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Investigation of Metal-assisted Si Etching for Fabrication of Nanoimprint Lithography Stamps

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This diploma work is dedicated to my family and friends.
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ABSTRACT

This diploma thesis deals with the investigation of the metal-assisted catalytic etching (MaCE) of Si. One of the main goals is to study fabrication of stamps for nanoimprint lithography using MaCE.

Formation of nanoporous silicon (PSi), Si nanowires (SiNWs) and three-dimensional nanostructures in Si by MaCE is demonstrated. For this purpose optical lithography, electron beam lithography (EBL), shadow mask evaporation and aerosol nanoparticles deposition techniques have been utilized. The etching rate and surface morphology of Si (with Au lift-off films as a catalyst) as functions of time and concentrations of chemicals are measured in the current diploma work using optical microscope and scanning electron microscopy (SEM). In the current thesis it is shown that Si structures with sub-150 nm lateral sizes, high aspect ratio (up to 1:21), well-defined shapes, and various complexity can easily be fabricated by means of MaCE process.
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INTRODUCTION

These days, high-aspect ratio silicon structures are attracting interest due to their potential application in broad areas ranging from electronics, photonics, and renewable energy to biomedical sensing. There have been attempts to create new low-dimensional silicon nanostructures, including Si nanowires, porous silicon, and related nanodevices. Silicon nanowires (SiNWs), for example, are very attractive nanostructures because of their unique one-dimensional nature and associated electrical, mechanical, and thermal properties. Currently, SiNWs have been successfully implemented in solar cells, chemical sensors and field-effect transistors. Porous silicon (PSi) is widely employed in applications such as silicon-based optoelectronics, photonic crystals, optical filters, membranes, and molecular sieves. Interest in PSi is explained due to the large surface-to-volume ratio.

There are a number of techniques to produce nanostructures in Si. Standard fabrication techniques include wet chemical methods utilizing both acids and bases and dry chemical methods such as ion etching and deep reactive ion etching. These techniques have two limitations: complex 3D shapes are difficult to produce and it is very hard to maintain high aspect ratio structures with varying degrees of complexity as feature sizes shrink into the nanoscale.

SiNWs are produced by different methods such as laser ablation, thermal evaporation, chemical vapor deposition, molecular beam epitaxy, chemical etching, and solution growth. Nevertheless, controllable and repeatable fabrication of SiNWs arrays is still a problem.

PSi is usually produced by anodic etching, with and without illumination, by chemical etching, and by photochemical etching. The last two techniques are used without external bias. Chemical etching is usually slow, non-reproducible, and unreliable.

In the current diploma work, an alternative “top-down” approach, metal-assisted wet-chemical Si etching (MaCE) [1-4], is considered as a promising solution to obtain high aspect ratio nanostructures with well-defined shapes, and various complexity. The named approach is also defined as a promising solution to achieve aligned SiNWs with control of the diameter, length, spacing and density, and to create the PSi with controllable sizes and density of pores.

There is an increasing interest in nanoimprint lithography (NIL) due to its capability to produce sub-10 nm features, process simplicity, high throughput and low cost. One of the main aims of the diploma work is to study fabrication of NIL stamps using MaCE. The resolution and quality of nanoimprint is determined entirely by the stamp so its fabrication is of tremendous importance for NIL-based technology. In the present diploma thesis it is demonstrated that the negative Si stamp comprising of sub-150 nm structures with well-defined shapes and various complexities can be fabricated using metal-assisted catalytic Si etching.
1.1. Metal-assisted chemical etching of Si

Metal-assisted chemical etching (MaCE) is an alternative to the dry etching method. This is a highly anisotropic process. MaCE has recently been applied to fabrication of high aspect ratio SiNWs [4-8], three-dimensional, well-defined nanostructures [9-12] and PSi [3, 13-16]. In MaCE, a metal catalyst such as Au, Pt, or Ag is deposited onto a silicon surface as either nanoparticles or a discontinuous thin film that locally increases dissolution of silicon in an etch solution of hydrofluoric acid (HF) and hydrogen peroxide (H₂O₂). A simplified schematic of the MaCE process is illustrated in Fig. 1.1.

![Schematic illustration of the MaCE process.](image)

**Figure 1.1.** Schematic illustration of the metal-assisted chemical etching of Si.

The process begins with a metal patterning on the Si substrate (Fig. 1.1b). The sample is then immersed into an etching solution, which typically consists of diluted hydrofluoric acid/hydrogen peroxide (HF / H₂O₂). Catalytic etching of the Si substrate under the metal layer results in “sinking” of the metal into the substrate (Fig. 1.1c).

![Schematic illustration of the autonomous Au particle movement.](image)

**Figure 1.2.** Schematic illustration of the autonomous Au particle movement in bulk Si.
The metal-assisted Si etching process is described as a catalytic conversion of chemical free energy into propulsive mechanical power [1]. And it could be explained in the following way (Fig. 1.2).

In the current work Au was used as a catalytic metal. Therefore the etching process should be considered for the case of a Au particle. It has been suggested that the surface of a Au particle facing the etching solution acts as the cathode [2-4], which catalyzes H₂O₂ reduction, consuming H and electrons (e⁻). It could be described by the following reactions:

Cathode (Au):

\[
\begin{align*}
H_2O_2 + 2H^+ + 2e^- & \rightarrow 2H_2O \\
2H^+ + 2e^- & \rightarrow H_2
\end{align*}
\]

The surface of the Au particle facing the Si works as the anode and it catalyzes Si oxidation, generating H and e⁻, which is described as:

Anode (Si):

\[
\begin{align*}
Si + 2H_2O & \rightarrow SiO_2 + 4H^+ + 4e^- \\
SiO_2 + 6HF & \rightarrow H_2SiF_6 + 2H_2O \\
Si + 4HF & \rightarrow SiF_4 + 4H^+ + 4e^-
\end{align*}
\]

A potential difference appears between the cathode and the anode. Electrons flow from the anode to the cathode. A local current flows in the opposite direction, from the cathode to the anode.

The overall spontaneous power-generating reaction could be written in the following way:

\[
Si + 2H_2O_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O + H_2
\]

So the etching process is localized in the regions covered by Au. Thus, the etching of Si under the Au-particle results in its “sinking” into the substrate.

1.2. Investigation and applications of MaCE

A number of publications are related to the formation of nanoporous silicon, Si nanowires and three-dimensional nanostructures in Si by the metal-assisted catalytic etching.

According to the literature (see below) metal-assisted Si etching depends on several parameters, for example:

- the type of deposited metal (Pt, Ag, Au, etc.)
- the dopant type and doping level (n- or p-type)
- etching time, temperature of etching and ambient illumination
- concentration of etchants (HF, H₂O₂, dilution)
Thereafter Si structures with different morphologies and properties can be produced by varying these parameters.

K. Peng et al. [1] has shown a dependence of the morphology of etched samples on the wafer crystal orientation (Fig. 1.3). They demonstrated that Si (100) wafer shows large area aligned SiNW arrays perpendicular to the Si surface after etching process. P-type Si (111) wafer gives both vertical and slanting aligned SiNW arrays. P-type (110) and n-type (113) wafers produce SiNWs at the angle or slanted to the Si surface. It characterizes the MaCE as an anisotropic process. Also they have shown that the etching rate of Si increases with increasing concentrations of HF and H₂O₂.

**Figure 1.3.** Cross-sectional SEM images of Ag particle-coated Si wafers after etching in aqueous HF/H₂O₂ solution for 30 min showing aligned Si nanowire arrays produced on: a) p-type 7–14Ω cm Si (100) wafer, b) p-type 5×10⁻³Ω cm Si (111) wafer, c) p-type 4–7Ω cm Si (110) wafer, and d) n-type 4–7Ω cm Si (113) wafer. Adopted from [1].

P.W. Bohn et al. [3] studied the dependence of the MaCE process on the type of deposited metal (Fig. 1.4). Their results showed that a much rougher and deeper structure is produced on Pt-coated Si than on Au-coated Si. The authors also found that PSi produced with Pt as a catalyst resulted in stronger photoluminescence (PL) than PSi made with Au. They concluded that the stronger PL can be seen from the Pt-coated area for the p⁺-wafer, while the
uncoated area produces stronger photoluminescence in the p⁺ sample. Strong PL-signal is also acquired from the Pt-coated areas on n⁺ silicon.

Figure 1.4. SEM images of (a) Au-coated Si (100) after etching in HF/H₂O₂ for 30 s and (b) Pt-coated Si (100) after etching in HF/H₂O₂ for 30 s. Adopted from [3].

An in-depth study of MaCE by J. Teva et al. [17] has demonstrated that for a given gold thickness the etch rate of (111) Si wafers is lower than for (100) Si wafers. For both types of wafers, the maximum etch rate is obtained when the gold film is about 40 – 50 nm thick (Fig. 1.5).

Figure 1.5. Measured etch rate \( \varepsilon_r \) versus the deposited gold thickness \( t_e \) for (111) and (110) Si wafers. Adopted from [17].

X. Duan et al. [5] demonstrated that the etch rate increases with increase of the H₂O₂ concentration and reaction time (Fig. 1.6).
Figure 1.6. SEM images show the evolution of silicon nanowire morphology from n-Si (100) with 0.008-0.02 Ω-cm resistivity in etchant solutions composed of 4.8 M HF and variable concentrations of H$_2$O$_2$ through a two-step reaction. (a) 0.1 M H$_2$O$_2$ for 30 min, (b) 0.1 M H$_2$O$_2$ for 60 min, (c) 0.15 M H$_2$O$_2$ for 30 min, (d) 0.15 M H$_2$O$_2$ for 60 min, (e) 0.2 M H$_2$O$_2$ for 30 min, (f) 0.2 M H$_2$O$_2$ for 60 min, (g) 0.3 M H$_2$O$_2$ for 30 min, and (h) 0.3 M H$_2$O$_2$ for 60 min. The scale bars for all SEM images is 10 μm. Adopted from [5].

SiNWs arrays with different morphologies can be produced for Si wafers with different doping levels and the same type of the surface orientation. N-B. Wong et al. have shown in [4] that the diameter, and length of the SiNWs on heavily doped wafers are relatively smaller than those on the lightly doped one (Fig. 1.7).
**Figure 1.7.** SEM images from p-Si (111) substrates: (a, b, c) from the lightly doped wafer and (d, e, f) from the heavily doped wafer. Insets: corresponding top views in high magnification. Adopted from [4].

![SEM images](image)

**Figure 1.8.** Schematic of steps involved in the fabrication of MaCE patterns of (a) porous silicon from discrete nanoparticles, (b) silicon nanowires from discontinuous metal films or high density nanoparticle layers, and (c) 3D silicon nanostructures from slightly discontinuous metal films. Adopted from [12].

G. Fedorov et al. [12] have shown the influence of the metal film morphology on the morphology of the Si structures after the etching process (Fig. 1.8).
The authors used a thin layer of amorphous carbon formed using electron beam induced deposition (aC EBID) for fabrication of either PSi (deposition of Au particles, Fig. 1.8a), or SiNWs (Au film should be discontinuous, Fig. 1.8b), or 3D silicon nanostructures (continuous Au film, Fig. 1.8c).

Various applications of nanostructures prepared by MaCE were demonstrated by different research groups. C. V. Thompson et al. reported [18] a fabrication of silicon nanopillar-based nanocapacitor arrays (Fig. 1.9).

![SEM images showing (a) a silicon nanopillar array after metal-assisted etching using an interference lithography-patterned gold layer as the catalyst and (b) capacitor array after thermal oxidation, seed layer deposition (tungsten), and Ni electrodeposition. Adopted from [18].](image)

**Figure 1.9.** SEM images showing (a) a silicon nanopillar array after metal-assisted etching using an interference lithography-patterned gold layer as the catalyst and (b) capacitor array after thermal oxidation, seed layer deposition (tungsten), and Ni electrodeposition. Adopted from [18].

S.-T. Lee et al. have shown how SiNWs produced by MaCE can be used for rechargeable lithium-ion battery anodes [19]. Z. A. K. Durrani et al. demonstrated fabrication of field-effect transistors using SiNWs prepared by MaCE [20]. Also, many research groups have shown that the PSi can be used for optics and photonics applications [7, 15-16].
1.3. Nanoimprint lithography and methods of stamp fabrication

Nanoimprint lithography is a parallel lithography method of direct transfer of prefabricated stamp patterns onto a resist spun on a substrate. Nanoimprint lithography combines low cost, high throughput and nanometer-scale resolution. Sub-10 nm features can be produced with this technique. Nanoimprint lithography allows a patterning of wafers up to 6 inches in diameter.

There are two main types of NIL:

- thermal NIL
- UV NIL

In this diploma work thermal NIL has been used. The basic process is illustrated in Fig. 1.10.

Figure 1.10. Schematic illustration of the thermal nanoimprint process.

The main steps of NIL are:

- fabrication of a stamp
- deposition of a resist on wafer by spin-coating
- matching of the stamp and prepared wafer
- heating of the stamp and the substrate up above the glass transition temperature of the resist
- pressing the stamp against the substrate with certain pressure
- imprinting of stamp structures onto a resist
- lowering the temperature below glass transition temperature and removing the stamp
- removing the residual layer by O₂ plasma ashing
- deposition of a metal layer
- lift-off process to remove resist and unwanted metal

Thermal nanoimprint lithography is also called hot embossing lithography.
Since the stamp pattern transfers onto a resist over the substrate it is impossible to obtain a quality and resolution of the imprinted pattern better than the corresponding characteristics of the stamp pattern. Thus a stamp fabrication method should be chosen carefully.

Various methods for the stamp fabrication have been developed [21-25] In this diploma work only few of them are considered:

1) Optimized electron beam lithography (EBL) and lift-off patterning of a Cr mask [21]
2) Aerosol deposition of W particles [21]
3) Direct stamp fabrication using HSQ [22]
4) Metal-assisted Si etching

1.3.1. Optimized electron beam lithography (EBL) and lift-off patterning of a Cr mask

This method of stamp fabrication is one of the commonly used ones. It starts with thermal oxidation of Si wafer to form 200-500 nm thick silicon oxide layer. The following process steps include cleaning of the SiO$_2$ surface by conventional organic solvents, spin-coating of a double layer e-beam resist followed by exposure in an EBL machine. After development of the resist and thermal evaporation of Cr mask, lift-off is performed to form metal mask. The NIL stamp features are transferred from the Cr mask into the silicon oxide by reactive ion etching step.

1.3.2. Aerosol deposition of W particles

The NIL stamps can be produced using direct deposition of W aerosol particles onto the thermally oxidized Si surface. The aerosols are used as etch mask in a subsequent RIE process step and allow formation of SiO$_2$ columns with the size of the W aerosols (about 20 to 100 nm). This approach is very simple and fast, since the EBL exposure is not used, but it is difficult to control deposition of the aerosols: the methods results in randomly formed columns in the stamps.

1.3.3. Direct stamp fabrication using HSQ

This method of fabrication of NIL stamps is based on newly developed negative e-beam resist hydrogen silsequioxane (HSQ). A number of research groups have shown that the resist had very small line width fluctuations compared to commonly used positive e-beam resists (PMMA and ZEP520). Line widths down to 10 nm were demonstrated. Biggest advantage of HSQ for fabrication of NIL stamps is its ability to convert to SiO$_x$ after exposure, development and annealing.
1.3.4. Metal-assisted chemical etching of Si

The MaCE process has been described above. It is important to note that a “negative” stamp for nanoimprint lithography is formed by means of this technique. The main difference between “positive” and “negative” stamp is that the percentage of the raised areas is high for a “negative” stamp and small for a “positive” stamp (Fig. 1.11).

**Figure 1.11.** Positive (a) and negative (b) stamps for the nanoimprint lithography.
2. EXPERIMENTAL PART

Different techniques were utilized to form Au catalysts for studies of metal-assisted etching of Si. These are shadow mask evaporation, aerosol particles deposition, optical lithography, and electron beam lithography (EBL). The main goal of the present diploma work is investigation of the MaCE process. For this purpose shadow mask evaporation and aerosol particles deposition were tested due to the simplicity of sample preparation, low cost and process purity. These techniques are also fast and resist free, which is very important when many experiments have to be performed. Fabrication methods to make Si nanowires and porous Si nanostructures have been developed during the study of MaCE using aerosol particles and shadow mask techniques.

Advantages of contact optical lithography are low cost, high throughput and moderately high resolution (limited by the wavelength of light). This technique was utilized to prepare the samples for in-depth studies of MaCE such as measuring etching rates and surface morphology of Si as functions of time and concentrations of chemicals (with Au lift-off films used as a catalyst).

Electron beam lithography is a high resolution but expensive technique with low throughput. Sub-10 nm structures can be obtained using this technique. Due to this the EBL was used only for the nanoimprint stamps fabrication.

2.1. Experimental details

One or two inch n-type Si (100) wafers with resistivity of 10 Ω·cm were used as substrates in all experiments.

Au was used as a metal catalyst in the current work. The thickness of the Au film was 20 nm and the evaporation rate was about 2.1 Å/s in all experiments. For evaporation of the Au film two systems were used. The evaporator Pfeiffer Classic 500 was utilized to produce discontinuous gold film. The evaporator AVAC was used to obtain a continuous gold film.

Aerosol gold particles were deposited using the aerosol nanoparticle system including both an evaporation/condensation source and the spark discharge generator Palas GfG 1000 [26-27]. Firstly, the size of the particles was selected using a differential mobility analyzer (DMA). The particles were deposited onto the substrate in an electric field. The nominal diameter of the particles was 70-80 nm. The particle density was about $6 \times 10^8$ cm$^{-2}$. The carrier gas was purified nitrogen throughout the aerosol process [appendix C].

A Karl Süss MJB 3 mask aligner was employed for the optical lithography patterning. The exposure was done during 5 s (11.5-12 mW/cm$^2$) with vacuum contact.

Prior to deposition of resists, the wafers were annealed at 180°C for 3 hours in an oven. A double layer resist system was used. After the deposition of the bottom layer (positive resist LOR 3A) by spinning, the wafers were baked at 160°C for 20 min in an oven. Wafers were
additionally baked at 115°C for 1.5 min using a hot plate after the deposition of the second layer (positive resist S1813). Following the exposure, the samples were developed in MF319 for 90 s, wafers were rinsed in deionized water and blown dry with nitrogen. The resist residuals were ashed in O₂ plasma for 8 s using a microwave asher (New PlasmaPreen). After the thermal evaporation of the Au film it was lifted-off in a Remover 1165 [appendix D].

For the EBL patterning, we employed a Raith 150 (Raith GmbH, Germany) equipped with a thermal field emission cathode and a laser interferometer stage. The EBL system was operated at 20 kV with an electron probe current of 36 pA. Different structures (including single pixel lines, single pixel dots and grids with different geometry) were exposed in a writing field of 200 x 200 μm² with step size 0.01 μm and different doses.

The wafers were cleaned in acetone and isopropanol followed by the spin-coating of the polymethylmethacrylate (PMMA 950 A5) resist. Afterwards the wafers were baked at 160°C for 10 min using a hot-plate.

Following the EBL exposure, the resist was developed in a mixture of methylisobutylketone / isopropanol (MIBK/ IPA 1:3) for 1 min, the wafers were rinsed in isopropanol and blown dry with nitrogen. Immediately after development, the resist residues were ashed in O₂ plasma for 8 s. Following the oxygen plasma ashing the Au film was thermally evaporated in the evaporator AVAC and lifted-off in Remover 1165 heated at 60°C using a hot plate [appendix E].

The etching was performed at room temperature and ambient illumination. Etch solutions were prepared directly before the etching process [appendix A].

Two types of etch solutions were primarily tested: a strong solution (“solution S”) and a week solution (“solution W”). Hydrofluoric acid, hydrogen peroxide and deionized water were taken in proportions of 4 ml : 1 ml : 8 ml (48% HF : 30% H₂O₂ : H₂O) for the “solution S” and in proportions of 4 ml : 1 ml : 40 ml (48% HF : 30% H₂O₂ : H₂O) for the “solution W”.

Clean, wide and low Teflon beakers were used as vessels for the solution of hydrofluoric acid, hydrogen peroxide and deionized water (HF/H₂O₂/H₂O). Firstly, a necessary amount of deionized water is poured into the baker. Then aqueous hydrogen peroxide (H₂O₂) is added to deionized water. The final step of the etch solution preparation was adding the aqueous hydrofluoric acid (HF) to the mixture of H₂O₂/H₂O. The chemicals, 48% hydrofluoric acid and 30% hydrogen peroxide, were supplied by Merck (Germany).

The surface morphology of the etched samples was characterized using optical microscopy (Axio Imager A1m, Carl Zeiss) in both bright and dark fields.
Scanning electron microscope (SEM) LEO/ZEISS 1560 was used for more detailed surface studies of the etched samples. Typically the accelerating voltage of the SEM was about 15 kV, and the work distance was varying from 3 to 6 mm. The SEM was used to characterize the surface morphology both in plane and cross sections. For better imaging conditions, the etched samples were sometimes tilted 30° or 45°.

For the imprint experiments, the 6-inch nanoimprinter (Obducat AB) was used. Typical thermal imprint conditions were 200°C and 50 bar for the imprint temperature and pressure, respectively. Details of the NIL experiments are given in appendix F.

2.2. Formation of Si nanowires using shadow gold mask

As discussed previously, SiNWs can be easily produced by MaCE [appendix B]. The 20 nm thick Au film was evaporated through a shadow mask. Advantages of the shadow mask technique are mentioned above. A metal film should be discontinuous for SiNWs growth. The best Au film morphology was obtained using the evaporator Pfeiffer (Fig. 2.1).

To obtain SiNWs the “solution S” was used and the etching time was 5 min in all experiments. Two groups of samples were prepared. The first group was with native oxide and the second group was without native oxide. The second group of samples was etched in diluted hydrofluoric acid (1:100) for 30 s to remove the native oxide.

MaCE of the two groups of samples showed no difference in the morphology of the etched Si. Thus, removal of the native oxide was not necessary.

Figure 2.1. Morphology of the Au film with thickness of 20 nm obtained using Pfeiffer evaporator (top view). Evaporation rate is about 2.1 Å/s.

During the MaCE process arrays of SiNWs appeared. The produced nanowires were about 25 nm in diameter and 6.8 μm long in case of the samples without native oxide (Fig. 2.2).
Figure 2.2. SEM images showing SiNWs resulting from metal-assisted etching in a solution of HF : H₂O₂ : H₂O (4 ml : 1 ml : 8 ml) for 5 min (cross-section). (a) large-field view and (b) detailed view revealing SiNWs dimensions of about 25 nm in diameter and 6.8 μm length.

The shadow mask technique has two main disadvantages. It has a very low resolution and it does not provide a close fit between the shadow mask and the substrate (Fig.2.3) and the gap can affect the shape of the deposited material. As a result, pattern edges are not well-defined. SEM images of etched samples prepared by the shadow mask technique are shown in Fig. 2.4. These images demonstrate that it is impossible to deposit a material layer with uniform thickness and well-defined edges using the shadow mask technique.

Figure 2.3. Schematic illustrating the process of material deposition using the shadow mask technique.
It was demonstrated that SiNWs can be easily produced by the MaCE process using the shadow mask technique. It is possible to control length of SiNWs by changing the etching time and the etch solution. It was also demonstrated that the removal of the native oxide is not necessary.

2.3. Nanoporous Si structures produced by MaCE

Two alternative methods showed that nanoporous Si structures can be produced by the metal-assisted chemical etching. The well-defined nanometer-sized gold particles were synthesized both by the aerosol technique (Fig. 2.5) and electron beam lithography.

The aerosol particles deposition technique has the same advantages as the shadow mask evaporation technique. The aerosol particles deposition technique also allows control over the density, shape and size of the particles. The aerosol nanoparticle system includes both a spark discharge generator (SDG) and an evaporation/condensation source (Fig. 2.6) [26-27]. The material is evaporated, then cooled to form condensates of nanoparticles in the
evaporation/condensation source. Particles of sizes ranging from 10 nm to about 100 nm can be produced. There is a commercial SDG (Palas GfG 1000) along with the high temperature furnace. The source can be selected just by rerouting the carrier gas.

The aerosols are transported by the carrier gas through a bipolar charger after being generated. A differential mobility analyzer (DMA) is used to make a size selection. Subsequently, the particle number concentration is measured by an electrometer. The deposition is done in the electrostatic precipitator.

Figure 2.6. Schematic of the aerosol nanoparticle system.

Directly after the deposition of the Au particles, the samples were etched in “solution S” for 5 min. (Fig. 2.7a, b). Au particles are expected to “sink” strictly orthogonal to the surface of a (100)-oriented Si substrate during the etching process. Figures 2.7a-b indicate unexpected particle displacements along the surface (in arbitrary directions). To improve the adhesion of Au particles to the Si surface the wafers were annealed at 350°C for 30 min before the etching process. The etching results did not show any effects of annealing (Fig. 2.7c-d).

Electron beam lithography allows creation of ordered arrays of nanometer-sized gold particles in contrast to the aerosol particles technique. Single pixel dots (SPDs) were exposed in a writing field of 200 x 200 μm² with a step size of 0.01 μm and dwell time of 281 μs. The size of the SPDs was about 80 nm. “Solution S” and etch time of 5 min were chosen as etch parameters. Figure 2.8 illustrates particles displacements along the surface during the etching process.
Figure 2.7. SEM images illustrating metal-assisted etched nanoporous Si structures in a solution of HF : H$_2$O$_2$ : H$_2$O (4 ml : 1 ml : 8 ml) for 5 min (top view). (a) large-field view and (b) detailed view of the sample etched without annealing. (c) large-field view and (d) detailed view of the annealed sample at 350°C for 30 min.

Figure 2.8. SEM images illustrating metal-assisted etched nanoporous Si structures in a solution of HF : H$_2$O$_2$ : H$_2$O (4 ml : 1 ml : 8 ml) for 5 min (top view).

It was shown that the etching process cannot be controlled for Au structures with a lateral size less than 80 nm due to the insufficient adhesion of Au to the Si surface. However, nanoporous Si structures can simply be produced both by the aerosol particles technique and electron beam lithography. These techniques allow control over the density, shape and size of the particles. Therefore, the porosity of the etched Si can also be controlled. Another advantage is that particles with a nominal diameter below 20–30 nm can be produced by both techniques.
A comparison of samples nanoporous Si structures prepared by the two different techniques has not shown a considerable difference in the morphology of the etched samples. Thus aerosol particle technique is much more attractive for the fabrication of the PSi than EBL due to the complexity of the lithographic process.

### 2.4. Study of kinetics of the MaCE process

Several experiments were performed with samples made by optical lithography [appendix D] for a study of the MaCE process. Advantages of optical contact lithography were described above.

Samples were etched in “solution W” for various times (30 s – 10 min) to measure the time dependence of the etch depth. Figure 2.9 shows SEM images of the etched samples for different etching times (the etch depth is in the range of 107 nm – 2.9 μm). The images demonstrate that mesa structures with well-defined shapes formed during the etching process. The morphology of the formed structures characterizes the metal-assisted etching as a high anisotropy process. Due to the discontinuity of the Au film (Fig. 2.10) the etching process results in formation of the SiNWs.
Figure 2.9. SEM images illustrating cross-sections of the etched samples made by optical lithography and subsequent O₂ plasma ashing. The etch solution is a mixture of HF : H₂O₂ : H₂O (4 ml : 1 ml : 40 ml). (a) etching time \( t_{\text{etch}} = 30 \text{s} \), etch depth \( h_{\text{etch}} = 107 \text{ nm} \), (b) \( t_{\text{etch}} = 1 \text{ min} \), \( h_{\text{etch}} = 274 \text{ nm} \), (c) \( t_{\text{etch}} = 3 \text{ min} \), \( h_{\text{etch}} = 758 \text{ nm} \), (d) \( t_{\text{etch}} = 5 \text{ min} \), \( h_{\text{etch}} = 1.15 \mu\text{m} \), (e) \( t_{\text{etch}} = 7 \text{ min} \), \( h_{\text{etch}} = 1.7 \mu\text{m} \), (f) \( t_{\text{etch}} = 10 \text{ min} \), \( h_{\text{etch}} = 2.9 \mu\text{m} \).

Figure 2.10. Morphology of the Au film with thickness of 20 nm obtained by the Pfeiffer evaporator (top view). The evaporation rate is about 2.1 Å/s.

Figure 2.11 shows the time dependence of the etch depth. It can be seen that the plot has almost a linear shape. Thus, the etching process begins immediately after immersing the wafers into the etch solution, without delay.
Figure 2.11. Time dependence of the etch depth of the samples etched in the solution of HF : H₂O₂ : H₂O (4 ml : 1 ml : 40 ml) for a different time (30 s – 10 min).

Samples were etched in different solutions of HF : H₂O₂ : H₂O with the etch time of 5 min (Table 2.1) to evaluate the dependences of the etch depth and morphology of the etched samples on the etchant concentration. All experiments were performed with samples prepared by optical lithography.

Table 2.1. Summary the etch solution recipes used in the current experiments.

<table>
<thead>
<tr>
<th>Concentration of the etchants, ml</th>
<th>Concentration ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>48% HF</td>
<td>30% H₂O₂</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
</tr>
</tbody>
</table>

Figures 2.12-2.14 display plots of the dependence of the etched depth on the etchant concentrations. It can be seen that the etch rate increases with increasing concentrations of hydrofluoric acid and hydrogen peroxide. Figure 2.13 demonstrates that the dilution of the etch solution results in a decreased etch rate.
Figure 2.12. Measured etch depth versus concentration of hydrofluoric acid in the solution of HF : H₂O₂ : H₂O (x : 4 : 40), ml. Etching time is 5 min.

Figure 2.13. Measured etch depth versus concentration of hydrogen peroxide in the solution of HF : H₂O₂ : H₂O (4 : x : 40), ml. Etching time is 5 min.
Hydrogen peroxide itself cannot etch silicon. Therefore, the etching of silicon should be catalyzed by the metal nanoparticles. During the etch process Au particles are partly oxidized by H\textsubscript{2}O\textsubscript{2} to produce a localized Au\textsuperscript{+} ion cloud near the gold particles [5]. These gold ions participate in the etching process by capturing electrons from silicon near the Au/Si interface. Thereby, the etching process is localized around the gold particles. Along with an increase of the H\textsubscript{2}O\textsubscript{2} concentration the concentration of Au\textsuperscript{+} ion increases. Therefore, the formation of the nanopits will go faster with the increase of H\textsubscript{2}O\textsubscript{2} concentration. The oxidation rate of Si also increases with increased H\textsubscript{2}O\textsubscript{2} concentration, leading to a higher etch rate of Si.

An increase of HF concentration in the etch solution will also increase the etch rate of Si since HF etches the oxidized Si faster.

Increasing the dilution of the etch solution corresponds to decrease of the HF and H\textsubscript{2}O\textsubscript{2} concentrations. With decreasing HF and H\textsubscript{2}O\textsubscript{2} concentrations the etch rate of Si decreases. Thus dilution of the etch solution results in a decrease of the Si etch rate.

The dependence of the morphology of the etched samples on the dilution of the etch solution has also been found. This dependence is shown in Fig. 2.15. It can be seen that the etched surface becomes less rough with increasing amount of water in the etch solution. Also, nanowires detach from each other as a result of adding water.
Figure 2.15. SEM images (left) and appropriative images from optical microscope (right) illustrating the dependence of the Si surface morphology on the amount of water in the etch solution of HF : H$_2$O$_2$ : H$_2$O (4 ml : 1 ml : x ml). Etching time is 5 min. (a, b) No wafer in the etch solution, (c, d) 8 ml of H$_2$O, (e,f) 20 ml of H$_2$O, (g, h) 30 ml of H$_2$O, (i, j) 40 ml of H$_2$O.
In the current work it was demonstrated that the Si nanostructures can be easily produced by MaCE. In Fig. 2.16 high aspect ratio nanocolumns are depicted. The Au grid pattern was made on the Si sample electron beam lithography. The grid consists of about 1.05 μm width lines and square openings with about 250 nm sites. Etching of the sample in “Solution S” for 10 min resulted in formation of regular structures with nanocolumns. It was demonstrated that nanocolumns of about 250 nm in diameter and 5.8 μm long appeared during the etching process after a given time. The geometry of the produced nanostructures corresponds to the aspect ratio of 1:21.

The well-defined Si nanostructures were produced by MaCE during the current work. Figures 2.17a-d show Si nanostructures produced by EBL and MaCE with a different geometry. The etch conditions were a solution of HF : H₂O₂ : H₂O (4 ml : 1 ml : 8 ml) and the etch time of 5 min. The resulting Si nanocolumns are 760 nm in width and 2.3 μm in length, which corresponds to the aspect ratio of 1:3 (Fig. 2.17b).
**Figure 2.17.** SEM images showing Si nanostructures produced by EBL and MaCE with different geometry. The pictures were taken with a tilt angle of 30°. The etch solution is a mixture of HF : H$_2$O : H$_2$O (4 ml : 1 ml : 8 ml) and the etch time is 5 min. (a) large-field view and (b) detailed view of Si nanocolumns of 760 nm width and 2.3 μm height, (c) single pixel lines of 110 nm widths, (d) numbers.

### 2.5. NIL stamps fabrication and imprint experiments

The nanoimprint lithography process starts with the stamp fabrication. As mentioned above the resolution and quality of the nanoimprint is determined entirely by the stamp so its fabrication is of tremendous importance for the NIL-based technology.

A stamp containing patterns of different design and sizes was fabricated (Fig. 2.18). It consists of a 200x200 μm$^2$ frame, single pixel lines (SPLs), single pixel dots, letters and numbers. The average depth of the sample was about 130 nm [appendix E].

Following the stamp fabrication and deposition of the anti-sticking layer nanoimprinting was performed. The preparation of the sample starts with cleaning of the wafer in acetone and isopropanol, blowing dry with nitrogen followed by spin-coating of the PMMA 950A4 resist. Afterwards the wafer was baked at 160°C for 10 min on a hot plate. The details of nanoimprint experiment are discussed in appendix F.

As discussed before, a “negative” stamp is formed by the MaCE. Figure 2.19 illustrates top-view optical (Fig. 2.19a-c) and SEM (Fig. 2.19d) images of the imprinted sample. The Au film was evaporated on the top of the sample for the investigation of the last one using SEM. The smallest imprinted features are about 150 nm width (SPL). It was demonstrated that the negative stamp made by EBL and MaCE produced promising imprint results.
Figure 2.18. SEM images of the Si based stamp for NIL produced by EBL and MaCE comprising different structures (grid, single pixel lines, single pixel dots, letters and numbers) with different geometry. The etch solution is a mixture of HF : H$_2$O$_2$ : H$_2$O (4 ml : 1 ml : 40 ml) and the etch time is 14 min.

Figure 2.19. (a, b) top-view optical images of the imprinted sample made both in bright (a) and dark (b) fields, respectively, (c) top-view optical and (d) SEM images of the imprinted sample covered by the Au film. The smallest features are about 150 nm width (SPL).
Figure 2.20 shows the Si based stamp made by EBL and MaCE. This stamp consists of numbers and five grids with different geometry. The smallest achieved structures are about 150 nm in width (Fig. 2.20b).

**Figure 2.20.** SEM images of the Si based stamp for NIL produced by EBL and MaCE comprising different structures (numbers and five grids with various geometry). (a) large-field view recorded with a tilt angle of 30°, (b) detailed top view of the Si based stamp showing the smallest achieved structures with a lateral size of about 150 nm. The etch solution is a mixture of HF : H₂O₂ : H₂O (4 ml : 1 ml : 40 ml) and the etch time is 25 min.
CONCLUSIONS

The current study shows that metal-assisted Si etching (MaCE) is a highly anisotropic process which can be used to obtain high aspect ratio nanostructures with well-defined shapes and various complexities. The process can be applied to produce aligned Si nanowires (SiNWs) with controlled height and to form porous Si (PSi) with certain size and density of pores.

During the study of the MaCE, fabrication methods to make Si nanowires and porous Si nanostructures have been developed using the shadow mask evaporation and aerosol particles deposition techniques, respectively. The investigation of the MaCE process demonstrates that Si nanostructures with aspect ratio of 1:21 can be made by means of this technique. Si nanowires of diameter 25 nm and 6.8 μm length were produced in the present work. Sub-150 nm structures were formed by the EBL and MaCE.

The etching rate and surface morphology of etched Si as functions of time and concentrations of chemicals have been studied in the present work.

It was found that dilution of the etch solution resulted in smaller surface roughness. Long etching time and decreased amount of water in the mixture of HF/H₂O₂/H₂O allows the formation of the high aspect ratio nanostructures. The morphology of the deposited metal film results in various Si nanostructures (including PSi, SiNWs, and 3D-Si structures).

The “negative” stamp for nanoimprint lithography has also been fabricated during the thesis work. The nanoimprinting has subsequently been performed and demonstrated promising results.
APPENDIX A

Process steps of the metal-assisted Si etching

Etch solution should be prepared directly before the etching process. Clean, wide and low Teflon beakers are used to produce a solution of 48% hydrofluoric acid/30% hydrogen peroxide / deionized water (48%HF / 30%H₂O₂ / H₂O). HF and H₂O₂ used in the present work were manufactured by Merck KGaA Company (Germany). Automatic pipettes are utilized for mixing the etch solution. The etch procedure is following:

1. A necessary amount of water is poured into the baker
2. An aqueous hydrogen peroxide is added to the water
3. An aqueous hydrofluoric acid is poured to the solution of H₂O₂/H₂O

In the current work mainly two types of the etch solution were tested, a strong solution ("solution S") and a week solution ("solution W") (Table 1). Etching process was performed at room temperature and illumination.

Table 1. Main types of the etch solutions used during work on the diploma.

<table>
<thead>
<tr>
<th>Type of the solution</th>
<th>Concentration of the etchants, ml</th>
<th>Concentration of the etchants, proportions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>48%HF</td>
<td>30%H₂O₂</td>
</tr>
<tr>
<td>&quot;Solution S&quot;</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>&quot;Solution W&quot;</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

Silicon samples covered by an Au-pattern are placed in the beaker containing etchant for different times, ranging from 30 s to 10 min. After the etching process is completed the samples are removed carefully from the beaker using Teflon tweezers. Due to hydrophobic properties of Si surface after etching, normally no solution is present on the samples after removal from the etchant. After etching, the samples are rinsed in DI water for at least 60 s. The samples are placed on a cleanroom cloth and blown dry with a nitrogen gun.

Following MaCE process etched samples are investigated firstly using the optical microscope Axio Imager A1m Zeiss, in both bright and dark fields. For a more detailed study of the etched samples the scanning electron microscope (SEM) LEO/ZEISS 1560 is used. Typically the accelerated voltage is 15 kV, work distance is varying from 3 to 6 mm. The SEM is used to characterize the surface morphology both in plane and cross sections. Etched samples can be tilted at the angle, ranging from 0° or 90°.

Au film is removed in the Au etch solution (a mixture of KI+I₂+H₂O) for 30 s. Samples are investigated once more using the scanning electron microscope LEO/ZEISS 1560 after the Au pattern removal.
APPENDIX B

Fabrication of the Si nanowires using the shadow mask technique

The process of the SiNWs fabrication consists of the following steps:

1. One inch n-type Si wafers with crystal orientation (100) and resistivity of 10 Ω·cm are used as a substrate. The removal of the native oxide is not necessary.

2. The shadow masks with round openings (300 μm, 500 μm or 700 μm in diameter) are carefully mounted onto the wafers.

3. Au film with the thickness of the 20 nm is deposited onto the wafers using the evaporator Pfeiffer Classic 500 with the evaporation rate of 2.1 Å/s. It is necessary to get a discontinuous metal layer.

4. Wafers are etched in the etch solution (Table 1).

Table 1. Etch conditions for the fabrication of SiNWs.

<table>
<thead>
<tr>
<th>Type of the solution</th>
<th>Concentration of the etchants, ml</th>
<th>Concentration of the etchants, proportions</th>
<th>Temperature</th>
<th>Illumination</th>
<th>Etching time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Solution S”</td>
<td>4 30%H₂O₂ 8</td>
<td>4:1:8</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
</tr>
</tbody>
</table>

5. Au film is removed in the Au etch solution (a mixture of KI+I₂+H₂O) 30 s.
APPENDIX C

Production of the porous Si using the aerosol particles technique

Aerosol gold particles are deposited using the aerosol nanoparticle system including both an evaporation/condensation source and the spark discharge generator Palas GfG 1000 onto one inch n-type Si wafers with crystal orientation (100) and resistivity of 10 Ω·cm. The size of the particles is selected using a differential mobility analyzer (DMA). The particles are deposited onto the substrate in an electric field. The density, shape and size of the particles can be different. In the current diploma work the nominal diameter of the particles was 70-80 nm and the particle density was about 6x10^8 cm^-2. The carrier gas is purified nitrogen throughout the aerosol process.

After that the gold particles deposition wafers are etched at the conditions described in Table 1.

Table 1. Etch conditions for the fabrication of PSi

<table>
<thead>
<tr>
<th>Type of the solution</th>
<th>Concentration of the etchants, ml</th>
<th>Concentration of the etchants, proportions</th>
<th>Temperature</th>
<th>Illumination</th>
<th>Etching time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Solution S”</td>
<td>4 1 8</td>
<td>4:1:8</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
</tr>
</tbody>
</table>

Following the etching process aerosol gold particles have to be removed in the Au etch solution (a mixture of KI+I_2+H_2O) for 30 s.
APPENDIX D

Process steps of the sample preparation using the optical lithography

The process starts with the baking of two inch n-type Si wafers with crystal orientation (100) and resistivity of 10 Ω·cm at 180°C for 3 hours in an oven. A double resists system is used to perform a good resist profile for the lift-off procedure.

Following the deposition of the bottom layer (positive resist LOR 3A) onto the wafers by spinning at 3000 rpm for 30 s, the wafers were baked at 160°C for 20 min in an oven. Wafers are additionally baked at 115°C for 1.5 min using a hot plate after the deposition of the second layer (positive resist S1813) by spinning at 5000 rpm for 30 s.

For the optical lithography patterning Karl Süss MJB 3 is used. The exposure procedure is performed during 5 s (11.5-12 mW/cm²). Vacuum contact should be used during the exposure.

After the exposure resists are developed in MF319 for 90 s, wafers are rinsed in deionized water and blown dry with nitrogen. The resist residuals are ashed in O₂ plasma for 8 s using a microwave asher (New PlasmaPreen). After the thermal evaporation of the Au film with the thickness of the 20 nm and at the evaporation rate of 2.1 Å/s it is lifted-off in the remover 1165 heated at 60°C.

Prepared samples are etched in different solutions and for a various time (Table 1) depending on the purpose of the investigation.

Table 1. Different etch solution recipes used for the estimation of the time dependence of the etch depth and dependences of the etch depth and morphology of the etched samples on the etchants’ concentrations.

<table>
<thead>
<tr>
<th>№</th>
<th>Concentration of the etchants, ml</th>
<th>Concentration of the etchants, proportions</th>
<th>Temperature</th>
<th>Illumination</th>
<th>Etching time, min</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48%HF 30%H₂O₂ H₂O</td>
<td>4:1:40</td>
<td>Room</td>
<td>Room</td>
<td>0.5</td>
<td>Time dependence of the etch depth</td>
</tr>
<tr>
<td>2</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4 4 40</td>
<td>Room</td>
<td>Room</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4 1 8</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4 1 20</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4 1 30</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4 1 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>4 2 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>4 4 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>4 8 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>4 16 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1 4 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2 4 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>8 4 40</td>
<td>Room</td>
<td>Room</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>16</td>
<td>4</td>
<td>40</td>
<td>4 : 1 : 10</td>
<td>Room</td>
<td>Room</td>
</tr>
</tbody>
</table>

Au film is removed in the Au etch solution (a mixture of KI+I$_2$+H$_2$O) within 30 s.
APPENDIX E

Nanoimprint stamp fabrication using the electron beam lithography

One inch n-type Si wafers with crystal orientation (100) and resistivity of 10 $\Omega\cdot$cm are cleaned in acetone and isopropanol, blown dry with nitrogen. Immediately after the cleaning a polymethylmethacrylate (950 PMMA A5) resist is deposited on a spinner at 6000 rpm for 30 s. After the deposition of the resist the wafers are baked at 160°C for 10 min using a hot-plate.

Exposure procedure is performed using the EBL - Raith 150 (Table 1). There can be a few patterning areas on the whole wafer and each patterning area can contain a frame, single pixel lines, single pixel dots and grids with a different geometry.

Table 1. EBL exposure parameters.

<table>
<thead>
<tr>
<th>Acc. Voltage, kV</th>
<th>Probe current, pA</th>
<th>Working distance, nm</th>
<th>Write field size, $\mu$m</th>
<th>Area exposure Step size, $\mu$m</th>
<th>Dwell Time, $\mu$s</th>
<th>Dose, $\mu$C/cm$^2$</th>
<th>SPL Step size, $\mu$m</th>
<th>Dwell Time, $\mu$s</th>
<th>Dose, $\mu$C/cm$^2$</th>
<th>SPD Dwell Time, $\mu$s</th>
<th>Dose, $\mu$C/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>35.8</td>
<td>6</td>
<td>200</td>
<td>0.01</td>
<td>9.7</td>
<td>350</td>
<td>0.01</td>
<td>40.85</td>
<td>1468</td>
<td>278</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Following the EBL exposure, the resist is developed in a mixture of methylisobutylketone/isopropanol (MIBK/IPA 1:3) for 1 min, rinsed in isopropanol and blown dry with nitrogen. The resist residuals are ashed in O$_2$ plasma for 8 s using a microwave asher (New PlasmaPreen). The evaporator AVAC is used for the deposition of the Au film which should be continuous. After the thermal evaporation of the Au film with the thickness of the 20 nm and at the evaporation rate of 2.1 Å/s it is lifted-off in the remover 1165 heated at 60°C.

Prepared samples are etched in different solutions and for various times (Table 2) dependently on the purpose.

Table 2. Different etch solution recipes used for the NIL stamp fabrication.

<table>
<thead>
<tr>
<th>№</th>
<th>Concentration of the etchants, ml</th>
<th>Concentration of the etchants, proportions</th>
<th>Temperature</th>
<th>Illumination</th>
<th>Etching time, min</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45%HF 40%H$_2$O$_2$ 5%H$_2$O</td>
<td>4:1:8</td>
<td>Room</td>
<td>Room</td>
<td>10</td>
<td>Deep etching, rough Si surface</td>
</tr>
<tr>
<td>2</td>
<td>45%HF 40%H$_2$O$_2$ 5%H$_2$O</td>
<td>4:1:40</td>
<td>Room</td>
<td>Room</td>
<td>25</td>
<td>Low roughness of the etched Si, low etch rate</td>
</tr>
</tbody>
</table>

Au film is removed in the Au etch solution (a mixture of KI+I$_2$+H$_2$O) for 30 s.
APPENDIX F

Process steps of the nanoimprint lithography

The anti-sticking treatment of the NIL stamp is a final step of the stamp fabrication. Monolayer of fluorinated alkyl derivatives i.e. tridecafluoro-(1, 1, 2, 2)-tetrahydrooctyl-trichlorosilane (F-TCS) is coated on the stamp surface. The deposition procedure is performed under the following conditions: temperature of a hot plate is 250°C, amount of F-TCS is 45 μL, and reaction time is 2 hours.

The size of the sample should be the same as the size of the stamp. One inch n-type Si wafer with a crystal orientation (100) and resistivity of 10 Ω·cm is cleaned in acetone and isopropanol, blown dry with nitrogen.

The wafer is baked at 160°C for 10 min using a hot plate after the deposition of the positive resist PMMA950A5 by spinning at 6000 rpm for 30 s.

The sample is carefully mounted onto the stamp and the nanoimprint procedure is started (Table 1).

Table 1. Nanoimprinting parameters.

<table>
<thead>
<tr>
<th>Imprinting temperature (°C)</th>
<th>Imprinting pressure (bar)</th>
<th>Imprinting time (s)</th>
<th>Demolding temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>50</td>
<td>600</td>
<td>80</td>
</tr>
</tbody>
</table>
REFERENCES
