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Supplementary Information

Low-Temperature, High-Speed Reactive Deposition of Metal Oxides for Perovskite Solar Cells

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Keywords: perovskite solar cells, metal oxide, NiO, nickel oxide TiO₂, titanium dioxide electron-beam evaporation, reactive, scalable, low-temperature.

Experimental methods:

Device fabrication

Materials – All materials were purchased from Sigma Aldrich unless otherwise stated. All solvents are anhydrous unless otherwise stated. All dry powders were stored in a N_2 glovebox antechamber.

Cleaning & Substrate Preparation – Patterned Tec 20 indium tin oxide (ITO) glass (Ossila) with 8 cells per substrate were cleaned by sonication in dilute 2 % Hellmanex solution, followed by dump rinsing in DI water and then sonication in isopropyl alcohol (IPA) for 15 minutes. Substrates were dried with N_2 and then UV-Ozone cleaned for 15 minutes to remove final organic residues prior to subsequent layer deposition. ITO substrates were then moved into an electron beam evaporation system inside a N_2 glovebox and pumped down to pressures not exceeding $2x10^{-6}$ mbar. An evaporation mask was used such that the metal oxides were deposited over the patterned ITO active area, but not on the ITO contacts. A quartz crystal microbalance was used to monitor the rate and thickness of each metal oxide deposition.

Reactive Oxide deposition – Nickel and titanium pellets were purchased from Kurt Lesker (¼ by ¼ inch, 99.995 % purity). For deposition, Ni pellets were placed directly in a copper hearth, while titanium pellets were placed inside a carbon crucible. The deposition sources were first preconditioned through a long, high power electron beam exposure using a wide sweep pattern. This created a pool of melted metal that was free from initial oxide impurities. During deposition, O_2 was first fed into the chamber at a partial pressure between from 5×10^{-5} mbar to 1.9×10^{-4} mbar. During evaporation the O_2 flow rate was maintained at the chosen constant partial pressure and substrates were rotated at approximately 10 rpm. Evaporation of the metal oxides was performed using a smaller electron beam pattern, at rates ranging from 0.3 to 10 Å/s, creating a 10 nm (unless otherwise stated) transparent film.

Triple Cation Perovskite (TC) – Triple-cation perovskites having a composition $CsI_{0.05}((FAPbI_3)_{0.83}(MAPbBr_3)_{0.17})_{0.95}$ were deposited from solution via the one-step antisolvent quenching method. The solution was prepared with 1 ml of mixed solvent (anhydrous n,n-dimethylformamide: dimethyl sulfoxide (DMF:DMSO) 4:1 volume ratio) containing formamidinium iodide, (FAI, 1 M, Greatcell), methylammonium bromide

(MABr, 0.2 M, Greatcell), lead(II) iodide, (PbI₂, 1.1 M, TCI) and lead(II) bromide (PbBr₂, 0.2 M, TCI) which was heated at 70 °C and intermittently vortex mixed for around 30 minutes before adding 50 μ l/ml of caesium iodide (CsI) in DMSO (1.5M concentration). This solution was filtered through a 0.2 μ m PTFE filter before being spin coated at 1000 rpm for 10 seconds then 6000 rpm for 20 seconds. 100 μ l of chlorobenzene (CB) was then rapidly dripped on the film surface 5 seconds before the end of the program. Films were annealed at 80 °C for 60 minutes inside a vacuum chamber or at 100 °C for 60 minutes in a N₂ atmosphere.

Acetonitrile Perovskite (Ac) – Methylamine bubbled acetonitrile perovskite solutions with composition MAPbI₃ were deposited via dynamic spin coating. A 0.5M suspension was prepared using 4 – 10 ml of anhydrous acetonitrile containing PbI₂ and methylammonium iodide (MAI, Greatcell) at a ratio of 1:1.06. The black suspension of powder in acetonitrile was then bubbled with dry methylamine to create a clear-yellow solution, as first demonstrated by Noel *et al.*¹ This solution was then filtered through a 0.2 µm PTFE filter before spin coating at 4000 rpm for 30 seconds. Films were annealed at 100°C for 60 minutes in a N₂ atmosphere.

 $PC_{60}BM/BPhen/Ag$ (*p-i-n* only) – a [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₀BM) solution (Ossila, 30 mg/ml in CB) which had been stirred overnight at 70 °C and then left to cool was filtered through a 0.2 µm PTFE filter before spin coating at 4000 rpm onto the perovskite film for 20 seconds. The substrates were annealed for 10 minutes at 90 °C in a N₂ filled glovebox. After cooling, a bathophenanthroline (Bphen) solution (0.5 mg/ml in IPA) was spin coated at 6000 rpm onto the substrates for 20 s. Devices were patterned using razor blade to allow contact to the ITO as required. Devices were completed by thermally evaporating a 100 nm Ag contact onto the surface of the Bphen.

Spiro-OMeTAD/Au (*n-i-p* only) – a 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) solution (Ossila, 86 mg/ml in CB) was prepared with each ml additionally containing 34 μ l of 4-tert-butyl-pyridine (tBP, 96.6%), 20 μ l of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 500 mg/ml in acetonitrile) and 11 μ l of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(II) di[hexafluorophosphate] (FK 209 Co(II) PF6, Dyesol, 300 mg/ml in acetonitrile). The solution was vortex mixed until dissolved and filtered through a 0.2 μ m PTFE filter before being spin coated at 4000 rpm onto the perovskite films for 30 seconds. Devices were left in a dark, dry desiccant chamber overnight and patterned using a razor blade to allow contact to the ITO as required. Devices were completed by thermally evaporating 80 nm Au patterned contacts onto the surface of the spiro-OMeTAD.

Device Encapsulation – Inverted p-i-n Devices were encapsulated as detailed in our previous work,² using a layer of polyvinylpyrrolidone, UV curable epoxy and a glass cover slip.

Device and Film Characterisation

AFM – An Asylum Research MFP 3D scanning probe microscope was used in AC mode with Bruker TESPA-V2 cantilevers (f_0 : 320 kHz and k: 42 N/m) for imaging. Typical scanning parameters included a scan rate of 0.5 – 1 Hz with 256 scan points/line.

XRD – X-ray diffraction data was collected on a Cu K α Bruker D8 ADVANCE X-ray powder diffractometer. The instrument was fitted with a motorised variable slit optic set to 0.3° opening and a high-resolution energy-dispersive Lynxeye XE detector. Scans of 100 nm metal oxide films on quartz, along with a quartz reference were collected at room temperature between 20° - 70° 2 θ , using a step size of 0.04° and step time of 12 s giving a total exposure time of 3.5 or 4.5 h.

XPS - The ITO substrates coated with NiO and TiO₂ before and after UVO treatment were mounted onto the sample holder with double sided carbon tape. For XPS analysis the samples were considered insulating despite their conductive coating as no path was made between the uppermost surface and the sample mount, so charge neutralisation was used. XPS analysis was performed using a Kratos Supra instrument with a monochromated aluminium source, with two analysis points taken per sample, each of area 700 µm by 300 µm. Survey scans were collected between 1200 to 0 eV binding energy, at 160 eV pass energy, 1 eV intervals, and 300 seconds/sweep with one sweep being collected. High-resolution O 1s, C 1s, Ni 2p or Ti 2p XPS spectra, and Ni LMM Auger spectra, were also collected at 20 eV pass energy and 0.1 eV intervals for each analysis point over an appropriate energy range, with one 300 second sweep for all spectra except the Ni LMM Auger which - given the extended eV range necessary - was collected for 450 seconds. The data collected was calibrated in intensity using a transmission function characteristic of the instrument (determined using software from The National Physical Laboratory) to make the values instrument independent. The data was then quantified using theoretical Schofield relative sensitivity factors. All high-resolution spectra were calibrated in units of eV by fixing the main C 1s peak to be 285.0 eV.

UV-Vis Transmission – An Ocean Optics DH-2000-BAL UV-VIS-NIR light source and HR2000+ES spectrometer were used to determine transmission of metal oxide films deposited onto quartz coated glass. The optical band gaps were determined by first calculating the absorption coefficient α (assuming zero reflection and interference) on

100 nm thick film using the Beer-Lambert law. This allowed a Tauc plot of $(\alpha h \upsilon)^2 [1/(cm^2 eV^2)]$ against $h\upsilon$ (eV) to be constructed.

Ellipsometry – Ellipsometry was performed using a spectroscopic ellipsometer (M2000v, J. A. Woollam Co., USA). Nickel oxide and titanium dioxide were deposited onto silicon substrates with a 410-420 nm thermal oxide (Ossila). Ψ , the ratio of the amplitude of incident and reflected light, and Δ , the ratio of the phase lag between incident and reflected light, were recorded over a wavelength range of 370 to 1000 nm. The metal oxide was considered to be homogeneous and the film had negligible absorbance across this range, and hence low extinction coefficients (k). As such, we were able to determine the thickness using a Cauchy model. The model was then used to extract the refractive index (n) of the film. The resultant fits for nickel oxide and titanium dioxide had mean square errors (MSEs) of 4.4 and 11.5 respectively.

Device Characterisation – Device performance metrics were determined in air using a Newport 92251A-1000 solar simulator, calibrated against an NREL certified silicon reference cell to an intensity of 100 mW/cm². Devices were illuminated through a 0.0256 cm² aperture mask. J-V curves were obtained using a Keithley 237 source measure unit, sweeping the applied bias at 0.4 V/s from 0.0 V to +1.2 V and 1.2 V to 0 V. The stabilised power output was measured by holding devices at their V_{mpp}. For all tables and boxplots, a minimum of 24 pixels were tested to determine average efficiency and standard deviation.

Supplementary Figures and Table



Figure S1: Tauc plots taken from transmission spectra for 100 nm reactive e-beam deposited NiO (black) and TiO₂ (blue) films, and NiO films after UVO treatment (red).



Figure S2: Refractive index (n) data between 370-1000 nm (1.24-3.35 eV) for a 10 nm thick film of reactive e-beam deposited NiO (black) and TiO₂ (blue), both deposited at 1 Å/s under a O_2 partial pressure of 1x10⁻⁴ mbar on top of a silicon oxide/silicon wafer.



Figure S3: XPS of NiO films before and after 15 minutes of UVO treatment. Solid black lines are measured sample. a) and b) are survey scans of NiO with background signal shown as dashed blue line, c) and d) high-resolution spectra of Ni2p peaks, and e) and f) high-resolution spectra of O1s peaks. O1s is characterised by 3 fitted component curves (red, blue, and orange dashed line), which are summed to make an envelope of fitted measured data

(dashed black line). Inset tables list the peak positions and any well-known identification of those peaks obtained from literature.



FigureS4: XPS of TiO_2 films before and after 15 minutes of UVO treatment. Solid black lines are measured sample. a) and b) are survey scans of TiO_2 with background signal shown as dashed blue line, c) and d) high-resolution spectra of Ti2p peaks, and e) and f) high-resolution spectra of O1s peaks. Ti2p is characterised by 2 fitted component curves (red, blue corresponding to $2p_{3/2}$ and $2p_{1/2}$ respectively), O1s is characterised by 3 fitted

component curves (red, blue, and orange dashed line). These components are summed to make an envelope of fitted measured data (dashed black line). Inset tables list the peak positions and any well-known identification of those peaks obtained from literature.



Figure S5: Current-voltage sweeps for PSCs with reactive e-beam deposited NiO HTM with a) 10 nm (black) and 20 nm (red) of NiO (deposited at 1 Å/s) with an AC MAPbI₃ active layer. b) 10nm of NiO deposited at a rate of 1 Å/s with a TC active layer, converted using a 100 °C (red) or alternative 80 °C vacuum (black) perovskite anneal. Dotted lines represent forward sweeps and solid lines represent reverse sweeps.



Figure S6: a) Current-voltage sweeps for p-i-n (black, red) and n-i-p (blue, purple) PSCs with 10 nm of reactive e-beam deposited NiO HTM and TiO₂ ETM respectively, using a TC $CsI_{0.05}((FAPbI_3)_{0.83}(MAPbBr_3)_{0.17})_{0.95}$ active layer. The perovskite precursor is either deposited directly onto the metal oxides (black, blue) or treated with UV-Ozone for 15 minutes (red, purple) prior to deposition of the perovskite. Dotted lines represent forward sweeps and solid lines represent reverse sweeps. b) Transmission spectra of 10 nm (black, red) and 100 nm (blue, purple) of NiO as deposited (black, blue), or with 15 minutes UVO treatment (red, purple). c) Transmission spectra of 10 nm (black, red) and 100 nm (black, blue), or with 15 minutes (red, purple).



Figure S7: X-ray diffraction patterns of 100nm thick TiO_2 films deposited onto quartz coated glass using the reactive e-beam process, before (black) and after (red) UVO treatment.

1x10 ⁻⁴	69.7 ±4.2	66.8 ± 2.6		1x10 ⁻⁴	0.99 ± 0.02	0.98 ± 0.03	
5x10 ⁻⁵	69.3 ± 1.5	68.2 ± 3.9		5x10 ⁻⁵	1.04 ± 0.01	0.99 ± 0.01	
TiO ₂							
PCE	0.5	2	10	Jsc	0.5	2	10
1.9x10 ⁻⁴	12.6 ± 1.1	11.9 ± 0.6		1.9x10 ⁻⁴	19.7 ± 1.06	20.0 ±0.5	
1x10 ⁻⁴	8.9 ± 3.0	11.0 ± 0.7	12.1 ± 1.0	1x10 ⁻⁴	18.6 ±1.8	19.5 ± 0.6	19.2 ± 0.9
5x10 ⁻⁵	12.1 ± 0.2	12.1 ± 0.8		5x10 ⁻⁵	20.0 ± 0.3	20.0 ± 0.3	
FF	0.5	2	10	V _{oc}	0.5	2	10
1.9x10 ⁻⁴	62. 5± 2.0	57.9 ± 1.4		1.9x10 ⁻⁴	1.02 ± 0.03	1.03 ± 0.02	
1x10 ⁻⁴	46.0 ±10.2	54.9 ± 2.1	60 ± 1.9	1x10 ⁻⁴	1.04 ± 0.02	1.03 ± 0.03	1.04 ± 0.02
5x10 ⁻⁵	58.2 ± 0.8	59.8 ± 1.7		5x10 ⁻⁵	1.04 ± 0.01	1.01 ± 0.04	

Table S1: Matrix of performance metrics (average \pm standard deviation) for p-i-n and n-i-p PSCs with reactive e-beam deposited NiO HTM and TiO₂ ETM respectively, using an 80 °C vacuum anneal for a TC CsI_{0.05}((FAPbI₃)_{0.83}(MAPbBr₃)_{0.17})_{0.95} perovskite active layer. The matrix is comprised of different O₂ partial pressures: 5x10⁻⁵ mbar, 1x10⁻⁴ and 1.9 x10⁻⁴ mbar and low (0.5 Å/s) and high (1.5 Å/s for NiO and 2 Å/s for TiO₂) evaporation rates for the metal oxides.

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