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Electronic Supporting Information

Scalable Route to $CH_3NH_3PbI_3$ Perovskite Thin Films by Aerosol Assisted Chemical Vapour Deposition

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Experimental Methods

All reagents were purchased form Aldrich chemical company UK, and used as received. Methylammonium iodide was synthesised by neutralising a saturated aqueous solution of methylamine with aqueous hydrogen iodide. The product was obtained as a white solid by removing the solvent, washing with diethyl ether and drying at 80°C. PbI_2 was prepared by reacting aqueous solutions of $Pb(NO_3)_2$ and KI in stoichiometric ratios, yielding a bright yellow solid. For a typical AACVD deposition of MAPI, PbI_2 (1.50 g, 3 mmol) and CH_3NH_3I (0.51 g, 3 mmol) were added to N,N-dimethylformamide (25 ml) and stirred for 1 hour. The resulting solution was placed in a glass vial and an aerosol mist generated using a 6 MHz ultrasonic transducer. The aerosol was transported to the reactor using a N_2 flow rate of at 0.6 l/min. The "barrier glass" substrate was supplied by NSG with *c*. 50 nm SiO_2 thick layer over 3 mm thick soda lime float glass. The barrier layer functions to prevent ion migration from the underlying glass. Substrates were 15 cm × 4 cm × 0.3 cm. A top plate was suspended 0.5 cm above the glass substrate to ensure a laminar flow. For MAPI depositions, the substrate temperature was kept at 200 °C. After the deposition of MAPI the substrates were cooled under a flow of nitrogen. Coated substrates were immediately transferred to a M-Braun UniLab drybox for storage prior to analysis. The coated glass substrate was cut into ca. 3 cm × 3 cm squares for subsequent analysis.

Where required, a TiO_2 layer was coated onto the glass from a solution of $Ti(O^iPr)_4$ in ethanol using AACVD at 500°C.

Single crystals of MAPI were produced by dissolving equimolar proportions of PbI_2 and CH_3NH_3I in a saturated solution of HI in water. The solution was heated to 120°C under flowing nitrogen. Once half of the solvent volume had been removed, the solution was cooled slowly to obtain black single crystals of MAPI.

Powder X-ray diffraction (PXRD) was carried out using a modified Bruker-Axs D8 diffractometer with Cu Kα source, parallel beam optics equipped with a PSD LynxEye silicon strip detector. The incident beam angle was kept at 1° and the angular range of the patterns collected was $10° < 2\theta < 66°$ with a step size of 0.05° counted at 0.5s/step.

UV/Visible/near-IR spectra were taken using Perkin Elmer Fourier transform Lambda 950 UV/Vis spectrometer over a wavelength range of 300 nm to 1000 nm in diffuse reflectance mode and the absorption coefficient (α) according to the Kubelka-Munk equation.

X-ray Photoelectron Spectroscopy (XPS) was carried out on a Thermo K-alpha spectrometer using X-rays from a 72 W Al Kα source which were monochromated using a toroidal quartz crystal and micro focused to a spot size of 400 μm on the sample surface. The instrument was operated in constant analyser energy (CAE) mode. A pass energy of 200 eV was used for survey scans and 50 eV for high resolution core level and valence band scans. A dual beam charge compensation method was used, applying both an electron flood gun and low energy Ar^+ beam to compensate for surface charging during measurement. Area mapping was carried out over a 5.0 x 2.5 cm area by moving the sample and acquiring spectra on a 72 point grid under computer control. Spectral data were processed using Thermo Avantage and CasaXPS. Charge correction was carried out using surface adventitious carbon set to 285.0 eV.

Computational Methods

All DFT calculations were performed using the VASP code. Interactions between the core and valence electrons described within the PAW method. The calculations were performed

using the Screened hybrid exchange functional HSE06, which yields a geometry and electronic structure in excellent agreement with recent PBEsol and GW calculations respectively. A planewave cutoff of 400 eV and a *k*-point sampling of Γ-centred 6×6×6 for the MAPI unit cell were used, with the ionic forces converged to less than 0.01 eV°A^{-1}.