

## Supporting information for

# Micro- and nanopatterning of functional materials on flexible plastic substrates via site-selective surface modification using oxygen plasma

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## Experimental Details

**Preparation of PDMS molds and substrates:** PDMS and curing agent (Sylgard 184) were purchased from Dow Corning Corporation and mixed in a mass ratio 10:1 and poured over the micro/nano-patterned silicon master that had been created by photolithography or e-beam lithography. For fabrication of planar PDMS substrates the mixture was poured over a silicon wafer functionalized with a monolayer of 1H,1H,2H,2H-perfluorooctylsilane. The PDMS was cured for 48 h at 70°C. After curing, the PDMS molds were removed from the master or the silicon wafer and cut into pieces of required size.

**Channel diffused plasma surface modification and surface modification through micro/nano stencils:** The PDMS molds with micro/nano-patterned features were gently pressed against the flexible substrates, so that the patterned side of the mold faced the substrate. The PDMS mold made conformal contact with the substrate via attractive Van der Waals forces. The substrate-mold assembly was transferred to an oxygen plasma cleaner (Harrick Plasma) operating at 25 W at a pressure < 1 mbar. The substrates were exposed to oxygen plasma for 10-15 minutes. After plasma etching the PDMS mold was peeled off the substrate and the substrates were used immediately for further deposition of functional materials.

In addition to PDMS molds, patterning experiments were also performed with silicon and silicon nitride micro- and nanostencils with regular arrays of perforations. Silicon microstencils with 6 μm perforations were fabricated in the MESA+ cleanroom following a fabrication process that has been reported elsewhere.<sup>[1]</sup> Silicon nitride nanostencils with perforation diameters of 200, 400, and 800 nm were obtained from Aquamarijn BV, Netherlands. Planar PDMS substrates were brought into conformal contact with the stencils and were exposed to oxygen plasma for 5 min. After plasma treatment the PDMS substrates were peeled off the stencil and immediately used for further deposition of functional materials.

**Patterning amorphous TiO<sub>2</sub>:** Ti(IV) isopropoxide (Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, >99.999%) was purchased from Sigma-Aldrich. Benzyl alcohol was purchased from Acros. The reactants were used as received and stored in a water-free environment. A solution of 0.2 mol/dm<sup>3</sup> Ti(IV) isopropoxide in benzyl alcohol

was prepared. 5  $\mu\text{L}$  of the solution was spin-coated at a speed of 2000 rpm for 2 min on plasma patterned substrates that had been exposed to water vapor prior to spin coating. After spin coating the substrates were again exposed to water vapor to convert the precursor to amorphous titania. The substrates were then dried at 60  $^{\circ}\text{C}$  for 2 h.

**Silver seeding for electroless deposition:** Plasma-patterned substrates were dipped in a 1 mM aqueous solution of silver nitrate (Arcos organics, purity 99.%) for 1 h to attach silver ions to the modified regions. After removing the substrates from solution they were washed in a stream of absolute ethanol, dried in a stream of nitrogen and annealed at 80  $^{\circ}\text{C}$  for 20 min, and then exposed to light for 30 min to ensure complete photoreduction of Ag ions. Ag deposited in the hydrophilic regions acted as seed layer for the electroless deposition of Ag and ZnO.

**Electroless deposition of ZnO:** Electroless deposition of ZnO was carried out as described in ref. [2]. 1.5 g of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich, purity 99%) and 0.058 g of dimethylamine borane (DMAB, Aldrich, purity 97%) were dissolved in 100 ml water. The solution was heated to 55 or 65  $^{\circ}\text{C}$  and the substrates were immersed in the solution for 15 min up to a few hours for ZnO thin film growth.

**Deposition of silver:** Ag deposition solutions (Silver enhancer A and Silver enhancer B) were obtained from Aldrich and mixed in equal proportions. The solution was diluted with water to 25%. The plasma patterned substrates were Ag seeded first and then placed in the solution for few minutes for Ag film growth.

**Solution phase growth of ZnO nanowires:** After the plasma surface modification process the substrates were immersed in a 0.2 M ethanolic solution of zinc acetate (Aldrich, purity 99.99%), taken out and allowed to dry at room temperature. The samples were kept in an oven at 80 $^{\circ}\text{C}$  for 1 h. An oxygen plasma treatment was employed for 5 minutes to convert the zinc acetate to ZnO seed particles. After seeding, ZnO nanowires were grown on the substrate as described in more detail in ref. [3].  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.15 g) and 0.07 g of hexamethylenetetramine (HMTA, Fluka, purity 99.5%) were mixed in 100 ml water. The solution was heated to 70-85  $^{\circ}\text{C}$ . The substrates were then placed floating upside down on the surface of the ZnO growth solution. ZnO nanowires were grown for 2 to 15 h, depending on the desired length of the nanowires.

**Conducting polymer micropatterns:** PEDOT/PSS [Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate)] was purchased from Sigma Aldrich. 50  $\mu\text{L}$  of PEDOT/PSS suspension was spin coated at a speed of 2000 rpm for 60 s on the plasma patterned substrates. After spin coating the PDMS substrates were heated to 70  $^{\circ}\text{C}$  for 15 min and stored for further analysis.

**Adsorption of gold nanoparticles:** (3-Aminopropyl)triethoxysilane ( $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-\text{C}_3\text{H}_6-\text{NH}_2$  (APTES, 98% purity) was purchased from Sigma Aldrich. The stencil oxidized PDMS substrates were soaked in a 0.5 wt% solution of APTES in absolute ethanol for 10 min. The substrates were removed from the solution, washed several times with absolute ethanol, and blow-dried in pure nitrogen stream. A colloidal solution of gold nanoparticles was prepared as described in ref. [4]. The

substrates were immersed in the gold nanoparticle solution for 12 h. The amine functional groups on the surface were protonated and electrostatically bound to the citrate ion coated gold nanoparticles.

**Characterization:** Prepatterned substrates and patterned materials were imaged using high resolution scanning electron microscopy (HR-SEM, Zeiss 1550) and tapping mode AFM. X-ray diffraction (XRD, Philips diffractometer PW 3020, Software XPert Data Collector 2.0e, Panalytical B.V., Almelo, The Netherlands) was used for phase determination of the patterns.

## References

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