Nanomachining using Gold

Creation of nanoparticle arrays and nanopores

Lennart de Vreede

NANOMACHINING USING GOLD

CREATION OF GOLD NANOPARTICLE ARRAYS AND NANOPORES

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1. Introduction

1.1 Motivation

One of the health targets of the Sustainable Development Goals set by the United Nations is to end the disease tuberculosis by 2030. [1] In 2015, 1 in 3 HIV-positive patients died because of tuberculosis. The death rate due to tuberculosis has already dropped by 47% worldwide between 1990 and 2015. The disease is caused by a bacteria called *Mycobacterium tuberculosis*, which typically enters the body via the airways to end up in the lungs. In the lungs it can multiply and cause an infection of the alveoli, or in other words, pneumonia. *Mycobacterium tuberculosis* can be active or latent. A risk of the latent state is the unawareness of the disease until long after infection, creating a chance of reactivation of the bacterial infection when the immune system of the host is weak. One of the targets of the Millennium Development Goals [2] was halting and reversing the tuberculosis epidemic. This goal has been met. The Sustainable Development Goals for health envision that apart from tuberculosis, also the epidemics of AIDS and malaria will end in 2030. Vaccination, drug development and diagnostics improvement are the key tools to achieve these goals. [3] A good candidate technology for diagnostics improvement could be nanotechnology. On the nanoscale, materials exhibit interesting properties such as plasmonic activity, which properties could potentially be used in a protocol for detection of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) of the infecting organisms.

1.2 Aim

The original aim of the STW project that this thesis forms part of, is to investigate if a cost effective point-of-care device can be manufactured which is able to fast and accurately detect the RNA of *Mycobacterium tuberculosis* from a humane sputum sample. The method is based on a plasmonic detection protocol for DNA/RNA developed at the NanoBioPhysics group at the University of Twente. [4] The work reported in this thesis was carried out as part of a collaboration between the BIOS Lab on a Chip group and the NanoBioPhysics group. The investigation of a manufacturing scheme for the RNA detection area within the point-of-care device thereby was the task of the BIOS Lab on a Chip group and the investigations related to the development of the assay RNA were set to be performed at the NanoBioPhysics group, [5] The benefit of a point-of-care approach for rooting out a disease like tuberculosis, is to take the diagnostics away from a centralized laboratory and into the field. In this way a human carrier of *Mycobacterium tuberculosis* can be identified sooner and treatment can be provided as soon as possible. A point-of-care device should be equipped with all required analysis steps, i.e. methods for cell lysis, DNA/RNA purification and DNA/RNA detection. As the reader will discover in this thesis,

the original aim was not met for the BIOS Lab on a Chip group, as the detection area could not be manufactured in the way designed. The research however led to the discovery of an interesting phenomenon which in future can find many applications, i.e. the formation of nanopores by heating gold on silica.

1.2.1 Ribonucleic acid

From elephants to bacteria, all living organisms are built up from cells. [6] Independent from the organism species, all cells have some components in common. Figure 1.1 shows a sketch of a prokaryotic cell, in this case a bacterial cell. It contains a cell membrane with cytoplasm, biomolecules and the DNA genome of the organism. Bacterial species differ from each other based on differences in the nucleic acid sequence of their DNA. DNA molecules and many other biomolecules play a crucial role in the metabolism of the organism and they are all found in the cytoplasm of the prokaryotic cell. These biomolecules contained in the bacteria include proteins, enzymes, RNA molecules and plasmids. Amongst these biomolecules RNA has several important functions. Messenger RNA is the intermediate molecule to translate the information stored in the DNA molecule to produce proteins and enzymes. Messenger RNA is the single stranded complementary replica of a double stranded DNA. [6] Apart from messenger RNA, ribosomal RNA (rRNA) exists in the cell, which is a structural component of the ribosome, the biomolecule essential for protein synthesis.

Figure 1.1 A schematic representation of the bacterial cell. Showing the cytoplasm with a variety of biomolecules like proteins. Also the DNA, RNA and plasmid are kept in the cytoplasm. [6]

Since the mycobacterium rRNA contains a sequence of nucleic acids that is specific for *Mycobacterium tuberculosis*, and active cells contain several 1000s of copies of this molecule, rRNA is a very interesting target for use in detection of tuberculosis. [7]

1.2.2 Plasmonics

The principle that will be used for detection is based on the plasmonic activity of gold nanoparticles. Plasmonic activity is caused by interaction of the electrons of a gold nanoparticle to an incident electromagnetic (light) wave as shown in figure 1.2. [8] The interaction with the electromagnetic wave induces an electron cloud resonance in the gold nanoparticle. The frequency at which the electron cloud resonates depends on the size of the particle, the material properties of the particle, the shape of the particle and the refractive index of the surrounding medium. Plasmonic resonance of the gold nanoparticles can be observed when they are inspected on a glass slide with dark field illumination using a microscope. Dark field microscopy prevents light transmission in the direction normal to the surface, hence the name dark field. Instead, the light arrives at an angle and enhances the contrast of objects on the stage surface by collection of scattered light off these objects. [9]

Figure 1.2 Left: schematic representation of dark field microscopy. [10] Right: A close-up demonstrating plasmonic resonance of the electron cloud and light scattering as a reaction to an incident electromagnetic wave. [11]

Interaction of the incident electromagnetic wave with the gold nanoparticle causes extinction of the electromagnetic wave. This extinction is the sum of light absorption causing heat production [12], and scattering. [5] Depending on the four criteria mentioned

above the absorbed and scattered light have specific wavelengths and intensities. In an example given by van Dijk, [8] a spherical gold nanoparticle in a medium with refractive index of $n = 1,5$ and a diameter of 20 nm has an absorption peak at a wavelength of $\lambda = 545$ nm but no scattering peak. A spherical gold particle with a diameter of 60 nm, also in a medium with refractive index $n = 1,5$ has an absorption maximum at a wavelength of $\lambda = 555$ nm and a scattering peak at a wavelength of $\lambda = 560$ nm. Figure 1.3 shows the colours in the visible spectrum and the accompanying frequencies. [13] The latter particle will thus appear under a dark field microscope as a source of green/yellow light. Since the wavelength of the scattered light is also a function of the refractive index of the environment, the principle of a sensor is created. Moreover, since gold does not react with oxygen, it is stable in typical experimental conditions encountered in sensing of biological samples making gold nanoparticles excellent candidates for plasmonic sensors.

Figure 1.3 The visible spectrum. The colors vary according to their wavelength. [13]

Figure 1.4 displays randomly distributed gold nanoparticles with an average diameter of 80 nm on a glass slide observed with dark field illumination microscope in air (refractive index $n = 1$). These gold nanoparticles with 80 nm diameter scatter the light at a wavelength of $\lambda = 525$ nm and thus appear green.

Figure 1.4 Randomly distributed gold nanoparticles on a glass slide. The background appears black in the dark field microscopy. The gold nanoparticles appear green.

1.2.3 Detection protocol

The *Mycobacterium tuberculosis* rRNA will be isolated from the cells by lysis in order to be used in the detection protocol, which is explained in figure 1.5. [14][15] The solution obtained from the lysed cells will be brought into contact with a transparent surface with RNA oligomer functionalized gold nanoparticles.

Figure 1.5 The proposed protocol by Verdoold et al. [4] An immobilized gold nanoparticle on a transparent surface is oligomer functionalized to capture sample RNA. After a washing step, to remove unbound oligomers, the sample material is added to allow RNA specific binding to the functionalized gold nanoparticle. Secondary nanoparticles, functionalized to hybridize to the remaining strand of the *Mycobacterium Tuberculosis* RNA, are then added. If hybridization of the sample material to the functionalized gold nanoparticle has taken place, the secondary functionalized gold nanoparticle is bound. This bond is made visible by dark field microscopy by a shift in the wavelength of the scattered light. [16]

The RNA oligomers will function as receptor. [4] The oligomers will be bound to the gold using a thiol bond. The oligomer sequence is tailored for specific capturing of the *Mycobacterium tuberculosis* RNA from the bulk lysed solution, without attachment of any other biomolecules from the lysed sputum sample. Once the *Mycobacterium tuberculosis*

RNA has bound, a secondary gold nanoparticle can be added. This secondary particle is functionalized with a second oligomer of synthetic RNA, which can hybridize with the remainder of the *Mycobacterium tuberculosis* RNA strand. Once hybridization has taken place, the two gold nanoparticles are bound together at close distance, causing the scattering wavelength peak to shift towards a higher wavelength by interaction of the electron clouds in the two nanoparticles. For an 80 nm gold nanoparticle the scattering wavelength at the binding of a suitably sized secondary gold particle shifts from green to red in the spectrum, as shown in figure 1.6. In principle, this method can be used for single molecule detection and is therefore suitable for the detection of very low concentrations of the RNA of *Mycobacterium tuberculosis*. Any hybridisation event with the gold nanoparticles on the surface would then become visible after addition of the secondary gold nanoparticles.

Figure 1.6 Secondary gold nanoparticles were bound to the gold nanoparticles from figure 1.4. The inset shows the resulting peak shift from green to red.

Verdoold et al. [4] use a random distribution of gold nanoparticles immobilized on the surface. The random distribution could lead to clustering of particles prior to sensing which could negatively affect the assay by decreasing the amount of detectable binding events. To optimise the detection, a regular, 5 μm evenly spaced, dense array of monodisperse gold nanoparticles of the optimal diameter would thus be preferable. This would maximize the number of detectable single binding events per unit surface while preventing gold nanoparticles from being too close. Manufacturing this array in a cost effective way is an important goal of the work reported in this thesis.

1.3 Approach

For manufacturing a sensor surface with a high density array of gold nanoparticles (80 nm diameter and 5 μm spacing), using a technology which is simple, cheap and reliable, several fabrication technologies were considered. Manufacturing of very small features can be done with cleanroom fabrication techniques, which are known from the field of microelectronics, such as lithography, etching, and deposition. Over the years a large

collection of fabrication technologies has been developed. A morphological analysis was performed to investigate which method is most suitable. The various techniques in the overview are given below as well as the morphological analysis.

1.3.1 Stretching a polydimethylsiloxane (PDMS) substrate

An array of gold nanoparticles could be created by placing a monolayer of gold nanoparticles on a stretchable PDMS substrate.[17] Millyard et al. reported on a self-assembled, 1-dodecanethiol coated, gold nanoparticle monolayer which is created on the interface of hexane and water. A transfer to a flexible substrate is performed and subsequent omnidirectional stretching of the substrate results in a spacing between the particles of a few 100 nm. However, to create the 5 μm pitch between the particles required for our application, the PDMS must be overstretched. This overstretching of PDMS results in cracking of the layer, which is an elegant method for the creation of nanochannels but in our case will cause irregularities in the formation of a controlled array. [18]

1.3.2 Nanosphere lithography and annealing

Nanosphere lithography is a very cost effective method for the fabrication of periodic arrays of nanoparticles. [19] A layer of polystyrene nanospheres can be deposited on a substrate surface by spin coating, drop coating or thermoelectrically cooled angle coating. [20][21][22] The densely packed polystyrene nanospheres can then function as a mask because through the voids between the spheres, evaporated or sputtered material can reach the surface. When the nanospheres are subsequently released from the surface, a periodic array of triangular nanostructures is left. The pitch between the features depends on the nanosphere diameter. Additional annealing of the features is also investigated and showed that nanometre sized particles could be formed from the triangular features. [23] The direct relation between the particle spacing and size however makes this method less suitable for our purpose.

1.3.3 Photolithography and annealing

Another cost effective method for array fabrication is by means of standard cleanroom technologies like photolithography and metal deposition. It is known that a uniform thin film of gold on a surface which is annealed by furnace or flame shows dewetting of the gold to form an irregular pattern. [24] A patterned thin film applied by standard cleanroom processing techniques, including photolithography, sputtering and lift-off, on a silica substrate could form a regular pattern. When followed by annealing at high temperatures, dewetting of the periodic gold patches into a periodic gold nanoparticle array should be

possible. [23] [25] Photolithography and annealing are cost-effective techniques, which can provide high volume production possibilities and low-complexity.

1.3.4 Electron beam lithography

Using an electron beam for writing a pattern guarantees a high accuracy, as the spot size of an electron beam is typically in the order of 10 nm in diameter. [26] A polymethyl methacrylate (PMMA) resist is coated on a substrate followed by a high energy electron beam bombardment of the PMMA in a high vacuum chamber. On the locations of bombardment the PMMA is crosslinked. [27] To ensure high precision when a pattern is written on an insulating substrate, a chromium coating is usually applied to avoid charge build-up of the substrate and uncontrolled crosslinking of the PMMA resist. Electron beam lithography is, in combination with evaporation of a gold layer, an interesting method to achieve the required 80 nm diameter gold nanoparticles. However, use and maintenance of an electron beam machine is costly in terms of purchase and maintenance. [27] Moreover, electron beam lithography requires a serial production strategy, as every single substrate has to be separately written.

1.3.5 Laser interferometric lithography

Laser Interferometric Lithography (LIL) is a maskless technique which uses a laser beam which is split up into two separate beams. [28] The two beams are recombined and an interference pattern is created, visualised as a sequence of bright and dark spots next to each other, depending on the shift of the phase. The widths of the bright and dark spots are similar and determined by the wavelength of the light. When the pattern is projected onto a photoresist coated substrate, the photoresist becomes more strongly exposed at the bright spots than at the dark spots. The intensity settings and phase of the laser beam are fixed. The substrate is then rotated 90° and exposed again. In this way the double exposed spots will be exposed just enough to be developed into holes in the photoresist layer. Feature sizes as small as 50 nm in diameter are feasible using LIL. However, since the widths of the bright and black spots are the same, the pitch between the exposed areas is comparable to the desired feature size. Therefore, a pitch of 5 µm will not be possible using laser interference lithography.

1.3.6 Polymer coated gold nanoparticles

A polymer-assisted method could be used for manufacturing of periodically spaced gold nanoparticle arrays. [29] When a gold nanoparticle is encapsulated in polystyrene-*b*-poly (HAuCl₄) diblock copolymer, self-assembly of the diblock copolymer evenly spaces the particles when deposited on a solid surface. A subsequent plasma treatment removes the diblock copolymers and an array of gold nanoparticles remains on the solid surface. A pitch

between particles of below 2 μm has been reported, however this result was obtained with assistance of electron beam writing. This method thus will need much development to be suitable for our purpose.

1.3.7 Nanoimprint Lithography

Nanoimprint lithography is a technique which uses a transparent silica master to imprint into a photoresist layer on a substrate. [30] The silica masters are usually made by means of electron beam writing and subsequent etching of the silica. Photopolymerization of the photoresist is performed by UV exposure when the master is imprinted into the photoresist layer. Since the masks are prepared using electron beam writing, feature sizes of 80 nm can easily be manufactured. However, nanoimprint lithography also requires dedicated equipment, with accompanying high cost of use and maintenance.

1.3.8 Shadow mask

The use of a shadow mask allows bulk processing of arrays. [31][32] A pattern of through holes in a thin layer is placed above a substrate. The substrate, together with the shadow mask are placed in a sputtering machine or metal evaporation clock and can be used to produce arrays. The membrane thickness should be thick enough to overcome buckling, which is membrane deformation due to internal material stresses, however thin enough to avoid clogging of the through holes during metal deposition. Buckling and bending of a template membrane could transfer undesired irregularities to the substrate. [33]

		Weight factor					
		Size Au-particle	Spacing Au-particle	Shape Au-particle	Tolerance	Bulk process	Sum
Fabrication technology	Stretch self-assembled GNP layer (balloon)	1	0	1	1	0	3
	Stretch polystyrene						
	Nanosphere lithography	3	3	1	1	3	11
	Photolithography and annealing	3	3	1	3	3	13
	E-Beam lithography	3	3	3	3	0	12
	Laser interferometric lithography	0	0	3	3	1	7
	Polymer coated gold nanoparticle	1	0	1	3	1	6
	Nano imprint lithography	3	3	3	3	1	13
Shadow mask	3	3	1	3	1	11	

Figure 1.5 A morphological analysis of nanoparticle array manufacturing methods. Zero points are awarded if the weight factor compared to technology is poor, 1 point if the weight factor compared to technology is acceptable and 3 points if the weight factor compared to technology is good.

A morphological analysis of the aforementioned techniques is shown in figure 1.5. The weight factors are: gold particle size, gold particle spacing, gold particle shape control, tolerance and the applicability of the technology in bulk processing. 0 points are awarded if the weight factor compared to technology is poor, 1 point if the weight factor compared to technology is acceptable and 3 points if weight factor compared to technology is good.

The photolithography and annealing method scores highest, followed by nanoimprint lithography and electron beam lithography. Then shadow masking, nanosphere lithography, laser interference lithography, polymer coated gold nanoparticles, and lastly the stretching of self-assembled gold nanoparticles follow. For this thesis we therefore focused on the photolithography and annealing method (chapter 2).

1.4 Thesis outline

This thesis describes the results of the attempt to manufacture an array of gold nanoparticles of 80 nm in diameter by using a photolithography and annealing approach to

create the detection area for rRNA of, for example, *mycobacterium tuberculosis* required for this project. The original aim of the project, to manufacture an array of gold nanoparticles and to reach a method for cost-effective, accurate and fast detection of rRNA has not been met. However, an interesting phenomenon was discovered instead that is further investigated.

In chapter 2 of this thesis the dewetting of photolithographically patterned gold by annealing is reported and discussed. The phenomena occurring during the dewetting, such as pinch-off, evaporation, crystallization and ridging are introduced and explained in more detail, which are followed by the experimental results.

In chapter 3 the creation of nanopores as a result of heating the photolithographically patterned gold is demonstrated and an explanation for this previously not reported phenomenon is given.

To enable a broader field of applications of the fabrication scheme developed in chapter 3, chapter 4 and 5 further develop the formation of nanopores in membranes. In chapter 4 the nanopore fabrication scheme is transferred from the original silicon oxide substrate to a silicon nitride membrane, resulting in a buckled membrane with nanopores after heat treatment. In chapter 5 the nanopore fabrication scheme is applied to silicon oxide membranes which are suspended in a silicon nitride membrane. Via this approach the buckling of the membrane no longer occurred after heat treatment. These developments were not related to applications for the detection of DNA/RNA.

The dewetting approach of chapter 2 did not result in the desired 80 nm diameter gold nanoparticles. Chapter 6 therefore reports on investigations in which electron beam lithography was as an alternative to the dewetting approach. A fabrication scheme for a microfluidic cell is also given in this chapter. Chapter 7 finally presents conclusions and a brief outlook.

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2. Dewetting of gold on fused silica

2.1 Introduction

As described in the first chapter, a regular array of gold nanoparticles is needed for the application in a photonic sensor for tuberculosis diagnosis. This chapter gives an overview of the experiments to use solid-state dewetting of gold on silica to create an array of gold nanoparticles with 80 nm diameter and a 5 μm spacing as needed for this sensor. An impression of such an array is shown in figure 2.1. The choice for silica as substrate material had a twofold reason. First, the substrate has to be transparent to enable optical detection. Second, silica has a melting temperature of 1713°C. Gold has a melting temperature of 1064°C and is known to start dewetting at temperatures around 400°C. [5] The substrate thus should provide a stable surface to dewet the gold at high temperatures. In order to ensure a cheap production process in view of the use in developing countries, a photomask of the smallest possible openings (600 nm) still allowing standard photolithography was employed.

Figure 2.1 Schematic representation of the gold nanoparticle array on a transparent substrate that needs to be manufactured. The diameter of the gold nanoparticles is 80 nm. The pitch between the gold nanoparticles is 5 μm .

2.2 Experimental

This experimental section describes the manufacturing processes used in the attempts to manufacture the 80 nm diameter gold nanoparticle array. Standard micro-manufacturing processes were used: first photolithography was performed, which was followed by

sputtering of gold, lift-off and a high temperature heat treatment. The choice for standard processes was made to decrease the final manufacturing costs in view of the final application which requires a cheap device.

The variable parameters for the 80 nm diameter gold nanoparticles in this chapter are;

- The deposited volume of gold
- Temperature of heat treatment
- Time of heat treatment
- Pressure during heat treatment

The volume of gold is controlled by the mask opening and the deposited gold layer thickness. The heating temperature and time are controlled by the settings of the furnace. The pressure is controlled by either working in ambient atmosphere or in a vacuum furnace at pressures down to 10^{-6} millibar.

2.2.1 Photolithography

In a micro - and nanofabrication process, cleanliness is essential. A single dust particle can unfortunately strongly influence the process steps and in the worst case one may have to discard the work.

The photolithography process is started with a standard cleaning of 100 mm diameter fused silica wafers in nitric acid (HNO_3) and hot nitric acid to remove any organic contamination from the wafer surface. The next step is a dehydration bake at 120 °C, to remove any residual water present on the wafer from the wet processing. After cooling of the wafers the photoresist is applied. The masks were designed to be used with positive photoresist. The resist is spin coated at 6000 RPM for 40 seconds and after a baking step of 1 minute at 95°C exposed to ultraviolet light with a dose of 12 mW/cm² through a photomask. Two types of mask were used in this work: a mask with circular openings of 2 µm in diameter and a mask with circular openings of 600 nm in diameter. The first mask was ordered from Deltamask B.V. Enschede. The second, with smaller features, ordered at Photonics Inc. The exposure time for the 2 µm mask openings was a standard setting of 4 seconds exposure. Using the mask with features of 600 nm in diameter means operating at a mask opening which is in the range of the wavelength of the near UV of the EVG 620 mask aligner which is 350-450 nm. This makes processing with the latter mask very close to the limitations of the equipment. An exposure time of 25 seconds is used. After exposure the substrates are developed using OPD4262 photoresist developer. After gold sputtering the wafers were stripped from photoresist by a lift-off process in acetone for 15 minutes. After lift-off the wafer was diced in 6 mm square chips.

2.2.2 Sputtered gold-layer uniformity

After photolithography a layer of gold was deposited onto the substrates using a sputtering clock. A power of 200 Watt, argon flow of 150 sccm and a pressure of $6,6 \times 10^{-6}$ millibar was used. The sputtering rate for gold at these settings is 47 nm/min. Quantification of the variation in the gold layer thickness, which would result in a variation of the final gold patches, was performed. The thickness non-uniformity on full wafers was determined by sputtering a layer of 60 nm thick on 3 wafers of which the results were averaged. The gold layer showed a thickness with below 0,3 nm variance across the wafers.

2.2.3 Anneal Furnace

The heat treatment is performed in a pottery furnace, suitable for high temperatures, manufactured by TOMA B.V. Volkel, The Netherlands. Figure 2.2 shows this furnace which has a maximum working temperature of 1200°C. The sample was placed on a ceramic table inside the furnace. After calibration the furnace showed a difference with the internal furnace thermocouple. The temperature, when the furnace is set for 1050°C, was actually found to be $1067^\circ\text{C} \pm 5^\circ\text{C}$.

Figure 2.2 The tabletop furnace from TOMA B.V.. Maximum working temperature 1200°C.

2.2.4 Vacuum furnace

A low pressure increases the gold evaporation rate, and can thus be used to decrease the gold nanoparticle size. [1] To enable experiments at lower pressures ranging from ambient pressure to $1,6 \times 10^{-6}$ millibar a vacuum tube furnace was used, which is shown in figure 2.3. The furnace was ordered from Nabertherm and was calibrated by the manufacturer.

The maximum temperature of the vacuum tube furnace is 1200°C. The vacuum pump used is a Pfeiffer Vacuum HiCUBE 80.

Figure 2.3 The vacuum tube furnace with connected vacuum pump. Maximum working temperature of the furnace is 1200°C.

2.3 Theory introduction

This section will address the various phenomena observed during the heat treatment. Starting as a gold patch, the gold atoms will become more and more mobile when heated and rearrangement of the gold atoms take place, which leads to dewetting of the gold from the silica. When this process takes place below the melting temperature of gold, it is known as solid-state dewetting, since the gold does not become liquid. A side-effect observed during dewetting is pinch-off. [2] This is the phenomenon that the gold layer not fully ends up as a single particle, but breaks up in smaller particles. The effect of pinch-off will be visible as small gold particles surrounding a larger central particle. Another observed phenomenon is ridging. [7] Ridging is the deformation of the silica surface on which the gold was patterned due to mobility of the silica. Finally, when gold nanoparticles are heated to close to their melting temperature, gold will evaporate, reducing the gold nanoparticle volume.

2.3.1 Interfacial energy

The air-gold-silica system has one gas phase and two solid phases. These phases are a sputtered layer of gold, a surface of silica, on which the gold is patterned and the air surrounding both solid phases. The reason for solid-state dewetting of the gold layer when heated is the fact that the initial system after sputtering is not at minimum interfacial energy

while the system strives for energy minimization. [8] The total interfacial energy is thereby determined by the contact area between the different phases and their respective interfacial energies.

The origin of the interfacial energy can be understood from figure 2.4, which depicts a slab of material (solid or liquid). Every atom in the bulk material experiences an equal attractive force in every direction from the surrounding atoms as depicted for atom b . Neighbouring atoms are however missing at the surface of the material, which results in a non-zero force balance for the surface atoms, as shown for atom a . This non-zero force F_r is directed into the material. The force is counteracted by a reactive force of the material, either stemming from small atomic displacements (solids) or a buildup of internal pressure in liquid droplets. These reactive forces are represented by the local force F_p .

Figure 2.4 The difference of atomic attractive forces F_b in bulk at point b and at the solid surface at point a . F_r represents the resultant force from the atomic forces F_a . Force F_r gives rise to a reaction force F_p which in a liquid droplet stems from the internal pressure acting from the bulk on the surface. As long as the system is in non-equilibrium, its atoms will rearrange to decrease surface energy and the system shape will develop towards the equilibrium shape.

2.3.2 Wetting

The situation described in 2.3.1 is valid in case the material borders a vacuum or gas, since no interaction with atoms from another phase is considered. When atoms of different phases interact (e.g. gold and silica), the interfacial energy will result from the $\text{SiO}_2\text{-SiO}_2$, $\text{SiO}_2\text{-Au}$ and Au-Au interactions, and energy minimization can involve reshaping of both materials, and the process can result in wetting or dewetting.

Wetting and dewetting of materials is a phenomenon which is probably best known from the behaviour of a liquid droplet on a solid surface. The surface energies of the droplet and the solid surface determine the final wetting condition and the accompanying contact angle. When a small amount of liquid has reached the stage in which it is in thermodynamic equilibrium with a solid, a macroscopic contact angle at the triple line is observed. This contact angle depends on the interfacial energies of the liquid-vapor (γ_{lv}), solid-liquid (γ_{sl}) and solid-vapor (γ_{sv}) interface. The Young-Dupré equation relates the individual interfacial energies with the observed contact angle,

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl}$$

Figure 2.5 A liquid droplet on a surface with its accompanying contact angle, following Thompson. [2]

A liquid on a solid surface, as shown in figure 2.5, thus forms a droplet with a specific contact angle θ determined by the three interfacial energies. In case of full wetting the contact angle is 0° , in case of partial wetting a contact angle of between 0° and 180° forms, in case of mostly wetting between 0° and 90° , and in case of mostly non-wetting between 90° and 180° , as shown in figure 2.6.

Figure 2.6 Three wettability conditions. a) full wetting, b) partial wetting and c) dewetting of a solid surface and liquid, following Thompson. [2]

2.3.3 Crystallization and surface energy

A sputtered gold film is in a metastable phase. When the gold film is heated, gold atoms become mobile and as a result reorganization and finally crystallization can be expected as the system moves to the lowest energy state. Gold has a face-centered cubic (fcc) unit cell and the gold crystals have multiple facets, making it a complex non-isotropic structure. The surface energies of the different crystal planes will vary depending on the orientation of the atomic arrangement. [3] A Wulff construction [4] (or a Winterbottom-construction when a crystal is located on a non-deformable substrate) can be used to visualize the crystal surface energies. An example of a Wulff plot is given in figure 2.7. It is a representation of the surface energies of the individual crystal planes as depending on the interatomic distances in the crystal lattice. A closer crystal stacking results in an energy minimum, which is depicted by a shorter vector normal to the crystal plane. The larger the interatomic distance, the higher the energy required for binding, the longer the vector depicted.

Figure 2.7 A Wulff plot, following Kaplan et al. [4], shows the atomic stacking of the crystal and deducts the surface energies from the internal atomic energies. The atomic energies are depending on the atomic spacing. If the spacing is large, more bond energy is required. For example if we follow the dashed normal line a we see it crosses three atoms with no space in between. This stacking is very tight, represented in a short vector a' normal to the dashed line. If we now follow the dashed line b we see gaps between the atoms, indicating more energy is required for those bonds. This results in a larger vector b' normal to dashed line b.

2.3.3.1 Thermal expansion strain

Gold and silica have a mismatch in thermal expansion coefficients. [4] Since heating of gold takes place on top of the silica surface a certain amount of mechanical stress is introduced in the system on heating. A formula for the strain ε_T thus generated was derived by Thompson [2] and gives,

$$\varepsilon_T = \int_{T_0}^T (\alpha_s - \alpha_f) dT + \varepsilon_0 \approx (\alpha_s - \alpha_f) \Delta T + \varepsilon_0$$

In this equation the thermal expansion coefficient of the substrate is given by α_s , and the thermal expansion coefficient of the film is given by α_f . ΔT represents the change in temperature, and ε_0 is the strain at the starting temperature. Since the thermal expansion coefficient of gold is much higher than that of silica, the resulting strain will be directed outward, against the dewetting direction. It is thus expected that this strain can be neglected as it will only temporarily delay the dewetting.

2.3.3.2 Atomic mobility in the liquid and solid state

The temperature at which the gold atoms leave their lattice position in the bulk of the material is known as the melting temperature, which in the case of gold is at 1064°C. At this temperature gold becomes a liquid. As we will see, dewetting already occurs at temperatures much lower than the melting point, depending on the gold layer thickness, implying atomic movement in the solid state. Solid-state dewetting of a 20 nm layer for example already occurs at 400°C. [5] In this case of solid-state dewetting the gold atoms at the surface, which are more mobile, will rearrange to minimize the system interfacial energy. It is not certain what exact shape the gold particles have in our system at temperatures that approach the melting point, Here we will assume a crystal shape with roughened edges. [6] The roughened edges result from the increased mobility of the gold atoms.

From the material datasheet from the fused silica supplier, PlanOptik GmbH, we know that the glass transition temperature of this fused silica glass lies around 1200°C, at which temperature the atoms will become more mobile. Some liquefaction of the silica surface is not ruled out in our experiments as the experimental temperatures are close to the glass transition temperature.

2.3.4 Ridging

Often deformation of a ceramic surface is seen when a metal droplet on its surface is heated. A ridge is formed around the droplet and the phenomenon is therefore known as ridging. [7] The ridging is explained by ceramic transport along the interface with the metal

(where it is assumed to have a higher mobility) by surface diffusion toward the vapor-liquid-solid triple line where it is deposited, a process that in its entirety is driven by interfacial energy minimization. A related phenomenon is thermal grooving of grain boundaries of crystalline metal films which occurs due to local differences in surface energies of the crystal plains involved. [8]

When a system of a gold crystal on a silica surface in air is not in equilibrium, the different phases experience a torque at the triple line which results from the different interfacial energies. If the silica is mobile, it will then be deposited in those locations where it reduces the torques between the different phases. The torques are given by $\partial\gamma/\partial t_i$, with γ as the interfacial energy (J/m^2) and t_i as the vectors in the plane of the i th ($i = 3$) interface. The vectors are normal to the triple line and pointing away from it. The systems final equilibrium will be reached if this torque terms disappear by material reorganization. This equilibrium is described by the Smith equation [4]

$$\gamma_{VL}/\sin \theta_S = \gamma_{SL}/\sin \theta_V = \gamma_{SV}/\sin \theta_L$$

Here θ is the angle of the different phases; vapor (v), silica (s) and gold (l). Ridging in metal ceramic systems occurs at a triple line. [10] The small dimensions of the systems used here allows rapid reshaping due to fast diffusional transport.

Figure 2.8 The process of ridge formation under a small gold crystal over time. The contact angle θ_L changes to θ'_L and the location of the triple line changes due to reorganization of the ceramic material at the metal-ceramic interface.

In figure 2.8 the interfacial deformation in the case no gold evaporates is shown. The volume of the metal in this case is assumed to remain unchanged. The ceramic substrate however allows material reorganization along the interface between the metal and the ceramic, resulting in a change of the contact angle from θ_L to θ'_L and of the location of the triple line.

2.3.4.1 Pinch-off

When a thin layer of metal undergoes solid-state dewetting, it is often found that small particles become separated at the edges of the layer as shown in figure 2.9. [2] The related phenomenon is called pinch-off. Pinch off occurs when, upon heating, the metal starts to move away from the vapor-liquid-solid triple line. The rearrangement of the metal upon heating is both upward and inward, creating a convex surface which increases in height above the initial height of the layer. The edge retracts and piles up metal on top, deforming the top layer directly behind this bulge due to the inward motion of the edge. The curvature is rising upward, while next to the upward curvature a valley is created because metal from the valley also accumulates towards the bulge. The combined effects are depleting the metal layer next to the bulge, leading finally to pinch-off of the metal layer. When the metal is sufficiently thick however, the triple line can retreat before breakup occurs. The edge retraction rate J of the metal upon heating is described as [3]:

$$J = - \left(\frac{D_s \gamma_f N_s \Omega}{kT} \right) \nabla_s \mu$$

Here D_s is the surface diffusion, γ_f the surface energy, N_s the number of surface atoms per area, Ω the atomic volume, k Boltzmann's constant, T the absolute temperature and μ the local surface curvature.

Figure 2.9 Process of pinch-off as described by Thompson. [2] Starting with a sharp edge in a), the liquid material both retracts and forms a round edge, higher compared to the starting height.

2.3.5 Gold evaporation

Meng et al. report that gold patches of 650 nm x 650 nm with a thickness of 20 nm when dewetting can be reduced to a controllable particle size down to 10 nm in diameter by evaporation (or sublimation). [1] Regulation of the pressure of the Argon in which the gold

is annealed provides the central processing parameter. In this case gold atoms evaporate out of the gold particle, decreasing the gold volume and contributing to the particle retreat from the initial triple line. Two consecutive mass transfer processes take place, namely first the evaporation at the gold particle surface and then the diffusion of the evaporated gold into its surroundings. In the paper it is calculated that the reduction rate of the radius of the metal nanoparticles R_{Au} is described by [1]:

$$-\frac{d(2R_{Au})}{dt} = \frac{2k}{\rho_l} \rho_v^{sat} \left[\frac{1}{1 + \alpha R_{Au} P} \right]$$

Here k is the evaporation rate constant, ρ_l the bulk density of the gold particle, ρ_v^{sat} the saturated vapor density, α a constant related to the diffusion coefficient of gold vapor atoms and P the environmental pressure. It is reported that the gold evaporation rate increases when working at a lower pressure.

2.4 Results and Discussion

To find the optimal conditions for dewetting to produce the desired array, various chips with deposited patches of gold were heated to temperatures of 500°C, 700°C and 900°C for 6, 12, 18, 24, 30 and 36 hours either at ambient or low pressure. Based on this work subsequently the higher temperature range of 990°C to 1030°C was investigated as well. The ramp-up time for the furnace experiments in every case is 1 hour. The shape from the initial photolithographically manufactured gold patches of either 600 nm or 2 μ m in diameter and various thicknesses, changes by the treatment. A diverse collection of solid-state dewetted gold particles results, as shown below. In some cases the result is a solid-state dewetted gold particle surrounded by even smaller gold particles, in some cases the result is a crystalline gold particle shape surrounded by a smooth surface and in some cases the result is a gold particle with the directly surrounding silica surface deformed. Below for every temperature measured the result of the 6 hours and 30 hours heat treatments are shown.

2.4.1 500°C temperature treatment

The images are made with a high resolution scanning electron microscope (HRSEM) and have been adjusted to have the same scale. A scale bar is given for each image set.

2.4.1.1 Ø 600 nm, 10 nm thickness

Figure 2.10a The result of heat treatment after 6 hours; Figure 2.10b the result after 30 hours. Scale bar in both cases represents 200 nm.

Figure 2.10 shows the results of dewetting of a gold layer with an initial diameter of 600 nm and an initial thickness of 10 nm which is heated to 500°C. Pinch-off effects, visible as small satellite particles, are observed regardless of the heating time, as expected because pinch-off occurs in the initial stages of heating. The average diameter of the measured central particle for 6 hours of heat treatment was 436 nm, with a standard deviation of 32 nm (n=8). The average particle diameter for 30 hours of heat treatment was 220 nm, with a standard deviation of 38 nm (n=8). These dimensions probably depend on the amount of gold which got pinched-off from the dewetting layer. It is seen that the shape of the central particle is irregular. We hypothesize that this is because at this temperature the thermal energy is insufficient to allow the retreating gold patch to overcome pinning barriers at the silica surface.

2.4.1.2 Ø 600 nm, 60 nm thickness

Figure 2.11a The result of heat treatment after 6 hours; Figure 2.11b the result after 30 hours. Scale bar in both cases represents 200 nm.

In figure 2.11 it is shown that heating of a gold layer with an initial thickness of 60 nm and diameter of 600 nm results in a single central particle after dewetting, without satellite

particles. Very little to no pinch-off has taken place as the initially thicker gold layer did not allow this and the dewetting thus has not reduced the central gold particle size. The shape of the gold particle is again irregular, for which we expect the same cause as in the previous case. The average particle diameter (of the measured central particle) for 6 hours of heat treatment was 624 nm, with a standard deviation of 67 nm (n=8). The average particle diameter for 30 hours of heat treatment was 610 nm, with a standard deviation of 91 nm (n=8). It can thus be concluded that at the temperature of 500°C not much evaporation takes place.

2.4.1.3 Ø 2µm, 10 nm thickness

Figure 2.12a The result of heat treatment after 6 hours; Figure 2.12b shows the result after 30 hours. Scale bar in both cases represents 500 nm.

Figure 2.12 shows that the dewetting of a 2 µm diameter patch with 10 nm initial thickness did not result in similar pinch-off as for the 600 nm mask opening used for fabrication of the structures shown in figure 2.10 and 2.11. The use of a deposited layer of 10 nm thickness thus not always leads to pinch-off. Reasons could be a difference in surface roughness of the substrate and/or small differences in deposited thickness. The average particle diameter (of the measured central particle) for 6 hours of heat treatment was 1285 nm, with a standard deviation of 128 nm (n=8). The average particle diameter for 30 hours of heat treatment was 641 nm, with a standard deviation of 41 nm (n=8).

2.4.1.4 $\varnothing$ 2 μ m, 60 nm thickness

Figure 2.13a The result of heat treatment after 6 hours; Figure 2.13b shows the result after 30 hours. Scale bar in both cases represents 500 nm.

Figure 2.13, where a 2 μ m diameter and 60 nm thick gold patch is heated to 500°C for different times, again results in irregularly shaped particles and the absence of pinch-off satellites. The average particle diameter (of the measured central particle) for 6 hours of heat treatment was 899 nm, with a standard deviation of 95 nm ($n=8$). The average particle diameter for 30 hours of heat treatment was 1270 nm, with a standard deviation of 202 nm ($n=8$).

If we compare the results of applying various thicknesses and mask diameters in the 500°C experiments, it can be concluded that dewetting occurred and that an irregular particle shape was obtained. The 10 nm layer thickness patches resulted in central particles of the smallest diameter due to pinch-off, however at the cost of the formation of satellite particles. Particles obtained above in all cases were too large for application as a plasmonic based sensor array.

2.4.2 700°C Temperature treatment

Below the results are shown for heating of gold patches at 700°C for different durations. Again a 600 nm diameter patch and a 2 μ m diameter patch were used at different initial thicknesses.

2.4.2.1 Ø 600 nm, 10 nm thickness

Figure 2.14a The result of heat treatment after 6 hours; Figure 2.14b shows the result after 30 hours. Scale bar represents 200 nm.

In contrast to the results at 500°C, the dewetting at 700°C of gold patches of 600 nm diameter and 10 nm thickness resulted in crystalline particle shapes, that no more have irregular boundaries. Pinch-off of the 10 nm thickness gold layer was however still observed, creating an area with small particles surrounding a central dewetted crystalline particle. The central particle average diameter obtained was 196 nm, with a standard deviation of 11 nm ($n=8$), for a heat treatment for 6 hours. For the 30 hours heat treatment the average particle diameter was 238 nm with a standard deviation of 22 nm ($n=8$). We explain the occurrence of crystalline shapes at this temperature, in contrast to the irregular shapes obtained at 500°C, by the fact that the energy of pinning barriers for the retreating meniscus can be overcome at the higher temperature. No significant evaporation seems to take place at these temperatures, as the longer heat treatment does not result in smaller particles.

2.4.2.2 Ø 600 nm, 60 nm thickness

Figure 2.15a The result of heat treatment after 6 hours; Figure 2.15b shows the result after 30 hours. Scale bar represents 200 nm.

When a thicker initial gold layer was used, no severe pinch-off was observed. The dewetted particles shown in figure 2.15 have a hexagonal crystalline shape and the average diameter of the particles was 318 nm with a standard deviation of 14 nm (n=8). For the 30 hours heat treatment the average diameter of the particles was 355 nm with a standard deviation of 30 nm (n=8). This is a larger diameter as compared to the 10 nm layer, which can simply be explained by the thicker initial layer and the absence of pinch off as observed from the 10 nm layer.

2.4.2.3 Ø 2µm, 10 nm thickness

Figure 2.16a The result of heat treatment after 6 hours; Figure 2.16b shows the result after 30 hours. Scale bar represents 200 nm.

When a 2 µm gold patch with a layer thickness of 10 nm was annealed at 700C, the result shown in figure 2.16 was obtained. A crystalline shape can be observed. Surprisingly some pinch-off was observed as well, where the pinched-off particles also have obtained crystalline shapes. The average diameter of the gold particle after heat treatment for 6 hours was 391 nm with a standard deviation of 21 nm (n=8).

2.4.2.4 Ø 2µm, 60 nm thickness

Figure 2.17a The result of heat treatment after 6 hours; Figure 2.17b shows the result after 30 hours. Scale bar represents 200 nm.

The results of the dewetting of gold patches of 2 μm diameter and 60 nm thickness shown in figure 2.17 show clear crystal planes on the gold particle. Particles had an average diameter of 625 nm with a standard deviation of 26 nm ($n=8$) for the 6 hours heat treatment. The heat treatment of 30 hours resulted in an average particle diameter of 612 nm with a standard deviation of 19 nm ($n=5$). The size of the particle thus was not observed to decrease over time, indicating that evaporation at a temperature of 700°C is not substantial.

2.4.3 900°C Temperature treatment

Below the results are shown for heating of gold patches at 900°C for different durations. Again a 600 nm diameter patch and a 2 μm diameter patch were used at different initial thicknesses.

2.4.3.1 Ø 600 nm, 10 nm thickness

Figure 2.18a The result of heat treatment after 6 hours; Figure 2.18b shows the result after 30 hours. Scale bar represents 200 nm.

The dewetting at 900°C resulted in gold particles with a crystalline shape, with examples shown in figure 2.18. Pinch-off of the gold layer was again observed, creating an area with smaller particles surrounding a central dewetted particle. The dewetted particles have an average diameter of 227 nm with a standard deviation of 12 nm ($n=8$). The average particle diameter for the 30 hours heat treatment was 119 nm with a standard deviation of 9 nm ($n=8$). At this temperature therefore a significant decrease of nanoparticle size is observed in time, which could be well due to gold evaporation.

2.4.3.2 Ø 600 nm, 60 nm thickness

Figure 2.19a The result of heat treatment after 6 hours; Figure 2.19b shows the result after 30 hours. Scale bar represents 200 nm

The dewetted particles shown in figure 2.19, obtained from an initial deposited layer thickness of 60 nm, have a hexagonal crystalline shape. No pinch off is observed. The average diameter of the particles was 384 nm with a standard deviation of 13 nm (n=8). Heat treatment at 30 hours resulted in an average particle diameter of 361 nm with a standard deviation of 15 nm. In contrast to the results of 2.4.3.1. (10 nm deposited thickness) no significant size reduction in time thus is observed.

2.4.3.3 Ø 2µm, 10 nm thickness

Figure 2.20a The result of heat treatment after 6 hours; Figure 2.20b shows the result after 30 hours. Scale bar represents 200 nm

Figure 2.20 shows the particles resulting from annealing a 2 µm gold patch with an initial layer thickness of 10 nm. A hexagonal crystalline shape can be observed. The average diameter of the gold particles is 362 nm with a standard deviation of 45 nm (n=8) after 6 hours heating, and 327 nm, with a standard deviation of 11 nm (n=8), after heating for 30 hours. No pinch-off was observed.

2.4.3.4 Ø 2µm, 60 nm thickness

Figure 2.21a The result of heat treatment after 6 hours; Figure 2.21b shows the result after 30 hours. Scale bar represents 200 nm

The crystalline particles resulting from dewetting of 60 nm thickness and 2 µm diameter patches are shown in figure 2.21. No pinch-off was observed. The average diameter was 580 nm with a standard deviation of 26 nm (n=8). The average diameter for the 30 hours heat-treated samples was 557 nm with a standard deviation of 23 nm (n=8).

2.4.4 Dewetting at 500 °C to 900 °C - Conclusions

The results of dewetting gold patches at different heating times and temperatures were given above. Concluding, it can be stated that the influence of heating time varying between 6 and 30 hours on the particle size is not significant. Particles obtained from the 500°C experiments have an irregular shape, showing that the gold cannot obtain a final crystalline shape, but rather remains in a metastable shape. We attribute this to contact line pinning which cannot be overcome by thermal energy at this temperature. The pinch-off observed of the 10 nm layer indicates that the layer stability depends on the initial layer thickness. 60 nm thick layers in almost all cases did not show pinch-off. Particles obtained after the 700°C heat treatment show clear crystallization of the gold, indicating that the energy barriers preventing crystallization at 500°C can now be overcome. In the entire temperature range of the experiments, the diameter of the particles did not significantly decrease over time between 6 and 30 hours, with the exception of the 600 nm diameter, 10 nm thick experiments at 900°C (pinch-off).

The conclusion of the above experiments is, that particles of 80 nm diameter could not easily be obtained, as layers of 10 nm thickness or less generally suffered from pinch-off, while evaporation did not sufficiently reduce the particle size for thicker layers. In section 2.4.5 we report on subsequent experiments that therefore were performed at higher temperatures and in section 2.4.7 on experiments at low pressure, in both cases to increase the evaporation rate.

2.4.5 Results obtained in 990°C - 1030°C temperature treatments

In figure 2.22 the results of experiments conducted in the 990°C - 1030°C temperature range are shown. The original patch size of the gold for each of these experiments was a 600 nm diameter disc of 10 nm layer thickness. The morphological map below shows top views and cross sections of the structures obtained. The original gold particles are in a number of cases absent.

Figure 2.22 Matrix of dewetted gold nanoparticles and resulting surface deformations obtained in temperature treatments between 990 °C and 1030 °C.

After these experiments crystalline gold particles are observed as well as fused silica surface deformations which we classified as ridging, indicating that the fused silica has become mobile at this temperature. Around the central particle in many cases multiple ridges can be observed. We expect that these have been formed during dewetting of the gold layer at locations where the gold temporarily became pinned. It is also observed that the gold particles become embedded in the silica, as expected because the material to form the ridge is supplied from beneath the gold particle. In several cases the silica has disappeared to greater depth close to the ridge than in the middle of the particle, evidencing a kinetic shape resulting from silica surface diffusion. Higher temperatures are seen to lead to stronger ridging and deeper embedding of the gold particle.

Close inspection of the results obtained at 990°C show other interesting phenomena. In figure 2.22 the image obtained at 990°C for 1 hour of heating shows a central particle of ~200nm diameter while at the perimeter of the original gold patch small surface deformations can be seen. Experiments for 3 hours at 990°C also show a particle of ~200 nm in diameter. 5 hours at 990°C however showed a slightly smaller diameter of ~155 nm and a ridge surrounding the particle.

Figure 2.23 AFM image of a ridge remaining after the gold was removed using aqua regia. The ridge shows a hexagonal shape and 6 small peaks can be seen on the ridge. Small ridges can be observed at the former perimeter of the gold patch. The original gold patch was 600 nm in diameter and 10 nm thick, and the sample was heated for 1 hour at 990°C. The scale bar represents 200 nm.

These surface deformations are on the location where at lower temperatures typically pinched off particles are present. Ridging has occurred at these locations and the pinched-off particles have created small ridges in the surface. Experiments at 1030°C for 1 hour

show a gold nanoparticle on the surface of 200 nm diameter. A longer heat treatment at 1030°C did not leave a gold nanoparticle on the surface. Therefore, for longer heating times at 1030°C evaporation can be assumed. A sample, heated to 990°C for 1 hour, is shown in figure 2.23, where the gold has been etched away using aqua regia. The central ridge shows 6 peaks. A possible explanation for this interesting shape can be found in crystal surface energy theory.

Firstly, the central particle can safely be assumed to have been crystalline during the ridging process, since for a particle of this size (~200 nm) melting point depression is not yet expected, and the temperature was below the melting point of gold. Some reports moreover state that a Au(111) plane will remain stable almost up to the bulk melting temperature. [9] The 6-peak ridge configuration observed then is theoretically expected when a hexagonal crystal becomes embedded in a deformable substrate. It results from the difference in interfacial energy on the crystal planes and the substrate on which the crystal is formed, compared to the interfacial energy of the edges of the crystal planes and the substrate. [10]

2.4.6. Heating between 990 °C and 1030 °C – Conclusions

From the results presented in figure 2.22 it can be concluded that heating at the higher temperatures leads to embedding of the gold in the fused silica substrate, which is progressive in time. The necessary size reduction by evaporation could thus not be obtained without the gold becoming embedded in the fused silica, which is expected to decrease the usefulness for plasmonic sensing. It was thus chosen to increase the evaporation rate at a lower temperature, for which purpose annealing experiments needed to be performed at lower pressure.

2.4.7 Low pressure high temperature annealing

As mentioned in section 2.3.5, gold evaporation will proceed faster at low environmental pressures. Heating in a vacuum tube furnace was therefore conducted at various low-pressures. The temperature settings for these experiments were 900°C, 950°C, 970°C and 1000°C. Air was used to regulate the pressure using a valve with air filter.

In figure 2.24 some particles are shown obtained after heating the substrate for 1 hour at 950°C at a pressure of 4.0×10^{-5} mbar. The original gold patches were 600 nm in diameter and 10 nm in thickness. No pinch-off was observed. The gold nanoparticles were measured individually using HRSEM. Particles with a diameter of 60 nm were obtained. Figure 2.25 shows two gold nanoparticles observed after heating for 1 hour at 900°C and 1 hour at

950°C at a pressure of 3.0×10^{-5} mbar. The average diameter obtained was 98nm with a standard deviation of 29 nm (n=10).

Figure 2.24 Two gold nanoparticles measured with HRSEM after heating at 950 °C for 1 hour at a pressure of 4.0×10^{-5} mbar. The scale bar represents 50 nm.

Figure 2.25 Two gold nanoparticles measured with HRSEM after heating at 900 °C for 1 hour and at 950 °C for 1 hour at a pressure of 3.0×10^{-5} mbar. The scale bar represents 50 nm.

The particles obtained in this process were suitable for application in the sensor and were therefore also optically investigated. The dark field image in figure 2.26 shows an array of green dots. As explained in chapter 1, a green color indeed indicates that the diameter of the gold nanoparticles in the array is <100 nm, and the figure shows that this occurs over a larger area.

Figure 2.26 Gold nanoparticles in array configuration scattering green light, indicating a diameter <100 nm. Particles were obtained by heating for 1 hour at 900°C , followed by heating for 1 hour at 950°C at a pressure of 3.0×10^{-5} mbar.

The scattered intensity at five gold nanoparticles was measured for air, water and saturated glucose solution and is presented in figure 2.27. By varying the refractive index of the surrounding medium of the gold nanoparticles, the plasmonic resonance of the gold nanoparticle will change. The peak position of the scattered light in air is at a wavelength $\lambda = 550$ nm. For water the peak positions shifts to $\lambda = 570$ nm, and for the saturated glucose solution (91g/100ml) the peak shifts to $\lambda = 590$ nm. The measurements were performed using a Olympus GX71 microscope with a 20x dark field objective, and a Ocean Optics QE650000 spectrometer. Exposure time 20 seconds.

Figure 2.27 The spectrum of five gold nanoparticles obtained using a heating process under vacuum. A peak shift of the gold nanoparticles is visible for air, water and saturated glucose solution, indicating the potential usefulness of the array for detection.

2.4.8 Process reproducibility

The process reported in section 2.4.7 led to a few useful arrays. However, reproduction of the results, to create multiple batches chips with arrays of gold nanoparticles, unfortunately was not successful. A hypothesis is that the non-reproducibility is due to an unknown contamination during the heating process in the vacuum oven. In our experience heat treatments in the vacuum oven were more vulnerable to contamination, probably because of the low oxygen pressure which did not lead to oxidation of hydrocarbons. However, other factors which could play a role are the wafer cleaning procedure, the lithographic

patterning, controlling the gold patch volume, variations in the ramp-up time of the furnace and temperature of the heat treatment, and the environment in which the experiment is performed. In this case the pressure was regulated with oxygen. To improve reproducibility all these points need to be tightly controlled. The use of standard photolithography and sputtering should be reconsidered in future experimentation to investigate whether it increases controllability of the gold patch shape and gold volume. Argon or nitrogen could also be added to the low-pressure setup, which could positively influence the evaporation rate of the gold upon heating. A novel lithography technique named Talbot lithography could potentially be a successful candidate, since this technique allows exposure of <100 nm features in a single exposure step. [11]

2.5 Conclusion

In this chapter the influence of the originally deposited gold patch thickness and diameter, heating temperature, heating time and environmental pressure were varied to investigate the manufacturing of a gold nanoparticle array of the desired specifications. A deposited layer thickness of 10 nm was found most of times to lead to pinch-off during dewetting, resulting in unsuitable arrays. The process thus has to rely on a significant particle size reduction by evaporation. The 500°C – 900°C temperature range does not show a significant decrease in particle diameter for heat treatments of 6 to 30 hours. Higher temperatures were seen to lead to gold embedding in the substrate. A particle array of the desired dimensions could finally be obtained by a combination of heating at 950°C and a reduced pressure, leading to an accelerated evaporation rate. Unfortunately these results were only obtained once and could not be reproduced. It therefore can be concluded that the initial volume of gold, after photolithographic patterning, is of great importance to the final gold nanoparticle dimensions. The method investigated in this chapter did not successfully create the 80 nm diameter gold nanoparticle array with 5 μm spacing. The gold nanoparticles were seen to embed into the surface and eventually, as explained further in chapter 3, create nanopores. In chapter 6 an alternative method was to create 80 nm diameter gold nanoparticles was therefore tried.

2.6 References

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3. Nanopore Fabrication by Heating Au-Particles on Ceramic substrates

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3.1 Introduction

In this chapter we show that gold nanoparticles, when heated to close to their melting point on substrates of amorphous SiO_2 , move perpendicularly into the substrate. Dependent on applied temperatures, we find that particles can become buried or leave nanopores of extreme aspect ratio (diameter ± 25 nm, length up to 800 nm) as sketched in figure 3.1. The process can be understood as driven by gold evaporation and controlled by capillary forces and we show that it can be controlled by temperature programming and substrate choice.

Figure 3.1, A schematic representation of a nanopore created in SiO_2 by heating a Au particle on its surface.

The production of nanometric tools has gained more and more interest in recent years. For instance the ability to investigate our very own genetic building blocks using nanopores, be it biological or solid-state, has fueled the demand for optimization of such tools. As mentioned above, we here present a scheme for manufacturing solid-state nanopores with potentially abundant applications. Through-hole nanopore arrays or single pores are for example of great practical use for applications in high-throughput DNA sequencing, [1] molecular sensing [2] and molecular separations [3]. Closed-end pores can for example be useful as a mold for atomic force microscope tips. Existing methods to create nanopores are either versatile but costly and labor intensive, such as ion-beam or electron-beam sculpting, or simple and cheap but lacking control, such as anodizing aluminum. Here we demonstrate a method that combines versatility with low cost.

3.2 Materials and Methods

Using conventional photolithographic patterning and gold sputtering a fused silica wafer with a thickness of 500 μm (PlanOptik GmbH, for properties see appendix 1, Table S12) was patterned with 10^6 circular gold islets (diameter 1 μm , pitch 5 μm). Subsequent heating was carried out in a programmable oven (TOMA TSD 12, Volkel, the Netherlands). Ramp-up time was one hour. No special cleanliness measures were taken. After the heat treatment the oven was switched off and passively left to cool. For characterization of the nanostructures an atomic force microscope (VEECO, Dimension 3100) was used as well as a HRSEM (FEI Sirion). To remove the gold from the surface to examine the area below the gold, we used gold etchant (Standard, 651818-500ML, Sigma Aldrich). For observation of pores and gold nanoparticles after the $1067^\circ\text{C} \pm 5^\circ\text{C}$ heat treatment the sample was cleaved and the cross section examined using the HR-SEM. To avoid charging effects of the isolating fused silica sample in the HR-SEM the samples were coated with a 2 nm gold-palladium layer prior to examination. Examination and verification measurements on figure 3.3a and 3.3b on the lattice structure of the SiO_2 were performed by electron diffraction spectroscopy and scanning tunneling microscopy. Handling of the sample required a Pt coating to be applied on the sample (NanoPhysics B.V. Enschede, The Netherlands). The membranes in figure 3.6a and 3.6b were manufactured from one side polished silicon wafers. These wafers dry-thermally oxidized at high temperature. The gold pattern was applied using photolithography, and covered with a 50 nm chromium layer. The backside of the wafer was patterned and the SiO_2 layer was etched using reactive ion etching, followed by wet etching of silicon by potassium hydroxide (KOH). The chromium is a protection layer during the KOH step so no SiO_2 will be removed. After etching the backside up to the SiO_2 membrane the chromium was stripped using an O_2 plasma treatment. The wafers were placed in an oven at $1067^\circ\text{C} \pm 5^\circ\text{C}$ to perform the nanopore formation. The amorphous Si_3N_4 layer in figure 3.6c was deposited by LPCVD. The rest of the process is the same as for the fused silica samples.

3.3 Experimental

An array of 10^6 circular gold patches of 18 nm thickness and 1 μm diameter on a substrate of fused silica glass (SiO_2) was heated in ambient air for several hours at $1067^\circ\text{C} \pm 5^\circ\text{C}$. Ramp up time from room temperature to $1067^\circ\text{C} \pm 5^\circ\text{C}$ was 1 hour. The moment the heat treatment ended the furnace was left to cool down passively to room temperature. The process was followed by inspection after different treatment times. We found that after initial dewetting, [4] hexagonal Au nanocrystals formed that became surrounded by an increasingly thick and high silica ridge (appendix 1 figures S1 and S2). The Au particles

then moved into the SiO_2 as shown in figure 3.2a, at a velocity of ~ 100 nm/hour while remaining connected to the substrate surface by a nanopore as shown in figures 3.2b and 3.2c.

Figure 3.2 High resolution scanning electron microscope (HRSEM) pictures at three stages of heat treatments at SiO_2 . (a) gold nanoparticle penetrating into the fused silica after 10 minutes at $1067^\circ\text{C} \pm 5^\circ\text{C}$ and (b) gold nanoparticle penetration into the glass and pore formation after 1 hour at $1067^\circ\text{C} \pm 5^\circ\text{C}$ (c) penetration after 3 hours at $1067^\circ\text{C} \pm 5^\circ\text{C}$. Scale bars represent 100 nm. Figures (a-c) were produced after fracturing the substrate. In graph (d) on the right, in black the measured nanopore length l versus heating time at $1067^\circ\text{C} \pm 5^\circ\text{C}$. Error bars represent standard deviation with $n = 6$. Red: predicted pore length based on a diffusional model with literature values for the Au vapor pressure and Au Knudsen diffusion coefficient. (appendix 1, section 3)

Experiments with the gold facing up and down showed a similar penetration, ruling out an influence of gravity. Nanopore direction was generally normal to the surface with pores slightly narrowing downward. Curved pores were occasionally observed at longer heating times and consequently greater lengths. Nanopores were approximately three times narrower than the diameter of the gold nanoparticles at their end. We observed the formation of nanopores up to a length of 840 nm and a final diameter of approximately 25 nm after 9 hours of heating at $1067^\circ\text{C} \pm 5^\circ\text{C}$. figure 3.2d shows the nanopore length over time for the $1067^\circ\text{C} \pm 5^\circ\text{C}$ heat treatment (black dots). Electron microscopy pictures of the

system did not show any morphological differences between the bulk SiO_2 and the SiO_2 surrounding the pore on the atomic level, ruling out recrystallization of SiO_2 (appendix 1, figure S4). Local X-ray spectroscopy showed no evidence of Au diffusion into the SiO_2 . The scanning transmission electron microscopy (STEM) cross-section image in figure 3.3 showed evidence of flat crystal facets, most markedly at top and bottom.

Figure 3.3 On the left (a) a STEM cross-section of a structure formed after 3 hours at $1067^\circ\text{C} \pm 5^\circ\text{C}$. On top it shows the ridge surrounding the nanopore entrance and at the bottom the gold nanoparticle. On the right (b) a close-up of the gold nanoparticle on the bottom of the pore. The close-up clearly shows the gold nanoparticle is not totally spherical. A flat surface can be seen on the pore side of the gold nanoparticle.

3.4 Mechanism

The temperature of 1067°C is slightly higher than the melting temperature of Au (1064°C). [5] At such temperatures substrate-supported Au forms nanocrystals where some crystal planes (notably the (111) plane) persist but others exhibit surface melting. Theory predicts that freestanding gold nanoparticles below 70 nm diameter will melt at 1050°C , while particles embedded in a solid matrix can either melt or exhibit superheating depending on the interfacial energies. [6] For gold nanoparticles embedded in SiO_2 some evidence for the latter is given in literature. [7] Close to the bulk melting temperature the Au(111) crystal plane is expected to still be solid, [8] while the remaining surfaces bordering air or SiO_2 can have one or several layers of mobile atoms, depending on the interfacial energies as mentioned above. [9] In literature ridge formation around metal particles on ceramics is frequently reported when the system is heated to about half the ceramic melting point. It is

explained by ceramic transport along the interface with the metal (where it is assumed to have a higher mobility) by surface diffusion towards the air/particle/ceramic triple line where it is deposited.[10] [11] [12] [13] [14] [15] Material will be deposited in those locations, where it reduces the torques between the different phases, $\partial\gamma/\partial\vec{t}_i$, where γ is the interfacial energy (J/m²) and $\vec{t}_i$ are the vectors in the plane of the i th ($i = 3$) interface, normal to the triple line and pointing away from it (the Herring equation). [12] [16] Final equilibrium is reached when the torque terms disappear by material reorganization, and is described by the Smith equation;

$$\frac{\gamma_{AG}}{\sin\theta_C} = \frac{\gamma_{AC}}{\sin\theta_G} = \frac{\gamma_{CG}}{\sin\theta_A},$$

where θ is the angle occupied by the respective phases – air (A), ceramic (C) and gold (G). [17]

Equilibrium as described by the Smith equation however is not reached in our system. Because the gold nanoparticle Au evaporates [18] [19] the Au will continuously retreat from the triple line again generating torque. We thus explain the observed structures by continuous remodeling of the ceramic to reduce the triple line torque resulting from Au evaporation. The small dimensions of our system make diffusional transport fast, allowing rapid reshaping. The pore shapes obtained essentially however are kinetic shapes and not equilibrium shapes, as only the ceramic around the Au is mobile, and the ceramic in the absence of Au is practically immobile. [20] The proposed mechanism for Au/SiO₂ is schematically shown in figure 3.4 which can be related to figures 3.2a-d and figure 3.3. The system strives for equilibrium, where the angles occupied by the three phases at the triple line as determined by the interfacial energies [7] [21] [22] are $\theta_S \sim 95^\circ$ for the SiO₂ angle, $\theta_G \sim 170^\circ$ for the Au angle, and $\theta_A \sim 95^\circ$ for the air angle (appendix 1, section 5). During the initial dewetting stage, this results in the formation of a series of ridges at the outer circumference of the hexagonal crystalline (figures 3.2a and appendix 1, S1 and S2), caused by SiO₂ transport to the triple line and alternating pinning and depinning of the Au. This phenomenon as described in literature is caused by an insufficient rate of ceramic transport as to keep up with the metal evaporation rate. [11] [13] Below a certain particle diameter a continuous SiO₂ ridge is formed when diffusional SiO₂ transport becomes sufficiently fast (figure S1).

Figure 3.4 A cross-sectional schematic representation of the pore formation process at $1067^{\circ}\text{C} \pm 5^{\circ}\text{C}$. a) Gold dewetting, directly followed by b-c) ridging of SiO_2 . d-f) Continuous Au evaporation and transport of SiO_2 to the triple line creates an increasingly narrow pore facing into the substrate. Continually maintaining angle θ_A .

Figure 3.5 At the pore end the triple line is positioned on the gold nanoparticle surface at the edges of the stable Au(111) plane, which occupies an angular diameter 2α . The resulting relation between particle diameter d and pore diameter $d_p = d \sin(\alpha)$. Pore narrowing rate with depth y is given by $d(d_p)/dy = -3/2 \sin^3(\alpha)$.

Initially the gold nanoparticle center is located above the SiO_2 substrate level and SiO_2 is deposited above the substrate level, figures 3.2a and 3.2b and figure 3.4. The Au in this stage forms a slight bulge, again shown in figures 3.2a and 3.2b and figure 3.4, in accordance with the equilibrium $\theta_A \sim 95^\circ$. In course of time the gold nanoparticle is observed to further penetrate into the SiO_2 , which can be explained by continued Au evaporation and SiO_2 transport from below the gold nanoparticle to the triple line. To satisfy the Smith equation for an embedded gold nanoparticle, the triple line must move to the top of the particle, thereby forming the cross-section of a pore. In view of the fact that the equilibrium $\theta_A \approx 95^\circ$ it is expected that the pore for a spherical gold nanoparticle will not close as $2\theta_A > 180^\circ$. We however also note that the gold nanoparticle displays crystal facets in the STEM cross section in figure 3.3. Assuming the top facet is the stable Au(111)

plane [23] and θ_s is close to its equilibrium value, the triple line will become pinned at the edge of the plane, since moving further inward will cause a step increase in energy by the change of θ_s as well as by a decrease in surface area of the low energy Au(111) plane. The angular diameter of the Au(111) facet then determines the pore dimension relative to the gold nanoparticle. If the angular diameter covered by the Au(111) plane measures 2α , a pore will result of width $d_p = d \sin(\alpha)$ shown in figure 3.5. Additionally kinetics can play a role in pinning the triple line at the boundary of the (111) facet, namely in case the solid Au(111) surface supports less ceramic material transport than the more mobile gold atoms at the other interfaces. Since the gold nanoparticle diameter decreases on deeper embedding by evaporation, the Au(111) facet and thereby the pore will narrow, while the pinning will prevent the pore from closing. It can be deduced (appendix 1, section 6) that the pore diameter in this stage is linearly dependent on pore length with a pore narrowing rate, $d(d_p)/dy = -3/2 \sin^3(\alpha)$, where y is the surface-normal coordinate. Thus, the Au progressively moves into the SiO₂, leaving a pore with a volume equal to the evaporated volume of Au and a narrowing diameter due to the decrease in d . We compared predictions by this theory with the observations. From figure 3.3, from the measured ratio of bead diameter (105 nm) and pore diameter (30 nm) the angular diameter of the Au(111) plane can be calculated as $2\alpha = 33^\circ$. Also, in figure 3.3 the measured pore contraction $d(d_p)/dy$ in the final 230 nm of pore growth is constant as theoretically predicted and equals -0.06, yielding $2\alpha \sim 35^\circ$. Both values are slightly higher than the value of $25\text{-}30^\circ$ found in literature for the (111) facet of Au crystals in vacuum. [23] In further support of this hypothesis, measurements on 12 pores showed a constant ratio for d_p/d for heating times between 1 and 9 hours (appendix 1, S7).

The above considerations described pore shape as predicted by equilibrium conditions at the triple line. We also considered the kinetics of pore formation, and investigated whether SiO₂ transport or Au evaporation/diffusion was rate limiting. Figure 3.2d plots the experimentally obtained values for the nanopore length as function of heating time. The figure also shows the curve predicted for the pore length increase when Au vapor diffusion is rate-limiting. The curve uses no fitting parameters and was calculated assuming a saturated Au vapor pressure at the gold nanoparticle, zero Au pressure at the nanopore exit and Knudsen-regime diffusion of Au (appendix 1, section 3). The Knudsen diffusion coefficient for the tapered pore was calculated using a diameter-weighted value. Measured values give $d = 2.32 \cdot t^{0.62}$ while theory predicts $d = 2.51 \cdot t^{0.53}$, and both are in satisfactory agreement in view of the absence of adjustable parameters. This leads to the conclusion that Au diffusion is rate-limiting. In support of this conclusion is the fact that the gold nanoparticle is almost spherical, indicating a constant interfacial energy and hence equilibration.

Alternative mechanisms for the pore formation were considered but rejected. SiO₂ removal by Au in the presence of Si has been observed and explained, but this process can be excluded since unbound Si is not present in our system. [24] The same holds for possible mechanisms based on local heating of gold nanoparticles by light absorption, since the black-body radiation curves of the oven at 900 °C and 1050 °C do not overlap with gold nanoparticle absorption cross-section. [25] [26] Local SiO₂ crystallization finally was eliminated as cause because it was not observed in the EM pictures (appendix 1, S4b).

3.5 Nanopore design

Figure 3.5 presents some guidelines for pore design. After an initial embedding phase in which a pore length $l = l_0$ is reached and particle diameter is d_0 , the triple line becomes pinned at the (111) plane and the pore narrowing rate becomes linear. As mentioned, pore diameter $d_p = d \sin(\alpha)$ and pore narrowing rate $d(d_p)/dy = - 3/2 \sin^3(\alpha)$. For the present material combination, the maximal pore length then follows as $l_{max} = 2d_0/(3\sin^2(\alpha)) + l_0$. For $d_0 = 100$ nm and $l_0 = 200$ nm, $l_{max} \cong 940$ nm. A control parameter for the pore diameter is thus the initial gold nanoparticle diameter, while the pore diameter decreases with pore length, becoming extremely small at great pore length. In the next section we will show preliminary experiments indicating that pore diameter can also be tuned by temperature programming.

3.6 Through-holes, Si₃N₄ nanopores and temperature programming

Heating an 10⁶ array of gold patches on a 100 nm thick SiO₂ membrane resulted in an array of through-holes within the bounds of the initially formed SiO₂ ridge (see figure 3.6a and 3.6b and appendix 1, S8).

Figure 3.6a The nanopore through-holes in a thermally-grown 100 nm thick SiO_2 film. Scale bar represents 5 μm . Figure 3.6b, A single through-hole captured with STEM. Au indicates some residual gold still present. The through-hole is shown in bright white. The light grey circular area indicates the scar of the initial gold patch. Scale bar represents 100 nm. Figure 3.6c, A cross-section of a fractured Si_3N_4 layer with a nanopore formed. Scale bar represents 100 nm.

The SiO_2 membranes with nanopore through-holes in figure 3.6a and 3.6b were visualized using STEM. The picture shows a bright white area, which is the through-hole. The light grey circular area is the material scar of the location where the gold patch of 600 nm diameter was applied. Some residual gold is also visible. Most of the gold nanoparticle therefore has very likely evaporated, with the evaporation expected to be high due to the short Au diffusion distance and the two-sided evaporation once the gold nanoparticle broke through the membrane. Heating an 10^6 array of gold patches on LPCVD grown amorphous Si_3N_4 for 6 hours at $1067^\circ\text{C} \pm 5^\circ\text{C}$ also produced pores, shown in figure 3.6c. As shown in the figure, pores were initially strongly tapered and short. For amorphous Si_3N_4 , the scarce literature available indicates that $\theta_c \ll 90^\circ$ (appendix 1, section 9), resulting in a predicted geometry that is different from SiO_2 . Further experimentation with heating gold patches on a Si_3N_4 layer to create through-holes is reported in chapter 4, also considering the oxidation of the substrate.

Heat treatment at the lower temperature of 900°C of gold on SiO_2 also showed ridge formation and gold penetration, albeit much slower (up to 50 nm pore depth after 24 hours, appendix 1, figure S10). Also more complicated programmed heat treatments were investigated to increase understanding of the mechanism. Heating temperatures were thereby chosen close to the melting point of bulk Au as it was expected that large changes would be observed around this point. Heating at 1100°C resulted in evaporation of all Au. Heating with the program (1 hour ramp-up, 10min 1067°C , 50 min 1087°C , 60min 1117°C , passive cool-down) resulted in entirely buried gold nanoparticles (appendix 1, figure S11). We interpret the closing of the nanopores and the resulting burying of the gold nanoparticles in this case as the result of melting of the Au(111) plane, removing the

pinning barrier. Programming the heat treatment as (1 hour ramp-up, 10min 1067°C, 50 min 1087°C, passive cool-down) and (1 hour ramp-up, 10min 1067°C, 110 min 1087°C, passive cool-down) gave pores that suddenly narrowed to very small diameter. The pore diameters observed in the last two cases were variable and occasionally very narrow (at the edge of the STEM resolution, of the order of 10 nm or even smaller). Whether precise temperature control will enable stable machining of very narrow pores must thus be subject of further investigation. At these higher temperatures more curved pores were observed, which we explain by the smaller size of the (111) plane and consequently the increasingly homogeneous environment of the particle. The large margin of error in our present measurements and the large uncertainty in the calculated phase angles at present however do not permit a quantitative comparison of theory and experiment.

The proposed manufacturing technique can in principle be applied to any metal/ceramic combination that on the macroscale exhibits ridging without chemical reaction. Examples of such combinations found in literature include metals on ceramics as for example Au, Al, Ni, Cu and Mg on Al₂O₃ and Pt on SrTiO₃, all under the proper partial oxygen pressures, [10] [11] [13] [27] but also of ceramics on metals. When the formation mechanism that we propose is correct, many factors play a role in the pore formation process, such as metal properties (molten or crystalline), substrate properties (amorphous or crystalline), chemical reactions between system components, including the atmosphere, and operating temperature. Recently, Curiotto et al. [15] for example described the formation of depressions of a few tens of nanometers when heating Cu on crystalline Al₂O₃. They explain the structures as resulting from Al₂O₃ transport along the ceramic substrate crystal plane. This suggests the possibility of anisotropic machining using this method. The easy manufacturing procedure and controllability of the present method, the wide applicability of the products formed and its potential application in a wide choice of materials is quite attractive.

3.7 References

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4. Nanopore fabrication in Silicon Oxynitride membranes by heating Au-Particles

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In this chapter we report the fabrication of nanopores in a silicon oxynitride (SiON) membrane by heating a silicon rich-silicon nitride (SiRN) membrane with a gold nanoparticle array deposited on its surface. The gold nanoparticle array was realized by photolithography and the membrane by wet-etching. The entire process is wafer scale. Nanopore through-holes of an average diameter of 150 nm were produced in a ~22 nm thick membrane. Membranes and nanopores were characterized by atomic force microscopy (AFM), scanning transmission electron microscopy (STEM) and x-ray photoelectron spectroscopy (XPS).

4.1 Introduction

Nanopores in thin membranes are of great interest for biosensing and separation processes with applications in sieving [1], molecular separation [2], DNA analysis [3] and DNA sequencing [4]. Creation of nanopores for such applications typically relies on a combination of a membrane fabrication method with an established nanopore formation technology like focused ion beam milling [5][6], track etching [7], electron beam writing [8], or dielectric breakdown [9]. Another method is to use dry etching processes combined with Au particles, where the etch rate is locally enhanced around the Au particle creating a nanopore. [10] In a recent paper we showed the fabrication of dead-end nanopores in SiO₂ by a novel technique based on gold nanoparticle penetration in fused silica upon heating, as well as preliminary results of the manufacturing of through-holes in a SiO₂ membrane [11]. Here we demonstrate a manufacturing process on the basis of this new technique that results in nanopore through-holes in membranes of SiON.

4.2 Materials and methods

The creation of the membranes with nanopores is depicted in figure 4.1. Low-stress (50 MPa) SiRN with a thickness of 36 nm was grown on p-type (100) one-side polished silicon wafers. Olin 906-12 photoresist was applied by spin coating at 6000 rpm, creating a 1 μ m thick photoresist layer. The photoresist layer was exposed with a dose of 12 mW/s using a mask containing 2 μ m circular features which were 5 μ m spaced. After photoresist

development and an ozone plasma treatment to remove any residual photoresist from the silicon nitride layer, gold with a thickness of 20 nm was sputtered. A lift off was done in acetone for 15 minutes. The substrate with the nitride and gold pattern was then again spin-coated with a photoresist layer, Olin 907-17 at 4000 rpm and after photolithography the chromium layer with a thickness of 40 nm was sputtered over the silicon nitride and gold pattern.

Photolithography was then performed on the non-polished backside of the wafer. The SiRN layer on the backside of the wafer then functioned as a potassium hydroxide (KOH) etch mask. The backside SiRN layer was plasma etched for 90 seconds (gas flow 25 sccm CHF_3 , 5 sccm O_2 , pressure 10 mTorr, power 60W). The wafers were etched up to the topside SiRN membrane using KOH 25% at 75°C for 8 hours. The chromium layer was removed with chromium etchant (Chrome etch n° 1, MicroChemicals GmbH). The wafer was then cleaved in 16 mm square chips. To create nanopore through-holes in the SiRN membranes, the chips were then placed in a furnace for a heat treatment for 6 hours. The furnace heated the samples to $1067^\circ\text{C} \pm 5^\circ\text{C}$.

Figure 4.1. A schematic representation of the nanopore through-hole fabrication protocol.

4.2.1 Characterization

The properties of the thin film before and after heat treatment were investigated using XPS and a series of etching experiment combined with ellipsometry. The etching was performed

in steps of one minute for a total of 10 minutes in KOH 25%, 75°C. After each minute of etching the layer thickness and refractive index were measured by ellipsometry using a J. A. Woollam ellipsometer. After 10 minutes of etching, three etch time intervals of 5 minutes were applied. The nanopores were inspected using scanning transmission electron microscopy.

4.3 Results and Discussion

4.3.1 Nanopores

In our previous research concerning Au penetration in SiO₂, we found that the heat treatment initially caused dewetting of the gold patches to form gold nanoparticles. This dewetting was followed by the particles penetrating the SiO₂ layer and forming dead-end nanopores in the bulk material. We proposed a mechanism based on a combination of gold evaporation coupled to continuous SiO₂ transport to the Au/SiO₂/air triple line driven by capillary forces, forming the pores. [11] In our present research, as in the case of SiO₂, we found that nanopores had formed in the membranes. The membranes also oxidized from SiRN into SiON during the heat treatment which was performed in ambient air. The proposed pore formation mechanism is shown in the schematic diagram in figure 4.2. In general the surface energy of the materials involved provides a specific air phase angle (θ_A) when a droplet of gold is placed on a ceramic surface [11, 12]. When the initial shape of the gold nanoparticle does not provide the desired angle between Au and the ceramic, ceramic material diffuses toward the Au/ceramic/air triple line to reach equilibrium, forming a ridge at the particle diameter. When gold continuously evaporates, this process proceeds over a long time, whereby continuously ceramic material is transported from below the gold to the triple line, leading to pore formation (see figure 4.2). When the ceramic material is a thin membrane, a through-hole is formed, as evidenced by the STEM pictures of figures 4.3b and 4.3c. Membranes of 80 by 80 μm square with 256 nanopatches of gold, after the heat treatment contained 256 nanopores with a spacing of 5 μm . To determine the size of the pores, STEM pictures of thirty holes were measured using ImageJ software. It was found that the shape was approximately circular with an area-averaged diameter of 167 nm and a standard deviation of 48 nm. Details of the size distribution are given in appendix 2, S1. Pores were always located inside the perimeter of the original deposited Au patch.

Figure 4.2 A schematic representation of the proposed nanopore through-hole formation mechanism. SiON migration to the triple line to maintain the angle θ_A between the gold and the SiON combined with continuous evaporation of gold creates the nanopores (modified from reference [11]).

Figure 4.3a. An overview of a SiON membrane with a nanopore through-hole array. Scale bar represents 20 μm . The membrane can be seen to be buckled. In figure 4.3b a single nanopore is shown, the scale bar represents 400 nm. Figure 4.3c shows the nanopore through hole, with in detail crystallites thought to be of Au and Au-Si, scale bar represents 200 nm. Figure 4.3d is a close-up of three crystallites.

4.3.2 Membrane oxidation and buckling

Figure 4.3a also shows that the (initially flat) membranes became buckled in the process. Membrane buckling on these scales is a result of internal material stresses. [13] A possible explanation is an oxidation of the SiRN layer, which will cause a volume increase. Such oxidation is expected since the heat treatment took place in ambient atmosphere. Oxidation of SiRN increases the membrane thickness and results in a layered configuration of SiO₂, SiON and SiRN. [14] Another possible cause of membrane buckling is the oxidation of the bare silicon on which the membrane is suspended after KOH etching. Finally, although expected to have only a minor contribution, also the creation of the nanopore through-holes can have an effect on buckling since it decreases the membrane stiffness. [15] To assess the oxidation state of the SiRN, the layer thickness and refractive index were measured by ellipsometry on the Si at a location adjacent to the membrane. Measurements before and after heat treatment showed that the layer thickness increased from 36 nm before to 42 nm after heat treatment. The layering of the oxidized SiRN layer was investigated in two ways. One method was by means of XPS, and the other method was by KOH etching at given time intervals followed by ellipsometry measurements of the layer. The graphs in figure 4.4a and 4.4b show the XPS measurements of the layer before and after the etching experiment. Figure 4.4a shows the layer before etching and reveals that the surface layer has 70% oxygen content and 30% silicon content (SiO₂). The subsequent gradual decline in oxygen content and increase in nitrogen content in the depth profile is evidence of a SiON layer. At a sputter depth of 30 nm the oxygen is removed and a silicon nitride layer remains (approximately 50% nitrogen and 50% silicon). Figure 4.4b shows XPS data of the surface after KOH etching. A ratio of 33% oxygen, 33% silicon and 30% nitrogen is observed (and 4% fluor and carbon content), indicating the presence of SiON.

Figure 4.4a The elemental content depth profile of the oxidized SiRN layer on the Si substrate before KOH etch. Atomic concentration is given for carbon (C1s), nitrogen (N1s), oxygen (O1s), fluor (F1s) and silicon (Si2p). Before sputtering O1s content is 70% and Si2p content 30%. With increasing sputter depth the ratio of oxygen and nitrogen content changes, indicating the presence of a gradient of SiON ending at 27nm depth and followed by a layer of SiN. At 45 nm sputter depth Si remained (Si2p). Figure 4.4b shows the atomic concentrations after KOH etch, removing the SiO₂ and leaving SiON and SiN on Si.

Figure 4.5 shows the measured layer thickness after subsequent etch steps. Two stages can clearly be distinguished. The first stage from 0 to 10 minutes shows an etching rate of 1.4 nm/min in which a 16 nm layer is etched away. The second stage, from minute 10 to minute 25 shows a much slower etch rate of 0.06 nm/min. [16] Ellipsometry data of the layer after 25 minutes etching show a refractive index of 2.06 of the remaining 25 nm thick layer. This value is in good agreement with the refractive index of SiRN, which ranges from 1.99 to 2.35. [17, 18] The etch rate of the second stage in KOH 25%, 75°C is 0.06 nm/min. These data compare well to the XPS data in figure 4.4a and 4.4b which showed a stacked layer of SiO₂, SiON, SiN and Si with a total thickness of 44 nm (at 44 nm sputter depth strong increase in Si content is shown). From the sputter depth profile we there concluded that the SiO₂ layer thickness is 16 nm, the SiON layer thickness 11 nm and the SiRN layer 17 nm. As shown more than half of the initial 44 nm thickness has thus converted into either SiO₂ or SiON. Since the oxidation of the membrane proceeded from two sides, we expect that the initial SiRN membrane has fully transformed into SiON. It is thus not surprising that the buckling induced by the heat treatment was still present after KOH etching.

Figure 4.5 The thickness of the oxidized layer on top of the silicon adjacent to the membrane after subsequent KOH etch steps of the indicated time, for 3 experiments. Linear fits to the data for the period before and after 10 minutes are shown. The decrease of layer thickness in the first 10 etch steps of 16 nm is the etching of the SiO_2 layer.

4.3.3 Nanopore formation mechanism

In STEM imaging a darker shade indicates either a denser material or a thicker layer. [18] On the other hand, when no material is present, the image appears white since electrons can then travel directly from the source to the detector. The STEM image of figure 4.3b shows that a circular area with a diameter of 2 μm (the original dimension of the deposited Au patch) has a lighter shade compared to the rest of the membrane. The 2 μm diameter area also has a high density of small crystalline shapes, while the direct area around the pore shows just a few larger crystals. AFM measurements of the former Au patch area show that it lies about 5 nm deeper than the remainder of the membrane. In figure 4.3c darker and lighter crystalline shapes can be distinguished close to the pore, as is clearly visible in the enlarged area in figure 4.3d.

Our hypothesis is, that the crystalline shapes in the 2 μm diameter area are crystallites of Au or Si or of Au-Si alloys. The Au crystallites could have formed due to break up of the Au patch, when it would show pinch-off instead of fully dewetting into a singular particle.

Also Si clustering during heat treatment can take place within SiRN layers. [18] Subsequent reactions between the Au and Si clusters from the SiRN membrane material are not ruled out. [20] Alloy formation between Au and Si is known to occur at higher temperatures. [21] The molar ratio of Si and N in a SiRN layer is 1.04, implying an excess of Si with respect to Si_3N_4 , [17] which could have alloyed with the Au.

Since oxidation plays an important role in this process, the lighter shaded circular area with dark crystals in the SiON surface at the original location of the patterned gold could be explained by oxidation of the initial SiRN layer. The 20 nm gold layer is likely to break up around 400°C. [22] Oxidation of the SiRN layer could have appeared during the ramp-up time of the furnace reaching the temperature at which dewetting of Au takes place. Within the circular area a darker ring around the nanopore can be observed, as shown in figure 4.3c. This ring is a ridge as mentioned in the discussion concerning figure 4.2 and is shown in an AFM picture in appendix 2, S2. This ridge formation occurs before pore formation as has been explained in our previous paper on Au nanopore formation in SiO_2 . After etching in 1%HF for 20 minutes the ridge disappeared (appendix 2, S3), while the rest of the 2 μm diameter area remained, indicating a ridge with high SiO_2 content. At the perimeter of the ridge large dark crystals can be seen and also at the perimeter of the pore large dark crystals are present. We expect here crystals could have grown larger because the surface was for a longer time in contact with the Au particle which retreated slowly after ridging started.

4.4 Conclusion

The method described here proves to be capable of creating nanopore through-holes in a ~20 nm thick SiON membrane. By starting the process with a 36 nm thick SiRN membrane with Au patches on top, a heat treatment by a combination of oxidation, capillary action and gold evaporation leads to wafer scalable nanopore through-hole formation. XPS measurements show oxidation of the original SiRN into SiON. Buckling of the membrane is also observed, which is a result of the consequent volume increase. We show a proof of principle of a new method for nanopore through-hole fabrication, potentially competing with methods like electron beam writing or ion beam milling.

4.5 References

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5. Nanopores created using an internal shadowmask process

In this chapter we report on the manufacturing of nanopore through-holes by heating gold nanoparticles on a silicon oxide (SiO_2) sheet, suspended in a silicon-rich nitride membrane (SiRN). Membrane patterning is performed using self-alignment by an internal shadow mask based process. A benefit of this approach is the ease at which downscaling of the lithographic features can be achieved. With a single alignment, a shadow mask is etched and metal is deposited. The nanopore through hole is then created after heating. In this chapter this scalable technique is applied to create non-buckled membranes by combining the compressive and tensile stress components in a SiO_2 /SiRN bilayer. Theory on the bilayer stresses is given in order to characterize the buckling. The nanopore through holes are characterized using ionic current measurements and electron microscopy techniques.

5.1 Introduction

The use of nanoporous membranes offers possibilities for example in sieving and filtration of liquid or gaseous mixtures. [1] [2] A regular distribution of nanopores can be of interest in schemes where quantification of the content of such liquids or gaseous mixtures is important. [3]

Moreover, a membrane with just a single nanopore, when in the order of <2 nm in diameter potentially has the ability to serve as sequencing tool for deoxyribonucleic acid (DNA). [4] In the research reported in this chapter nanopores in a membrane were manufactured by heating a gold patch on a silica membrane to $1064^\circ\text{C} \pm 5^\circ\text{C}$, a scheme that was reported in chapter 3 and 4 and that was published in two papers. [5] [6] Nanopore creation in bulk SiO_2 has been characterized but a transfer of this technique to a membrane appeared problematic due to buckling of the membrane as a result of the heat treatment. Incorporation of the stress components of SiO_2 and SiRN allows creation of non-buckled membranes. [7]

To overcome the problem of membrane buckling, a 40 nm thick SiO_2 layer suspended in a 200 nm thick SiRN membrane will be used. [8] [9] The heating of a SiO_2 membrane to high temperatures will result in an increase of compressive stresses in the membrane. [10] However, since the SiO_2 is suspended in SiRN in this case, it is expected the compressive stress is compensated by the tensile stress in the SiRN.

Compared to established nanopore fabrication techniques, for example electron beam writing and ion beam milling, our method enables fast, high volume processing and omits the use of complex equipment. [11] [12] For characterization of the nanopores created by heating gold nanoparticles, high resolution scanning electron microscopy (HRSEM),

transmission electron microscopy (TEM) and ionic current measurements through the nanopores will be performed.

5.2 Materials and Methods

5.2.1 Manufacturing

The processing steps used for manufacturing are given in figure 5.1. We use a 380 μm thick silicon (100) wafer. A SiO_2 layer of 40 nm is grown on each side by dry oxidation at 1000°C, followed by deposition of 200 nm thick silicon nitride. To create the membranes from the SiO_2/SiRN bilayer, the backside of the wafer is patterned by photolithography. Olin 907-17 positive photoresist is spin coated on the surface after which the wafer is UV-exposed for 4 seconds with a dose of 12 mW/cm^2 . Development takes place in OPD4262 for 2 x 45 seconds followed by dry etching of the SiO_2/SiRN bilayer. (Plasma etch, time: 4 minutes, 5 sccm O_2 , 25 sccm CHF_3 sccm, 10mTorr, 60W). Afterwards the photoresist is stripped in nitric acid (HNO_3) and the SiO_2/SiRN bilayer functions as a mask for the silicon etch in potassium hydroxide (KOH 25%, 75°C). The KOH etches 350 μm deep so that a silicon layer of 30 μm remains. The substrates are cleaned using RCA2 solution ($\text{H}_2\text{O}:\text{HCl}:\text{H}_2\text{O}_2$, 80°C) to remove KOH residue from the substrate, followed by low-pressure chemical vapor deposition (LPCVD) of a 10 nm thick layer of poly-silicon. The poly-silicon covers both sides of the wafer, and will be oxidized so a layer of 4-5 nm thick silicon oxide is grown on top of the SiRN. Again an Olin 907-17 positive photoresist layer is applied on the silicon oxide (from polysilicon) to pattern the topside of the membrane with 2 μm circular features, which are evenly spaced by 5 μm . UV-exposure for 4 seconds with a dose of 12 mW/cm^2 and development in OPD4262 are performed, followed by a 2 minutes 1% HF etch step which patterns the silicon oxide (from poly-silicon) on top of the SiRN. The photoresist layer is stripped from the oxidized polysilicon by acetone and isopropanol, followed directly by a tetramethylammonium hydroxide (TMAH) etching step to etch through the remaining polysilicon onto the silicon nitride. The silicon nitride is etched using phosphoric acid (85% H_3PO_4 , 180°C). The 85% H_3PO_4 etches the 200 nm silicon nitride isotropically and thus creates a shadow mask from the polysilicon layer. SiO_2 etches 10 times slower than SiRN in 85% H_3PO_4 , 180°C. [13] This opens the option to stop the etching when the 40 nm thick SiO_2 sheet is reached during the etch process. This “internal” shadow mask is used for patterning of the gold which will be deposited both onto the newly exposed 40 nm thick SiO_2 sheet and on rest of the SiO_2/SiRN bilayer.

Figure 5.1 Process flow of the manufacturing process.

In order to prevent damage to the SiO₂/SiRN bilayer with the patterned gold a layer of Parylene C with a thickness of 1 µm is applied to protect this side of the substrate. The parylene C is resistant to 1%HF and also to TMAH. This allows removal of the oxidized poly-silicon on the backside using 1%HF and removal of silicon by TMAH up to the 40 nm thick SiO₂ membrane. After removal of the Parylene C with oxygen plasma the substrate is diced into 12 mm square separate chips using a Disco Dicing DAD321. In this process the membranes could get damaged by the high pressure spray of the dicing blade cooling water, or during peel off from the dicing foil. Therefore, to protect the membranes from breaking during the dicing process, the gold patterned side of the wafer and membranes are spin coated with 10 µm thick AZ9260 photoresist, before being mounted on a dicing frame using foil. After dicing the chips are placed in acetone. The AZ9260 will dissolve and the dicing foil is lift-off from the chips. A high temperature treatment at 1064°C for 6 hours in ambient atmosphere (TOMA TSD 12, Volkel, the Netherlands) is performed to create the nanopores through the SiO₂. After the heat treatment a gold etch is performed (Gold etchant, Standard, 651818-500ML, Sigma Aldrich) to avoid interference from the gold while measuring the ionic current through the nanopore (see later). After removal of the gold, a piranha (H₂SO₄:H₂O₂, 80°C) cleaning for 10 minutes is performed, followed by a 20 minutes O₂ plasma cleaning. Directly after the plasma cleaning the chip is put in a beaker with demineralized water to circumvent any filling issues of the nanopore in the conductance measurements.

5.2.2 Membrane

Thin films contain compressive or tensile stress due to the material properties and the method of how the film is applied. In the case of SiO₂ the residual stress is a compressive stress, for the case of SiRN this is a tensile stress. With these properties combined one could create a stable, non-buckled bilayer membrane of SiRN and SiO₂, where the SiRN forms a ridged support and the SiO₂ can be used for nanopore creation. Removal of the Si below a SiO₂/SiRN bilayer results in a freely suspended membrane mounted to the Si on the sides of the membrane. Following Popescu et al. [7] a value for the critical stress S_{cr} , in a SiRN monolayer membrane can be found using:

$$S_{cr} = \frac{h^2}{a^2} \frac{E}{1 - \nu^2}$$

Here the membrane thickness is given as h , and the area of the membrane as a . E represents the Young's modulus, and ν Poisson's ratio. For the calculation of the critical stress the values for the mechanically stable 200 nm thick SiRN layer are used, the values for the 40 nm thick SiO₂ layer are neglected. For the total stress, S_{tot} , the values of both the SiO₂ and

SiRN layers are used. Buckling appears above the critical stress S_{cr} . To predict the total stress S_{tot} , the residual stresses of SiO_2 and SiRN should be known to calculate [7]:

$$S_{tot} = \frac{S_{\text{SiO}_2} * h_{\text{SiO}_2} - S_{\text{SiRN}} * h_{\text{SiRN}}}{h_{\text{SiO}_2} + h_{\text{SiRN}}}$$

The thicknesses of the layers are given as h_{SiO_2} and h_{SiRN} in the membrane stack. Calculation of the stresses is given in the Results and Discussion section.

5.2.3 Characterization

Characterization of nanopores in the membrane is performed using high resolution scanning electron microscopy (HRSEM) to investigate morphology. To verify through-hole creation, transmission electron microscopy (TEM) was used. A second method used to verify whether through-hole nanopores were created was by measuring the ionic conductance of the membrane when suspended in solution. The setup for the conductance measurements is shown in Figure 5.2. The chip containing the nanopores was clamped by two O-rings. The reservoirs are filled with the 1M KCl solutions and the electrodes are placed in the trans- and cis-reservoirs.

For the transmembrane conductance measurements two reference electrodes were used (Calomel, XR110 13311-A03). Prior to each series of measurements an inspection of the electrodes was performed by submerging them both in a 1M KCl solution to verify if there is no voltage offset between the two electrodes and a low ohmic connection to the solution. Cyclic voltammetry was then used to apply a voltage profile to the electrodes and measure the current through the membrane.

Figure 5.2 Ionic current measurement setup.

5.3 Results and Discussion

5.3.1 Manufacturing

Figure 5.3a and 5.3b show one of the twenty 25 x 25 μm SiO_2/SiRN bilayer membranes before and after heat treatment respectively. Each chip contains 20 silicon nitride membranes in total.

Figure 5.3a The SiO_2/SiRN bilayer membrane before heat treatment. Figure 5.3b The surface covered with gold nanoparticles after annealing for 6 hours at 1064°C. The membrane contains 30 SiO_2 membranes with 2 μm diameter, Figure 5.3c: a single SiO_2 membrane after gold etch showing 6 nanopores, Figure 5.3d and 5.3e: close-ups of the nanopores in the square areas indicated in 3c.

Each silicon nitride membrane is supporting 30 individual, 2 μm diameter, SiO_2 sheets. The entire surface of the SiO_2/SiRN bilayer membrane is covered with dewetted gold particles after heat treatment. We assume, based on previously published results that a thin layer of silicon oxynitride could have formed on the SiRN during the heating in ambient atmosphere. [5] The HRSEM image in figure 5.3c shows an individual SiO_2 membrane, after gold etching, where six nanopores can be observed.

The chips have been placed in gold etchant to remove all gold particles. The formation of multiple pores can be explained by the break-up from the originally continuous gold film on the SiO_2 due to pinch-off, as explained in chapter 2. [14] The separate gold nanoparticles will then each penetrate the SiO_2 membrane, forming nanopores. Figures 5.3d and 5.3e show a close-up of areas containing nanopore(s). Both the SiO_2 membrane and the SiRN surface show ridges as a result of ceramic migration under the gold nanoparticles, whereby a hexagonal shape represents the hexagonal crystalline gold nanoparticle. [5]

5.3.2 Membrane

Figure 5.3a and 5.3b show no buckling before and after heat treatment. This indicates that the total stress in the membrane is still below the critical stress value, above which buckling would occur. A 25 x 25 μm membrane, with a SiO_2 thickness of 40 nm and a SiRN thickness of 200 nm has a critical stress of 29,8 MPa, while a total stress of 16,7 MPa is calculated. The presence of the nanopores and the possible densification of the SiRN as a result of heat treatment has not been taken into account for these calculations.

5.3.3 Characterization

Evidence of nanopore through-hole formation is also given by TEM imaging, shown in figures 5.4a-d. The average size of the nanopores measured by TEM was 102 nm in diameter, with a standard deviation of 37 nm ($n=26$). The nanopore diameters were estimated from 14 of the 30 SiO_2 sheets in figure 5.4a. Extrapolation of the number of nanopores per SiO_2 patch would result in 56 nanopores per membrane and thus a total of 1120 nanopores per chip. However, apart from by microscopic observations, the number of nanopores per chip was also determined via the trans-membrane conductivity measurements. Five different chips were measured in the trans-cis setup, whereby four chips contained membranes with nanopores and one chip served as reference. Each chip has 20 membranes, each 25 by 25 μm squared, with 30 SiO_2 sheets with nanopores. A voltage sweep was applied from -5mV to +5mV at a rate of 1 mV/s and the resulting ionic current through the membrane was measured. Figure 5.5 shows the cyclic voltammetry curves of the closed membrane serving as reference (*Chip 1*) in green, and for the membranes with nanopores (*Chip 2-5*). The ionic current through the chips with membranes ranged from -

0.8 μA to +0.8 μA as can be observed in Figure 5.5. The conductance of each chip was calculated as the average slope of the CV curves by a MATLAB script and was found to be $\sim 0.15 \text{ mS}$.

Figure 5.4a TEM image of the full silicon nitride membrane. Figure 5.4b a single SiO_2 membrane. Figure 5.4c an open nanopore. Figure 5.4d, close-up of the nanopore through hole shown in Figure 5.4c.

Figure 5.5. Cyclic voltammetry graph of 5 measured chips. Chip 1 contained no nanopores, chip 2-5 did contain nanopores.

For ease of calculation, each pore was assumed to be a cylindrical resistor and the membrane was assumed to be electrically equivalent to an array of pores in parallel not influencing each other. The total conductance of the chip is then equal to the sum of all pore conductances. The conductance for a single pore with diameter d was calculated using [15]:

$$G_{pore} = \sigma \left(\frac{4h}{\pi d^2} + \frac{1}{d} \right)^{-1}$$

The bulk solution conductivity σ was set to 10.8 S/m (for 1 M KCl at room temperature), and each pore was assumed to have a conductivity equal to this bulk conductivity. The 26 pore diameters which were observed in the TEM measurements served as an input for this

calculation, which resulted in a mean pore conductivity of $0.78\ \mu\text{S}$ with a standard deviation of $0.34\ \mu\text{S}$.

Using this calculated pore conductance and the measured membrane conductance, the total number of nanopores in the chips is estimated to be 235 with a standard deviation of 115 nanopores. The characterization using TEM mentioned above provided a measure for the average nanopore diameter of 102 nm and a nanopore count of 1120 nanopores per chip. The estimate from the ionic current measurements thus was almost 5 times less compared to the estimation based on the TEM results. The exact number of nanopores thus remains unclear.

5.4 Conclusion

The internal shadow mask process presented here can be used to expose small features and as such is expected to be able to create even smaller nanopores in thinner membranes, since the process is easily downscalable. The process presented here relies on a single mask exposure step for each side of the wafer. A single alignment step is advantageous since it reduces alignment errors and thus increases yield. This approach could potentially, in combination with an established sub-micrometer lithography technique like laser interference lithography [16] or using Talbot lithography [17] and by simply varying the bilayer thicknesses and the gold layer thickness, create nanopores with low-nanometer dimensions. We further demonstrated that the combination of a SiO_2/SiRN bilayer membrane prevents buckling caused by heating, which is needed to create the nanopores in the SiO_2 membranes by gold penetration.

5.5 References

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6. Flow cell and array electron beam patterning

6.1 Introduction

As described in chapter 1, the aim was to develop a fast and accurate method for detection of tuberculosis by designing a diagnostic point-of-care device based on plasmonic sensing with a gold nanoparticle array. This way a mobile tool can be brought to the possibly infected patients and diagnosis can be performed. [1] Mobility of the equipment requires a device no larger than a coffee mug, and the facility of interfacing with a laptop computer. Since the detection method for tuberculosis is nano- and microtechnology-based, space requirements should easily be met for the microfluidic sensor chip. A flow cell with a microfluidic channel of 500 μm wide, 20 μm high and few millimeters long, in which the array of 80 nm diameter gold nanoparticles with a spacing of 5 μm is contained, will be used to run the diagnostics protocol. The sample will be flown through this cell and applied to the gold nanoparticle surface as part of the proposed assay. [2] A process to package the array by using SU-8 foil, once the array is manufactured into a flow cell, is applied. [3] As explained in chapters 2 and 3, the method to manufacture the array by heating of gold nanoparticles caused rearrangement of the underlying substrate and gold embedding. In this chapter we first report preliminary results on a flow cell incorporating randomly distributed gold nanoparticles. We subsequently report on preliminary experiments to manufacture gold nanoparticle arrays using an alternative route with electron-beam patterning. With the current state of the art in electron beam patterning, writing features of 20 nm in diameter is feasible. [4] [5] Though this method is much more expensive than the heating method we attempted before, it was necessary as the heating method proved to be unsatisfactory and not reproducible.

6.2 Materials and Methods

6.2.1 Flow cell manufacturing

The flow cell was constructed using randomly distributed gold nanoparticles, and in a later phase was also suited for the incorporation of the regular gold nanoparticle array. The process flow for manufacturing the flow cell is shown in figure 6.1. A substrate was laminated and patterned with I-HE dry resist powderblast foil (Harke Group, Bochum Germany). After powderblasting of the through holes an SU-8 foil was laminated on the bottom surface of the top substrate followed by a bake step for 5 minutes at 95°C. Patterning of the SU-8 foil was done using photolithography, with a UV exposure time of 45 seconds. UV exposure was followed by a post exposure bake. The substrates were

ramped up to 95°C (5 minutes at 50°C, 5 minutes at 65°C and 5 minutes at 85°C). The substrates were then left to cool down to below 50°C before taking them off the hot plate. This is done to prevent stress formation in the SU-8 layer. The bottom substrate was cleaned using acetone and IPA and was given an oxygen plasma treatment for 5 minutes. The substrate was then coated with a 3-aminopropyltriethoxysilane (APTES) coating to serve as an adhesion layer for the gold nanoparticles. [2]

Figure 6.1 Fabrication process of the flow cell. In column 1 the topside of the flow cell is prepared. Powderblast holes are made and SU-8 epoxy foil is applied and patterned using lamination and lithography. In column 2 the bottom part is prepared by APTES coating followed by deposition of gold nanoparticles on the surface.

The bonding of the SU-8 layer to the top plate was performed using a heated press (Carver Inc., USA). The temperature of the press plates is set at 150°C and the pressure is set at 17800 N. The substrates are pressed together for 6 hours. The bonded substrates are mounted on a dicing frame by applying a slab of foil on the powderblasted side of the bonded substrates, connecting the bonded substrates to the dicing frame. In this way no contaminants from the cooling water of the dicing blade will enter the microfluidic channels of the chip. The bonded substrates are finally diced into 10 mm x 20 mm chips using a Disco DAD321 dicing machine.

6.2.2 Electron beam manufacturing of a gold nanoparticle array

Writing of the wafer scale pattern was done with an EBP system from Raith at the Kavli institute in Delft, the Netherlands. The wafer scale design was such that from one wafer, 50 chips of 10 mm x 20 mm could be made. Per chip two arrays of 2,6 mm x 7 mm were written. Figure 6.2 shows a sketch of the bottom part of the chip design.

Figure 6.2 Sketch of the bottom part of the chip design.

When using electron beam patterning, a high power electron beam crosslinks poly methyl methacrylate (PMMA, MicroChem, Corp.). [6] The crosslinked PMMA is developed with MIBK:IPA developer (MicroChem, Corp.) When electron beam writing is used on a substrate, the conductivity of the substrate plays an important role. In this case the pattern needs to be written on an insulating SiO_2 substrate. If no measures are taken, drift due to surface charging will then result in patterning errors. For this reason a conducting anti-charging layer of chromium with a thickness of 40 nm thick is deposited on the SiO_2 surface by means of sputtering.[4] A schematic overview of the process is given in figure 6.3. The fused silica wafers are cleaned using a standard cleanroom wafer cleaning protocol of two times 5 minutes cleaning in nitric acid (HNO_3), followed by 10 minutes cleaning in hot 95°C HNO_3 . After rinsing and dry spinning, a 5 minutes UV ozone cleaning is performed. A layer of 40 nm chromium was then sputtered (200W, Ar flow 150 sccm). A

layer combination of poly methyl glutarimide (PGMI) and PMMA is used to create a lift-off mask for the gold nanoparticle arrays. PGMI (MicroChem, Corp.) 7% was applied by spin coating in two steps, 5 seconds at 500 rpm and 55 seconds at 2500 rpm, followed by a bake step on a hotplate for 5 minutes at 200°C. Subsequently, 2% PMMA 950K was applied by spin coating in two steps, 5 seconds at 500 rpm and 55 seconds at 6000 rpm, followed by a bake step on a hotplate for 30 minutes at 175°C. Squares of 10x10mm² were then exposed with the E-beam using a spot size of ~80 nm (79nm, 151nA, 400μm aperture and 100kV) and a dose of 50000 μC/cm². The PMMA layer was then developed using MIBK: IPA developer for 60 seconds followed by development of the PGMI using MF321 (MicroChem, Corp.) for 12 seconds. The substrates were rinsed in demineralized water, followed by spin drying. A UV/ozone treatment followed, after which a chromium etch step was performed (Chrome etch n° 1, MicroChemicals GmbH). Then a 70 nm thick gold layer was deposited by vapor deposition in a Balzers BAK 600 apparatus. After deposition the PMMA was lift-off using sonication and N-methyl-2-Pyrrolidone (NMP), followed by 15 minutes in acetone, a demineralized water rinse and dry spinning. The patterned chromium layer was then removed by stripping in chromium etch (Chrome etch n° 1, MicroChemicals GmbH). The substrate is mounted on a dicing frame by applying a slab of foil on the processed side of the substrate, connecting the substrate to the dicing frame. Via this procedure no contaminants from the cooling water of the dicing blade will affect the patterned surface. The substrate is then diced into chips using a Disco DAD321 dicing machine. After chip separation the chips are cleaned using oxygen plasma. In the case of the flow cell, the bonded substrates are mounted as a whole.

Figure 6.3 The process for electron beam writing on an insulating substrate

6.2.3 Characterization of the gold nanoparticle array

The characterization of the gold nanoparticle arrays was done using three different methods. By means of dark field microscopy an estimate for the coverage can be found. Atomic force microscopy (AFM) is used to obtain information about the height of the deposited layer. High resolution scanning electron microscopy (HRSEM) was used to obtain information about the size and shape of the deposited gold nanoparticles.

6.3 Results and Discussion

6.3.1 Flow cell manufacturing

The flow cell manufacturing was successful, and a completed flow cell is shown in figure 6.4a. A chip holder was manufactured to allow placing the flow cell in the inverted microscope shown in figure 6.4b. Apart from optical access, the chip holder allows easy fluidic connectivity via nanoport connectors and fused silica tubing (Inacom Inc.). Using this setup, a pilot assay was performed using the randomly distributed gold nanoparticles.

Figure 6.4a The glass/SU-8/glass chip incorporating the flow cell with gold nanoparticle array; figure 6.4b The chip holder in which the flow cell chip is placed. A random distribution of gold nanoparticles in a 1,5 mm wide flow cell channel is shown in figure 6.4c, where the field of view is 400 x 350 μm .

In this assay no binding of the secondary gold nanoparticles was observed. A possible explanation could be that the SU-8 foil on heating released some volatile solvents which

covered the gold nanoparticles on the surface, so no binding could take place when the assay was performed. Further experiments are necessary to pinpoint the cause of the non-binding and to improve the manufacturing procedure.

6.3.2 Electron beam manufacturing of a regular gold nanoparticle array

A chromium etch (Chrome etch n° 1, MicroChemicals GmbH) was performed for 2 minutes after which inspection was done using dark field microscopy and HRSEM imaging. In both cases very few gold nanoparticles were found, in the range of 18% coverage. In the dark-field microscopy image of figure 6.5 the bright spots are gold nanoparticles and the remaining blue dots are unknown residual material.

The low coverage of the gold nanoparticles could be due to the removal procedure of the PMMA and PGMI resist, where a lift-off was performed in an ultrasonic bath with NMP, followed by rinsing with acetone and demineralized water. The high energy of the ultrasonic bath can well have been sufficient to remove the gold from the substrate, as no bonding material had been applied between the substrate and the gold.

Figure 6.5 The gold nanoparticle array after chromium strip. In the array some gold nanoparticles are visible (bright spots), while residual material is visible in the remaining array spots (blue spots).

Inspection of the sample surface with atomic force microscopy showed a residual layer after chromium stripping from the surface. Figure 6.6 shows three takes of the substrate. Each take a closer look at one of the chromium etched locations. A ridge of 20 nm height was visible surrounding the location where the initial chromium etch was performed. It is very likely the blue spots which are visible in the dark field image in figure 6.5 are in fact these circular features. Moreover since also after oxygen plasma treatment for 15 minutes there were no more particles visible on the substrate surface.

Figure 6.6 Three takes of the substrate surface after chromium strip. Each take a closer look. Circular ridges are found on the location where the chromium was initially etched.

Before the chromium layer had been stripped, inspection with AFM was performed and the result is shown in figure 6.7. It was found that the gold nanoparticles have a height of 70 nm and are located on the fused silica substrate surface. Before the chromium etch step they are still surrounded by the chromium layer.

Figure 6.7 AFM image of a single gold nanoparticle prior to chromium etching. In the direct surroundings of the gold nanoparticle the chromium was etched during manufacturing (see figure 6.3).

Figure 6.8a, Gold nanoparticles in the array prior to chromium etching, observed by HRSEM. As in the dark-field microscopy image of figure 6.4 a low coverage is observed. Figure 6.8b, a single triangular shaped gold nanoparticle, surrounded by chromium.

Figures 6.8a and 6.8b show HRSEM pictures of the array. The array of gold nanoparticles shown in figures 6.5-6.8 does not have the desired properties. The coverage of the gold nanoparticles in the array is low (18%) and the gold nanoparticle shape, which will be of influence on the plasmonic signal, is triangular instead of the desired spherical shape whereby the ribs of the triangle have a length of between 140 nm and 160 nm ($n=8$). The triangular shape appeared to be a result of the writing protocol which was chosen for the electron beam, which itself has a triangular shape. A circular exposure pattern could have been created when the electron beam would move in a circle. This small difference in protocol would however have increased the writing time five times. Therefore, in this case, the exposure was performed without the circular motion, and a fast single exposure was done, resulting in a shape similar to the shape of the electron beam, triangular in this case.

Based on figure 6.7 and 6.8 the volume of the triangular particle is estimated to be 394000 nm^3 . This is equal to the volume of a spherical particle with a diameter of 90 nm. An anneal step at 700°C for 1 hour, with 1 hour ramp-up time, was performed to create a spherical particle. After examination of three samples no gold particles were found.

6.4 Conclusions

A flow cell was successfully manufactured, based on a sandwich design of glass, SU8 and glass. The secondary gold nanoparticle binding protocol however proved unsuccessful in this cell and the process needs further optimization. The use of an electron beam to create the gold nanoparticle array was only partly successful. The patterning of the PMMA layer and the subsequent development of the PMMA and PGMI were well controlled.

Nonetheless, the writing protocol of the electron beam resulted in triangular openings and therefore triangular gold nanoparticles. Since the size and the shape of the gold nanoparticle determine their plasmonic resonance peak, and the size and shape of the gold nanoparticles were not according to the required specifications. The array, apart from the problematic process, would not have been functional. The etching of the chromium through the holes was adequate, in view of the fact that a large area of chromium was etched away from below the PGMI resist. The adhesion of the gold to the substrate proved to be problematic and removal of the gold nanoparticles from the substrates is expected to have happened during sonication.

The anneal experiment performed with the electron beam patterned substrate did not show any gold particles after a 700°C heat treatment. It remains unclear whether these gold nanoparticles have been removed from the surface during the wet processing steps or as a result of the heat treatment.

6.5 References

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7. Conclusions and Outlook

Nanotechnology is settling in more and more in our everyday lives, and has the potential to have a positive impact on the quality of life. This thesis describes the methods, experiments and results of research performed to investigate a low-cost method for fabrication of a nanotechnology-based tool for point-of-care diagnostics of tuberculosis. In this diagnostic device a plasmonic sensor would be used consisting of a large ($\sim 10^6$) array of gold nanoparticles with diameters in the order of 80 nm. The equipment which is used for fabrication of patterns and features on the nanoscale, such as this array, is usually costly due to operating and maintenance costs. For this reason we aimed to use a simple and cheap manufacturing method for the gold nanoparticle arrays, namely the dewetting of photolithographically prepatterned gold. This approach unfortunately proved unsuccessful as described in chapter 2. Later we therefore resorted to the use of the (expensive) electron beam writing tool. Since also this method however failed, the aim of this thesis was not met: the gold nanoparticle array fabrication process was not delivered using either the dewetting of prepatterned gold method or electron beam writing. No experimentation with bacterial DNA or RNA on a micromachined gold nanoparticle array has therefore been performed as a result of this.

The research however yielded other useful results: we found that the heat treatment of the prepatterned gold did allow nanomachining using gold.

Dewetting is the rearrangement of a patch of gold atoms on a substrate driven by minimization of the interfacial energy to form a smaller patch. It occurs when heating the gold to higher temperature. This technique is explained in chapter 2, where also experiments are reported where the gold patch thickness and diameter, heating temperature, time and environmental pressure were varied in a number of ways to obtain an array that would meet the specifications as a functional tool for diagnostics. Phenomena related to the temperature treatment at temperatures higher than 900°C, like evaporation and ridging were found and described making use of imaging techniques like atomic force microscopy (AFM), high resolution scanning electron microscopy (HRSEM) and spectroscopy. A particle array of the desired dimensions, which would be able to function in a diagnostics tool, was obtained by a combination of heating gold at 900°C and 950°C in a low pressure environment. The low pressure led to an accelerated evaporation rate when dewetting the gold patches. This result was unfortunately only once observed, and could not be reproduced. Therefore it was concluded that at present reproducibility of the obtained results was not proven sufficiently. It is advised to further investigate the dewetting

approach in the future, as it potentially does offer a cheap and simple method for nanoparticle array fabrication.

It was found that dewetting at a temperature above 1000°C led to the gold embedding in the fused silica (SiO_2) substrate and the creation of a dead-end nanopore above the embedded gold particle. This surprising result is reported in chapter 3. We ascribe it to migration of the SiO_2 under and around the gold particle to the gold/air/ SiO_2 triple line and simultaneous evaporation of the gold at the high temperatures. The nanopore manufacturing technique can in principle be applied to any metal/ceramic combination that on the macroscale exhibits ridging without chemical reaction. Examples of such combinations include metals on ceramics such as for example Au, Al, Ni, Cu and Mg on Al_2O_3 and Pt on SrTiO_3 , all under the proper partial O_2 pressures but also of ceramics on metals. The easy manufacturing procedure and controllability of the presented nanopore formation mechanism, the wide applicability of the products formed and its potential application in a wide choice of materials is quite attractive. It was also envisaged that by implementation of the technique to a thin membrane, this method could potentially be a low-cost and versatile replacement for conventional through-hole nanopore manufacturing methods.

A transfer of the technology was then performed from the SiO_2 substrate onto a silicon rich silicon nitride (SiRN) substrate. A SiRN membrane is mechanically more stable compared to SiO_2 because of the internal stress component. For SiO_2 this stress component is compressive, for SiRN this stress component is tensile. The method described in chapter 4 proves to be capable of creating nanopore through-holes in a ~40 nm thick silicon oxynitride (SiON) membrane. By starting the process with a 36 nm thick SiRN membrane with Au patches on top, a heat treatment by a combination of oxidation, capillary action and gold evaporation leads to wafer scalable nanopore through-hole formation. Imaging of the nanopore through holes was done using scanning transmission electron microscopy (STEM). X-ray photoelectron spectroscopy (XPS) measurements show oxidation of the original SiRN to SiON. Characterization of the layer composition was also performed with a potassium hydroxide (KOH) etch. Buckling of the membrane is also observed, which is a result of the consequent volume increase combined with the internal compressive stress of SiO_2 . The transformation of the membrane material from SiRN to SiON was not expected, as well as the stress induced buckling as a result of this transformation. In this chapter we showed the proof of principle of a new method for nanopore through-hole fabrication, potentially competing with methods like electron beam writing or ion beam milling. A buckled membrane can be used, for example, as a valve in a microfluidic setup where the membrane deflection can be used to switch between modes.

To overcome the membrane buckling, an approach was investigated in which a 40 nm thick SiO₂ membrane was suspended in a 200 nm thick SiRN membrane. This approach is described in chapter 5. Again on heating nanopore through holes were created in the SiO₂, as was the case for the nanopore formation in bulk SiO₂ described in chapter 3. The nanopores were characterized using HRSEM, transmission electron microscopy (TEM) and ion current measurements. The process presented here relies on a single mask exposure step for each side of the wafer. The internal shadow mask process presented here can easily be scaled down. It can in future thus be used to expose smaller features which, in combination with thinner membranes, is expected to enable the creation of even smaller diameter nanopores. This single alignment step can be beneficial because it can reduce alignment errors and thus positively impact the yield of the process. The method described in chapter 5 has the potential to create, when combined with a technique like the novel Talbot lithography, nanopores close to, or even in the single nanometer regime. Moreover, by applying variation in the layer thickness of the SiO₂/SiRN bilayer, any desirable pore length through the SiO₂ layer, depending on the initial deposited SiO₂ layer thickness, can be manufactured.

Fabrication of a flow cell and a gold nanoparticle array using electron beam writing, was investigated and explained in chapter 6. The flow cell was assembled using a patterned intermediate layer of SU-8. In this cell an assay was attempted but did not appear successful, possibly due to solvent released from the used materials. This approach to constructing a flow cell therefore in future needs to be optimized.

The conclusion of chapter 2 had been that at present a reliable cost effective approach to manufacturing the gold nanoparticle array for the diagnostics tool was not found via heating of gold patches on a fused silica substrate. For the manufacturing of the gold nanoparticle array electron beam writing was therefore chosen as alternative technique because, apart from a single success, the dewetting approach resulted in gold nanoparticles that either became embedded or that had a diameter too large for plasmonic sensing. A result of electron beam writing was that the gold nanoparticles were triangular, which also influences their plasmonic behavior. An anneal step could have solved this problem, since the volume of the triangular particles, with a height of 70 nm and rib lengths of the triangle of 150 nm length gives a similar volume compared to a sphere with a diameter of 90 nm. For future experimentation a technique like Talbot lithography should be considered for creation of the array gold nanobeads.

The nanopore membranes which were developed using the nanopore creation method presented in chapters 3 to 5 could find application in the field of sieving or ultrafiltration when multiple nanopores are needed in array configuration. The method also conveniently

enables the creation of single nanopores. Single nanopores can be highly useful in the field of single molecule translocation and sensing. For example, the nanopores created in SiO_2 , via the method presented in this thesis, could be used to mimic biological ion channels by adding fluid lipid bilayers to the nanopores sidewalls. Another advantage is the use of SiO_2 and SiRN, which both find applications as optical waveguide materials, potentially opening up a range of new detection methods by incorporating light to measure biomolecule pore translocation and sensing experiments. The manufacturing method furthermore has the large advantage that the location of the nanopore or nanopores can be chosen at will by prior photopatterning.

Preliminary results on temperature programming for pore formation were shown in appendix 1. They show that very small pores can be machined by using higher temperatures, and that some programming of the pore diameter might be possible. This offers the potential of tuning nanopore properties for molecular separations.

In chapter 3, 4 and 5 we showed that pores could be created using gold on SiO_2 and SiON. Ridging however is known from many other metal/ceramic combinations, and these could in future all be investigated for pore formation.

8. List of Publications

8.1 Journal articles

L. J. de Vreede, A. van den Berg and J. C. T. Eijkel, *Nanopore fabrication by heating Au-Particles on Ceramic substrates*, Nano Lett. 15(1):727-731, 2015.

L. J. de Vreede, M. Schmidt-Muniz, A. van den Berg and J. C. T. Eijkel, *Nanopore fabrication in silicon oxynitride membranes by heating Au-particles*, J. Micromech. Microeng. 26:037001, 2016.

L. J. de Vreede, J. W. Berenschot, N. R. Tas, W. T. E. van den Beld, J. T. Loessberg-Zahl, A. van den Berg and J. C. T. Eijkel, *Nanopores Created using an Internal Shadowmask Process*, accepted oral presentation at IEEE-NEMS 2016 Conference, Sendai, Japan; to be submitted to Micro & Nano Letters

8.2 Conference contributions

L. J. de Vreede, A. van den Berg and J. C. T. Eijkel, *Can Gold sink into Silica Glass?*, NanoCity 2015 (Poster presentation), October 5-6, Amersfoort, The Netherlands.

L. J. de Vreede, A. van den Berg and J.C.T. Eijkel, (2014) *Evaporation driven nanomachining to fabricate nanopores in SiO₂* at microTAS 2014, San Antonio, TX, USA (pp. 1844-1846)

L. J. de Vreede, A. van den Berg and J. C. T. Eijkel, *Evaporation driven nanomachining*, NanoCity 2014 (Poster presentation), October 27-28, Utrecht, The Netherlands.

L.J. de Vreede, K. Göeken, R. Gill, A. van den Berg and J.C.T. Eijkel, *Fabrication of gold-nanoparticle arrays using photolithography and thermal dewetting* at MicroTAS 2013, Freiburg, Germany (pp. 1418-1420)

8.3 Other articles

Y.Xie, D. Bos, L.J. de Vreede, H.L. de Boer, M.J. van der Meulen, M. Versluis, A.J. Sprenkels, A. van den Berg and J.C.T. Eijkel
High-efficiency ballistic electrostatic generator using microdroplets
Nature Comm. 5:3575, 2014

T. Nguyen, Y. Xie, L.J. de Vreede, A. van den Berg, J.C.T. Eijkel

Highly enhanced energy conversion from the streaming current by polymer addition

Lab Chip 13:3210-3216, 2013

Appendix 1

Figure S1: (a) 3D-AFM image of the rim surrounding the nanopore entrance after the 900°C heat treatment. (b) cross-sectional profile heights from the data of figure S1a. The white dashed lines in the insets represent the profile scan direction.

Figure S2: A gold particle of larger volume which was heated to $1067^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for 1 hours, showing ridge formation on the left side of the rim initiated before the gold particle and thus the rim reached its final size and shape. This is evidence the SiO_2 rim copies the shape of the gold.

Section 3: Pore length as function of time

The pore volume V_p with pore length y grows by

$$\frac{dV_p}{dy} = \frac{\pi}{4} d_p^2(y)$$

where $d_p(y)$ is the pore width at the gold nanoparticle surface. In the calculations we take for the pore width

$$d_p(y) = d_{p,0} - 0.06y$$

where the factor 0.06 is the experimentally determined value for pore contraction with pore length.

The evaporation flux from a pore of length y is

$$J(y) = \frac{1}{R(y)} \frac{\Delta p}{RT} V_m$$

where $R(y)$ is the diffusion resistance for a pore of length y . Along the diffusion path the diffusion resistance is a function of y , which we express in a local resistivity ρ_y :

$$\rho_y = \frac{4}{\pi d_{p,y}^2} \cdot \frac{1}{D_y}$$

with the local pore width $d_{p,y}$ and local diffusion coefficient D_y . The latter can be derived as follows. The mean free path of gold atoms in ambient air at $1.013 \cdot 10^5$ Pa and $1067^\circ\text{C} \pm 5^\circ\text{C}$ can be calculated as 298 nm. Since the pore diameter is always smaller than 60 nm, the Knudsen number is always larger than 5 and we can assume Knudsen diffusion. The Knudsen diffusion coefficient is given by

$$D_y = \frac{d_{p,y}}{3} \sqrt{\frac{8RT}{\pi M_A}}$$

where M_A is the molecular weight of Au (0.197 kg/mol).

We then obtain the diffusion resistance $R(y)$ by integrating the resistivity ρ_y over the pore length y

$$R(y) = \int_0^y \rho_y dy = \frac{4}{\pi d_{p,y}^2} \cdot \frac{1}{D_y}$$

Finally we derive the rate of pore growth by realizing that $J = dV_p/dt$:

$$\frac{dy}{dt} = \frac{dV_p}{dt} \cdot \frac{dy}{dV_p} = \frac{1}{R(y)} \frac{4}{\pi d_p^2(y)} \frac{\Delta p}{RT} V_m$$

$$R(y) \frac{\pi d_p^2(y)}{4} dy = \frac{\Delta p}{RT} V_m dt$$

We then obtain the pore length as function of time by integrating

$$R(y) \int_0^y \frac{\pi d_p^2(y)}{4} dy = \frac{\Delta p}{RT} V_m t$$

Hereby we use for Δp , the vapor pressure of Au at 1050°C, the value of $1.6 \cdot 10^{-3}$ Pa. (Lide, D.R.; CRC Handbook of Chemistry and Physics (CRC Press, Boca Raton, FL, 2003), and for the molar volume of Au, V_m , we take 10^{-5} m³/mol.

Figure S4: Image of the cross section of the pore. (a) showing the pore with 5 measurement locations for the EDS measurements (b) close-up of the filled pore. In the red circle Pt crystals are visible, which filled the pore. The Pt was coated in the pore and on the surface to prepare the substrate for STEM handling. The SiO₂ does not show any crystallinity, confirming its amorphous phase.

Section 5: Triple line angles from the Smith equation

Au/SiO₂/Air

For the Au/air interfacial energy we adopt the value of 1138 mJ/m² (Ricci E.; Novakovic R.; Wetting and surface Tension Measurements on Gold alloys, Gold Bull. 34, 41 (2001)). For the SiO₂/Air interfacial energy we take the value of 260 mJ/m² (Brunauer, S.; Kantro, D.L.; Weise, C.H.; The surface energies of amorphous silica and hydrous amorphous silica,

Can. J. Chem. 34, 1483-1496 (1956)). To derive the Au/SiO₂ interfacial energy, we base ourselves on macroscopic contact angle measurements which show an angle of 143° at 1353 K (Ricci E.; Novakovic R.; Wetting and surface Tension Measurements on Gold alloys, Gold Bulletin 34, 41 (2001)), resulting in a work of adhesion between Au and SiO₂ of 227 mJ/m². In combination with the Au/air interfacial energy of 1138 mJ/m² we then find a value for the Au/SiO₂ interfacial energy of 1171 mJ/m². The Smith relation is then satisfied for $\theta_{\text{air}} = 90^\circ$, $\theta_{\text{SiO}_2} = 103^\circ$ and $\theta_{\text{Au}} = 167^\circ$

Section 6 Rate of pore diameter decrease

Theory predicts that in its final growth phase, the pore diameter is $d \sin(\alpha)$, with d the gold nanoparticle diameter and 2α the angular diameter of the (111) gold plane. This implies that the following equality holds:

$$dV_{\text{GNP}} = d \left(\frac{1}{6} \pi d^3 \right) = - \frac{\pi (d \sin \alpha)^2}{4} dy,$$

where y is the coordinate normal to the substrate surface. This yields for the bead diameter

$$\frac{d(d)}{dy} = - \frac{3}{2} \sin^2 \alpha,$$

and for the pore diameter

$$\frac{d(d_p)}{dy} = \frac{d(d \sin \alpha)}{dy} = - \frac{3}{2} \sin^3 \alpha$$

From measurements on the EM picture (figure 2) we find the pore contraction speed $d(d \sin \alpha_G)/dy$ in the final 229 nm of the pore to be constant and equal to -0.06. This yields $2\alpha = 35^\circ$.

Figure S7: The ratio of pore diameter over gold nanoparticle diameter for 12 pores, obtained for different heating times from SEM pictures after fracturing the substrate. The ratio remains approximately constant and equal to 0.26 during the heating time. This value is slightly lower than the value obtained from the EM picture (0.29, figure 3.2). This is in accordance with the fact that it is probably slightly underestimated as the fracture most often will not occur exactly through the heart of the pore. Imaging resolution of the scanning electron micrographs introduces further uncertainty. The slope of the linear fit shown did not significantly differ from zero ($P > 0.95$).

Figure S8: HRSEM image of a tilted view of an array of nanopores in a 100nm thick SiO₂ membrane. The SiO₂ was thermally grown from a silicon substrate. The SiO₂ layer was subsequently etched free from the Si in order for a free standing membrane to remain. Subsequently gold was patterned by photolithography and the nanopores were created through heat treatment at 1050°C (ramp up time 1 hour, residential time 1 hour). Scale bar represents 5 μm . Inset shows a STEM image of a single pore, which is the same as figure 3b. Scale bar represents 100 nm.

Section 9: Triple line angles from the Smith equation for Au/Si₃N₄/Air

The interfacial energy of the Si₃N₄ interface can be deduced from the above-cited values for the Au/air interfacial energy, the Si₃N₄ interfacial energy, for which 46 mJ/m² is reported (L.S. Čerović and S.K. Milonjic, Adsorption of n-Alkanes on Silicon Nitride Nanopowder, J. Am. Ceram. Soc., 88, 1875–1878 (2005)) and the reported value of 157° for the contact angle of molten Au on Si₃N₄ (Ljungberg and Warren, Wetting of Silicon Nitride with selected metals and alloys, Ceram. Eng. Sci. Proc. 10, 1655-1666 (1989)). The last two data result in a value for the Si₃N₄/Au interfacial energy of 1090 mJ/m². Application of these data to the Smith equation results in $\theta_{\text{air}} = 165^\circ$, $\theta_{\text{Si}_3\text{N}_4} = 15^\circ$ and $\theta_{\text{Au}} = 179^\circ$. The calculated phase angles are extremely sensitive to errors in these input data because $\gamma_{\text{GC}} + \gamma_{\text{AC}} \approx \gamma_{\text{GA}}$.

For example, for a 1 degree change of the contact angle to 158° , $\theta_{\text{Si}_3\text{N}_4}$ becomes 35° . A second caveat involves the possibility of oxidation of the Si_3N_4 surface at the high temperatures used in air, which would modify the interfacial properties.

Figure S10: Left nanocrystal indentation versus heating time at 900°C. Right nanocrystal volume versus heating time at 1050°C Error bars represent standard deviation with n=4.

Figure S11: HRSEM image of a tilted view of (a) Heating at 10min 1050°C, 50 min 1070°C and (b) 10min 1050°C, 110 min 1070°C gave pores that suddenly narrowed to very small diameter. (c) Heating at (10min 1050°C, 50 min 1070°C, 60min 1100°C) resulted in entirely buried gold nanoparticles. Scalebar represents 100 nm.

Table S12: Table showing the chemical data for the fused silica substrates

Trace elements (ppm)

Al	Fe	K	Li	Cu	Na	B	Ca	Mg	P	Ti	OH
20	0,4	1	1,4	0,01	1,5	0,2	0,5	---	---	---	120-260

From: PlanOptik GmbH

Appendix 2

Supplementary information:

The supplementary information for the technical note “Nanopore Fabrication in Silicon Oxynitride Membranes by Heating Au-Particles consists of 3 figures.

Figure S1a Part of the SiON membrane with pores. In figure S1b the amount of pores per patch area are given.

Figure S2a AFM image of a pore, located within the perimeter of the deposited gold patch. Figure S2b shows the step height measured at the transition highlighted in figure S2a.

Figure S3 The result after 20 minutes 1%HF etch. The ridge has been etched away while a 2μm diameter area of SiON still remains. Scale bar represents 1μm.

Samenvatting

Dit proefschrift behandelt het proces van het “dewetten” van photolithografisch aangebracht goud op een transparant silicium oxide substraat. Goudschijfjes met een diameter van 2 micrometer of 600 nanometer en met een dikte variërend tussen 10 en 60 nanometer worden vervolgens verhit tot ca. 1064 °C. Het oorspronkelijke doel van deze methode was om een transparant oppervlak te bezetten met een regelmatig array van gouddeeltjes met een diameter van 80 nanometer en een onderlinge afstand van 5 micrometer. Dit oppervlak zou vervolgens gebruikt gaan worden voor detectie van biomoleculen als deoxyribonucleotide acid (DNA) en ribonucleic acid (RNA) om ziektes als *mycobacterium tuberculosis* te detecteren. Een methode om dit te doen met een array van gouddeeltjes was in het verleden ontwikkeld in de NanoBioPhysics groep op de Universiteit Twente, en was gebaseerd op een oppervlak dat was bedekt met random geïmmobiliseerde gouddeeltjes. Het gebruik van een regelmatig array zou de detectielimiet naar verwachting sterk verlagen.

Een gouddeeltje van 80 nm diameter op een transparant oppervlak is groen van kleur wanneer het wordt bekeken met een donkerveld microscoop. Wanneer de grootte, vorm, materiaalsamenstelling of de brekingsindex van het medium rondom het gouddeeltje verandert, wordt dit zichtbaar door een kleurverandering. De voorgestelde methode maakt gebruik van deze eigenschappen om DNA of RNA van bacteriën of virussen te detecteren. Eerst wordt een DNA of RNA molecuul aan het gouddeeltje gebonden dat zo is gemaakt dat het specifiek bindt aan de helft van het DNA of RNA dat gedetecteerd moet worden (zoals het RNA van de *mycobacterium tuberculosis*). De volgende stap is, dat het te onderzoeken monster over de gouddeeltjes wordt gespoeld. Na de hechting van het te detecteren DNA en RNA uit het monster aan het gouddeeltje wordt een tweede, kleiner (40 nm diameter) gouddeeltje over het oppervlak gespoeld dat geprepareerd is met de andere helft van het RNA of DNA van het detecteren DNA of RNA. Wanneer dit tweede deeltje bindt (wat alleen kan als het DNA/RNA van de bacterie is gebonden), verandert de kleur van het gouddeeltje in de donkerveldmicroscoop van initieel groen naar rood. De principes van dit proces worden uiteengezet in hoofdstuk 1 van dit proefschrift. Door het proces op silicium oxide uit te voeren, en een heel regelmatig array van gouden nanodeeltjes te maken zou in een latere fase detectie in een microfluidische opstelling kunnen worden gerealiseerd met een buitengewoon lage detectielimiet. Zo ver is het project wat betreft de detectie niet gekomen. Fabricage van de regelmatige array van gouddeeltjes in een enkele keer door dewetting lukte uiteindelijk slechts een maal onder lage druk condities in een vacuum oven. Het proces bleek helaas niet reproduceerbaar en hierdoor heeft geen RNA of DNA meting plaats kunnen vinden gebaseerd op de voorgestelde detectiemethode. De redenen waarom

de voorgestelde methode niet lukte leidden echter tot een nieuwe onderzoekslijn die in het proefschrift uitgebreid worden beschreven.

Gaandeweg het experimentele proces, waarin verschillende volumes goud op siliciumoxide werden verhit naar temperaturen variërend tussen 500 °C en 1064 °C, zoals omschreven in hoofdstuk 2, kwam aan het licht dat het gouddeeltje bij hoge temperaturen in het omringende siliciumoxide zakt. De verklaring die we hiervoor geven is dat het onderliggende siliciumoxide via het contactvlak met het goud naar de zijkant van het gouddeeltje wordt getransporteerd. Op deze manier wordt een gaatje gegraven onder het goudbolletje waar het goud in wegzakt, terwijl een rand siliciumoxide rond het gouddeeltje wordt opgebouwd. Dit proces bleek bekend te staan in de literatuur als “ridging”. Het “ridging” volgt op het “dewetten” van goud en beiden vinden plaats omdat het gouddeeltje en het silicium oxide zich in een metastabiele toestand bevinden, bepaald door hun vorm en de onderlinge oppervlakte-energiën. Indien de hoeveelheid goud constant zou blijven, zou een evenwicht op een bepaald moment worden bereikt. Echter, de hoge temperatuurbehandeling vindt bij hoge temperatuur (dicht bij het smeltpunt van goud, 1064 °C) plaats, en hierdoor zal ook een zekere mate van verdamping plaatsvinden. Het verdampen van het goud zorgt ervoor dat evenwicht continue *niet* bereikt wordt. Hierdoor is het mogelijk dat het goud deeltje naast dat het kleiner en kleiner wordt ook steeds dieper en dieper het siliciumoxide in zinkt en op deze manier een zogenaamde nanoporie creëert. Het goudvolume neemt hierbij af naar gelang de tijd waarin de materialen verhit worden. De achtergrond van deze nanoporievorming door het verhitten van goud op siliciumoxide is beschreven in hoofdstuk 3.

Nadat mogelijk is gebleken dat (doodlopende) nanoporiën kunnen worden gemaakt in een keramisch materiaal middels patroneren met goud en vervolgens verhitten, is gekeken of het ook mogelijk is om nanoporiën te maken dwars door een keramisch membraan. Wanneer nanoporiën door een membraan kunnen worden gemaakt biedt dit bijvoorbeeld de mogelijkheid om, gebaseerd op het principe van een Coulter counter, moleculen te tellen in een vloeistofoplossing. Hoofdstuk 4 omschrijft hoe goud wordt gepatroneerd op een siliciumnitride membraan dat vervolgens wordt verhit tot 1064 °C. Voor het membraan is daarbij 40 nanometer dik siliciumnitride gekozen om de mechanische stabiliteit van het membraan te waarborgen. Het resultaat is dat het siliciumnitride wordt omgezet in siliciumoxynitride door oxidatie, terwijl tegelijkertijd nanoporiën worden gevormd in het membraan op de plaats waar goud heeft kunnen “dewetten”. De gemiddelde diameter van de poriën bleek 170 nanometer. De omzetting naar siliciumoxynitride zorgt voor een compressieve stress in het membraan waardoor het membraan na de hoge temperatuur

behandeling plooien vertoonde. Dit kan het membraan enigszins flexibel maken wat potentieel problemen kan veroorzaken tijdens metingen.

Om een membraan zonder plooien te maken is het fabricageproces vervolgens aangepast. In hoofdstuk 5 wordt uitgelegd waarom er is gekozen voor een dubbellaag van siliciumnitride met daaronder siliciumoxide. De laagdikte voor het siliciumnitride is nu 200 nanometer en de laagdikte voor het siliciumoxide 40 nanometer. Deze keuze voor een dubbellaag heeft geresulteerd in vorming van een laag van siliciumoxynitride op het 200 nanometer dikke siliciumnitride membraan en nanoporiën in het silicium oxide gedeelte van het membraan. Door de penetratie van het goud waren daarnaast nanoporiën met een gemiddelde diameter van circa 102 nanometer gecreërd. De keuze voor een dubbellaags membraan brengt het voordeel met zich mee dat een groot aantal parameters, zoals maskeropening, laagdikte van het silicium oxide, laagdikte van het silicium nitride en laagdikte van het goud c.q. het volume van het goud kan worden gevarieerd. Dit schept de mogelijkheid om nanoporiën van allerlei lengte (silicium oxide laagdikte) en diameter (goud laagdikte) te maken in relatief stress-arme (ten gevolge van de silicium nitride laagdikte) membranen.

In hoofdstuk 6 wordt een nieuwe poging aangewend om, nu via het paterneren met een electronenbundel, een array van 80 nm goud deeltjes met een 5 micrometer onderlinge afstand te verkrijgen. Een substraat van siliciumoxide is voorzien van een 100 nanometer dikke chroomlaag alvorens een resistlaag wordt aangebracht. Voor het schrijven met een electronenbundel is namelijk een electrisch geleidende laag nodig om drift van de electronenbundel tijdens het schrijven te voorkomen. Na het schrijven van het patroon zal de chroomlaag geëtsd worden in een chroomets bad. Hierdoor kan er goud op de plekken waar het chroom is weggeëtsd worden gedeponneerd. Dit wordt dan gevolgd door het verwijderen van de resistlaag en de chroomlaag. Dit proces bleek helaas problematisch omdat de chroomlaag niet homogeen werd geëtsd in het etsbad, waardoor uiteindelijk een niet homogene matrix van gouddeeltjes zou ontstaan. De fabricage van een microfluidische chip met het gewenste goudarray is om deze reden niet gelukt.

Samenvattend, een stabiele en reproduceerbare technologie voor fabricage van een array van 80 nanometer goud deeltjes met een onderlinge afstand van 5 micrometer is niet ontwikkeld. Echter, een nog niet eerder omschreven methode voor fabricage van nanoporiën is wel ontwikkeld en is het belangrijkste product van het werk dat wordt behandeld in dit proefschrift. Conclusies en aanbevelingen naar aanleiding van dit werk staan uiteindelijk omschreven in hoofdstuk 7.

Dankwoord

“Nou, laten we het dan maar gaan doen!”

Het is 16 december 2011 en Jan spreekt zijn goedkeuring uit over mijn wens om een promotie opdracht te gaan doen. De woorden staan mij bij alsof ze gisteren uitgesproken zijn. Het heeft mijn koers verlegd in een zeer positieve zin. Dit maakt dat ik zeer dankbaar ben.

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Annemiek, lieve schat! Dankjewel dat je mijn leven zo enorm verrijkt, alles is leuker met jou erbij!

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