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Electronic Supplementary Information

Surface-related properties of perovskite $CH_3NH_3PbI_3$ thin films by aerosol-assisted chemical vapour deposition

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Experimental Section

Prior to thin film deposition, cleaning of 1.1 mm borosilicate glass (2.5 cm × 2.5 cm, Corning Eagle 2000) was carried out with detergent, water, propan-2-ol, and dried in air. Vicks paediatric mini ultrasonic humidifier was used as the nebuliser. The PbI_2 (99%, Sigma Aldrich), DMF (>99%, Sigma Aldrich) and CH_3NH_3I (Solaronix) were used as received. The N_2 (99.9 %, BOC Gases) flow rate was controlled using a Platon NGX glass variable area flowmeter. An IEC - type K thermocouple was used to measure the surface temperature of the carbon block.

Deposition of Thin films: As illustrated in Fig S1, a cold-walled horizontal-bed AACVD reactor was used to deposit $CH_3NH_3PbI_3$ on borosilicate glass. Prior to conducting any experiments, system was continuously purged with N_2 for 2-3 hrs, to reduce moisture and any contaminants. In the first stage, wet PbI_2 films were deposited at 30 °C using an aerosoled 0.14 M solution of PbI_2 in DMF for 1 hr. After evaporating DMF at 70 °C for 5 minutes (second stage), a CH_3NH_3I solution (0.27M) was introduced into the system (via aerosol) for 1 hr at 220 ^{o}C (third stage). The N_2 carrier gas (flow rate = 0.6 l/min) was passed through the reactor during all of the experiment. After deposition, films were immediately removed from the reactor and transferred to a N_2 glovebox for further manipulation.

Characterisation

X-ray powder diffraction measurements were performed on a Bruker D8 using Cu Kα radiation (λ = 1.5406 Å). A field emission scanning electron microscope (FESEM, Lyra3, Tescan, Czech

Republic) with an accelerating voltage of 20 kV was used to characterise the films. Reflection and transmission measurements were carried out using an Aquila nkd 8000 spectrophotometer between 400 - 1000 nm at an incident angle of 30° using s polarisation. Photoluminescence studies were performed on a single beam spectrometer (Jobin−Yvon TRH1000), with an edge filter and a thermoelectric-cooled multichannel CCD detector (Horiba Synapse) using an excitation wavelength of 532 nm. The surface chemistry of deposited films was investigated using X-ray photoelectron spectroscopy on a Thermos Scientific ESCALAB 250Xi spectrometer equipped with a monochromatic Al Kα (1486.6 eV) X-ray source. Samples were etched in argon for 10 sec to remove any surface contaminants.

The ellipsometric data were obtained using J.A. Woollam Company VASE ellipsometer and J.A. Woollam Completease software was used for the data analysis. Ellipsometric characterisation provides several parameters such as thickness, refractive index (n) and extinction coefficient (k) of the films. The ψ (the ratio of the amplitude diminutions) and Δ (the phase difference induced by the reflection) measurements were carried out at three incident angles 65°, 70°, 75° over the spectral range of 300-1700 nm (0.73 - 4.13 eV). It should be noted that the measurement of the ψ and Δ at three angles are valuable but adding experimental measurement such as intensity transmission measured independently of ψ and Δ can helps to determine the unique optical model.[1] The Bruggeman effective medium approximation (EMA) were used to fit the layers including the glass substrate, the $CH_3NH_3PbI_3$ film and voids.

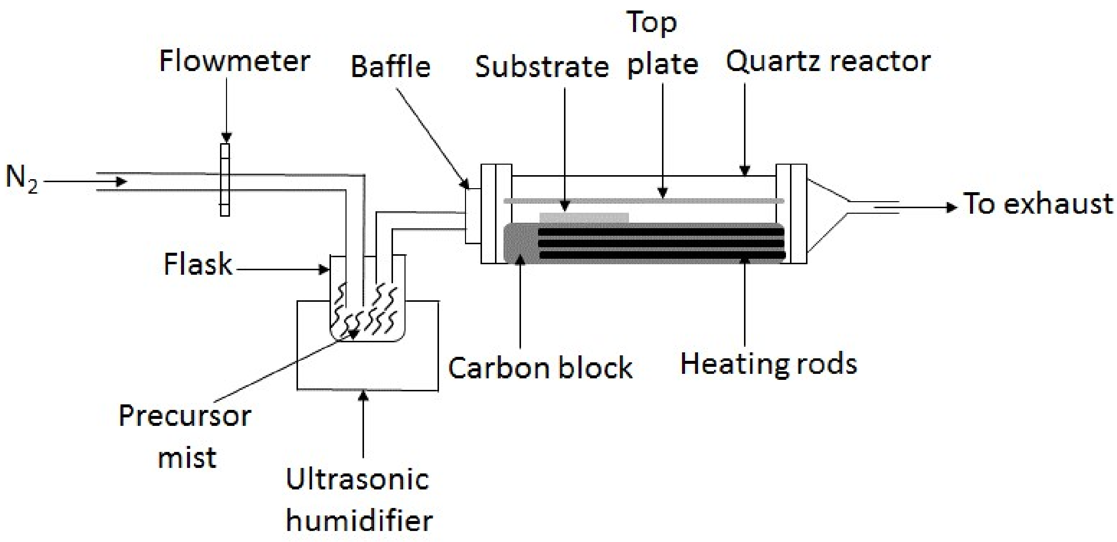

Fig. S1 A schematic illustration of the AACVD process used in this work.

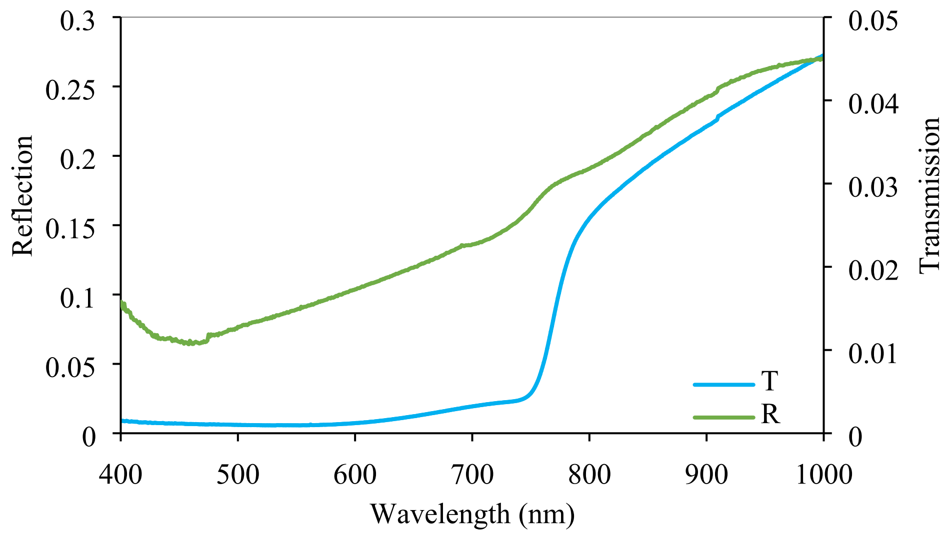

Fig. S2 Transmission and reflection of deposited $CH_3NH_3PbI_3$ thin films.

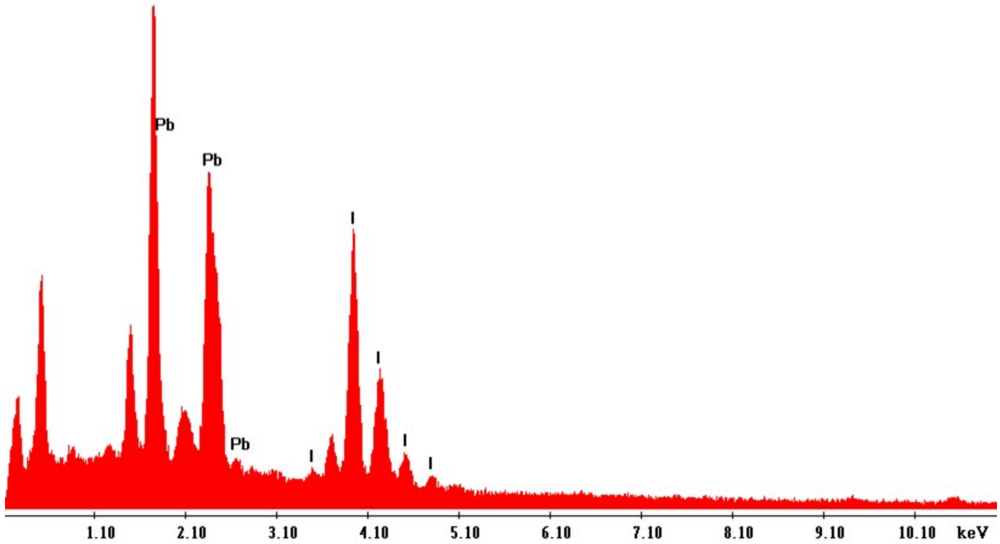

Fig. S3. A typical EDAX spectrum of $CH_3NH_3PbI_3$ thin films.

Table S1 A comparison of experimental and reference 2-theta values.

Experimental 2θ (°)	Calculated Reference 2θ(°)[2]	Index
14.69	14.22	110
20.56	20.16	200
25.13	24.6	202
29.02	28.67	310
32.46	32.14	310
35.58	35.19	312
39.39	40.58	224
41.18	40.99	400
43.76	43.6	330
53.05	53.02	510

References

(1) R. A. Synowicki, *Thin Solid Films,* 1998, **313–314**, 394–397.

(2) Solar Cells - New Approaches and Reviews Edited by Leonid A. Kosyachenko, Publisher: InTech, Chapter 3, p86.