Chapter 6

Fabrication of PhC gas sensor structures

For the fabrication of the PhC gas sensor structures the macroporous Si material system was chosen. After a brief description of the state-of-the-art of this fabrication process at the onset of this work the further development necessary for the realization of PhC gas sensor structures is presented in the subsequent section. These developments are essentially etching of deep (≥ 450 µm), parallel pores, realization of the different taper concepts discussed in chapter 5 and aspects of device integration.

6.1 Why macroporous Si?

For PhCs in the IR spectral region the dielectric materials used for their realization have to be transparent, i.e., have negligible absorption in that wavelength range. Furthermore it must be possible to periodically structure these materials on an appropriate length scale, i.e., on the order of a few µm. Si fulfills both requirements. As a semiconductor with an electronic band gap of 1.1 eV it is transparent from the FIR spectral region down to a wavelength of $\lambda = 1.1 \text{ µm}$. Furthermore, Si is the dominating material in today’s microelectronics industry and a lot of experience and methods for Si structuring exist. Unfortunately, these conventional methods are well suited for lateral structuring, i.e., features in the x-y-plane, but allow only rather shallow vertical

![Figure 6.1](image_url)

Figure 6.1: (a) p-type macroporous Si Kielovite structure [74]; (b) Si Lincoln-Log structure [75]; (c) [110] and [111] facets of a Si inverse opal structure [76]; (d) porous Si membrane [77].
6.1 Why macroporous Si?

features to be realized. For PhCs, however, it is necessary to realize high aspect ratio structures in Si along the vertical, i.e., along the z-direction. Several techniques to realize PhC structures in Si have been developed and some results are shown in fig. 6.1. The structure in fig. 6.1a is called Kielovite, named after the German city in which it was invented and realized by photo-electrochemically etching pores into [111] oriented p-type silicon [74]. Unfortunately this pore growth regime is not very stable resulting in limited structuring along the vertical direction.

Another possibility for structuring of Si along the z-axis is the so-called Lincoln-Log structure shown in fig. 6.1b fabricated by Lin et. al [75]. In this layer-by-layer approach the structure is fabricated by depositing a layer of SiO$_2$, subsequent lithographical pattern definition, dry etching of the defined trenches, followed by infiltration of poly-crystalline Si into the trenches. By repeating this procedure a 3D PhC can be obtained. But due to the time consuming nature of this approach (≈ 2...4 weeks per layer) the largest so far realized Lincoln Log possessed only 4 repetitions of the unit cell along the z-direction.

Another technique, that manages to get along without complex and costly lithography steps, is based on self-organization of colloidal particles and subsequent infiltration of the structure with Si followed by removal of the colloids, as shown in fig. 6.1c [76]. While such structures can in principle be built having several dozens of unit cells in the vertical direction, their major shortcoming is the relatively high defect concentration resulting from the fabrication process.

The structure shown in 6.1d was produced by using conventional semiconductor processing techniques. After patterning the Si by dry etching the sacrificial layer underneath was removed resulting in a free standing Si membrane with an incorporated W1 PhC waveguide. The fabrication of such a structure is rather straightforward but its disadvantages are mechanical instability and only low achievable aspect ratios.

Unfortunately, the above described methods cannot be used for the realization of a PhC-based gas sensor because the interaction volume realizable with the above procedures is too small, mainly due to the limits in vertical structuring depth. A method that allows Si structuring in the x-y-plane as well as along the vertical z-direction is the macroporous Si fabrication process, demonstrated by Lehmann and Föll [47][46], which is described in the following section.

Figure 6.2: SEM micrographs of defect structures in a hexagonal lattice of air pores in Si. a) Point defect or cavity. b), c) Straight and bent linear defects. d) Y-branch.
6.2 Macroporous Si for PhCs: state-of-the-art in 2002

Fabrication of macroporous Si structures to realize bulk 2D PhCs has been a well established technique at the Max Planck Institute of Microstructure Physics (MPI MSP) in Halle at the beginning of the PhC gas sensor project in 2002. It was shown that an aspect ratio of $\approx 20$ is sufficient to treat the macroporous structures as real 2D PhCs, i.e., the extension along the $z$-direction parallel to the pores does not have a significant influence on the PhBS. For the lattice constants typically used so far ranging from 0.5-1.5 $\mu$m a pore depth of less than 100 $\mu$m was therefore sufficient. The structures were typically characterized by IR reflection measurements perpendicular to the pores. The interfaces for the optical measurements were realized by cleaving the macropore arrays along either $\Gamma K$ or $\Gamma M$ directions, which in turn were oriented along the Si [110] directions. The incorporation of single point and W1 line defects in hexagonal macropore arrays had been realized. Furthermore, in a cooperation with the group of H. van Driel in Toronto it was shown that it is possible to measure transmission through a PhC consisting of up to about 180 pore rows. This catwalk of macropores had been realized by post-processing the PECE macropore array using lithography and a subsequent dry etching process [78]. A few examples of the above described structures are given in fig. 6.2.

6.3 PECE of deep pore arrays

For realization of macroporous Si structures to be used as the interaction volume in PhC-based gas sensors, structures with aspect ratios as high as possible should be used. An IR light source to be used in a PhC-based gas sensor should be broadband and cheap. This excludes the use of, e.g., QCLs, light emitting diodes (LED) or lead-salt-lasers. Therefore the likely IR light source will be a simple thermal emitter. Radiation coming from such a thermal emitter is rather divergent. To couple an appreciable amount of it into the PhC - even with the help of some optical elements - the macroporous structure should be as high as possible.

The physical limit for the maximum pore depth is given by the thickness of standard 4-6 inch diameter Si wafers ($\approx 525$ $\mu$m) minus the absorption length of the (IR) light used to create the electronic holes for the PECE process (a few $\mu$m). Deeper pores could in principle be realized by using standard Si wafers with a thickness of about 700 $\mu$m. But taking into account fabrication time and cost issues, an increase in pore depth is not attractive because for standard PECE conditions using HF with a concentration of 5wt% and temperatures around 10$^\circ$C typical etch times of 10-16 hours are necessary to etch 400-450 $\mu$m deep macropores. For pores with a depth of 700 $\mu$m the etching time would be on the order of 24-30 hours. Furthermore, the quality of thick Si wafers concerning electronic hole lifetime in the material is a critical issue when it comes to PECE of deep pores.

The functionality of the PhC interaction volume in a spectroscopic gas sensor depends on the PhC’s band structure. The PhBS in turn depends on the distribution of the dielectric material. For the fabrication of the macroporous Si structures this means that deep macropores with parallel walls and smooth pore surfaces have to be etched. While the pore walls can be smoothened after the PECE by growth of thermal oxide and a subsequent HF-dip, the parallel shape of the pores has to be realized already during the PECE process.
Figure 6.3: PECE of deep macropore arrays. a) Electrical breakdown pores used as depth markers. b) $c_a$ (bottom) and $c_b$ (top) in the Lehmann model for some surfactants used in this work as a function of temperature. NIS1: non-ionic surfactant very similar to the one used by Lehmann, NIS2: new non-ionic surfactant, AIS: anionic surfactant, MAIS (MNIS): mix of anionic and non-ionic surfactants, dominated by anionic and non-ionic surfactant, respectively.

The empirical model of Lehmann\[49] underlying the software controlling the PECE process is based on a 2nd order polynomial relation between the pore depth $l_{\text{pore}}$ and growth time $t_l$ necessary to achieve this depth according to

$$t_l = c_a l_{\text{pore}} + c_b l_{\text{pore}}^2$$

with parameters $c_a$ and $c_b$ to be determined from the experiment. Using Lehmann’s values for $c_a$ and $c_b$, significant deviations of sometimes more than 20% - depending on the detailed PECE parameters - of the measured pore depth compared to the desired pore depth were found. The effect was more pronounced for deep macropores with $l_{\text{pore}} > 150 \, \mu m$. In addition it was found that the deviation strongly depends on the type of surfactant added to the electrolyte.

To determine the parameters $c_a$ and $c_b$ relevant for the PECE of deep macro pores in this work, depth markers were set during the PECE process by suddenly increasing the externally applied voltage by 20 V for 1 min\[1]. This leads to the formation of sharp features as shown in fig.6.3a. Their positions along the macropore have been determined using SEM and were then related to the instance of time during PECE when the increased voltage was applied. A least-square-fit using (6.1) to this data yields the parameters $c_a$ and $c_b$ shown in fig.6.3b.

Addition of surfactants to the electrolyte is necessary to avoid formation of gas (H₂) bubbles on the surface of the sample which would prevent HF exchange between the HF reservoir and

\[1\]Depth markers produced by this technique allow a much more precise determination of the marker’s position along the pore axis than utilization of conventional depth markers realized by diameter variations of the macropores. It was verified that these unconventional depth markers do not significantly alter the PECE process and therefore yield the same results as in case of diameter modulated macropores.
the macropores, thereby leading to inhomogeneous etching. Two types of surfactants were used: anionic and non-ionic. The concentrations of the surfactants in the electrolyte were chosen to allow stable macropore growth\(^2\). Addition of anionic surfactant (AIS)\(^3\) of concentration \(c_{AIS}\) leads to slower pore growth than expected while addition of non-ionic surfactant\(^4\) (NIS1, NIS2) of concentrations \(c_{NIS,1}\) and \(c_{NIS,2}\) results in deeper pores than anticipated. The increase in growth speed was less pronounced for NIS1. The surfactant NIS1 is similar to the one originally used by Lehmann et al., but due to environmental concerns no longer available. To ensure the applicability of the concepts developed in this work for potential large scale production of macroporous Si-based PhC gas sensors investigation of the PECE process using the nowadays available successor of NIS1, namely NIS2, was necessary.

Furthermore it can be seen in fig.\(6.3\)b that in the case of a mixture of non-ionic (\(MNIS\)) and anionic (\(MAIS\)) surfactants added to the electrolyte the dominant species, i.e., the species being present with the higher effective concentration, determines the behavior of the pore growth speed. While the values for \(c_a\) are similar for all kinds of surfactants, there is a striking difference in the values for \(c_b\) for (mainly) non-ionic and (mainly) anionic surfactants.

Grüning related the meaning of the coefficient \(c_a\) to the inverse of the initial growth speed of the macropore and \(c_b\) to the inverse of the diffusion constant \(D_{HF}\) of the HF molecules within the macropores \[^80\]. The data derived in this work is not in agreement with her findings because one would expect an increase in HF diffusion with increasing temperature. For the \(c_b\) of the anionic surfactants the opposite is found while for the \(c_b\) of the non-ionic surfactants no temperature dependence of the \(c_b\) is found. Furthermore, within the model of Grüning, dark currents lead to an additional reduction in pore growth speed. Dark currents arise from HF consumption along the pore wall, i.e., Si etching, at the pore wall/HF (not the pore tip/HF) interface and are on the order of a few \(\mu\)A/cm\(^{-2}\). As a consequence the HF concentration along the pore is further reduced and the growth speed according to (4.33) is reduced and the pore walls are no longer parallel but wedged. This effect becomes important especially for deep pores with large surface area. Based on this model, the faster (slower) etching using non-ionic (anionic) surfactant corresponds to lower (higher) dark currents for the non-ionic surfactant. However, experiments show that the dark currents are higher for the non-ionic surfactant \[^79\]. The lower dark current in the case of anionic surfactant could be explained by an increase in surface potential at the HF/Si interface due to the presence of the anionic species at this interface, thereby aggravating the tunneling of electrons from the electrolyte into the Si. Another observation is that the pore diameter is usually significantly smaller \((\gtrsim 25\%)\) than the desired one when using anionic surfactants. From the slower growth rate for anionic surfactants mentioned above one would however expect a larger pore diameter. This is a hint towards a change in the valence \(n_{val}\) (compare (4.33)) depending on the type of surfactant used. The observed different behaviors of the anionic and the non-ionic surfactants is not due to changes of the pH-value of the electrolyte depending on the surfactant used, because all the surfactants had approximately the same pH-value of 7-7.5.

Grüning did not specify which/what kind of surfactant and in which concentration was used for her investigations. In addition her goal was to model the PECE behavior using HF concentration and temperature. The influence of different surfactants was neither included in her model nor in

\(^2\) Stable macropore growth could not be achieved with cationic surfactants \[^79\].

\(^3\) SLS: Sodium dodecyl sulfate, \(C_{12}H_{25}NaO_4S\), \(c_{AIS} = 0.1\) mM

\(^4\) \(c_{NIS,1} = c_{NIS,2} = 1\) ml/90 l HF (5-7wt%)
6.4 Realization of PhC tapers in the macroporous Si material system

6.4.1 Adiabatic PhC Taper

As the PECE of macropores in n-type Si provides the freedom to define the pore pattern geometry by lithography, the adiabatic taper concept described in 5.4.1 was implemented by combining regular hexagonally arranged pores together with pores arranged in a distorted hexagonal lattice. An SEM micrograph of the situation is shown in fig. 6.5. The green region exhibits pores arranged in a regular hexagonal pattern. This region is intended to be used for gas detection. The regions highlighted in red have pores arranged in distorted hexagonal lattices and are intended to be used for coupling incoming light either along $\Gamma K_1$ or $\Gamma M_2$ directions. In these regions the hexagonal lattice is distorted along the coupling direction ($\Gamma K_1$ and $\Gamma M_2$, respectively, as shown in fig. 5.4b). The taper shown is rather abrupt, consisting of only one intermediate step of one pore row (framed by the dotted line) with lattice constant $a_i$ between the coupling lattice constant $a_c$ and $a_0 = 4.2 \, \mu m$.

Within all regions and also at the interfaces between coupling and detection regions macropore...
growth was found to be stable. This can be mainly considered as a consequence of the only slight disturbance of the ideal, i.e., undistorted hexagonal lattice case.

### 6.4.2 Anti-Reflection-Layer: PECE of deep trenches

The above described realization of an adiabatic PhC taper by distortion of the hexagonal lattice is similar to PECE of perfectly ordered macropore arrays in terms of etching pores next to pores - with a minor change in symmetry and interpore distances.

For the realization of the ARL during PECE it was necessary to go a step further. A trench has to be etched next to an ordered array of macropores, within a distance of less than one lattice constant of the ordered pore array. Such a procedure disturbs the PECE process by far more than the adiabatic taper scheme. The approach and the results are presented in the following part of this chapter.

Keeping in mind the design rule of constant porosity within a unit cell stated in 5.4.2.1 the ARL layer can be realized by lithographically defining a trench to be etched next to the last row of pores of the interaction volume as schematically depicted in fig. 6.6a. The thickness \( t_{\text{ARL}} \) of the remaining ARL - as defined in the theoretical design in section 5.4.2 - is given by the distance of the edge of the trench and the center of the adjacent pores as shown in fig. 6.6b. By lithography the \( x-y \)-positions of the pores and the trench are fixed. But the width of the etched trench depends on the \( r/a \) ratio chosen during PECE according to

\[
t_t = \frac{\pi \left( \frac{t}{a} \right)^2 (2t_{\text{ARL}} - 0.5)}{\sqrt{3} - 2\pi \left( \frac{t}{a} \right)^2} \tag{6.2}
\]

with the symbols used in fig. 6.6a. As a consequence the intended \( r/a \) ratio necessary for spectral overlap of the PhC gas sensing mode with the gas absorption frequency has to be taken into account when defining the position of the trench on the lithography mask. Because the above arguments are based on simple geometric considerations and the assumption of a homogenous distribution of charge carriers it is not expected that the desired ARL thickness is precisely achieved.

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5 Equipotential surfaces for this situation are shown in fig. 7.2
6.4 Realization of PhC tapers in the macroporous Si material system

Figure 6.6: Realization of the ARL during PECE. a) Design principle b) SEM micrographs of the etch pits for the macropores and the trenches in a Si wafer. Left: overview. Right: zoom revealing ARLs with different thicknesses. The yellow and blue circles mark a region with smaller lattice constant for the lateral confinement discussed in 5.4.2 and markers allowing distinction of the individual devices on the wafer, respectively.

Figure 6.7 depicts successfully etched, 450 µm deep trenches next to arrays of hexagonally arranged macropores. Both, the macropores as well as the trenches grow stable. However, an increase in roughness of the ARL surface is observed with increasing depth. This issue is discussed in 7.1. Due to the observance of the before stated design rules, stable trench-next-to-macropores-growth could be achieved by using PECE parameters comparable to the parameter set used for the fabrication of pure macropore arrays.

However, it is clear that constant porosity in the bulk PhC and the ARL/trench regions is a necessary but not sufficient prerequisite to achieve stable macropore/trench growth. If the system is disturbed too much by, e.g., creating too thick ARLs with \( t_{\text{ARL}} \gtrsim 10 \) µm the PECE process becomes unstable. As a result dying of trenches or branching of pores and trenches is observed as shown in fig.6.8.

\(^6\)Christophersen et al. also report on the growth of deep trenches using PECE [83]. But they did not lithographically define trenches to be etched but were investigating Si dissolution and underetching at the edge of a large masked area. Their trenches were only several 10 µm deep and the shape was strongly wedged.
Figure 6.7: Deep trenches next to macropores realized by PECE (SEM micrographs). a) Lithographically prestructured n-Si wafer (top view). b) Trench and adjacent macropore array after PECE. c) Side view of the cleaving edge through the macropore array. d) Side view of the cleaving edge perpendicular to the trench. (trench highlighted by the red dotted line) e) Side view of the cleaving edge parallel to the trench. (The broken trench surface at the bottom is a consequence of cleaving.)

PECE of trenches, which was originally investigated to enable highly efficient coupling to macroporous Si PhC structures, opens the possibility to realize additional interesting structures. Figs 6.9a and d show how PECE trenches next to macropore arrays can be used to precisely define thin...
6.5 Fabrication of macroporous Si membranes

As shown in fig. 1.3, a macroporous Si membrane through which the gas can flow is needed for the realization of a PhC-based spectroscopic gas sensor. For this purpose the bulk Si remaining below the PECE pores has to be removed. Several approaches have been investigated in the framework of this thesis.

Conventional approach: wet etching using KOH/TMAH and SiO₂ passivation layer: The remaining Si below the macropores can be removed by wet etching from the wafer backside using...
Fabrication of PhC gas sensor structures

Figure 6.10: Post-PECE macroporous Si membrane fabrication methods. a) Conventional approach using wet etching from the backside and pore wall passivation layers. b) Membrane detachment by thermal SiO\textsubscript{2} growth and subsequent HF dip applied to pores that were widened during PECE at the bottom.

KOH, as depicted in fig.6.10a. To prevent the porous structure also being etched the pore walls have to be passivated by a KOH resistant layer. Typically a thermal oxide of 100-200 nm thickness is used. But the selectivity of KOH with respect to Si and SiO\textsubscript{2} is only on the order of 150-200:1 [49]. This makes large scale (≈cm\textsuperscript{2}) fabrication of macroporous membranes a difficult task. To increase the selectivity and thereby the reproducibility of this process other wet etchants such as EDP or TMAH could be used. The etch contrast for Si and SiO\textsubscript{2} of TMAH (25% wt) at 60°C amounts to more than 15000. However, the Si etch rate of TMAH is about 2.5 times lower compared to KOH of the same concentration and temperature, resulting in increased fabrication time.

Wet etching using KOH/TMAH and alternative passivation layers: The disadvantage of some alternative wet etchants is their high toxicity and their complex handling compared to KOH. Therefore in this work the approach of alternative passivation layers was investigated. One possibility is to use SiN deposited by low pressure chemical vapor deposition (LP-CVD) which increases the etch contrast by almost a factor of 1000 [49]. Although it was possible to deposit about 50 nm thick SiN layers even in about 350 μm deep macropores and use it as etch stop, it turned out that SiN has strong absorption in the wavelength region of interest (≈ 10 μm). Another possibility is to infiltrate the pores by polymers that are KOH resistant using the wetting method developed by Steinhart et al. [85]. The drawback of this method is that the polymer layer is not completely closed so that KOH can penetrate through the polymer layer and etch away the pore walls.

Wet etching using HF and thermal oxidation: An alternative method for the fabrication of macroporous Si membranes is shown in fig.6.10b. The bottom part of the macropores is widened during PECE. Subsequent repetition of thermal oxide growth and HF-dip cycles leads to the connection of the widened bottom part of the pores and finally to the release of the membrane structure. The main advantage of his approach is that large scale (≈cm\textsuperscript{2}) membrane formation can be achieved relatively well controlled. The widening of the pores during the oxide growth/HF-dip cycles has to be taken into account during PECE with respect to the desired pore diameter.

In-situ membrane fabrication during PECE: Within the framework of this thesis a third membrane fabrication method was developed. It allows in-situ realization of macroporous Si membranes and is depicted in fig.6.11. The porosity for a hexagonal array of macropores is given by 4.32. From this it follows that a porosity of 100% (corresponding to removal of all Si atoms in a certain
6.5 Fabrication of macroporous Si membranes

etch depth) is achieved for $r/a \geq 0.525$. By choosing the corresponding etch current density according to (4.30), overlap of neighboring macropores can be achieved and a macroporous Si membrane is formed. However, the PECE process is not in a stable regime for such extreme conditions. As a consequence the bottom part of the pores does not grow as nicely as in the stable PECE regime. This can be seen in the larger inset of fig. 6.11 where an SEM micrograph of the bottom of a membrane fabricated in-situ at the end of PECE is shown. The pore ends are rather brittle and Si fragments cover parts of the membrane. They can be easily removed by mechanical treatment (e.g., scraping) and/or blowing with pressurized air or nitrogen. The smaller inset shows a photograph of a macroporous Si membrane with 2 cm diameter fabricated by this technique. This method offers the advantage, that no complex post-PECE process steps are necessary for membrane fabrication. Furthermore, large-scale ($\approx$cm$^2$) membrane fabrication is possible. For typical wafer sizes of 6 or 8 inch diameter, however, this method might not be applicable, since the necessary power supplies and illumination apparatus able to deliver the required high currents are no off-the-shelf components.