Chapter 4

Etching Macroporous Silicon in the Sub-Micrometer Range

Under applied aspects the properties of a photonic crystal structure should match a wavelength region used in the telecommunication industry. For the transport of data around the globe optical fibers are used. In order to bridge large distances the attenuation in the fibers has to be minimized. An optimal window is found around a wavelength of 1.55 µm, the so-called ‘C band’ (C stands for conventional, 1530 – 1565 nm). For larger wavelengths the infrared absorption increases the attenuation whereas in the smaller wavelength regime the Rayleigh scattering (attenuation is inversely proportional to the fourth power of the wavelength) is most pronounced.

Based on the 3D photonic crystal design shown in Fig. 3.6b an appropriate structure was etched in macroporous silicon as described in section 3.4.4. This structure with a lattice constant \( a \) of 1.5 µm shows stop bands in the region of 3 µm wavelength [107]. Changing the position of the photonic stop band from 3 µm to 1.5 µm for the same design means that the dimensions of the crystal structure have to be changed by the same factor. Or to be more precise: In order to relate the center frequency \( (\omega a/2\pi c = 0.488) \) of the photonic crystal with the telecommunication wavelength \( \lambda \) of 1.55 µm the lattice constant \( a \) has to be chosen to be \( a = 0.488 \lambda = 0.756 \mu \text{m} \). From the scalability of the Maxwell’s equations it results that the band structure calculation can be adapted to arbitrary lattice constants \( a \) as long as the value of \( \varepsilon \) remains unchanged for the frequency region under consideration (cf. section 3.3). The calculations in Fig. 3.6a were done for \( \varepsilon = 11.7 \) which is equivalent to a refractive index of \( n = 3.42 \) corresponding to wavelengths larger than six micrometers. When approaching the electronic band gap at \( \lambda = 1.1 \mu \text{m} \) the dielectric constant of silicon changes considerably. For the case of 1.55 µm wavelength the dielectric constant changes to \( \varepsilon = 12.1 \) (according to a refractive index of \( n = 3.48 \)). As can be seen in Fig. 4.1 the change in the dielectric constant has only a minor impact and therefore the assumptions above hold true. In conclusion, in order to make macroporous silicon competitive for photonic crystal device fabrication the lattice constant has to be reduced to lattice constants in the range of several hundred nanometers. The etching process for structures with a sub-micrometer lattice constant as well as the utilization of the obtained results as optical devices are discussed in this chapter.
Figure 4.1: Comparative analysis of the photonic band structure for the design of overlapping air spheres (cf. section 3.4.4). While a dielectric constant of $\varepsilon = 11.7$ corresponds to a wavelength of several micrometers, the dielectric constant increases when approaching the electronic band gap. At a wavelength of 1.55 $\mu$m the dielectric constant has changed to $\varepsilon = 12.1$. In the table, gap position and size are compared to each other for the two different dielectric constants. The band gap shifts slightly towards lower frequencies for the higher dielectric constant. Because of the enhanced dielectric contrast the width of the band gap is enlarged.

4.1 Etching of Straight Pores

For the experiments presented in this chapter phosphorus doped n-type silicon wafers from Wacker Siltronic AG oriented in $\langle 100 \rangle$ direction were used. The resistivity of the material was nominally $0.1 \pm 0.013 \Omega \cdot \text{cm}$ corresponding to a doping density of $8 \cdot 10^{16} \text{cm}^{-3}$. The silicon was grown in a float zone process and the wafers measured $300 \pm 15 \mu$m in thickness and 100 mm in diameter. Rectangular pieces of 20 to 25 mm side length were cleaved out of the wafer to fit into the etching cell (cf. Fig. 1.1). At the front side of the wafers a mask of KOH etch pits was defined with a lattice constant of $a = 700 \text{nm}$. The pores were arranged in a hexagonal symmetry.

The introduced simple cubic photonic crystal structure cannot be realized with a hexagonal pore arrangement. However, at this point the etching behavior in the sub-micrometer range is studied and therefore the lattice geometry is of minor interest. It could be even argued that a hexagonal lattice is more advantageous since it has a higher symmetry than a square lattice and therefore also the pore etching should be more homogeneous and stable.

The current-voltage characteristic measured between two points at the wafer back side showed a nonlinear behavior with a resistance in the range of several kiloohms to megaohms. Hence, an ohmic back side contact had to be established prior to the etching process. Therefore, the following procedure was applied at the edge of each sample: First, two small areas of the back side were ground with fine abrasive paper. Then, a gallium-indium eutectic (Alfa Aesar, gallium-indium eutectic 99.99%, gallium : indium 75.5 : 24.5 wt%) was applied and ground into the silicon to provide a high conductivity contact. After this procedure the excess material was removed. In order to test the quality of this process the resistance between the two contacts was measured with a common circuit analyzer. Resistance values less than 20 $\Omega$ were considered to be sufficient to use the prepared sample in the etching process. Since the HF-containing etching solution corrodes the gallium-indium contact it has to made sure that the etching cell is clean and dry and that the contacts are only created at the edge of the sample outside the sealing rings (cf. Fig. 1.1).
At first, the etching of straight pores with different diameters and aspect ratios should be considered. In principal, the parameters obtained for the etching of pores at larger lattice constants can be transferred: The critical current density $J_{PS}$ is dependent on HF concentration and temperature of the etching solution. Unless otherwise noted the HF concentration was 5 wt% and the temperature was kept constant at 10°C. The porosity $p$ for a given ratio of the pore radius $r$ to the lattice constant $a$ is independent of the lattice constant (cf. Eq. 1.8, e.g. for $r = 0.25a$). Therefore, the etching current density $J$ remains at the same value, too (cf. Eq. 1.7). The voltage was set to $V = 2$ V. As a surfactant, SDS (0.1 mM) was added to the etching solution.

With these preconditions straight pores of different porosities were etched. Stable pore growth over a depth of at least 50 µm could be achieved for pore diameters between 240 nm ($r/a = 0.17$) and 480 nm ($r/a = 0.34$) (Figs. 4.2a and b).\(^1\) This corresponds to porosity values of 11% and 43%, respectively. Pores with diameters out of this range tended to stop growing or grew together. Analyzing the cross section pictures of several pores gave a standard deviation of 14% for the pore diameter.

Pores with a length of up to 200 µm were etched without a significant lack of pore uniformity. That is equivalent to two-thirds of the wafer thickness and to an aspect ratio of pore length to pore diameter of about 700 : 1. In Fig. 4.2c a 100 µm deep etched sample is shown. The pore diameter is $280 \pm 30$ nm corresponding to an aspect ratio of about 360 : 1. Almost every pore is completely etched and they are all of the same length. In the cross section picture (Fig. 4.2c) two missing pores could be identified separated by approximately 90 pores in between. This means that 99.99% ($1 - 1/90^2$) of the pores have been etched. This value could be confirmed statistically by measuring at different positions of the sample. However, a few pores could be found that differ by thirty percent of the mean pore diameter, e.g. the smallest diameter was 190 nm and the largest was 370 nm. This indicates the existence of parameters that locally disturb the self-stabilizing pore etching process. The influence of several parameters was explored more in detail for modulated pore structures as presented in the next section.

\(^1\)In contrast to the discussion in the next sections, no microporous layer can be seen on the sample walls. The sample was stored under ambient atmosphere for a day and the microporous layer was oxidized. Prior to the SEM an HF-dip was performed to lower the influence of statics. So, also the microporous layer was removed.
4.2 Etching of Modulated Pores

Diameter-modulated pores can be obtained by a modulation of the back side illumination intensity (cf. section 3.4.4). Additionally, the surfactant was changed from SDS to NCW (0.17 mM) since NCW was proven to be more suited for modulated pore growth. In Fig. 4.3a the etching current density is given for a single modulation. It consists of three sections: In the increasing part more charge carriers are provided and the pore is widened in diameter. The reverse is true for the second part: During the decrease of the etching current the pore shrinks in diameter since less charge carriers are available. In the following constant current part, time is given for the system to recover into a steady state. In Fig. 4.3b the result is shown for ten repetitions of this etching profile. The pores are sinusoidally shaped. Their form does not follow directly the applied profile. As already observed for larger lattice constants it is very smooth without sharp spikes [109]. The reason is the altered condition in the SCR. If the current is increased charge carriers are accumulated in the region of the pore tip. In order to consume these additional charge carriers the pore increases in diameter until an equilibrium is established again between provided charges and pore diameter. During this transition time, however, more charge carriers are present at the pore tip than can be consumed. Thus, the focusing effect of the SCR is lowered and therefore the passivation of the pore walls is diminished. The defect electrons do not only react at the tip of the pores but also in areas that were already etched before and the pore shape becomes smeared out.

Another important observation is, that the pores differ in diameter and length. This was also observed for the straight pores in the last section. Furthermore, these two parameters appear to be...
4.3 Influence of the Lithography

In the two previous sections the etching of straight and sinusoidally shaped pores was presented. Now, the observed behavior of the correlation between the pore diameter and its length will be discussed. Because this correlation is independent of the pore shape as well as the etched depth, the conclusion is drawn that this disorder effect cannot be prevented by changing the parameters in the etching process itself. Rather, this disorder must be induced by an inherent ordering parameter. Since the initial ordering is given by the KOH etch pits, this extrinsic parameter should be considered more in detail in this section.

Fig. 4.5 shows a comparison of two hexagonal lattices with a lattice constant of 700 nm and 4 µm, respectively. Thereby, the 4 µm lattice belongs to a charge of wafers that has been shown to yield perfectly aligned pores with equal diameters and lengths (cf. Fig. 1.4 on page 10). Although the hexagonal arrangement of the etch pits is clearly visible in both lattices, the 700 nm lattice exhibits a higher degree of disorder. The parameters used for the definition of disorder are the area of the etch pits (defined by their side lengths) and the distribution of the etch pits in the plane. SEM micrographs of the surface were taken for the analysis. To minimize the influence of aberrations only a quadratic region in the center of the SEM pictures was considered for the analysis. Via setting a threshold the pictures were transformed to binary images with one color value for the etch pit areas and the second one for the unetched area. The image analysis of the threshold picture gave a value for each etch pit area. Furthermore, the absolute position of the etch pit center was also determined. Statistical treatment of the obtained data gave the values presented in table 4.1.

4.3 Influence of the Lithography

Connected: Pores with a larger mean diameter are also a little bit longer than those with a smaller diameter. Nevertheless, all pores were etched and they show the same dependencies between diameter and length (Fig. 4.3c).

The found set of parameters was also suited for the growth of deeper pores. Instead of ten modulations the given profile was repeated for 40 times (Fig. 4.4). Still, there are no pores which stop growing or grow together. This emphasizes that the etching process takes place in a stable state within the applied parameters. Furthermore, the offset in length between thicker and thinner pores remains constant and therefore it is independent of the overall pore length. Thus, it can be concluded that this disorder is not caused by the etching process. Instead, an inherent property of the material itself must cause this effect, as discussed in the following section.
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Figure 4.5: The lithographically defined hexagonal lattice for a lattice constant of a) 700 nm and b) 4 µm. The comparison between the two lattices shows that the 700 nm lattice suffers from a significantly higher disorder of the etch pits regarding their size and position.

Table 4.1: Comparison between the hexagonal lattice with 700 nm lattice constant and the one with 4 µm. The statistical analysis revealed that the etch pit positions possess the same standard deviation while the deviation of the edge lengths in the 700 nm lattice are comparatively higher.

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>0.7 µm</th>
<th>4 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Edge length</td>
<td>0.45 ± 0.06 µm ̂ ± 13%</td>
<td>2.20 ± 0.06 µm ̂ ± 2.6%</td>
</tr>
<tr>
<td>Position</td>
<td>△x = △y = 1.5%</td>
<td>△x = △y = 1.5%</td>
</tr>
</tbody>
</table>

Because the etch pits are etched into the ⟨100⟩ oriented silicon by KOH it was assumed that the etch pits have a quadratic shape. Thus, a value and an error for the edge length of the etch pits can be derived from the analysis of the etch pit area. As can be seen in table 4.1 the absolute error of 60 nm for the edge lengths is the same for both lattices. This gives a comparatively higher standard deviation of 13% for the 700 nm lattice compared to the 4 µm lattice with a standard deviation of 2.6%.

The second parameter under consideration was the position of the etch pit. Therefore, the coordinates of the center of the areas were related to a perfectly aligned hexagonal lattice and the deviation was calculated. Remarkably, it is the same relative error of 1.5% for each lateral direction in both lattices. So it can be concluded that the reason for the observed disorder is due to the higher variation of the etch pit edge lengths in the 700 nm lattice.

In the following it should be argued in which way the initial etch pit conditions affect the pore diameters. As revealed by the considerations above, the etch pit diameter of the 700 nm lattice shows a deviation of 13%. After lithographically defining a mask the etch pits are anisotropically etched with KOH. The angle between the wafer surface and the formed {110} faces is 54.7° and crystallographically defined. Thus, the visible etch pit diameter from the top view is directly related to the depth of the etch pit: An increased etch pit diameter is related to a deeper etch pit and vice versa. This can be seen in Fig. 4.6a. A cross section of a 700 nm sample is shown and differently sized etch pits can be distinguished. As a result, there is an offset △z in depth between smaller and larger pores.

The surface conditions also affect the form of the SCR, as schematically shown in Fig. 4.6b. A
silicon surface with differently sized etch pits (black line) transfers this variation also to the form of the SCR, represented by an equipotential line (red line). In the vicinity of the large etch pit the SCR extends deeper into the silicon and thus more charge carriers are collected. The smaller etch pit is somewhat behind and collects less defect electrons. Fortunately, the adaption of the SCR ensures a stable pore growth despite the unequal etch pit sizes. The pores regulate their diameter in accordance with the amount of collected charge carriers. The etching speed is independent of their diameter and thus the initial offset remains constant.

Another effect related to this issue concerns the modulation profile. Since the pore etching starts in different depths, the diameter modulation reproduces also this offset. This can be seen by carefully checking Fig. 4.3b or Fig. 4.4: A pore with a very large diameter next to a very small pore forms its modulation maxima slightly deeper than the modulation maxima of the small pore. The reason for this phenomenon is apparent: If the porosity is changed during the etching then this changes the pore diameter at the pore tip. However, due to the etch pit induced variations of the etch front depth, the porosity change takes place in different depths.

The results presented in this section emphasize the importance of a perfectly prepatterned silicon surface. Although most of the pores are etched, an initial disorder in the etch pit lattice propagates into the pore length and diameter. It acts as a source for instabilities and renders the etching of precisely arranged and equally shaped pores impossible. Thereby, the standard deviation of 14% found for the pore diameters in section 4.1 is comparable to the obtained standard deviation of 13% for the etch pit edge lengths. This confirms the proposed interaction between etch pit and pore morphology. A detailed analysis, where differently sized etch pits were introduced intentionally can be found in Ref. [110].

### 4.4 Etching of Strongly Modulated Pores

In section 3.4.4 the realization of a 3D photonic crystal structure with macroporous silicon was shown. In addition to the current modulation a strong modulation of the voltage is the crucial factor to obtain a pore profile with sharp kinks (Figs. 3.7a and b). This design is necessary for the subsequent pore widening process. The modulated pores with a lattice constant of 700 nm
Figure 4.7: Cross section SEM micrographs of modulated macroporous silicon with a lattice constant of $a = 700\,\text{nm}$. a) After oxidation and treatment in NH$_4$F a highly porous slightly modulated pore structure is obtained. In the background the modulated pore walls of the next row can be seen. b) Modulated pores etched with a current density and voltage profile directly transferred from two micrometer lattice constant with lengths scaled by factor $0.7/2$. The result is a disordered pore growth with corroded pore walls.

Presented so far offer a smooth sinusoidal shape only and are not suitable for the isotropic pore widening process. In Fig. 4.7a a smoothly modulated pore structure, e.g. as presented in Fig. 4.3b, was oxidized for two hours at $900\,\text{°C}$ and after that the oxide layer was removed in NH$_4$F. Still, a slight modulation is visible. The black areas in the regions of the thin pore walls denote that a breakthrough towards neighboring pores was established. Thus, the hexagonal pore arrangement is clearly visible. The modulation intensity of the pore diameter, however, is too weak for 3D photonic crystal applications.

The modulation profile shown in Fig. 3.7e produced a well-shaped pore profile for a lattice constant of $2\,\mu\text{m}$. As discussed in section 4.1 for straight pores, the current densities can be transferred to arbitrary lattice constants. For a fixed $J_{PS}$ the porosity is preserved independently from the lattice constant. This holds also true for a modulated porosity. Only the length scale of the modulation has to be adapted to the new lattice constant. In this particular case the lengths of the profile in Fig. 3.7e were scaled by a factor 0.35 to go from a lattice constant of $a = 2\,\mu\text{m}$ to $a = 700\,\text{nm}$. The result (Fig. 4.7b) is clearly different from the expected one: Although sharp kinks are visible the pores tend to leave their preferred growth direction and the walls appear to be corroded.

For a systematic study of how the different parameters influence the pore etching process an asymmetric profile was applied (Fig. 4.8a). In contrast to the profile for sinusoidally modulated pores (Fig. 4.3a), the increasing current density part is now longer with respect to the decreasing one. Furthermore, a strong voltage modulation was applied with a maximum voltage of three volts during the low current density part. Although the higher voltage should increase the focusing effect of the charge carriers to the pore tip, the resulting pores still show a sinusoidal shape (Fig. 4.8b).

In former works it has been observed that the choice of the surfactant has a strong influence on the obtained pore shape [111, 109, 26, 27]. While straight pores are preferentially etched with SDS (anionic surfactant), for the modulated ones NCW (nonionic surfactant) is used (cf. section 1.2). Nevertheless, the modulated pore etching was also carried out with SDS instead of NCW. In Figs. 4.8c and d the resulting pore shape is shown for a sample etched with an identical
4.4 Etching of Strongly Modulated Pores

Figure 4.8: For etching pores with sharp kinks, beside the current density also the applied voltage has to be modulated. a) The current density and voltage profile for a single pore modulation. b) SEM cross section view of the resulting pores when NCW is used as surfactant. c) The same modulation profile etched with SDS as surfactant instead of NCW exhibits a clearly different pore shape. d) Magnified version of the pore modulation. Three different areas can be distinguished: A bright area (bulk silicon), covered by a dark-gray film of varying thickness (microporous silicon), and the pore presented by the dark area in the middle and at the border.

The modulation profile. Fig. 4.8d shows a magnified version of the SDS-etched pores. The bright areas represent the remaining silicon. It is slightly modulated in its thickness comparable to the NCW-etched sample in Fig. 4.8b. In addition, a layer is found covering the whole silicon pore wall. It is of lower contrast and develops a sponge-like structure. Furthermore, it shows no dependence on crystal orientation. Therefore, this layer could be identified to be microporous silicon. This could also be proved by luminescence measurements. The contour of this layer forms a drop-shaped pore with a maximum diameter of 430 nm and a minimum diameter of 200 nm. While this kind of surface could be interesting for surface chemistry because of the large surface-to-volume ratio of the microporous layer, it is not suitable for photonic applications. The effective dielectric constant of microporous silicon is considerably lower and therefore only a low dielectric contrast to the air-filled pore is established. The refractive index $n_{ps}$ of a microporous silicon layer can be roughly approximated to:

$$n_{ps} = (n_{si} - 1) (1 - p) + 1 \tag{4.1}$$

For a porosity $p$ of 70% the microporous silicon layer has a refractive index of 1.7 in contrast to

---

2Only the situation at the pore bottom is different: While in the case of NCW (Fig. 4.8b) the etching was stopped directly after the last modulation, for SDS a section of constant current density and voltage was added.
Pores in n-type silicon are etched in an HF containing etchant for current densities below $J_{PS}$ under anodic bias. In the case of meso- and macroporous silicon the etched pore walls are passivated due to the SCR. The formation of microporous silicon, however, is not explained via a SCR but due to a quantum confinement effect [15]. If particle movement is restricted in one or more dimensions due to a potential wall, the energy of the particle increases. This is the definition of quantum confinement. In microporous silicon, the remaining walls have thicknesses of only a few nanometers. As a result, the band gap energy increases compared to bulk silicon and an additional energy barrier for the holes is established. If the energy of this barrier exceeds the bias-dependent energy of the holes, the walls get depleted. They are passivated and the etching stops [24]. The size scale which marks the transition between unrestricted charge carrier movement and the presence of quantum confinement effects is the Bohr radius of an exciton. In crystalline bulk silicon the Bohr radius of an exciton is about five nanometers [16].

With this short explanation of microporous silicon formation the question of the difference between the two surfactants can be answered. For comparison, two samples with straight pores of 200 µm depth were grown: One with SDS added and the other with NCW (Fig. 4.9). For SDS (left image) the typical microporous layer is visible on the pore walls. It has a constant thickness. Such a layer is not visible in the case of NCW (right image). Comparing the pore diameter between the beginning of the pores (top) and their end (bottom) reveals that the pore diameter is constant (0.75 µm) in the case of SDS but changes from 1.16 µm in the beginning to 0.98 µm at the end in the case of NCW. The reason for that is a post-etching of the pore walls due to dark currents. For SDS, these dark currents are significantly lower [26]. A microporous layer forms and passivates the pore walls. No further etching takes place. In an NCW containing etchant the formation of a
microporous layer seems to be hindered or, rather, the microporous layer is dissolved immediately after the formation.

The following two assumptions could explain this phenomenon. Firstly, the higher dark currents in NCW lead to a higher porosity of the microporous layer. Secondly, the resulting smaller pore walls are completely oxidized and removed in the HF containing etchant. This happens just before the microporous layer is thick enough to passivate the pore walls. In the case of SDS the pore wall thicknesses of the micropores are higher due to a lower dark current density. The layer can increase in thickness before it is completely dissolved. Charge carriers cannot (or only at a strongly decreased rate) pass this layer. The dissolution of the microporous layer is stopped or at least the dissolution rate is significantly lowered so that no post-etching induced pore widening could be identified from the SEM micrographs.

This crude explanation was not further checked since a detailed investigation of the surfactant and its electrochemistry was not realized in the frame of this work. However, it could be learned that the microporous layer visible in the SDS containing etchant can be seen as an intermediate step to the etching in NCW. The microporous layer shows the intended shape with sharp kinks.

In Fig. 4.10 the modulation of the last pore in an SDS containing etchant is analyzed more in detail. Three samples were etched with the modulation profile given in Fig. 4.8a. The first five modulations were etched completely. Afterwards, the process was stopped at three different points during the sixth modulation. The first picture (Fig. 4.10a) represents the condition in the beginning of the pore formation. The voltage is at maximum while the current density is at minimum (depth of 0 µm in Fig. 4.8a). A small channel with only a few ten nanometers in diameter forms, assisted by the high voltage that produces additional charge carriers due to breakdown. The pore walls of the last complete modulation are still free from a thick microporous layer.

A second picture (Fig. 4.10b) was taken at a depth of 0.2 µm. The current density is increasing to enlarge the diameter of the new pore. The voltage has diminished to its normal value to avoid instabilities due to further generation of breakdown charge carriers. In contrast to the first picture, the fifth modulation is now completely covered with a microporous layer like the preceding modulations.

The third picture (Fig. 4.10c) represents the situation at maximum current density (depth of
Figure 4.11: SEM cross section of modulated macropores etched with an increased voltage. The pore shape has a higher modulation amplitude but the pores are corroded due to the increased voltage. a) Overview. b) Detailed view. c) In this table the modulation amplitude of the sample etched with an increased voltage of 4 V maximum is compared with the result in Fig. 4.8b for 3 V maximum voltage.

<table>
<thead>
<tr>
<th>Peak Voltage</th>
<th>Diameter [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 V</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.38</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.52</td>
</tr>
<tr>
<td>Ratio</td>
<td>1:1.37</td>
</tr>
</tbody>
</table>

0.3 µm). The pore diameter has reached its maximum. The length, however, will be adjusted during the last steps of the pore modulation while the current density is decreased and the voltage is raised to form a new pore at the bottom. The thickness of the microporous layer of the last complete modulation has slightly increased once again.

While up to the last but one modulation the pore walls are already covered with a microporous layer, the last modulation does not show this feature. This can be seen also in Figs. 4.8c and 4.9 at the bottom of the pores. Since the local current density at the pore tip is always \( J_{PS} \), the pore bottom is electropolished and no microporous layer can be found. But immediately after the formation of a new pore the preceding modulation is affected and a microporous layer is formed. In contrast to the straight pore formation in SDS (Fig. 4.9), the thickness of the microporous layer changes with the modulation. This indicates an additional charge carrier transport beside that of dark currents through the pore walls. In other words, the passivation of the pore wall is not working properly. Charge carriers that are meant to be focused to the pore tip can pass this region and dissolve already etched areas. This effect is most pronounced during the beginning of a new pore formation process. Hence, the pore wall passivation can be accomplished with a higher voltage at this point.

Therefore, the applied voltage was raised from three to four volts in the beginning. The minimum voltage of two volts remained unchanged (cf. Fig. 4.8a). Because the voltage decreases linearly from four to two volts, the voltage is higher during the first 0.2 µm of the new pore formation. As predicted by the considerations above the thickness of the microporous layer could be diminished. The obtained pore shape – already etched in NCW containing etching solution – is shown in Fig. 4.11. In comparison to Fig. 4.8b the ratio of minimum to maximum pore diameter is increased from 1.4 to 1.9 (cf. Fig. 4.11c). The pore walls, however, appear to be corroded (Fig. 4.11b). A further increase in the applied voltage amplified this phenomenon.

An increased voltage means an increase in the electrical field strength, too. In the case of the small pores with only a few ten nanometers radius of curvature, the local electric field strength is significantly increased. Therefore, the threshold for generating charge carriers by tunneling is lowered. During the time of increased voltage the chance of initiating a local current burst is
enhanced. This is visible in the diminishing diameter part of a modulation: Small side pores are etched and corrode the pore walls.

To summarize this section, the etching of strongly diameter-modulated pores in highly doped n-type silicon works close to physical limits. On the one hand an increased voltage is necessary to etch a tiny pore in the beginning that can be widened afterwards. On the other hand the high doping density limits the increase of voltage due to the generation of charge carriers by tunneling. However, the doping density itself defines the width of the SCR and is thus not freely adjustable. The open question is, whether a change in the doping density can significantly improve the etching conditions or not. Therefore, the next section is dealing with the space charge region and their dependency on doping density and pore geometry.

4.5 Space Charge Region and Breakdown

In Eq. 1.1 the width of the SCR is dependent on voltage and doping density. But the derivation of this equation is only true for a planar silicon-electrolyte interface. The presented case of small pores with a radius of curvature of only some ten nanometers is quite different from that. Due to the hemispherical-like bent pore tip the electric field strength is locally increased and can exceed the limit of electric breakdown. In silicon with a doping density of \( N_D = 8 \cdot 10^{16} \text{ cm}^{-3} \) considered in this chapter, this limit is reached at a breakdown electric field strength \( E_{bd} = 5.7 \cdot 10^5 \text{ V/cm} \).

Based on Ref. [113] it can be calculated using the following approximation:

\[
E_{bd} = \frac{4 \cdot 10^5}{1 - \frac{1}{3} \cdot \lg(N_D / 1 \cdot 10^{16})}
\] (4.2)

where the doping density \( N_D \) is taken in units of \( \text{cm}^{-3} \) and \( E_{bd} \) in \( \text{V/cm} \). The assumption of a planar interface is not a valid approximation for small radii of curvature anymore. Therefore, this section will discuss the relation between the applied voltage, the doping density, the influence of the pore tip geometry, and the resulting SCR.

The differential form of Gauss’ law in electrostatics for a linear medium is

\[
\overrightarrow{\nabla} \cdot \overrightarrow{E}(\vec{r}) = \frac{\rho(\vec{r})}{\varepsilon \varepsilon_0}
\] (4.3)

with \( \rho(\vec{r}) \) the free electric charge density, \( \varepsilon = 11.9 \) the dielectric constant of silicon and \( \varepsilon_0 \) that of free space. The electric field \( \overrightarrow{E}(\vec{r}) \) can be derived from the scalar electric potential field \( \varphi(\vec{r}) \):

\[
\overrightarrow{E}(\vec{r}) = -\nabla \varphi(\vec{r})
\] (4.4)

Thus, Eq. 4.3 can be expressed as

\[
\triangle \varphi(\vec{r}) = -\frac{\rho(\vec{r})}{\varepsilon \varepsilon_0}
\] (4.5)

which is the Poisson equation with \( \triangle \) being the Laplace operator.

It is assumed that all dopants in the SCR are ionized. This is the so-called depletion approximation and can be justified by the potential drop over the SCR (cf. section 1.2). That gives \( \rho(\vec{r}) = -eN_D \) for \( 0 \leq r \leq W_{SCR} \) with \( e \) the elementary charge and \( N_D \) the doping density. The
Figure 4.12: Schematic cross section of the silicon-electrolyte interface in spherical geometry. The SCR ranges from the interface \( r = r_0 \) until a depth of \( r = r_0 + x_d \) with \( r_0 \) the radius of curvature.

First integration of Eq. 4.5 gives the electric field. In the case of a planar silicon-electrolyte interface \( \vec{r} = r \) it has its maximum at the interface \( r = 0 \) and is linearly decreasing towards zero at \( r = W_{SCR} \).

Integrating Eq. 4.5 for a second time gives the potential \( \varphi (r) \) which is proportional to \( r^2 \). The bias applied between electrolyte and silicon drops over the SCR and thus the width of the SCR is determined (cf. Eq. 1.1).

To reproduce the conditions at the pore tip more precisely, Eq. 4.5 has to be solved for spherical geometry\(^3\):

\[
\Delta \varphi (r) = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d}{dr} \varphi (r) \right] = -\frac{eN_D}{\varepsilon \varepsilon_0} \tag{4.6}
\]

The boundary conditions for the integration can be seen in Fig. 4.12: The SCR ranges from \( r = r_0 \) to \( r = r_0 + x_d \) and the electric field and the applied voltage drop from maximum at \( r = r_0 \) to zero at \( r = r_0 + x_d \), i.e. \( E (r_0 + x_d) = 0 \) and \( V (r_0 + x_d) = 0 \) \([114]\). Integration from \( r = r_0 + x_d \) to \( r = r_0 + x \) of Eq. 4.6 gives the electric field in the SCR:

\[
E (r) = \frac{eN_D}{3 \varepsilon \varepsilon_0} \left[ \frac{(r_0 + x_d)^3}{r^2} - r \right] = -\frac{d}{dr} \varphi (r) \tag{4.7}
\]

The relation between potential drop and width of the SCR is obtained by the second integration over the same interval:

\[
V (r) = \frac{eN_D}{6 \varepsilon \varepsilon_0} \left[ -3 (r_0 + x_d)^2 + \frac{2(r_0 + x_d)^3}{r} + r^2 \right] \tag{4.8}
\]

As written in section 1.2 the effective voltage consists of the the built-in potential of the contact, the applied voltage and the thermal voltage \((kT/e)\). It is assumed that the voltage drop takes

\[^3\text{The full Laplace operator in spherical coordinates: } \triangle = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}.\]
place only over the SCR, i.e. for $r_0 \leq r \leq r_0 + x_d$. Therefore, Eq. 4.8 simplifies to:

$$\frac{6\varepsilon_{0}V}{eN_D} = \frac{2}{r_0}x_d^3 + 3x_d^2$$

(4.9)

This cubic function can be solved with the formula of Cardano [115]. For the limit of a planar interface (i.e. $r_0 \to \infty$) Eq. 4.9 transforms to Eq. 1.1.

In table 4.2 certain values are listed that can be calculated with the presented equations. In the first column the values for silicon with a resistivity of $1\ \Omega\ \text{cm}$ are given. This material is known to produce modulated shapes with strong kinks (cf. section 3.4.4) and has been optimized during a former doctoral thesis [26]. Analyzing the growth of strongly modulated pores revealed that a tiny pore with a radius $r_0$ of about 100 nm is formed in the beginning and widened afterwards to obtain the desired shape. This ratio $r_0/a = 0.05$ is taken as the basis for the calculations in table 4.2. In the second column the material with a lattice constant of 700 nm is presented. The corresponding radius of curvature with the same ratio $r_0/a = 0.05$ is then $r_0 = 35$ nm. During the formation of the small pore the applied voltage was $V = 5$ V for $a = 2\ \mu m$ and $V = 4$ V for $a = 700$ nm. The width of the flat SCR $W_{SCR}$ is calculated with Eq. 1.1. For the calculations, the voltage was corrected by the built-in potential of the silicon-electrolyte interface (0.5 V).

Under the assumption of a flat interface the critical field strength of electric breakdown $E_{bd}$ corresponds to a breakdown voltage of $V_{bd}^{^{\text{flat}}}$, dependent only on the doping density $N_D$. $V_{bd}^{^{\text{flat}}}$ can be calculated from Eq. 4.7 with $r = r_0$ and $r_0 \to \infty$

$$E = \frac{eN_D}{\varepsilon_{0}x_d}$$

(4.10)

whereas $E = E_{bd}$ and $x_d$ is replaced by the width of the SCR of a planar junction (Eq. 1.1):

$$V_{bd}^{^{\text{flat}}} = \frac{E_{bd}^2 \varepsilon_{0}}{2eN_D}$$

(4.11)

The derivations presented above for a spherical junction introduce an additional dependence on the radius of curvature $r_0$. For a spherically curved interface a significantly smaller width of the SCR $W_{SCR}^{^{\text{sphere}}}$ is obtained. Therefore, the electric field strength increases and the breakdown conditions are reached at a considerably lower breakdown voltage $V_{bd}^{^{\text{sphere}}}$. In the case of the material with $2\ \mu m$ lattice constant the formation of a small pore takes place at a voltage close to the breakdown voltage $V_{bd}^{^{\text{sphere}}} = 5.29$ V of a spherical junction. This unstable regime close to the breakdown voltage lasts only for a short time (cf. section 3.4.4 and Fig. 3.7). With increasing pore diameter and decreasing voltage a stable pore growth is ensured again.

A pore with the same radius of curvature of $r_0 = 100$ nm etched in the 700 nm material would give a $V_{bd}^{^{\text{sphere}}}$ of 3.98 V. The reason for the lower breakdown voltage is the higher doping density. However, this radius is too large for the purpose of strongly modulated pore shapes and has to be scaled-down to $r_0 = 35$ nm in the 700 nm material as mentioned above. Thus, the breakdown voltage is further reduced to $V_{bd}^{^{\text{sphere}}} = 2.05$ V due to the changed geometry (cf. second column in table 4.2).

The width of the SCR is the important number which characterizes the field conditions during the formation of the pores. Especially the initial small pore in the beginning of a new modulation
Table 4.2: Table of factors that determine the electric conditions in the vicinity of the pore tip.

<table>
<thead>
<tr>
<th></th>
<th>optimized material</th>
<th>material under consideration</th>
<th>$W_{\text{SCR}}^{\text{sphere}} / a = 0.258$ at $V = 4\text{V}$</th>
<th>$W_{\text{SCR}}^{\text{sphere}} / a = 0.258$ at $V \geq V_{\text{bd}}^{\text{sphere}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ [nm]</td>
<td>2000</td>
<td>700</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>$N_D$ [cm$^{-3}$]</td>
<td>5 \cdot 10^{15}</td>
<td>8 \cdot 10^{16}</td>
<td>3.2 \cdot 10^{16}</td>
<td>2 \cdot 10^{16}</td>
</tr>
<tr>
<td>$\rho$ [Ω cm]</td>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>$E_{\text{bd}}$ [V/cm]</td>
<td>3.6 \cdot 10^{5}</td>
<td>5.7 \cdot 10^{5}</td>
<td>4.8 \cdot 10^{5}</td>
<td>4.5 \cdot 10^{5}</td>
</tr>
<tr>
<td>$V$ [V]</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>2.7</td>
</tr>
<tr>
<td>$W_{\text{SCR}}^{\text{flat}}$ [nm]</td>
<td>1088</td>
<td>240</td>
<td>380</td>
<td>380</td>
</tr>
<tr>
<td>$V_{\text{bd}}^{\text{flat}}$ [V]</td>
<td>86.9</td>
<td>13.5</td>
<td>23.9</td>
<td>32.5</td>
</tr>
<tr>
<td>$r_0$ [nm]</td>
<td>100</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>$r_0/a$</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>$W_{\text{SCR}}^{\text{sphere}}$ [nm]</td>
<td>516</td>
<td>129</td>
<td>181</td>
<td>181</td>
</tr>
<tr>
<td>$W_{\text{SCR}}^{\text{sphere}} / a$</td>
<td>0.258</td>
<td>0.184</td>
<td>0.258</td>
<td>0.258</td>
</tr>
<tr>
<td>$V_{\text{bd}}^{\text{sphere}}$ [V]</td>
<td>5.29</td>
<td>2.05</td>
<td>2.14</td>
<td>2.20</td>
</tr>
</tbody>
</table>

is the crucial point for a strongly modulated pore shape. In the optimized material of 2 µm lattice constant the width of the spherical curved SCR is 0.258 in units of the lattice constant while it is only 0.184 for the 700 nm lattice. This means that in the latter case the expansion of the SCR into the material is reduced. For the given doping density $N_D = 8 \cdot 10^{16}$ cm$^{-3}$ a voltage of $V = 9.3$ V would be necessary to enlarge the SCR accordingly.

According to Eq. 4.9 the width of the SCR is dependent on the applied voltage and the doping density for a fixed radius of curvature. In the following it is assumed that a width of the SCR equal to the conditions in the 2 µm material would be an optimum for the pore growth. Therefore, in the last two columns of table 4.2 two different scenarios for the same ratio $W_{\text{SCR}}^{\text{sphere}} / a = 0.258$ as in the 2 µm lattice are discussed.

In the third column the voltage is set to $V = 4$ V. Thus, the required doping density for the case
4.6 Photonic Stop Band at 1.5 µm Wavelength

With the hexagonal pore arrangement and the obtained shape of modulated structures presented so far a photonic crystal with a complete 3D photonic band gap cannot be realized (cf. section 3.4.4). However, the fabrication of structures that possess photonic stop bands in the mod-
4.7 Summary

This chapter discussed the possibility to shrink the lattice constant of macroporous silicon to a range applicable for optical applications in the 1.55 µm wavelength region and the limitations involved in creating 3D structures. Straight pores could be etched with large aspect ratios and thus the realization of 2D photonic crystals is feasible. The observed disorder in pore diameter and length was proven to be caused by the lithographically defined mask. To circumvent this problem, the lithography has to be improved in its accuracy. The deviation of the etch pit positions and their diameter should vary within only a few ten nanometers which is feasible with today’s masking.
processes.

The etching of diameter-modulated structures was also presented. A homogeneous pore growth with a ratio of minimum to maximum diameter of $1:2$ was realized. Furthermore, optical characterization of the samples emphasized the utilization of the obtained structures for photonic crystal applications.

In comparison to former works the structures with 700 nm lattice constant cannot yet compete with the lower doped material. There, diameter modulation ratios of $1:4$ and even more are possible, as shown for instance in chapter 2 and section 3.4.4. Especially the strong modulation of the pore diameter is a limiting fact in the design of structures so far. Therefore, this chapter dealt intensively with the SCR model and the electric field conditions at the pore tip. The phenomenological observations were corroborated by calculations and a recommendation for a properly doped material was given. An optimized material with proper doping density and uniform mask will result in a higher homogeneity of the macroporous samples.

Nevertheless, physical limitations in the etching process become more and more dominant at this sub-micrometer size scale. Thus, a couple of other parameters have to be considered carefully as well. For instance, the composition of the etchant and especially the influence of type and concentration of the surfactant need further investigations. For reliable results the obvious limitations due to lithography and doping should be solved first.