Nanomachining

Regular Noble Metal/Ceramic Structures
for Catalytic Applications

Hai Le The

NANOMACHINING REGULAR NOBLE METAL/CERAMIC STRUCTURES FOR CATALYTIC APPLICATIONS

HAI LE-THE

NANOMACHINING REGULAR NOBLE METAL/CERAMIC STRUCTURES FOR CATALYTIC APPLICATIONS

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Multiscale Catalytic Energy Conversion

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1

Introduction

1.1 | Netherlands Center for Multiscale Catalytic Energy Conversion

The Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC) has been established since 2014 from a ten-year Gravitation programme directly funded by the Dutch Ministry of Education, Culture and Science (OCW).¹ The ultimate aims of the MCEC are to develop highly efficient catalysis processes, and to optimize existing catalysis processes for the production of future materials and fuels. Within MCEC, the research is conducted at all relevant scales, from the atomic level of the catalyst materials to the level of the actual reactors, with a combination of different scientific disciplines of chemistry, physics, and engineering. Moreover, MCEC also interconnects internationally renowned scientists and talented researchers from three universities with their own long-term research strategies: Sustainability (Utrecht University), Energy (Eindhoven University of Technology), and Nanotechnology (University of Twente).²

The research within MCEC has been divided over several scientific and technological challenges, which focus on the fundamentals of catalytic processes at different scales: nanoscopic, mesoscopic, and macroscopic. Multidisciplinary frontier research projects are fostered by interconnecting these challenges. In MCEC, all the research projects are categorized into six so-called project clusters, i.e. Biomass Conversion, Syngas Conversion, Future Methodologies in Catalysis & Solar Fuels, Fluidic Systems, Nanoreactors, and Nanobubbles, in which every project cluster is coordinated by two MCEC members. In addition, every research project is supervised by at least two MCEC members from different backgrounds and disciplines in order to foster possible multidisciplinary collaborations and knowledge transfer.²

1.2 | Noble metal nanostructures and their applications

In the past decades, noble metal nanostructures have been used extensively in both academic research and industry. With controllable sizes and shapes, fabricated noble metal nanostructures possess extraordinary optical, electrical, and catalytic properties,^{3,4} making them suitable for a wide range of applications in chemical and biological sensing,⁵⁻⁷ fuel and solar cells,^{8,9} surface-enhanced Raman scattering (SERS),¹⁰⁻¹⁶ and catalysis.¹⁷⁻²⁰ Among many different structural configurations, arrays of ceramic-supported noble metal nanoparticles²¹⁻²⁴ and periodic noble metal nanogaps^{11-16,25} are the most intensively studied structures, especially for sensing, catalysis, and SERS applications.

It has been found that the reduction in size of the noble metal nanoparticles, for example gold (Au) and platinum (Pt) nanoparticles, to sub-10 nm leads to an enormously enhanced catalytic activity.²⁶ Not only the

nanoparticle size and shape, but also the interaction of the nanoparticle with its support material is thought to strongly affect the catalytic activity.²⁷ However, supported nanoparticles have been found to be unstable under the reaction conditions due to their aggregation, thus resulting in blocking of active sites and deactivation.²⁸ Therefore, structures with regular and uniform noble metal nanoparticles on support substrates are highly demanded for catalysis studies as a better control in the uniformity and distribution of the nanoparticles can lead to a better control of their properties. Such arrays of supported noble metal nanoparticles can serve as model systems to investigate their thermal stability and catalytic properties.²⁹

A significant reduction in the gap spacing, i.e. much smaller than the incident wavelength, of the noble metal nanogaps on the other hand results in remarkable optical properties.³⁰ A strongly confined electromagnetic field is found to be generated at the region of the noble metal nanogaps caused by localized plasmon.³¹ This leads to an excellent enhancement of the signals for the surface plasmon-based sensing, thus enabling the detection of even a single molecule.^{11,12}

Although having a large number of applications, reproducible fabrication of uniform and dense arrays of these noble metal nanostructures over large areas on ceramic substrates such as glass, fused-silica, and thermally oxidized silicon, has been considered challenging at low-cost, especially without the use of metallic adhesion layers. Therefore, there is a need for robust fabrication techniques for wafer-scale patterning of uniform and dense arrays of noble metal nanoparticles and nanogaps at high throughput and low-cost.

1.3| Aim of the thesis

The aim of this thesis is to develop enabling techniques for patterning regular noble metal/ceramic nanostructures over large areas at low-cost and to apply such nanostructures in microfluidic devices for catalysis study of ceramic-supported noble metal nanoparticle arrays. In the course of the investigation another aim arose, namely understanding the mutual interaction of noble metals with ceramic substrates.

1.4| Collaborations

Being encouraged by the great opportunities for interdisciplinary collaboration within MCEC, many collaborations were successfully established during this research with researchers from different research groups. Details of the main collaborators are listed below, whereas details of the scientific output are given in the publication list.

Mesoscale Chemical Systems group (University of Twente)

Together with [dr. ir. Niels R. Tas](#), [ing. Erwin Berenschot](#), and [dr. ir. Roald M. Tiggelaar](#), we developed many techniques for large-area fabrication of regular noble metal/ceramic nanostructures at low-cost. The mutual interaction of noble metals with ceramic substrates upon treating with ultraviolet (UV)-ozone or oxygen (O_2) plasma was also investigated in close collaboration.

BIOS Lab-on-a-Chip group (University of Twente)

High-quality tunable gold nanogap arrays were prepared for [Jasper J. A. Lozeman](#) to study surface-enhanced Raman scattering.

Together with [dr. Corentin B. M. Tregouet](#), we further explored the engulfment mechanism of Au and Pt nanoparticles into silica substrates. By controlling the engulfment process of Pt nanoparticles into oxidized silicon substrates, we developed a technique for patterning ceramic membranes with dense through-hole nanopores.

Free-standing and sub- μm thickness polydimethylsiloxane (PDMS) through-hole membranes were prepared for [Martijn P. Tibbe](#) to study the cell culturing on these membranes in a Transwell-like set-up.

Together with [Juan Wang](#), hierarchical structures were fabricated using droplet-based microfluidics, which can be used for hydrophobic coating and molecular detection.

Physics of Fluids group (University of Twente)

Glass-supported gold microhole arrays were prepared for [dr. Pengyu Lv](#) to study the growth and detachment of oxygen bubbles induced by gold-catalyzed decomposition of hydrogen peroxide.

Arrays of gold nanoparticles supported on cone-shaped silica features were prepared for [prof. dr. Yuliang Wang](#), and [Mikhail Zaytsev](#) to study the gas-bubble growth around laser-irradiated, water-immersed plasmonic nanoparticles.

Janus particles at various sizes were prepared for [dr. Alvaro Marin](#), [dr. Maziyar Jalaal](#), and [dr. Borge ten Hagen](#) to study the self-propelling of Janus particles in evaporating liquid droplets.

Inorganic Chemistry and Catalysis group (Utrecht University)

Silica-supported noble metal nanoparticle arrays were prepared for [Anne-Eva Nieuwelink](#) to perform trial catalytic experiments.

PhotoCatalytic Synthesis group (University of Twente)

Microreactors integrated with a noble metal nanoparticle array were fabricated, and catalytic experiments were performed with the help of [Devin O'Neill](#). The measurement system was built by [ing. Robert Meijer](#).

1.5| Thesis outline

The outline of this thesis is as follows. In **Chapter 2**, a plasma shrink-etching technique is presented that enables large-area fabrication of nanostructures, i.e. dots or lines, with tunable dimensions down to sub-30 nm. The starting point for the shrink-etch fabrication is the nanostructures patterned by UV-based displacement Talbot lithography (DTL). By combining this DTL-based shrink-etching technique with dry etching, wet etching, and thin film deposition techniques, in **Chapter 3** we report a robust and high-yield fabrication method for wafer-scale patterning of high-quality arrays of dense gold nanogaps at low-cost. These nanogaps are successfully applied for SERS experiments. In **Chapter 4**, by combining DTL with an inclined argon ion beam etching technique, we report a robust method for large-scale fabrication of highly ordered size-tunable noble metal nanoparticles, both of gold and platinum, supported on oxidized silicon substrates without metallic adhesion layers. To explore the mutual interaction of gold thin films with the surface of oxidized silicon substrates, in **Chapter 5** we investigate their adhesion to the substrate surface upon treating with UV-ozone or oxygen plasma. In **Chapter 6**, we present an analysis of the engulfment of platinum nanoparticles into oxidized silicon substrates upon high temperature annealing. We show that this phenomenon enables the fabrication of dense arrays of solid-state through-hole nanopores with diameters down to sub-30 nm. In **Chapter 7**, we show an effort of using microfluidic technology for catalysis study of ceramic-supported noble metal nanoparticle arrays. Finally, conclusions and recommendations on the basis of each chapter are given in **Chapter 8**.

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2

Shrinkage Control of Photoresist Nanocolumns*

A method to fabricate large-area arrays of nanocolumns without a deep-ultraviolet (UV) laser source is reported. This method allows high-yield fabrication of $3\times 3\text{ cm}^2$ arrays of sub-30 nm nanocolumns made of bottom antireflection layer coating (BARC) by combining displacement Talbot lithography (DTL) using a monochromatic UV beam (365 nm wavelength) with plasma etching techniques. DTL is used to manufacture an initial pattern of periodic photoresist nanocolumns with a diameter of approximately 110 nm. N_2 plasma can transfer this pattern at a 1:1 ratio to BARC nanocolumns. We find

that reactive O₂/N₂ plasma etching on the other hand can shrink the BARC nanocolumns to sub-30 nm dimensions. The shrink-etching process can be reproducibly controlled by tuning the gas flow ratio and the etching time. It is highly remarkable that the verticality of these BARC nanocolumns remains during O₂/N₂ plasma shrink-etching. Combining the etching of O₂/N₂ plasma with N₂ plasma allows us to produce BARC nanocolumns with over the entire diameter range from 110 nm to sub-30 nm. Our fabrication approach enables large-footprint fabrication of size-tunable periodic nanostructures that have many potential applications in photonics, electronics, biosensors, smart surfaces, catalysis, and biomedical analysis.

*This chapter is based on the publication: [Le-The, H.](#); Berenschot, E.; Tiggelaar, R. M.; Tas, N. R.; van den Berg, A.; Eijkel, J. C. T. Shrinkage control of photoresist for large-area fabrication of sub-30 nm periodic nanocolumns. *Advanced Materials Technologies* **2017**, 2, 1600238.

2.1| Introduction

Nanotechnology in recent decades has provided opportunities to synthesize nanomaterials and to pattern nanostructures. The enormous increase in nanotechnology applications in physics, chemistry, biological/medical applications, and in materials science, leads to the requirement for robust, high-yield fabrication techniques to precisely pattern nanostructures over large-areas and at low-cost.^{1,2} Near-UV based optical lithography techniques such as projection lithography and proximity lithography allow to pattern structures in the sub-micrometer range, but are limited to approximately 0.35 μm feature size.³ Fabricating using these techniques to achieve the critical dimension requires dedicated systems, which are difficult to operate reproducibly. Several techniques have been successfully utilized to meet the great demand for surface patterning at the nanoscale, including electron beam lithography (EBL),^{4,5} ion beam lithography (IBL),⁶ laser interference lithography (LIL),⁷⁻⁹ nanoimprint lithography,^{10,11} and nanosphere lithography.¹¹⁻¹⁴ EBL and IBL provide the opportunity to produce feature sizes as small as 10 nm, but require conducting substrates and delicate operating systems. Moreover, because of their low throughput they are not suitable for batch production. LIL – with the use of the interference of two coherent laser beams – can produce periodic nanopatterns down to approximately 20 nm over large-areas. Although featuring high-yield fabrication, this technique requires high system stability in order to achieve reproducible fabrication. Nanoimprint lithography is also suitable for large-footprint nanopatterning at low-cost; however, it requires flat substrates and an additional step to remove the residual polymer layer. Nanosphere lithography relies on the self-assembly of colloidal spheres, but this leads to a lack of control, and hence is not applicable for large-area fabrication of periodic nanostructures.

Another direct way to decrease the feature size is to decrease the wavelength of the illumination sources. Using a laser source with a shorter exposure wavelength, e.g. 157 nm or 193 nm, photolithography could possibly produce sub-50 nm features.¹⁵ Using extreme ultraviolet lithography interferometry with a synchrotron source wavelength of 13 nm, the fabrication of 19 nm lines and spaces, and 38 nm period gratings has been demonstrated.^{16,17} Although these techniques can provide excellent resolution-enhancement in downscaling the feature size, they require high-cost and complex operating systems that are not widely available.

Recently, Talbot lithography has been used as an alternative for patterning high-resolution periodic nanofeatures.¹⁸⁻²⁰ This technique relies on the near-field diffraction effect that was first observed by Talbot.²¹ When illuminating a periodic pattern (grating) with monochromatic light, its image is repeated at

periodic distances away from the grating plane. This distance, termed the Talbot distance, is proportional to both the square of the grating period and the reciprocal of the wavelength.²² Although effective, Talbot lithography is limited by the very small Talbot distances of the self-images, which requires extremely flat substrates and precise control of the distance from the mask to the substrate. Significant progress was reported by Solak *et al.* with the introduction of an improved version of this technique, termed displacement Talbot lithography (DTL).²³ During the illumination of the mask using a monochromatic UV beam (365 nm wavelength), after a period of time the substrate is displaced within a DLT-range at around a set gap distance from the mask. The substrate is then scanned through the self-images of the pre-defined periodic structures on the mask at every Talbot distance. Therefore, this effective technique could provide rapid wafer-level patterning of high-resolution periodic nanostructures, i.e. regular patterns of lines, holes or dots in photoresist, without the need for flat substrates and the absolute distance between the mask and the substrate. For the high-resolution patterning of photoresist nanostructures using this technique, a bottom anti-reflection layer coating (BARC) is required. BARC is used to absorb the light passing through the photoresist layer to reduce the interference effect caused by the reflection of light on the Si wafer surface.^{24,25} Despite being a powerful nanopatterning technique, UV based DTL is limited in its application to nanostructures of hundreds of nanometers. Thus, patterning sub-100 nm periodic nanostructures by applying the DTL technique then still requires a deep-UV laser, i.e. an ArF laser operating at 193 nm.

In this chapter, we report an alternative robust method to fabricate sub-100 nm periodic nanocolumns using the DTL technique but without the need for a deep-UV laser source. Combining DTL using a UV beam source (365 nm wavelength) with plasma etching techniques enables us to produce periodic nanocolumns made of BARC at various sub-100 nm diameters from the pre-defined 110 nm photoresist nanocolumns patterned by DTL. We have demonstrated the fabrication of large-area arrays of BARC nanocolumns at diameters ranging from 110 nm to sub-30 nm, by combining various plasma etchings (N_2 , O_2 , and O_2/N_2 plasmas) and by tuning the etching parameters such as O_2/N_2 gas flow ratios and varying the etching time. Using our fabrication approach, well-defined BARC nanocolumns with diameters as small as 28 nm and high aspect ratios up to 5.3 over large-areas of $3 \times 3 \text{ cm}^2$ were reproducibly fabricated with high uniformity.

2.2 | Materials and methods

2.2.1 | Patterning photoresist nanocolumn arrays

4-inch Si wafers (525 μm thick, single side polished, Okmetic, Finland) were immersed in a 1% hydrofluoric acid (HF) solution to remove the native oxide, and dehydrated on a hotplate at 125°C for 10 min to remove the solvent. A BARC layer (186 ± 2 nm thick) (AZ BARLi II 200, MicroChem GmbH) was spin-coated on the Si wafers at 3000 rpm for 45 s, followed by baking at 185°C for 1 min. The Si wafers were then spin-coated with positive photoresist (PR) PFI88 solution diluted 1:1 with propylene glycol methyl ether acetate (PGMEA) (Sumitomo Chemical Co., Ltd., Japan) at 4000 rpm for 45 s (200 ± 3 nm thick), followed by pre-exposure baking at 90°C for 1 min (**Figure 2.1**). Two exposures were implemented for each Si wafer by using Displacement Talbot Lithography (PhableR 100C, Eulitha, Switzerland)²³ with a phase shift mask at an exposure dose of 1 mW cm⁻². The phase shift mask with a 3×3 cm² linear grating period of 250 nm made of fused-silica was bought from Eulitha. This linear grating were etched into a fused-silica substrate to provide an approximately 180° phase shift between the light transmitted through the lines and the spaces. As a result, a strong Talbot effect can be obtained at a suitable distance from the mask.²³ The Si wafer was mounted on a vacuum chuck with a gap of approximately 65 μm from its surface to the mask. For each exposure of 45 s, the Si wafer was displaced a DLT-range of 3 μm around the gap distance after every 20 s during the illumination of the mask by a monochromatic UV beam. The mask was rotated an angle of 90° relative to the Si wafer for the second exposure. After two exposures, the Si wafers were post-exposure baked on a hotplate at 110°C for 1 min, followed by developing in the OPD4262 developer for 30 s and rinsing with de-ionized (DI) water to complete the fabrication of PR nanocolumn arrays.

2.2.2 | Chamber cleaning and etching implementation

The etching chamber was cleaned completely before running each plasma etching process using cleanroom tissues with acetone, and then dried using a nitrogen gun to remove all the residual materials from the previous etching process. Before etching, a patterned Si wafer was broken into pieces, and one piece was selected for the high-resolution scanning electron microscope (HR-SEM) observation of the cross-sectional view. Pieces were assembled back into the wafer shape for the etching process in a parallel plate reactive ion etching system (in-house built Tetske system, NanoLab Cleanroom, The Netherlands) (Appendix A: **Figure A1**). Regularly checking the selected piece using a HR-SEM was done after every etching time-step.

Figure 2.1. Fabrication process of a 3x3 cm² array of PR nanocolumns using DTL.

2.2.3 | Plasma etching of photoresist and BARC layers

To measure the etching rates of PR and BARC in various gas plasmas, Si wafers were coated with a PR PFI88 layer (4000 rpm for 45 s, baked at 90°C for 1 min) or with AZ BARLi II 200 (3000 rpm for 45 s, baked at 185°C for 1 min), followed by plasma etching using the TETSKE system at the wafer-level, 13 mTorr, and 25 W. Three gas plasmas were used, namely 50 sccm N₂, 50 sccm O₂, and 50/50 sccm O₂/N₂, at the above etching settings with etching time-steps of 2 min for the N₂ plasma, and 30 s for the O₂ plasma and O₂/N₂ plasma.

2.2.4 | Patterning BARC nanocolumn arrays

3x3 cm² arrays of PR nanocolumns made by DTL were subsequently etched in the TETSKE system to pattern BARC nanocolumn arrays. The etching was conducted at the wafer-level, 13 mTorr, 25 W using three gas plasmas, i.e. 50 sccm N₂, 50 sccm O₂, 50/50 sccm O₂/N₂. The etching time-step was 2 min for 50 sccm N₂ plasma etching, and 30 s for 50 sccm O₂ and 50/50 sccm O₂/N₂ plasma etching.

2.2.5 | Shrink-etching with different O₂/N₂ gas flow ratios

Si wafers with patterns of 3x3 cm² PR nanocolumn arrays were shrink-etched using different O₂/N₂ gas flow ratios (10/50, 20/50, 30/50, 40/50, and 50/50 sccm) at wafer-level, 13 mTorr, and 25 W with an etching time-step of 30 s.

2.2.6| Characterization

All high-resolution scanning electron microscope (HR-SEM) images were taken using a FEI Sirion microscope (United States) at a 5 kV acceleration voltage and a spot size of 3. The cross-sectional HR-SEM images were obtained at an angle of 20° with tilt correction applied. Each error bar was calculated from the standard deviation of at least five measurements

2.3| Results and discussion

2.3.1| Patterning photoresist nanocolumn arrays

Figure 2.2(a) shows HR-SEM images of the fabricated PR nanocolumn array. Well-defined PR nanocolumns were obtained that had vertical sidewalls as shown in the cross-sectional image. The top-view HR-SEM image shows a well-controlled pattern of PR nanocolumns (250 nm pitch) with a high uniformity in terms of diameter distribution (**Figure 2.2b**). The diameter of the PR nanocolumns was approximately 110 nm with a small variation (1 standard deviation) of 3 nm. Five selected areas over the 3×3 cm² array were also measured and showed well-fabricated and well-controlled PR nanocolumns, though the diameter variation was slightly larger, i.e. 4.7 nm (Appendix A: **Figures A3-A4**). This could be due to the imperfection of the mask made by electron beam lithography which was then transferred directly to the patterns. The loss of focus and drifting of the HR-SEM images²⁶ during a slow scan speed could also probably add to the inaccuracy for further image processing and analysis by using ImageJ software. All these features indicate a robust fabrication process.

Figure 2.2. (a) Top-view (scale bar 2 μm) and cross-sectional (scale bar 1 μm) HR-SEM images of periodic PR nanocolumns patterned by DTL. (b) Diameter distribution of the PR nanocolumns with a close-up image inserted (scale bar 200 nm).

2.3.2 | Plasma etching of bottom antireflection layer coating

To subsequently transfer the fabricated PR nanocolumn arrays into the BARC layer, plasma etching was chosen as a suitable technique. Plasma etching is considered as an excellent approach for transferring PR structures patterned from the lithography process to BARC layers because of its high etch-rate selectivity for BARC over PR. With a minimum resist loss, it thus allows further processing the substrates.^{27,28}

Figure 2.3. Thickness measurement of (a) PR and (b) BARC layers etched in various gas plasmas versus etching time at wafer-level, 13 mTorr, and 25 W. The linear fit curves are associated with the slopes of the lines.

Table 2.1. Etching rates of PR (PFI88 1:1 PGMEA) and BARC (AZ BARLi II 200) in different gas plasmas obtained at wafer-level, 13 mTorr, and 25 W.

Plasma etching	PFI88 1:1 PGMEA (nm min ⁻¹)	AZ BARLi II 200 (nm min ⁻¹)
50 sccm N ₂	17.4	23.4
50 sccm O ₂	86.4	95.4
50/50 sccm O ₂ /N ₂	91.2	93.0

We first investigated the etching rate of un-patterned PR and BARC layers in the TETs machine using various gas plasmas, i.e. 50 sccm N₂ plasma, 50 sccm O₂ plasma, and 50/50 sccm O₂/N₂ plasma, all at 13 mTorr and 25 W. The etching was conducted at the wafer-level in a clean etching chamber in order to prevent the loading effect and the redeposition of residual materials deposited on the chamber wall from the previous processes (Appendix A: **Figure A2**). **Figure 2.3** shows the measured thicknesses of the PR and BARC layers on the Si wafers versus the etching time. For all gas plasmas, a linear decrease in the thicknesses of the PR and BARC layers was observed with increasing etching time, as evidenced by the almost perfect linear fit curves (Appendix A: **Figures A5-A6**, and **Equations A1-A6**). The etching rates of the PR and BARC found at these etching settings are shown in **Table 2.1**.

A considerable etch-rate selectivity of BARC over PR (1.34) was achieved in 50 sccm N₂ plasma. This significant difference in etching rates was also reported by Gupta *et al.*,²⁷ who attributed it to the difference in molecular structure between BARC (AZ BARLi) and PR (i-line photoresist). The i-line photoresist is a novolac (phenol-formaldehyde) based resist containing aromatic rings, methyl and hydroxyl groups, whereas the molecular structure of the BARC contains oxygen atoms in maleic anhydride units and nitrogen atoms in N-substituted maleimide units, without the hydrocarbon rings. As a result, the concentration of oxygen atoms in the BARC is much higher than in the PR, i.e. 39.8% versus 13.3%. In the literature, the relation between etching selectivity and PR structure has been repeatedly investigated. An increase in the number of oxygen atoms in monomer units was reported to increase the etching rates of metal-free organic materials.²⁸ Using various dry etching techniques such as argon ion-beam, oxygen ion-beam, and oxygen plasma etching, Gokan *et al.* investigated the etching rates of various resist materials. They found that the measured etching rates are proportional to the " $N/(N_c - N_o)$ factor", where N , N_c , and N_o are the total number of atoms, the number of carbon atoms, and the number of oxygen atoms in a monomer unit, respectively.²⁸ In the presence of oxygen atoms, the carbon atoms in polymers are volatilized easily during the plasma etching.²⁹ Another possible reason for the difference in the etching rates could be the presence of nitrogen atoms in the BARC material. Huang *et al.* reported that when polymers containing nitrogen were etched in a reducing gas plasma such as N₂, the nitrogen atoms cause an increase in the etching rate, by a mechanism similar to that behind the presence of oxygen atoms in polymers.³⁰

In 50 sccm O₂ plasma, the etching rates of the PR and BARC were sharply increased compared to those in 50 sccm N₂ plasma, though the etching rate of the BARC was still higher than that of the PR. The physical bombardment of highly energetic neutrals and ions breaks the chemical bonds of polymers, and atomic oxygen or molecular oxygen can easily react with the polymer carbon to form volatile carbon oxides.³¹ However, when using a plasma mixture of 50/50 sccm O₂/N₂, the etching rate of the PR slightly increased compared to that in the O₂ plasma, whereas the etching rate of the BARC slightly decreased. We attribute this to a decreased oxygen concentration, since – because of the fixed pressure of 13 mTorr – adding nitrogen resulted in a decrease in the oxygen concentration. For the BARC, the increased etching rate caused by the N₂ plasma could not compensate and as a result, the overall etching rate dropped. For the PR, we explain the only slightly altered etching rate at the decreased oxygen concentration by the fact that the aromatic rings in the molecular structure of the PR could form stable structures on the surface in the O₂ plasma, thereby preventing the chemical reactions.^{30,31} Also, the N₂ plasma

enhanced the physical bombardment to remove these stable structures, leading to a significant increase in the overall etching rate.

Figure 2.4. Patterning of periodic BARC nanocolumns using N_2 plasma etching. PR nanocolumns were etched in 50 sccm N_2 plasma at wafer-level, 13 mTorr, and 25 W, to transfer to BARC nanocolumns. (a) Cross-sectional HR-SEM images of the nanocolumns at different etching times. Scale bars represent 200 nm. (b) Geometric measurement and calculation of the structures.

Figure 2.4(a) shows the cross-sectional HR-SEM images of periodic PR nanocolumns etched in 50 sccm N_2 plasma at different etching times, together with sketches for illustration. After 8 min of etching, the PR nanocolumns were completely transferred to the underlying BARC layer, resulting in BARC nanocolumns with straight sidewalls. The diameter of the nanocolumns remained largely unchanged during the etching process, though the formation of nano-sharp tips was observed. These results indicate that there was no etching in the lateral direction, which means the N_2 plasma etching was probably purely by physical bombardment. The physical bombardment of high energy particles has indeed been reported to lead to the formation of nano-sharp tips.³² The geometric parameters of these nanocolumns versus the etching times were also measured and are shown in Figure 2.4(b). Using the etching rates of the PR and BARC as previously established in 50 sccm N_2 plasma etching, we also calculated the remaining thickness of the BARC layer and the height of the nanocolumns versus the etching time (Appendix A: Figure A7 and Equations A7-A9). The calculated curves showed a good agreement with the measurement results. The height of the nanocolumns increased with the increasing etching time because the etching rate of the PR is much lower than that of the BARC. The rate of increase was 0.10 nm s^{-1} , in accordance with the

measured etching rate of the PR (0.29 nm s^{-1}) subtracted from that of the BARC (0.39 nm s^{-1}). After a 477 s etching time, the BARC layer was completely etched, after which time the height of the nanocolumns decreased at a rate of the PR etching rate since the PR still remained on the top of the nanocolumns. The differences between the measurement results and the calculation results could be explained by the errors in the height measurement using the HR-SEM, as well as the formation of the nano-sharp tips which had not been taken into account.

We also investigated the etching of PR nanocolumn arrays in 50 sccm O_2 plasma, and in the mixture plasma of 50/50 sccm O_2/N_2 . **Figures 2.5(a)** and **2.5(b)** show the cross-sectional HR-SEM images of the PR nanocolumn arrays etched in the O_2 plasma and O_2/N_2 plasma at different etching times, respectively. For both etching processes, it was observed that the PR nanocolumns were transferred into the BARC layer, while simultaneously shrinking in diameter. Well-defined nanocolumns with vertical sidewalls were again obtained, although this time without the formation of nano-sharp tips. We can explain the results as follows. The presence of oxygen probably broke chemical bonds in the nanocolumn tips due to chemical reactions. The shrinking of the nanocolumns in the O_2 plasma was slightly faster than that in the mixture plasma due to the higher etching rate of the BARC obtained in pure oxygen plasma. After 150 s etching, the PR nanocolumns were shrink-etched into BARC nanocolumns of diameters of $24.7 \pm 3 \text{ nm}$ (in 50 sccm O_2 plasma) and $27.7 \pm 2.2 \text{ nm}$ (in 50/50 sccm O_2/N_2 plasma) as shown in **Figures 2.5(c)** and **2.5(d)**, respectively. Similar calculation of the remaining BARC thickness and the nanocolumn height was performed as reported above, based on the measured etching rates of the PR and BARC in 50 sccm O_2 and 50/50 sccm O_2/N_2 plasmas (Appendix A: **Figure A7** and **Equations A10-A17**). The calculated values show a good fit with the measured values. A significant difference in the nanocolumn height between the measured values and the calculated values after 120 s etching in the O_2 plasma was observed. This could be explained by a rapid breakage of molecular bonds in the tips, and the bending of the nanocolumns due to a higher etching rate which resulted in narrower nanocolumns (see discussion in **Figure 2.6**). Highly vertical sub-30 nm BARC nanocolumns with aspect-ratios as high as 5.3 were achieved in 50/50 sccm O_2/N_2 plasma after 150 s etching.

Figure 2.5. Patterning of periodic BARC nanocolumns using O₂, or O₂/N₂ plasma etchings. PR nanocolumns were etched in (a) 50 sccm O₂ plasma or (b) 50/50 sccm O₂/N₂ plasma at wafer-level, 13 mTorr, and 25 W. Cross-sectional HR-SEM images of the nanocolumns at different etching times at the etching parameters in (a) and (b). Scale bars represent 200 nm. (c-d) Geometric measurement and calculation of the structures obtained in (a) and (b), respectively.

The uniformity of the BARC nanocolumn arrays fabricated by using different gas plasma etchings was also investigated. **Figure 2.6** shows the top-view and cross-sectional HR-SEM images of the fabricated BARC arrays. Highly uniform arrays of well-fabricated BARC nanocolumns were obtained for 50 sccm N₂ and 50/50 sccm O₂/N₂ plasma etchings, as shown in **Figures 2.6(a)** and **2.6(c)** respectively (Appendix A: **Figures A9-A10**, and **Table A1**). Smaller BARC nanocolumns were achieved in 50 sccm O₂ plasma etching, though the nanocolumns were bent. Moreover, many BARC nanocolumns were fallen down due to their weak adhesion with the Si surface (**Figure 2.6b**). Insufficient cleaning of the etching chamber could create “nanograss” surfaces caused by redeposition of materials from previous etching processes, as shown in **Figure 2.7**. Such redeposited materials could also slow down or even terminate the shrinking process (Appendix A: **Figure A2**). In addition, at the etching time-step of 30 s, no significant influence of the corona effect on the resulting nanocolumns has been observed in our etching processes.³³

Figure 2.6. Top-view (scale bar 2 μm) and cross-sectional (scale bar 1 μm) HR-SEM images of BARC nanocolumn arrays fabricated by using different gas plasmas: (a) 50 sccm N_2 for 8 min, (b) 50 sccm O_2 for 150 s, and (c) 50/50 sccm O_2/N_2 for 150 s, at wafer-level, 13 mTorr, and 25 W.

Figure 2.7. Comparison of the etching results obtained in a cleaned etching chamber and in an uncleaned etching chamber. Scale bars represent 200 nm. Nanogrowth was formed when etching in the uncleaned chamber due to the redeposition of residual materials deposited on the chamber wall from the previous etching.

The influence of the O_2/N_2 gas flow ratio on the mixture plasma etching was investigated by changing the O_2 flow rate (V_{O_2}) while keeping the N_2 flow rate at 50 sccm. PR nanocolumn arrays were shrink-etched in O_2/N_2 plasma at wafer-level, 13 mTorr, and 25 W with different gas flow ratios of O_2/N_2 (Appendix A: **Figure A11**). The diameter and height of the nanocolumns were determined after every 30 s of etching time from the cross-sectional images obtained by HR-SEM, as shown in **Figure 2.8**. An increase in the O_2 flow rate resulted in an enhanced shrinking of the nanocolumns, especially at O_2 flow rates above 10 sccm (**Figure 2.8a**). At a 10 sccm O_2 flow rate, even after 180 s etching the column diameter remained larger than 60 nm. For O_2 flow rates of 20 sccm or above, the decrease in the column diameter was faster than at a 10 sccm O_2 flow rate. Moreover, this decrease in the column diameter was almost independent of O_2 flow rate, up to an etching time of 120 s. When increasing the etching time by another 30 s to 150 s, differences in shrinking were

observed. The diameter of the nanocolumns significantly decreased from ~58 nm to ~38 nm ($V_{O_2} = 40$ sccm), or from ~59 nm to ~28 nm ($V_{O_2} = 50$ sccm), whereas the column diameter only slightly decreased from ~65 nm to ~55 nm for both the O_2 flow rates of 20 sccm and 30 sccm. Etching these nanocolumns for another 30 s also resulted in sub-30 nm nanocolumns, though the column height was significantly decreased (**Figure 2.8b**). Beyond a 150 s etching time, the remaining BARC layer was etched away completely while the nanocolumn was etched from the top, thus shortening the nanocolumns. The most efficient etching recipe for shrinking was using the mixture plasma of 50/50 sccm O_2/N_2 for 150 s where sub-30 nm BARC nanocolumns were obtained at the highest aspect ratio of 5.3. Using 10/50 sccm O_2/N_2 plasma to continuously shrink these nanocolumns at a lower rate could possibly lead to even narrower nanocolumns, though we would then expect a slight decrease in the uniformity of the nanocolumn distribution.

Figure 2.8. Measurement of (a) the diameter and (b) the height of the PR nanocolumns shrink-etched in O_2/N_2 plasma versus etching time. The etching was conducted at wafer-level, 13 mTorr, and 25 W with different O_2/N_2 gas flow ratios.

2.3.3 | Patterning BARC nanocolumns at a particular diameter

To fabricate BARC nanocolumn arrays at a particular diameter, we combined the etching in the mixture plasma of O_2/N_2 with the N_2 plasma, as shown in **Figure 2.9**. The PR nanocolumns were first shrink-etched in 50/50 sccm O_2/N_2 plasma for 60 s to produce nanocolumns at a diameter of 81.2 ± 1.4 nm. These nanocolumns were subsequently etched in 50 sccm N_2 plasma for 4 min to remove the remaining BARC layer (96 ± 2 nm) but without changing the nanocolumn diameter (80.9 ± 1.6 nm). We also observed the formation of nano-sharp tips caused by etching in the N_2 plasma. Importantly, the values predicted by calculation showed a good match with the measurement results, indicating that a similar design recipe could be followed for the fabrication of particular nanocolumn diameters (Appendix A: **Figure A8** and **Equations A18-A21**). When

etching in 50/50 sccm O_2/N_2 plasma, the nanocolumn height slightly increased at a rate of $+0.03 \text{ nm s}^{-1}$, while the BARC thickness sharply decreased with the rate of -1.55 nm s^{-1} (see **Figure 2.5d**). On the other hand, when etching in 50 sccm N_2 plasma, the nanocolumn height strongly increased at a rate of $+0.10 \text{ nm s}^{-1}$, while the thickness of the remaining BARC slowly decreased at a rate of -0.39 nm s^{-1} (see **Figure 2.4b**). We thus expect that this etching combination will enable us to easily fabricate well-defined periodic BARC nanocolumns that have vertical sidewalls and diameters ranging from approximately 110 nm to sub-30 nm.

Figure 2.9. Patterning of periodic BARC nanocolumns at a designed diameter of 80 nm by combining O_2/N_2 plasma etching with N_2 plasma etching. PR nanocolumns were etched in 50/50 sccm O_2/N_2 plasma, and then in 50 sccm N_2 plasma at wafer-level, 13 mTorr, and 25 W. (a) Cross-sectional HR-SEM images of the nanocolumns at different etching times. Scale bars represent 200 nm. (b) Geometric measurement and calculation of the structures.

For the shrink-etching process, the shrinkage of the nanocolumn diameter was mostly caused by oxygen plasma (**Figure 2.5c**). Minor effects have been observed when adding N_2 plasma (**Figure 2.5d**). Therefore, upon using another i-line photoresist, the shrinkage of the PR nanocolumns in oxygen plasma needs to be reconducted, which can then be used as a new reference. In addition, our study revealed that for the highest uniformity in nanocolumn height the etching rate of the photoresist is close to that of BARC (**Table 2.1**). Therefore, in case of use of another resist, the flow rate ratio of oxygen to nitrogen needs to be

adjusted to obtain this condition of highest uniformity on the complete specimen area. Finally, our technique is not limited to the manufacturing of nanocolumns. Using our technique, we also demonstrated the shrinkage control of PR nanolines of 90 nm to BARC nanolines of 45 nm in width (Appendix A: Figure A12).

2.4 | Conclusion

In summary, we have successfully demonstrated a robust fabrication method that enables large-footprint fabrication of sub-30 nm periodic BARC nanocolumns without the need for a deep-UV laser illuminating source. Combining O₂/N₂ plasma etching with N₂ plasma etching at different etching times allowed us to fabricate 3×3 cm² arrays of BARC nanocolumns at different diameters ranging from sub-30 nm to approximately 110 nm, and with high control ability. Our fabrication method combines DTL using a monochromatic UV beam (365 nm wavelength) with plasma etching techniques that are simple in operation, hence making it suitable for large-area batch production at low-cost. We believe the sub-30 nm nanopatterning method reported in this chapter will provide an enabling approach for rapid patterning of 30–110 nm periodic nanostructures which are needed for many applications, including optoelectronic devices,³⁴ photonic sensors,³⁵ biosensors,³⁶ nanosieve membranes,³⁷ and energy applications.³⁸ In fact, elsewhere we report on the fabrication of high-density arrays of sub-15 nm silicon quantum dots using the combination of DTL-nanolithography and wet chemical etching steps.³⁹

2.5 | References

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3

Wafer-scale Fabrication of High Quality Tunable Gold Nanogaps*

We report a robust and high-yield fabrication method for wafer-scale patterning of high-quality arrays of dense gold nanogaps, combining displacement Talbot lithography based shrink-etching with dry etching, wet etching, and thin film deposition techniques. By using the self-sharpening of $\langle 111 \rangle$ -oriented silicon crystal planes during the wet etching process, silicon structures with extremely smooth nanogaps are obtained. Subsequent conformal deposition of a silicon nitride layer and a gold layer results in dense arrays of narrow gold nanogaps. Using this method, we successfully fabricate

high-quality Au nanogaps down to 10 nm over full wafer areas. Moreover, the gap spacing can be tuned by changing the thickness of deposited Au layers. Since the roughness of the template is minimized by the crystallographic etching of silicon, the roughness of the gold nanogaps depends almost exclusively on the roughness of the sputtered gold layers. Most importantly, our fabricated Au nanogaps show a significant enhancement of surface-enhanced Raman scattering (SERS) signals of benzenethiol molecules chemisorbed on the structure surface, at an average enhancement factor up to 3.0×10^8 .

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3.1| Introduction

Nanometer-sized metallic nanogaps made of gold (Au) or silver (Ag) have found many applications including biomedical and chemical sensing,¹ surface-enhanced Raman spectroscopy,²⁻⁷ and nonlinear optics⁸ due to their remarkable electrochemical and optical properties. For the surface-enhanced Raman spectroscopy, the intensity of the Raman scattering signal is boosted due to the modified emission of the scattering signal and the improved excitation of the studied molecules caused by the near-fields generated in metallic nanogap regions.⁹ To significantly enhance signals, the gap spacing needs to be much smaller than the incident wavelength.¹⁰ As a result, a strongly confined electromagnetic field is generated in the nanogap region by localized plasmons.¹¹ Using metallic nanogap structures, local enhancement factors up to 10^9 have been achieved, thus enabling the detection of a single molecule.^{2,3} Many methods have been reported to fabricate metallic nanogap structures, such as electron beam lithography (EBL),⁵ EBL-based angular deposition,⁴ electrochemical deposition,¹² electromigration,¹³ break junction,^{14,15} and atomic layer deposition (ALD).^{2,7} EBL-based methods offer a high feasibility in designing the size, position, shape and orientation of the metal nanogaps. However, their feature of serial patterning limits their use for high-yield and low-cost fabrication of large-area metal nanogap arrays. Moreover, the quality of the metal nanogaps strongly depends on the sidewall roughness of the patterned resist structures, which is mostly limited by the properties of the resist.^{4,5} Other indirect methods, such as electrochemical deposition, electromigration, and break junction, can produce very narrow metal nanogaps down to 5 nm.¹²⁻¹⁵ However, using these methods it is difficult to design a reproducible fabrication process, and thus they are unsuitable for mass production at low-cost. ALD has recently come to be considered as an effective method to pattern well-defined metal nanogaps as narrow as 3 nm.^{2,7} However, the fabrication process involves many complicated steps, which makes it time consuming. Additionally, the metal nanogaps patterned by the ALD technique cannot be rapidly reproduced, whereas other template-based methods allow the metal nanogaps to be reused by replacing the metal layer sputtered over the template surface. Therefore, there is a need for a robust fabrication technique for wafer-scale patterning of dense metal nanogap arrays at high throughput but low-cost.

Recently, a compelling technique for patterning periodic nanostructures has been reported by Solak *et al.*, termed displacement Talbot lithography (DTL).¹⁶ Using this technique with a monochromatic UV beam (365 nm wavelength) allows high-yield patterning of highly ordered photoresist (PR) nanostructures, *i.e.* lines, holes or dots, with dimensions down to approximately

100 nm, over full wafer areas. However, patterning PR nanostructures smaller than 50 nm using this technique still requires the use of a deep-UV laser, *i.e.* an ArF laser at 193 nm wavelength. To overcome this limitation, we developed a robust technique for shrink-etching the patterned PR nanostructures using a mixture of O₂/N₂ plasma.¹⁷ As a result, bottom antireflection coating (BARC) nanostructures with dimensions down to sub-30 nm could be reliably fabricated from the initially patterned PR nanostructures.

In this chapter, we report and demonstrate a robust and high-yield method for wafer-scale patterning of dense arrays of tunable Au nanogaps, combining the DTL-based shrink-etching technique with dry etching, wet etching, and thin film deposition techniques. Silicon (Si) structures consisting of extremely smooth nanogaps were fabricated by combining the dry etching process with the self-sharpening of <111>-oriented Si crystal planes during the wet etching process. Such etching combination has been reported and used to fabricate various Si-based structures.¹⁸⁻²¹ Subsequent conformal deposition of a silicon nitride layer and a gold layer resulted in dense arrays of high-quality gold nanogaps over full wafer areas. The gap spacing can be tuned down to 10 nm at high uniformity by changing the Au layer thickness. Moreover, we showed the potential of our fabricated Au nanogaps for surface-enhanced spectroscopy by measuring SERS signals of benzenethiol (BT) molecules chemisorbed on the structure surface.

3.2 | Materials and methods

3.2.1 | Patterning periodic 50 nm BARC nanolines

A BARC layer of 187 ± 2 nm (AZ BARLi II 200, MicroChem GmbH), and a PR layer of 200 ± 1.5 nm (PFI88 photoresist diluted 1:1 with propylene glycol methyl ether acetate (PGMEA), Sumitomo Chemical Co., Ltd., Japan) were spin-coated on the surface of an oxidized (~ 30 nm thick SiO₂) 4-inch Si wafers (525 μ m thick, P-type, <100>, single side polished, Okmetic, Finland), followed by baking at 185°C for 1 min and 90°C for 1 min, respectively (**Figure 3.1a**). DTL (PhableR 100C, Eulitha, Switzerland) was utilized to pattern PR nanolines of approximately 110 nm in width (250 nm pitch) at an exposure dose of 1 mW cm^{-2} for 75 s, using a wafer-scale phase shift mask of 250 nm grating period purchased from Eulitha (**Figure 3.1b**). After the exposure, the oxidized Si wafer was post-exposure baked on a hotplate at 110°C for 1 min, developed in the OPD4262 developer for 1 min, and rinsed with DI water to complete the fabrication of PR nanoline arrays (**Figure 3.1c**). It is worth mentioning that the patterned PR nanolines were aligned to the [100] crystal orientation of the Si wafers – PR nanolines were patterned perpendicularly to the primary flat of the

Si wafers. Subsequently, these PR nanolines were shrink-etched into ~ 50 nm BARC nanolines, using a two-step reactive plasma etching process, i.e. 50/50 sccm O_2/N_2 plasma for 1 min and 45 s, and 50 sccm N_2 plasma for 2 min (**Figure 3.1d**). These plasma etching processes were conducted using a parallel plate reactive ion etching system (in-house built TETSke system, NanoLab Cleanroom, The Netherlands) at wafer-level, 13 mTorr, and 25 W.¹⁷

3.2.2 | Patterning periodic Cr nanolines using lift-off process

A thin Cr layer of approximately 6 nm was deposited over the surface of the patterned wafer using a sputtering system (in-house built T'COathy system, NanoLab Cleanroom, The Netherlands) (**Figure 3.1e**). The sputtering process was conducted at 200 W, and a pressure of 6.6×10^{-3} mbar adjusted by using an argon (Ar) flow. Subsequently, a lift-off process was performed in a 99% HNO_3 solution, followed by sonication in DI water for 10 min. As a result, periodic Cr nanolines of approximately 200 nm in width (250 nm pitch) were fabricated on the surface of the oxidized Si wafer (**Figure 3.1f**). These Cr nanolines were then used as a hard mask for further processing of both the SiO_2 masking layer and the bulk Si substrate.

3.2.3 | Patterning high-quality SiN nanogaps

Reactive plasma etching was used to directionally etch the SiO_2 masking layer and the bulk Si substrate, which resulted in periodic Si nanotrenches of ~ 50 nm in width and ~ 150 nm in depth (**Figure 3.1g-h**). This plasma etching was also conducted in the TETSke system at wafer-level, 25 sccm fluorocarbon (CHF_3), 5 sccm O_2 , 10 mTorr, and 25 W for 13 min. Thereafter, the Cr mask was removed completely in a Cr etchant solution (Cr etch 200, MicroChemicals GmbH), leaving the SiO_2 nanolines as a masking layer (**Figure 3.1i**). After rinsing with DI water and drying with N_2 , the patterned wafer was cleaned in the O_2 plasma (TePla 300, PAV TePla AG, Germany) at 500 W for 20 min. Subsequently, the fabricated Si nanotrenches were etched in a 25% KOH solution at $75^\circ C$ for 15 s (**Figure 3.1k**), cleaned using the standard RCA-2 cleaning process, and immersed in a 50% HF solution for 10 min to completely remove the SiO_2 masking layer, thus leaving only the Si structures as a template for the deposition of a low stress silicon nitride (SiN) layer.

Prior to the deposition of the SiN layer, the wafer was completely cleaned in a 99% HNO_3 solution for 10 min, in a 69% HNO_3 solution at $95^\circ C$ for 10 min, in DI water using a quick dump rinser, and spin-dried to prevent any cross-contamination. A thin SiN layer of approximately 35 nm was deposited over the Si template by using low-pressure chemical vapor deposition (LPCVD) in a high temperature tube furnace (Tempress Systems, Inc., The Netherlands) at $850^\circ C$

for 40 min (**Figure 3.1L**). The thickness of the deposited SiN layer was measured using an ellipsometry system (M-2000UI, J.A. Woollam Co., United States) at an angle of 75°.

3.2.4 | Patterning high-quality tunable Au nanogaps

Au layers at different thicknesses were deposited over the SiN-coated Si templates by using the T'COathy sputtering system at 200 W, 6.6×10^{-3} mbar.²² By adjusting the sputtering time, Au nanogaps of different gap spacings down to ~10 nm were fabricated over full wafer areas (**Figure 3.1m**). It is worth mentioning that all the deposited Au layers were treated with UV-ozone (PR-100 UV-ozone Photoreactor, UVP Inc., United States) for 5 min.

High-resolution scanning electron microscopy (HR-SEM) images were taken by using a HR-SEM system (FEI Sirion microscope, United States) at a 5 kV acceleration voltage and a spot size of 3. The surface roughness of the deposited Au layers was determined from atomic-force microscopy (AFM) images (scan field: 500×500 nm²), recorded in contact modes using an AFM system (Dimension Icon, Bruker Corp., United States) in air.

Figure 3.1. Fabrication process of high-quality sub-10 nm Au nanogap arrays.

3.2.5 | Finite-difference time-domain simulations

The plasmonic behavior of the Au nanogaps was simulated by using finite-difference time-domain (FDTD) method by means of a commercial software package (Lumerical Solutions Inc., FDTD solutions). The dimensions of the Au nanogap structures were determined from the HR-SEM images (see **Figures 3.6c-e**). Given the translational symmetry of the structures, two-dimensional FDTD simulations were performed. Conformal mesh (mesh accuracy 4) and mesh refinement were used to define the structure with a minimum mesh size of 0.1 nm. Antisymmetric boundary conditions were used in both boundaries in the x-axis to simulate an infinitely periodic array of Au nanogaps, thus reducing the computational time. Perfectly matched layer (PML) boundary conditions with a steep angle profile were selected along the y-direction, which, ideally,

absorb all incident light without creating any back reflections. A plane wave source propagating in the y -direction with an electric field parallel to the x -direction was employed to excite the surface plasmons. Convergence test was made to determine the optimum distance between the SERS structure and the PML boundary conditions in the y -axis ($2\ \mu\text{m}$). The values of the dispersion relations for the different materials used (Au and Si) were extracted from the literature.²³ To represent the dispersion relation of the Si_3N_4 material, a Cauchy model²⁴ with coefficients of $B = 1.9832$, $C = 0.0096$, and $D = 6 \times 10^{-4}$ extracted from the characterization of a Si_3N_4 layer by ellipsometry, was used. The auto shutoff intensity was fixed at 1×10^{-6} , and an excitation wavelength of 785 nm was used in the simulations.

3.2.6 | Reflection measurements

Reflection measurements were performed on different Au nanogap samples featuring different gap spacings, i.e. $\sim 30\ \text{nm}$, $\sim 20\ \text{nm}$, and $\sim 10\ \text{nm}$, in order to determine the reflection minimum of the different gap spacings. The reflection measurements were conducted by using a microscope (Leica DM6000 FS microscope fitted with an Ocean Optics HR4000 detector) with a bright light source (Leica type 11307072060). A 100x magnification, and a numerical aperture of 0.9 was used for the measurements. A continuous gold substrate was used as a background for the reflection measurement.

3.2.7 | Surface-enhanced Raman scattering measurements

For the Raman measurements, a confocal Raman microscope (WITec Alpha300R, Germany) fitted with an UHTS300 spectrometer was used. The laser wavelength was chosen based on the result of the reflection measurements. Two different laser sources were used for the Raman measurements, i.e. a laser with an excitation wavelength of 785 nm (Topica Photonics XTRA 785nm single frequency diode laser), and a laser with a wavelength of 532 nm (WITec 532 nm laser). The laser was focused on the substrate using a lens with a 100x magnification, and a numerical aperture of 0.9. The Raman microscope was operated in a backscatter configuration. The elastically backscattered excitation beam was filtered from the spectrum using an edge filter. Polarization of the light beam with respect to the sample was controlled by rotating the sample using a rotation plate for rough alignment and a half-wave dish for precise alignment. The integration time was 100 ms, and the power applied was 20 mW. It has to be noted that the measured signals were stable at this applied power. For the samples, a $5 \times 5\ \mu\text{m}$ map of 2500 measurements was created, in which for every point in the map the enhancement factor was calculated. For

the reference BT sample, a total of nine measurements were performed and averaged before being used to calculate the enhancement factor.

In this chapter, BT molecule was chosen as a reference molecule as it is generally accepted as a reference molecule to determine SERS enhancement factors in literature.²⁵⁻²⁷ Moreover, it can form a well-defined monolayer over the structure surface, and has strong Raman peaks. A monolayer of BT molecules was deposited on the Au nanowires by immersing the Au nanogaps in a 10 mM solution of BT molecules in ethanol for 15 hours. Before immersing completely in the solution, the Au nanogaps were slowly immersed perpendicularly to the solution surface so that the solution could enter all Au nanogaps by capillary flow. Subsequently, the Au nanogaps were rinsed with ethanol, and dried with N₂ gas. After the functionalization of the Au nanogaps, SERS Raman spectra were measured. In addition, a neat BT solution in a glass vial was also measured using the same power and same integration time as for the SERS measurements, which was then used to determine the enhancement factor.

3.2.8 | Determination of enhancement factor

A large variety of methods have been reported to determine the enhancement factor of a SERS substrate.²⁸ However, each of them has its own advantages and disadvantages, and the reported enhancement factors vary widely depending on the method used. In this chapter, we used a method reported and used by Pilot *et al.*,²⁷ Le Ru *et al.*,²⁸ and Lin *et al.*²⁹ In this method, the enhancement factor is calculated by comparing the normalized results of a SERS structure, functionalized with a reference molecule, against the normalized results of the neat solution of the same reference molecule. The enhancement factor is approximated from the following equation:²⁷

$$EF = \frac{C^{Raman} \cdot I^{SERS}}{C^{SERS} \cdot I^{Raman}} \times \eta^N, \quad (3.1)$$

where C^{Raman} is the amount of the BT molecules per unit of volume in the neat BT solution. The value of C^{Raman} can easily be calculated by dividing the density of the liquid by the molecular weight, and subsequently multiplying it with the Avogadro number. This results in a C^{Raman} of 5.88×10^{21} molecules cm⁻³. C^{SERS} is the surface density of the BT monolayer on the surface of the Au nanogaps. The surface density of the BT monolayer on a flat gold surface has been reported in literature,³⁰ and is 6.80×10^{14} molecules cm⁻². Using this value and the estimated surface of the Au nanogaps, the surface density of the BT monolayer on the surface of our fabricated Au nanogaps can be calculated. I^{RAMAN} is the integrated intensity of the 999cm⁻¹ peak in the neat BT solution, and I^{SERS} is the integrated intensity of the same peak of the SERS sample. η^N is the integrated area of the

normalized collection efficiency of the instrument. It must be noted that the value for C^{SERS} corresponds to that of a flat surface, while in our case we use nanowires, causing a slight overestimation of the enhancement factor.

The normalized collection efficiency was obtained by taking several Raman spectra of a Si wafer at different positions along the z-axis. For each spectrum, the area of the Si peak at 520 cm^{-1} was then obtained, and then normalized against the area found at the focal point.

3.3 | Results and discussion

3.3.1 | Patterning periodic 50 nm BARC nanolines

Figure 3.2(a) shows the HR-SEM images of periodic PR nanolines patterned on an oxidized Si wafer applying DTL. The top-view image shows well-fabricated PR nanolines (250 nm pitch) with a high uniformity in terms of the line width. The width of the PR nanolines was approximately 114 nm with a relatively small variation (standard deviation) of 2 nm. For the uniformity measurement of the fabricated PR nanolines, four areas were selected over a full wafer area (Appendix B: **Figures B1-B2**). The cross-sectional image shows a highly vertical PR sidewall, thus indicating a robust fabrication process achieved by applying the DTL technique.

Figure 3.2. Top-view (scale bar: 1 μm) and cross-sectional (scale bar: 500 nm) HR-SEM images of (a) periodic PR nanolines, and (b) $\sim 50\text{ nm}$ BARC nanolines shrink-etched from the patterned PR nanolines.

Figure 3.2(b) shows the HR-SEM images of BARC nanolines shrink-etched using a mixture O_2/N_2 plasma, starting from the patterned PR nanolines. It is remarkable that the BARC nanolines were found to be still uniform over a full wafer area (Appendix B: **Figure B3**), and that their sidewalls remained highly vertical after the shrink-etching process, as shown in the cross-sectional image. These periodic BARC nanolines of 50 ± 3 nm in width were subsequently used as a template to pattern Cr nanolines by using a lift-off process.

3.3.2 | Patterning periodic Cr nanolines using lift-off process

Figure 3.3(a) shows a top-view HR-SEM image of periodic Cr nanolines (~ 6 nm thickness) patterned on the surface of an oxidized Si wafer. A high width uniformity of the fabricated Cr nanolines was obtained over a full wafer area (Appendix B: **Figure B4**), with an average width of approximately 50 nm. It is worth mentioning that the lift-off process was conducted in a 99% nitric acid (HNO_3) solution as BARC cannot be dissolved in acetone. Moreover, the patterned wafer needs to be immersed immediately into DI water for sonication after the immersion in the HNO_3 solution as drying the wafer before the sonication could result in the permanent sticking of unwanted Cr residues on its surface (**Figure 3.3b**). Such Cr residues are attributed to the collapse of a Cr layer deposited on the sidewall of the BARC nanolines during the sputtering process. In addition, deposition of a thick Cr layer of approximately 12 nm also made it difficult to obtain the complete lift-off of Cr (**Figure 3.3c**). We attribute this to the fact that the Cr layer completely covered the BARC nanolines, thus preventing the diffusion of HNO_3 to completely dissolve the BARC.

Figure 3.3. (a) Top-view HR-SEM image of periodic Cr nanolines with ~ 50 nm spacing fabricated by using a lift-off process. (b) Unwanted Cr residues caused by drying the wafer before the sonication in DI water. (c) A thick deposited Cr layer (~ 12 nm thick) resulted in an undesired structure after the lift-off process. Scale bar represents 1 μm .

3.3.3 | Patterning high-quality SiN nanogaps

Figure 3.4(a) shows the HR-SEM images of Si nanotrenches after directionally dry etching the bulk Si in a parallel plate reactive ion etching system (in-house built Tetske system, NanoLab Cleanroom, The Netherlands). From the cross-

sectional image, a well-defined pattern of Si nanotrenches that have a relatively vertical sidewalls is seen, indicating an anisotropic etching process. Moreover, the top-view image shows no damage to the area that is protected by the Cr layer after the etching process. This indicates that a continuous Cr layer was formed at the thickness of approximately 6 nm, and that this Cr layer was sufficient to withstand the etching of the SiO₂ masking layer and the bulk Si substrate for 13 min (~150 nm deep in Si). It is clear from the cross-sectional image that the top edge of the SiO₂ masking layer was slightly damaged. We attribute this damage to the faceting formation at these SiO₂ edge regions during the dry etching process. However, such damage was not found to affect the formation of Si structures after the wet etching in a potassium hydroxide (KOH) solution (**Figure 3.4b**). A high uniformity of the etched profile into the sidewall of the Si nanotrenches was obtained, in which the etching virtually ceased at <111>-oriented Si crystal planes (etching rate of 12.5 nm min⁻¹). It is worth noting that over-etching of the wafer in the KOH solution could lead to the formation of undesirable v-grooves in the bulk Si substrate (Appendix B: **Figure B5**). After wet etching of the SiO₂ masking layer, a dense array of extremely smooth Si nanogaps of approximately 120 nm (250 nm pitch) was obtained (**Figure 3.4c**). Since the roughness effects of the patterned Cr nanolines and SiO₂ masking layer on the quality of the Si nanogaps are eliminated by the subsequent crystallographic etching of Si, using this Si template for further patterning of Au nanogaps significantly improves their quality.

Figure 3.4. Top-view (scale bar: 1 μm) and cross-sectional (scale bar: 500 nm) HR-SEM images of the fabricated (a) Si nanotrenches after dry etching, (b) Si structure after wet etching in the KOH solution, and (c) after wet etching of the SiO₂ masking layer.

Figure 3.5 shows the HR-SEM images of a fabricated Si template after coating with a SiN layer. The top-view image shows well-defined SiN nanolines with high uniformity in width (~200 nm) and periodicity (~250 nm) (Appendix B:

Figure B6). It can be observed from the cross-sectional image that the SiN layer (~ 35 nm thick) was conformally deposited over the Si template, resulting in very smooth and uniform SiN nanogaps of approximately 50 nm (**Figure 3.5b**).

Figure 3.5. (a) Top-view (scale bar: 500 nm) and (b) cross-sectional (scale bar: 200 nm) HR-SEM images of a fabricated Si template coated with a SiN layer.

Figure 3.6. (a) Top-view (scale bar: 1 μ m) and cross-sectional (scale bar: 200 nm) HR-SEM images of a fabricated array of Au nanogaps. (b) A close-up HR-SEM image (scale bar: 200 nm) shows well-defined Au nanogaps with a gap spacing of approximately 10 nm. The gap spacing was tuned from (c) ~ 30 nm to (d) ~ 20 nm, and (e) ~ 10 nm by increasing the thickness of the deposited Au layers from ~ 67 nm to ~ 90 nm, and ~ 113 nm, respectively. Scale bars represent 200 nm.

3.3.4 | Patterning high-quality tunable Au nanogaps

Figure 3.6(a) shows the HR-SEM images of a dense array of high-quality Au nanogaps fabricated by sputtering a Au layer over the SiN-coated Si template. A high uniformity in the gap spacing of the fabricated Au nanogaps was obtained over a full wafer area (Appendix B: **Figure B7**). It is clearly shown in the cross-sectional image that the sputtered Au layer completely covered the structure surface. It is worth mentioning that no metallic adhesion layer was used to improve the adhesion of the sputtering Au layer with the SiN surface. Therefore, the adverse effects caused by metallic adhesion layers on the optical and electrical properties of pure Au were eliminated.^{31,32} **Figure 3.6(b)** shows a close-up top-view HR-SEM image of Au nanogaps after the sputtering of a Au layer approximately 113 nm thick. Well-defined Au nanogaps of approximately 10 nm were fabricated at the periodicity of 250 nm. Since the roughness of the template was minimized by the crystallographic etching of Si, the roughness of the Au nanogaps depended almost exclusively on the roughness of the sputtered Au layers. Decreasing the thickness of the Au layer was found to decrease its roughness (Appendix B: **Figures B8-B10**),³³ though the gap spacing became wider (**Figures 3.6c-e**). Additionally, our SiN-coated Si template can be reused by replacing the Au layer with another fresh layer, without damaging the template material or altering its dimensions.

3.3.5 | Finite-difference time-domain simulations

Figure 3.7 shows the finite-difference time-domain (FDTD) simulation results of the local field intensity enhancement factor at Au nanogaps with different gap spacings at the excitation wavelength of 785 nm. The color scale represents the normalized amplitude of the enhanced electric field $|E|$ with respect to the amplitude of the incoming electric field $|E_0|$. As can be seen in **Figure 3.7**, the reduction of the gap spacing resulted in an increase in the enhanced electric field at the Au nanogap region, which can be explained from the increasing surface plasmon resonance (SPR) strength when decreasing the gap spacing.^{34,35} Similar results have also been reported for different structures when reducing the gap spacing.^{35,36} In addition, **Figure 3.7(c)** clearly shows that there are two major regions of the enhanced electric field generated within the ~10 nm Au nanogaps. Awang *et al.* reported a similar observation when simulating the electric field distribution within the gap of the Au nanograting pairs supported on the SF10 glass substrate,³⁶ which they attributed to the corner effect of the structure.

Figure 3.7. FDTD-simulated distribution of the local field intensity enhancement factor ($|E|^2/|E_0|^2$) at the wavelength of 785 nm for Au nanogaps of (a) ~ 30 nm, (b) ~ 20 nm, and (c) ~ 10 nm. The yellow dashed lines indicate the SiN boundary.

3.3.6 | Surface-enhanced Raman scattering measurements

Figure 3.8(a) shows the reflectance spectra measured on various Au nanogap samples containing different gap spacings. A red shift and formation of a second peak at ~ 525 nm were observed in the spectra when reducing the gap spacing. The appearance of such second peak at lower wavelengths has been reported in the literature, both for two nanoparticle systems³⁷ and nanowires.⁵ Romero *et al.* attributed the formation of these peaks to the strong interactions of single particle multipoles.³⁸ However, it has to be noted that the explanation of Romero *et al.* was based on the two nanosphere system.

Figure 3.8(b) shows the SERS signals measured on various Au nanogap samples containing different gap spacings of ~ 30 nm, ~ 20 nm, and ~ 10 nm, after coating a monolayer of BT molecules. As can be seen at the 999 cm^{-1} peak in **Figure 3.8(c)**, there is a slight increase in the measured signal with decreasing gap spacing from ~ 30 nm to ~ 10 nm. It might be surprising that the enhancement in the electric field strength in the simulated gap region (see **Figure 3.7**), which is about 10-fold from the ~ 20 nm to ~ 10 nm gaps, causes only a relatively small increase in the measured signal. However, this can be explained by the fact that the fraction of the scattered signal that reaches the objectives ($NA = 0.9$, $\alpha_{adm} \approx 64^\circ$) decreases with an increasingly narrow gap and consequently lower escape angle. It must furthermore be noted that the BT monolayer forms only on the sample surface after drying (white lines in **Figure 3.7**), so that the high field enhancement in the entire gap in the ~ 10 nm Au nanogaps does not contribute to the measured SERS signal (Appendix B: **Figures B11-B12**). It is thus expected that the ~ 10 nm Au nanogaps are especially useful for measuring in solution.

Figure 3.8. (a) Reflectance spectra and (b) SERS signals measured on Au nanogap arrays of ~30 nm, ~20 nm, and ~10 nm gap spacing, with (c) a close-up image. (d) Calculated enhancement factors of the spectra obtained from the measurements over a $5 \times 5 \mu\text{m}^2$ area for the ~10 nm Au nanogaps.

It is worth mentioning that all the Au nanogaps were slowly immersed perpendicularly to the BT solution surface before immersing completely in the solution. We expect that the solution could wet the entire Au nanogaps by the capillary flow. This procedure was followed because immersing the Au nanogaps into the BT solution, parallel to the solution surface, resulted in a significant drop in the signal intensity, especially for the ~10 nm Au nanogaps (Appendix B: **Figure B13**). We attribute this to a lack of penetration of the solution with analyte molecules to the region of the nanogaps, caused by the hydrophobic nature of Au. Therefore, in that case, although there is a strongly enhanced electric field at this region (see **Figure 3.7**), a lower SERS signal is generated, leading to a significant drop in the totally obtained signal. This would imply that the method of sample introduction is an important factor in the present SERS structures.

To investigate the homogeneity of the enhancement over the structure surface, a map of $5 \times 5 \mu\text{m}^2$ containing 2500 excitation points (50 lines containing

50 points per line) was constructed, and the enhancement factor was calculated using **Equation 3.1**. As shown in **Figure 3.8(d)**, for the Au nanogaps of ~ 10 nm gap spacing, a relatively high uniformity in the enhanced factor was obtained. For the structures with gap spacings of ~ 30 nm and ~ 20 nm, the maps of the enhancement factor are shown in Appendix B: **Figure B14**.

The average enhancement factors calculated by averaging 2500 spectra of each map were $\sim 2.4 \times 10^8$, $\sim 2.4 \times 10^8$, and $\sim 3.0 \times 10^8$ for the Au nanogaps of ~ 30 nm, ~ 20 nm, and ~ 10 nm, respectively (Appendix B: **Figure B15**). In addition, it is noteworthy that for the second, smaller peak at around 525 nm in the reflectance spectra, no signal was observed when excited by a 532 nm laser (Appendix B: **Figure B16**).

3.4 | Conclusion

In summary, we report a robust method for wafer-scale patterning dense arrays of high-quality Au nanogaps, combining DTL-based shrink-etching with dry etching, wet etching, and thin film deposition techniques. Using this fabrication method, SiN-coated Si templates with extremely smooth SiN nanogaps were fabricated over full wafer areas, which were then used as a template to pattern high-quality Au nanogaps by sputtering a Au layer over the structure surface. The quality of the Au nanogaps was significantly enhanced by minimizing the roughness of the template used for the Au deposition. By varying the thickness of deposited Au layers, we successfully demonstrated the fabrication of high-quality tunable Au nanogaps down to ~ 10 nm gap spacing over full wafer areas. Our fabricated Au nanogaps showed a significant enhancement of SERS signals (up to 3.0×10^8) of BT molecules chemisorbed on the nanogap surface compared to those obtained when using a pure BT solution. Moreover, using the FDTD simulation allowed us to predict the location of the hot-spot regions. As a result, a tailored sample introduction procedure was introduced for our fabricated Au nanogap arrays in order to obtain good SERS signals, especially for the ~ 10 nm Au nanogaps. In addition, the simulations indicated that the ~ 10 nm and ~ 20 nm Au nanogap arrays are expected to give higher enhanced signals when measuring in solution as the enhanced electric field in between the gap is then fully employed. With its simple operation, our fabrication method is suitable for the high-yield and low-cost patterning of high-quality tunable Au nanogaps that can be used in many applications, including biomedical and chemical sensing,^{3,4} and surface-enhanced spectroscopy.^{6,39}

3.5 | References

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4

Large-scale Fabrication of Highly Ordered Sub-20 nm Noble Metal Nanoparticles*

Periodic noble metal nanoparticles offer a wide spectrum of applications including chemical and biological sensors, optical devices, and model catalysts due to their extraordinary properties. For sensing purposes and catalytic studies, substrates made of glass or fused-silica are normally required as supports, without the use of metallic adhesion layers. However, precise

patterning of such uniform arrays of silica-supported noble metal nanoparticles, especially at sub-100 nm in diameter, is challenging without adhesion layers. In this chapter, we report a robust method to large-scale fabricate highly ordered sub-20 nm noble metal nanoparticles, i.e. gold and platinum, supported on silica substrates without adhesion layers, combining displacement Talbot lithography (DTL) with dry etching techniques. Periodic photoresist nanocolumns at diameters of approximately 110 nm are patterned on metal-coated oxidized silicon wafers using DTL, and subsequently transferred at a 1:1 ratio into antireflection layer coating (BARC) nanocolumns with the formation of nano-sharp tips, using nitrogen plasma etching. These BARC nanocolumns are then used as a mask for etching the deposited metal layer using inclined argon ion beam etching. We find that increasing the etching time results in cone-shaped silica features with metal nanoparticles on the tips at diameters ranging from 100 nm to sub-30 nm, over large areas of $3\times 3\text{ cm}^2$. Moreover, subsequent annealing these sub-30 nm metal nanoparticle arrays at high temperature results in sub-20 nm metal nanoparticle arrays with approximately 10^{10} uniform particles.

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4.1 | Introduction

Noble metal nanoparticles (NPs) have been studied intensively due to their widespread applications in both academic research and industry. The reduction in size of noble metal particles, for example gold (Au) and platinum (Pt) particles, to the nanoscale results in extraordinary properties, especially optical and catalytic properties.^{1,2} The most compelling optical property of metallic NPs is their localized surface plasmon resonance (LSPR).³ When excited by incident light, the conduction electrons in metallic NPs are stimulated to collectively oscillate at a resonant frequency, thus absorbing the incident light at a specific wavelength. By manipulating this LSPR property of metallic NPs, especially in an ordered arrangement, various applications have been demonstrated including optical devices,⁴ chemical and biological sensors,^{5,6} fuel and solar cells,^{7,8} and surface-enhanced Raman spectroscopy (SERS),⁹ showing the great benefits of using noble metal-NP arrays. Besides having excellent optical properties for sensing purposes, noble metallic NPs at diameters of a few or tens of nanometers have also shown enormously high catalytic activity. Haruta *et al.* first observed that supported Au nanoparticles at the diameter of approximately 5 nm possess extremely high catalytic activity for the oxidation of carbon monoxide even at temperatures far below 0°C.¹⁰ The particle size and shape, composition, oxidation state, and the interaction of the particle with its support are attributed to strongly affect the catalytic activity simultaneously.¹¹ However, under chemical reactions, metallic NPs have found to be unstable due to the sintering of particles which results in blocking of active sites and deactivation.¹² Therefore, for catalysis studies, highly ordered and uniform metallic NPs on support substrates are highly demanded as better control in the uniformity and distribution of the metallic NPs leads to better controlled properties. Such arrays of supported metallic NPs can serve as model systems to investigate their thermal stability and catalytic properties.¹³ Therefore, the aim of this study is to fabricate arrays of supported noble metal nanoparticles with diameters of several tens of nanometers that can be used for gas-phase catalysis studies.

Although having a large number of applications as outlined above, large-scale uniform arrays of noble metal NPs with tunable sizes down to 20 nm and supported on ceramic substrates such as glass, fused-silica or oxidized-silicon, are difficult to fabricate, especially without the use of metallic adhesion layers. For top-down fabrication of Au and Pt nanostructures, a metallic adhesion layer, i.e. titanium (Ti) or chromium (Cr), is normally required to improve their adhesion to the substrates, preventing the removal of the structures.¹⁴ However, such adhesion layers could result in undesired reactions with Au and Pt, i.e. interdiffusion and alloying, and thus affect their structural and optical

properties.^{15,16} The many techniques that have been utilized to pattern such arrays can be classified into two main categories which are direct patterning techniques and template-assisted techniques. Conventional direct patterning techniques such as electron beam lithography (EBL),¹⁷ ion beam lithography (IBL),¹⁸ and dip pen lithography^{19,20} provide opportunities to precisely control the particle size and shape, and their interspacing. However, these techniques require dedicated systems which are costly expensive, and thus not widely accessible. Moreover, their use of serial patterning limits their throughput at a relatively low yield, making them not suitable for mass production of large-area arrays. Another direct patterning technique, laser interference lithography (LIL), allows high-yield patterning of large footprint arrays.²¹ However, this technique requires a high stability of the operation system in order to obtain reproducible fabrication. Template-assisted techniques are based on the idea of using templates such as block copolymers,^{22,23} shadow masks,²⁴ nanoimprint molds,²⁵ and monolayer of polystyrene spheres²⁶ for patterning metal nanoparticle arrays. Using such templates, arrays of metallic NPs can be fabricated through self-assembly,²⁷ or by metal deposition methods such as evaporation, sputtering, and electrochemical deposition.²⁸ These techniques however come with their own drawbacks. Self-assembled block copolymers are normally difficult to precisely control at the nanoscale over large areas. The use of shadow masks requires additional steps for making the masks which are time-consuming. Moreover, significant efforts are needed in order to pattern metal nanoparticle arrays over centimeter-scale areas because of the fragility of the mask. The use of nanoimprint mold suffers from its contact with the substrate, which can lead to the significant degradation of the mold over time. Self-assembly of polystyrene spheres, on the other hand, allows very little control over particle orientation and geometric pattern variation.

Recently, an alternative top-down nanopatterning technique has been reported by Solak *et al.*, termed displacement Talbot lithography (DTL). It allows for rapid fabrication of highly ordered nanostructures at the wafer scale, i.e. periodic photoresist patterns of lines, holes or dots, with a high yield.²⁹ However, when DTL is used with a monochromatic UV beam (365 nm wavelength), only photoresist nanostructures with feature sizes of a few hundreds of nanometers can be fabricated, which can be utilized as a mask for fabricating metal nanoparticle arrays. In fact, patterning arrays of metal nanoparticles with diameters below 50 nm is still challenging.

In this chapter, we report and demonstrate a robust fabrication method that allows rapid patterning of highly ordered noble metal (Au and Pt) nanoparticles supported on oxidized silicon substrates, without the need of metallic adhesion layers. Our fabrication method combines UV-based DTL with subsequent plasma and ion beam etching techniques, enabling us to fabricate

3×3 cm² arrays of Au and Pt nanoparticles with diameters in the range from sub-20 nm to 100 nm, supported on cone-shaped silica features.

4.2 | Materials and methods

4.2.1 | Wet thermal oxidation of silicon wafers as support substrates

For all fabrication processes, silicon wafers with a thick thermal oxide layer of approximately 1.1 μm were used as support substrates for the metal nanoparticles. They were prepared by the wet thermal oxidation of conventional (100) 4-inch silicon (Si) wafers (525 μm thick, single side polished, Okmetic, Finland). All the Si wafers were completely cleaned before running the wet thermal oxidation process to prevent cross-contamination. In detail, Si wafers were immersed in a 99% nitric acid (HNO₃) solution for 10 min, and in a 69% HNO₃ solution at 95°C for 10 min. These Si wafers were then rinsed with deionized (DI) water using a quick dump rinser. Subsequently, Si wafers were immersed in a 1% hydrofluoric acid (HF) solution to remove the native oxide, rinsed in DI water again, and spin-dried. The Si wafers were then loaded into a high temperature tube furnace (Model 287, Tempres Systems, Inc., The Netherlands), using a quartz carrier to implement the wet oxidation at 1150°C for 2 hours and 40 minutes. During the oxidation process, the flow rate of a mixture of water vapor and nitrogen gas was fixed at 2 ℓ min⁻¹. The ramping and cooling rates were set at 10°C min⁻¹ and 7°C min⁻¹, respectively.

4.2.2 | Patterning periodic BARC nanocolumns with nano-sharp tips

Figure 4.1 shows the fabrication process of periodic BARC nanocolumns on a metal-coated oxidized Si wafer. Briefly, a thin metal layer made of gold or platinum was deposited on the oxidized Si wafer using an ion-beam sputtering system (in-house built T'COathy system, NanoLab Cleanroom, The Netherlands). The sputtering processes were performed at 200 W, and a pressure of 6.6×10⁻³ mbar which was adjusted using an argon (Ar) flow. Periodic nanocolumns at a diameter of approximately 110 nm were patterned by using UV-based DTL (PhableR 100C, Eulitha) in a photoresist (PR) layer of 200 ± 1.5 nm (PFI88 photoresist diluted 1:1 with propylene glycol methyl ether acetate (PGMEA), Sumitomo Chemical Co., Ltd.), and subsequently transferred at a 1:1 ratio into a bottom anti-reflection layer coating (BARC) layer of 187 ± 2 nm (AZ BARLi II 200) by using nitrogen (N₂) plasma etching.³⁰ The plasma etching of BARC was conducted using a parallel plate reactive ion etching system (in-house built TETSke system, NanoLab Cleanroom, The Netherlands) at wafer-level, 13 mTorr, and 25 W for 8 min.

Figure 4.1. Fabrication process of periodic BARC nanocolumns with nano-sharp tips, supported on a metal-coated oxidized Si wafer. (a) A metal layer was sputtered on an oxidized Si wafer. (b-d) Periodic photoresist nanocolumns were patterned by DTL, and (e) subsequently etched in N₂ plasma to directly transfer to (f) BARC nanocolumns with PR nano-sharp tips.

4.2.3 | Argon ion beam etching for patterning metal nanoparticle arrays

To further process the deposited metal layer, argon ion beam etching (IBE) was performed in an etching system (IBE, Oxford i300, Oxford Instruments PLC, United Kingdom) at 5 sccm Ar, 300 eV, and 50-55 mA. We first investigated the etching rate of individual layers of different materials, i.e. SiO₂, PR, BARC, Au, and Pt, in this IBE system at different beam incident angles. Thicker layers of PR and BARC were used for this investigation of the etching rate. PR layers (299.3 ± 1.8 nm) and BARC layers (245.8 ± 1.5 nm) were spin-coated on oxidized Si wafers at 2000 rpm for 45 s, followed by baking at 90°C and 185°C, respectively. Au and Pt layers were also deposited on oxidized Si wafers, using the T'COathy system at 6.6×10^{-3} mbar, and 200 W for 2 min. The etching rate at each etching angle was determined by comparing the thickness of the initial layer with that of the layer etched for 3 min. The thicknesses of the PR and BARC layers were determined from the images taken using a high-resolution scanning electron microscope (HR-SEM, FEI Sirion microscope, United States) at a 5 kV acceleration voltage and a spot size of 3. The thicknesses of the metal layers and the thermal oxide layers were measured using an ellipsometer system (M-2000UI, J.A. Woollam Co., United States) at an angle of 75°. The surface roughness was determined from atomic-force microscopy (AFM) images (scan field: 500×500 nm²), recorded in contact modes using an AFM system (Dimension Icon, Bruker Corp., United States) in air.

For fabricating the metal nanoparticle arrays, the metal-coated wafers with the patterned BARC nanocolumns were subsequently inclined etched in the IBE system (Oxford i300) at 5 sccm Ar, 300 eV, and 50-55 mA (**Figure 4.2**). The etching time was increased with an etching time-step of 3 min, and the structure was regularly checked using the HR-SEM after every etching time-step. Over-etching the SiO₂ substrate resulted in metal nanoparticles supported on cone-shaped silica features.

Figure 4.2. Patterning an array of metal nanoparticles supported on cone-shaped silica features. A metal-coated oxidized Si wafer with patterned BARC nanocolumns was inclined-etched by ion beam etching. Increasing the etching time resulted in a silica-supported metal nanoparticle array.

4.3 | Results and discussion

4.3.1 | Periodic BARC nanocolumns with nano-sharp tips

Figure 4.3(a) shows the HR-SEM images of periodic BARC nanocolumns fabricated on a gold coated oxidized Si wafer. The cross-sectional HR-SEM image shows successful fabrication with highly vertical BARC sidewalls as well as formation of PR nano-sharp tips. We attribute the tip formation to the physical bombardment of high energy particles during N₂ plasma etching. For resist material, a dependence of the etching rate on the angle of ion incidence was reported, in which the highest etching rate occurred at an angle around 50°-60°. ³¹ Therefore, etching the PR nanocolumns at normal ion incidence causes facet formation at an angle directly corresponding to the angle of the maximum etching rate, resulting in the formation of PR nano-sharp tips. The close-up image clearly shows the BARC nanocolumns with the PR nano-sharp tips at an angle of $58 \pm 2^\circ$ (**Figure 4.3b**). It is highly remarkable that the BARC nanocolumns with the PR nano-sharp tips – called BARC nanocolumns – were found to have an extremely high uniformity in the column height over the entire area of 3×3 cm², namely 251.4 ± 1.5 nm. The top-view HR-SEM image shows a lower, but still high uniformity in the diameter (110 ± 3 nm) and periodicity of 250 nm (**Figure 4.3a**). The narrow distribution in the diameter indicates a highly controllable fabrication process (**Figure 4.3b**). The uniformity of the BARC nanocolumns over the entire area of 3×3 cm² was also investigated by repeating

the measurement at five selected areas within the array. Well-defined and highly ordered BARC nanocolumns with a high uniformity in the height and diameter were obtained over the large area of $3 \times 3 \text{ cm}^2$ (Appendix C: **Figures C1-C3** and **Table C1**).

Figure 4.3. (a) Top-view (top, scale bar: 1 μm) and cross-sectional (bottom, scale bar: 500 nm) HR-SEM images of periodic BARC nanocolumns fabricated on a gold coated oxidized Si wafer, and (b) the corresponding column diameter distribution with a close-up image inserted (scale bar: 200 nm).

4.3.2 | Sputtering and optimization of Au and Pt thin films

In the close-up image (**Figure 4.3b**), a discontinuous Au layer was observed. We attribute this to the insufficient thickness of approximately 8.9 nm of the deposited Au layer in the sputtering system at 6.6×10^{-3} mbar, and 200 W for 10 s. Although a longer sputtering time results in a continuous Au layer, a thicker deposited Au layer leads to an increase in size and volume of the fabricated Au nanoparticles. Moreover, an increase in metal layer thickness could enlarge the surface roughness (R_a), caused by the increase in the Au crystallographic grain size.³² This is also the case for sputtered Pt.³² A large surface roughness of the deposited metal layers could lead to non-uniform arrays of metal nanoparticles. Therefore, Au and Pt layers with optimized thicknesses are needed to achieve uniform metal nanoparticle arrays. We thus investigated the thickness and surface roughness of metal layers deposited at various sputtering times in the T'COathy system at 6.6×10^{-3} mbar, and 200 W.

Figure 4.4(a) shows the measured thickness of the deposited metal layers as function of the sputtering time. From the linear fit curves, the sputtering rates of Au and Pt could be determined as 45.0 nm min^{-1} and 22.5 nm min^{-1} , respectively. At a 5 s sputtering time, a large variation in the layer thickness between the measured value and the linear fit curve was observed. We attribute this difference to the inaccuracy of the ellipsometer system at this Au layer thickness. At this sputtering time Au nanoclusters formed on the

substrates, and such discontinuous layer (**Figure 4.4b**) can lead to an inaccurate thickness measurement. It is furthermore clearly observed in **Figure 4.4(a)** that there was an offset thickness in our sputtering system, i.e. for sputtering time of 0 s the linear fit does not pass the origin. This could result from the metal deposition during the pre-sputtering process for cleaning the target, or an unexpectedly high sputtering rate when opening the shutter between the target and the substrate.

Figure 4.4(b) shows the average surface roughness (R_a) of the deposited metal layers measured over an area of $500 \times 500 \text{ nm}^2$ (Appendix C: **Figures C4-C5**). Up to 10 s sputtering time, the surface roughness of the Au layers was high, which we explain by the formation of Au nanoclusters, growing over time. A significant decrease in the surface roughness was observed for a sputtering time above 10 s, which we contribute to the subsequent formation of a continuous Au layer. For a sputtering time range from 15 s to 30 s, the surface roughness increased only slightly due to the increase in the Au crystallographic grain size. For platinum, a continuous layer was readily formed at a shorter sputtering time of 5 s, due to its much smaller crystallographic grain size compared to gold.³² Beyond a 5 s sputtering time, there was only a minor variation in the surface roughness of the deposited Pt layers. From these obtained results, for Au and Pt layers optimal sputtering times of 15 s and 5 s were selected for further patterning our metal nanoparticle arrays because these times yield continuous, metallic films with a low surface roughness. The thicknesses of these Au and Pt layers were approximately 12.5 nm and 4.5 nm, respectively.

Figure 4.4. (a) Thickness of deposited metal layers and (b) their corresponding surface roughness versus sputtering time. Inserted top-view HR-SEM images in (b) (scale bar: 200 nm) show the morphological appearance of the deposited metal layers at various sputtering times.

4.3.3 | Argon ion beam etch rate at various beam incident angles

There are two common problems encountered with ion beam etching which are the strong dependence of the etching rate of materials on the beam incident angle, and redeposition of back-sputtered materials on the surface of steep features. Therefore, the etching rate of the used materials as function of the beam incident angle is needed in order to obtain an optimal etching recipe for particular structures, especially at the nanoscale. In this work, we investigated the etching rate versus the beam incident angle of five materials, i.e. SiO₂, PR, BARC, Au, and Pt (**Figure 4.5a**). As the beam incident angle increases from normal incidence, the etching rate of SiO₂, PR, and BARC reached a maximum for an angle between 50° to 70°, subsequently decreasing at glancing angles. This behavior is well-known from literature.³³⁻³⁵ Lee³⁵ attributed this initial increase in the etching rate to an increase in the probability of collisions that results in atoms possessing momentum components directed away from the material surface. At high incident angles, the incoming ion beam is spread over a large surface area, resulting in a decreased ion flux, and hence a reduction in the etching rate. Moreover, at glancing angles the purely elastic reflection of the primary incident ions increases significantly, leading to a sharp decrease in the etching rate. In contrast to SiO₂, PR, and BARC, the etching rate of Au and Pt showed a maximum at the normal incidence, and the etching rate decreases with increasing incident angle. A similar behavior in the etching rate of Au and Pt as a function of the beam incident angle has been observed by Gosset *et al.*,³¹ who attributed this to the used ion energy of 500 eV, which is rather low. Increasing the ion energy to 2-50 keV would lead to a more classic IBE behavior of these materials, in which their etching rates increase with the increasing incident angle.³⁶

As shown in **Figure 4.5(a)**, the etching rate of PR was much lower than that of BARC for the entire range of beam incident angles (Appendix C: **Figure C6**). We attribute this to the difference in the molecular structure and composition of PR (i-line photoresist) and BARC (AZ BARLi).³⁷ Compared to BARC, PR contains a novolac (phenol-formaldehyde) resin with aromatic rings, and a diazonaphthoquinone (DNQ) sensitizer,³⁸ giving the PR a much larger molecular weight than BARC. Moreover, the DNQ sensitizer acts as a dissolution restrainer for the unexposed novolac resin after baking, leading to difficulty in breaking the chemical bonds in the PR. The highest etching rate of SiO₂ was approximately 12.6 nm min⁻¹, which is almost three times lower than that of BARC (**Table 4.1**). We explain this large difference to the fact that SiO₂ has much stronger covalent bonds than BARC and PR,³⁹ requiring a larger amount of energy for breaking the bonds. **Figure 4.5(a)** also shows that the maximum etching rate of Au was nearly two times higher than that of Pt, although these

materials have a similar crystallographic structure (FCC), and almost the same atomic mass. The difference in the etching rate of these materials has also been reported in literature.^{31,40} It can be attributed to the difference in the metallic bonding strength between Au atoms and Pt atoms, which is measured by the enthalpy of atomization. In the third series of transition metal, the enthalpy of atomization first increases with increasing number of d electrons up to six electrons per atom, i.e. the half-filled s+d band, and subsequently decreases.⁴¹ Below six d electrons, only bonding orbitals are filled, leading to the enhancement of cohesive energy, while further filling of electrons results in the occupation of the antibonding orbitals, leading to the decrease in the cohesive energy. In addition, Pt atoms possess 10 valence electrons ($5d^9 6s^1$), while Au atoms possess only 1 valence electron ($6s^1$). The higher the number of valence electrons, the stronger the bond among atoms becomes due to the stronger attractive force of the nucleus on the valence electrons.

Figure 4.5. (a) Etching rate of five materials (PR, BARC, SiO₂, Au, and Pt) as function of the beam incident angle. (b) Etching selectivity of PR, BARC, Au, and Pt with respect to SiO₂ versus beam incident angle.

For patterning uniform metal nanoparticle arrays, a high uniformity in the nanocolumn height and the shape of the nano-sharp tips remaining during the etching process is a crucial requirement. Since the nano-sharp tips are used as an etching mask (**Figure 4.2**), a low etching selectivity of BARC and PR with respect to SiO₂ is needed in order to reduce their damage during the over-etching of the substrate, i.e. SiO₂. Moreover, the etching rates of Au and Pt, and their selectivities with respect to SiO₂ need to be high enough in order to etch through the deposited metal layer and to remove the redeposited metal on the nanocolumn sidewall. **Figure 4.5(b)** shows the etching selectivity of PR, BARC, Au, and Pt with respect to SiO₂ as function of the beam incident angle, separated into three domains. The etching rates of these materials and their selectivities at the beam incident angles in domain 1 ($0^\circ \leq \theta \leq 20^\circ$) fulfill the

above stated requirements. Therefore, in our chapter, three angles within this domain were selected for further patterning arrays of Au and Pt nanoparticles, i.e. 0°, 10°, and 20°.

Table 4.1. Etching rate of five materials (PR, BARC, SiO₂, Au, and Pt) at various beam incident angles.

Material	Etching rate (nm min ⁻¹)							
	0°	5°	10°	15°	20°	40°	60°	80°
PR	14.4	16.2	17.2	18.6	19.1	21.8	25.6	15.6
BARC	22.3	23.2	23.3	23.5	23.7	25.3	34.5	24.7
SiO ₂	7.4	7.4	7.6	7.7	8.3	11.2	12.6	6.2
Au	21.6	20.9	20.7	21.5	21.4	17.6	11.0	4.4
Pt	11.5	11.0	11.0	11.4	11.3	9.9	6.0	1.6

4.3.4 | Silica supported size-tunable metal nanoparticle arrays

Figure 4.6 shows the etching results for periodic BARC nanocolumns patterned on Au-coated oxidized Si wafers at three beam incident angles of 0°, 10°, and 20°. At a normal beam incidence, it was difficult to remove the Au that was redeposited on the sidewall of the BARC nanocolumns, which resulted in a relatively low uniformity of the structural geometry. Moreover, perpendicular bombardment of high energy Ar ions on the BARC nano-sharp tips leads to the rapid removal of these tips. As a result, at an etching time of 12 min, no Au nanoparticles remained on the cone-shaped silica features. Increasing the beam incident angle to 10° resulted in a faster removal of the redeposited Au, and a considerable increase in the uniformity of the structures.

Figure 4.6. Cross-sectional HR-SEM images (tilt correction at 20°) of BARC nanocolumns inclined-etched in the IBE system at different beam incident angles versus the etching time. Over-etching the Au-coated substrate resulted in Au nanoparticles supported on cone-shaped silica features, indicated by the yellow areas. The red arrow indicates the removal of a BARC nano-sharp tip caused by the breaking of the sample for SEM observation. Scale bars represent 200 nm.

As can be seen in **Figure 4.6**, the highest structural uniformity was obtained at an etching angle of 20° . We attribute this to the rapid removal of the redeposited Au, and the significant decrease in the physical bombardment of Ar ions on the BARC tips under this inclined etching angle. A low etching of the BARC nano-sharp tips leads to precise control of the fabrication of the metal nanoparticles with the etching time. Therefore, in this work, a beam incident angle of 20° was selected for further investigation on the patterning of Au and Pt nanoparticles arrays.

Figure 4.7. Top-view HR-SEM images of (a,c) Au and (b,d) Pt nanoparticles (bright spots) supported on cone-shaped silica features at different etching times, recorded with back-scattered electrons. The close-up cross-sectional images (scale bar: 100 nm) inserted in (a-b) show the geometry of the structure after etching at particular etching times. The black spots in (a) indicate that the BARC nano-sharp tips remained during the etching process. (b) These BARC tips were completely removed by using oxygen plasma cleaning for 20 min at 500 W. (c-d) Arrays of sub-30 nm Au and Pt nanoparticles, respectively. (e) Diameter measurement of Au and Pt nanoparticles versus the etching time. Scale bars represent 200 nm.

Figure 4.7 shows top-view HR-SEM images of arrays of Au and Pt nanoparticles supported on cone-shaped silica features after various etching times. After every etching time, it is remarkable that the BARC nano-sharp tips

were preserved during the etching process with a high uniformity in the shape and the height, as can be seen in the close-up image inserted in **Figure 4.7(a)** (Appendix C: **Figure C7**). These BARC tips could subsequently be removed by using an oxygen plasma (TePla 300, PVA TePla AG, Germany) at 500 W for 20 min (**Figure 4.7b**). From **Figure 4.7(b)** recorded with back-scattered electrons, we could also again confirm the continuity of the sputtered Pt layer at 5 s in the T'COathy system. The size of Au and Pt nanoparticles could be varied from the original ~ 110 nm to sub-30 nm by increasing the etching time up to 12 min and 30 s and 13 min, respectively (**Figures 4.7c** and **4.7d**). A high uniformity in the particle diameter was obtained for both Au and Pt nanoparticles after etching at particular etching times (Appendix C: **Figures C8-C9**, and **Table C2**). It is remarkable that the Au and Pt nanoparticles remained without damage after the oxygen plasma cleaning process (Appendix C: **Figure C9**). For an etching time of 12 min and 30 s, and 13 min, arrays of sub-30 nm Au and Pt nanoparticles were obtained with a high uniformity in particle diameter, 28.1 ± 1.5 nm and 25.9 ± 1.2 nm, over the patterned 3×3 cm² areas, respectively (Appendix C: **Figure C10**). A further increase in etching time of 30 s resulted in arrays of sub-20 nm Au and Pt nanoparticles, though with a considerable decrease of uniformity in particle diameter distribution, 15.1 ± 2.5 nm and 13.6 ± 3.1 nm, respectively (**Figure 4.7e** and Appendix C: **Figure C11**).

Subsequent annealing in air (TSD-12 furnace, Toma, The Netherlands) of sub-30 nm Au and Pt nanoparticle arrays at 300°C (Au) and 600°C (Pt) for 1 h resulted in sub-20 nm Au and Pt nanoparticle arrays at a high uniformity in the particle diameter, 13.0 ± 1.6 nm and 13.2 ± 1.1 nm, respectively (Appendix C: **Figure C12**). It is highly remarkable that these annealed sub-20 nm Au nanoparticle arrays were found to be very stable in water using a quick dump rinser for 10 min, i.e. flowing water (Appendix C: **Figure C13**). We attribute this to the significant increase in the adhesion of Au nanoparticles with silica substrate after this annealing process.⁴² Our fabrication method could also be used to pattern sub-100 nm Au nanoparticle arrays from an initially 45 nm thick Au layer. On the other hand, an initially 22.5 nm thick Pt layer resulted in the destruction of the BARC nano-sharp tips during the etching process (Appendix C: **Figure C14**). We attribute this to the approximately two times lower etching rate of Pt versus Au and BARC, which makes the removal of the redeposited Pt on the sidewall of the BARC nanocolumns more difficult. Consequently, the BARC nano-sharp tips were removed faster than the redeposited Pt. Heating such arrays of sub-100 nm Au nanoparticles lead to the formation of sub-100 nm Au nanocrystals with facets supported on curve-shaped silica features (Appendix C: **Figure C15**). The annealed sub-100 nm Au nanocrystal array was found to be very stable in flowing water for 10 min (Appendix C: **Figure C16**), and could be used to study gas-bubble growth around laser-irradiated, water-

immersed plasmonic nanoparticles.⁴³ In fact, although non-annealed Au nanoparticles revealed insufficient adhesion in flowing water, we expect that their adhesion is sufficient for our intended gas-phase catalysis study.

4.4 | Conclusion

In conclusion, we successfully demonstrated a versatile top-down nanofabrication method for patterning large-scale arrays of highly ordered noble metal nanoparticles supported on oxidized silicon substrates, without the need of metallic adhesion layers. Our fabrication method combines UV-based DTL with a N₂ plasma etching technique and an Ar ion beam etching technique. The N₂ plasma etching technique is used to pattern periodic BARC nanocolumns with nano-sharp tips that are used as a mask for further patterning metal nanoparticles from the metal layer deposited on SiO₂ substrates, using an inclined Ar ion beam etching technique. Upon applying this method to films of 12.5 nm Au or 4.5 nm Pt, we fabricated 3×3 cm² arrays of Au or Pt nanoparticles supported on cone-shaped silica features at various diameters. By tuning the inclined etching time, the particle diameters could be varied from sub-30 nm to 110 nm. Annealing such sub-30 nm metal nanoparticle arrays at high temperature resulted in sub-20 nm metal nanoparticle arrays with high uniformity in the particle diameter. By using a post-annealing process, we significantly enhanced the adhesion of Au nanoparticles with the silica substrate. The annealed Au nanoparticles were found to be very stable in flowing water.

As our fabrication method relies only on dry etching techniques – physical bombardment with ions or atoms of nitrogen and argon – we believe that this method can be extended to pattern size-tunable nanoparticle arrays of different metal-support combinations. In case of thicker films, i.e. 100 nm Au, we have the opportunity to transfer our Au nanoparticle arrays to substrates with a stronger adhesion. With its easy and flexible operation, our fabrication method presents an enabling technique for rapidly patterning highly uniform arrays of size-tunable metal nanoparticles over large areas that can be used in biological/chemical applications, e.g. trace analyte detection,⁴⁴ dopamine sensing,⁴⁵ and protein and cell surface analyses.^{46,47}

Our ongoing research focuses on integration of these fabricated arrays of silica-supported Au and Pt nanoparticles into microreactor chips. Different gas-phase chemical reactions will be conducted in these chips, for various particle size distributions, for investigating the influence of particle size on their catalytic activity and the mass transfer effect at the particle surface.^{2,48}

4.5 | References

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5

Enhancement of Noble Metal Adhesion to Silica Using UV-ozone Treatment*

We found that continuous films of gold (Au) on oxidized silicon (SiO_2) substrates, upon treatment with ultraviolet (UV)-ozone, exhibit excellent adhesion to the SiO_2 support. Importantly, the enhancement is independent of micro- or nanostructuring of such nanometer thick films. Deposition of a second Au layer on top of the pretreated Au layer makes the adhesion stable for at least

5 months in environmental air. Using this novel treatment method enables us to large-scale fabricate various SiO₂-supported Au structures at various thicknesses with dimensions spanning from a few hundreds of nanometers to a few micrometers, without the use of additional adhesion layers. We explain the observed adhesion improvement as polarization-induced increased strength of Au^δ-Si^{δ+} bonds at the Au-SiO₂ interface due to the formation of a gold oxide monolayer on the Au surface by the UV-ozone treatment. Our simple and enabling method thus opens new routes for patterning Au micro/nanostructures on SiO₂ substrates without intermediate metallic adhesion layer, which is critical for biosensing and nanophotonic applications.

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5.1| Introduction

Micro/nanostructures made of Au supported on fused-silica or oxidized silicon (SiO_2) substrates have attracted much interest in recent years due to their wide range of potential applications such as chemical and biological sensors,¹⁻³ optical devices,⁴ localized surface plasmon resonance spectroscopy,⁵ and surface-enhanced Raman spectroscopy (SERS).⁶ However, fabrication of such structures has been considered challenging, due to the inherently poor adhesion of Au to SiO_2 .⁷ Generally, an additional metallic adhesion layer, for example titanium (Ti) or chromium (Cr), is used to improve the adhesion of the Au films. However, it is reported that such adhesion metals deteriorate the optical and electrical properties of pure Au.⁸⁻¹⁰ Several other methods have been explored to enhance the adhesion of Au on substrates such as plasma treatment of the substrates with different gases,^{11,12} post-irradiation with high energetic ion beam,¹³ and spin-casting of organic layers.¹⁴⁻¹⁶ Although improving the Au adhesion, these methods either require a complex treatment process, a dedicated deposition system, or an additional adhesion layer.

In this chapter, we report a novel method to significantly enhance the adhesion of deposited Au films to SiO_2 substrates, by using a post-deposition UV-ozone treatment. The chapter is structured into three sections. In the first section, we describe how post-deposition treatment of SiO_2 -supported Au films with UV-ozone results in an exceptional increase in their adhesion strength, compared to an untreated Au film. Deposition of a second Au film on top of the pretreated Au film is furthermore found to strongly extend the duration of adhesion. In the second section, we show that this novel treatment method can be used to fabricate various well-adhering Au micro/nanostructures at various thicknesses on SiO_2 substrates, without any adhesion layers. In the third section, we propose the mechanism causing this adhesion enhancement, which is an increased strength of $\text{Au}^\delta-\text{Si}^{\delta+}$ bonds at the Au- SiO_2 interface due to the formation of a charge-polarized gold oxide layer on the Au surface upon UV-ozone treatment.

5.2| Materials and methods

5.2.1| Patterning Au microdots using a shadow mask

A shadow mask containing arrays of microholes with diameters ranging from 200 μm to 600 μm was bought from Multi Leiterplatten GmbH, Germany. Using this shadow mask, arrays of Au microdots were patterned directly on oxidized ($\sim 1.1 \mu\text{m}$ thick SiO_2) 4-inch Si wafers (525 μm thick, Okmetic, Finland), using an ion-beam sputtering system (home-built T'COathy system, MESA+, NanoLab Cleanroom, The Netherlands) (Figure 5.1a).¹⁷ It is worth noting that there was

no treatment of the oxidized Si wafers prior to the shadow masked deposition. The sputtering processes were conducted at 200 W, and a pressure of 6.6×10^{-3} mbar adjusted by an argon (Ar) flow. The thickness of the deposited Au layers was varied by changing the deposition time. These Au microdot arrays were used to quantify the strength of the adhesion enhancement using the tape test.

5.2.2 | Adhesion measurement using tape test

There are several existing techniques for measuring the adhesion of thin films such as the tape test, pull test, topple test, and scratch test.¹³ Among them, the tape test is the simplest technique. A piece of adhesive tape is pressed onto the film surface, and the film is considered to have passed the test, i.e. good adhesion, if it remains on the support surface after peeling off the tape. It is worth mentioning that the classical Scotch tape test¹⁸ was inapplicable for our fabricated Au microdots due to their thin thickness. Therefore, a modified method of this Scotch tape test, herein named tape test, was used by sputtering a second continuous Au layer ~24 nm thick over the wafer surface with the patterned Au microdots before applying the tape (**Figures 5.1b-c**). In this work, a commercial adhesive tape (3M Scotch Magic Tape, United States) of 19.1 mm in width was used to test the adhesion of periodic Au microdots patterned on SiO₂ substrates. A piece of tape was applied to the surface of the sputtered second Au layer containing the Au microdots, and subsequently peeled off perpendicularly to the surface. All images of the Au microdots before and after the tape test were captured by using a bright field microscope, and converted into grayscale images – Au microdot areas are converted in black pixels – in order to be analyzed by using ImageJ software. The strength of the adhesion was quantified by comparing the remaining black pixels after the test to the number before.

5.2.3 | Patterning Au micro/nanostructures on oxidized Si substrates

Periodic microlines/holes made of a positive PR (OiR 907-17i, Fujifilm, Japan) were patterned on SiO₂ substrates by using a conventional lithography process with a mask alignment system (EVG620, EV Group, Austria). However, for patterning periodic PR nanolines/holes, UV-based displacement Talbot lithography (DTL, PhableR 100C, Eulitha, Switzerland) was utilized.¹⁹ Details of the fabrication process are shown in **Figure 5.3**. A PR layer of 200 ± 1.5 nm (PFI88 photoresist diluted 1:1 with propylene glycol methyl ether acetate (PGMEA), Sumitomo Chemical Co., Ltd., Japan) was patterned using the DTL technique with a photo-mask purchased from Eulitha. The patterned PR nanostructures were subsequently transferred at a 1:1 ratio into a bottom anti-

reflection layer coating (BARC) layer of 187 ± 2 nm (AZ BARLi II 200) by using nitrogen (N_2) plasma etching. The plasma etching of BARC was conducted in a reactive ion etch (RIE) system (home-built TETSke system, MESA+, NanoLab Cleanroom, The Netherlands) at wafer-level, 13 mTorr, and 25 W for 8 min.

These PR micro/nanostructures were then used as templates for patterning Au micro/nanostructures using a lift-off process. To improve the duration of the adhesion strength of the patterned Au micro/nanostructures, a combination of a two-step sputtering process of Au with an intermediate UV-ozone treatment was used. A Au layer of approximately 13 nm was sputtered over the PR structures, treated with UV-ozone for 5 min. Subsequently a second Au layer (~24 nm thick) was sputtered on top of the UV-ozone treated Au layer, followed by lift-off in a 99% HNO_3 solution.

5.2.4 | Characterization

The thickness of the deposited Au layers and formed gold oxide films were measured by ellipsometry (M-2000UI, J.A. Woollam Co., United States) at an angle of 75° . The surface roughness of the deposited Au layers was measured by atomic-force microscopy (AFM, Dimension Icon, Bruker Corp., United States) with a contact mode in air. HR-SEM images were captured with a high-resolution scanning electron microscope (FEI Sirion, United States) at a 5 kV acceleration voltage and a spot size of 3. The contact angles of a DI water drop on Au surfaces were measured by using an interfacial tension meter (OCA 15 Pro, Dataphysics Instruments GmbH, Germany) at ambient temperature. TEM specimens were prepared by using a focused ion beam (FIB) system (FEI Nova 600 NanoLab FIB, United States). The TEM analysis was performed with a Philips CM300ST-FEG TEM system (The Netherlands) at 300 kV acceleration voltage.

5.3 | Results and discussion

5.3.1 | Strength of the adhesion

Au microdot arrays were patterned directly on the surface of oxidized Si wafers using a shadow mask (**Figure 5.1a**, and Appendix D: **Figures D1-D3**). Their adhesion was measured with a modified tape test using a second Au layer sputtered on the microdot array (**Figure 5.1b-c**). The adhesion strength was quantified by comparing the remaining Au area after the tape test, to the initial area of the patterned Au microdots. Different experimental sequences ('cases') were conducted for investigating the Au adhesion to the SiO_2 substrate, as given in **Table 5.1**.

Figure 5.1. Schematic diagram of (a) the fabrication process for patterning periodic Au microdots using a shadow mask, and the procedure for quantifying the adhesion strength of (b) Au microdots treated with UV-ozone, and (c) Au microdots without the UV-ozone treatment.

Table 5.1. Different experimental sequences ('cases') for determination of the Au adhesion to SiO₂ using the tape test.

Cases	Description
1	~13 nm thick Au microdots.
2	~13 nm thick Au microdots treated with UV-ozone for 5 min.
3	~13 nm thick Au microdots treated with UV-ozone for 5 min, and immersed in DI water for 10 min.
4	~24 nm thick Au microdots treated with UV-ozone for 5 min.
5	~13 nm thick Au microdots treated with UV-ozone for 5 min, and immersed in ethanol for 10 min.
6	~13 nm thick Au microdots treated with UV-ozone for 5 min, immersed in ethanol for 10 min, cleaned with nitric acid (HNO ₃), and re-treated with UV-ozone for 5 min.
7	~13 nm thick Au microdots treated with UV-ozone for 5 min, and stored for 2 weeks.
8	~13 nm thick Au microdots treated with UV-ozone for 5 min, covered with a second Au layer of ~24 nm thick through the shadow mask, and sonicated in ethanol for 2 hours.

Figure 5.2. Fraction of remaining Au area versus the diameter or area-to-perimeter ratio of Au microdots after the tape test for cases 1-4 (see Table 5.1).

Figure 5.2 shows the fraction of remaining Au area as function of the diameter of fabricated Au microdots after the tape test for the cases 1-4 of Table 5.1. Case 1 indicates the inherently poor adhesion of Au to SiO₂⁷: without the UV-ozone treatment, the Au microdots of all diameters were completely removed (Appendix D: Figure D4). Case 2 shows the effect of the 5 minute UV-ozone treatment: now between 83% and 96% of Au area remained attached, depending on the Au microdot diameter (Appendix D: Figures D5-D7).²⁰

Case 4 shows that the adhesion effect depends on the Au thickness: increasing the thickness of the Au microdots to approximately 24 nm results in a decrease in the adhesion strength (Appendix D: Figures D11-D13). We found in this case that the center part of almost all Au microdots was removed, leaving only their circumference on the SiO₂ surface, especially for large Au microdots.

Importantly, deposition of a second Au layer on top of the pretreated Au layer of ~13 nm thick caused the adhesion to remain stable in the environmental air for more than 5 months (Appendix D: Figures D14-D15). This observation, which is considered in more detail in the mechanism section, allowed stable patterning of well-adhering thick gold layers without additional adhesion layers, which we used for micro/nanopatterning of various Au structures.

5.3.2 | Patterning Au micro/nanostructures on oxidized Si substrates

Au micro/nanostructures with a stable and strong adhesion to the surface of oxidized Si wafers, could be manufactured by a combination of lithography with a two-step sputtering of stacked Au layers and an intermediate UV-ozone treatment (Figure 5.3).

Figure 5.3. Fabrication process for patterning well-adhering Au nanostructures supported directly on the surface of oxidized Si wafers, without additional adhesion layers.

Figure 5.4 shows the top-view optical and high-resolution scanning electron microscope (HR-SEM) images of ~ 37 nm thick Au dot and line structures, patterned directly on the surface of oxidized Si wafers. The patterns were well defined over large areas of 5×5 mm², with high uniformity and excellent adhesion. It is noteworthy that there were no defects observed in the patterned structures, indicating that the Au adhesion to the oxidized Si substrate remained stable during all processing steps. Without applying the UV-ozone treatment, removal of several Au microdots was observed (Appendix D: Figure D16). Also, a ~ 90 nm thick Au layer sputtered on a UV-ozone treated ~ 13 nm thick Au layer showed stable adhesion, which could be patterned using wet etching (Appendix D: Figure D17).

The post-deposition UV-ozone treatment also opens a direct way of patterning Au structures on oxidized Si substrates from a thin Au layer less than 13 nm thick by using patterned UV-ozone exposure and thereby controlling the formation areas of gold oxide (Appendix D: Figure D18 and Video D1).

Interestingly, we also observed an enhancement in the adhesion of Pt to SiO₂ after UV-ozone treatment. Although no further characterization has been performed, we used this treatment to pattern Pt nanodots/lines supported directly on the surface of oxidized Si wafers (Appendix D: Figure D19).²¹ We also

have preliminary evidence that this treatment technique can be further extended to increase the adhesion of Au or Pt, to other ceramic substrates, such as a silicon nitride coated silicon wafer.

Figure 5.4. Top-view optical images (scale bar: 50 μm) of periodic (a) Au microdots ($\sim 2\ \mu\text{m}$ diameter), (b) Au microlines ($\sim 2\ \mu\text{m}$ width) with the inserted top-view HR-SEM images (scale bar: 5 μm), and top-view HR-SEM images (scale bar: 5 μm) of periodic (c) Au nanodots ($\sim 346\ \text{nm}$ diameter), (d) Au nanolines ($\sim 286\ \text{nm}$ width) with the inserted close-up HR-SEM images (scale bar: 1 μm).

5.3.3 | Mechanism of the adhesion enhancement

As the mechanism for the adhesion enhancement, we propose a polarization-induced increased interaction strength at the Au-SiO₂ interface when gold oxide is formed at the air-Au interface during UV-ozone treatment (**Figure 5.5**). The reaction of oxygen with Au surfaces has been reported to induce the transfer of electrons from the Au bulk into the adsorbed oxygen layer.²² This electron transfer has also been described by Sun *et al.*,²³ where details of the interaction of adsorbed atomic oxygen with Au surface atoms were studied intensively using the Hückel theory, and density functional theory (DFT) calculations.

We hypothesize that this electron transfer causes an increased Au-Si bonding strength at the Au-SiO₂ interface. This hypothesis is schematically

depicted in **Figure 5.5**, and is based on the work of Bauer *et al.*²⁴ and Sun *et al.*²⁵ These authors investigated the interaction between Au and SiO₂, the former authors by soft-x-ray photoemission spectroscopy and the latter by DFT. Both reported evidence for the formation of Au-Si bonds with a polarization Au^{δ-}Si^{δ+}. As this polarization implies partial electron transfer to the Au layer, we expect that these Au-Si bonds will be strengthened when gold surface oxidation causes partial electron transfer from the Au to the bound oxygen.

Figure 5.5. Schematic diagrams of the mechanism for the adhesion enhancement of (a) ~13 nm thick Au microdots, and (b) ~24 nm thick Au microdots with the oxidized Si substrate.

The formation and removal of gold oxide was confirmed by different methods. Ellipsometer data obtained after 5 min UV-ozone treatment were in accordance with the growth of a gold oxide layer of approximately 2.0 ± 0.2 Å, consistent with the approximate thickness (2 Å) of a monolayer of Au-O bonds.²⁶ The change in the peak intensity of the reflectance spectrum measured on the Au surface after the UV-ozone treatment (Appendix D: **Figures D20-D21**) without a significant change in the Au surface roughness is consistent with the formation/reduction of a gold oxide layer.²⁶⁻²⁸ Measurements of the contact angle (CA) of a DI water drop on a Au surface after the UV-ozone treatment were also in accordance with the formation of a gold oxide layer (Appendix D: **Figure D22**).²⁶

It is known that gold oxide is reduced in ethanol.^{26,29} We therefore immersed the UV-ozone treated Au microdots in ethanol for 10 min, and found that the enhanced adhesion had vanished (Case 5, **Figure 5.6** and Appendix D: **Figure D23**). Re-treating the sample with UV-ozone restored the adhesion, though with a considerable drop in the adhesion strength, especially for small Au microdots (Case 6, **Figure 5.6** and Appendix D: **Figures D24-D26**). Our measured contact angle (CA) of a DI water drop on a Au film re-treated with UV-ozone also indicates the renewed formation of a gold oxide layer (Appendix D: **Figure D22**).

Decomposition of gold oxide over time in the environment is reported in literature.³⁰ We stored a Si wafer with UV-ozone treated Au microdots in

environmental air for 2 weeks before the tape test (Case 7, **Figure 5.6**). **Figure 5.6** shows that all fabricated Au microdots were removed after the tape test (Appendix D: **Figure D27**), indicating the loss of the adhesion strength over time in air, consistent with a gold oxide origin of the effect.

Quite remarkably, deposition of a second Au layer on top of the pretreated Au layer of ~ 13 nm thickness resulted in a major extension in the duration of its adhesion to the SiO_2 substrate. The adhesion of stacked Au layers remained stable in environmental air for more than 5 months (Appendix D: **Figures D14-D15**). Arrays of Au microdots fabricated using this stacked Au layer configuration were found to pass the tape test after sonication at room temperature in ethanol for 2 hours (Case 8, **Figure 5.6** and Appendix D: **Figure D28**). This is consistent with an embedded gold oxide layer that is insensitive to reduction during the sonication. A stable and strong adhesion of these Au microdots to the SiO_2 surface was obtained (Appendix D: **Figures D29-D31**). It is worth noticing that the embedded gold oxide layer could not be seen in an image recorded with transmission electron microscopy (Appendix D: **Figure D32**), probably due to its extremely low thickness of 2.0 ± 0.2 Å measured by ellipsometry.

Figure 5.6. Fraction of remaining Au area versus the diameter or area-to-perimeter ratio of Au microdots after the tape test for cases 5-8 (see **Table 5.1**).

A further experiment supported our hypothesis of a charge-based mechanism for the adhesion. We applied an electrical potential in water (Appendix D: **Figure D33**) to stacked Au films (a ~ 24 nm Au layer sputtered on an UV-ozone treated ~ 13 nm Au layer), supported on amorphous fused-silica

substrates. Applying a negative potential to the stacked Au films resulted in their immediate detachment from the SiO₂ support, whereas they remained attached upon applying a positive potential. We attribute this detachment to the destabilization of the Au^{δ-}Si^{δ+} bonds at the Au-SiO₂ interface by the additional negative charges.^{31,32}

Finally, we believe that the enhanced adhesion observed for Pt can also be explained by the proposed mechanism. Charge polarization at the interface of Pt-oxide support has been reported elsewhere.^{33,34}

5.4 | Conclusion

In summary, we report an enabling technique to significantly enhance the direct adhesion of gold to oxidized silicon, solely by a UV-ozone treatment of the deposited Au films or structures. The observed excellent enhancement of the adhesion can be explained as polarization-induced increased Au-SiO₂ interaction at their interface due to the formation of gold oxide on the Au/air interface upon UV-ozone treatment. By embedding the gold oxide layer in between two sputtered Au layers, the adhesion increase becomes durable and independent of the influence of the surrounding environment, i.e. gases or solutions. This enables the fabrication of SiO₂ supported Au micro/nanostructures, which strongly adhered to the substrate after storing for more than 5 months in environmental air, or sonication in ethanol for 2 hours. With its simple operation, our fabrication technique provides a new route for patterning of various Au micro/nanostructures at different thicknesses supported directly on SiO₂ substrates, without the need of additional adhesion layers. The absence of such adhesion layers is highly favored for biosensing and nanophotonic applications.

5.5 | References

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31. Reaction of Au with Si at the Au-SiO₂ interface was eliminated as no increase in the surface roughness of the SiO₂ substrate after removing the UV-ozone treated Au film (Appendix D: **Figure D34**).
32. It was found that the adhesion of thicker Au films of approximately 24 nm thickness could be increased when treating with O₂ plasma. An explanation can be that the thicker gold oxide layer formed (14.4 ± 0.09 Å measured by ellipsometry) in this case still leads to a significant charge polarization at the Au-SiO₂ interface despite the thicker Au film. The O₂ plasma was conducted at 500 W for 10 min using a plasma system (TePla 300, PAV TePla AG, Germany).
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6

Engulfment Control of Platinum Nanoparticles into Oxidized Silicon Substrates*

We found that platinum (Pt) nanoparticles, upon annealing at high temperature of 1000°C, are engulfed into amorphous fused-silica or thermal oxide silicon substrates. The same phenomenon was previously published for gold (Au) nanoparticles. Similar to the Au nanoparticles, the engulfed Pt nanoparticles connect to the surface of the substrates through

conical nanopores, and the size of the Pt nanoparticles decreases with increasing depth of the nanopores. We explain the phenomena as driven by the formation of platinum oxide by reaction of the platinum with atmospheric oxygen, with platinum oxide evaporating to the environment. We found that the use of Pt provides much better controllability than the use of Au. Due to the high vapor pressure of platinum oxide, the engulfment of the Pt nanoparticles into oxidized silicon (SiO_2) substrates is faster than of Au nanoparticles. At high temperature annealing we also find that the aggregation of Pt nanoparticles on the substrate surface is insignificant. As a result, the Pt nanoparticles are uniformly engulfed into the substrates, leading to an opportunity for patterning dense nanopore arrays. Moreover, the use of oxidized Si substrates enables us to precisely control the depth of the nanopores since the engulfment of Pt nanoparticles stops at a short distance above the SiO_x/Si interface. After subsequent etching steps, a membrane with dense nanopore through-holes with diameters down to sub-30 nm is obtained. With its simple operation and high controllability, this fabrication method provides an alternative for rapid patterning of dense arrays of solid-state nanopores at low-cost.

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6.1 | Introduction

Solid-state nanopores have attracted much scientific interest due to their excellent properties including size-tunability, high reliability and stability, easy modification and integration.¹⁻⁴ Among potential applications in sensing,⁵ separation,⁶ purification,^{7,8} solid-state nanopores are intensively used for DNA sequencing and protein detection.⁹⁻¹¹ Many methods have been reported to fabricate solid-state nanopores, which can be separated in two categories namely high-energy beam sculpting¹²⁻¹⁴ and conventional manufacturing.¹⁵⁻²⁰ Although high-energy beam based methods can precisely produce nanopores in silicon nitride or silicon oxide with diameters down to approximately 1 nm, these methods are time- and labor-intensive, and require dedicated systems. Therefore, high-yield fabrication of solid-state nanopore arrays is not possible at low-cost. Conventional methods, for example mask etching,^{15,17} nanoimprinting,¹⁶ electrical breakdown,¹⁹ offer a high production rate, but lack precise control of both reproducibility and pore dimensions. Surwade *et al.* reported the fabrication of a nanoporous graphene film by using oxygen plasma etching of graphene.⁸ Although nanopores with the diameter of 0.5-1 nm can be produced, this fabrication method is limited to graphene only. Therefore, a robust and simple fabrication method for high-yield patterning of dense arrays of solid-state nanopores at low-cost is necessary.

Recently, de Vreede *et al.* reported the engulfment of Au nanoparticles into amorphous fused silica substrates at high temperature.²¹ Annealing at approximately 1050°C, Au nanoparticles are found to become engulfed perpendicularly into the substrates, leaving a nanopore connection to the substrate surface. Using this observed phenomenon, closed-end nanopores with diameters of approximately 25 nm, and lengths up to 800 nm were fabricated into amorphous fused-silica substrates. Although this proved a simple method for making solid-state nanopores through membranes,²² it is difficult to precisely control the uniformity in the engulfment depth of Au nanoparticles, or the dimension and uniformity of the nanopores. Moreover, the aggregation of Au nanoparticles at high temperature limits the use of this method for making dense arrays of solid-state nanopores.

In this chapter, we report an alternative method to fabricate dense arrays of silicon oxide nanopores by annealing Pt nanodots supported directly on the surface of oxidized Si substrates at high temperature. The use of Pt nanoparticles leads to an opportunity for patterning dense nanopore arrays due to their insignificant aggregation at high temperature compared to Au nanoparticles. In addition, the use of oxidized Si substrates enables us to precisely control the depth of the nanopores since the engulfment of Pt nanoparticles stops above the SiO_x/Si interface. Using this combination with

subsequent etching steps, we successfully demonstrate the fabrication of dense arrays of silicon oxide nanopore through-holes with diameters down to sub-30 nm.

6.2 | Materials and methods

6.2.1 | Patterning dense arrays of Pt nanodots on oxidized Si substrates

Figure 6.1 shows the fabrication process for patterning arrays of Pt nanodots supported on the surface of thermally oxidized (~ 100 nm thick SiO_2) 4-inch Si wafers (525 μm thick, single side polished, Okmetic, Finland), without the use of additional adhesion layers. Briefly, ultraviolet (UV)-based displacement Talbot lithography (DTL, PhableR 100C, Eulitha, Switzerland) was used to pattern periodic ~ 300 nm diameter nanoholes with ~ 400 nm pitch into a positive photoresist (PR) layer of 200 ± 1.5 nm thickness (PFI88 photoresist diluted 1:1 with propylene glycol methyl ether acetate (PGMEA), Sumitomo Chemical Co., Ltd., Japan). These nanoholes which were subsequently transferred at a 1:1 ratio into a bottom anti-reflection layer coating (BARC) layer of 187 ± 2 nm thickness (AZ BARLi II 200) by using nitrogen (N_2) plasma etching in a parallel plate reactive ion etching system (in-house built TETSKE system, NanoLab Cleanroom, The Netherlands) at wafer-level, 13 mTorr, and 25 W for 8 min.²³ These PR/BARC nanoholes were then used as a template for the fabrication of Pt nanodots using a lift-off process. To improve the adhesion strength of Pt with SiO_2 , the patterned wafer was treated with UV-ozone (PR-100 UV-ozone Photoreactor, UVP Inc., United States) for 5 min after the sputtering of a Pt layer using an ion-beam sputtering system (in-house built T'COATHY system, NanoLab Cleanroom, The Netherlands).²⁴ By performing the lift-off process in a 99% nitric acid (HNO_3) solution, dense arrays of Pt nanodots supported on the surface of oxidized Si wafers were obtained.

6.2.2 | High temperature annealing of Pt nanodots on oxidized Si substrates

The fabricated Pt nanodots were annealed at high temperature by using a furnace (TSD-12 furnace, Toma, Netherlands) in environmental air. Different annealing recipes were conducted to investigate the effects of the annealing temperature and time on the dewetting of Pt nanodots into Pt nanoparticles, and the engulfment of the Pt nanoparticles into the oxidized Si substrates. It is worth mentioning that the furnace was closed completely during the annealing processes.

Figure 6.1. Fabrication process for patterning Pt nanodots (~ 300 nm diameter, ~ 400 nm pitch) supported directly on the surface of oxidized Si wafers, combining DTL with a lift-off process.

Figure 6.2. Fabrication process for patterning dense arrays of through-hole sub-30 nm nanopores. (a) Pt nanoparticles sunk into an oxidized Si substrate upon annealing at high temperature. (b) Wet etching of the bulk Si substrate, and subsequently (c) dry etching of the SiO_2 layer from the backside. (d) Wet etching of Pt nanoparticles to open the through-hole nanopores.

6.2.3 | Manufacturing membranes with dense arrays of sub-30 nm nanopores

Figure 6.2 show the fabrication process for manufacturing membranes with dense arrays of through-hole sub-30 nm nanopores, using the prior engulfment of Pt nanoparticles into an oxidized Si substrate. Briefly, an oxidized Si substrate containing engulfed Pt nanoparticles (Figure 6.2a) was wet etched in a 25% potassium hydroxide (KOH) solution at 75°C , to selectively remove the bulk Si from the backside (Figure 6.2b). Thereafter, a dry etching process of SiO_2 was conducted from the backside of the sample in the TETSKE system using a mixture plasma of 25 sccm fluoroform (CHF_3) and 5 sccm oxygen (O_2) at 10 mTorr, and 60 W for 1 min and 30 s, to thin down the SiO_2 layer to reach the Pt nanoparticles (Figure 6.2c). Subsequent etching of the sample in a mixture

solution of 30% HNO_3 and 27% hydrochloric acid (HCl) at a ratio of 1:9:20 – $\text{HNO}_3\text{:HCl:H}_2\text{O}$ at 90°C , for 10 min, resulted in a removal of the Pt nanoparticles, thus opening the nanopores (**Figure 6.2d**).

6.2.4 | Characterization

High resolution scanning electron microscope (HR-SEM) images were captured by using a FEI Sirion microscope (United States) at a 5 kV acceleration voltage and a spot size of 3. The surface topography of structures was measured by using an atomic-force microscopy (AFM, Dimension Icon, Bruker Corp., United States) in contact mode in air. The thickness of the sputtered Pt layers and the SiO_2 layers was measured by using an ellipsometer system (M-2000UI, J.A. Woollam Co., United States) at an angle of 75° . Sample for transmission electron microscopy (TEM) was prepared by using a focused ion beam (FIB) system (FEI Nova 600 NanoLab FIB, United States). The TEM specimen was measured by using a TEM system (FEI Tecnai F20, United States) at a 200 kV acceleration voltage

6.3 | Results and discussion

6.3.1 | Patterning dense arrays of Pt nanodots on oxidized Si substrates

Figure 6.3 shows the HR-SEM images of periodic Pt nanodots supported on the surface of an oxidized Si wafer, without additional adhesion layers. The top-view HR-SEM image shows a well-fabricated pattern of Pt nanodots (400 nm pitch) of approximately 300 nm in diameter (**Figure 6.3a**). It is remarkable that all the Pt nanodots remained on the substrate surface after the lift-off process in the HNO_3 solution, thus indicating a good adhesion of Pt to SiO_2 obtained after treating the patterned wafer with UV-ozone for 5 min (see **Figure 6.1**). The thickness of the sputtered Pt layer measured using the ellipsometer system was approximately 12.5 nm. The cross-sectional HR-SEM image shows residues of Pt at the edge of the patterned Pt nanodots (**Figure 6.3b**). This phenomenon is typically encountered when using the lift-off process, and is caused by the sticking of unwanted metals deposited on the sidewall of PR patterns.²⁵ The fabricated Pt nanodot arrays were subsequently used to investigate the dewetting and engulfment process into the oxidized Si substrates by annealing at different temperatures.

Figure 6.3. (a) Top-view (scale bar: 2 μm), and (b) cross-sectional (scale bar: 1 μm) HR-SEM images of periodic Pt nanodots supported directly on the surface of an oxidized Si wafer, with a close-up HR-SEM image (scale bar: 500 nm).

6.3.2 | High temperature annealing of Pt nanodots on oxidized Si substrates

Figure 6.4 shows the HR-SEM images of Pt nanodots after annealing at different temperatures, i.e. 700°C, 800°C, 900°C, 1000°C, for 5 h (Appendix E: **Figure E1**). It clearly shows that the shape and dimension of the Pt nanodots changed after annealing at 700°C for 5 h, indicating Pt mobility and consequent dewetting at this relatively low temperature (700°C) when compared to the melting temperature of Pt ($\sim 1768^\circ\text{C}$). Such dewetting of Pt nanodots on SiO_2 surfaces at low temperature has been reported in literature.²⁶ Increasing the annealing temperature to 800°C resulted into Pt nanoparticles with a more hemispherical shape. However, annealing at 900°C for 5 h led to a significant reduction in the Pt nanoparticle circumference (Appendix E: **Figures E2-E3**). We attributed this to the evaporation of platinum oxide via the oxidation of platinum at this temperature (900°C).^{27,28} **Figure 6.5** shows that these Pt nanoparticles started to become engulfed into the SiO_2 layer, though at a relatively low uniformity. Several Pt nanoparticles were found to be completely engulfed, whereas other Pt nanoparticles had a ridge formation of SiO_2 around their perimeter (Appendix E: **Figures E2-E3**). Remarkably, these Pt nanoparticles were uniformly engulfed into the SiO_2 layer with only insignificant aggregation when compared to Au nanoparticles after annealing at 1000°C for 5 h (Appendix E: **Figure E4**). Such a higher thermal stability of Pt nanoparticles compared to Au nanoparticles on SiO_2 substrates has also been observed by other investigators.^{29,30} By the engulfment, closed-end conical nanopores were formed in the SiO_2 layer with

an end diameter of sub-10 nm and a length of approximately 185 nm. It is noted that the thickness of the initial 100 nm thick SiO_2 layer further increased during the annealing process. Details of the proposed engulfment mechanism are given in the next section. It is worth mentioning that the engulfment of all Pt nanoparticles stopped at a defined distance above the SiO_x/Si interface, thus leading to a precise control of the nanopore depth over large areas. This could be because the layer under the Pt nanoparticle is not fully oxidized to SiO_2 ,³¹ or because stress is formed in this layer,³² which then leads to a decrease in the mobility of silicon oxide around the Pt nanoparticle surface. Both mechanisms could explain the termination of the engulfment of the Pt nanoparticle.

Figure 6.4. Top-view (scale bar: 1 μm) and cross-sectional (scale bar: 500 nm) HR-SEM images of Pt nanodots after annealing at different temperatures for 5 h. For all annealing processes, the ramp-up time was fixed at 2 h, and the furnace was passively cooled down to room temperature after heating.

Figure 6.5. AFM (scan filed: $2 \times 2 \mu\text{m}^2$) images of Pt nanodots after annealing at different temperatures for 5 h.

6.3.3 | Mechanism of the engulfment of Pt nanoparticles in oxidized Si substrates

To investigate the engulfment mechanism of the Pt nanoparticles into oxidized Si substrates, we measured the cross-section of an engulfed Pt nanoparticle connected to the substrate surface through a nanopore, using a transmission electron microscopy (TEM). A clear evidence of a flat crystal facet was observed at the upper side of the engulfed Pt nanoparticle (**Figure 6.6**). A similar formation of crystal facets at the top of engulfed Au nanoparticles has been observed and reported by de Vreede *et al.*²¹ In their paper, the engulfment of Au nanoparticles is attributed to the continuous evaporation of Au causing a constant change in the structural geometry, thus leading to the continuous migration of silica from below the Au nanoparticle to the triple line at its top in order to maintain equilibrium. As a result, the Au nanoparticle moves perpendicularly into the substrate. Assuming the Au evaporation was rate-limiting for the process, the engulfment depth as function of the annealing time could in good approximation be predicted.²¹ This model did not include a description for the migration of silica along the nanoparticle, which process was recently modeled as driven by diffusiophoresis of Au in a nanometer thin viscous layer surrounding the Au nanoparticles.³³ We attribute the engulfment of Pt nanoparticles in oxidized Si substrates to comparable processes. It has to be noted that the platinum oxide evaporates faster than gold in atmospheric oxygen at high temperature as its vapor pressure is one order of magnitude higher than that of gold.³⁴ Further experimental verification is ongoing in order to confirm the reliability of the model, especially for the engulfment of Pt nanoparticles.³⁵ In addition, the influence of oxygen on the engulfment process can be further investigated by annealing the Pt nanoparticles in inert gases, i.e. N₂ or Ar.

In this chapter, we apply the engulfment of Pt nanoparticles into oxidized Si substrates (**Figure 6.7**) to fabricate dense arrays of through-hole sub-30 nm nanopores in a silicon oxide layer, combining wet etching and dry etching techniques (see next section).

Figure 6.6 (a) Cross-sectional TEM images of a Pt nanoparticles sunken into an oxidized Si substrate with (b) the corresponding close-up image of the Pt nanoparticle.

Figure 6.7. Formation of nanopores into oxidized Si substrates caused by the engulfment of Pt nanoparticles upon annealing at high temperature.

6.3.4 | Manufacturing membranes with dense arrays of sub-30 nm nanopores

Figure 6.8 shows HR-SEM images of an array of nanopores fabricated in a silicon oxide (SiO_2) layer of approximately 160 nm thickness. The top-view HR-SEM image (**Figure 6.8a**) taken at the edge of the Si substrate (red dash line) shows a clear difference in the contrast between the through-hole nanopores (black) created into the free-standing SiO_2 area and the closed-end nanopores (grey). This indicates the success of the pore opening process from the backside of the SiO_2 layer (see **Figure 6.2**). From the observation, almost all nanopores were opened ($\sim 95\%$). In addition, a well-ordered pattern of through-hole nanopores was obtained. The cross-sectional image (**Figure 6.8b**) confirms the opening of

the nanopores with diameters down to sub-30 nm (Appendix E: **Figure E5**). The average top-diameter of the nanopores was approximately 31.9 nm with a variation (standard deviation) of 6.5 nm. The through-hole nanopores have a conical shape due to the continuous evaporation of the Pt nanoparticles during the engulfment. Further optimization and timing of the etching processes, especially of the final SiO_2 dry etching step, is expected to produce through-hole nanopores of even smaller end-diameters as the closed-end nanopores had end-diameters in the sub-10 nm range (Appendix E: **Figure E6**). Moreover, subsequent conformal deposition of a silicon nitride layer or an aluminum oxide layer can also probably reduce the nanopore diameter.¹⁰

Figure 6.8. (a) Top-view (scale bar: 500 nm) and (b) cross-sectional (scale bar: 500 nm) HR-SEM images of periodic through-hole sub-30 nm nanopores created in a thick SiO_2 layer of approximately 160 nm, with a close-up image (scale bar: 100 nm).

6.4 | Conclusion

In summary, we report an alternative method to fabricate solid-state nanopores into oxidized Si substrates by annealing Pt nanodots supported directly on the substrate surface at high temperature. Compared to the previous approach using Au, we found that Pt nanoparticles were engulfed faster into the oxidized Si substrates, even though Pt has a higher melting temperature ($\sim 1768^\circ\text{C}$) than Au ($\sim 1064^\circ\text{C}$). We attribute this to the formation and subsequent evaporation of volatile platinum oxide in atmospheric environment. In addition, the aggregation of Pt nanoparticles was found to be insignificant compared to that of Au nanoparticles annealed at the same temperature, thus leading to an opportunity to pattern dense regular arrays of solid-state nanopores. Moreover, the use of oxidized Si substrates enables us to precisely control the depth of the nanopores since the engulfment of Pt nanoparticles stops above the SiO_x/Si interface. Using the engulfment of Pt nanoparticles into oxidized Si substrates, we fabricated dense arrays of through-hole nanopores in a free-standing SiO_2 layer with sub-30 nm pore diameter. With its simple operation,

our fabrication method provides an alternative for rapid patterning of dense arrays of solid-state nanopores at low-cost.

6.5 | References

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7

Fabrication of Microreactors Integrated with Noble Metal Nanoparticle Arrays and Initial Experiments

We apply microfluidic technology for catalysis study by fabricating microreactors integrated with noble metal nanoparticle arrays. The fabricated microreactor consists of a top part made of glass that is anodically bonded to a bottom part containing an array ($3 \times 3 \text{ cm}^2$) of gold nanoparticles supported on an oxidized silicon substrate. For the top part, a microchamber and two flow distribution channels are wet-etched into the glass substrate, whereas the connections are fabricated by using a powder blasting process. The fabricated microreactors are used to perform a simple gas-phase reaction on chip, which is the oxidation of carbon monoxide. By using the two distribution channels, the fluid flow is uniformly distributed inside the microchamber, thus providing homogenous reaction conditions. The product of the reaction is monitored continuously using a mass spectrometer connected directly to the outlet of the microreactor. The use of such microreactors provides opportunities to precisely control the reactant flows, especially at very low flow rates, and to maximize the volume ratio of products to reactants which can enhance the detection sensitivity.

7.1| Introduction

Microreactors have been widely used in recent years as tools for analytical chemistry and chemical synthesis of organic/inorganic materials and metal nanoparticles.^{1–3} The use of microreactors provides a precise control of mass and heat transfer.⁴ Moreover, the reduction in reactor size leads to not only a lower energy consumption, but also to a smaller amount of by-products and reagents consumption compared with conventional methods.⁵ This offers controllable methods for high-yield production of chemicals at high selectivity and consistency. In addition, using microreactors enables the exploration of new chemical windows and the study of reaction kinetics, as well as provides the chance to conduct reactions which are difficult to perform in batch.^{6,7}

Various designs of microreactors are reported in literature,¹ which can be categorized into two groups: chip-based microreactors and microcapillary reactors. Although requiring many fabrication steps, chip-based microreactors provide capabilities to conveniently integrate multiple functions into one chip, and to connect in a facile manner to other microfluidic devices. The fabrication process of the chip-based microreactors is mainly adapted from the microelectronics industry.⁸ Various materials including silicon-based inorganic materials, borosilicate glass, ceramics, polymers, and stainless steel are used for the fabrication of such microreactors.³ Borosilicate glass based microreactors^{9,10} offer the advantage of visualizing the chemical reaction progress due to their transparency, however the difficulty in creating high aspect ratio structures limits their structural design. Moreover, the low thermal conductivity of glass leads to a difficulty in providing homogeneous heating conditions for chemical reactions inside the microreactors. Although being nontransparent, silicon based microreactors^{11,12} offer a high efficiency of heat exchange. In addition, high aspect ratio microchannels in silicon can easily be fabricated using dry etching techniques. Polymer-based microreactors^{13,14} can be easily fabricated using soft lithography, injection molding, and embossing, though they cannot be used to perform chemical reactions of corrosive fluids at high temperature and high pressure. Stainless steel based microreactors^{15,16} offer the opportunity to operate at high temperature and high pressure, but they are nontransparent and difficult to scale down in size, especially to the micrometer scale.

In this chapter, we report the fabrication of microreactors integrated with noble metal nanoparticle arrays for catalysis study. The designed microreactor consists of a top part made of glass containing a microchamber and two distribution channels, which is anodically bonded to a bottom part containing

an array of gold (Au) nanoparticles supported on an oxidized silicon substrate. The fabricated microreactors were used to perform the oxidation of carbon monoxide on chip. The product of the reaction is monitored continuously by using a mass spectrometer (MS) connected directly to the outlet of the microreactor.

7.2 | Materials and methods

7.2.1 | Microreactor design

Figure 7.1 shows the schematic design of a microreactor integrated with a noble metal nanoparticle array. The designed microreactor consists of a top part made of glass containing a microchamber and two distribution channels anodically bonded to a bottom part containing an array of noble metal nanoparticles supported on an oxidized silicon substrate. Since the area of the fabricated array of noble metal nanoparticles is fixed at $3 \times 3 \text{ cm}^2$ (see **Chapter 4**), the size of the microchamber is also designed at $3 \times 3 \text{ cm}^2$ with a depth of $25 \text{ }\mu\text{m}$ (microchamber volume of $22.5 \text{ }\mu\text{l}$). For each distribution channel, the main channel is split equally into 32 branch channels with the channel width of $50 \text{ }\mu\text{m}$ and the channel depth of $25 \text{ }\mu\text{m}$. The use of these two distribution channels is to uniformly distribute the reagent flow inside the microchamber. For the connection to the main channels, fused-silica capillaries are glued into channels previously made into the glass top part by powder blasting.

Figure 7.1. Schematic design of a microreactor integrated with a noble metal nanoparticle array. The close-up image shows details of the microchamber of $3 \times 3 \text{ cm}^2$ connected with two distribution channels.

7.2.2 | Simulation of the designed microreactor using COMSOL Multiphysics

To study the fluid flow behavior in the designed microreactor (estimated Reynolds number ≈ 9), the physical model of laminar flow was used in our COMSOL Multiphysics simulations.¹⁷ For simplification, air was used as the simulated fluid in a three-dimensional model of the microreactor. The fluid flow was assumed to be steady, compressible, and with the Maxwell slip boundary condition.^{18,19} The fluid flow rate at the inlet was fixed at 0.3 ml min^{-1} , whereas a fixed pressure of 0 Pa was set the outlet (reference pressure: 1 atm). Due to the symmetry of the designed microreactor, only half the distribution channel (Figure 7.2) and half the microchamber (Figure 7.3) were simulated.

Figure 7.2. Half of the distribution channel together with the dimensions, and a zoom-in meshing in COMSOL Multiphysics.

Figure 7.3. Half of the microchamber together with the dimensions, and a zoom-in meshing in COMSOL Multiphysics. The fluid flow into this half of the microchamber was distributed uniformly by 16 branch inlets from the half of the distribution channel.

7.2.3 | Fabrication of the designed microreactor

Figure 7.4 shows the fabrication process of the designed microreactor. Details of the patterning process for the bottom part, which has the array of Au nanoparticles ($\sim 10^{10}$ particles of approximately 20 nm in diameter) supported on an oxidized silicon substrate are given in Chapter 4, Figures 4.1-4.2. For the

top-part of the microreactor, a microchamber and two distribution channels were wet-etched into a glass substrate, whereas the connections were fabricated by using a powder blasting process. Briefly, 4-inch borosilicate glass wafers (1 mm thick, double-side polished, PlanOptik AG, Germany) were cleaned completely before sputtering chromium (Cr) and gold (Au) layers to enhance the adhesion of this stacked Au/Cr layer to the wafer surface. For the cleaning process, the glass wafers were immersed in a 99% nitric acid (HNO_3) solution for 10 min, in a 25% potassium hydroxide (KOH) solution at 75°C for 10 s, in a 99% HNO_3 solution again for 10 min, in deionized (DI) water using a quick dump rinser, and finally spin-dried with nitrogen (N_2) gas. After the cleaning process, a Cr layer of approximately 25 nm was sputtered over the wafer surface, followed by the sputtering of a Au layer of approximately 135 nm. All the sputtering processes were conducted in an ion-beam sputtering system (in-house built T'COathy system, NanoLab Cleanroom, The Netherlands) at 200 W, and a pressure of 6.6×10^{-3} mbar. Subsequently, a positive photoresist (PR) layer (OiR 907-17i, Fujifilm, Japan) was spin-coated over the wafer surface at 4000 rpm, followed by baking at 95°C for 1 min. The exposure process was performed by using a mask alignment system (EVG620, EV Group, Austria) for 5 s at an intensity of 12 mW cm^{-2} , and with hard contact mode. Thereafter, the glass wafer was post-baked at 120°C for 1 min, followed by developing in a OPD4246 solution for 1 min and rinsing with DI water to complete the fabrication of PR structures, i.e. a microchamber and two distribution channels, on the Au/Cr coated glass wafer (**Figure 7.4a**).

To further pattern the stacked Au/Cr layer, argon (Ar) ion beam etching (IBE) was performed in an etching system (Oxford i300, Oxford Instruments PLC, United Kingdom) at 5 sccm Ar, 300 eV, 50-55 mA for 12 min (**Figure 7.4b**). Subsequently, the patterned wafer was immersed in a 25% hydrogen fluoride (HF) solution for 25 min to wet-etch the glass substrate, thus forming the microchamber and the distribution channels (**Figure 7.4c**). Thereafter, the glass wafer was immersed in a 99% HNO_3 solution for 5 min to remove the PR structures, followed by wet-etching of the stacked Au/Cr layer using Au and Cr etchant solutions. To completely clean the patterned wafer, a standard RCA-2 cleaning process was done in a mixture solution of 27% hydrochloric acid (HCl) and 30% hydrogen peroxide (H_2O_2) at a ratio of 1:1:5 – HCl: H_2O_2 : H_2O at 80°C for 10 min.

To pattern a mask for the powder blasting process, a plastic foil (MX5020, DuPont Electronic Technologies, United States) was laminated on the wafer surface by using a laminator (GBC 3500 Pro Series, United States) at 70°C. The

exposure was conducted by the EVG620 system for 4 s with soft contact mode, followed by developing in water at 45°C for 100 s and spin-drying with N₂ gas (**Figure 7.4d**). Subsequently, the patterned wafer was powder-blasted using an in-house built system (BIOS Lab-on-a-Chip Group, The Netherlands) with a x-scan rate of 5 mm s⁻¹, a y-scan rate of 0.5 mm s⁻¹, and a pressure of 5 bar (**Figure 7.4e-f**). After removing the foil, the glass wafer was sonicated in water for 20 min to completely remove the remaining residues (**Figure 7.4g**). Before applying the anodic bonding to the bottom-part containing an array of Au nanoparticles, the patterned wafer was cleaned in 99% HNO₃ solution for 10 min, in a 25% KOH solution at 75°C for 10 s, in a 99% HNO₃ solution again for 10 min, in DI water using a quick dump rinser, and finally spin-dried with nitrogen (N₂) gas. The anodic bonding was conducted in an anodic bonder EV-501 (EV Group, Austria) at 400°C, with a voltage of 340 V and no applied pressure for 20 min. After a dicing process (DAD3220, Disco Corporation, Japan) to obtain the microreactor, polymicro fused-silica capillaries (ID: 100 μm, OD: 360 μm, Inacom instruments BV, The Netherlands) were glued into the connections using the Araldite glue (Huntsman Corporation, United States), and passively dried at room temperature in environmental air for at least 1 day (**Figure 7.4h**).

Figure 7.4. Fabrication process of the designed microreactor. (a) Patterning PR structures on a Au/Cr coated glass wafer, and subsequently (b) dry etching of the Au/Cr layer for (c) wet etching of the glass substrate. (d) Patterning a foil mask for (e-f) powder blasting the connections. (g) Removing the foil and (h) anodic bonding the top part with the bottom part containing an array of Au nanoparticles supported on an oxidized Si substrate. The fused-silica capillary was glued into the connections of the microreactor. The fabrication process of the bottom-part was shown in **Chapter 4, Figures 4.1-4.2**.

Before applying the anodic bonding to the bottom part of the reactor containing an array of Au nanoparticles, the patterned wafer was cleaned in 99% HNO₃ solution for 10 min, in a 25% KOH solution at 75°C for 10 s, in a 99%

HNO₃ solution again for 10 min, in DI water using a quick dump rinser, and finally spin-dried with nitrogen (N₂) gas. The anodic bonding was conducted in an anodic bonder EV-501 (EV Group, Austria) at 400°C, with a voltage of 340 V and no applied pressure for 20 min. After a dicing process (DAD3220, Disco Corporation, Japan) to obtain the microreactor, polymicro fused-silica capillaries (ID: 100 µm, OD: 360 µm, Inacom instruments BV, The Netherlands) were glued into the connections using Araldite glue (Huntsman Corporation, United States), and passively dried at room temperature in environmental air for at least 1 day (**Figure 7.4h**).

7.2.4|Catalysis measurement

A simple reaction, i.e. the oxidation of carbon monoxide, was performed in the fabricated microreactors to investigate the catalytic properties of the patterned Au nanoparticle arrays. The product of the reaction is monitored continuously by using a mass spectrometer (OmniStar GSD 320, Pfeiffer Vacuum Benelux B.V., The Netherlands) connected directly to the outlet of the microreactor (**Figure 7.5**). The flow rates of the carbon monoxide (CO) and the oxygen (O₂) were fixed at 3 ml min⁻¹ and 1.5 ml min⁻¹, respectively. The flow rates of the gas mixture of CO and O₂ through the microreactor, and the argon (Ar) with which was mixed after exiting the reactor were fixed at 0.3 ml min⁻¹ and 10 ml min⁻¹, respectively. During the measurement, the microreactor was heated at 80°C using a hotplate. Moreover, the flow of the gas mixture of CO and O₂ through the microreactor was opened for 8 min and closed for 10 min in a repeated manner using the mass flow controller connected before the inlet of the microreactor (MV-FIC-303, see **Figure 7.5b**) in order to vary the residence time of the CO/O₂ mixture in the microreactor. The flow rate of the gas mixture – gases from the outlet of the microreactor and the Ar – into the MS was fixed at 1 ml min⁻¹ due to the limitation in the mass spectrometer design. The addition of Ar to the reactor mixture is to protect the MS from explosion risks of CO when operating the MS.

a

b

Figure 7.5. (a) Photograph and (b) schematic diagram of the setup for measuring the oxidation of carbon monoxide in the fabricated microreactors.

7.3| Results and discussion

7.3.1| Simulation results

Figure 7.6 show the simulated profiles of velocity and pressure of the fluid flow in one half the designed microchamber. As can be seen in the velocity profile (**Figure 7.6a**), the fluid flow is homogeneously distributed inside the microchamber from the 16 branch inlets of the distribution channel. It is worth noting that only in the area close to these inlets (less than 400 μm) the fluid

velocity is not homogeneous. **Figure 7.6(b)** shows a relatively small pressure drop in the microchamber (~ 106 Pa), which can be neglected compared to the pressure drop in each distribution channel (36 kPa). In summary, the simulation results indicated that the use of these two distribution channels provides virtually homogenous reaction conditions inside the designed microchamber.

Figure 7.6. (a) Velocity profile, and (b) pressure profile of the fluid flow in one half of the designed microchamber simulated using COMSOL Multiphysics.

7.3.2 | Fabrication of the designed microreactor

Figure 7.7a shows the photograph of a well-fabricated microreactor. It is worth noticing that applying a higher anodic bonding voltage of 400 V or pressure at the center of the microchamber during the bonding process resulted into a permanent bond area in the center of the microchamber. Moreover, complete dicing through the connections (powder-blasted channels) led to a penetration of water into the microchamber, which can potentially contaminate the Au nanoparticles. To prevent this, a combination of dicing and breaking of the chip on the side containing the connections was performed.

The top-view HR-SEM image at the area of the distribution channel shows a well-defined channel with a smooth surface of the microchamber area after the wet etching process (**Figure 7.7b**). **Figure 7.7c** shows a good connection between the powder-blasted channel and the distribution channel. It has to be noted that due to the parabolic profile of the power-blasted channel its depth needs to be larger than 450 μm to allow the fused-silica capillary (360 μm outer

diameter) to be fitted into it. To prevent the blocking of the fused-silica capillaries by the glue, they were first inserted into the connection channels (the power-blasted channels) before the glue was applied, so that glue could fill the gap between the fused-silica capillaries and the connection channels by capillary flow.

Figure 7.7. (a) Photograph of a fabricated microreactor. (b) Top-view HR-SEM image at the area of the distribution channel, and (c) a close-up image at the powder-blasted connection.

Figure 7.8. Signals measured using the mass spectrometer when performing the reaction in (a) a blank microreactor, and in (b) a microreactor integrated with an array of Au nanoparticles of approximately 20 nm diameter.

7.3.3 | Catalysis measurement

Figure 7.8 shows the signals measured using the mass spectrometer when performing the reaction in the fabricated microreactors. The signal obtained from the microreactor integrated with an array of Au nanoparticles of approximately 20 nm diameter (**Figure 7.8b**) was similar to that obtained from the blank microreactor (**Figure 7.8a**). The formation of carbon dioxide (CO_2) catalyzed by the Au nanoparticles was therefore not clearly observed from the measured signal. The obtained signal of the CO_2 in both the blank and the Au nanoparticle reactor was probably from the non-catalyzed combustion of the carbon monoxide, as it was equal in both cases. This indicates that the fabricated Au nanoparticles had insufficient catalytic activity at the operating

temperature of 80°C. The low catalytic activity of these fabricated Au nanoparticles could probably due to their large size (~20 nm diameter), which has been reported elsewhere.^{20–24} In the following section we estimate this limitation. Moreover, these Au nanoparticles could be contaminated during the fabrication process, thus resulting in blocking their active sites.²⁵

7.3.4| Estimation of the CO₂ formation catalyzed by the fabricated Au nanoparticle arrays

We roughly estimated the expected formation of CO₂ catalyzed by our fabricated Au nanoparticle arrays based on the catalytic activity of supported 20 nm Au nanoparticles obtained from literature.²⁶ The turnover frequency (TOF) for CO oxidation over supported Au nanoparticles of 20 nm in diameter was reported to be approximately 0.01 s⁻¹.²⁶ We assumed that only the Au atoms located at the interfacial circumference of the 20 nm Au nanoparticle (semi-spherical shape) supported on the SiO₂ substrate are active,²¹ which are ~230 active sites per particles. It has to be noted that we hereby probably overestimated the number of active sites per Au nanoparticle by assuming all Au atoms at the interfacial circumference are active. A decrease in the number of active sites can lead to a significant decrease in the catalytic activity of the Au nanoparticles. For an entire fabricated array of ~10¹⁰ Au nanoparticles, there are therefore ~23×10¹¹ active sites. The number of CO₂ molecules catalyzed by the fabricated Au nanoparticle array is then 23×10⁹ molecules/s. Therefore, the fraction of the catalyzed CO₂ molecules to the totally estimated molecules of other gases (CO, O₂, and Ar: ~4.2×10¹⁸ molecules/s) after mixing with Ar is 5.5×10⁻⁹, which is 0.055 ppm. This roughly estimated number is much lower than the detection limit of the used MS of approximately 1 ppm. This can explain our experimental observation of a lack of catalyzed CO₂ signal using the current set-up and operating conditions.

7.4| Conclusion

In summary, we report the fabrication of microreactors integrated with Au nanoparticle arrays. The fabricated microreactor consists of a top part made of glass containing a microchamber and two distribution channels anodically bonded to a bottom part containing an array of Au nanoparticles supported on an oxidized silicon substrate. By using two distribution channels, the fluid flow was uniformly distributed inside the microchamber, thus providing homogenous reaction conditions. The use of our fabricated microreactors provides opportunities to precisely control the reactant flows, especially at very low flow rates, and to maximum the volume ratio of products to reactants. The

conclusion from the preceding section was that the catalytic activity was insufficient by a factor of about 20.

7.5 | Recommendations

Although the formation of CO₂ catalyzed by the fabricated Au nanoparticles was not observed in the preliminary results, there is much room for improvement and investigation. Further cleaning the fabricated Au nanoparticle arrays, using arrays of smaller Au nanoparticles, e.g. sub 5 nm in diameter, or using Pt instead of Au^{22,26} is expected to improve the catalytic activity of the nanoparticles. A redesigned microreactor integrated with a local microheater can allow the use of a higher operating temperature, which will normally double the reaction rate for every 10°C rise in temperature.²⁷ In addition, operating the measurement at stopped-flow conditions with a higher temperature and pressure is expected to give better results. **Figure 7.9** shows a possible modification of the setup for the measurement at stopped-flow conditions, using a switching valve (SMV).

Figure 7.9. Schematic diagram of the possible modification of the setup for measuring the oxidation of carbon monoxide in the fabricated microreactors at stopped-flow conditions.

7.6 | References

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8

Summary and Recommendations

Summary and recommendations for each chapter in this thesis are given here.

8.1 | Summary

The research work presented in this thesis was aimed at developing enabling techniques for patterning regular noble metal/ceramic nanostructures over large-areas at low-cost. The direct aim of this work was to apply such nanostructures in microfluidic devices for catalysis study of ceramic-supported noble metal nanoparticle arrays. In the course of the investigation a third aim arose, namely understanding the mutual interaction of noble metals with ceramic substrates.

Although many technologies used for top-down nanopatterning of regular nanostructures have been investigated intensively, fabrication of highly ordered nanostructures with sub-100 nm dimensions over large-areas at low-cost using a conventional ultraviolet (UV, 365 nm wavelength) light source has been considered challenging. To make this possible, we combined UV-based displacement Talbot lithography (DTL), which enables large-area nanostructures patterning (dots or lines) but with a dimensional limit of 100 nm, with a plasma shrink-etching technique that allowed tunable dimensions down to sub-30 nm (**Chapter 2**). We can transfer directly the DTL-patterned photoresist (PR) nanostructures into a bottom antireflection coating (BARC) layer at a 1:1 ratio using N_2 plasma, or at smaller dimensions using O_2/N_2 plasma. It is highly remarkable that the verticality of the PR/BARC nanostructures remained preserved during the shrink-etching process. Combining the etching of an O_2/N_2 plasma with a N_2 plasma allowed us to reproducibly pattern PR/BARC nanostructures with tunable dimensions from 110 nm to sub-30 nm. With the easy and flexible operation, our fabrication method is suitable for large-area mass production of sub-100 nm periodic nanostructure at low-cost.

Combining the DTL-based shrink-etching technique reported in **Chapter 2** with dry etching, wet etching, and thin film deposition techniques, we reported a robust and high-yield fabrication method for wafer-scale patterning of high-quality arrays of dense gold (Au) nanogaps at low-cost (**Chapter 3**). Using the self-sharpening of $\langle 111 \rangle$ -oriented silicon crystal planes during the wet etching process, we fabricated silicon structures with extremely smooth nanogaps. Subsequent conformal deposition of a silicon nitride layer and a Au layer resulted in dense arrays of high-quality gold nanogaps. The gap spacing of the fabricated Au nanogaps could be easily tuned down to ~ 10 nm over full wafer areas by varying the thickness of deposited Au layers. Since the roughness of the template was minimized by the crystallographic etching of silicon, the roughness of the Au nanogaps depended almost exclusively on the roughness of the sputtered Au layers. Notably, our SiN-coated Si template can be reused by replacing the Au layer with another fresh one, without damaging the

template material or altering its dimensions. Most importantly, the fabricated Au nanogaps showed a significant enhancement of surface-enhanced Raman scattering (SERS) signals of benzenethiol (BT) molecules chemisorbed on the nanogap surface, at an average enhancement factor up to 3.0×10^8 .

In **Chapter 4**, we reported a robust technique to large-scale fabricate highly ordered size-tunable noble metal nanoparticles, i.e. gold and platinum, supported on oxidized silicon substrates without metallic adhesion layers, combining UV-based DTL (see **Chapter 2**) with inclined argon (Ar) ion beam etching techniques. Upon applying this technique, we successfully fabricated $3 \times 3 \text{ cm}^2$ arrays of Au or Pt nanoparticles supported on cone-shaped silica features at various diameters. By tuning the inclined etching time, the particle diameters could be varied from sub-30 nm to 110 nm. Moreover, annealing such sub-30 nm metal nanoparticle arrays at high temperature resulted in sub-20 nm metal nanoparticle arrays with high uniformity in the particle diameter, and good particle adhesion. These well-ordered noble metal nanoparticles were used as model catalysts for catalysis study in combination with microfluidic technology mentioned in **Chapter 7**.

In another effort to explore the mutual interaction of sputtered Au with the surface of oxidized silicon (SiO_2) substrates, we found that continuous Au films on SiO_2 substrates upon treatment with ultraviolet (UV)-ozone reveal an excellent enhancement of adhesion to the SiO_2 support (**Chapter 5**). Importantly, the enhancement is independent of the micro- or nanostructuring of such nanometer thick films. Continuous Au films with a thickness less than $\sim 13 \text{ nm}$ possess an extraordinarily strong adhesion after 5 min UV-ozone treatment. It is remarkable that this high adhesion effect vanishes when rising the samples with ethanol for 10 min. On the basis of this observation as well as other observations, we attributed the increased adhesion to the formation of an gold oxide layer. By depositing a second gold layer after UV-ozone treatment, thereby embedding the hypothesized gold oxide layer in between two sputtered Au layers, the adhesion increase becomes durable and independent of the influence of the surrounding environment, i.e. gases or solutions. The observed excellent enhancement of the adhesion can be tentatively explained as polarization-induced increased Au- SiO_2 interaction at their interface due to the formation of the gold oxide on the Au surface. This novel technique enabled us to large-scale fabricate various SiO_2 -supported Au micro/nano-sized structures, i.e. lines and dots, at dimensions spanning from a few hundreds of nanometers to a few micrometers, without the use of additional adhesion layers. Our enabling technique thus opens new routes for patterning Au micro/nanostructures on SiO_2 substrates, which are highly favored for biosensing and nanophotonic applications due to the absence of metallic adhesion layers.

In **Chapter 6**, we found that platinum (Pt) nanoparticles, upon annealing at high temperature of 1000°C, are engulfed into amorphous fused-silica or thermal oxide silicon substrates. Similar to the previously reported engulfment of Au nanoparticles, the engulfed Pt nanoparticles connect to the surface of the substrates through conical nanopores, and the size of the Pt nanoparticles decreases with increasing depth of the nanopores. We explain the phenomena as driven by the formation of volatile platinum oxide by reaction of the platinum with atmospheric oxygen, with the platinum oxide evaporating to the environment. We found that the use of Pt provides much better controllability than the use of Au. Due to the high vapor pressure of platinum oxide, the engulfment of the Pt nanoparticles into oxidized silicon (SiO₂) substrates is faster than of Au nanoparticles. At high temperature annealing we also found that the aggregation of Pt nanoparticles on the substrate surface is insignificant, in contrast to the aggregation of Au nanoparticles. As a result, the Pt nanoparticles are uniformly engulfed into the substrates, leading to an opportunity for patterning dense nanopore arrays. Moreover, the use of oxidized Si substrates enables us to precisely control the depth of the nanopores since the engulfment of Pt nanoparticles stops at a short distance above the SiO_x/Si interface. Using this method, we obtained, after subsequent etching steps, a membrane with dense nanopore through-holes with diameters down to sub-30 nm. With its simple operation and high controllability, this fabrication method provides an alternative for rapid patterning of dense arrays of solid-state nanopores at low-cost.

In **Chapter 7**, we applied microfluidic technology for catalysis study by fabricating microreactors integrated with noble metal nanoparticle arrays. The fabricated microreactor consists of a top-part made of glass containing a microchamber and two distribution channels anodically bonded to a bottom-part containing an array (3×3 cm²) of noble metal nanoparticles supported on an oxidized silicon substrate. The fabricated microreactors were used to perform the oxidation of carbon monoxide on chip. By using the two distribution channels, the flow was uniformly distributed inside the microchamber, thus providing homogenous reaction conditions. The use of our fabricated microreactors provides opportunities to precisely control the reactant flows, especially at very low flow rates, and to maximize the volume ratio of products to reactants.

In **Appendix F**, we reported a robust and simple technique for large-scale fabrication of free-standing and sub-μm thin PDMS through-hole membranes, combining soft-lithography with reactive plasma etching techniques. Using this fabrication technique, we successfully demonstrated the fabrication of free-standing PDMS membranes at various sub-μm thicknesses down to 600 ± 20 nm, and nanometer-sized through-hole (810 ± 20 nm diameter) densities, over

areas as large as 3 cm in diameter. By its simple procedure, our fabrication technique provides an enabling technique for large-scale and rapid patterning of sub- μm PDMS through-hole membranes, which is suitable for high-yield production at low-cost. Furthermore, we demonstrated the potential of our membranes as cell-culture substrates for biomedical applications by culturing endothelial cells on the membranes in a Transwell-like set-up.

8.2 | Recommendations

There are several aspects that need to be taken into consideration for further improving the experimental work and understanding the mechanism behind several of the observed phenomena in future research.

Although the DTL-based shrink-etching technique (**Chapter 2**) showed that highly ordered nanocolumns/lines with tunable dimensions from 110 nm to sub-30 nm can be fabricated uniformly over large-areas of $3\times 3\text{ cm}^2$ using a combination of the PFI88 photoresist and the AZ BARLi II 2000, applying this technique for another kind of photoresist is expected to require additional investigation and optimization. For DTL, the exposure dose and time need to be tuned in order to get well-defined PR nanostructures. For the plasma shrink-etching process, the shrinkage of the patterned nanostructures is mostly caused by oxygen plasma, whereas minor effects have been observed when adding N_2 plasma. Therefore, only the shrinkage in oxygen plasma needs to be optimized for the new PR nanostructures.

Optimizing the deposition process of Au layers over the SiN-coated Si templates is expected to further improve the quality of the Au nanogap arrays (**Chapter 3**). Decreasing the sputtering power can lead to a lower sputtering rate, resulting in a smaller roughness of the sputtered Au layers. This leads to an opportunity to pattern Au nanogaps down to sub-10 nm with a high uniformity in gap spacing. In addition, the effects of the quality of deposited Au, i.e. sputtered Au versus evaporated Au, on the quality of the fabricated Au nanogaps, and thus the SERS signals, also need to be investigated. Moreover, although the post-deposition UV-ozone treatment improves the adhesion of the deposited Au layers to the template surface, the influence of the gold oxide layer formed on the Au surface on the SERS signals needs to be evaluated.

For full-wafer patterning of supported noble metal nanoparticle arrays (**Chapter 4**), it is necessary to investigate the uniformity of the nanoparticle size etched in the Ar ion etching system over the full-wafer areas. Moreover, our reported technique is expected to be extendable for patterning size-tunable nanoparticle arrays of different metal-support combinations since it relies only on dry etching techniques. In addition, the effects of UV-ozone or O_2 plasma

treatment on the catalytic properties of these noble metal nanoparticle arrays also need to be investigated.

Although the post-deposition UV-ozone treatment showed an excellent enhancement in the adhesion of Au to SiO₂, the mechanism of this observed phenomena has not yet been fully understood (**Chapter 5**). Further investigation of the thickness of the gold oxide layer formed on the surface of gold layers of different thicknesses is essential. The effects of other polar molecules absorbed on the gold surface on the adhesion strength could form good reference material comparison. Moreover, the thickness ratio of the formed gold oxide layer to the deposited gold layer needs to be taken into account in order to further understand the Au-layer thickness dependence of the adhesion strength. In addition, simulation of the interaction and charge transfer at the Au-SiO₂ interface is expected to give a better understanding of the phenomenon.

By annealing the Pt nanoparticles in inert gases, i.e. nitrogen (N₂) or Ar, the influence of oxygen and water concentration on the engulfment process can be investigated (**Chapter 6**). Further optimization and timing of the etching processes, especially of the final SiO₂ dry etching step, is expected to produce through-hole nanopores of even smaller end-diameters, because the closed-end nanopores possessed end-diameters in the sub-10 nm range. Moreover, subsequent conformal deposition of a silicon nitride layer or an aluminum oxide layer can probably further reduce the nanopore diameter. Also, studying the behavior of Pt nanoparticles on other ceramic supports, i.e. silicon nitride, alumina, and titania, at high temperature annealing is needed to further understand the observed phenomenon.

Further cleaning the fabricated Au nanoparticle arrays, using arrays of smaller Au nanoparticles, e.g. sub 5 nm in diameter, or using Pt instead of Au is expected to improve the catalytic activity of the nanoparticles (**Chapter 7**). A redesigned microreactor integrated with a local microheater can allow the use of a higher operating temperature, which will normally double the reaction rate for every 10°C rise in temperature. Operating the measurement at stopped-flow conditions with a higher temperature and pressure is expected to give better results. The effect of particle size and different metal-support combinations are important and need to be investigated. In addition, investigation of the reaction using the engulfed noble metal nanoparticle arrays is also expected to give additional information about mass transport of reactants/products inside the nanopores, and its influences on the reaction.

Despite the fact that biological cells can grow well on the fabricated PDMS membranes in the Transwell-like set-up (**Appendix F**), measurement of the mechanical properties, e.g. elasticity and rigidity, of the PDMS membranes is necessary to study their influence on the behavior of the cells. Moreover, using

another type of photoresist, e.g. Olin Oir 907-35 (Arch Chemicals Inc., United States), can result in a thicker photoresist layer (3.5 μm). This will lead to an opportunity to pattern higher photoresist columns, and thus thicker PDMS through-hole membranes. As a result, PDMS membranes with larger through-holes over large areas could be fabricated, possessing altered mechanical properties.

Appendix A

Shrinkage Control of Photoresist Nanocolumns

A.1| Chamber cleaning and etching implementation

We used a parallel plate reactive ion etching system (in-house built TEske system, NanoLab Cleanroom, The Netherlands) to conduct all our plasma etching processes, as shown in **Figure A1**. Before each etching process, the etching chamber was cleaned completely using cleanroom tissues with acetone several times, and dried with a nitrogen gun. Insufficient cleaning could cause redeposition of the residual materials on the Si-surface during the etching process, leaving nanograss surfaces (**Figure A2**). The etching process was always done at wafer-level to prevent the effects of etching load on the etching results. For structural investigation, the Si wafer was broken in pieces, and one piece was selected for the HR-SEM observation of the cross-section view. Pieces were collected back into the wafer shape for the etching process (**Figure A1**). This procedure was repeated after each etching time-step.

Figure A1. TEske system used for the plasma etching process and etching implementation.

Figure A2. Formation of a nanograss surface after 8 min N_2 plasma etching due to insufficient cleaning. Scale bar represents 200 nm. The etching was conducted at wafer-level, 13 mTorr, and 25 W with 50 sccm N_2 .

A.2 | Uniformity measurement of PR nanocolumn arrays

The uniformity of PR nanocolumn arrays fabricated by displacement Talbot lithography (DTL) was investigated. A Si wafer with a pattern of $3 \times 3 \text{ cm}^2$ was measured by using a high-resolution scanning electron microscope (HR-SEM). Five different areas within the pattern were chosen for observing the top-view and cross-section view (**Figure A3**). The top-view HR-SEM images were then used to analyze the diameter distribution of the PR nanocolumns within these selected areas using ImageJ software. The cross-sectional HR-SEM images show well-fabricated PR nanocolumns with vertical alignment over these areas. The top-view HR-SEM images show a good control over the diameter and periodicity of the fabricated PR nanocolumns (**Figure A4a**). The distribution in PR nanocolumn diameters shows only slightly difference among the measured areas (**Figure A4b**).

Figure A3. A $3 \times 3 \text{ cm}^2$ array of PR nanocolumns patterned on a Si wafer using DTL. The white squares indicate the areas selected for measuring the uniformity of the fabricated PR nanocolumns.

Figure A4. (a) Top-view (scale bar 2 μm) and cross-sectional (scale bar 1 μm) HR-SEM images of the selected areas, and (b) the corresponding diameter distribution of the PR nanocolumns.

A.3 | Plasma etching of PR and BARC layers

Figure A5 shows the thicknesses of PR layers etched at wafer-level, 13 mTorr, and 25 W in different gas plasmas, which are 50 sccm N₂, 50 sccm O₂, and 50/50 sccm O₂/N₂. Photoresist PFI88 layers were spin-coated on Si wafers at 4000 rpm for 45 s, followed by baking at 90°C for 1 min. The etching time-steps were 2 min for the N₂ plasma, and 30 s for the O₂ plasma and O₂/N₂ plasma.

Figure A5. Cross-sectional HR-SEM images of the PR thickness at different etching times in different gas plasmas: (a) 50 sccm N₂, (b) 50 sccm O₂, and (c) 50/50 sccm O₂/N₂. Scale bars represent 200 nm.

Based on the measured thickness of the PR layers as function of the etching time in different plasma etchings, the corresponding fit curves were calculated as follows:

$$\text{In 50 sccm N}_2 \text{ plasma: } T_{PR(N_2)} = -0.29 \cdot t + 201.3 \quad (\text{A1})$$

$$\text{In 50 sccm O}_2 \text{ plasma: } T_{PR(O_2)} = -1.44 \cdot t + 202.5 \quad (A2)$$

$$\text{In 50/50 sccm O}_2/\text{N}_2 \text{ plasma: } T_{PR(O_2/N_2)} = -1.52 \cdot t + 203.0 \quad (A3)$$

where T_{PR} (nm) is the thickness of the PR layers, and t (s) is the etching time.

Figure A6. Cross-sectional HR-SEM images of the BARC thickness at different etching times in different gas plasmas: (a) 50 sccm N₂, (b) 50 sccm O₂, and (c) 50/50 sccm O₂/N₂. Scale bars represent 200 nm.

The etching of the BARC layers (AZ BARLi II 200) was also investigated using the same etching settings, as shown in **Figure A6**. BARC layers were spin-coated on Si wafers at 3000 rpm for 45 s, followed by baking at 185°C for 1 min. Similarly, the fit curves of the BARC thicknesses etched in different plasmas were obtained:

$$\text{In 50 sccm N}_2 \text{ plasma: } T_{BARC(N_2)} = -0.39 \cdot t + 185.0 \quad (A4)$$

$$\text{In 50 sccm O}_2 \text{ plasma: } T_{BARC(O_2)} = -1.59 \cdot t + 184.4 \quad (A5)$$

$$\text{In 50/50 sccm O}_2/\text{N}_2 \text{ plasma: } T_{BARC(O_2/N_2)} = -1.55 \cdot t + 186.4 \quad (A6)$$

where T_{BARC} (nm) is the thickness of the BARC layers, and t (s) is the etching time.

A.4 | Nanopatterning BARC nanocolumn arrays

Figure A7. Cross-sectional HR-SEM images of periodic PR nanocolumns at different etching times in different gas plasmas: (a) 50 sccm N₂, (b) 50 sccm O₂, and (c) 50/50 sccm O₂/N₂. Scale bars represent 200 nm. The etching was conducted at wafer-level, 13 mTorr, and 25 W with the etching time-steps of 2 min for the N₂ plasma, and 30 s for the O₂ plasma and O₂/N₂ plasma.

A.4.1 | Geometric calculation of PR nanocolumns etched in N₂ plasma

The initial thickness of the BARC layer and the PR nanocolumn height were measured by using HR-SEM (**Figure A7a**), which are 186.0 nm and 198.0 nm, respectively. Based on the etching rate of the BARC in 50 sccm N₂ plasma (see **Equation A4**), the BARC thickness $T_{\text{BARC}(\text{N}_2)}$ versus the etching time t is calculated as follows:

$$T_{\text{BARC}(\text{N}_2)} = -0.39 \cdot t + 186.0 \quad (\text{A7})$$

From **Equation A7** follows that the BARC layer is completely etched when $t = 477$ s. Because the etching rate of the PR in 50 sccm N₂ plasma is lower than that of the BARC (see **Equations A1** and **A4**), the nanocolumn height is increased for an increasing etching time. When $0 \leq t \leq 477$ s, the nanocolumn height is calculated by:

$$h_{(\text{N}_2)} = +0.10 \cdot t + 198.0 \quad (\text{A8})$$

From **Equation A8** follows that the nanocolumn height is 245.7 nm for an etching time of 477 s, which is larger than the initial BARC thickness of 186.0 nm. Thus, PR still remains on the top of the nanocolumns. Continued etching of these nanocolumns results in decreasing the nanocolumn height with a rate of -0.29 nm s^{-1} , which is the PR etching rate in 50 sccm N₂ plasma (see **Equation A1**). Therefore, when $t > 477$ s the nanocolumn height versus the etching time is:

$$h_{(\text{N}_2)} = -0.29 \cdot t + 384.0 \quad (\text{A9})$$

A.4.2 | Geometric calculation of PR nanocolumns etched in O₂ plasma

The initial BARC thickness and the PR nanocolumn height measured by HR-SEM (**Figure A7b**) are 185.2 nm and 198.8 nm, respectively. Based on the BARC etching rate in 50 sccm O₂ plasma (see **Equation A5**), the thickness of the BARC layer versus the etching time is:

$$T_{\text{BARC}(\text{O}_2)} = -1.59 \cdot t + 185.2 \quad (\text{A10})$$

From **Equation A10** follows that $T_{\text{BARC}(\text{O}_2)} = 0$ when $t = 116$ s. For $0 \leq t \leq 116$ s, the nanocolumn height increases with a rate of $+0.15 \text{ nm s}^{-1}$, which is calculated from the etching rates of the PR and BARC in 50 sccm O₂ plasma (see **Equations A2** and **A5**). The nanocolumn height versus the etching time is then:

$$h_{(\text{O}_2)} = +0.15 \cdot t + 198.8 \quad (\text{A11})$$

From **Equation A11** follows that $h_{(\text{O}_2)} = 216.2$ nm when $t = 116$ s. For $t > 116$ s, the nanocolumn height decreases with a rate of -1.44 nm s^{-1} , which is the PR

etching rate in 50 sccm O₂ plasma (see **Equation A2**). For $t > 116$ s, the nanocolumn height is given by:

$$h_{(O_2)} = -1.44 \cdot t + 383.2 \quad (A12)$$

From **Equation A12** follows that when $t = 138$ s the nanocolumn height is decreased to the initial BARC thickness of 185.2 nm. Therefore, for $t > 138$ s the nanocolumn height is then decreasing with a rate of -1.59 nm s^{-1} , which is the etching rate of the BARC in 50 sccm O₂ plasma (see **Equation A5**).

$$h_{(O_2)} = -1.59 \cdot t + 403.9 \quad (A13)$$

A.4.3 | Geometric calculation of PR nanocolumns etched in O₂/N₂ plasma

The initial thickness of the BARC layer and the PR nanocolumn height measured by HR-SEM (**Figure A7c**) are 185.8 nm and 198.6 nm, respectively. From **Equation A6**, the etching rate of the BARC in 50/50 sccm O₂/N₂ plasma is -1.55 nm s^{-1} . Therefore, the thickness of the BARC layer versus the etching time can be calculated by:

$$T_{\text{BARC}(N_2/O_2)} = -1.55 \cdot t + 185.8 \quad (A14)$$

From **Equation A14** follows that $T_{\text{BARC}(O_2/N_2)} = 0$ when $t = 120$ s. For $0 \leq t \leq 120$ s, the nanocolumn height versus the etching time is computed by using the etching rates of the PR and BARC in 50/50 sccm O₂/N₂ plasma (see **Equations A3** and **A6**):

$$h_{(N_2/O_2)} = +0.03 \cdot t + 198.6 \quad (A15)$$

From **Equation A15** follows that $h_{(O_2/N_2)} = 202.2 \text{ nm}$ when $t = 120$ s. Then, for $t > 120$ s, the nanocolumn height is decreasing with a rate of -1.52 nm s^{-1} , which is the etching rate of the PR in 50/50 sccm O₂/N₂ plasma (see **Equation A3**).

$$h_{(N_2/O_2)} = -1.52 \cdot t + 384.6 \quad (A16)$$

From **Equation A16** follows that when $t = 130$ s the nanocolumn height is decreased to the initial BARC thickness of 185.8 nm. Therefore, for $t > 130$ s the nanocolumn height is decreasing with a rate of -1.55 nm s^{-1} , which is the etching rate of the BARC in 50/50 sccm O₂/N₂ plasma (see **Equation A6**). The nanocolumn height is then calculated by:

$$h_{(N_2/O_2)} = -1.55 \cdot t + 388.9 \quad (A17)$$

A.4.4 | Geometric calculation of PR nanocolumns etched in O₂/N₂ and N₂ plasmas

Figure A8. Cross-sectional HR-SEM images of the PR nanocolumns at different etching times, (a) etched in 50/50 sccm O₂/N₂ plasma for 60 s, and (b) subsequently etched in 50 sccm N₂ plasma for 4 min. Scale bars represent 200 nm. The etching was conducted at wafer-level, 13 mTorr, and 25 W.

The initial BARC thickness and the PR nanocolumn height measured by HR-SEM (**Figure A8**) are 187.0 nm and 200.0 nm, respectively. When etching in 50/50 sccm O₂/N₂ plasma, the etching rate of the BARC is -1.55 nm s^{-1} (see **Equation A6**). Therefore, for $0 \leq t \leq 60 \text{ s}$ the BARC thickness as function of the etching time is calculated as follows:

$$T_{\text{BARC}(\text{N}_2/\text{O}_2)} = -1.55 \cdot t + 187.0 \quad (\text{A18})$$

The height of the nanocolumns is increased with a rate of $+0.03 \text{ nm s}^{-1}$, which is calculated by using the etching rates of the PR and BARC in 50/50 sccm O₂/N₂ plasma (see **Equations A3** and **A6**). Thus, for $0 \leq t \leq 60 \text{ s}$, the nanocolumn height is:

$$h_{(\text{N}_2/\text{O}_2)} = +0.03 \cdot t + 200.0 \quad (\text{A19})$$

When $t = 60 \text{ s}$, the remaining BARC thickness and the nanocolumn height are 94.0 nm and 201.8 nm, respectively. Subsequently etching these nanocolumns in 50 sccm N₂ plasma for 4 min, i.e. $60 \text{ s} < t \leq 300 \text{ s}$, the BARC thickness versus the etching time is calculated by using the etching rate of the BARC in 50 sccm N₂ plasma (see **Equation A4**).

$$T_{\text{BARC}(\text{N}_2)} = -0.39 \cdot t + 117.4 \quad (\text{A20})$$

During this time, the nanocolumn height increases with a rate of $+0.10 \text{ nm s}^{-1}$, which is calculated by using the etching rates of the PR and BARC in 50 sccm N_2 plasma (see **Equations A1 and A4**). Therefore, for $60 \text{ s} < t \leq 300 \text{ s}$, the nanocolumn height is given by:

$$h_{(\text{N}_2)} = +0.10 \cdot t + 196.4 \quad (\text{A21})$$

A.5| Uniformity measurement of BARC nanocolumns

Figure A9. Top-view (scale bar $2 \mu\text{m}$) and cross-sectional (scale bar $1 \mu\text{m}$) HR-SEM images at the selected areas of a BARC nanocolumn array fabricated by using a mixture plasma of 50/50 sccm O_2/N_2 for 150 s, at wafer-level, 13 mTorr, and 25 W.

Figure A10. Close-up cross-sectional HR-SEM images of BARC nanocolumns at the selected areas. Scale bars represent 200 nm.

Table A1. Uniformity measurement in diameter and height of BARC nanocolumns at the selected areas in **Figure A10**. The variation was calculated from the standard deviation of the measured values.

Area	1	2	3	4
Column diameter (nm)	29.7 ± 0.4	29.3 ± 0.5	29.7 ± 0.5	30.7 ± 0.7
Column height (nm)	146.8 ± 1.7	147.6 ± 3.1	143.8 ± 4.1	150.2 ± 4.1

A.6 | Shrink-etching with different O₂/N₂ gas flow ratios

Figure A11. Cross-sectional HR-SEM images of periodic PR nanocolumns shrink-etched in the mixture plasma with different O₂/N₂ gas flow ratios at different etching times. Scale bars represent 200 nm. The etching was conducted at wafer-level, 13 mTorr, and 25 W with the etching time-step of 30 s.

A.7 | Nanopatterning BARC nanolines at a particular width

We used our fabrication method to shrink nanolines of 90 nm to 45 nm in width (**Figure A12**). The initial nanolines of approximately 90 nm were patterned using displacement Talbot lithography with an exposure time of 100 s (exposure dose of 1 mW cm^{-2}). These nanolines were etched in 50/50 sccm O_2/N_2 plasma, and then in 50 sccm N_2 plasma at wafer-level, 13 mTorr, and 25 W.

Figure A12. Patterning of periodic BARC nanolines to a target width of 45 nm by combining O_2/N_2 plasma etching with N_2 plasma etching. Initial PR nanolines of 90 nm in width were etched in 50/50 sccm O_2/N_2 plasma, and then in 50 sccm N_2 plasma at wafer-level, 13 mTorr, and 25 W. Cross-sectional HR-SEM images show the nanolines at different etching times. Scale bars represent 200 nm.

Appendix B

Wafer-scale Fabrication of High Quality Tunable Gold Nanogaps

B.1| Uniformity measurement of fabricated PR and BARC nanoline arrays

Figure B1. A wafer-scale array of PR nanolines patterned on an oxidized Si wafer. Four areas indicated by white squares were selected for the uniformity measurement of the fabricated PR nanolines.

Figure B2. Top-view HR-SEM images of the fabricated PR nanolines at the four selected areas (see **Figure B1**). Scale bars represent 1 μm .

Figure B3. Top-view HR-SEM images of the fabricated BARC nanolines at the four selected areas (see **Figure B1**). Scale bars represent 1 μm .

B.2| Uniformity measurement of fabricated Cr nanoline arrays

Figure B4. Top-view HR-SEM images of the fabricated Cr nanolines at the four selected areas (see **Figure B1**). Scale bars represent 1 μm .

B.3 | Wet etching of bulk Si substrates

Figure B5. Cross-sectional HR-SEM image of undesired v-grooves in bulk Si substrate caused by over etching in the KOH solution. Scale bar represents 100 nm.

B.4 | Uniformity measurement of fabricated SiN nanogap arrays

Figure B6. Top-view HR-SEM images of the fabricated SiN nanogaps at the four selected areas (see **Figure B1**). Scale bars represent 1 μm .

B.5 | Uniformity measurement of fabricated Au nanogap arrays

Figure B7. Top-view HR-SEM images of the fabricated Au nanogaps at the four selected areas (see **Figure B1**). Scale bars represent 1 μm .

B.6 | Surface roughness measurement of sputtered Au layers

Figure B8. AFM images (scan field $500 \times 500 \text{ nm}^2$) of Au layers deposited on the surface of oxidized Si wafers at different thicknesses.

Figure B9. Top-view HR-SEM image (scale bar 2 μm) of a dense array of sub-20 nm Au nanogaps with a close-up image (scale bar: 200 nm), fabricated by sputtering a Au layer of approximately 90 nm thick over the SiN coated Si template.

Figure B10. Top-view and cross-sectional HR-SEM images of the fabricated Au nanogaps with different gap spacings of (a) ~ 30 nm, (b) ~ 20 nm, and (c) ~ 10 nm. Scale bars represent 500 nm.

B.7 | Finite-difference time-domain simulations

We estimated the normalized SERS intensity from the local electromagnetic enhancement generated in our Au nanogaps by analyzing the near-field distributions at 785 nm (excitation) and 852 nm (BT Raman shift at $\sim 999 \text{ cm}^{-1}$) wavelengths (see **Figure B11**). The normalized SERS intensity – SERS intensity enhancement – was calculated as follows (Ru *et al.* 2009):

$$\text{Normalized SERS intensity} = \frac{|E|_{785\text{nm}}^2 \cdot |E|_{852\text{nm}}^2}{|E_0|_{785\text{nm}}^2 \cdot |E_0|_{852\text{nm}}^2} \quad (\text{B1})$$

where $|E|$ is the locally enhanced electric field and $|E_0|$ is the incident electric field calculated for 785 nm, and 852 nm wavelengths.

Due to the exponential decay of the enhanced near field, only the molecules adsorbed on the surface of the SERS structures can show the increased Raman scattering intensity. Therefore, we calculated the expected normalized SERS intensity from only a monolayer of BT covered completely the surface of our Au nanogaps (white lines in **Figure B11**). The thickness of a BT monolayer coated on a Au surface was estimated using Materials Studio software (Accelrys Inc., United States), which is approximately 0.8 nm. The SERS-enhanced intensities integrated over the thickness of the considered BT monolayer were 4.1×10^6 , 8.2×10^6 , and 2.3×10^7 for Au nanogaps of ~ 30 nm, ~ 20 nm, and ~ 10 nm, respectively (**Figure B12**). This indicated that although there was a significant increase in the enhanced electric field in the simulated gap region, only a relatively small increase in the calculated SERS intensities due to the presence of a BT monolayer.

Despite of the fact that the simulations proved to be useful for understanding the origin of the behavior differences of our Au nanogaps of different gap spacings – the simulations follow the expected trend from the experimental measurements – no absolute comparison between the calculated SERS intensity and the measured SERS intensity is intended. Because our calculated SERS intensity includes only the contribution from the local field enhancement, without considering the chemical enhancement. Moreover, the simulations were performed using a two-dimensional model, which was simplified from the three-dimensional structure of the fabricated Au nanogaps.

Figure B11. FDTD-simulated distribution of the local field intensity enhancement factor ($|E|^2/|E_0|^2$) for Au nanogaps of (a) ~30 nm, (b) ~20 nm, and (c) ~10 nm at excitation (785 nm) and Raman (852 nm or 999cm^{-1}) wavelengths. The yellow dashed lines indicate the SiN boundary, whereas the white lines indicate the BT monolayer.

Figure B12. FDTD-simulated distribution of the SERS intensity ($|E|^4$) for Au nanogaps of (a) ~30 nm, (b) ~20 nm, and (c) ~10 nm. The yellow dashed lines indicate the SiN boundary, whereas the white lines indicate the BT monolayer.

B.8 | Surface-enhanced Raman scattering measurements

Figure B13. SERS signals measured on Au nanogaps of ~ 30 nm, ~ 20 nm, and ~ 10 nm gap spacing. All the Au nanogaps were immediately immersed into the BT solution, parallel to the solution surface.

Figure B14. Calculated enhancement factors of the obtained spectra over a $5 \times 5 \mu\text{m}^2$ area for Au nanogaps of (a) ~ 30 nm and (b) ~ 20 nm.

Figure B15. (a) Simulation of the allowed angle range of our fabricated Au nanogaps. (b) Estimation of the reachable surface of the Au nanogaps (red lines). It is worth noting that in case of ~ 10 nm gaps the scattering signal from the cavity under the gap cannot reach to the detector. Therefore, the surface of this cavity did not consider in the totally estimated surface. Scale bars represent 100 nm.

Figure B16. SERS signal of ~ 10 nm Au nanogap array with an excitation laser of 525 nm. High fluorescence background is visible, but no signal of BT is observed (2500 scan average).

Appendix C

Large-scale Fabrication of Highly Ordered Sub-20 nm Noble Metal Nanoparticles

C.1| Uniformity measurement of fabricated BARC nanocolumn arrays

A BARC nanocolumn array of $3 \times 3 \text{ cm}^2$ fabricated on a gold coated oxidized Si wafer was investigated. Periodic BARC nanocolumns were transferred directly at a 1:1 ratio from pre-patterned PR nanocolumns by using N_2 plasma etching in a parallel plate reactive ion etching system (in-house built TETSKE system, NanoLab Cleanroom, The Netherlands) at wafer-level, 10 mTorr, and 25 W for 8 min. The uniformity of these fabricated BARC nanocolumns was analyzed by measuring their geometric dimensions at five different selected areas (Figure C1).

Figure C2(a) shows top-view and cross-sectional HR-SEM images of the BARC nanocolumns taken at these selected areas. The cross-sectional HR-SEM images show well-defined BARC nanocolumns with highly vertical sidewall over these selected areas. The formation of nano-sharp tips was also observed, which is attributed to the physical bombardment of high energy particles during N_2 plasma etching. The top-view HR-SEM images show a high uniformity in the diameter and periodicity of the fabricated BARC nanocolumns. The diameter distributions of the BARC nanocolumns analyzed by ImageJ software within these top-view images show only a slightly difference in the diameter variation.

Figure C1. A BARC nanocolumn array ($3 \times 3 \text{ cm}^2$) patterned on a gold-coated oxidized Si wafer. Five areas indicated by white squares were selected for the uniformity measurement of the fabricated BARC nanocolumns.

Figure C2. (a) Top-view (scale bar: 1 μm) and cross-sectional (scale bar: 500 nm) HR-SEM images of the fabricated BARC nanocolumns at the five selected areas, and (b) the corresponding column diameter distributions.

To quantitatively analyze the uniformity in diameter and height of the fabricated BARC nanocolumns, close-up cross-sectional HR-SEM images at these selected areas were taken (**Figure C3**). At each selected area, the average column diameter and height were calculated from at least five measured values; and the variation was calculated as the standard deviation of these measured values (**Table C1**).

Figure C3. Close-up cross-sectional HR-SEM images of the fabricated BARC nanocolumns at the five selected areas. Scale bars represent 200 nm.

Table C1. Uniformity measurement in diameter and height of the fabricated BARC nanocolumns in **Figure C3**. The variation was calculated as the standard deviation.

Area	0	1	2	3	4
Column diameter (nm)	110.2 ± 1.7	110.6 ± 1.4	110.8 ± 1.3	110.7 ± 0.7	110.6 ± 1.3
Column height (nm)	251.4 ± 1.5	249.8 ± 1.9	250.6 ± 1.6	251.6 ± 0.8	250.8 ± 1.1

C.2 | Surface roughness measurement of sputtered Au and Pt layers

All sputtering processes were conducted by using an ion-beam sputtering system (in-house built T'COathy system, NanoLab Cleanroom, The Netherlands) at a pressure of 6.6×10^{-3} mbar, and 200 W. The thickness of the deposited metal layers was varied by adjusting the sputtering time. **Figures C4** and **C5** show atomic force microscopy (AFM) and HR-SEM images of the deposited Au and Pt layers at different sputtering times, respectively. For both Au and Pt layers, the surface roughness (R_a) measured in AFM images increased with the increasing layer thickness. We attribute this to an increase in the Au or Pt crystallographic grain size as the layer thickness increases. In addition, the small crystallographic grain size in the Pt layers led to a much lower surface roughness compared to the Au layers.

Figure C4. AFM (scan field 500×500 nm²) and top-view HR-SEM (scale bar: 200 nm) images of Au layers deposited at different times on oxidized Si substrates.

Figure C5. AFM (scan field 500×500 nm²) and top-view HR-SEM (scale bar: 200 nm) images of Pt layers deposited at different times on oxidized Si substrates.

C.3| Etching of PR and BARC layers at various beam incident angles

PR layers (299.3 ± 1.8 nm) and BARC layers (245.8 ± 1.5 nm) were spin-coated on oxidized Si wafers at 2000 rpm for 45 s, followed by baking at 90°C and 185°C, respectively. The etching rate at each etching angle was determined by comparing the initial layer with the layer after etching for 3 min. The thicknesses of the PR and BARC layers were determined from the images taken using a HR-SEM (FEI Sirion microscope, United States) at a 5 kV acceleration voltage and a spot size of 3 (**Figure C6**).

Figure C6. Cross-sectional HR-SEM images of PR and BARC layers etched in an IBE system (Oxford i300) at various beam incident angles for 3 min. The etching was conducted at 5 sccm Ar, 300 eV, and 50-55 mA. Scale bars represent 200 nm.

C.4| Patterning Au or Pt nanoparticle arrays using inclined Ar ion beam etching

Au and Pt nanoparticle arrays were fabricated by etching the periodic BARC nanocolumns patterned on Au or Pt -coated SiO_2 substrates in the IBE system at a beam incident angle of 20° (**Figure C7**). It is remarkable that the BARC nano-sharp tips remained during the etching process with a high uniformity in the shape and the height. The size of the Au and Pt nanoparticles can be varied by changing the etching time, as shown in **Figure C8**. A high uniformity in the particle diameter was obtained for both Au and Pt nanoparticles after etching at particular etching times (**Table C2**).

Figure C7. Cross-sectional HR-SEM images of BARC nanocolumns inclined etched in the IBE system at different etching times. The etching was conducted at 5 sccm Ar, 300 eV, 50-55 mA, and at a beam incident angle of 20°. Over-etching the metal-coated SiO_2 substrate resulted in (a) Au and (b) Pt nanoparticles supported on cone-shaped silica features, indicated by the yellow and white areas, respectively. The BARC nano-sharp

tips remained during the etching process. The red arrows indicate the removal of the BARC nano-sharp tips caused by the breaking of samples for SEM observation. Scale bars represent 200 nm.

Figure C8. Top-view HR-SEM images of (a) Au and (b) Pt nanoparticles (bright spots) supported on cone-shaped silica features at different etching times, recorded with back-scattered electrons. The Au and Pt nanoparticle arrays were fabricated by etching the periodic BARC nanocolumns supported on Au or Pt-coated SiO₂ substrates in the IBE system at a beam incident angle of 20°. The black spots in (a) indicate that the BARC nano-sharp tips remained during the etching process. These BARC tips were removed by using oxygen plasma cleaning for 20 min at 500 W (b). Scale bars represent 200 nm.

Table C2. Uniformity measurement in the diameter the fabricated Au and Pt nanoparticles in **Figure C8**. The variation was calculated from the standard deviation of at least five measured values.

Etching time (min)	6	8	10	12
Au nanoparticle diameter (nm)	110.8 ± 5.3	80.2 ± 1.5	58.4 ± 1.2	34.3 ± 1.1
Pt nanoparticle diameter (nm)	115.5 ± 7.5	82.0 ± 1.9	61.6 ± 1.3	38.0 ± 1.0

Figure C9 shows the diameter measurement of Au and Pt nanoparticles after inclined etching in the IBE system for 12:30 min (12 min and 30 s) and 13 min, respectively. Sub-30 nm Au and Pt nanoparticles were obtained with a high uniformity in the particle diameter, 28.1 ± 1.5 nm and 25.9 ± 1.2 nm, over the patterned 3×3 cm² areas, respectively.

Figure C9. Close-up top-view HR-SEM images of sub-30 nm Au and Pt nanoparticles (bright spots) supported on cone-shaped silica features at the etching time of 12:30 min (12 min and 30 s) and 13 min, respectively. The BARC tips were removed by using oxygen plasma cleaning for 20 min at 500 W (TePla 300, PAV TePla AG, Germany). Scale bars represent 100 nm.

Figure C10 shows the top-view HR-SEM images at the selected areas (**Figure C1**) of a fabricated array of sub-30 nm Au nanoparticles supported on the cone-shaped silica features, which has a high uniformity in the particle diameter.

Increasing the etching time with 30 s, sub-20 nm Au and Pt nanoparticles were fabricated, though at a considerable decrease of the uniformity in the particle size distribution, 15.1 ± 2.5 nm and 13.6 ± 3.1 nm, respectively (**Figure C11**). In addition, several BARC nano-sharp tips were removed at these etching times, leading to direct exposure of the Au and Pt nanoparticles to high energy Ar ions. As a result, the Au and Pt nanoparticles were etched away from those cone-shaped silica features.

Figure C10. Top-view HR-SEM images at the selected areas of a fabricated array of sub-30 nm Au nanoparticles supported on the cone-shaped silica features. Scale bars represent 200 nm.

Figure C11. Top-view HR-SEM images (scale bar: 200 nm) with close-up images (scale bar: 100 nm) of sub-20 nm (a) Au and (b) Pt nanoparticles (bright spots) supported on cone-shaped silica features at the etching time of 13 min, and 13 min and 30 s, respectively.

Subsequent annealing of sub-30 nm Au and Pt nanoparticle arrays at 300°C and 600°C for 1 h resulted in sub-20 nm Au and Pt nanoparticle arrays with a high uniformity in the particle diameter, 13.0 ± 1.6 nm and 13.2 ± 1.1 nm, over the patterned 3×3 cm² areas, respectively (Figure C12).

Figure C12. Top-view HR-SEM images with close-up images of sub-20 nm (a) Au and (b) Pt nanoparticles (bright spots) supported on cone-shaped silica features after heating at 300°C (Au) and 600°C (Pt) for 1 h, respectively. Scale bars represent 100 nm.

C.5 | Adhesion investigation of the fabricated Au nanoparticle arrays

An adhesion test for two fabricated arrays of Au nanoparticles supported on the silica features was conducted. An array of sub-30 nm Au nanoparticles supported on cone-shaped silica features, and an array of sub-20 nm Au nanoparticles fabricated by annealing the sub-30 nm Au nanoparticle array at 300°C for 1 h were chosen for the text. These arrays were rinsed with deionized (DI) water using a quick dump rinser for 10 min, and subsequently checked with the HR-SEM (**Figure C13**). It is highly remarkable that the annealed sub-20 nm Au nanoparticle arrays was found to be very stable in water.

Figure C13. Top-view HR-SEM images of (a) sub-30 nm Au nanoparticles and (b) sub-20 nm Au nanoparticle arrays before and after water rinsing in a quick dump rinser for 10 min

C.6| Inclined etching BARC nanocolumns patterned on thick Au and Pt layers

Thick layers of Au (45.0 nm) or Pt (22.5 nm) were sputtered directly on the oxidized Si wafers using the T'COathy system. Periodic BARC nanocolumns were patterned on these wafers, and subsequently etched in the IBE system at different etching times. The etching was performed at 5 sccm Ar, 300 eV, 50-55 mA, and at a beam incident angle of 20°. As can be seen in **Figure C14**, the BARC nano-sharp tips remained during the etching process in case of a thick Au layer, whereas they were completely destroyed in case of a thick Pt layer. We attribute this to the low etching rate of Pt, which is approximately two times less than that of Au and BARC. Therefore, it was difficult to get rid of the Pt redeposition on the sidewall of BARC nanocolumns. Consequently, the BARC nano-sharp tips were removed faster than the redeposited Pt.

Figure C14. Cross-sectional HR-SEM images of BARC nanocolumns inclined etched in the IBE system at different etching times. These BARC nanocolumns were patterned on thick deposited layers of (a) Au (45.0 nm) and (b) Pt (22.5 nm). The etching was conducted at 5 sccm Ar, 300 eV, 50-55 mA, and at a beam incident angle of 20°. Scale bars represent 200 nm.

After an etching time of 9 min, an array of Au nanoparticles fabricated using a 45 nm thick Au layer (**Figure C14a**) was heated in air from room temperature to 1100°C, and passively cooled down. Before the heating treatment, the BARC nano-sharp tips were removed by using oxygen plasma cleaning for 20 min at 500 W (TePla 300 plasma etcher). During heating at high temperature, the Au nanoparticles and the cone-shaped silica features were dewetted to form sub-100 nm Au nanocrystals supported on curve-shaped silica features (**Figure C15**). This fabricated sub-100 nm Au nanocrystal array was also found to be very stable in water rinsing for 10 min (**Figure C16**).

Figure C15. (a) Cross-sectional HR-SEM image (scale bar: 1 μ m) of sub-100 nm Au nanocrystals supported on curve-shape silica features. (b) A close-up image and (c) an image recorded with back-scattered electrons (scale bar: 100 nm) indicate the Au nanocrystals (bright spots).

Figure C16. (a) Top-view HR-SEM images of sub-100 nm silica-supported Au nanocrystals, after water rinsing in a quick dump rinser for 10 min. (b) Image recorded with back-scattered electrons indicates the Au nanocrystals (bright spots). Scale bars represent 200 nm.

Appendix D

Enhancement of Noble Metal Adhesion to Silica Using UV-ozone Treatment

D.1| Adhesion measurement using tape test

Figure D1. A shadow mask on the surface of an oxidized ($\sim 1.1 \mu\text{m}$ thick SiO_2) 4-inch Si wafer.

Figure D2. Top-view optical images of initial Au microdot arrays patterned by using the shadow mask. The diameter of the Au microdots is given on the vertical axis. Scale bars represent 1 mm.

Figure D3. Grayscale images of the initial Au microdot arrays patterned by using the shadow mask. Scale bars represent 1 mm.

Table D1. Different cases for measuring the Au adhesion to SiO₂ using the tape test.

Cases	Patterning ~13 nm thick Au dots	Patterning ~24 nm thick Au dots	UV-ozone treatment for 5 min	Water immersing for 10 min	Depositing a second ~24 nm Au layer	Tape test
Case 1	✓				✓	✓
Case 2	✓		✓		✓	✓
Case 3	✓		✓	✓	✓	✓
Case 4		✓	✓		✓	✓

Case 1:

Figure D4. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, without the UV-ozone treatment. (a) Au microdots patterned on an oxidized Si wafer by using a shadow mask. (b) Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. (c) Pressing tape over the Au surface. (d-e) Peeling off the tape.

Case 2:

Figure D5. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, with the UV-ozone treatment for 5 min. **(a)** Au microdots patterned on an oxidized Si wafer by using a shadow mask, and subsequently treated with UV-ozone for 5 min. **(b)** Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. **(c)** Pressing tape over the Au surface. **(d-e)** Peeling off the tape.

Figure D6. Top-view optical images of the Au microdot arrays, after the tape test in case 2 (see **Figure D5**). Scale bars represent 1 mm.

Figure D7. Grayscale images of the Au microdot arrays, after the tape test in case 2 (see Figure D6). Scale bars represent 1 mm.

Case 3:

Figure D8. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, with the UV-ozone treatment for 5 min, and subsequently rinsing with DI water for 10 min. (a) Au microdots patterned on an oxidized Si wafer by using a shadow mask, treated with UV-ozone for 5 min, and subsequently rinsed with DI water for 10 min. (b) Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. (c) Pressing tape over the Au surface. (d-e) Peeling off the tape.

Figure D9. Top-view optical images of the Au microdot arrays, after the tape test in case 3 (see **Figure D8**). Scale bars represent 1 mm.

Figure D10. Grayscale images of the Au microdot arrays, after the tape test in case 3 (see **Figure D9**). Scale bars represent 1 mm.

Case 4:

Figure D11. Adhesion measurement of ~ 24 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, with the UV-ozone treatment for 5 min. **(a)** Au microdots patterned on an oxidized Si wafer by using a shadow mask, and subsequently treated with UV-ozone for 5 min. **(b)** Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. **(c)** Pressing tape over the Au surface. **(d-e)** Peeling off the tape.

Figure D12. Top-view optical images of the Au microdot arrays, after the tape test in case 4 (see **Figure D11**). Scale bars represent 1 mm.

Figure D13. Grayscale images of the Au microdot arrays, after the tape test in case 4 (see Figure D12). Scale bars represent 1 mm.

Figure D14. Preparation of a Au layer consisting of a gold oxide layer embedded between two sputtered Au layers, supported on an oxidized Si wafer. A protection mask was used during the UV-ozone treatment to create treated and untreated areas. After the sputtering of a second Au layer of ~ 45 nm thick over the sample surface, the sample was stored in environmental air for 5 months before the tape test.

Figure D15. Adhesion measurement of a supported Au layer consisting of a gold oxide layer embedded in between two sputtered Au layers, after storing in environmental air for 5 months (see **Figure D14**) (a) A ~ 13 nm thick Au layer was sputtered directly on the surface of an oxidized Si wafer. Left-half of the wafer was covered by a shadow mask during the UV-ozone treatment for 5 min. (b) Removal of the shadow mask after the UV-ozone treatment: the change in the color of the UV-ozone treated area indicates the formation of a gold oxide layer. (c) Sputtering of a continuous Au layer of ~ 45 nm thick over the wafer surface. The sample was then stored in environmental air for 5 months (d) Pressing tape over the Au surface. (e-f) Peeling off the tape.

D.2 | Patterning gold structures on oxidized Si substrates

Figure D16. Top-view optical images of $\sim 2\ \mu\text{m}$ diameter Au microdot arrays patterned (a) with UV-ozone treatment, and (b) without UV-ozone treatment. Scale bars represent $20\ \mu\text{m}$.

Figure D17. Photograph images of Au structures patterned directly on an oxidized ($\sim 1.1\ \mu\text{m}$ thick SiO_2) 4-inch Si wafer using wet etching of Au. (a) A $\sim 13\ \text{nm}$ thick Au layer was deposited on the wafer surface, treated with UV-ozone, followed by sputtering another $\sim 90\ \text{nm}$ thick Au layer. (b) A shadow mask was used for standard UV lithography process. (c) Positive photoresist patterns after developing in the OPD4246 developer. (d) Au structures after wet etching in the gold etchant and removing the photoresist, showing well-defined Au structures without any damage.

Figure D18. (a) A shadow mask was applied to the surface of an oxidized Si wafer coated with a ~ 13 nm thick Au layer during the UV-ozone treatment for 5 min, and (b) a photograph image of the wafer surface after removing the shadow mask.

Figure D19. Top-view HR-SEM images of ~ 10 nm thick (a) Pt nanodots of ~ 300 nm in diameter, and (b) Pt nanolines of ~ 190 nm in width patterned directly on the surface of oxidized Si wafers without using any additional adhesion layers. Scale bars represent $2\ \mu\text{m}$.

D.3| Characterization of Au surfaces

Figure D20. AFM images (scan field 1x1 μm²) of (a) a ~24 nm thick Au layer deposited on the surface of an oxidized Si wafer, and its surface after (b) treating with UV-ozone for 5 min, and (c) subsequently rinsing with ethanol for 10 min.

Figure D21. Reflectance spectra of untreated Au surface (blue curve), and UV-ozone treated Au surface (red curve). A Au layer of ~13 nm thick was sputtered on the surface of an oxidized (~1.1 μm thick SiO₂) Si wafer.

Figure D22. Measurement of the contact angle (CA) of a water drop on (a) the surface of a ~24 nm thick Au layer sputtered on the surface of an oxidized Si wafer, and on the same sample after (b) treating with UV-ozone for 5 min, (c) treating with UV-ozone for 5 min, and immersing in ethanol for 5 min, and (d) treating with UV-ozone for 5 min, immersing in ethanol for 5 min, cleaning with HNO₃, and re-treating with UV-ozone for 5 min. Scale bars represent 1 mm.

D.4| Effect of ethanol on the adhesion

Case 5:

Figure D23. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, with the UV-ozone treatment for 5 min, and subsequently rising with ethanol for 10 min. (a) Au microdots patterned on an oxidized Si wafer by using a shadow mask, treated with UV-ozone for 5 min, and subsequently rinsed with ethanol for 10 min. (b) Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. (c) Pressing tape over the Au surface. (d-e) Peeling off the tape.

Case 6:

Figure D24. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer. **(a)** Au microdots patterned on an oxidized Si wafer by using a shadow mask, treated with UV-ozone for 5 min, subsequently rinsed with ethanol for 10 min and cleaned with HNO_3 , and finally re-treated with UV-ozone for 5 min. **(b)** Pressing tape over the surface of the continuous Au layer of ~ 24 nm thick sputtered over the wafer surface containing the treated Au microdots. **(c-d)** Peeling off the tape.

Figure D25. Top-view optical images of the Au microdot arrays, after the tape test in case 6 (see **Figure D24**). The Au microdots of 200 μm in diameter were completely removed after the tape test. Scale bars represent 1 mm.

Figure D26. Grayscale images of the Au microdot arrays, after the tape test in case 6 (see **Figure D25**). Scale bars represent 1 mm.

D.5 | Effect of storage time on the adhesion

Table D2. Case for measuring the effect of storing time on the Au adhesion to SiO₂ using the tape test.

Case	Patterning ~13 nm thick Au dots	UV-ozone treatment for 5 min	Storing for 2 weeks	Depositing a second ~24 nm Au layer	Tape test
Case 7	✓	✓	✓	✓	✓

Case 7:

Figure D27. Adhesion measurement of ~ 13 nm thick Au microdots on a ~ 1.1 μm thick oxidized Si wafer, treated with UV-ozone and stored for in environmental air 2 weeks. (a) Au microdots patterned on an oxidized Si wafer by using a shadow mask, treated with UV-ozone for 5 min, and subsequently stored in environmental air for 2 weeks. (b) Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. (c) Pressing tape over the Au surface. (d-e) Peeling off the tape.

D.6 | Effect of gold oxide embedding on the adhesion

Figure D28. Fabrication process for patterning periodic Au microdots consisting of a gold oxide layer embedded in two sputtered Au layers using the shadow mask.

Table D3. Case for measuring the effect of embedded gold oxide on the adhesion using the tape test. Au microdots consisting of a gold oxide layer embedded in between two sputtered Au layers (see **Figure D28**), were sonicated in ethanol for 2 hours before the tape test.

Case	Patterning ~13 nm thick Au dots	UV-ozone treatment for 5 min	Depositing Au (24 nm thick) on the 13 nm Au dots through the shadow mask	Sonication in ethanol for 2 hours	Depositing a second ~24 nm Au layer	Tape test
Case 8	✓	✓	✓	✓	✓	✓

Case 8:

Figure D29. Adhesion measurement of supported Au microdots consisting of a gold oxide layer embedded in between two sputtered Au layers, after the sonication in ethanol for 2 hours (a) Au microdots were fabricated by using a process shown in **Figure D28**, and subsequently sonicated in ethanol for 2 hours (b) Sputtering of a continuous Au layer of ~ 24 nm thick over the wafer surface. (c) Pressing tape over the Au surface. (d-e) Peeling off the tape.

Figure D30. Top-view optical images of the Au microdot arrays, after the tape test in case 8 (see **Figure D29**). Scale bars represent 1 mm.

Figure D31. Grayscale images of the Au microdot arrays, after the tape test in case 8 (see Figure D30). Scale bars represent 1 mm.

Figure D32. TEM image of a stacked Au layer on the surface of a native oxide Si substrate. A gold layer of ~ 13 nm was sputtered on the substrate surface, and subsequently treated with UV-ozone for 5 min. Thereafter, a second Au layer of ~ 24 nm was sputtered on top of the previously treated Au layer. A thin silicon oxide layer (native oxide) was used to prevent undesired charge accumulation during the TEM imaging. Scale bars represent 5 nm.

D.7| Chronoamperometry

Figure D33. Set-up and results of chronoamperometry experiments for the verification of the adhesion mechanism.

D.8| Characterization of SiO₂ surfaces

Figure D34. AFM images (scan field 100×100 nm²) of (a) an oxidized Si substrate, and (b) the same substrate after removing an UV-ozone treated Au film using Au etchant.

Appendix E

Engulfment Control of Platinum Nanoparticles into Oxidized Silicon Substrates

E.1 | High temperature annealing of Pt nanodots on oxidized Si substrates

Figure E1. (a) Annealing recipes of Pt nanodots at different temperatures for 5 h, and (b) the corresponding thickness of the silicon oxide (SiO₂) layer after each annealing process.

Figure E2. AFM (scan filed: 2x2 μm²) images of Pt nanodots after annealing at different temperatures for 5 h.

Figure E3. Structural dimensions measured along the blue line and the red line (see Figure E2), after annealing the Pt nanodots at different temperatures for 5 h.

E.2 | Manufacturing membranes with dense arrays of sub-30 nm nanopores

Figure E4. Cross-sectional HR-SEM images of SiO₂-supported (a) Pt nanodots and (b) Au nanodots after annealing at 1000C for 5 h. The diameter and thickness of Au nanodots was kept the same as Pt nanodots. Scale bars represent 500 nm.

Figure E5. Cross-sectional HR-SEM image of periodic through-hole sub-30 nm nanopores created in a thick SiO₂ layer of approximately 160 nm. Scale bar represents 200 nm.

Figure E6. Cross-sectional HR-SEM image of a closed-end nanopore created by the engulfment of a Pt nanoparticle into the SiO₂ layer. Scale bar represents 100 nm.

Appendix F

Large-scale Fabrication of Free-standing PDMS Through-hole Nanomembranes*

Free-standing polydimethylsiloxane (PDMS) through-hole membranes have been studied extensively in recent years for chemical and biomedical applications. However, robust fabrication of such membranes with sub- μm through-holes, and at a sub- μm thickness over large-areas is challenging. In this appendix, we report a robust and simple method for large-scale fabrication of

free-standing and sub- μm PDMS through-hole membranes, combining soft-lithography with reactive plasma etching techniques. First arrays of sub- μm photoresist (PR) columns were patterned on another spin-coated sacrificial PR layer, using conventional photolithography processes. Subsequently, a solution of PDMS:hexane at a 1:10 ratio was spin-coated over these fabricated arrays. The cured PDMS membrane was etched in a plasma mixture of sulfur hexafluoride (SF_6) and oxygen (O_2) to open the through-holes. This PDMS membrane can be smoothly released with a supporting ring by completely dissolving the sacrificial PR structures in acetone. Using this fabrication method, we demonstrated the fabrication of free-standing PDMS membranes at various sub- μm thicknesses down to $600 \pm 20 \text{ nm}$, and nanometer-sized through-hole ($810 \pm 20 \text{ nm}$ diameter) densities, over areas as large as 3 cm in diameter. Furthermore, we demonstrated the potential of our membranes as cell-culture substrates for biomedical applications by culturing endothelial cells on the membranes in a Transwell-like set-up.

*This appendix is based on the publication: [Le-The, H.](#); Tibbe, M. P.; Loessberg-Zahl, J.; Palma do Carmo, M.; van der Helm, M. W.; Bomer, J. G.; van den Berg, A.; Leferink, A. M.; Segerink, L. I.; Eijkel, J. C. T. Large-scale fabrication of free-standing and sub- μm PDMS through-hole membranes. *Nanoscale* **2018**, *10*, 7711–7718.

F.1| Introduction

Free-standing through-hole nanomembranes have attracted great attention over the past decade due to their wide range of applications¹⁻⁴ including sterile filtration (bacteria and viruses), cell sorting, biomolecular separation, and biomimetic microfluidic devices, termed organs-on-a-chip systems, such as gut-on-a-chip,⁵ lung-on-a-chip,⁶ and blood-brain barrier-on-a-chip.⁷ Such nanomembranes have been fabricated from various materials including silicon-based inorganic materials,^{8,9} and polymers.¹⁰⁻¹³ Nanomembranes made of silicon (Si) or silicon nitride (SiN_x) can be fabricated at various thicknesses ranging from few nanometers to a few hundreds of nanometers, possessing nano through-holes of a few tens of nanometers.⁸ However, fabrication of such through-hole nanomembranes requires dedicated patterning systems such as electron-beam lithography,¹⁴ laser interference lithography,¹⁵ or focused ion-beam milling,¹⁶ which is expensive and labor intensive. Moreover, these inorganic nanomembranes are very fragile under applied pressure and mechanical contact, thus resulting in the difficulty to fabricate/handle large-scale areas. This also leads to the difficulty in the integration of the fabricated nanomembranes with other micro/nanofluidic systems made of polydimethylsiloxane (PDMS) or glass/fused-silica. Nanomembranes made of polymers, e.g. PDMS, on the other hand have the advantages of being economic and easy to integrate into lab-on-a-chip systems.^{6,17-19} Due to its great advantages of low costs, chemical resistance, flexibility, gas permeability, optical transparency, and high molding capability, PDMS has become one of the most widely used polymers in various fields, especially for lab-on-a-chip or micro total analysis systems.²⁰ However, large-area fabrication of free-standing and sub- μm thick PDMS membranes with nanometer-sized through-holes has been considered challenging.

A number of methods has been reported to fabricate PDMS through-hole membranes such as imprinting,²¹ manual punching,²² and spin-coating on SU-8 molds.^{23,24} However, these fabrication methods are accompanied each by their own drawbacks. The imprinting process involves pressing a positive pillar mold into a pre-polymer layer coated on a flat surface. The dependence of the required pressure on the pre-polymer viscosity however leads to the difficulty in reliably fabricating uniform PDMS nanomembranes over large-areas. In addition, insufficient applied pressure could lead to undesirable closed holes rather than complete through-holes. A manual punching process involves punching a needle gauge through a continuous PDMS membrane, which is time consuming. Moreover, handling of membranes at the nanoscale for the punching process is rather difficult, thus making it not suitable for high-yield patterning PDMS through-hole nanomembranes over large footprints. A spin-

coating process can be used, based on the coating of PDMS solution at a high spinning speed over a patterned SU-8 column array, resulting in a PDMS layer thinner than the column height. Subsequently demolding the cured PDMS layer from the SU-8 mold results in a PDMS through-hole membrane. However, the difficulty in fabrication of SU-8 columns at sub- μm diameter ranges limits its use for fabricating PDMS membrane with nanometer-sized through-holes.

Using a hierarchical mold under applied pressure, Cho *et al.* reported the fabrication of flexible and free-standing nanomembranes made of ultraviolet-curable resins.²⁵ Based on the dewetting of the resins into the hierarchical mold, nanomembranes with various nano through-hole sizes from 50 nm to 800 nm, and shapes (dots or lines) were fabricated. Combining hierarchical structures with a microfluidic chip, Tahk *et al.*²⁶ reported an alternative fabrication method for patterning multiscale PDMS through-hole membranes. Their chip was fabricated by plasma bonding the top part of a microfluidic chip made of PDMS with a nanocolumn patterned substrate. Injecting pre-polymer and subsequently curing the PDMS solution inside the microfluidic chip resulted in the formation of membranes with through-holes size ranging from a hundred nanometers to a hundred micrometers. By gently separating the chip bonding via cutting, sub- μm PDMS membranes with nano through-holes were peeled off from the PDMS chip. Although being able to fabricate free-standing and through-hole nanomembranes, these fabrication methods^{25,26} requires hierarchical molds consisting of patterned nanocolumns. Patterning such molds is labor intensive, and requires dedicated patterning systems which are expensive. In addition, an additional coating of anti-sticking layers on the molds prior to the injection of the pre-polymer is needed in order to release the nanomembrane from the mold.

Recently, Kang *et al.* reported a compelling technique that allows rapidly patterning free-standing and continuous PDMS nanomembranes over large-areas.²⁷ Using a mixture solution of PDMS and hexane, PDMS nanomembranes at various thicknesses from 70 nm to a few hundreds of nanometers could be fabricated on a sacrificial photoresist (PR) layer by spin-coating at very high speed of 6000 rpm. By gluing a thick PDMS ring used as a support on the membrane surface, and subsequently dissolving the PR layer in acetone, a free-standing and continuous PDMS nanomembrane supported on the PDMS ring was obtained over large-areas up to 6 cm in diameter. The use of a PDMS support ring prevented the folding of the membrane, thus providing an opportunity to smoothly release the nanomembrane from the dissolved PR layer.

Further improving the fabrication technique reported by Kang *et al.*,²⁷ we present a robust fabrication method that allows rapid patterning of free-standing PDMS membranes with periodic sub- μm through-holes at various sub-

μm thicknesses. Our fabrication method combines the soft lithography technique with an easy operation reactive plasma etching technique, and thus is suitable for mass production at low-cost. Using this method, we demonstrate the fabrication of free-standing and sub- μm PDMS membranes over large footprints of 3 cm in diameter, possessing periodic sub- μm through-holes of 810 ± 20 nm in diameter at different hole interspacings of 3 μm , 5 μm , and 10 μm . Additionally, we demonstrate the potential of this membrane as a cell-culture substrate for biomedical applications by culturing endothelial cells on the membranes in a Transwell-like set-up.

F.2| Materials and methods

F.2.1| Patterning sub- μm PR column arrays on a sacrificial PR layer

Figure F1 shows the process for fabricating free-standing and sub- μm PDMS through-hole membranes. A positive PR layer (OiR 907-17i, Fujifilm, Japan) of 1.71 ± 0.04 μm thickness destined as sacrificial layer was spin-coated on a Si wafer (525 μm thick, single side polished, Okmetic, Finland) at 4000 rpm for 30 s, followed by baking on a hot-plate at 95°C for 2 min. Subsequently, an extremely thin titanium (Ti) layer (~ 3 nm) was sputtered on the coated PR layer, using a ion-beam sputtering system (in-house built T'COathy system, NanoLab Cleanroom, The Netherlands)²⁸ at a pressure of 6.6×10^{-3} mbar, and 200 W (**Figure F1a**). This Ti layer was used to prevent the intermixing of the first PR layer with the second PR layer of approximately 1.7 μm , which was spin-coated at 4000 rpm for 30 s and followed by baking on a hot-plate at 95°C for 1 min (**Figure F1b**). At this sputtered thickness a discontinuous Ti layer was obtained. Moreover, it is mentioned here that an extremely thin layer of hexamethyldisilazane (HMDS) was spin-coated on the surface of Ti-coated PR layer before spin-coating the second PR layer. This HMDS layer is used to increase the adhesion of the patterned PR structures with the substrates.²⁹ A photo-mask made of quartz containing arrays of 1 μm chromium (Cr) discs with three different pitches, i.e. 3 μm , 5 μm , and 10 μm , was fabricated in-house by using a mask-making system (DWL 2000 Laser Lithography System, Heidelberg Instruments, Germany). The exposure process was conducted by using a mask alignment system (EVG620, EV Group, Austria) for 3 s at an intensity of 12 mW cm^{-2} , and with vacuum contact mode. The vacuum was always kept at 0.75 bar during the exposure process to ensure a good contact of the mask over the entire wafer, thus increasing the reproducibility of the fabrication process. Thereafter, the wafer was post-baked on a hot-plate at 120°C for 15 s, followed by developing in the OPD4246 developer for 1 min, and rinsing with de-ionized

(DI) water to complete the fabrication of sub- μm PR column arrays on another, sacrificial, PR layer (**Figure F1c**).

F.2.2 | Patterning sub- μm PDMS through-hole membranes

A solution of PDMS prepolymer with curing agent (10:1) was diluted with hexane at a 1:10 (PDMS:hexane) ratio, and subsequently degassed for at least 2 h. This PDMS:hexane solution was then spin-coated over the fabricated PR column arrays at 6000 rpm for 3 min (**Figure F1d**). After baking the Si wafer in an oven at 80°C for at least 3 h, a plasma etching process of the PDMS membrane was conducted in a parallel plate reactive ion etching system (in-house built Tetske system, NanoLab Cleanroom, The Netherlands)³⁰ at 47 sccm SF_6 , 17 sccm O_2 , 50 mTorr, and 100 W to decrease the thickness of the PDMS membrane and open the through-holes (**Figure F1e**). Reactive plasma etching was chosen for etching PDMS because it allows to precisely control the etching time, and the etching rate by tuning the amount of gas mixture and power.³¹ This leads to the opportunity to uniformly etch PDMS layers at the nanoscale. The thickness of the membrane could be thinned down to sub- μm by increasing the etching time. By comparing the thickness of the initial membrane with that of the membrane after etching, the etching rate of the cured PDMS:hexane was determined. The membrane thicknesses were measured from the images taken using a high-resolution scanning electron microscope (HR-SEM, FEI Sirion microscope, United States) at a 5 kV acceleration voltage and a spot size of 3. In addition, the surface roughness of the membrane etched at various etching times was measured from atomic force microscopy (AFM) images (scan field: $1 \times 1 \mu\text{m}^2$), recorded in contact mode using an AFM system (Dimension Icon, Bruker Corp., United States) in air. After the etching process, a three-dimensional (3D)-printed ring used as a support was glued onto the surface of the membrane using PDMS solution, followed by baking in an oven at 80°C for at least 2 h. Acetone was spread over the membrane surface to completely dissolve the PR columns and the sacrificial PR layer by the diffusion through the discontinuous Ti layer, enabling a smooth detachment of the PDMS through-hole membrane with the 3D-printed ring (**Figure F1f**).

F.2.3 | Cell culture on the PDMS membrane in a Transwell-like set-up

To show the cell culture compatibility of our sub- μm PDMS through-hole membranes, human umbilical vein endothelial cells (HUVECs, passage 4-6) were seeded onto PDMS membranes that were mounted to Transwell inserts from which the traditional polycarbonate membrane was removed. Prior to cell seeding, PDMS membranes were coated with a $10 \mu\text{g mL}^{-1}$ rat tail collagen-I

(Corning, NY, United States) in 1x phosphate buffered saline (PBS, Merck, Germany) solution. HUVECs (Lonza, Switzerland) were seeded statically in a concentration of 15×10^4 cells mL^{-1} in endothelial cell growth medium (ECGM, Merck, Germany). 600 μL ECGM was pipetted into the wells of a 24-well plate after which 100 μL HUVEC suspension was added on top of the PDMS membrane. After 7 days, cell viability was assessed by use of a live/dead viability assay according to manufacturer's protocol. Cell morphology was visualized after 7 days by staining the actin filaments and nuclei with ActinGreen™ and NucBlue™ (both Invitrogen) respectively by adding a drop of each staining solution to each membrane. A traditional Transwell insert with a polycarbonate membrane was utilized as a control on cell viability and cell morphology. Both the cell viability and the cell morphology were imaged with fluorescence microscopy (EVOS, Hatfield, PA, United States).

Figure F1. Fabrication process of a free-standing and sub- μm thick PDMS through-hole membrane. (a) PR1 was spin-coated on a Si wafer, and a Ti layer was sputtered directly on the coated PR layer. (b-c) PR2 was coated and array of sub- μm columns was patterned into this layer using conventional photolithography. (d) A solution of PDMS:hexane at a 1:10 ratio was spin-coated over the fabricated PR column array. (e) Plasma etching of the PDMS membrane was conducted in a reactive ion etching system to open the through-holes. (f) Releasing the PDMS through-hole membrane in acetone using a 3D-printed ring as a support.

F.3| Results and discussion

F.3.1| Patterning sub- μm PR column arrays on a sacrificial PR layer

Figure F2 shows the HR-SEM images of arrays of sub- μm PR columns with different pitches of 3 μm , 5 μm , and 10 μm , fabricated on PR1. The cross-sectional HR-SEM images shows successful fabrication of periodic PR columns with a sloped sidewall profile, which is typical for positive PR structures.³² It is

highly remarkable that the presence of Ti layer tremendously decreased the intermixing of the PR2 with the PR1. Therefore, no significant efforts on the optimization of the heating time and temperature for the PR1 were required. A rough surface was observed after the development of the PR2. We attribute this to the discontinuity of the sputtered Ti layer of approximately 3 nm, which led to the deformation of the Ti layer and the local PR surface mixing when spin-coating the PR2 at high speed (4000 rpm) on the PR1. The black spots and the white rings in the top-view HR-SEM images indicate the flat-top and the sidewall slope profile of the PR columns, respectively. A considerable uniformity in the flat-top diameter (809 ± 20 nm) and periodicity of the fabricated PR columns were obtained for all arrays (Supplementary **Figure S1**). The 2.5% relative standard deviation could probably stem from the imperfection of the fabricated mask, or the inaccuracy in image processing and analysis using ImageJ software.³³ The close-up image in **Figure F2(a)** shows the shape of a fabricated PR column, which has a flat-top (810 nm diameter) and a sloped sidewall profile. In summary, these images indicate a robust and highly controllable fabrication process.

Figure F2. Top-view (scale bar: 10 μm) and cross-sectional (scale bar: 5 μm) HR-SEM images of sub- μm PR column arrays with different pitches of (a) 3 μm , (b) 5 μm , and (c) 10 μm , fabricated on top of PR1. The black spots and the white rings in the top-view images indicate the flat-top and the sidewall slope of the PR columns, respectively. The close-up image (scale bar: 1 μm) in (a) shows the shape of a fabricated PR column, which has a sub- μm flat-top indicated by a red circle, and a sloped sidewall profile.

F.3.2 | Spin-coating of PDMS:hexane solution over sub- μm PR column arrays

Figure F3 shows the cross-sectional HR-SEM images of sub- μm PR column arrays, spin-coated with the PDMS:hexane (1:10) solution, followed by baking at 80°C for 3 h. At a high spinning speed of 6000 rpm for 3 min, the PDMS:hexane solution was uniformly spread over the surface, and homogeneously covered all the PR columns. It is worth mentioning that the thickness of the PDMS layer after curing was much smaller than the height of

the fabricated PR columns, i.e. $1.35 \pm 0.02 \mu\text{m}$ versus $1.71 \pm 0.04 \mu\text{m}$, respectively. However, a thin PDMS layer was found to cover the flat-top of the PR columns. The red arrow in **Figure F3(a)** indicates the unexpected breaking of this thin film caused by breaking the sample for SEM observation. The coverage of such PDMS thin film over the top of microcolumns when spin-coating PDMS solution over microcolumn arrays is a typical problem reported in literature.^{34,35} It can be attributed to the flexibility of PDMS, leading to the ductility of PDMS thin films. The cross-sectional views of the holes of the PDMS membranes **Figures F3(a)** and **F3(b)** show truncated cone-shaped holes, which were replicated from the periodic sub- μm PR columns as master molds. The difference in the size of the holes observed in **Figures F3(a)** and **F3(b)**, and the deformation of the membrane surface observed in **Figure F3(c)** probably came from the stretching of the membranes when breaking the sample for SEM observation. In addition, a low surface roughness ($R_a = 0.45 \text{ nm}$ over an area of $1 \times 1 \mu\text{m}^2$) of the PDMS membranes measured using an AFM indicated a smooth membrane surface after the spin-coating and curing processes (Supplementary **Figure S2**).

Figure F3. Cross-sectional HR-SEM images of PR column arrays with different pitches of (a) $3 \mu\text{m}$, (b) $5 \mu\text{m}$, and (c) $10 \mu\text{m}$, coated with the cured PDMS:hexane (1:10) solution. The red arrow in (a) indicates the breaking of the PDMS thin film covered on the flat-top of the PR columns – inserted image in (b) – which was caused by breaking the sample for SEM observation. Scale bars represent $2 \mu\text{m}$.

F.3.3| Through-hole opening using reactive plasma etching of PDMS

Figure F4 shows the cross-sectional HR-SEM images of sub- μm PR column arrays coated with PDMS, which were etched at various etching times in the TETske system. From the observation, a uniform etching of PDMS layer was obtained for all arrays. By etching the thin PDMS film covered on the flat-top of the PR columns, the holes were opened after an etching time of 15 s. By increasing the etching time, membranes with a thickness of $600 \pm 20 \text{ nm}$ were obtained at an etching time of 60 s. At a thickness less than $1 \mu\text{m}$, the effective Young's modulus of PDMS has been reported to significantly increase to approximately 8 MPa, which is ten times higher than that of a thick PDMS layer of 0.5 mm .³⁶

This effective Young's modulus of a sub- μm PDMS is comparable to that of a tissue culture plastic (TCP) substrate, i.e. ~ 10 MPa.³⁷ The average thicknesses of the PDMS through-hole membranes at various etching times are presented in **Table F1**. It is clearly observed that the standard deviation calculated from the measured thickness values of the membranes was relatively large. We attribute this mainly to the errors in the thickness measurement of the exact values due to the stretching of the membranes caused by the breaking of samples for cross-sectional SEM measurement (Supplementary **Figure S3**).

Figure F4. Cross-sectional HR-SEM images of PDMS-coated PR column arrays with different pitches of (a) 3 μm , (b) 5 μm , and (c) 10 μm , etched at various etching times. Scale bars represent 2 μm . (d) AFM images (scan field: $1 \times 1 \mu\text{m}^2$) of the PDMS membrane surface with the measured roughness (Ra) at various etching times. The inserted HR-SEM image in (d) shows a close-up image (scale bar: 200 nm) of a hole on the surface of the PDMS membrane observed after the etching process.

Figure F4(d) shows the average surface roughness (Ra) of a PDMS membrane at various etching times, which was measured over an area of $1 \times 1 \mu\text{m}^2$ (Supplementary **Figure S4**). A slight increase in the surface roughness from 0.67 nm to 3.01 nm was observed with an increase in the etching time from 15 s to 60 s, respectively. This is a typical problem encountered with plasma etching, which is based on the physical bombardment of high energy particles.³² The close-up HR-SEM image in **Figure F4(d)** shows a nanohole on the surface of

the PDMS membrane, which was observed only after the etching process. From the observation in **Figures F4(a)** and **F4(c)** the number of these nanoholes did not increase with the increase in the etching time (Supplementary **Figure S5**). Therefore, we attribute these nanoholes to nanobubbles trapped inside the PDMS membranes. These nanobubbles were probably created during the spin-coating of this solution over the fabricated PR arrays at the high speed of 6000 rpm. By etching the top layer of the membrane, these nanoholes became exposed to the membrane surface. In addition, after etching for 60 s, sulfur (S) residues were found on the PDMS membrane surface by using energy dispersive X-ray spectrometry (EDS), though at a relatively low percentage of approximately 1.5 wt% (Supplementary **Figure S6**).

Figure F5. Etching rate of the cured PDMS:hexane as function of the etching time. The inserted sketches and HR-SEM images (scale bar: 1 μ m) show the geometry of the structures etched at various etching times.

Table F1. Thickness measurement of the PDMS through-hole membranes at various etching times.

Etching time (s)	Membrane thickness (nm)	Standard deviation (nm)
0	1345	20
15	1170	26
30	940	20
45	749	23
60	600	20

Figure F5 and **Table F1** show the etching rate of the cured PDMS:hexane versus the etching time. From the linear fit curve, the etching rate of the cured

PDMS:hexane (1:10) solution could be determined as 740 nm min^{-1} . The inserted HR-SEM images in **Figure F5** show that the curvature of the PDMS layer around the PR columns increased with the increasing etching time. Moreover, the opening of the through-holes also increased with the decrease in the membrane thickness due to the sidewall sloop profile of the fabricated PR columns.

F.3.4 | Releasing of the sub- μm PDMS through-hole membranes

Figure F6 shows top-view optical and HR-SEM images of a free-standing and sub- μm PDMS membranes with through-holes of $810 \pm 20 \text{ nm}$ in diameter, with different hole interspacings of $3 \mu\text{m}$, $5 \mu\text{m}$, $10 \mu\text{m}$. No cracking or breaking of the large-area membranes was observed upon releasing them with the 3D-printed ring from positive PR structures in the acetone, thus indicating this procedure enables a smooth detachment (**Supplementary Figure S7**). It is worth mentioning that the free-standing membranes (3 cm in diameter) were vibrating continuously during the observation using the optical microscope, probably due to air convection. This led to a significant change in the observed color of the light transmitted through the through-holes, which are indicated by red circles in the close-up optical image. The black holes in the HR-SEM images again indicate a through-hole membrane.

F.3.5 | Cell culture on the sub- μm PDMS through-hole membranes

After successful release of the sub- μm PDMS through-hole membranes and mounting of the membranes on a support ring to create a Transwell-like culture set-up (**Supplementary Figure S8**), the Transwell was fully immersed in 70% ethanol for 2 h, and subsequently in PBS solution for 1 h. After this sterilization process, cells were added on top of the membrane and allowed to adhere and proliferate. **Figure F7(a)** shows top-view fluorescent images of the cells on the membrane after a live/dead staining. It can be observed that most of the cells ($\sim 94\%$) were viable (green) after 7 days (**Supplementary Figures S9-S10**). The number of dead cells (red) ($\sim 6\%$) were relatively low and comparable with that of the same cells cultured on a Transwell permeable support (Corning Inc., USA), i.e. $\sim 8\%$ (**Supplementary Figure S11**). From this result can be concluded that the membranes do not induce any acute cytotoxic response. From **Figure F7(b)**, the cell morphology was observed as normal with most cells showing an endothelial-like bipolar spread morphology. There were no abnormalities found in the morphology of the cell nuclei. Similar cell morphology was observed when these cells are cultured on a TCP substrate (**Supplementary Figure S12**). Therefore, this membrane can be considered as a cell culture substrate in studies where, for example, the role of direct-cell contacts or paracrine

signaling between compartmentalized co-cultures is of interest. The membrane would in this case be a model of the basal lamina and allow for both sprouting of cells' filopodia through the through-holes and the fast diffusion of soluble factors from one compartment to the other by passing through the sub- μm length of the through-holes.

Figure F6. Top-view optical (top) and HR-SEM (bottom) images of the free-standing and sub- μm PDMS through-hole membranes with different hole interspacings of (a) 3 μm , (b) 5 μm , (c) 10 μm . Scale bars represent 5 μm .

Figure F7. Top-view fluorescent images of cultured cells on sub- μm PDMS through-hole membranes. (a) A live/dead staining combined with nuclei staining (NucBlue™) after 7 days shows a relatively high number ($\sim 94\%$) of viable cells (green) with a relatively low number of dead cells (red). (b) This merged image of the PDMS membrane (grayscale after bright field imaging) and an ActinGreen™ and NucBlue™ staining, shows the spread morphology of the cells on the membrane. Scale bars represent (a) 400 μm and (b) 50 μm .

F.4 | Conclusion

In summary, we report and demonstrate a robust and simple method for fabricating free-standing and sub- μm PDMS through-hole membranes over large-areas, combining soft lithography with reaction plasma etching techniques. Using this method, we fabricated free-standing PDMS membranes at various sub- μm thicknesses over areas as large as 3 cm in diameter, possessing periodic sub- μm through-holes of 810 ± 20 nm in diameter at different hole interspacings of 3 μm , 5 μm , and 10 μm . By its simple procedure, our fabrication method provides an enabling technique for large-scale and rapid patterning of sub- μm PDMS through-hole membranes, which is suitable for high-yield production at low-cost.

Furthermore, we demonstrated the use of our fabricated PDMS membranes as a cell culture substrate for biomedical applications by culturing endothelial cells on the membranes in a Transwell-like set-up. Future work with this setup will allow us to further characterize the mechanical properties, permeability and transport selectivity of the membrane.³⁶ In addition, the effect of our membrane on co-cultures of multiple cell types on opposite sides of the membrane can be conducted.¹²

Our research into integration of these fabricated PDMS through-hole membranes into microfluidic chips is also ongoing. For example, we wish to use these membranes as part of the blood-brain barrier-on-a-chip shown in the supplementary information (Supplementary **Figure S13**).³⁸ In this device, the quality of the cultured cell layer and its response to mechanical cues can be easily studied by measuring the trans endothelial electrical resistance (TEER).⁷

F.5 | References

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F.6| Supplementary

F.6.1| Uniformity measurement of fabricated sub- μm PR column arrays

The uniformity of the sub- μm PR columns in each fabricated array was measured from the top-view HR-SEM images (**Figure S1**). A high uniformity in the periodicity of the fabricated PR columns was obtained for all arrays. The flat-top diameter distribution of the PR columns analyzed by ImageJ software within the top-view HR-SEM images show a relatively small variation. This could probably come from the imperfection of the mask that was directly transferred to the patterned PR columns. In addition, the inaccuracy in the image processing and analysis using ImageJ software could also contribute to the errors.

Figure S1. Top-view (scale bar: 10 μm) and cross-sectional (scale bar: 5 μm) HR-SEM images of periodic sub- μm PR column with different pitches of (a) 3 μm , (b) 5 μm , and (c) 10 μm , fabricated on the first, sacrificial, PR layer (PR1), and their corresponding flat-top diameter distribution. The black spots and the white rings in the top-view images indicate the flat-top and the sloped sidewall of the PR columns, respectively. The close-up image (scale bar: 1 μm) in a) shows the shape of a fabricated PR column, which has a sub- μm flat-top indicated by a red circle, and a sloped sidewall profile.

F.6.2 | Spin-coating of PDMS:hexane solution over sub- μm PR column arrays

Figures S2(d) and S2(f) show an atomic force microscope (AFM) image and the corresponding HR-SEM image of the surface of a PDMS membrane coated on a sub- μm PR column array, respectively. A low surface roughness (R_a) of 0.45 nm over a scan field of $1 \times 1 \mu\text{m}^2$ indicated a smooth membrane surface after the spin-coating and curing processes. The close-up HR-SEM image in Figure S2(f) again confirmed the smoothness of the membrane surface.

Figure S2. Cross-sectional HR-SEM images (scale bar: 5 μm) of PR column arrays with different pitches of (a) 3 μm , (b) 5 μm , and (c) 10 μm , coated with the cured PDMS:hexane (1:10) solution. (d) An AFM image (scan field: $1 \times 1 \mu\text{m}^2$) of the surface of a spin-coated PDMS membrane, and (f) a corresponding top-view HR-SEM image (scale bar: 200 nm).

F.6.3 | Reactive plasma etching of PDMS

Figure S3 shows the cross-sectional HR-SEM images of a PDMS-coated PR column array with the pitch of 5 μm , after etching for 30 s. The close-up HR-SEM image shows the peeling off and the stretching of the membrane ($\sim 960 \text{ nm}$ thick) caused by breaking the sample, thus resulting in larger through-holes.

Figure S3. Cross-sectional HR-SEM image (scale bar: 20 μm) of a PDMS-coated PR column array with the pitch of 5 μm , after etching for 30 s. The close-up HR-SEM image (scale bar: 10 μm) shows the peeling off and the stretching of the membrane ($\sim 960 \text{ nm}$ thick) caused by breaking the sample, which resulted in larger through-holes.

Figure S4 shows AFM images of the surface of a PDMS membrane etched at various etching times, and their corresponding top-view HR-SEM images. A slightly increase in the membrane surface roughness from 0.67 nm to 3.01 nm was obtained with an increase in the etching time from 15 s to 60 s, respectively. Such increase in the membrane surface roughness could also be observed in the top-view HR-SEM images.

Figure S4. AFM images (scan field: $1 \times 1 \mu\text{m}^2$) of the surface of a PDMS membrane etched at various etching times, and their corresponding top-view HR-SEM images (scale bar: 200 nm).

Figure S5. Top-view HR-SEM images of the surface of PDMS membranes, etched at various etching times. The PDMS:hexane (1:10) solution was spin-coated over (a) a PR column array (5 μm pitch), or on (b) a sacrificial photoresist layer. Scale bars represent 2 μm .

Figure S5 shows the top-view HR-SEM images of the surface of PDMS membranes etched at various etching times. After the etching process, nanoholes were only observed on the membrane surface coated over an PR column array (**Figure S5a**). It is clearly seen that the number of these nanoholes

slightly increased in the beginning (from 15 s to 30 s etching time), and subsequently decreased significantly with the increasing etching time. We attribute these nanoholes to the nanobubbles trapped inside the PDMS membranes. These nanobubbles were probably created during the spin-coating of this solution over the fabricated PR arrays at the high spinning speed of 6000 rpm. No nanohole observed on the membrane surface coated on a continuous photoresist layer indicated a sufficient degassing process of the PDMS:hexane solution (**Figure S5b**).

Figure S6 shows the energy dispersive X-ray spectrometry (EDS) spectrum and elemental quantitative data measured on a PDMS membrane surface after etching for 60 s. Sulfur (S) residues were found on the PDMS membrane surface, though at a relatively low percentage of approximately 1.5 wt%.

Figure S6. EDS spectrum and elemental quantitative data measured on a PDMS membrane surface after etching for 60 s. The inserted HR-SEM image shows the measured area (scale bar: 500 μm).

F.6.4 | Releasing of the sub- μm PDMS through-hole membranes

Figure S7. Sketch of sub- μm PDMS through-hole membranes, which are free-standing on a 3D-printed ring used as a support. The inserted images show real optical images of the released PDMS membranes over large-areas of 3 cm in diameter.

Figure S8. Photograph of a sub- μm PDMS through-hole membrane, mounted on a support ring to create a Transwell-like culture set-up.

G.6.5 | Cell culture on the sub- μm PDMS through-hole membranes

Figure S9. Bright-field optical images of cultured cells on sub- μm PDMS through-hole membranes, captured at different days using an inverted microscope. Scale bar represents 200 μm .

Figure S10. Live/dead viability assay of HUVECs cultured on a PDMS membrane for 7 days. **(a)** Overlay image of viable cells stained with Calcein AM (green), necrotic cells stained with Ethidium Homodimer (red) and Nuclei are stained with NucBlue™ Live ReadyProbes™ reagent (blue). **(b)** Greyscale image of the Calcein AM staining, imaged by use of a Green Fluorescent Protein filter cube. **(c)** Greyscale image of the nuclei staining NucBlue™ using a DAPI filter cube. **(d)** Greyscale image of dead cells stained by Ethidium Homodimer and imaged using a Red Fluorescent Protein filter cube. Scale bars represent 400 μm .

Figure S11. Live/dead viability assay of HUVECs cultured on a Transwell permeable support (Corning Inc., USA) for 7 days. **(a)** Overlay image of viable cells stained with Calcein AM (green), necrotic cells stained with Ethidium Homodimer (red) and Nuclei are stained with NucBlue™ Live ReadyProbes™ reagent (blue). **(b)** Greyscale image of the Calcein AM staining, imaged by use of a Green Fluorescent Protein filter cube. **(c)** Greyscale image of the nuclei staining NucBlue™ using a DAPI filter cube. **(d)** Greyscale image of dead cells stained by Ethidium Homodimer and imaged using a Red Fluorescent Protein filter cube. Scale bars represent 400 μm .

Figure S12. Bright field images of HUVECs cultured on **(a)** a sub- μm through hole PDMS membrane and **(b)** a tissue culture plastic (TCP) substrate. No significant differences in cell morphology are observed. Images are taken 24 hours after cell seeding. Scale bars represent 400 μm .

F.6.6 | Integration of the PDMS membranes into microfluidic chips

Figure S13. (a-c) Fabrication process for transferring a fabricated PDMS membrane to a PDMS microfluidic chip. (d) A close-up optical image at the channel intersection separated by the PDMS through-hole membrane. Scale bar represents 800 μm .

Figures S13(a-c) shows the fabrication process for transferring a fabricated PDMS membrane to a PDMS microfluidic chip using a supporting Transwell. Briefly, the bottom part of the PDMS chip was treated with O_2 plasma to activate its surface. Subsequently, a PDMS membrane mounted on a Transwell was brought into contact with the PDMS chip surface, thus resulting in a nice bond of the PDMS membrane with the bottom part surface of the PDMS chip. After releasing the Transwell, the bottom part of the PDMS chip with the PDMS membrane was aligned and bonded to the top part of the PDMS chip, which was already treated with O_2 plasma. The final PDMS chip was put in an oven at 60°C for at least 1 h to achieve a good bonding. Figure S13(d) shows the testing result of the fabricated PDMS chip. The mixture solution of phosphate buffered saline (PBS) and blue food dye with 3 μm diameter particles was flowed into the bottom channel of the PDMS chip at $1 \mu\text{l min}^{-1}$. Whereas, only PBS solution was flowed into the top channel at the same speed of $1 \mu\text{l min}^{-1}$. When the pure PBS solution flowed over the PDMS membrane, the blue food dye in the bottom channel went through the though-holes of the PDMS membrane to the top channel. This resulted in a mixture solution of PBS with blue food dye in the top channel. From the observation, the 3 μm particles were only flowed in the bottom channel without crossing the PDMS membrane with sub-micron through-holes.

Publication List

Peer-reviewed Journal Publications

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Samenvatting

Het onderzoek dat beschreven wordt in dit proefschrift had als doel het ontwikkelen van geordende patronen van edelmetalen en keramische nano-structuren, over een groot oppervlak en tegen een lage prijs. Het hoofddoel van dit onderzoek was om de bovengenoemde nano-structuren toe te passen in microfluidische systemen voor het bestuderen van katalytische reacties. Gedurende het onderzoek ontstond er nog een doel, namelijk het begrijpen van de wederzijdse interactie tussen de structuren van edelmetaal en de keramische substraten.

Hoewel veel technologieën die worden gebruikt voor top-down nano-patterning van geordende nano-structuren intensief zijn onderzocht, is de fabricage van zeer geordende nano-structuren met afmetingen kleiner dan 100 nm over het algemeen een uitdaging. De innovatie van het onderzoek van dit proefschrift is gelegen in het fabriceren van deze structuren over grote oppervlakken, tegen lage kosten en met behulp van een conventionele ultraviolette (UV, 365 nm golflengte) lichtbron. Om dit te realiseren, is de op ultraviolet licht gebaseerde Verplaatsing-Talbot-lithografie (DTL) gebruikt. Deze DTL techniek maakt het mogelijk om nano-structuren in de vorm van stippen of lijnen over een grote oppervlakte te fabriceren. De kleinste dimensies voor patronen die bereikt kunnen worden met DTL is normaal gesproken 100 nm. Door gebruik te maken van een nieuw ontwikkelde plasma krimp-ets techniek bleek het mogelijk om de dimensies van de structuren te variëren en over te brengen naar nog kleinere afmetingen. De combinatie van deze twee technieken maakte het mogelijk om structuren te verkrijgen met afmetingen kleiner dan 30 nm (**Hoofdstuk 2**). De DTL-gepatroneerde fotoresist (PR) nano-

structuren konden direct worden overgebracht op een *bottom antireflection coating* (BARC) laag in een 1:1 verhouding met behulp van stikstof (N_2) plasma. Voor structuren met kleinere dimensies werd een zuurstof/stikstof (O_2/N_2) plasma gebruikt. Het is interessant om op te merken dat de verticale structuur van de PR / BARC-nanostructuren bewaard blijft tijdens het krimp-etsproces. Door het etsen met een O_2/N_2 -plasma te combineren met een N_2 -plasma konden we de PR/BARC-nano-structuren reproduceerbaar fabriceren. Afmetingen van de aparte nanostructuren konden daarbij worden gevarieerd van 110 nm tot kleiner dan 30 nm. Met zijn eenvoudige en flexibele productiestappen is onze fabricagemethode geschikt voor grootschalige massaproductie van periodieke nanostructuren kleiner dan 100 nm tegen lage kosten.

Door de combinatie van de op DTL-gebaseerde krimp-etstechniek, die beschreven staat in **Hoofdstuk 2**, met droog etsen, nat etsen en dunne film depositie technieken, is er een robuuste en hoog rendement fabricagemethode ontwikkeld. Deze fabricagemethode kan vervolgens worden gebruikt om hoogwaardige arrays, met een grote dichtheid van metallisch gouden (Au) nanogaps, tegen lage kosten te fabriceren (**Hoofdstuk 3**). Gebruikmakend van de eigenschappen van de $\langle 111 \rangle$ georiënteerde siliciumkristalvlakken tijdens een nat etsproces worden er zeer scherpe vlakken gecreëerd, met als resultaat dat er silicium nano-structuren met zeer weinig oneffenheden in de nanogaps worden gevormd. Vervolgens wordt een uniforme depositie van een siliciumnitride (SiN) laag en een goudlaag (Au) uitgevoerd, met als resultaat een reeks van hoogwaardige Au-nanogaps. De grootte van de Au-nanogaps kunnen eenvoudig worden afgesteld tot een minimum van ~ 10 nm door de dikte van de gedeponeerde Au-laag te variëren. Omdat de ruwheid van het oorspronkelijke SiN-gecoate Si-sjabloon geminimaliseerd wordt door het nat-etsen van het kristallijn silicium, hangt de ruwheid van de Au-nanogaps bijna uitsluitend af van de ruwheid van de gesputterde Au-laag. Het SiN-gecoate Si-sjabloon kan makkelijk worden hergebruikt door de Au-laag te vervangen, zonder het sjabloonmateriaal te beschadigen of de afmetingen te wijzigen. Een belangrijk resultaat was dat de gefabriceerde Au nanogaps een significante verhoging vertoonden van het Surface Enhanced Raman scattering (SERS) signaal van benzeenthiole (BT) -moleculen. Het signaal van deze BT moleculen, chemisch geadsorbeerd op het oppervlak van nanogaps, vertoonde een versterkingsfactor tot 3.0×10^8 .

In **Hoofdstuk 4** rapporteerden we een robuuste techniek om op grote schaal geordende nanostructuren van edelmetalen zoals goud en platina te fabriceren. De afmetingen van deze structuren kunnen in hoge mate worden gevarieerd. De structuren worden ondersteund door geoxideerde siliciumsubstraten en hechten aan het oppervlak zonder dat er

metaaladhesielagen worden gebruikt. De fabricage wordt gedaan met UV gebaseerde DTL (zie **Hoofdstuk 2**) gecombineerd met argon (Ar) ionenbundel etstechnieken, die het meest efficiënt bleek wanneer toegepast onder een specifieke hoek. Door het toepassen van deze techniek hebben we met succes een oppervlakte van $3 \times 3 \text{ cm}^2$ Au of Pt nanostructuren gefabriceerd, die door kegelvormige silica nanostructuren van variabele diameter worden ondersteund. Door de etstijd van het argon etsen te variëren, konden de diameters van de structuren worden aangepast tussen afmetingen van kleiner dan 30 nm tot 110 nm. Bovendien leidt het annealen van dergelijke metalen nano-structuur arrays met structuurtjes kleiner dan 30 nm bij hoge temperatuur tot metalen nano-structuur arrays die kleiner dan 20 nm zijn, met hoge uniformiteit van de deeltjesdiameter en goede hechting aan het substraat. Deze geordende edelmetaal nano-structuren worden gebruikt als modelkatalysatoren voor katalyse onderzoek, in combinatie met de microfluidische technologie genoemd in **Hoofdstuk 7**.

In een poging om beter inzicht te krijgen in de onderlinge interactie van het gesputterde Au met het oppervlak van de geoxideerde silicium (SiO_2) substraten, bleek dat continue Au-films op SiO_2 -substraten na behandeling met een ultraviolet–ozon plasma een uitstekende verbetering van de hechting aan het SiO_2 -substraat vertoonden (**Hoofdstuk 5**). Belangrijk is dat de verbeterde adhesie onafhankelijk is van de afmetingen van de micro- of nano-structuren zolang de dikte in de orde van nanometers is. Continue Au-films met een dikte van minder dan $\sim 13 \text{ nm}$ bezitten hierdoor een buitengewoon sterke hechting na 5 minuten UV-ozonbehandeling. Het is opmerkelijk dat dit sterke hechtingseffect verdwijnt wanneer de monsters gedurende 10 minuten met ethanol worden gespoeld. Op basis van deze waarneming en andere waarnemingen, hebben we de toegenomen hechting aan de vorming van een goudoxidelaag toegeschreven. Door een tweede goudlaag te deponeren op de UV-ozonbehandelde eerste laag wordt de adhesietoename duurzaam en onafhankelijk van de invloed van de omringende omgeving, d.w.z. gassen of oplosmiddelen. We schrijven dit toe aan de inbedding van de veronderstelde goudoxidelaag tussen twee gesputterde Au-lagen. In meer detail hebben we de hypothese dat de waargenomen versterking van de adhesie kan worden verklaard door een verhoogde Au- SiO_2 -interactie op het grensvlak als gevolg van een polarisatie van de goudlaag door de vorming van het goudoxide op het Au-oppervlak. Deze nieuwe techniek stelde ons in staat om op grote schaal verschillende SiO_2 -ondersteunde structuren met Au micro/nano afmetingen te fabriceren zonder gebruik van een metalen adhesielaag. Met deze techniek konden daardoor structuren, lijnen en punten, met dimensies van enkele honderden nanometers tot enkele micrometers zonder het gebruik van extra adhesielagen worden gefabriceerd. Onze techniek creëert nieuwe

mogelijkheden voor de vormgeving van Au micro/nano-structuren op SiO₂-substraten. Deze goud nano-structuren zijn erg gewild voor biosensing en nanofotonische toepassingen, vanwege de afwezigheid van de metalen adhesielagen.

In **Hoofdstuk 6** hebben we gevonden dat platina (Pt) nanodeeltjes, na annealen bij een hoge temperatuur van 1000°C indalen in amorf kwartsglas of thermische oxide silicium substraten. Vergelijkbaar met de eerder gerapporteerde indaling van Au-nanodeeltjes, blijven de ingedaalde Pt-nanodeeltjes via conische nanoporiën in contact met het oppervlak van de substraten en neemt de afmeting van de Pt-nanodeeltjes af met toenemende diepte van de nanoporiën. We leggen dit verschijnsel als volgt uit: het transport van de platinadeeltjes wordt gedreven door de vorming van vluchtig platinaoxide, dat ontstaat doormiddel van de reactie van het platina met atmosferische zuurstof, waarbij dit platinaoxide verdampt naar de omgeving. Dit fenomeen was eerder aangetoond voor goud, maar we vonden dat het gebruik van Pt een veel betere beheersbaarheid biedt van dit fenomeen dan het gebruik van Au. Vanwege de hoge dampspanning van platinaoxide is de indaling van de Pt-nanodeeltjes tot geoxideerde silicium (SiO₂) -substraten sneller dan van de Au-nanodeeltjes. Bij het annealen op hoge temperatuur vonden we ook dat de aggregatie van Pt-nanodeeltjes op het substraatoppervlak onbeduidend is, in tegenstelling tot de aggregatie van Au-nanodeeltjes. Dientengevolge worden de Pt-nanodeeltjes uniform ingesloten in de substraten, wat leidt tot een mogelijkheid voor het fabriceren van dichte nanopore arrays. Bovendien stelt het gebruik van geoxideerde Si-substraten ons in staat de diepte van de nanoporiën nauwkeurig te regelen, aangezien de indaling van de Pt-nanodeeltjes op korte afstand boven het SiO_x/Si-grensvlak stopt. Met behulp van deze methode verkregen we, na opvolgende ets stappen, een membraan met een grote dichtheid van nanoporiën met diameters tot kleiner dan 30 nm. Met deze makkelijk beheersbare en eenvoudig uit te voeren methode biedt deze fabricagemethode een alternatief voor snelle patterning van dichte arrays van nanoporiën in siliciumoxide tegen lage kosten.

In **Hoofdstuk 7** hebben we microfluïdische technologie toegepast voor katalyseonderzoek. Microreactoren zijn gefabriceerd en geïntegreerd met arrays van edelmetaal nanodeeltjes. De gefabriceerde microreactor bestaat uit een bovenste deel van glas, dat een microkamer en twee distributiekkanalen bevat, die anodisch gebonden zijn aan een onderste deel, dat een array (3×3 cm²) van edelmetaal nanodeeltjes bevat op een substraat van geoxideerd silicium. De gefabriceerde microreactoren werden gebruikt om de oxidatie van koolmonoxide op de chip uit te voeren. Door gebruik te maken van de twee distributiekkanalen was de stroom gelijkmatig verdeeld in de microkamer, waardoor homogene reactieomstandigheden werden gecreëerd. Het gebruik

van deze microreactoren biedt mogelijkheden om de reactantstromen nauwkeurig te regelen bij zeer lage stroomsnelheden en om de volumeverhouding van producten tot reactanten te maximaliseren.

In **Appendix F**, hebben we een robuuste en eenvoudige techniek voor grootschalige fabricage van vrijstaande en sub- μm dunne PDMS-membranen vermeld. Hierbij hebben we de soft-lithografie techniek gecombineerd met reactieve plasma-etstechnieken. Met behulp van deze gecombineerde fabricagetechniek hebben we met succes de fabricage aangetoond van vrijstaande PDMS-membranen, met verschillende diktes onde de micrometer, tot 600 ± 20 nm. De poriën in het membraan hadden een diameter van 810 ± 20 nanometer over gebieden van 3 cm in diameter. Door de eenvoudige procedure biedt onze fabricagetechniek de mogelijkheid voor grootschalige fabricage van sub- μm PDMS membranen, die geschikt zijn voor productie met hoge opbrengst tegen lage kosten. We hebben het potentieel van onze membranen als celweeksubstraten voor biomedische toepassingen aangetoond door endotheel cellen op de membranen te kweken in een Transwell-achtige opstelling.

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Appendix F

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About the Author

Hai Le-The was born on 24 March 1989 in Bien Hoa city, Vietnam, where he completed his primary education at the Phan Dinh Phung school in 1999, and his secondary education at the Tam Hoa school in 2004. In 2004, he passed the entrance exam of the Luong The Vinh high school for the gifted students, where he focused his study mostly on physics and mathematics. After finishing in 2007, he became a student of Bach Khoa University – one of the best technical universities in Vietnam – with major in Electronics and Telecommunication Engineering. He graduated his Bachelor in 2012 with the first-class honor degree, in which he was ranked first among 600 students graduated in that year. In August 2012, he was granted the Norwegian Quota Scholarship Scheme for doing his Master in Micro- and Nanosystems Technology at University of South-Eastern Norway in Norway. There he started his early stage of research on Lab-on-a-Chip and Microfluidic fields under the supervision of prof. dr. philos. Frank Karlsen. He joined in a research project, named Intelligent Health and Care Technology, in which he worked in close collaboration with researchers from NorChip AS and ORP companies. After completing his Master, he went back to Vietnam in 2014, and worked as a researcher at the Institute for Computational Science (INCOS) of the Ton Duc Thang University for 5 months, where he continued his research in Microfabrication and Microfluidics. In April 2015, he joined the BIOS Lab-on-a-Chip group, MESA+ Institute for Nanotechnology at the University of Twente in the Netherlands as a PhD candidate in a research project within the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC). His PhD research focused on nanomachining regular noble metal/ceramic structures for catalytic applications, in which he worked in close collaboration with many researchers from different research groups involved in the MCEC. His PhD research was supervised by his promotor: prof. dr. Jan C. T. Eijkel and prof. dr. ir. Bert M. Weckhuysen, and co-promotor: prof. dr. ir. Albert van den Berg. During his PhD, he also got married with Hoa Thi Khanh Tran on 16 April 2017 in Vietnam.

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