

Selective deposition of silver and copper films by condensation coefficient modulation

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Experimental Procedures

Master fabrication. A silicon master having an array of holes was produced by standard photolithography: a clean silicon wafer was spin coated with a uniform layer of photoresist (S1818, 300 rpm for 5 s and 4000 rpm for 20 s); after baking at 115°C it was exposed to ultraviolet light (130 mJ/cm²) under a chromium/quartz mask and developed in MF319 developer for 35 s. The patterned photoresist layer was used as a mask for the etching process and then was removed. The final structure was either an array of circular holes having a diameter $d \sim 2.5 \mu\text{m}$, spacing $s \sim 4 \mu\text{m}$ and height $h \sim 1.5 \mu\text{m}$ or grids having line width, $a \sim 0.5\text{-}1.4 \mu\text{m}$, spacing, $s \sim 13\text{-}18.5 \mu\text{m}$ and height $h \sim 1.7 \mu\text{m}$. The master was coated with a (1H,1H,2H,2H-perfluorooctyl)trichloro silane (FTS) layer deposited from the vapour phase at a low pressure to help replica detachment. This first step was performed just once and then the master could be replicated several times.

Polydimethylsiloxane stamp. The silicon master was replicated with polydimethylsiloxane (PDMS, Sylgard 184) to produce the stamp for the microcontact printing procedure. Base and curing agent were mixed (10:1 w/w), degassed and poured onto the master. After curing at $\sim 80^\circ\text{C}$ for $\sim 1\text{h}$ the polymerised stamp was gently peeled off the master.

Substrate cleaning. Glass substrates ($18 \times 18 \text{ mm}$) were cut from 1.2 mm thick glass microscope slides (Academy) and $18 \times 18 \text{ mm}$ PET substrates were cut from a roll (Hostapan GN4600, MITSUBISHI POLYESTER FILM). For devices $12 \times 12 \text{ mm}$ glass substrates with an 8 mm wide ITO strip were purchased from Thin Film Devices Inc. with an ITO stated thickness of $145 \text{ nm} \pm 10 \text{ nm}$ and a sheet resistance of $15 \pm 3 \Omega \text{ sq}^{-1}$. These types of substrates were cleaned by ultrasonic agitation in a diluted solution of surfactant, deionized water and IPA for 30 min each. Glass substrates were exposed to acetone vapours for 10 s, while PET substrates were rinsed with acetone. After drying with a stream of nitrogen, glass and PET slides were treated with UV/O cleaner respectively for 15 and 10 minutes.

Adhesive layer. Immediately after cleaning, the substrates were coated with a layer promoting metal adhesion (i.e. with a condensation coefficient of 1): (a) 10-15 nm molybdenum trioxide (denoted MoO_{3-x} because evaporated molybdenum oxide is partially reduced) were evaporated at $0.1\text{-}0.3 \text{ \AA/s}$ or (b) 0.3% w/v PEI/water solution was spin coated at 5000 rpm for 60 s, then substrates were annealed at 100°C for 20 minutes.¹

Micro-contact printing. The ink was a 1-3 mM FTS/toluene solution. It is fundamental to use laboratory grade toluene, inevitably containing a small amount of water allowing the FTS to polymerise in solution so that a thick layer of FTS is printed and not only a monolayer. The PDMS stamp was inked for 1 minute, then thoroughly dried with nitrogen and put in contact with the substrate for 40 s.

Metal evaporation. Ag and Cu were deposited directly onto the printed surfaces (thickness 15-85 nm, rate 1-6 Ångstrom per second).

Washing. To remove the silane layer from the holes samples were coated with a 0.2 M tetrabutylammonium fluoride/tetrahydrofuran solution left acting for a few seconds, then spun at

around 1000-2000 rpm and a few DI water droplets were dispensed onto the surface during spinning.

Morphological and elemental characterization of patterned samples. AFM imaging was performed using an Asylum Research MFP-3D operated in tapping mode to study the morphology of the printed substrates and the patterned metal layers. The height of the FTS features and the depth of the apertures was evaluated using WXS software². Scanning electron microscopy (SEM) imaging was performed using ZEISS Gemini500 with an accelerating voltage of typically 2-10 kV to evaluate the presence of metal particles inside the holes and the compactness of the continuous metal layer. EDXS spectra were recorded using an Oxford Instruments Si-Li detector unit on the SEM instrument, at an accelerating voltage of 6 or 10 keV. Transmission electron microscopy (TEM) specimens were prepared using conventional mechanical polishing followed by cryo-ion milling to electron transparency using Ar⁺ at 6 keV. A final low-energy milling step was performed at < 2 keV to minimize surface damage. The final thickness of samples was estimated to <30 nm. The structure of the samples were analysed using a JEOL ARM200F TEM/scanning TEM (STEM) with a Schottky gun operating at 200 kV. Annular dark-field (ADF) STEM measurement was performed with probe and image aberration CEOS correctors. ADFSTEM images were obtained using a JEOL annular field detector with a probe current of approximately 23 pA, a convergence semi-angle of ~25 mrad, and an inner angle of 45–50 mrad. An Oxford Instruments X-MaxN 100TLE windowless silicon drift detector (SSD) was used to perform STEM-EDX analysis. Far-field total transmittance of patterned metal films were measured over the wavelength range of 300–1100 nm using 150 mm Spectralon Integrating Sphere coupled to PerkinElmer LAMBDA high performance series of UV/vis spectrometer. The incident beam passed through the substrate first.

Characterization of uniform films on 3.2 cm² substrates. Far-field total transmittance of metal films on glass were measured over the wavelength range of 300–1100 nm using 150 mm Spectralon Integrating Sphere coupled to PerkinElmer LAMBDA high performance series of UV/vis spectrometer. The incident beam passed through the substrate first. Scanning electron microscopy (SEM) imaging was performed using ZEISS Gemini 500 with an accelerating voltage of typically 2-10 kV to evaluate the presence of metal on the spin coated Si substrates. EDXS spectra were recorded using an Oxford Instruments Si-Li detector unit on the SEM instrument, at an accelerating voltage of 10 keV. The surface energy was computed from the values of the static contact angles of 1-2 μ L DI water and hexadecane droplets measured with a drop shape analysis system (Krüss, DSA100). The total surface energy γ , given by the sum of dispersive (superscript *d*) and polar (superscript *p*) components, is derived from equation 1^{3,4}:

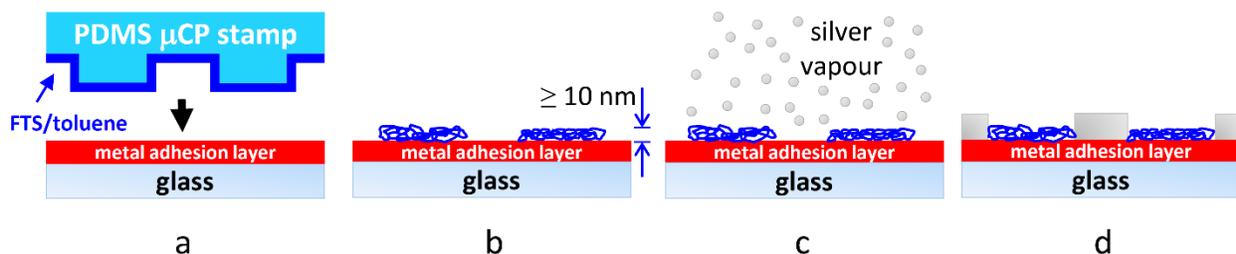
$$\left((1 + \cos \theta)(\gamma_i^d + \gamma_i^p) \right) = 2 \left(\sqrt{\gamma_i^d \gamma_s^d} + \sqrt{\gamma_i^p \gamma_s^p} \right) \quad (1)$$

where θ is the static contact angle of the probe liquid, the subscripts *i* and *s* refer to the probe liquid and the surface respectively.

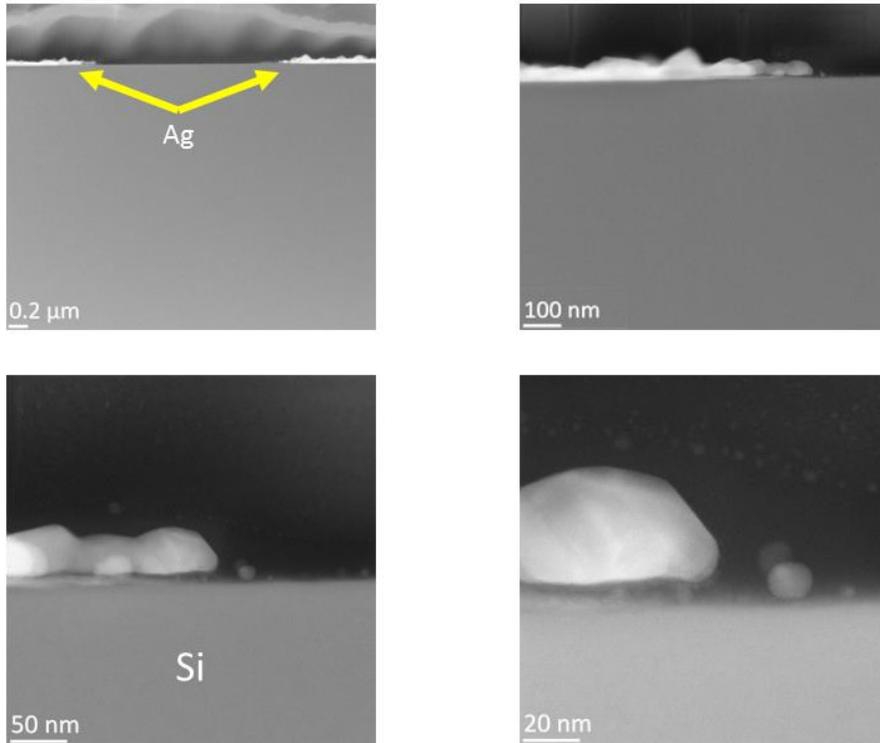
Fabrication of semitransparent OPV Devices. PEDOT:PSS (poly(3,4-ethylenedioxythiophene) Al 4083 by Ossila) was spincoated on ITO glass slides at 4000 rpm for 30 seconds and the annealed

at a temperature higher than 100°C for at least 10 minutes. PCE12 (Poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)], Ossila), ITIC-m (3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene, Ossila) and PC₇₀BM ([6,6]-Phenyl-C71-butyric acid methyl ester, Ossila) were mixed in 1:1:0.2 mass ratio to make a 20 mg mL⁻¹ solution in chlorobenzene (99%) and 1,8-diiodooctane (1%) and deposited by spin-coating from a static start at 2000 rpm for 60 s to form the photoactive layer followed by annealing at 110 °C for 10 minutes. A ZnO ink (5.6% w/v) in IPA was purchased from Infinity PV and a diluted solution (0.7% w/v) was spun at 1000 rpm for 60 s followed by annealing at 120 °C for 10 min. These coated substrates were micro-contact printed with a freshly made FTS/toluene 1mM solution with a PDMS stamp featuring a regular array of circular pillars. The printing was performed in air by keeping the sample exposure as short as possible. Reference devices were exposed to air for the same time. After printing a 17 nm thick Ag layer was thermal evaporated at 1 Å/s through a shadow mask to give an electrode area of 0.06 cm². The same 0.7% w/v ZnO/IPA ink as previously used was spun at 1000 rpm for 60 s followed by annealing at 80 °C for 10 min. Finally a flat PDMS film (~200 μm thick) was laminated on the ZnO layer after exposure to UV/O₃ for 10 minutes.

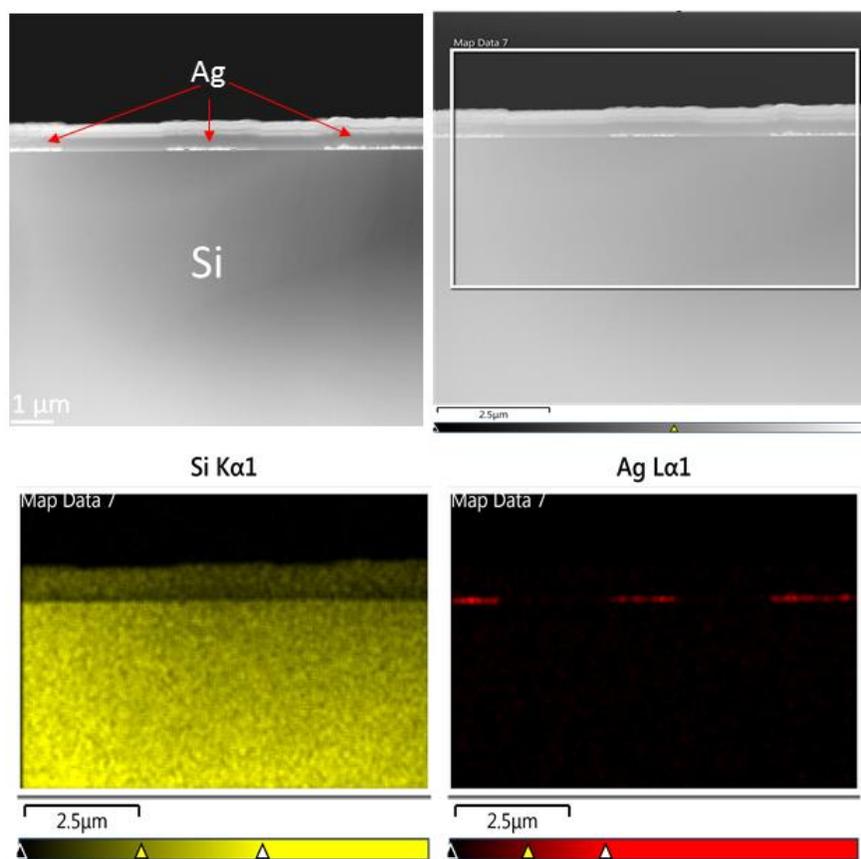
Characterization of OPV Devices. Current density–voltage testing was performed in the dark and under 1 sun simulated solar illumination using a Keithley 2400 source measurement unit and a custom Labview interface using an ABET technologies Sun 2000 Solar Simulator. The intensity was set to 100 mW cm⁻² over the AM 1.5G solar spectrum. The light source was calibrated using a calibrated silicon diode. OPV devices were measured through a mask having a pixel area of 0.0288 cm² when the ITO side was shined and without any mask when light was shined on the PDMS side.



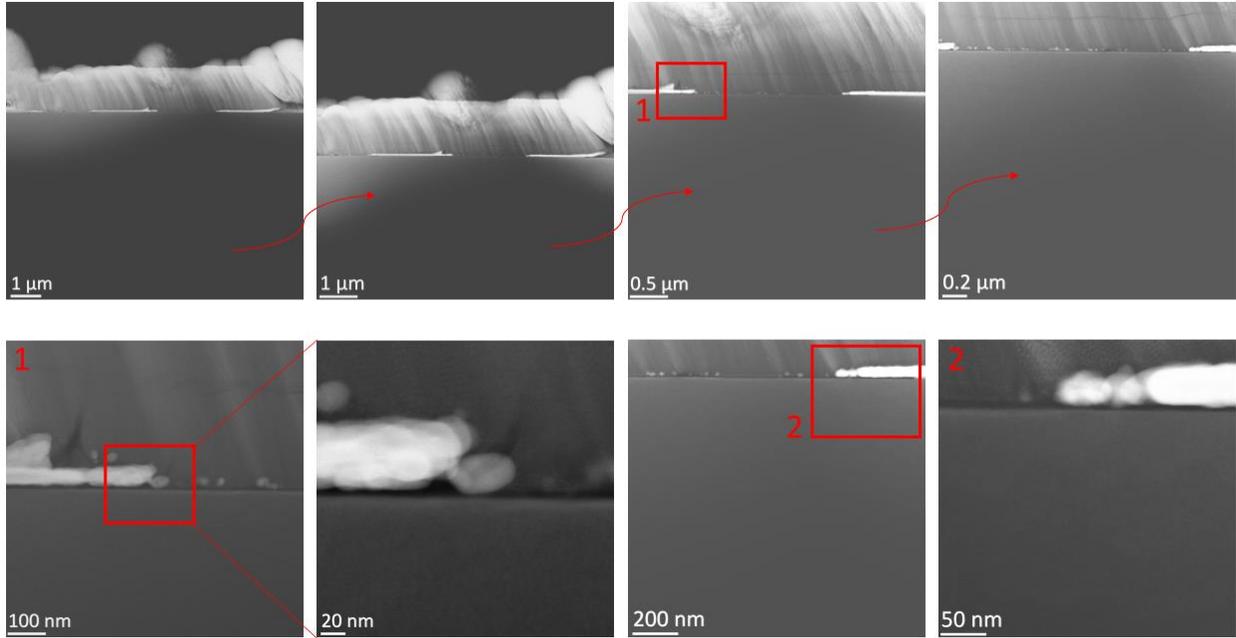
Supplementary Fig. 1. Schematic of selective metal deposition process based on a micro-contact printed organofluorine layer: a) A polydimethylsiloxane (PDMS) stamp having micron-sized pillars is inked with a mM (1H,1H,2H,2H-perfluorooctyl)trichlorosilane (FTS) solution and brought into contact with the substrate coated with a high *C* adhesive layer for the metal (molybdenum oxide or polyethylenimine); b) A printed pattern of FTS with thickness of ≥ 10 nm; c) Metal deposition over the whole substrate by vacuum thermal evaporation; d) Selective condensation of silver only where the FTS layer is not.



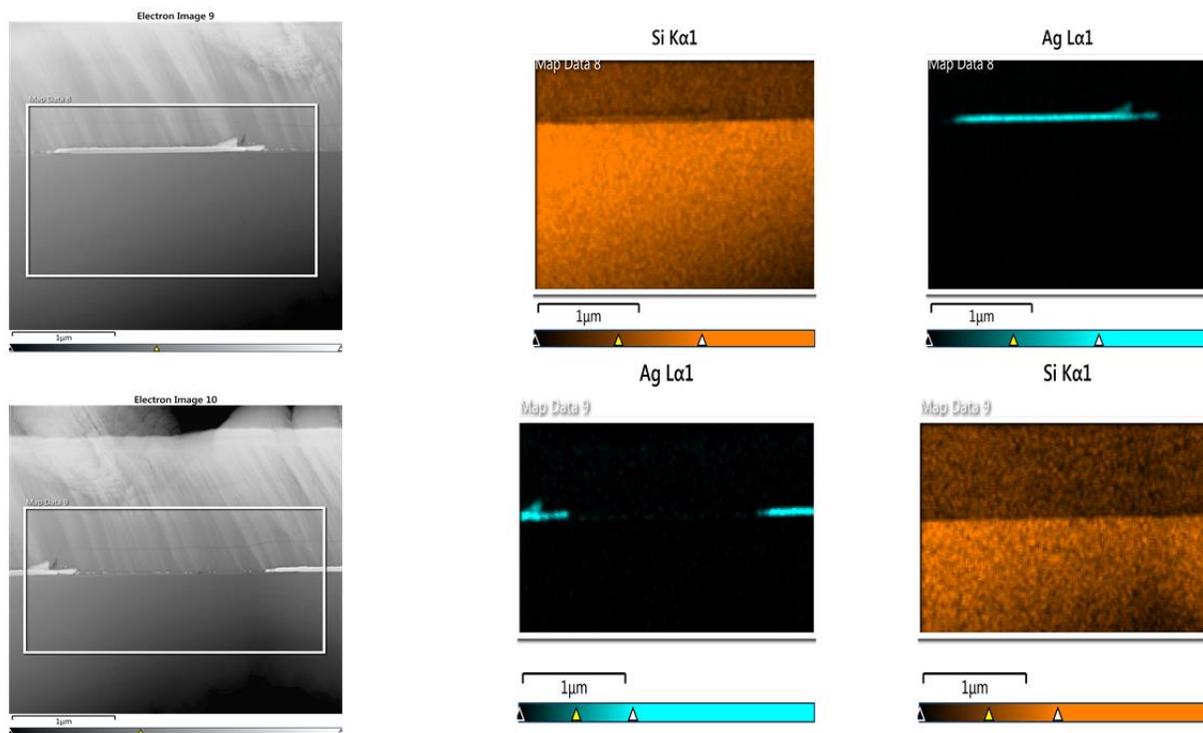
Supplementary Fig. 2. Cross-sectional Scanning TEM (STEM) images of a 2.5 μm aperture in a 15 nm thick Ag film on a MoO_{3-x} (10 nm)|Si substrate fabricated using a micro-contact printed FTS selective deposition layer.



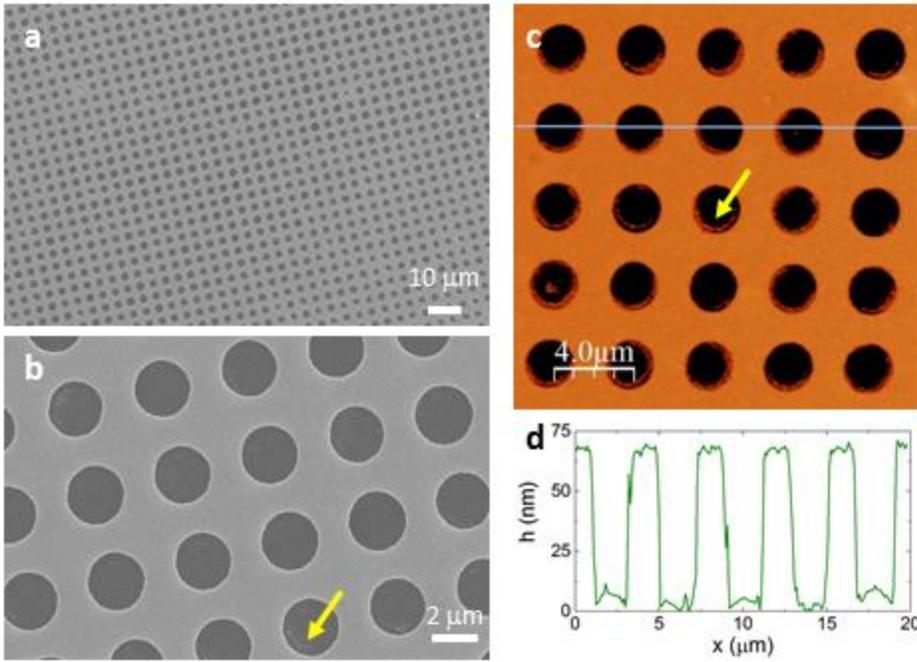
Supplementary Fig. S3. Cross-sectional Scanning TEM (STEM) images and corresponding energy dispersive X-ray spectroscopy (EDXS) element maps of a 2.5 μm aperture in a 15 nm thick Ag film on a MoO_{3-x} (10 nm)|Si substrate fabricated using a micro-contact printed FTS selective deposition layer.



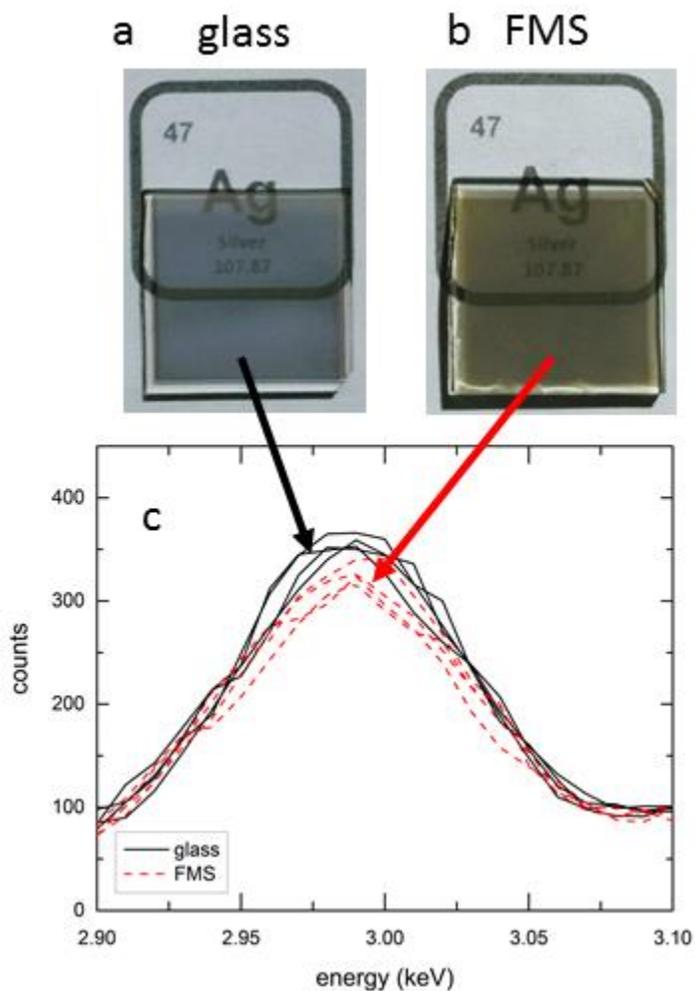
Supplementary Fig. 4. Cross-sectional Scanning TEM (STEM) images of a 2.5 μm aperture in a 50 nm thick Ag film on a MoO_{3-x} (10 nm)|Si substrate fabricated using a micro-contact printed FTS selective deposition layer.



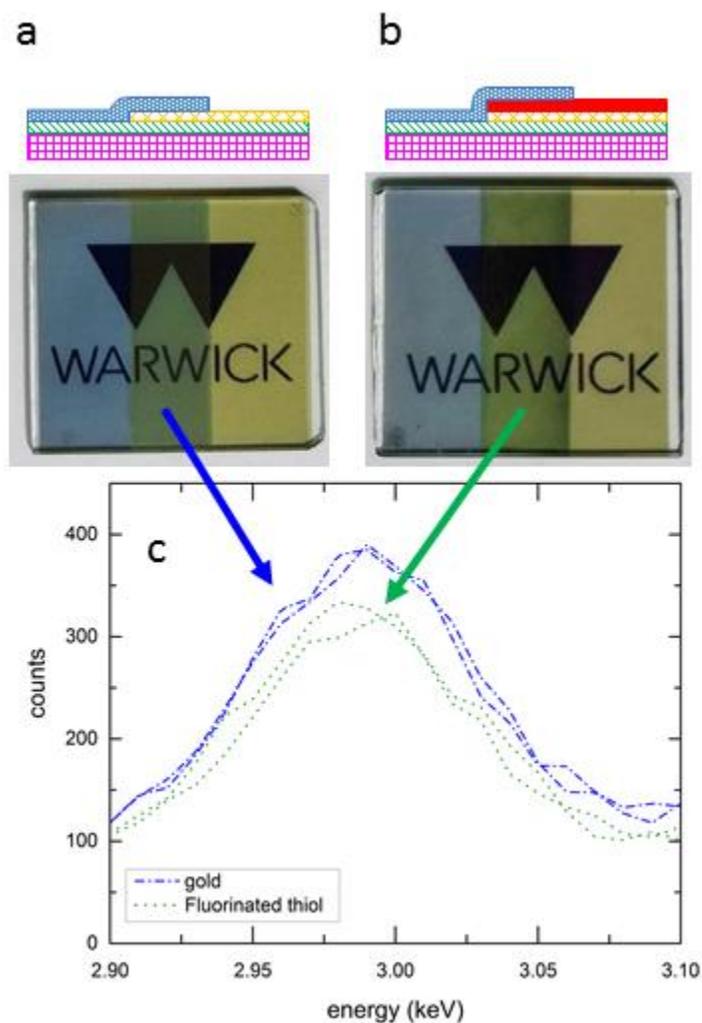
Supplementary Fig. 5. Cross-sectional Scanning TEM (STEM) images and corresponding energy dispersive X-ray spectroscopy (EDXS) element maps of a 2.5 μm aperture in a 50 nm thick Ag film on a MoO_{3-x} (10 nm)|Si substrate fabricated using a micro-contact printed FTS selective deposition layer.



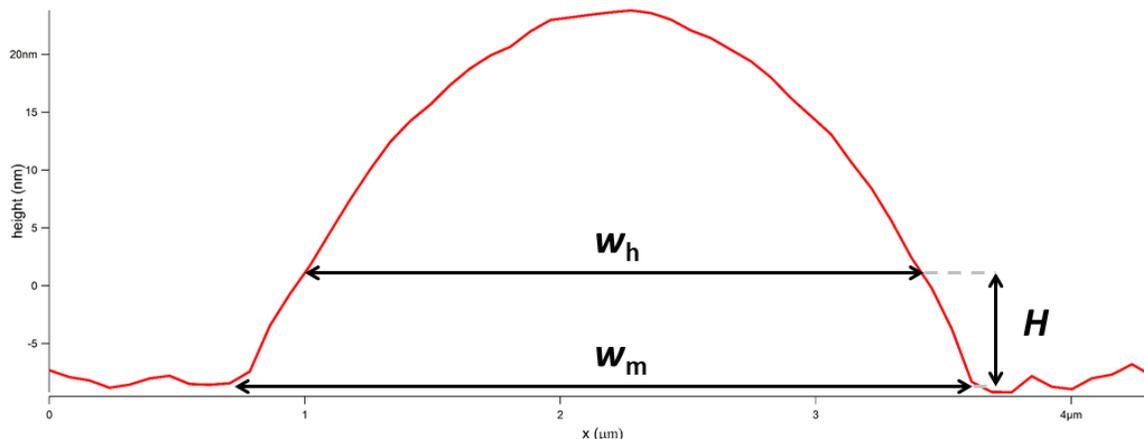
Supplementary Fig. 6. Characterization of 2.5 μm diameter apertures in a Ag film with a nominal thickness of 85 nm supported on a MoO_{3-x} (10 nm) glass substrate, fabricated using a micro-contact printed FTS selective deposition layer. **a-b**, SEM images. **c**, AFM scan and **d**, height profile along the line drawn in image **c**.



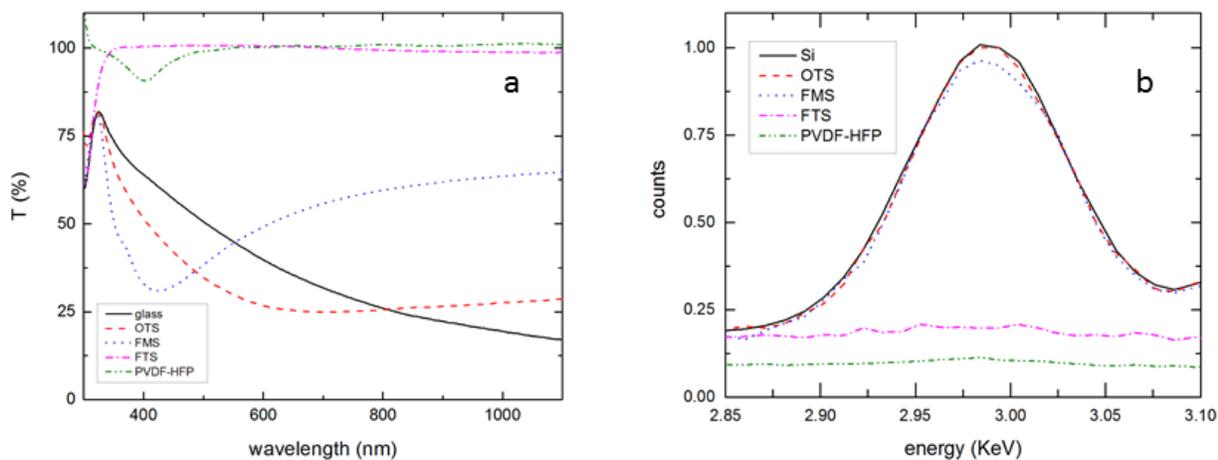
Supplementary Fig. 7. Silver evaporation onto fluorinated silane monolayers on glass. a) Photograph of 15 nm Ag evaporated onto a glass substrate. b) Photograph of 15 nm Ag evaporated onto a glass substrate derivatized with a monolayer of 1H,1H,2H,2H-perfluorooctyldimethylchlorosilane (FMS). c) EDXS for the Ag peak acquired from samples a) and b). It is evident from the photographs and from comparison of the EDXS spectra that a monolayer of fluorinated silane is not sufficient to block Ag condensation.



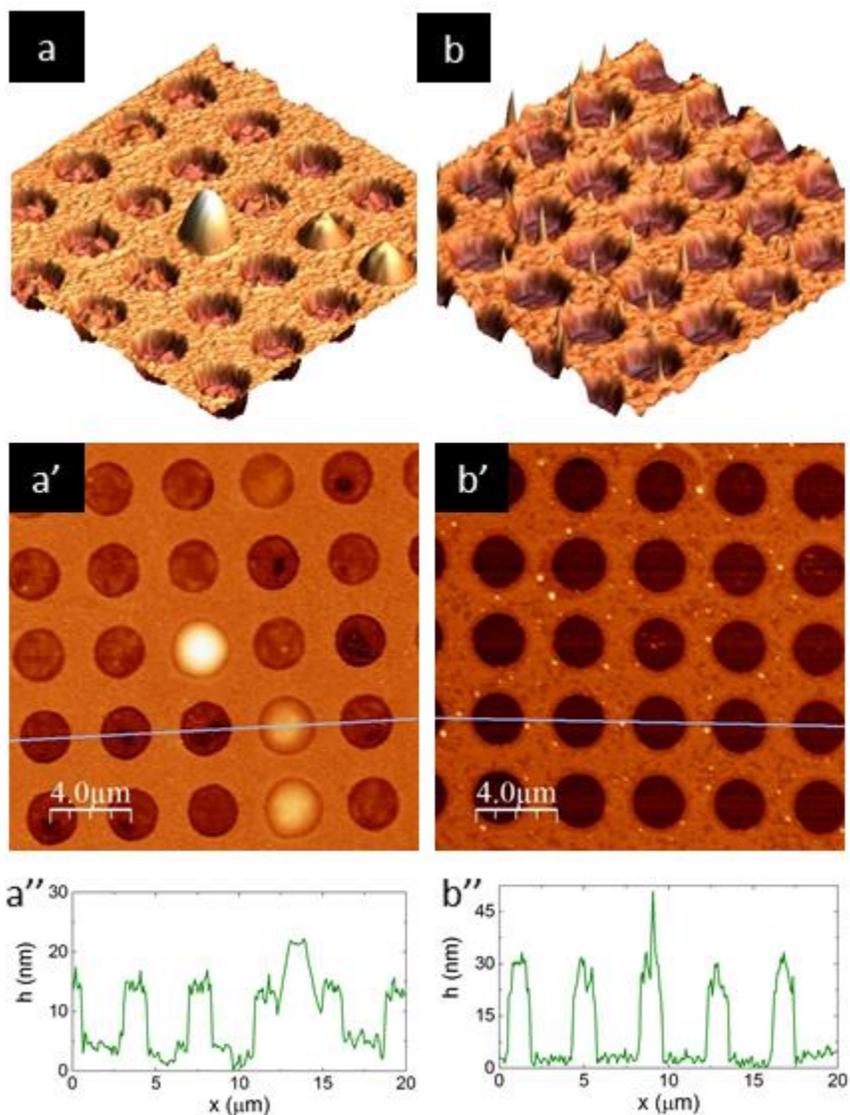
Supplementary Fig. 8. Silver evaporation onto fluorinated thiol monolayers on gold. a) and b) include schematic cross-sections and photographs of a pair of samples produced to test whether a single fluorinated monolayer is enough to suppress silver condensation. Both a) and b) comprise a glass substrate (purple in the sketch) functionalized with a mixed molecular adhesive layer ([(3-mercaptopropyl) trimethoxysilane (MPTMS) and (3aminopropyl)trimethoxysilane (APTMS))] (green in the sketch) to facilitate deposition of an optically thin gold film (yellow in the sketch). The rightmost two-thirds of both a) and b) were coated with a 11 nm thick layer of gold by thermal evaporation (yellow in the sketch). The whole of sample b) was then dipped in a 1 mM ethanol solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol forming a densely packed fluorinated monolayer (red in the sketch) on the gold film. Finally, the leftmost two-thirds of both samples a) and b) were coated with 12 nm of silver as measured by a quartz crystal microbalance adjacent to the samples. By comparing pictures a) and b) it is evident (already by eye) that Ag is deposited both on the pristine gold and on the gold film coated with the fluorinated thiol monolayer, since the central stripe is green in both samples a) and b). c) EDXS Ag peak acquired from the central stripes of samples a) and b). The intensity of both peaks is similar meaning that a single fluorinated thiol monolayer is not effective to prevent Ag deposition.



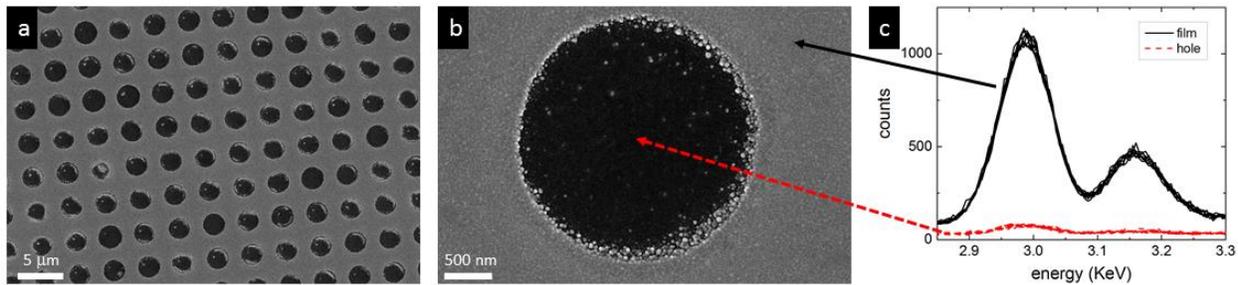
Supplementary Fig. 9. Typical profile of an FTS mound (measured using an AFM) used to evaluate the FTS thickness required to prevent Ag and Cu deposition (H) by considering the width of the printed mounds (w_m) and the width of the holes formed after metal evaporation (w_h). According to this method the critical thickness is 8.4 ± 1.6 nm (average and standard deviation from a sample of 75).



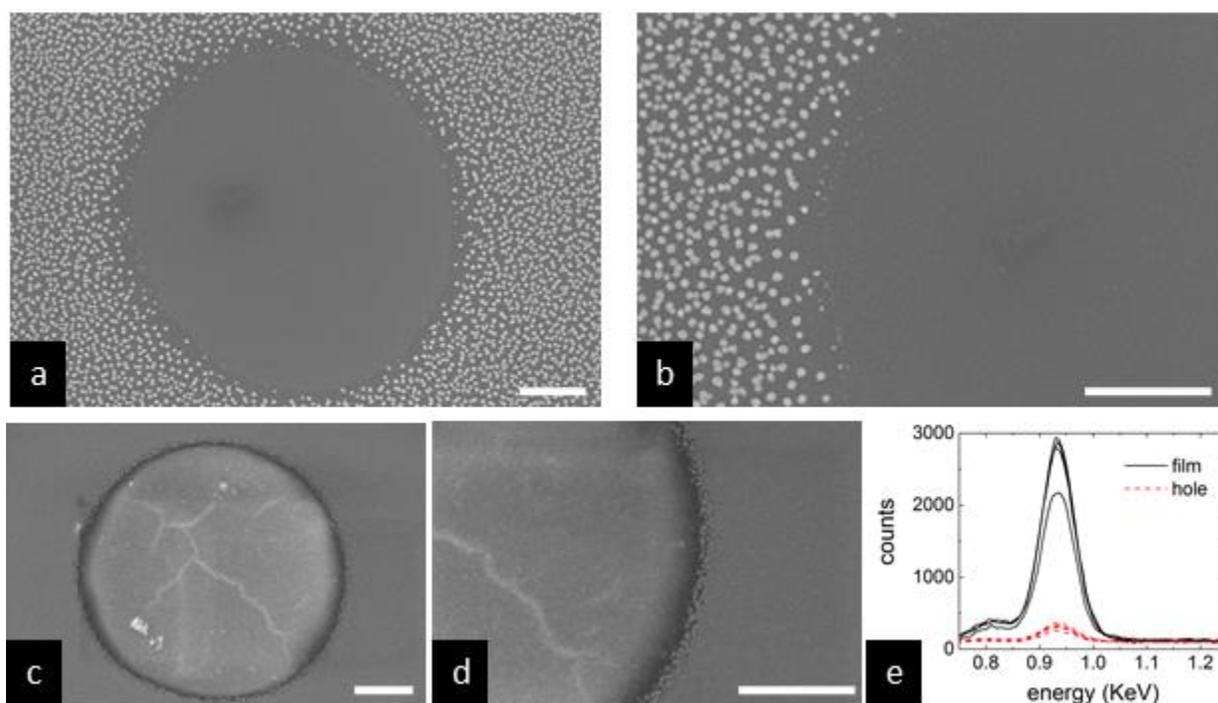
Supplementary Fig. 10. Characterisation of 15 nm Ag evaporated onto glass and silicon substrates with: (dashed red) a spin cast OTS film with thickness > 10 nm; (dotted blue) a monolayer of 1H,1H,2H,2H-perfluorooctyldimethylchlorosilane (FMS); (dash/dotted pink) a spin cast FTS film with thickness ≥ 10 nm; (dashed /dotted green) a spin cast PVDF-HFP film with thickness ≥ 10 nm. a) Transmittance spectra referenced to bare glass. b) Normalised EDXS Ag peak.



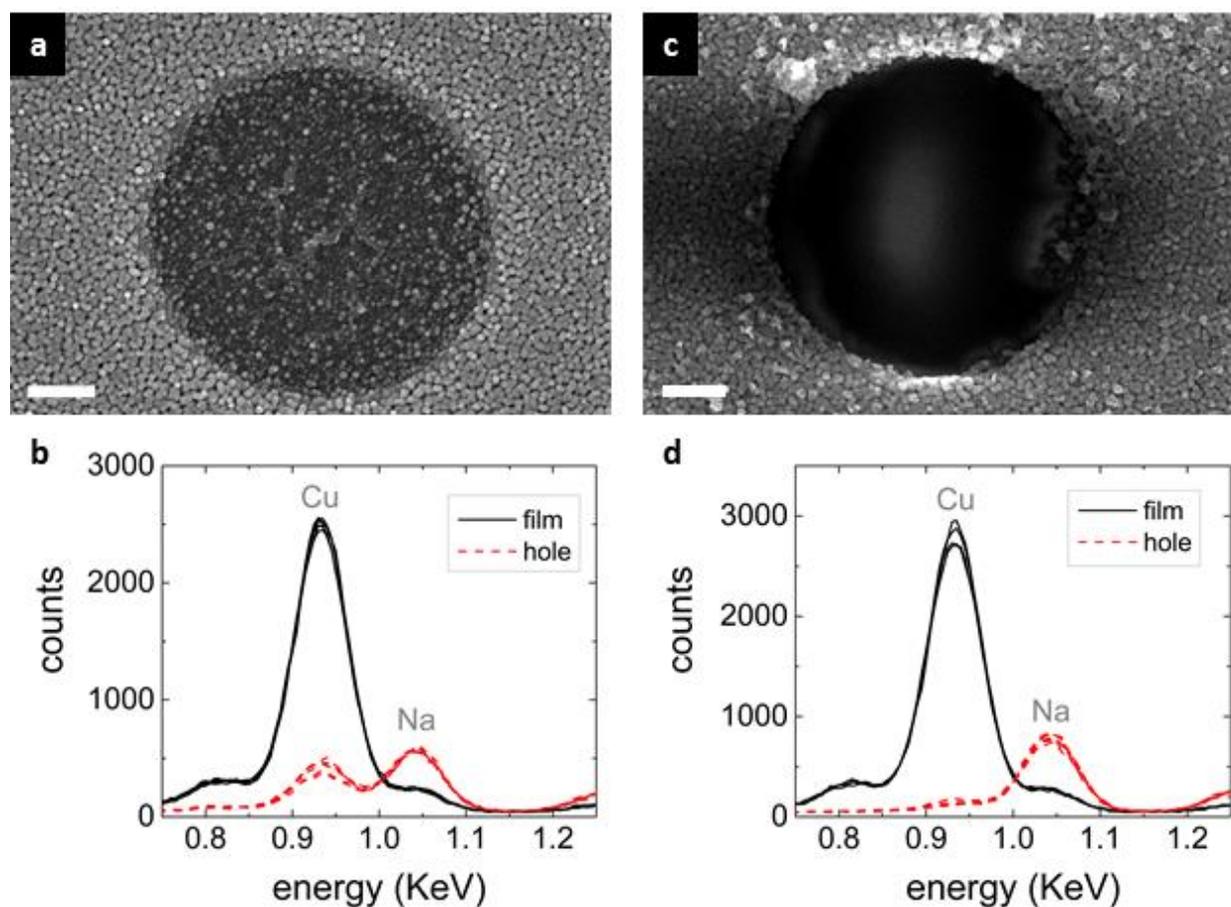
Supplementary Fig. 11. Atomic force microscope (AFM) images of a patterned 15 nm thick Ag layer. a) after metal evaporation; b) after rinsing with tetrabutylammonium fluoride/tetrahydrofuran and water. Cross-sections a'' and b'' are the cross-sectional profiles along the line drawn on the corresponding image (a' and b'). This washing process removes both the silane and underlying MoO_{3-x} layer and so the depth of the holes is equal to the thickness of the evaporated MoO_{3-x} and Ag films after rinsing.



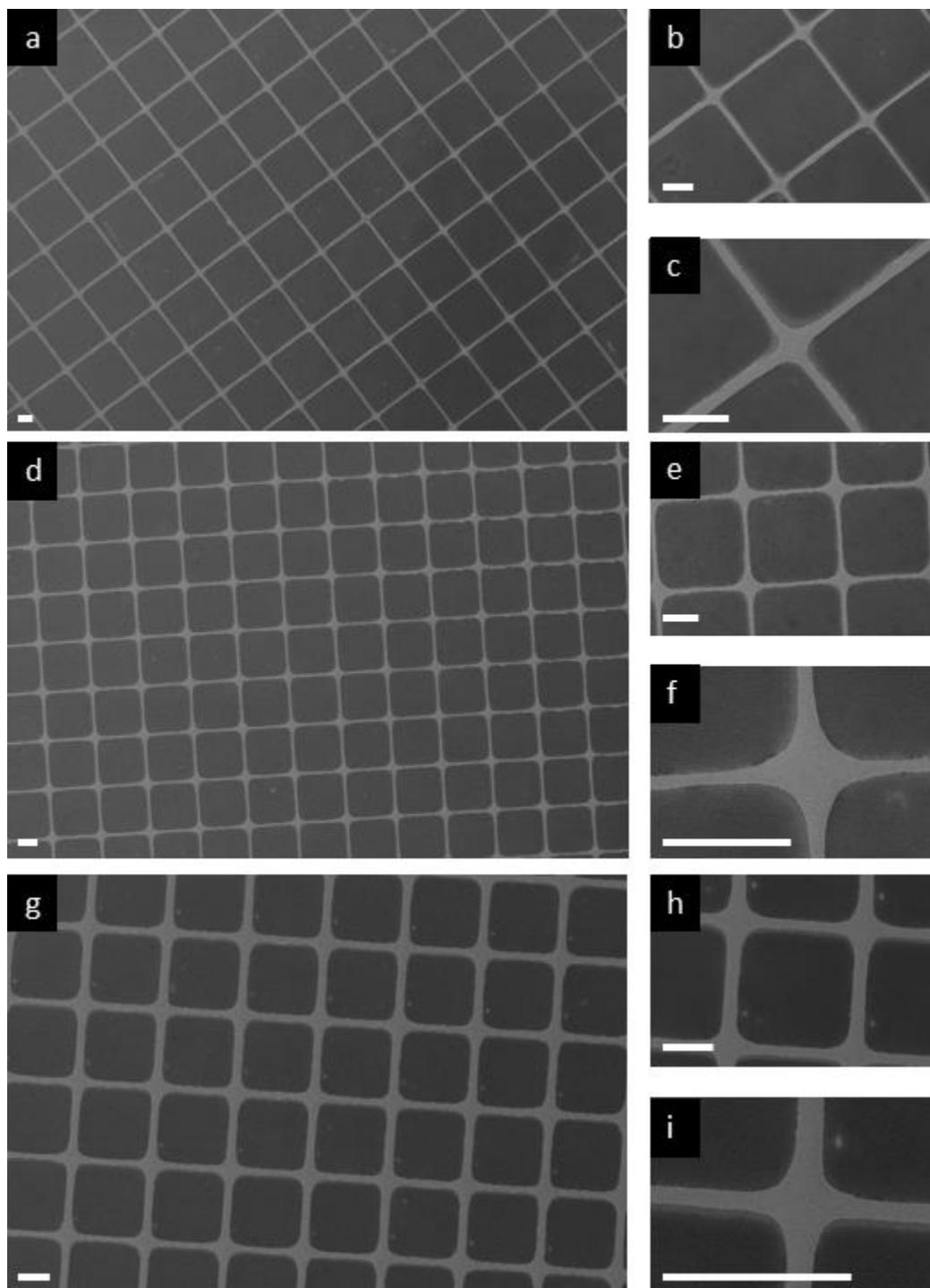
Supplementary Fig. 12. Characterization of a 70 nm Ag film deposited at 5.5 Angstroms per second onto a MoO_{3-x} | glass with a printed FTS layer. a) and b) SEM images c) Ag peaks from the EDXS spectra acquired either from within an aperture (dashed red) or from the continuous metal region (continuous black).



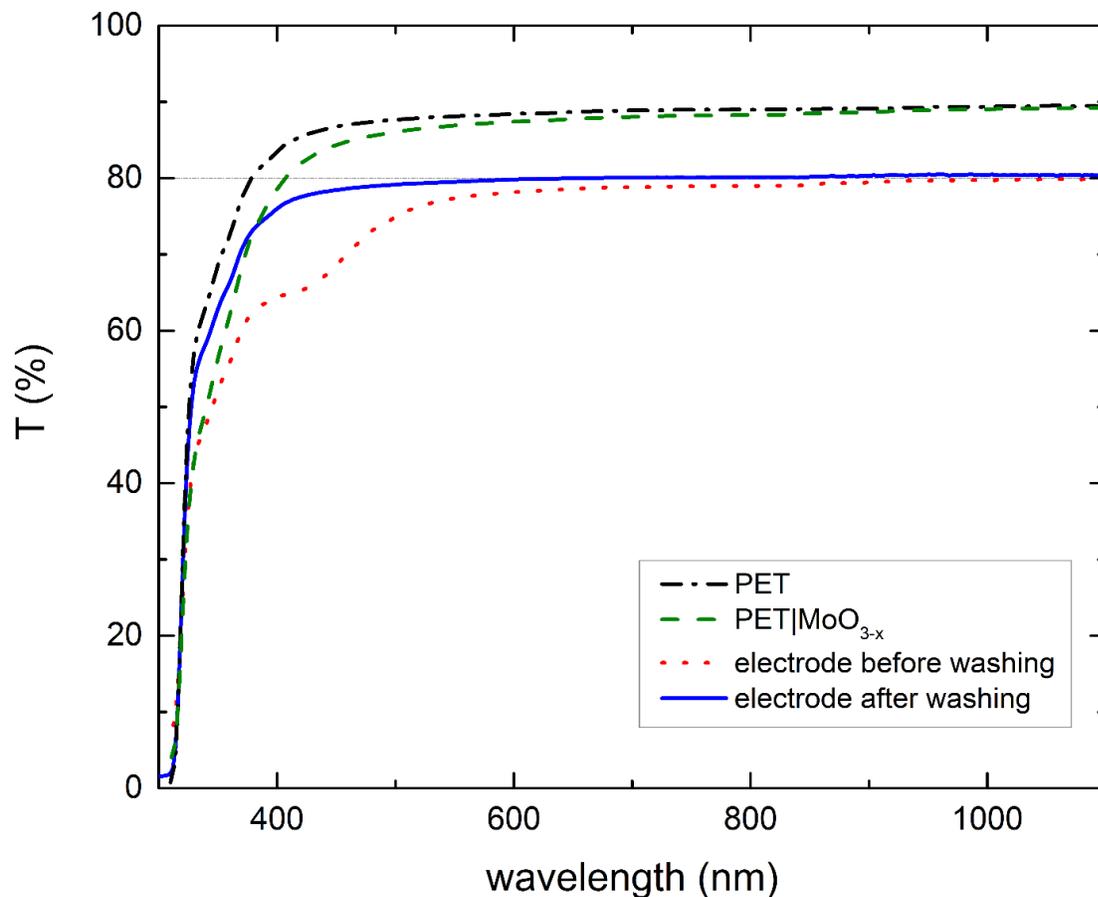
Supplementary Fig. 13. Selective deposition of Cu on various substrates using a micro-contact printed (perfluorooctyl)trichlorosilane (FTS) layer. a, b, SEM images of a 10 nm Cu film deposited by thermal evaporation onto a MoO_{3-x} / glass printed with an FTS pattern comprising a regular array of circles. c, d, SEM images of 15 nm Cu evaporated onto micro-contact printed PEI coated PET substrate. e, Spatially resolved EDAX elemental analysis probing the Cu content inside and outside an aperture in a 15 nm thick Cu film evaporated on a PEI / PET substrate. Scale bars correspond to 500 nm.



Supplementary Fig. 14. Characterization of apertures in a Cu film with nominal thickness 85 nm supported on a MoO_{3-x} (10 nm)|glass substrate printed with FTS using microcontact printing. a) SEM image. b) Spatially resolved EDAX elemental analysis probing the Cu content inside and outside an aperture. c) SEM image after washing with a 0.2M tetrabutylammoniumfluoride/THF solution and water. d) Spatially resolved EDAX elemental analysis probing the Cu content inside and outside an aperture after sample washing. Scale bars correspond to 500 nm.

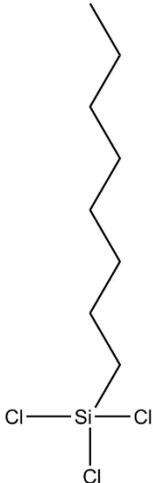
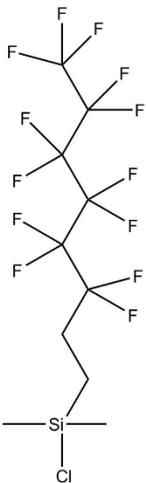
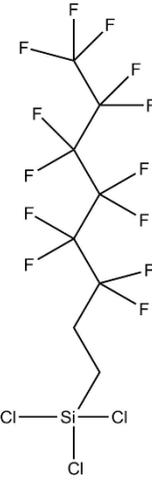
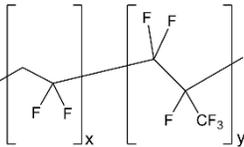
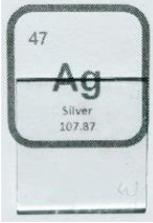


Supplementary Fig. 15. SEM images of 40 nm thick Ag grids supported on a MoO_{3-x} (10 nm)|PET flexible substrate printed with FTS using micro-contact printing. Scale bars: 5 μm .



Supplementary Fig. 16. Transmittance spectra of a grid electrode produced by printing an FTS pattern of squares onto a MoO_{3-x} (10nm) | PET substrate and evaporating 50 nm Ag. The grid lines are 1 μm wide and 50 nm thick. The grid spacing is 18.5 μm which corresponds to 10% metal coverage. These electrodes have an average absolute transparency across the wavelength range 400-1100 nm of ~78% although 12% of the incident light is attenuated by the PET substrate and MoO_{3-x} adhesion layer due to reflection and absorption.

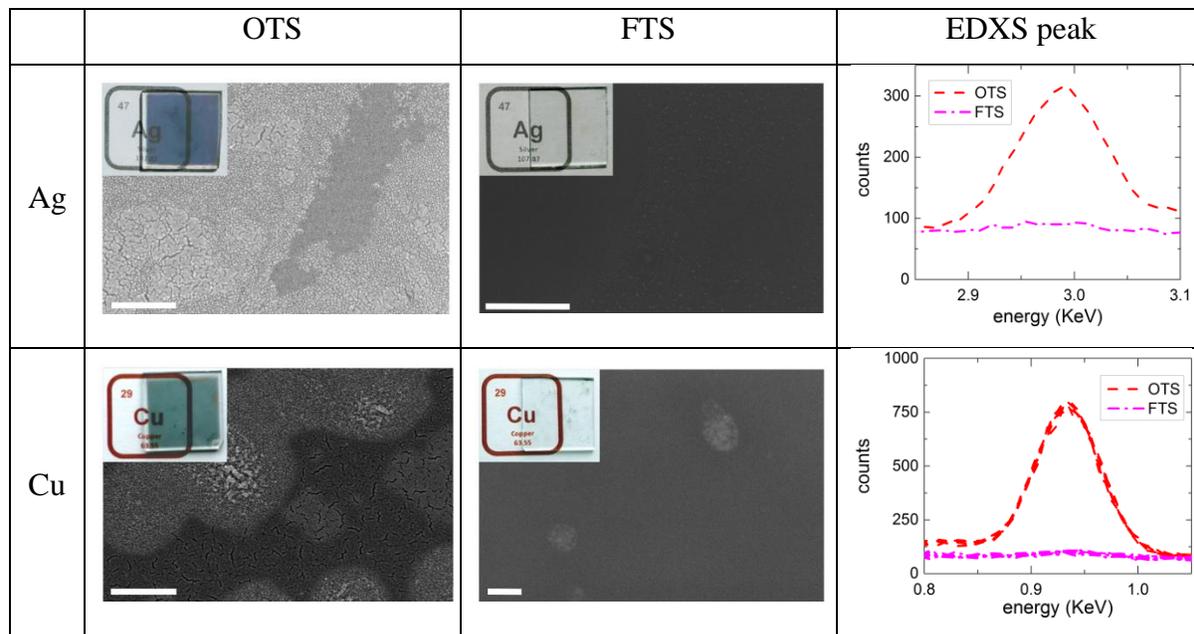
Supplementary Table 1. Surface energy of 3.2 cm² glass substrates coated with different organic layers, and corresponding photographs after vacuum deposition of Ag equivalent to a nominal thickness of 15 nm. OTS (octyltrichlorosilane) and FTS ((1H,1H,2H,2H-perfluorooctyl)trichlorosilane) were deposited by spin coating from a 1:3 v/v silane/toluene solution; PVDF-HFP (poly(vinylidene fluoride-co-hexafluoropropylene), (-CH₂CF₂-)_x[-CF₂CF(CF₃)-]_y) was deposited by spin and drop of a 100 mg/mL polymer/acetone solution and FMS (1H,1H,2H,2H-perfluorooctyldimethylchlorosilane) was deposited from the vapour phase. The colour of optically thin silver (and copper) films depends strongly on the film morphology, due to excitation of localised surface plasmonic resonant excitations in the visible part of the spectrum that occur when the metal film is on non-uniform thickness. The colour of silver films can range from blue/green to brown/red depending on the morphology.

	glass	OTS	FMS (monolayer)	FTS	PVDF-HFP
Molecule					
Surface energy (mJ m ⁻²)		27.1±0.5	21.3±0.7	13.2±0.9	30±1
sample					

Supplementary Table 2. Diameter of printed FTS mounds (w_m) and holes in evaporated Ag and Cu films (w_h) determined from AFM image analysis.

	Width (μm)	Standard deviation (μm)	Number of features
FTS mounds	2.61	0.11	140
Holes in 15 nm thick Ag	2.46	0.14	60
Holes in 85 nm thick Ag	2.45	0.09	70
Holes in 15 nm thick Cu	2.43	0.09	100
Holes in 85 nm thick Cu	2.50	0.09	115

Supplementary Table 3. HR-SEM images and corresponding EDXS spectra of silicon substrates coated with a > 10 nm thick layer of trichlorosilane (OTS or FTS) deposited from a concentrated toluene solution, followed by thermal evaporation of 15 nm Cu or Ag. Scale bars = 500 nm. Insets: Photographs of 3.2 cm^2 glass substrates coated with a > 10 nm thick layer of trichlorosilane (OTS or FTS) deposited from a concentrated toluene solution, followed by 15 nm metal.



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