# Supporting Information

# Large-Scale Synthesis of Highly Uniform Silicon Nanowire Arrays Using Metal-Assisted Chemical Etching (MACE)

*Fedja J. Wendisch,* [1] *Marcel Rey,* [2] *Nicolas Vogel,* [2] *Gilles R. Bourret* [1,]*

[1] Department of Chemistry and Physics of Materials, University of Salzburg, Jakob Haringer Strasse 2A, A-5020 Salzburg, Austria

[2] Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg, Cauerstrasse 4, 91058 Erlangen, Germany

*E-mail: gilles.bourret@sbg.ac.at

## Table of Content

## Materials and chemicals

All chemicals and solutions were used without further processing, unless noted otherwise. Acrylic acid (99.0 %), ammonium persulfate (98.0 %), styrene (99.0 %), potassium iodide (puriss. p.a., reag. ISO, reag. Ph. Eur. 99.5 %) and Triton X-100 (laboratory grade) were purchased from Sigma Aldrich, USA. Colloidal PS particles with 1500 diameter (2.5 w%) were purchased from Polysciences Inc., USA. For the synthesis of the PS colloidal particles, styrene was purified by adding a 10 wt. % NaOH solution in a volume ratio 1:1. After vigorous shaking, the aqueous phase was discarded and the styrene phase purified by passing through an aluminum oxide powder column. The water used was double deionized using a MilliQ system with a resistivity of 18 MΩ. Acetone (technical grade), calcium chloride (90-98 %, Technical), ethanol (euro denaturated 96 %), iodine (99.8 %, crystals, ACS, resublimed) and methanol (99.8 %, ACS grade) were purchased from VWR, Europe. Hydrofluoric acid (40 %, EMSURE) and hydrogen peroxide (30 %, ACS grade) were purchased from Merck. Calcium gluconate monohydrate (pure Ph. Eur., USP) were purchased from AppliChem. N-doped Silicon wafers ((100), resistivity 1-30 Ω cm) were commercially purchased from Si Materials, Germany.

## Synthetic protocols

### Colloidal sphere synthesis

PS colloidal particles were synthesized, self-assembled at the air-water interface and used as mask as described elsewhere.[1–3] In short, PS colloidal particles with a diameter of $d$ = 590 nm and $d$ = 1100 nm were synthesized by a surfactant-free emulsion polymerization. Using a 500 mL triple-neck round-bottom flask with reflux condenser 250 mL of MilliQ water were heated to 80 °C. The water was degassed 30 min with nitrogen gas. 40 g styrene (for $d$ = 1100 nm) or 20 g styrene (for $d$ = 590 nm) was added to the water phase under constant stirring. 0.4 g of the comonomer acrylic acid dissolved in 5 mL MilliQ water was added to the mixture. After 5 min 0.1 g ammonium persulfate, dissolved in 5 ml MilliQ water, was added. The reaction was carried out for 24 h at 80 °C. After cooling to room temperature the dispersion was filtered and purified by centrifugation and redispersion and dialysis.[1]

PS colloidal particles with $d$ = 1500 nm were commercially purchased.

$SiO_2$-PNiPAm core-shell particles with an inner diameter of 160 nm (±10 nm) and a shell of 480 nm were synthesized as described elsewhere.[4]

### Preparation of substrates

Colloidal sphere monolayer were obtained by self-assembly at the water-air interface and by spin coating. The substrates were either used directly (2” wafers) or cut to the appropriate size using a glass cutter. Prior to self-assembly, the substrates were cleaned *via* sonication in acetone, ethanol and MilliQ water for 4 min each, followed by an oxygen plasma treatment (50 W, 10 mL/min, 4 min) to render the surface clean and hydrophilic.

## Self-Assembly at the water/air interface

Prior to self-assembly at the water/air interface, the PS colloidal particles (*d* = 590 nm, *d* = 1100 nm) were cleaned and purified by three centrifugation-redispersion steps. [5] Typically, 2 mL of the PS solution was mixed with 20 mL MilliQ water and 20 mL ethanol (absolute) and centrifuged at 4000 rpm for 15 minutes. The supernatant was removed, and the PS colloidal particles were redispersed in 20 mL MilliQ water and 20 mL ethanol (absolute). The procedur was repeated three times. The final redispersion was done with 1 mL MilliQ water and 1 mL ethanol (absolute).

For the spreading onto the water/air interface a syringe pump (Landgraf HLL LA120) was used (Figure S1). A 1 mL syringe was filled with 500 µL PS spheres and 500 µL ethanol (absolute) for the 1100 nm PS colloidal particles and with 750 µL PS sphere solution and 250 µL ethanol (absolute) for the 590 nm PS colloidal particles. A big beaker (Ø = 140 mm; height: 70 mm) was filled with MilliQ water and a syringe was bent with a 90 ° angle and placed in such way that half of the opening at the syringe tip was immersed in the water. During self-assembly, the dispersions were added slowly (1-30µl/min) via the syringe to the air/water interface to minimize disturbance. When the water surface was fully covered by a monolayer, the syringe pump was turned off. Silicon substrates were immersed in the water phase and elevated under a shallow angle to transfer the monolayer. The substrates were left to dry in air on top of a tissue and at an angle of ~ 45 °. After removal of each sample, the syringe pump was turned on again, and additional PS colloidal particles were added to the interface via the syringe pump to replenish the interfacial assembly. Several substrates (~ 10 – 15) can be pulled out until the process has to be started again, by filling up the solution in the syringe and renewing the water in the large beaker. The procedure delivered large-area colloidal crystals with grains in the mm² range (Figure S2).

The $SiO_2$-PNiPAm core-shell particles were self-assembled at the water/air interface using a Langmuir-Blodgett trough (KSVNIMA) (area = 243 $cm^2$, width = 7.5 cm) with Delrin barriers and the surface pressure was measured by a Wilhelmy plate. Four substrates were mounted vertically onto the dipper and the trough was filled with Milli-Q water. The core-shell particle suspension was diluted to 0.5 wt.%, mixed with 30 wt.% ethanol as the spreading agent, and spread at the water/air interface of the trough using a regular 100 μL pipette. After 10 min of equilibration, the barriers were compressed to a constant surface pressure of 30 mN/m while the dipper was lifted by 0.8 mm/min. After deposition, the $SiO_2$-PNiPAm core-shell particles were exposed to oxygen plasma for 10 min to remove the organic PNiPAm shell, leaving a non-close packed array of silica particles at the surface.[4]

### Self-Assembly using spin coating

Spin coating was performed with PS colloidal particles with $d$ = 1500 nm. The colloidal dispersion (2.5 w%) was first concentrated *via* centrifugation (6000 rpm for 20 min). Then, the spin coating dispersion was prepared by mixing the concentrated PS colloidal dispersion with a methanol:Triton x-100 (400:1) mixture with a ratio of 1:3 (PS conc : methanol-Triton X100). 40 – 100 μl of the dispersion was added onto the surface of the substrate (depending on the substrate size) and spun at 3500 rpm for 3 min (acceleration of 100 rpm) on a Laurell WS-650SZ-6NPP/LITE. Spin Coating led the formation of monolayers, albeit with lower surface coverage (around 70-80 %), smaller grains and more holes and multilayers (Figure S2).

### Size reduction of the colloidal monolayers

After the deposition of monolayers, oxygen plasma etching can be used to reduce the size of the individual PS colloidal particles and thereby produce non-close-packed monolayers. The size of the PS colloidal particles defines the final diameter of the silicon nanowire. Typically, samples were etched at 50 W using a FEMTO plasma oven from Diener Electronics. The chamber was evacuated to ~ 0.1 mbar and oxygen gas was added with a flow of 4 mL/min. The etching duration was adjusted to the desired SiNW diameter. For a PS sphere monolayer with $d = 590$ nm, a 14 minutes treatment resulted in a reduction to $d = 410$ nm. The size reduction is straight-forward and the size of the spheres decreases linearly with the etching time.

### Metal film deposition

After converting the close-packed sphere monolayer into a non-close packed architecture, a thin metal film is deposited by sputter coating or thermal evaporation. The spheres protect the surface from the metal and a metal hole array is created. Gold was used for all substrates in this work, due to its excellent chemical stability.

Before gold sputtering a thin adhesion layer of Al-doped ZnO was sputtered directly on the non-close packed colloidal monolayer, using a Clustex 100M sputtering system from Leybold Optics. The substrates were fixed on the sample holder and inserted into the reaction chamber. The chamber was evacuated to around $1*10^{-6}$ mbar. Sputtering was performed for 1 second using Argon gas at a pressure at $3*10^{-3}$ mbar and a power in the 75-200 W range depending on the PS particle size. After sputtering of the adhesion layer, gold was immediately sputtered using a Cressington Sputter Coater 108 auto (gold target from PLANO GmbH, B7701, $d = 57$ mm, $t = 0.4$ mm). The chamber was evacuated to 0.1 mbar and flushed with Argon gas. Evacuation and flushing were performed twice to have a clean atmosphere. Deposition was started at 0.1 mbar with a current of 40 mA during 200 s.

### Removal of the colloidal template

After metal deposition, the PS particles were removed using adhesive tape (Scotch Magic Tape). The adhesive tape was carefully placed on top of the substrate and then brought into contact with the backside of a tweezer or by using a finger (Figure S3). A gold film without patterning, i.e. corresponding to an area where no PS spheres were present before the gold sputtering, usually delaminated during the removal of adhesive tape. To avoid gold film delamination the tape removal was always initiated at a patterned side of the substrate. Finally, the substrates were cleaned from residual tape with oxygen plasma using the Emitech K1050x at 50 W for 5 min with an oxygen flow of 10 mL/min.

### Synthesis of Si nanowire arrays *via* metal-assisted chemical etching (MACE)

MACE was used to prepare Si nanowire (SiNW) arrays by immersing the Si/Au hole array substrates in an aqueous $HF/H_2O_2$ mixture. [2, 3, 6] *Caution: Appropriate safety precautions have to be observed when working with hydrofluoric acid (HF): HF is a contact poison! The experimental build up is shown in Figure S4.* All HF steps were performed inside a HF specific fume hood, using HF resistant plastic or Teflon tools, beakers and butyl gloves (Butoject 897+ from Honeywell). For safety precautions a 2 L beaker was filled with 1 L liquid calcium gluconate, as quick washing of the exposed skin in the event of an accident can significantly limit the damages caused by HF. In addition, a 2.5 % calcium gluconate gel (C-gel) was commercially bought for the same purpose and kept close to the hood where the experiment was performed. A second 2 L beaker was filled with 1 – 1.5 L of calcium chloride ($CaCl_2$) aqueous solution. $CaCl_2$ scavenges the toxic fluoride ions by quickly forming an inert precipitate of $CaF_2$, thus significantly reducing the toxicity of the HF waste and reducing the chances of HF poisoning and contaminations. The various HF etchings and subsequent rinsing were carried out in plastic beakers in a plastic box inside the fume hood. Different home-made 3D printed polymer (polylactic acid, PLA) sample holders were prepared to avoid using tweezers, allowing reproducible etching of several samples at the same time (Figure S4). At the end of the experiment, all pieces of equipment used were fully immersed into the calcium chloride solution, thoroughly rinsed with deionized water, dried and stored inside a fume hood until further use.

The MACE solution was freshly prepared before etching and was composed of 10 mL of hydrofluoric acid, 10 mL of MilliQ water and 0.75 mL of hydrogen peroxide ($H_2O_2$). The substrates were placed on a home-made 3D printed polymer sample holder and immersed in the solution. Etching was done without stirring: the samples stayed still in the sample holder. Typical etching duration were between 2-30 minutes depending on the desired wire length. The substrates were then rinsed three times in MilliQ water and once in ethanol. After MACE etching, the substrates were immersed into a solution of 20 mL of MilliQ water and 4 mL of hydrofluoric acid to remove porous $SiO_2$ that can be formed on the sidewalls during MACE. After the HF treatment the substrates were rinsed three times in MilliQ water in separate beakers, once in ethanol and finally dried in air. The silicon micro- or nanowire arrays were characterized with scanning electron microscopy (SEM) and stored for later use. The gold film at the bottom of the array can be removed in an aqueous $KI/I_2$ solution (10 wt.% KI, 5 wt.% $I_2$) within 30 minutes.

## Characterization Methods

### Scanning Electron Microscopy (SEM)

Secondary electron (SE) and back-scattered electron (BSE) images of the arrays were acquired using a Zeiss Ultra Plus 55 at a working distance of ~ 2.5 - 4 mm, equipped with an InLens SE detector, an InLens BSE detector (EsB) and an angle selective BSE detector (AsB) located below the pole piece. The accelerating voltage was adjusted between 1 and 10 kV depending on the sample to limit charging.

### Calculation of the gold coverage and the normalized Au/Si/etchant interface length

The gold coverage and wire density were calculated assuming 100 % defect-free monolayer. The interface length was calculated by taking the circumference of a wire multiplied by the number of wires for a specific substrate area. The interface length shown in Figure 5b (main text) was normalized to the largest calculated value, obtained for a hexagonal close-packed wire array with 590 diameter and a 590 nm pitch, corresponding to a 9.31 % Au coverage.

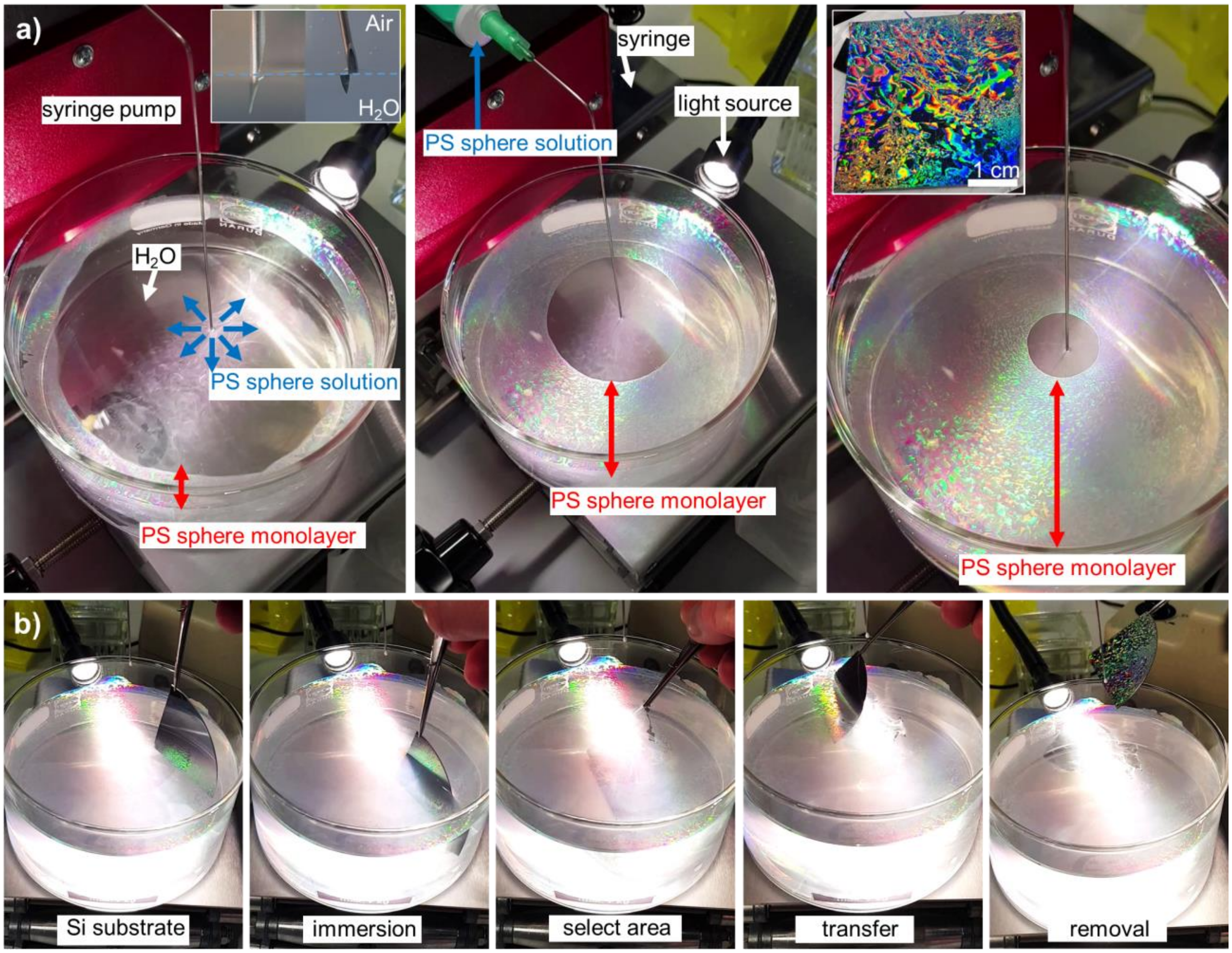


**Figure S 1. Self-Assembly of a PS sphere monolayer (*d* = 1100 nm) on the water-air interface and transfer to a Si substrate.**

(a) Growth of a PS sphere monolayer. First Image: The PS sphere solution is added to the air/water interface using a syringe pump. Inset shows the immersion of the syringe tip from side and front at the water-air interface. Second Image: Structural colors (diffraction) occurring from the close-packed, enable a simple, visual quality control of the assembly process. Third image: Nearly finished monolayer on the water surface. The Inset shows a PS colloidal monolayer on a large Si substrate. (b) Transfer of a PS sphere monolayer onto a Si substrate by manual immersion and withdrawal of the substrate. A light source under a shallow angle illuminates the air/water interface to increase the visibility of the interfacially assembled monolayer.

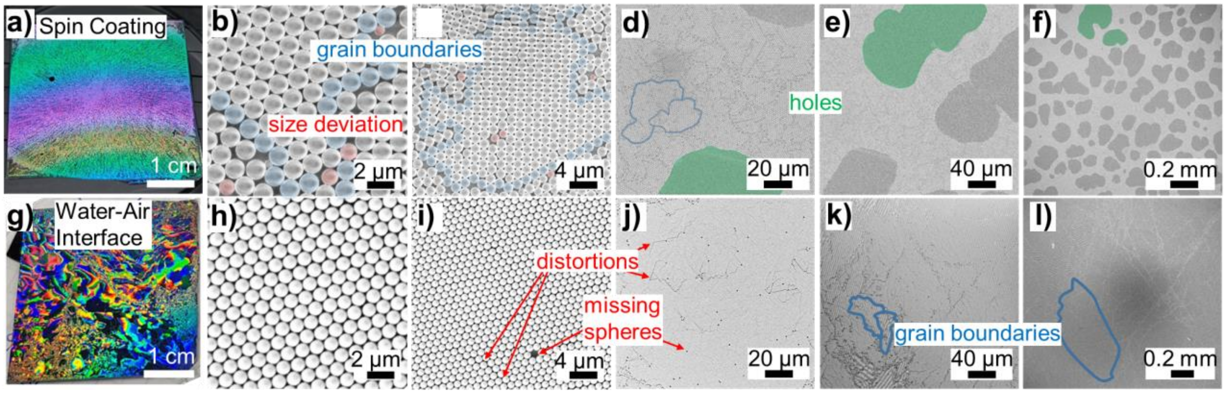


**Figure S 2. Polystyrene colloidal monolayer after spin coating and self – assembly at the water-air interface.**

Typical defects, like grain boundaries or holes, from the self-assembly process are shown in color at different magnifications. (a-f) PS Monolayer with *d* = 1500 nm after spin coating. (a) Photograph with illumination. (b-f) Secondary electron SEM images in different magnifications. (g-l) PS Monolayer with *d* = 1100 nm after self-assembly on the water-air interface. (g) Photograph with illumination. (h-l) Secondary electron SEM images in different magnifications. For spin coating a commercial PS solution with a larger size deviation was used.

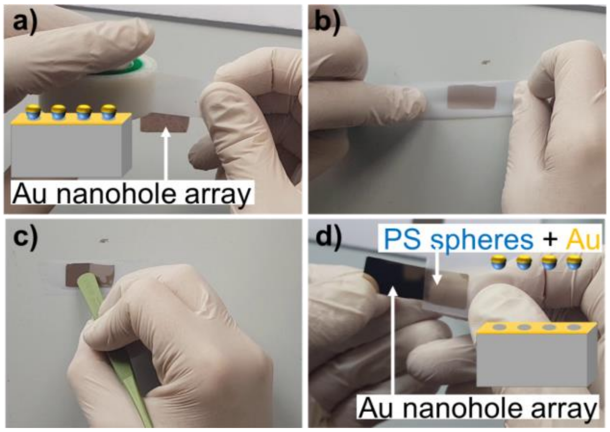


**Figure S 3. Removal of colloidals using adhesive tape.**

(a) Substrate after gold sputtering. The PS spheres are covered with gold. (b) Adhesive tape (Scotch Magic Tape) is placed on the sample. (c) The adhesive tape is brought into contact. (d) The adhesive tape with the PS spheres is removed and the gold nanohole array remains on the surface of the Si.

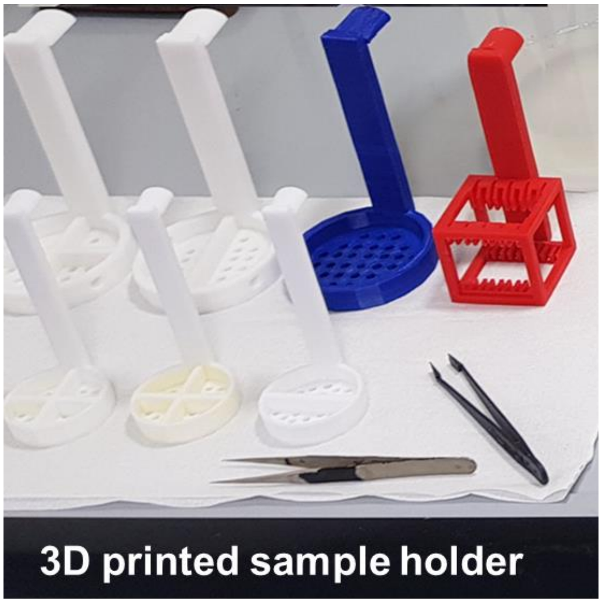


**Figure S 4. HF resistant 3D printed sample holders (polylactic acid, PLA).**

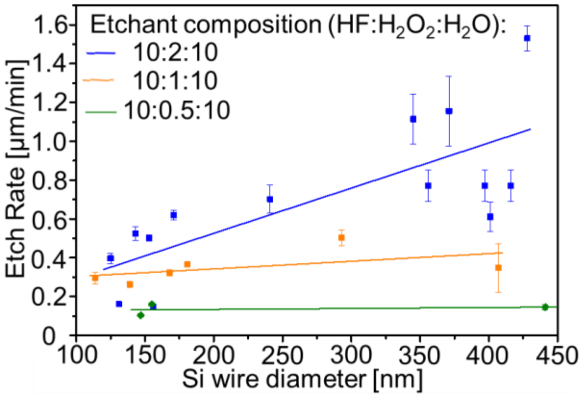


**Figure S 5. Effect of etchant concentration.**

Etching rate in dependence of the Si nanowire diameter for etchants with different composition. *p* = 590 nm, AZO: 150 W 1 s, Au: 40 mA 150 s.

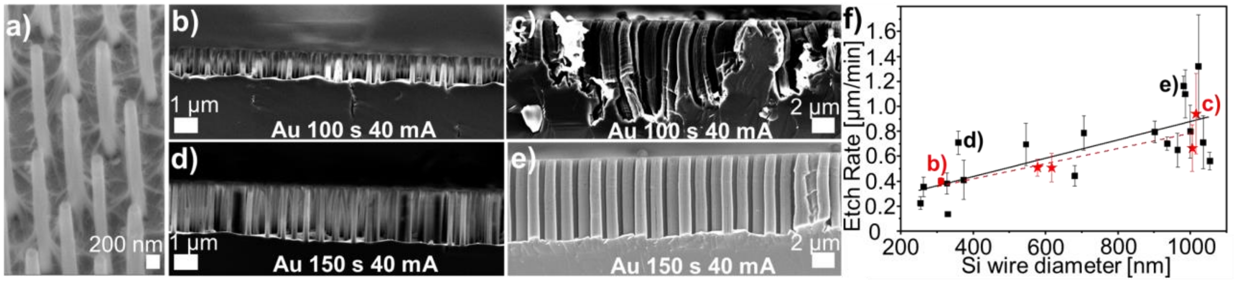
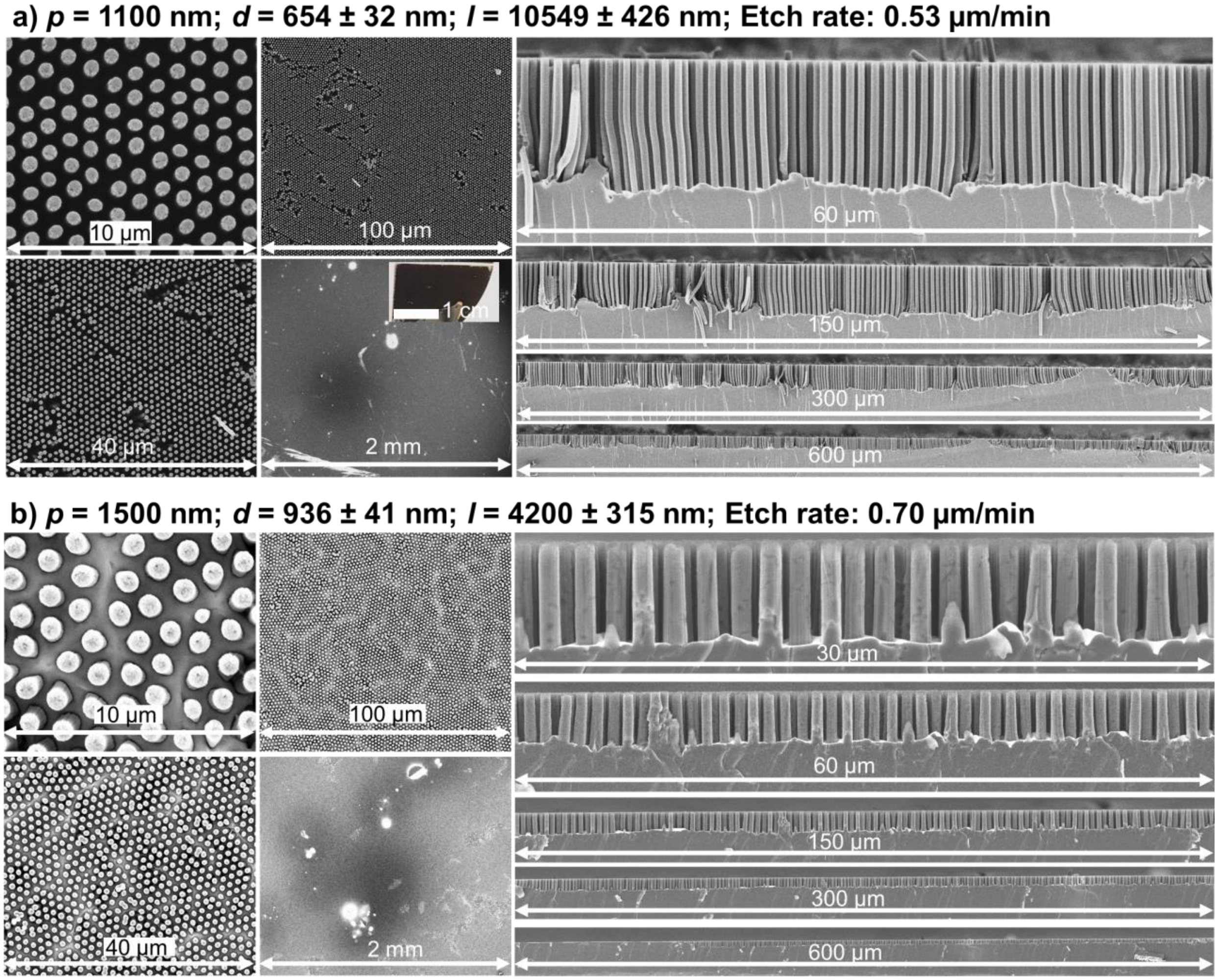


**Figure S 6. Influence of gold film thickness.**

(a-e) Secondary electron SEM images. (a) Etching with a porous gold film (Ti: 3 nm, Au: 20 nm), leads to unwanted thin nanowires (bundled to the big ones). (b-e) SEM images of substrates with different gold thicknesses but similar geometry, AZO thickness and etchant composition. Initial PS sphere size: 1500 nm; AZO 75 W 1 s; MACE etchant composition 10:2:10 ($HF:H_2O_2:H_2O$) for 6 min; (b, d) and (c, e) have comparable diameters. (f) Etching rate in dependence of Si wire diameter for substrates shown in (b-e). The red symbol indicates substrates with a thinner gold film (Au 100 s 40 mA) and stars indicate a broken gold film, like the one in (c). While the thin gold film was not stable above 0.4 µm/min, the thicker gold film (Au 150 s 40 mA) showed good stability.



a) *p* = 1100 nm; *d* = 654 ± 32 nm; *l* = 10549 ± 426 nm; Etch rate: 0.53 µm/min

b) *p* = 1500 nm; *d* = 936 ± 41 nm; *l* = 4200 ± 315 nm; Etch rate: 0.70 µm/min

**Figure S 7. Large-scale homogeneity of Si wire arrays fabricated with MACE and colloidal lithography.**

Secondary electron top view or cross-sectional SEM images at different magnifications. The insets shows photographs of the substrates. (a) AZO: 100 W 1s; Au 200 s 40 mA; HF:$H_2O_2$:$H_2O$: 10:0.75:10 for 20 min. Prepared with PS spheres. (b) AZO: 75 W 1 s, Au 200 s 40 mA, HF:$H_2O_2$:$H_2O$ 10:2:10 for 6 min. Prepared with PS spheres.

## References

1. Vogel, N.; Goerres, S.; Landfester, K.; Weiss, C. K.; A Convenient Method to Produce Close- and Non-close-Packed Monolayers using Direct Assembly at the Air-Water Interface and Subsequent Plasma-Induced Size Reduction. *Macromol. Chem. Phys.*, **2011**, 212, 16, 1719–1734. DOI: http://dx.doi.org/10.1002/macp.201100187.
2. Wendisch, F. J.; Abazari, M.; Mahdavi, H.; Rey, M.; Vogel, N.; Musso, M.; Diwald, O.; Bourret, G. R.; Morphology-Graded Silicon Nanowire Arrays via Chemical Etching: Engineering Optical Properties at the Nanoscale and Macroscale. *ACS Appl. Mater. Interfaces*, **2020**, 12, 11, 13140–13147. DOI: http://dx.doi.org/10.1021/acsami.9b21466.
3. Wendisch, F. J.; Saller, M. S.; Eadie, A.; Reyer, A.; Musso, M.; Rey, M.; Vogel, N.; Diwald, O.; Bourret, G. R.; Three-Dimensional Electrochemical Axial Lithography on Si Micro- and Nanowire Arrays. *Nano Lett.*, **2018**, 18, 11, 7343–7349. DOI: http://dx.doi.org/10.1021/acs.nanolett.8b03608.
4. Tang, J. S. J.; Bader, R. S.; Goerlitzer, E. S. A.; Wendisch, F. J.; Bourret, G. R.; Rey, M.; Vogel, N.; Surface Patterning with $SiO_2$@PNiPAm Core-Shell Particles. *ACS omega*, **2018**, 3, 9, 12089–12098. DOI: http://dx.doi.org/10.1021/acsomega.8b01985.
5. Rey, M.; Yu, T.; Guenther, R.; Bley, K.; Vogel, N.; A Dirty Story: Improving Colloidal Monolayer Formation by Understanding the Effect of Impurities at the Air/Water Interface. *Langmuir*, **2019**, 35, 1, 95–103. DOI: http://dx.doi.org/10.1021/acs.langmuir.8b02605.
6. Wendisch, F. J.; Oberreiter, R.; Salihovic, M.; Elsaesser, M. S.; Bourret, G. R.; Confined Etching within 2D and 3D Colloidal Crystals for Tunable Nanostructured Templates: Local Environment Matters. *ACS Appl. Mater. Interfaces*, **2017**, 9, 4, 3931–3939. DOI: http://dx.doi.org/10.1021/acsami.6b14226.