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Supporting information

Room-temperature $CuAlO_2$ hole interfacial layer for efficient and stable planar perovskite solar cells

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Experimental

Materials preparation

Preparation of polycrystalline $CuAlO_2$ ceramic sputter target

The ceramic target was prepared following our previously reported method[1]. Appropriate proportions of 1:1 ratio of 96 % aluminum secbutoxide and 98 % copper(II)acetate precursors were measured into a 500 ml 2-neck schlenk flask fitted with a condenser. The reaction was processed under dry nitrogen due to the alkoxide's sensitivity to atmospheric moisture. The resulting volatile by-product of the reaction was allowed to reflux at 180 °C for 12 hrs. The volatiles were then drawn off under vacuum into a 25 ml flask. The reaction was propagated ontill all the volatiles were completely drawn off. The resulting dry powder was calcined at 450 °C to allow a complete decomposition of any remaining organic components. The calcined powder was milled using a planetary ball mill at 400 rpm for 5 hrs. The milled powder was then annealed at 900 °C for 2 hrs to obtain a pure phase $CuAlO_2$ delafossite crystal structure. The annealed powder was again milled under thesame milling condition and made into a pellet at 20 MPa. The pellet was further annealed at 900 °C for 2 hrs to obtain a firm and rigid ceramic structure. The obtained ceramic target had a diameter of 5 cm and a thickness of 4 mm.

Synthesis of methylammonium iodide (CH_3NH_3I)

The synthesis was done according to reported procedure[2] with modifications. 38 ml of methylamine (33 wt. % in absolute ethanol) was mixed with 40 ml of hydroiodic acid (57 wt. % in aqueous solution) in 100 ml of ethanol in a schlenk flask. The hydroiodic acid was added in a dropwise manner to form the reaction mixture. The reaction was carried out at 0 °C in an ice bath for 2 hrs under dry nitrogen atmosphere. As the reaction progressed, the originally yellowish mixture became clear and colourless. At the end of the processing time, the solvent was removed by using a rotary evaporator at 60 °C. A white crystalline powder was obtained as the product. The product was then recrystallized using a ratio 1:1 mixture of diethyl ether and ethanol. The sample was further washed twice with diethyl ether and finally dried for 24 hrs at 60 °C in a vacuum oven. The pure sample obtained was stored in the glove box for subsequent use.

Device fabrication

Cleaning of ITO glass substrates

Commercially available pre-patterned 1.6x1.4 cm^2 ITO substrates were cleaned preliminarily with soap and deionized (DI) water and then sequentially with ethanol and acetone in an ultrasonic bath each for 15 min. The cleaned substrates were then dried in the oven at 110 °C for 30 min.

Prepartion of a:$CuAlO_2$ thin films

The cleaned substrates were mounted on the sample stage in the sputter vacuum chamber. The prepared polycrystalline $CuAlO_2$ ceramic target was carefully placed on the d.c. source. The chamber was pumped down to a base pressure of $2.6x10^{-4}$Pa. The capman pressure was set at 3 mTorr. The $CuAlO_2$ target was initially exposed to 10 min of Argon (Ar) bombardment for contaminants on its surface to be removed. For the deposition, a d.c. power of 100 W was used and pure Ar was used as the sputter gas. The target to substrate distance was kept at about 120 mm. Platen motion was set at 20 rpm. The deposition was conducted at room temperature for a varied period of 100, 200, 300 and 400 sec to obtain a:$CuAlO_2$ thin films of 5, 10, 15 and 20 nm respectively.

Deposition of PEDOT:PSS layer

PEDOT:PSS layers were deposited onto the sputtered a:$CuAlO_2$ films by filtering it through a 0.45 μm filter and spin-coating at 4500 rpm for 40 min. The resulting film was then annealed in open air on a hot plate at 140 °C for 20 min to give a PEDOT:PSS layer of 40 nm. PEDOT:PSS was also directly depositied on the ITO layer without the introduction of the a:$CuAlO_2$ layer following the same deposition conditions for the purpose of fabricating reference devices.

Preparation of $CH_3NH_3PbI_{3-x}Cl_x$ absorber layer

The $CH_3NH_3PbI_{3-x}Cl_x$ absorber layer was deposited onto the PEDOT:PSS layer using one step spin coating method. A mixture of the already synthesised CH_3NH_3I (256 mg) and 99 % $PbCl_2$ (149 mg) was agitated in anhydrous DMF (1 ml) overnight at 60 °C to allow it dissove and form a homogenous solution prior to device fabrication. The homogenous solution was deposited on the PEDOT:PSS layers at 4000 rpm for 40 sec. The films obtained was thereafter annealed by gradually increasing the annealing temperature by 10 °C every 10 min interval starting from 60 °C to 100 °C. The annealing process was then kept for 40 min at 100 °C. Dark brownish films were obtained. This procedure was carried out in the dry nitrogen filled glove box.

Preparation of $CH_3NH_3PbI_3$ absorber layer

The $CH_3NH_3PbI_3$ absorber layer was separately grown on pristine a:$CuAlO_2$ (15 nm), pristine PEDOT:PSS (40 nm) and a:$CuAlO_2$ (15 nm)/PEDOT:PSS (40 nm) layers by two-step spin-coating method. To achieve this, PbI_2 (460 mg) was placed in anhydrous DMF (1 mL) and CH_3NH_3I (200 mg) was placed in isopropanol (20 mL). They were then agitated overnight to yield well dissolved and homogenous solutions prior to device fabrication. A layer of PbI_2

solution was deposited on the aforementioned layers with a spin-coating speed of 3000 rpm for 40 sec. The substrates were then annealed at 70 °C for 30 min. The obtained PbI_2 films were allowed to cool to room temperature. They were then dipped into the prepared CH_3NH_3I solution for 20 sec to allow a reaction between the PbI_2 and CH_3NH_3I. Excess CH_3NH_3I was rinsed off using isopropanol. The obtained films were finally annealed at 100 °C for 20 min.

Deposition of PCBM

20 mg of PCBM was placed into 1 ml chlorobenzene and stirred at room temperature overnight on a magnetic stirrer to give a homogenous solution prior to device fabrication. The solution was spin coated on the $CH_3NH_3PbI_{3-x}Cl_x$ and $CH_3NH_3PbI_3$ absorber layers at 2000 rpm for 40 sec without annealing. This process was also carried out in the dry nitrogen filled glove box.

Deposition of Silver top electrode

100 nm thick Ag electrode was finally deposited on the PCBM layers by vacuum evaporation to complete the device fabrication. The samples were carefully mounted on the sample holder in the vacuum chamber of a Kurt J. Lesker thermal evaporation system. The vacuum chamber was pumped down to10^{-6} Pa and the deposition carried out at the rate of 3 Å/sec. A shadow mask was used to achieve an Ag electrode area of 0.0725 cm^2.

Characterization

Temperature dependent crystal phase transition analysis was carried out to ascertain the structural composition of the ceramic target, the resulting a:$CuAlO_2$ thin films and the perovskite layers by an X ray diffraction technique using PANalytical designed Empyrean X ray diffractometer in the phase scan and thin film modes with Cu Kα radition $\lambda = 0.154056$ nm at 40 mA and 40kV. The secondary cut-off of the amorphous thin films with varied film thicknesses were characterized to obtain their workfunctions using KRATOS AXIS Ultra DLD photoelectron spectrometer in the ultraviolet range. The transmittance of the ITO and ITO/a:$CuAlO_2$ layers were compared by using PerkinElmer UV/Vis spectrophotometer which was also used to obtain the exitation wavelength of the $CH_3NH_3PbCl_{3-x}I_x$ layer from its absorption spectrum. Photoluminescence measurement was carried out by using French HORIBA Jobin Yvon company fluorescence spectrophotometer. The effective coverage of the ITO by the a:$CuAlO_2$ layer was confirmed from images obtained by using FEI designed Quanta 200 FEG scanning electron microscope (SEM) under high vacuum. The thicknesses of a:$CuAlO_2$ and PEDOT:PSS films were determined by AFM technique using Veeco atomic force microscope which was also used in the tapping mode to characterise their surface morphologies. The conductivities of the prepared a:$CuAlO_2$ and PEDOT:PSS films were measured by using Lake Shore Cryotronics 7600 Electromagnet Series Hall Measurement System at a temperature range of 273 K to

300 K. Electrical impedance spectroscopy (EIS) was conducted to study the interface charge transport in the perovskite solar cells using Wayne Kerr 6500B precision impedance analyzer equipped with Zman EIS analysis software at the V_{oc} of the devices. The photovoltaic properties of the perovskite solar cell fabricated such as current density-voltage (*J*-*V*) characteristics and external quantum efficiency (EQE) were measured using American Newport company photovoltaic test system equipped with Newport 91160 solar simulator (300 W xenon lamp and an AM 1.5 filter) set at an intensity of 100 mW/cm^2 and a Keithley semiconductor parameter analyzer. Dark current density-voltage (*J*-*V*) characteristics were also measured using the same equipment.

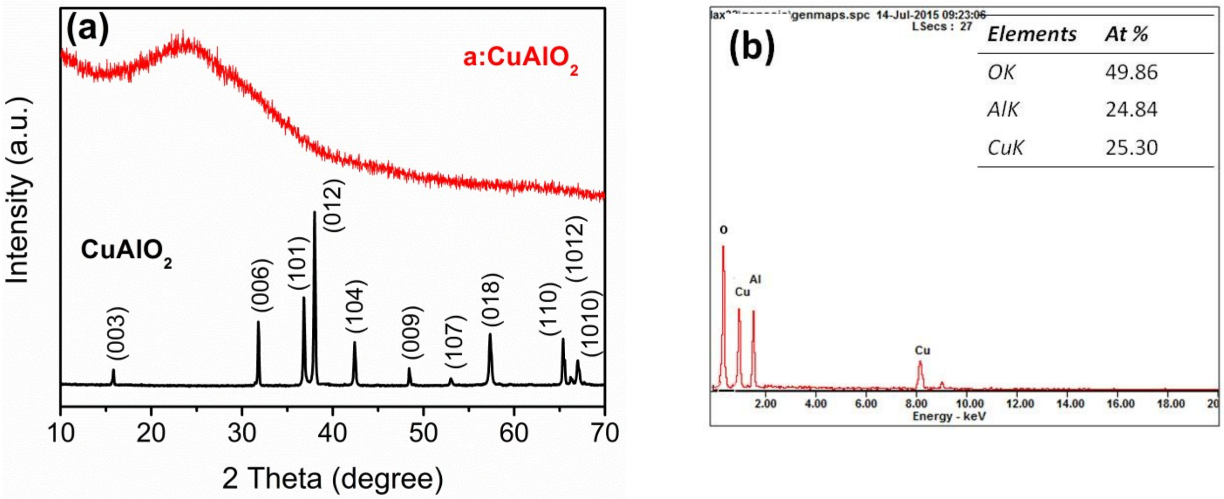

Fig. S1. (a) XRD patterns of a representative a:CuAlO$_2$ and the pure delafossite crystal phase of the CuAlO$_2$ ceramic target and (b) typical EDX spectrum confirming Cu:Al:O atomic ratio 1:1:2 for a:CuAlO$_2$.

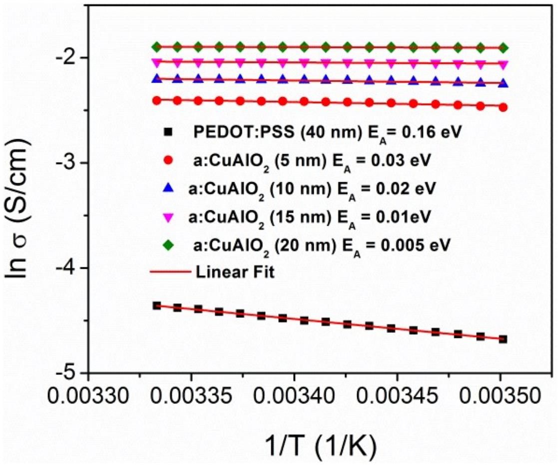

Fig. S2. Arrhenius plots of the PEDOT;PSS film and a:CuAlO$_2$ with the various film thicknesses showing the variation of logarithmic conductivity as a function of inverse of temperature.

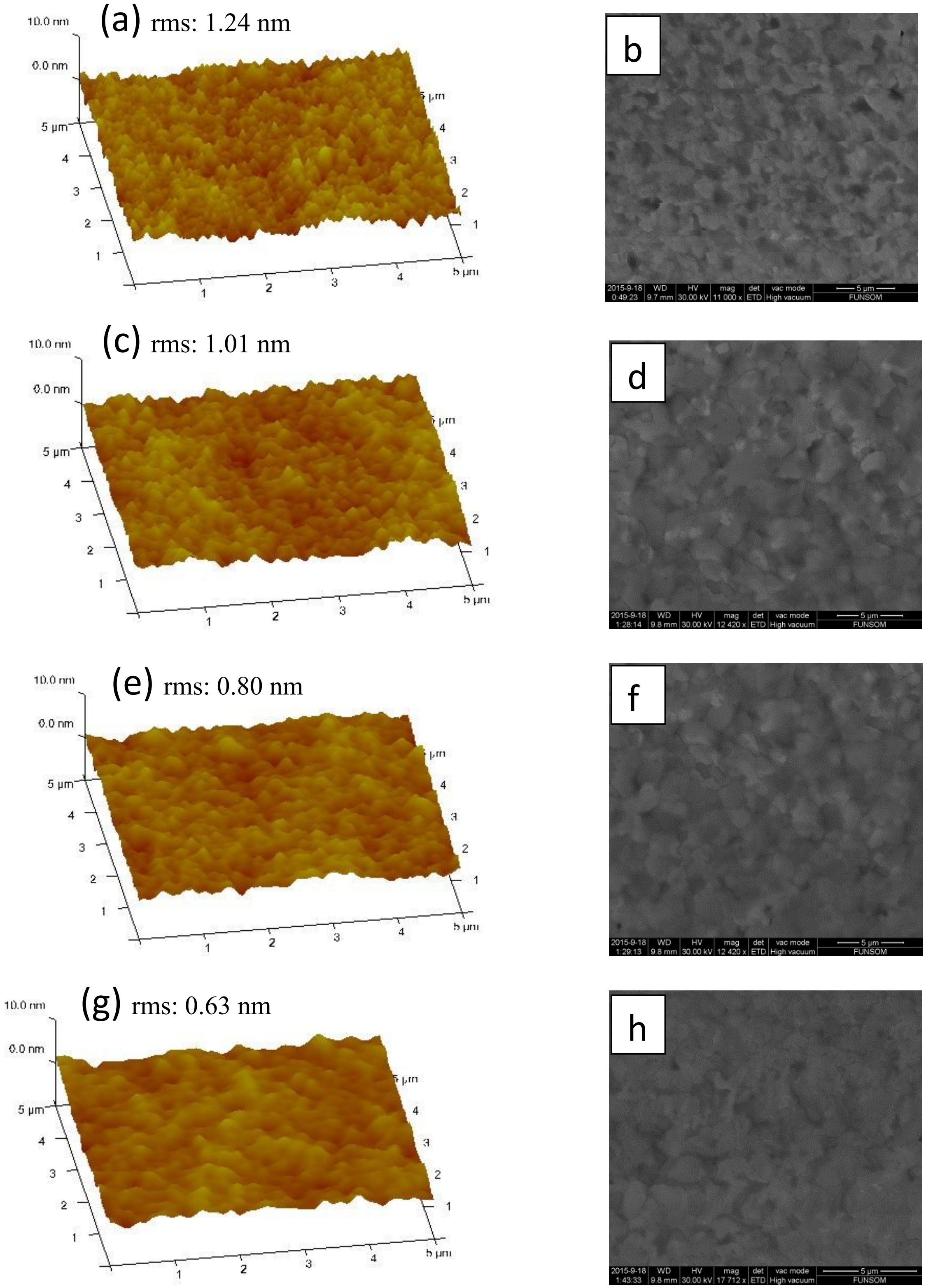

Fig. S3. (a) and (b), (c) and (d), (e) and (f), (g) and (h) presenting the tapping mode AFM and plan view SEM images of 5 nm, 10 nm, 15 nm and 20 nm a:CuAlO$_2$ films respectively on ITO substrates. A reduction in surface roughness is observed as the film thickness increases.

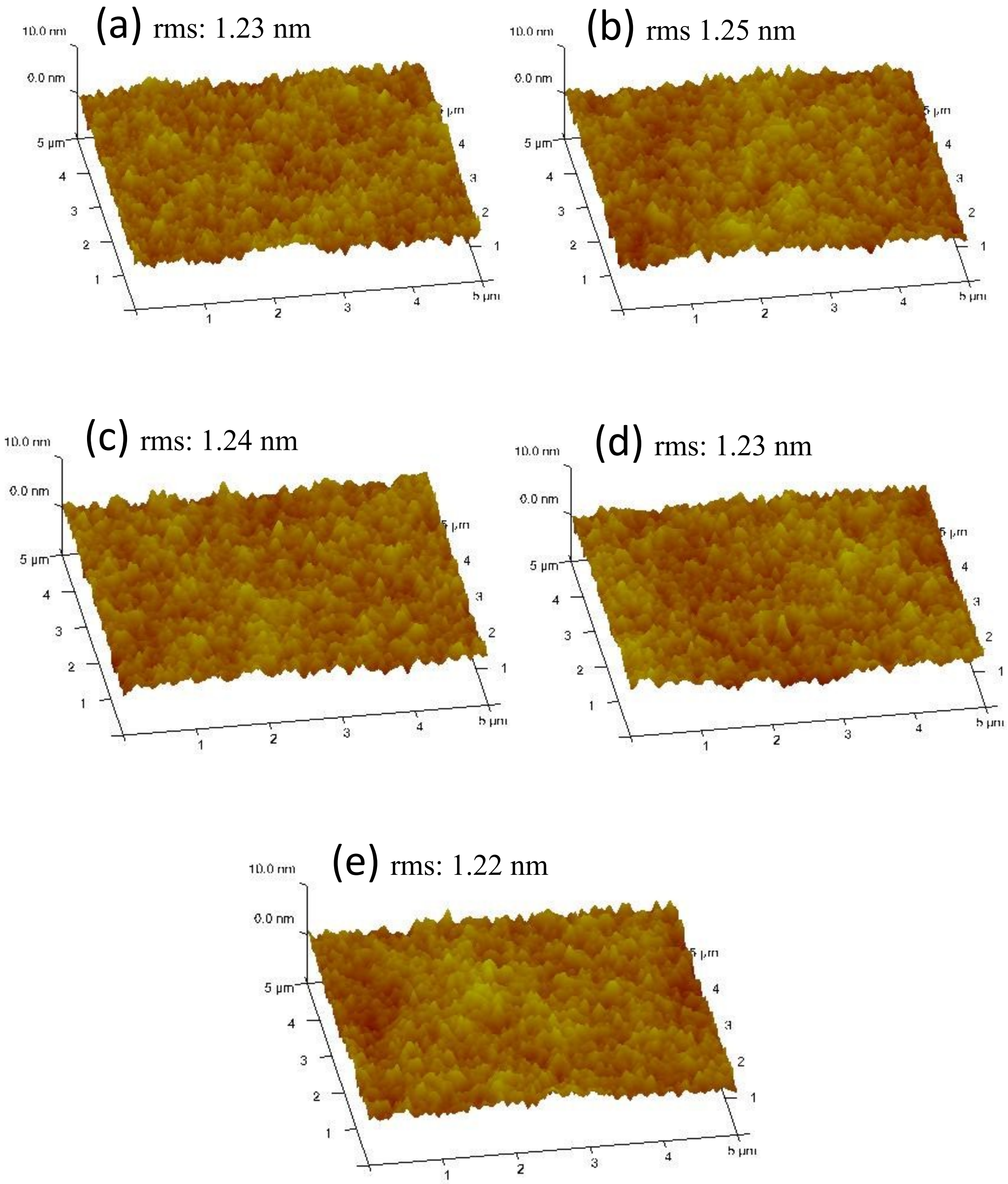

Fig. S4. The tapping mode AFM images of (a) pristine PEDOT:PSS and PEDOT:PSS deposited on (b) 5 nm, (c) 10 nm, (d) 15 nm and (e) 20 nm a:$CuAlO_2$ films with comparable surface roughness.

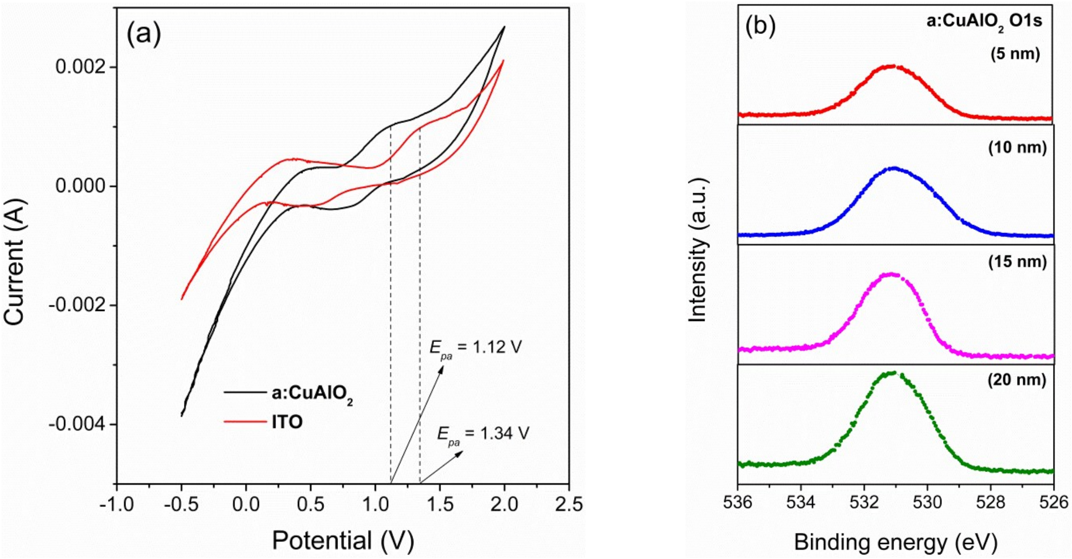

Fig. S5. (a) Cyclic voltammogram of bare ITO and a representative a:$CuAlO_2$ in 0.1 M KCl. (b) O 1s XPS core level spectra of various thicknesses of sputtered a:$CuAlO_2$ on ITO showing varied intensities.

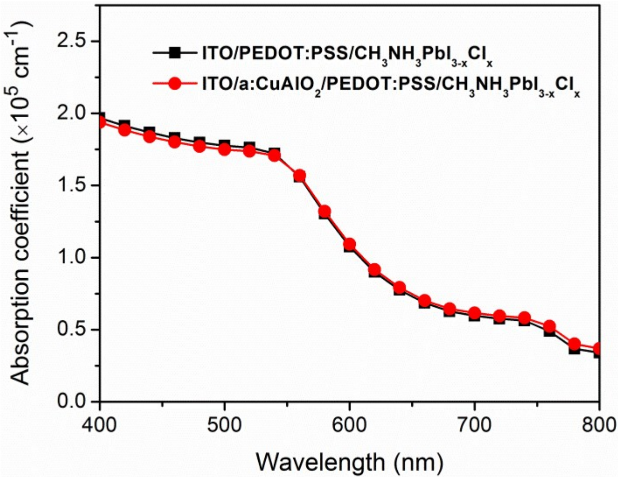

Fig. S6. Absorption spectra of ITO/PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$ and ITO/a:$CuAlO_2$/PEDOT:PSS/$CH_3NH_3PbI_{3-x}Cl_x$ films.

Table S1. EIS parameters of the perovskite solar cells with and without a:$CuAlO_2$.

	Without a:$CuAlO_2$	With a:$CuAlO_2$			
		5 nm	10 nm	15 nm	20 nm
R_s (Ω)	5.97	4.86	4.32	3.23	3.67
R_{CT} (Ω)	384.03	330.14	290.68	221.77	251.33
C_{CT} (F)	5.06E-6	5.23E-6	5.51E-6	5.89E-6	5.72E-6

References

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