ADVANCED MATERIALS

Supporting Information

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Monocrystalline Nanopatterns Made by Nanocube Assembly and Epitaxy

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SUPPLEMENTARY INFORMATIONS

All reagents were purchased from Sigma Aldrich if not stated otherwise.

Nanocubes synthesis

Nanocubes were synthesized according to a previously reported procedure *[1]*. Briefly, 5 mL of a 0.235 M solution of AgNO3 was prepared in pentanediol, and 40 µl of 0.043 M CuCl2 in pentanediol was added. A solution of 20 g/L of PVP (molecular weight ~ 55.000) was prepared in pentanediol. 500 µl of the AgNO3 solution was added every minute to 10 mL of pentanediol at 195 ºC in an oil bath, followed by the injection of 320 µL of PVP every 30 s. The reaction was stopped after 5 cycles by placing the reaction vial in an ice bath, to yield monodisperse nanocubes of ~75 nm in size. The nanocube solution was washed several times in ethanol and water, passed one time through 450 nm filters and four times through 220 nm filters (Durapore). The solution was then washed four more times in ethanol and re-dispersed in ~2 mL of ethanol.

Template fabrication

A nanopattern consisting of 500 µm long lines with widths in the range 50-150 nm was defined by electron beam lithography on an HSQ layer (30 nm on a silicon substrate) that was used as an etch mask to produce 50 nm high lines of silicon. The etch was performed in presence of O_2 and HBr (Oxford PlasmaPro100 Cobra). After HSQ removal in 5% HF, the silicon master was then oxidized with oxygen plasma (Diener Zepto) for 5 min, and then silanized with 1H, 1H, 2H, 2H-Perfluoro-octyltriethoxysilane in a desiccator for 24 h, in the presence of traces of acetic acid, to make the substrate hydrophobic *[2]*. A Polydimethylsiloxane (PDMS) solution (Wacker Elastosil RT 601 A) was prepared in a 10:1 ratio with respect to the curing agent, and 50 µL was added to the hydrophobic substrate. A 1 mm thick glass slide that was silanized with (3-Aminopropyl)triethoxysilane was placed on top of the PDMS liquid solution. The curing was carried out for 1h at 80 ºC. After careful removal of the silicon master, the PDMS-glass substrate containing the negative pattern of the silicon master was placed in ethanol for several days before being used, to clean from unreacted species *[2]*.

Assembly

A home-built setup was used to perform the assembly of nanocubes on the PDMS template, in a similar fashion to previously reported systems *[3]*. The assembly solution was prepared by diluting the nanocube solution (8 µL) in 88 µL of ethanol and 8 µL of deionized water. Briefly, 15 µL of the assembly solution was added to the template placed on a temperature controller. A glass slide connected to a motorized linear stage was placed on the nanocube solution at a distance of ~300-500 µm from the template surface. The glass slide was pulled at a speed of 50-100 µm/min. The temperature was kept in the range 25-28 ºC.

Transfer

After assembly in the PDMS trenches was complete, the transfer substrate was placed on the temperature controller, and 15 µL of ethanol was added. The PDMS template containing the assembled nanocubes was approached to the new substrate until full contact was achieved. The temperature was raised to 50-80 ºC, and the PDMS template was slowly removed, while the assembled nanocubes were transferred to the new substrate. This is possible because of the low surface energy of PDMS, compared to many substrates of interest such as silicon dioxide.

Chemical welding

After the nanocubes were transferred, the substrate was placed for 5 minutes in acetone and subsequently in isopropanol for 5 minutes, rinsed in water and blow-dried with N_2, to remove any residuals. The substrate was then exposed to 0.1 M $NaBH_4$ for 15 minutes and rinsed in water, to remove any PVP left on the nanocube surface after the synthesis *[4]*. A solution containing diamminesilver(I) complex was prepared as the silver source and a glucose/methanol solution as the reducing agent, according to a previously published protocol *[5]*. 100 µL of the silver complex diluted in a 1:10 ratio in water was added to 1086 µL of deionized water. 63 µL of the glucose/ methanol solution was added and then vortexed for 10 s (welding solution). The substrate was then placed in the growth solution for 90 s. The substrate was removed, rinsed in water and dried under a stream of N_2. The substrate was exposed to a quick RTA treatment *[5]* for 5 s to release any stress formed at the interface due to slight nanocube misalignment. Three 1 mm-thick glass slides were used to space the substrate with assembled nanocubes from the support substrate, to reduce the conductive heat. The temperature reached during the short RTA process, was estimated by sandwiching a thermocouple between two silicon substrates lying on three 1 mm-thick glass slides. A value of ~400 °C was measured over a time of 3 s.

Alternative welding conditions are reported in fig. S1, showing the effect on the nanocube shape. Fig. S1A shows the results of welding performed in four steps, alternated by rinsing and drying of the samples, with a four times lower silver precursor concentration (exposure time 1 minute per step; without RTA). Figure S1B shows nanocube welding in one step at an exposure time of 60 s (no RTA). Figure S1C shows the result of one-step nanocube welding performed at ten times larger Ag precursor concentration (30 s, no RTA). Figure S1D shows segments of assembled Ag nanocubes before and after welding with the optimized procedure described above.

Si_3N_4 membrane fabrication

A silicon wafer with 30 nm low-stress Si_3N_4 (Silchem) was processed to obtain backside etch windows by photolithography and plasma etching. Subsequently, the wafers are immersed in KOH etching solution (30%) at 60 °C until all the silicon is removed between the opening of the backside nitride mask and the continuous front side nitride film. The procedure results in squared suspended Si_3N_4 membranes in between a rigid silicon frame.

TEM characterization

Bright-field high-resolution transmission electron microscopy (HR-TEM) analysis was performed with a cubed FEI Titan equipped with aberration correction for imaging and operated at 300 kV.

Device fabrication

UV lithography was employed to fabricate electrode pads to measure the electrical conductivity of welded lines. A double layer of LOR1A (200 nm) - SU1805 (800 nm) was spun on the substrate before exposure. A positive mask with electrode pads was employed (fig. S4). After developing, a 150 nm layer of silver was thermally evaporated. After lift-off in NMP at 60 ºC, the devices were measured with an Agilent B2902A source/measure unit.

CL measurements and data analysis

Cathodoluminescence imaging spectroscopy measurements were performed in a FEI XL-30 SFEG (30 keV electron beam, ~1 nA current) equipped with a home-built CL system *[6]*. An aluminium parabolic mirror collects the emitted light and directs it outside of the microscope to an optical setup equipped with a liquid-nitrogen-cooled back-illuminated silicon CCD array (Princeton Instruments Spec-10 100B). We correct for the system response of the setup by using transition radiation from single crystal aluminium as a reference *[6]*. A linear polarizer (Moxtek PUBB01A50M) in the optical beam path is used to obtain polarization-resolved measurements. To account for the change in polarization upon reflection from the curved mirror, we spatially filter the emission with a 3 mm wide vertical slit, selecting the central part of the mirror which does conserve the emission polarization *[7, 8]*. For all spectral measurements we collect a substrate reference and a dark reference spectrum where we blank the electron beam, subtracting this from the data in the post-processing stage. The spectrum shown in Fig. 3A is averaged over 50 camera pixels.

FDTD simulations

Numerical simulations of 3D electromagnetic field distributions were performed using a commercial software package (Lumerical Solutions Inc.). A plane wave incident under normal incidence was employed as excitation source, and the scattering spectrum and field profile were recorded. The silver lines were lying on a 30 nm thick Si_3N_4 substrate. The optical constants for silver came from CRC. The field profile was recorded at half-height of the lines. The mesh size was 0.5 nm in every direction.

Resistivity model

The plot presented in fig. S5 was obtained by implementing the Mayadas-Shatzkes model, that takes into account the effect of grain boundaries and surface scattering on the conductivity *[5, 9]*.

FFT analysis of HRTEM images

The FFT of the HRTEM images in Fig. 2 was performed by using a commercial software (ImageJ).

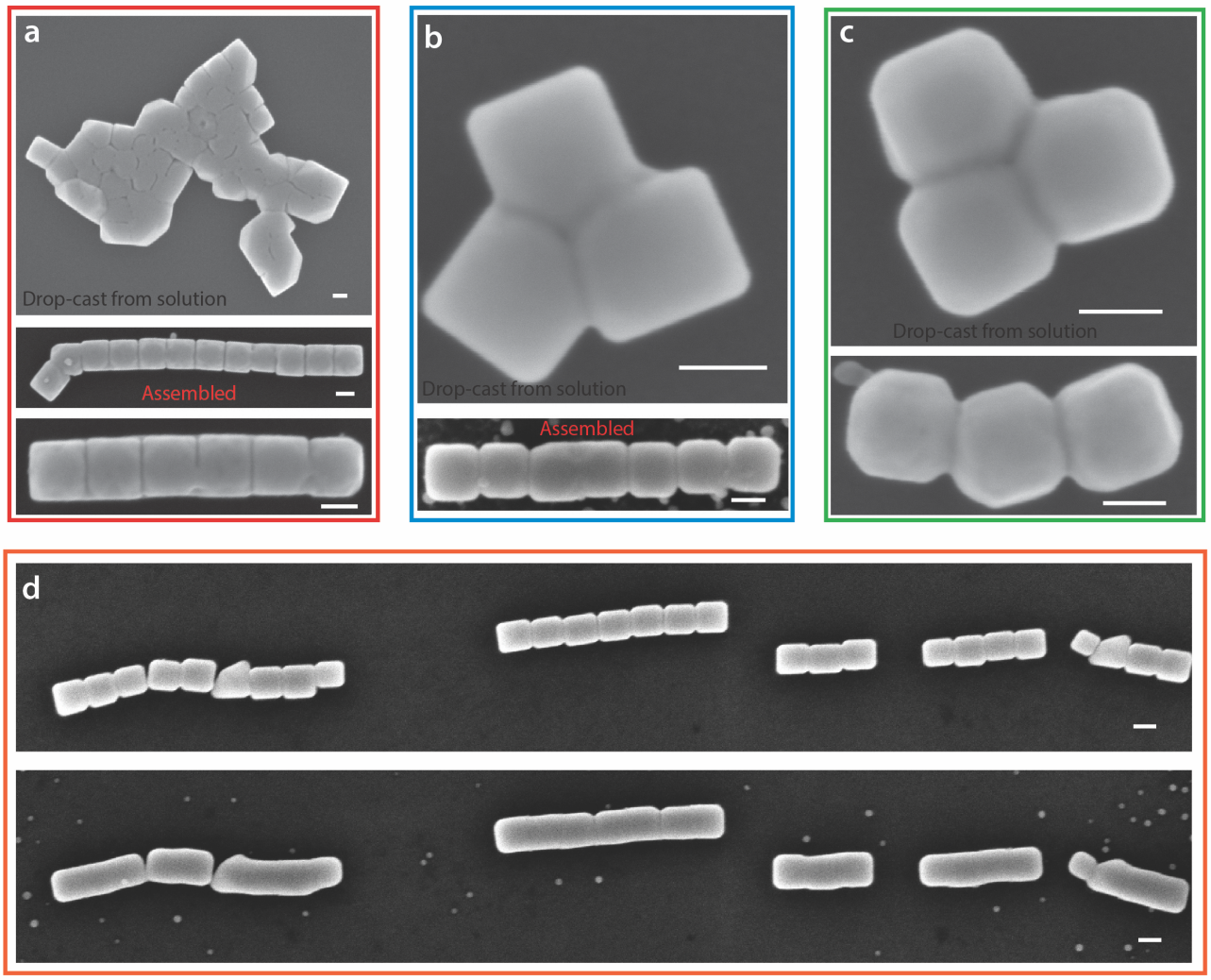

Fig. S1. Chemical nanowelding. a, Multistep welding, consisting of 4 consecutive exposures of 1 minute to a welding solution where the concentration of the diamminesilver complex(I) was one-fourth of the one described in the Methods. **b,** One-step welding, consisting of a single exposure of 60 s to the welding solution described in the Methods. **c,** One-step welding, consisting of a single exposure of 30 s to a welding solution where the concentration of the diamminesilver complex(I) was ten times larger than the one described in the Methods. **d,** Silver nanocube segments, before (top image) and after (bottom image) welding according to the optimized process described in the Methods (90 s exposure to the welding solution + 5 s RTA). The scale bars are 50 nm.

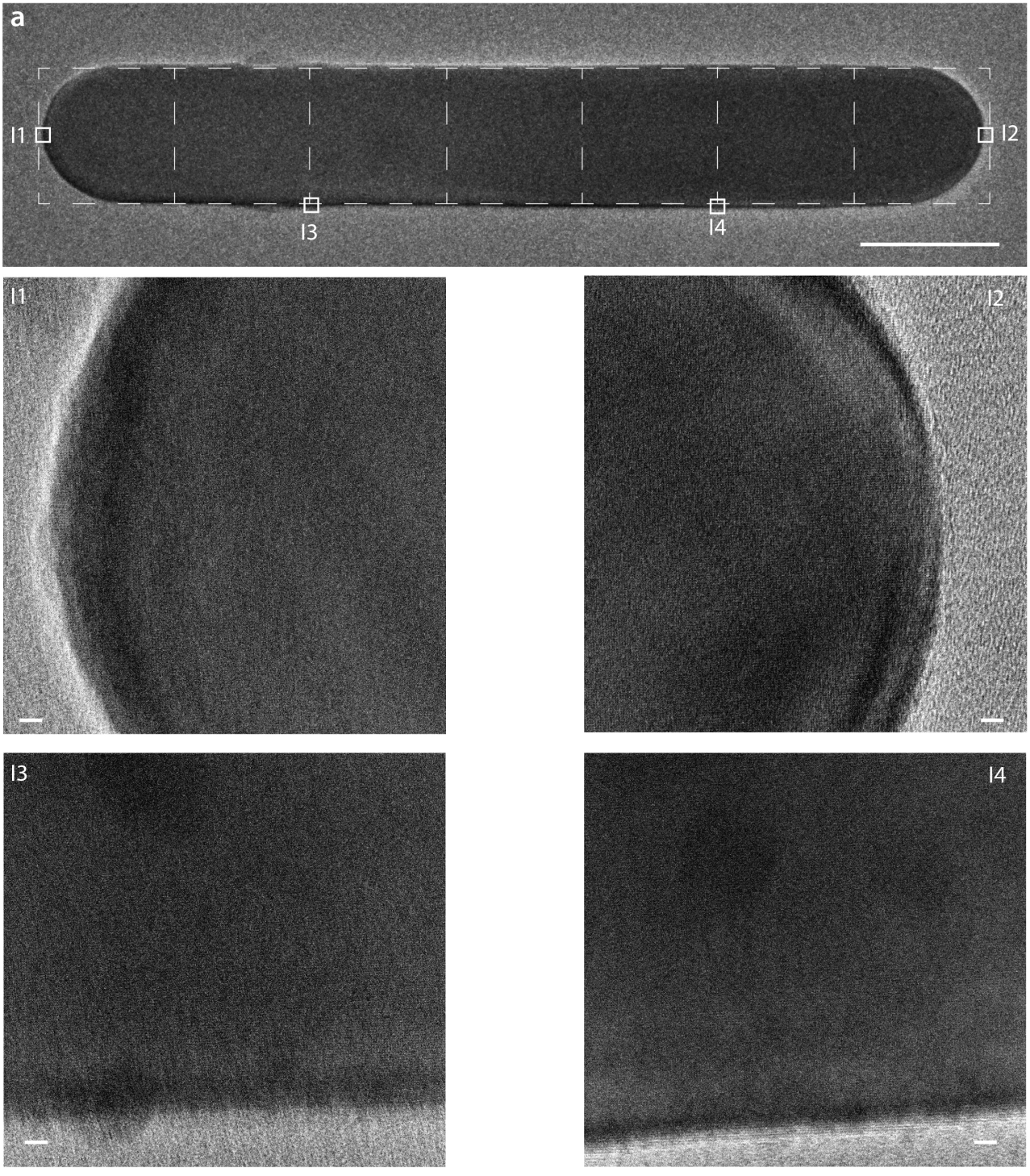

Fig. S2. TEM measurements of a wire composed of 7 silver nanocubes. a, Overview image (the scale bar in is 75 nm). Images I1 to I4 are HRTEM images of the regions indicated by the solid squares in **a**. The scale bars are 2 nm.

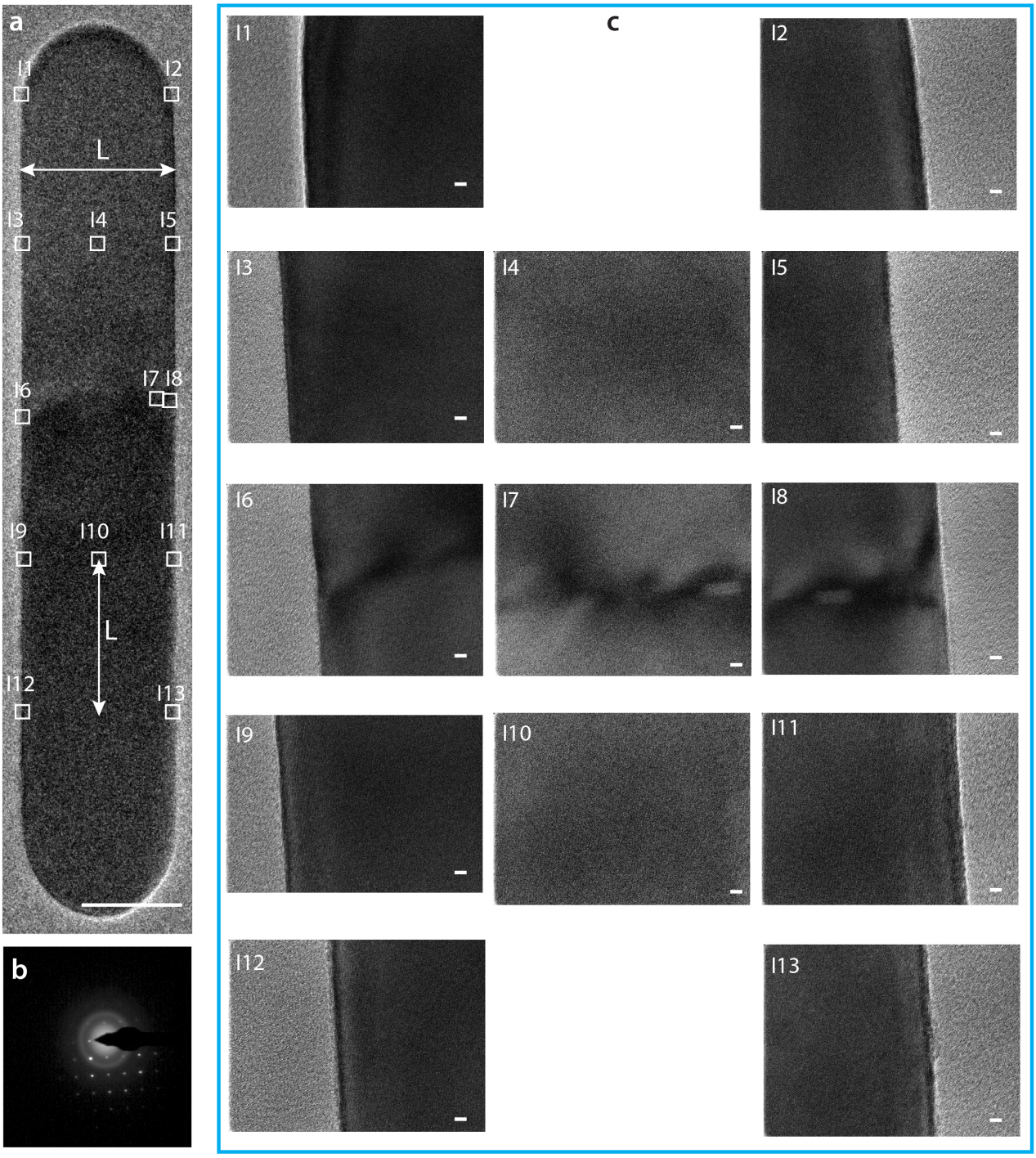

Fig. S3. TEM measurements of a silver wire. a, Overview image (the scale bar is 50 nm). **b,** SAED pattern of the silver wire. **c,** HRTEM images of the areas I1-I13 indicated by the solid squares in **a**. The scale bars are 2 nm.

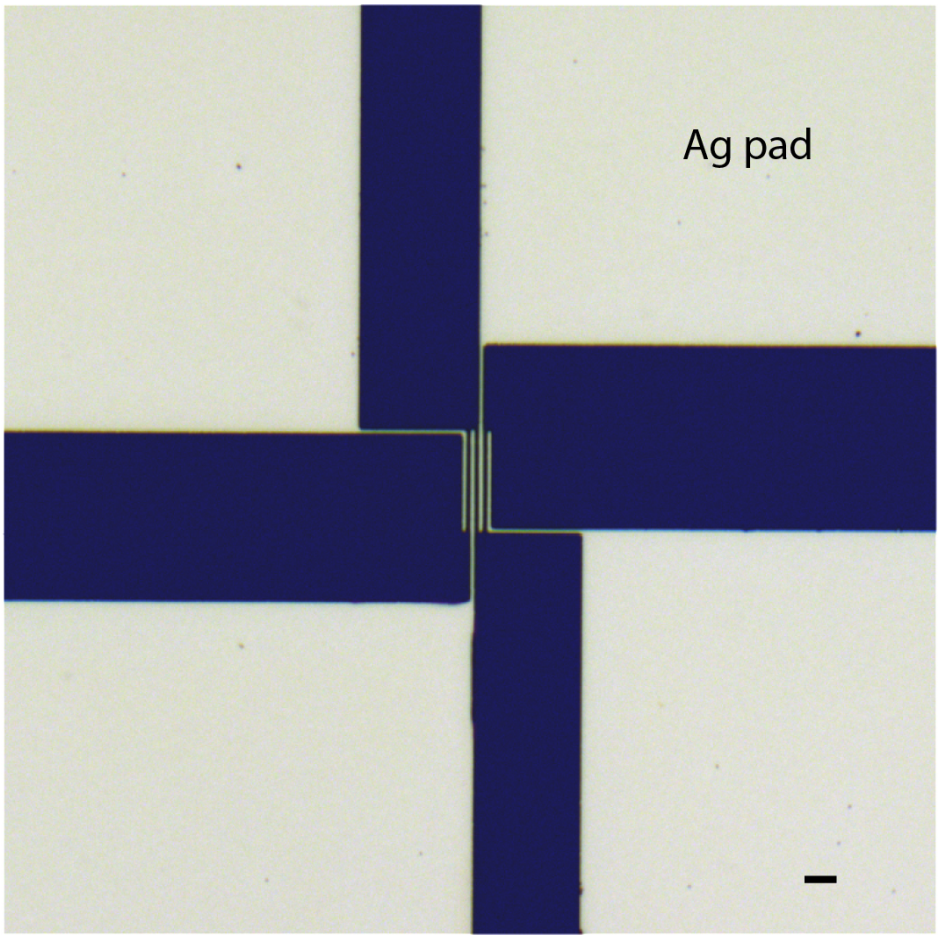

Fig. S4. Contact pads. Bright field optical image of Ag contact pads (white) used for electrical measurements. The scale bar is 15 μm.

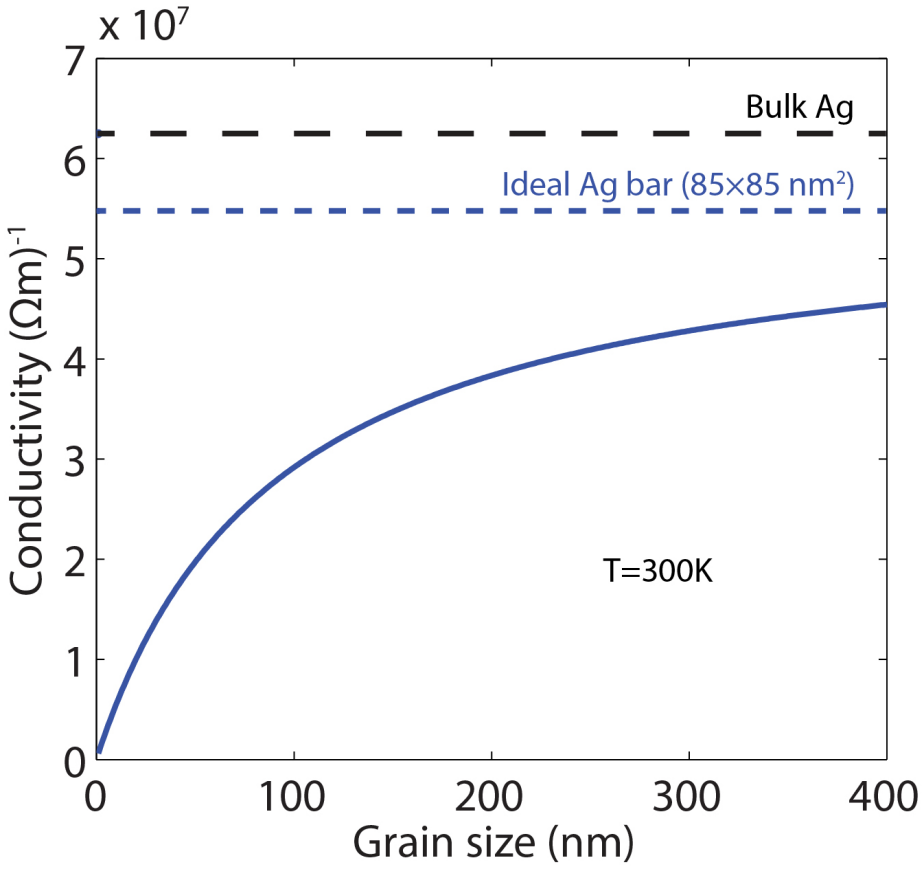

Fig. S5. The effect of grain size. Conductivity as a function of the average grain size for silver, calculated with the Mayadas-Shatzkes model, assuming a reflection coefficient of R = 0.57; the contribution of surface scattering is also included, with a specularity parameter p = 0.5. The dashed lines correspond to monocrystalline Ag with (blue) and without (black) surface scattering (Ref. 9).

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