Supporting information for

Sub-50 nm patterning of functional oxides by soft lithographic edge printing

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A. Experimental Methods

Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98% purity), copper (II) nitrate ($Cu(NO_3)_2$, 99.9% purity) and iron(III)nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98% purity) were purchased from Sigma Aldrich. Poly acrylic acid (M_w = 1800 g/mol) was obtained from Aldrich.

PDMS and curing agent (Sylgard 184) were purchased from Dow Corning Corporation and mixed in a ratio 10:1 and poured over the micro/nano-patterned silicon master (created by photolithography or e-beam lithography). The PDMS was cured at a temperature of 70°C for 48 h. After curing, the PDMS stamps were removed from the master and cut into pieces of desired size prior to use. The PDMS stamps were treated with oxygen plasma (Harrick plasma) at 24 W for 30-120 s to increase the surface energy of PDMS and promote its wetting by PAA during the spincoating process.[R1]

p-Type silicon substrates were cleaned with piranha solution (a mixture of H_2O_2 and H_2SO_4 in 1:3 volume ratio). The substrates were washed several times with de-ionized water after piranha cleaning and stored in de-ionized water. Prior to use, the substrates were taken out from de-ionized water and blow-dried in a nitrogen stream. PAA solutions with different concentrations (0.5, 0.75, 1, 1.5 and 3 wt%) were made in de-ionized water. The solutions were spincoated onto the PDMS stamps at 3000, 4000 and 5000 rpm. After spin coating the polymer films were allowed to dry for 5 min at room temperature. Multiple coatings were applied to make thicker polymer films, with intermediate drying at room temperature before each next coating. The PDMS stamps were then gently placed on the substrates and pressed with a gentle force to transfer the patterns. The substrates were then dried at 80°C for 5-10 min on a hot plate and peeled off from the substrate to obtain a pattern of PAA-metal salt complex. Solutions of 0.5 wt % PAA and 0.75 wt% metal salt and a spin coating speed of 5000 rpm were used when working with stamps with nanometer-scale features of 400 nm or less. Higher concentrations and lower rotational spincoating yielded thicker films on the stamp which were not suitable for edge transfer printing. After patterning the polymer film, the substrates were heat-treated at 620°C for 1 h in a tube furnace (Nabertherm, Germany) to remove the polymers and obtain the final metal oxide patterns.

ZnO nanowires were grown on edge transfer printed ZnO-patterned substrates as described in more detail in ref. [R2]. $Zn(NO)_3 \cdot 6H_2O$ (0.15 g) and hexamethylenetetramine (0.07 g; HMTA, Fluka, purity 99.5%) were mixed in 100 ml water. The solution was heated to 70-85 °C. The substrates were then

placed floating upside down on the surface of the ZnO precursor solution. ZnO nanowires were grown for 2 to 15 h, depending on the desired length of the nanowires.

Patterns of polymers and oxides were imaged using high resolution scanning electron microscopy (HR-SEM, Zeiss 1550). Atomic Force Microscopy (AFM; Veeco Dimension Icon) was used to determine the surface morphology. Tunneling current AFM (TUNA) was used to map the conductivity of patterned surfaces.[R3] X-ray diffraction (XRD, Philips diffractometer PW 3020, Software X'Pert Data Collector 2.0e, Panalytical B.V., Almelo, The Netherlands) was used for phase determination of the patterns.

B. Lap shear test

A lap shear test was performed to obtain average values of the adhesion force between the dried water-soluble polymer adhesive (PAA), and the participating surfaces, i.e. SiO_2 and oxygen plasma treated PDMS using a Zwick Z1.0/TH1S tensile tester. A schematic configuration of the test specimens used in the lap shear test is shown in **Figure S1**. Glass-PAA-glass and PDMS-PAA-PDMS test specimens with similar dimensions and polymer film thicknesses with similar adhesive areas were prepared as shown in the schematic configuration. The test specimens were placed between the grips of the testing machine and pulled until failure occurred. The maximum failure load was recorded using software testXpert V10.0. The lap shear strength (τ) of the adhesive joint is given by the formula

$$\tau = P/bL, \qquad (1)$$

where P is the maximum failure load, b the joint width and L the joint length.

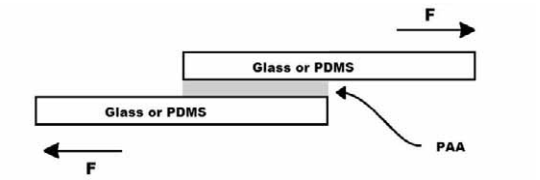

Figure S1: Schematic configuration of the test specimens used for the lap shear test to determine approximate values of adhesion forces between water soluble polymers and participating substrates.

C. Examples of Fe_2O_3, ZnO and NiO nanopatterns

Figure S2 shows a HR-SEM image of a Fe_2O_3 ring pattern, and an XRD pattern of a thin film fabricated using the same precursor solution (1.5 wt% PAA + 1 wt% $Fe(NO_3)_3 \cdot 9H_2O$). The sample was annealed at 620 ^oC to convert the precursor pattern into Fe_2O_3.

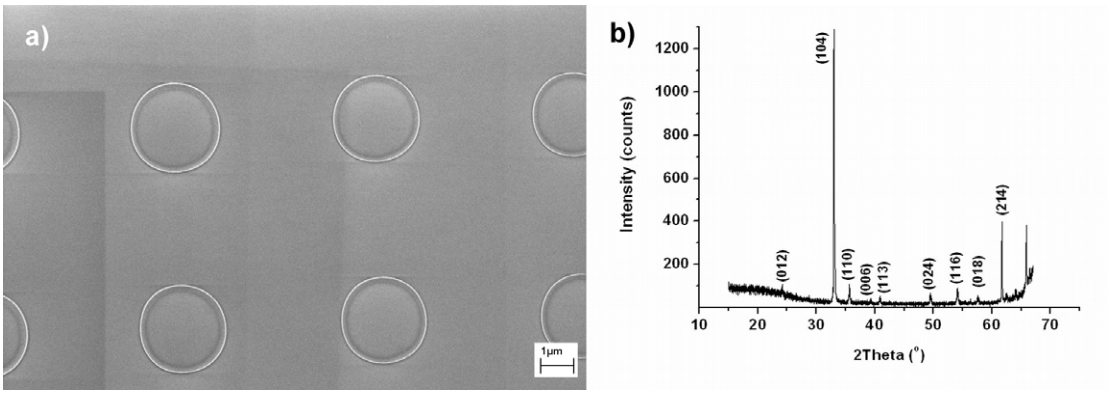

Figure S2: a) Fe_2O_3 ring pattern with a ring width of 250 nm; b) XRD pattern of Fe_2O_3 thin film.

Figure S3 shows a tapping mode AFM image and a height profile of ZnO line patterns fabricated using a PDMS stamp with line width and spacing of ~4 μm. Figure S3c and S3d show a ZnO ring pattern with a ring width of 80 nm, and a NiO pattern with a line width of 300 nm.

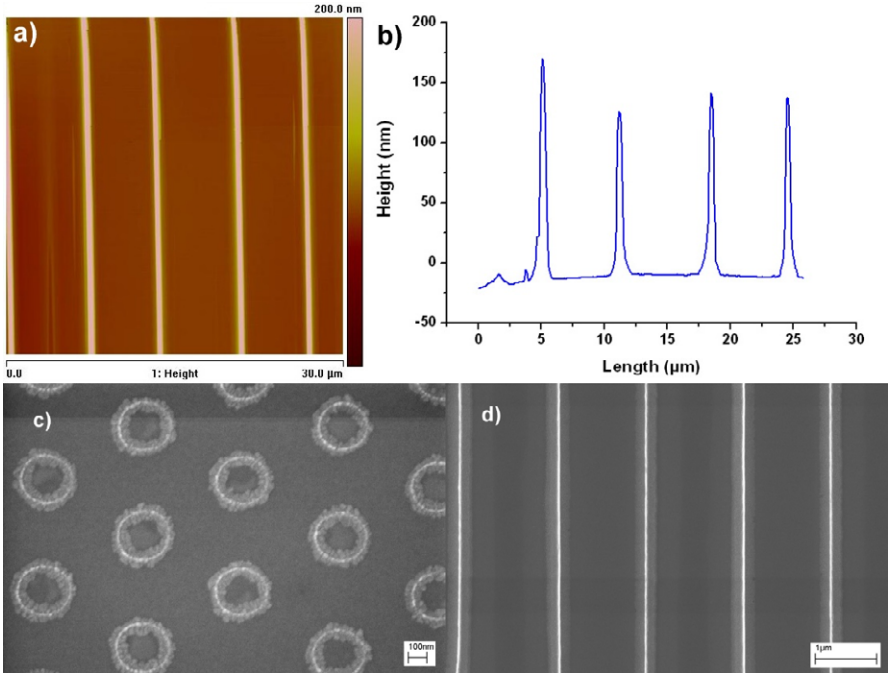

Figure S3: a) Tapping mode AFM image and (b) tapping mode height profile of ZnO line pattern with a line width of 600 nm and a spacing of ~ 4 μm; c) 80 nm ZnO ring patterns; d) 300 nm NiO line pattern.

References

[R1] C. Donzel, M. Geissler, A. Bernard, H. Wolf, B. Michel, J. Hilborn, E. Delamarche, *Adv. Mater.*, 2001, **13**, 1164.

[R2] L.E. Greene, M. Law, J. Goldberger, F. Kim, J.C. Johnson, Y. Zhang, R.J. Saykally, P. Yang, *Angew. Chem. Int. Ed.* 2003, **42**, 3031.

[R3] Veeco AFM manual, Application Modules, Nanoscope V7-B (004-1020-000).