristina Roldán-Carmona^{a,b,†}, Olga Malinkiewicz^{a,†}, Alejandra Soriano^a, Guillermo Mínguez Espallargas^a, Ana García^c, Patrick Reinecke^{c,d}, Thomas Kroyer^c, M. Ibrahim Dar^c, Mohammad Khaja Nazeeruddin^c and Henk J. Bolink^{a*}

Methods

Materials

Aqueous dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP Al 4083) were obtained from Heraeus Holding GmbH and used as received. poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD) was purchased from ADS Dyesource. PbI₂ was purchased from Aldrich and used as is, CH₃NH₃I was prepared similar to a previously published method¹, in brief: *CH₃NH₃I, was synthesized by reacting 21.6 ml methylamine (40%wt in water, Aldrich) and 30 ml hydroiodic acid (57 wt% in water, Aldrich) in a 250 ml round-bottomed flask at 0 °C for 2 h with stirring. The white precipitate was recovered by evaporation at 50C for 1 h. The product, methylammonium iodide (CH₃NH₃I), was dissolved in ethanol, filtered and recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h.*

Device preparation

Devices were prepared on cleaned AZO/Ag/AZO on PET substrates, by spincoating a thin layer of PEDOT:PSS from the commercial aqueous dispersion (1200rpm 30sec and a short annealing at 150 °C result in 70 nm thickness). On top of this layer a thin film of polyTPD was deposited from a chlorobenzene solution (10 mg ml⁻¹) using spincoating. Then the substrates were transferred to a vacuum chamber integrated into an inert glovebox (MBraun, <0.1 ppm O₂ and <0.1 ppm H₂O) and evacuated to a pressure of 1 × 10⁻⁶ mbar. The sublimation of the perovskite was performed using a vacuum chamber of MBraun integrated in an inert glovebox (MBraun). Temperature controlled evaporation sources from Creaphys fitted with ceramic crucibles were employed to sublime the CH₃NH₃I and the PbI₂. The sources are directed upwards with an angle of approximately 90 ° with respect to the bottom of the evaporator. The substrates were placed at a distance of 20 cm from the top of the evaporation

sources. Shutters are present at the evaporation sources and below the substrate holder. Three quartz microbalance sensors are present in the chamber, two monitoring the rate of each evaporation source and a third one at the height of the substrate holder. After the ceramic crucibles were loaded with the $\text{CH}_3\text{NH}_3\text{I}$ and the PbI_2 the chamber was evacuated to a base pressure of 1×10^{-6} mbar. Fresh $\text{CH}_3\text{NH}_3\text{I}$ was used for each evaporation. After the base pressure was reached, the $\text{CH}_3\text{NH}_3\text{I}$ crucible was heated to 70 °C. At this temperature, all three quartz sensors gave a signal. We were, however, unable to calibrate the sensor by measuring the thickness of a deposited $\text{CH}_3\text{NH}_3\text{I}$ film. Therefore, an alternative process was used. Upon stabilization of the sensor reading the crucible containing the PbI_2 was heated. Only at PbI_2 evaporation temperatures in excess of 200 °C were dark brown films obtained. The film thickness of the perovskite film was monitored using quartz sensor nr 3 (at the height of the substrate holder). Perovskite films were prepared at different PbI_2 evaporation temperatures, increasing with 10 degrees from the predetermined 200 °C. In this way the optimum films were obtained at an evaporation temperature of the PbI_2 crucible of 250 °C. The PCBM layer was deposited using a chlorobenzene solution of 10 mg ml^{-1} in ambient conditions using a meniscus coater and a coating speed of 10 mm/ second. The device was completed by the thermal evaporation of the top metal electrode under a base pressure of 2×10^{-6} mbar to a thickness of 100nm. The solar cells (active area of 0.12 cm^2) were characterized inside the inert glovebox.

Characterization

GIXRD data were collected at room temperature in the 2θ range 5–50 ° on an Empyrean PANalytical powder diffractometer, using $\text{Cu K}\alpha 1$ radiation. Typically four repeated measurements were collected and merged into a single diffractogram. Pawley refinements², were performed using the TOPAS computer program³ and revealed an excellent fit to a one-phase model with a tetragonal cell ($a = 8.80(2)$, $c = 12.57(2)$ Å) and space group $I4/mcm$. Additional peaks corresponding to the ITO substrate were also observed.

Scanning Electron Microscopy

Film thickness was investigated using a high-resolution scanning electron microscope (MERLIN, Zeiss) and micrographs were acquired using an in-lens secondary electron detector. Prior to analysis, the sample was coated with 12 nm carbon to minimize the charging effect.

Device characterization

Solar cells were illuminated by a white light halogen lamp in combination with interference filters for the EQE and J-V measurements (MiniSun simulator by ECN the Netherlands). A black mask was used to limit the active area of the device. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode. An estimation of the short-circuit current density (J_{sc}) under standard test conditions was calculated by convolving the EQE spectrum with the AM1.5G reference spectrum, using the premise of a linear dependence of J_{sc} on light intensity. Current-voltage (J-V) characteristics were measured using a Keithley 2400 source measure unit. All characterization was done in a nitrogen filled glove box (<0.1 ppm O_2 and <0.1 ppm H_2O) without exposure to ambient atmosphere.

Notes and references

^a Instituto de Ciencia Molecular, Universidad de Valencia, C/ Catedrático J. Beltrán 2, 46980 Paterna (Valencia), Spain. henk.bolink@uv.es

^b Department of Physical Chemistry and Applied Thermodynamics, Campus Rabanales, Ed. C3, University of Cordoba, 14014, Spain.

^c Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany.

^d Freiburg Materials Research Center (FMF), Stefan-Meier-Strasse 21, 79104 Freiburg, Germany

^e Laboratory of Photonics and Interfaces, Swiss Federal Institute of Technology (EPFL), Station 6, Lausanne, CH 1015, Switzerland.

‡ These authors contributed equally to this work.

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