Chapter 13
Macroporous Silicon

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Abstract Macroporous silicon is a material system ideally suited for the fabrication of tubular structures on the micrometer size scale. With nanometer precision on an arbitrarily sized area, millions to billions of identically shaped objects can be produced. In a modified way it is even possible to alter the shape of the structures in situ, i.e. to grow three-dimensionally modulated structures. The fabrication of macroporous silicon is based on a classical top down approach. Starting from bulk material, regular pore structures are formed in an electrochemical etching process. The underlying fabrication method is a parallel process which makes the production of macroporous silicon scalable to large areas and therefore economically attractive. In this review an introduction is given to the method of etching macroporous silicon while the growth of straight and modulated pores is explained in more detail. In conjunction with suitable post treatment steps a variety of applications for macroporous silicon has been realized from which a selection will be presented here.

The condemned live longer. And so does silicon. It is yet the material par excellence for making our modern live a complex one. It was often heard that the time has come for a new age beyond silicon. But meanwhile, silicon has learned numerous tricks, e.g. superconductivity [1, 2], spin transport [3], and even active emission of photons [4–7] and their modulation [8] is feasible. In the course of time and with all the efforts put in the field of silicon also a porous form of silicon was fabricated and investigated thoroughly. In the scope of this book we are interested in a material system that can provide us with regularly shaped and well controlled arrays of pores. The advantage of having a porous material based on silicon is obvious: All the knowledge and techniques established in silicon industry can be applied to this material system as well. Especially the ease of growing a native oxide on silicon was one key to make silicon the most popular material nowadays. In addition, silicon has the advantage to be nontoxic and biocompatible.

Macroporous silicon is a material system ideally suited for tubular structures on the micrometer size scale. With nanometer precision on an arbitrary area, millions to billions of identically shaped objects can be produced. In a modified way it is even
possible to alter the shape of the structures in situ, i.e. to grow three-dimensionally modulated structures. The fabrication of macroporous silicon is based on a classical top down approach. Starting with a bulk material, regular pore structures will be produced just by removing part of the material in an electrochemical etching process. Important to mention at this point is the fact that the underlying fabrication method is a parallel process. Thus macroporous silicon is scalable to large areas and therefore economically attractive.

The chapter is divided into two parts. At first, we give an introduction to the method of etching macroporous silicon. The growth of straight and modulated pores will be considered in detail, achievable material parameters are discussed, and different methods are presented suitable for modifying the obtained structures for certain applications. Secondly, we will concentrate on a selection of applications realized with macroporous silicon.

**13.1 Introduction**

The formation of porous silicon in an anodization setup is known since the 1950s from the pioneering work by Uhlir and Turner at Bell Labs [9, 10]. But it took more than 30 years when Lehmann and Föll invented an electrochemical etching process to produce arrays of ordered macropores in silicon [11]. Other groups followed, and this new topic was established as an important field in material science.

The etching of silicon and therefore the “growth” of pores into silicon covers several orders of magnitude. According to the IUPAC nomenclature for porous materials [12], structures with a pore width below two nanometers are called microporous. Their formation needs to be described quantum mechanically [13]. The mesoporous structures range from 2 to 50 nm. Bigger pores are referred as macropores.

The obtained pore morphology is dependent on the properties of the silicon (doping, resistivity, and orientation), the composition of the electrolyte (organic, anorganic, and concentration), and external parameters such as temperature, voltage and illumination. Beside numerous review articles that can be found in literature (e.g. [14, 15]), a book written by V. Lehmann is highly recommended for a more detailed study of the electrochemistry of silicon [16].

Among the different ways of fabricating porous silicon, macroporous structures etched in an aqueous solution of hydrofluoric acid (HF) allow to design the sample parameters specifically. This method has developed to a well understood and viable tool for device and template fabrication. One significant advantage is the possibility to produce ordered pore arrays with defined diameters and lengths. The pore diameters can be adjusted between a few hundred nanometers and several micrometers. Remarkably is the potential to etch pores of a few hundred micrometers in depth. Thus aspect ratios of 500:1 and even more can be obtained without losing the ordering and the defined shape of the pores. The underlying mechanisms of the macropore formation in silicon will be discussed in more detail in the following.
13.2 Etching of Macroporous Silicon

13.2.1 Fundamentals

The basic ingredients for the fabrication of macroporous silicon can be defined as follows: Most obviously silicon is needed. For reasons that will be discussed later on, n-type doped silicon with an adapted resistivity is preferred. The wafers must be grown in a float-zone process. This ensures a charge carrier life time sufficiently long to realize diffusion lengths in the order of the wafer thickness. In addition, this raw material should receive a lithographically defined and etched prepatterning. Moreover, a highly doped backside contact is needed. Low concentrated HF with some surfactant added is used in the chemical process. Furthermore, an anodization setup is needed that provides control over voltage and backside illumination of the substrate.

13.2.1.1 Space Charge Region

Starting with the bulk material, structures are designed by dissolving part of the silicon – a typical top-down approach. In Fig. 13.1a a sketch of an anodization setup is shown. The silicon wafer is clamped between two parts of a PVC cell (inert to low concentrated HF). One side (hereinafter called front side) of the wafer is exposed to the HF. Such an intersection between a moderately doped semiconductor and an ionic liquid resembles a behavior similar to a Schottky contact. The electrochemical potential between both materials will adjust by forming a Helmholtz double layer. In the electrolyte, the charge carriers are mobile and can therefore screen the electric field within a few nanometers. In the semiconductor, free charge carriers can only be generated from the fixed donor-atoms. The density of these dopants is much lower.

Fig. 13.1  (a) Sketch of an electrochemical etching setup for the growth of macroporous silicon. (b) An enlarged view of the situation at the bottom of the pores: The SCR extends to the dotted line in the silicon, so this region is depleted and the minority charge carriers are focused to the pore tips
than the charge carrier density in the electrolyte. Consequently, the electric field evolves inside the silicon and forms a space charge region (SCR) (Fig. 13.1b). For the case of a planar interface, the width of this region $W_{SCR}$ can be estimated to

$$W_{SCR} = \sqrt{\frac{2\varepsilon \varepsilon_0 U}{eN_D}}$$

(13.1)

where $\varepsilon$ is the dielectric constant of silicon, $\varepsilon_0$ the permittivity of the free space, $e$ the elementary charge and $N_D$ the density of dopants. The voltage $U$ is the difference between the built-in potential of the silicon-HF contact and the external applied voltage. There is no reference electrode in this setup because the voltage drop over the SCR is significantly larger than the electrochemical potential. Furthermore, the chemical reaction is limited by the charge carriers generated due to the backside illumination.

Although Eq. (13.1) is only valid for a one-dimensional geometry, it is a good approximation for the width of the SCR for pores within the micrometer range. For example, a moderate doping density of $10^{15}$ cm$^{-3}$ and a voltage of 2 V would result in a width of the SCR of 1.6 $\mu$m.

13.2.1.2 Electrochemistry

In Fig. 13.2 the current-voltage profile of an n-type silicon-electrolyte junction is depicted. The forward-biased regime (negative potential) is characterized by a charge carrier flow of majority charge carriers (electrons) from the silicon to the electrolyte. This case is of minor interest because it only leads to the reduction of H$^+$-ions and hence hydrogen is produced in the electrolyte.

In the anodic regime where the voltage is reversed, two different processes can be distinguished. The border between these two regions is defined by the critical current

![Fig. 13.2](image-url)  
**Fig. 13.2** Schematics of the I–V curve of an illuminated reverse-biased Si-HF contact. The critical current density $J_{PS}$ marks the transition from divalent to tetravalent dissolution. The limitation of the overall current density to values below $J_{PS}$ by illumination from the backside adjusts the diameter of the pores.
density $J_{PS}$. It was found experimentally that $J_{PS}$ is dependent on HF concentration and temperature [17]. For current densities below $J_{PS}$ divalent dissolution of silicon takes place:

$$\text{Si} + 4\text{HF}_2^- + \text{h}^+ \rightarrow \text{SiF}_6^{2-} + 2\text{HF} + \text{H}_2 + \text{e}^- \quad (13.2)$$

Thereby, two charges per dissolved silicon atom can be measured in the electric circuit: One defect electron ($\text{h}^+$), moving from the silicon to the electrolyte and one electron ($\text{e}^-$), moving in the opposite direction through the interface. Current densities exceeding the critical value $J_{PS}$ will involve four minority charge carriers. A tetravalent dissolution occurs:

$$\text{Si} + 2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{SiO}_2 + 4\text{H}^+ \quad (13.3)$$

The formed silicon dioxide is instantaneously removed by the HF from the electrolyte. Both, the divalent and the tetravalent reaction lead to a dissolution of silicon. But only the first reaction (Eq. 13.2) etches pores into silicon because the divalent dissolution shows a strong dependence on the crystal orientation.

The model presented here is sufficient to describe the etching process and the obtained results. Nevertheless, this continuum-like theory is based on macroscopical findings. A detailed description on an intrinsic time and length scale is given by the current-burst model. It can be found for instance in the review by Föll et al. [14].

### 13.2.1.3 Etching Speed

HF concentration and temperature are not only important for the magnitude of $J_{PS}$. They also determine the etching speed of the whole process. Increasing both quantities enhances the etching speed. However, it has turned out that moderate values will give the best results. For example, an etching speed of nearly 1 $\mu$m/min is obtained for an acid concentration of 5% and an electrolyte temperature of 10°C.

### 13.2.1.4 Porosity

As mentioned before, n-type doped silicon is used for this process. Therefore, the defect electrons which are needed in the dissolution process (Eqs. 2 and 3) are the minority charge carriers. Generated by, for example, backside illumination with an LED-array, the minority charge carriers are obtained from electron-hole pairs. Due to the applied voltage, the holes will diffuse towards the front side and take part in the dissolution of silicon.

For sufficiently high current densities the dissolution reaction is limited by the chemistry. This situation is represented by the curve in Fig. 13.2. Lower
currents can be adjusted by a decreased backside illumination intensity. Experiments show that the etching speed is unaffected by an altered current density. With less charge carriers available, however, the etched area decreases and therefore also the porosity p of the sample. This correlation is summarized in the following equation:

\[ p = \frac{J}{J_{PS}} \]  

(13.4)

This means that the porosity p of a sample can be adjusted by the current density J. It is controlled by the backside illumination intensity independently from the voltage.

### 13.2.1.5 Pore Wall Passivation

The width of the SCR is a critical factor in the etching process. It prevents the pore walls from being post-etched. In the SCR there are no free charge carriers available. The silicon is depleted and therefore no charge transfer through the silicon-electrolyte interface is possible. As can be seen in Eq. (13.1) the width \( W_{SCR} \) can be adjusted by the voltage \( U \) and the doping density \( N_D \). Controlling \( W_{SCR} \) by the voltage is limited to small changes only: A decreased voltage will diminish the focusing effect of the charge carriers towards the pore tips. In contrast, an increased voltage leads to a higher amount of dark currents that cannot be controlled. Consequently, the preferred way is to tune the \( W_{SCR} \) by the doping density of the material.

### 13.2.1.6 Lithography

In contrast to the anodization of metals (e.g. aluminum, titanium) the growth of macropores in silicon is not a self-ordering process. The pores would not form a periodic arrangement naturally. The pore position, however, can be predefined by lithography and subsequently etching in potassium hydroxide (KOH). The obtained etch pits then work as nucleation sites for the pore growth (Fig. 13.3a). The advantage of this process is that one is not only restricted to a hexagonal pore arrangement. Rather, the prepatternning can be varied in the pore arrangement and pore size, having a specific impact on several applications as shown below.

Although the etching process is not a self-ordering process, it is a self-organizing one. For a given doping density, applied voltage and backside illumination an average porosity and pore diameter will arise. Therefore, the lithography has to fit with the intrinsic material parameters. The passivation of the pore walls and thus the prevention of the pore walls from being post-etched is a consequence of the SCR. For a stabilized pore growth the remaining silicon between neighboring pores should be completely depleted from charge carriers. From this requirement a rule of thumb can be derived for the lattice constant of the lithography: The interpore distance \( a \) has to be chosen twice as large as the width \( W_{SCR} \). It implies, that higher doped material is preferentially used for smaller interpore distances and vice versa.
13.2.2 Etching of Straight Tubular Structures

In the previous section the basic model of macroporous pore etching in n-type silicon was presented. The most important points should be summarized once again:

- for ordered pore composition, a prepatterning with a certain mask design is necessary
- the SCR is responsible for pore wall passivation
- the etching speed is dependent only on acid concentration and temperature
- the porosity and therefore the pore diameter is controlled by the backside illumination intensity

With these four points at hand and in mind one can understand the formation of macropores: A given sample with a defined mask is etched at a speed determined by temperature and acid concentration with an interpore distance fixed by the mask and a pore diameter given by the intensity of the backside illumination.

13.2.2.1 Stability

Concerning the stability of the etching process several points are relevant. Firstly, the etching speed is affected by the electrolyte temperature. To avoid inhomogeneities during the etching the temperature has to be kept constant within 0.1 K. Another important point is the fact that during the pore etching HF-molecules are consumed and hydrogen is produced. To avoid hydrogen bubbles to stick at the surface the electrolyte can be stirred or pumped. In addition, some surfactant should be added.

The consumption of HF-molecules can be neglected as long as the volume of the electrolyte is large compared to the dissolved volume of silicon. However, things are different at the micrometer scale inside the pores. While a pore is growing, the
exchange of reactants with the HF-basin at the front side of the sample becomes more and more affected by diffusion processes. A concentration gradient establishes between the pore bottom and the opening of the pore at the sample surface. Consequently, with a lower concentration the etching speed slows down and also the critical current density \( J_{PS} \) diminishes. According to Eq. (13.4), a decreasing \( J_{PS} \) results in an increasing porosity \( p \) if the illumination intensity and thus the current density \( J \) is kept constant. The pores grow larger in diameter and finally – for \( J_{PS} < J \) – electropolishing sets in. To avoid this situation one has to establish a correction parameter for the illumination intensity in dependence on the pore depth. In that way, a uniform pore pattern with aspect ratios of several hundreds to one can be obtained.

After defining the starting conditions with a pattern of pore nucleation sites, the etching process itself is self-stabilizing. The porosity is controlled by the current density \( J \) over the entire etched surface. Thus there is no direct control mechanism for each individual pore. The self-stabilizing effect is based on the fact, that the HF concentration determines the growth velocity. Let us assume a situation in which one pore is somewhat ahead of the surrounding ones. This pore will then collect more charge carriers because of its enlarged SCR. However, the excess of consumed charge carriers will also decrease the concentration of the HF in this pore. As a consequence, the growth velocity is reduced and the offset to neighboring pores is compensated. Analogous argument holds for pores staying behind the surrounding ones. Because of this feedback interaction the pore depth is the same for all pores (Fig. 13.3b).

13.2.2.2 Surface Roughness

The adjustment of the effective current density controlled by the backside illumination is done over the whole etched area. However, the local current density at the tip of the pore is always \( J_{PS} \). Consequently, the bottom of the pore is electropolished and a very smooth surface is obtained (Fig. 13.4). In contrast, the pore walls exhibit a layer of microporous silicon with a certain roughness. The reason for this layer can be found in a kind of post etching process. While at the outermost pore tip electropolishing occurs the current drops gradually along the pore wall and therefore the already etched pore walls are being post-etched. Both, the divalent and the tetravalent dissolution of silicon as shown in Eqs. (13.2) and (13.3) take place simultaneously. This is experimentally confirmed by the fact that the number of charge carriers required for the dissolution of one silicon atom is around 2.7. Additionally, there is always a certain amount of dark currents, e.g. charge carriers generated by tunneling processes. Therefore, the thickness as well as the roughness of this microporous layer depends on the applied voltage as well as on the mixture of the electrolyte.

13.2.2.3 Limits

Naturally, the question arises what are the limits of this process? It appears in Eq. (13.1) that any width \( W_{SCR} \) can be obtained just by the proper doping of the
material. In lowly doped material, large interpore distances and pore diameters can be realized, e.g. etching of pore diameters up to 100 μm were reported [19]. For small interpore distances, highly doped substrates are required. The pore formation process then is limited by electrical breakdown, because the critical voltage at which charge carriers are generated by electrical breakdown approaches only a few volt. It has to be considered that the local electric field strength at the pore bottom is increased due to the curvature of the pore tip. In this case the field strength is significantly higher than that for a planar interface. This effect is most pronounced in the small interpore distance region and limits the lowest lattice constant which can be realized to a value of about 500 nm.

The same argumentation is true for the pore diameters. With a fixed doping density and a given lattice constant pores with diameters close to the interpore distance are possible (Fig. 13.5a). The limit for diameters that are small compared to the interpore distance is determined by the critical local breakdown voltage. If the pores are too small in diameter the resulting small radius of curvature would locally boost the electrical field strength and unintentional charge carrier generation can no longer be prevented. Furthermore, charge carriers can bypass the region of the pore tip and post-etch the pore walls. Therefore, small pores with diameters of only a few hundred nanometers or even less can be grown, but the pore walls show a ragged and non-uniform surface (Fig. 13.5b). Mesoporous pore growth resulting in sponge-like structures occurs and the continuum model discussed so far is not valid any longer.

13.2.3 Pores with Modulated Diameter

So far, the formation of straight pores with a constant diameter was demonstrated. With regard to Eq. (13.4) we learned that the porosity of a sample can be tuned
by the current density $J$. Moreover, we used this dependence to compensate for the concentration loss of the acid due to diffusion effects in the pores.

With rethinking this dependence, we can find a way to alter the pore shape while manufacturing. In contrast to the slow and steady adjustment necessary for diffusion compensation, the current density is now strongly modulated on a timescale of seconds to minutes. In combination with a periodic variation of the voltage, a pore shape with sharp kinks can be obtained. With this rather fast adjustment of the current as well as the voltage, the formation of diameter-modulated pores does no longer occur in the steady-state region of stable pore growth. Nevertheless, highly ordered three-dimensionally modulated structures can be obtained with this method. The mechanisms responsible for the pore growth will be presented in a detailed form in the following sections.

### 13.2.3.1 Current-Only Modulation

In a first approach a periodically modulated current profile is applied to the backside illumination LED array. In proportion to that, the minority charge carrier density is also modulated and therefore the amount of defect electrons at the pore tip changes. In Fig. 13.6a an applied sawtooth-like current profile is shown while the voltage is kept constant at 1.8 V. The obtained pore shape belonging to this profile is shown in Fig. 13.6b. The diameter of the pore changes in a sinusoidal form between 1 and 1.4 $\mu$m. The shape of the pores did not follow directly the applied current profile and the shape of the pores is very smooth without sharp spikes. 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. However, since the pore cannot adjust its diameter to a certain value instantaneously, it has to increase. With these additional charges the
focusing effect of the SCR is lowered and therefore the passivation of the pore walls is diminished [20]. 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.

13.2.3.2 Voltage-Assisted Current Modulation

To overcome the impact of the modified charge carrier density, the SCR itself has to be adjusted as well. According to Eq. (13.1) the width of the SCR $W_{SCR}$ – and therefore its capability of focusing incoming charges – is dependent on the voltage. A higher voltage will enlarge the width of the SCR and vice versa. However, an increased voltage brings the electrical condition at the pore tip closer to the limit of breakdown. This effect – dependent on the doping level of the silicon and the pore geometry – destabilizes the pore growth and is therefore not a general solution to this problem. Only a combination of both, stable and unstable etching steps is capable of producing uniform pores with a sharp modulation. A detailed description of strongly modulated pore etching is given in the following.

In Fig. 13.7 a three-dimensionally modulated structure with sharp kinks and a symmetric shape is shown. The square lattice has a lattice constant of $a = 1.5 \, \mu\text{m}$ and the same modulation length. As an example we will observe the growth of one single modulation of this structure. The current-voltage profile that was applied while etching the structure is shown in Fig. 13.8b: The black curve is the etching current density, the blue one the applied voltage for one period. To visualize the progress of the pore formation the pore growth was stopped at seven different points of the modulation. For every point the sample cross section was looked at in an SEM (Fig. 13.8a). The obtained pore shape was redrawn and is schematically reproduced in Fig. 13.8c.

In the beginning (point 1) a new pore with a small diameter at the bottom should be grown. The mechanism used for this purpose is quite different from
the macropore etching described above. As can be seen in Fig. 13.8b the voltage is increased by a large amount that locally exceeds the critical breakdown value. Additional charge carriers in the vicinity of the pore bottom are generated by tunneling. Combining both, the charge carriers generated by illumination and the charge carriers generated by tunneling due to the locally increased electric field strength, a nanometer scaled pore in the [100] – direction (point 2) is obtained. This process of pore generation by breakdown voltage is stable only for some 10 nm. After that, the voltage has to be reduced again. Otherwise the pores would start to branch or die and the ordering would be lost. Simultaneously, the current density is increased (points 3 up to 7). As expected the pore grows larger in diameter.

In Fig. 13.8c the contour of the pore is redrawn for every point. It can be seen that the etching takes place not only at the outer region of the pore tip. Also regions already etched get widened in their diameter. Furthermore, the sharp kink that marks the beginning of a new pore is propagating slightly with increasing pore depth. This can be seen best comparing the shapes of point 2 and point 7 in Fig. 13.8c. While for the last steps (points 5–7) the position of this kink remains stable, it has changed significantly during the formation and etching of the small pore (points 2–4). During the formation of the small pore more charge carriers can propagate between neighboring pores. Despite the increased width of the SCR not all of them are directed to the tip of the evolving pore and therefore they hit the surface at regions beyond the etch front. As a result, the already etched parts are widened and the position of the kink moves.

The current density has reached its maximum value at point 7. The voltage was raised again while approaching the maximum current density. This can help to protect the side walls from being etched too much because the majority of the charge carriers is focused to the pore tip. After this final point the current density is switched to zero for a short time. During this stage remaining charge carriers can be consumed. In addition, time is given for the diffusion of reactants and the relaxation of the electrolyte to normal concentration.

In contrast to the sinusoidally shaped pores (Fig. 13.6), strongly modulated pores with sharp kinks require a modulation of the current density and an adaptation of the
Fig. 13.8 (a) SEM pictures of the evolution of one etched pore at seven different points of the modulation profile. It starts with a tiny pore that is widened afterwards. (b) The current-voltage profile for one modulation, the black curve denotes the current density, the blue curve the voltage. (c) Visualized pore shape acquired from the pictures in (a) [20]

SCR via the applied voltage. Thereby, the steady-state regime is left and even unstable conditions are used for the pore formation. A detailed understanding of these processes nevertheless allows the fabrication of highly ordered diameter-modulated pore structures [21].
13.2.4 Nonuniform Pore Growth

The structures presented so far were equally sized in interpore distance and pore diameter. In the following, the controlled introduction of a nonuniformity should emphasize the complexity but also the versatility of the macroporous silicon etching process.

The prestructured mask of the sample under consideration is shown in Fig. 13.9a: A square lattice with a lattice constant of 6 μm and a base consisting of two different sizes of etch pits. The larger etch pit has a side length of 3 μm while for the smaller one two differently sized etch pits are examined: 0.56 and 0.76 μm, respectively. The depth of the etch pits differs because of the anisotropic etching process in KOH during the prepatterning. The pore with the larger diameter is 2.1 μm deep and has therefore an offset compared to the smaller pore of 1.7 and 1.6 μm, respectively.

The etching behavior of this mask type was systematically studied, varying the size of the small etch pit, the applied voltage, and the doping density. It was shown

![Figure 13.9](image)

Fig. 13.9 (a) Bird’s eye view of a square lattice with an alternating sequence of two differently sized pores (3 and 0.56 μm, respectively) and an offset between larger and smaller etch pits. (b) Stable pore growth could be observed for at least 100 μm resulting in pores with different diameters and lengths. (c) Measured offset depending on the pore depth, the applied voltage, and the initial pit size of the small pore. (d) SEM image of a modulated macroporous silicon sample with two-pore lattice. The maxima in diameter for the thick pore occur at a different depth than that for the thin pore [22].
that a stable pore growth of at least 100 μm in depth is possible [22]. In Fig. 13.9b a more detailed view is given for the bottom part of a sample with a small etch pit of 0.76 μm side length: There are thicker as well as thinner pores and there is an offset in the length between them. Interestingly, the ratio of the pore diameters equals the side length ratio of the etch pits. Roughly speaking, the large etch pits start with a larger diameter and thus collect more charge carriers than the small ones. Therefore, the diameter ratio of the small and large pores can be adjusted by the side length of the etch pits.

In Fig. 13.9c the evolution of the offset between the two types of pores is shown for different parameters. For an applied voltage of 3.5 V the offset strongly diminishes during the first ten micrometers and then steadily decreases at a rate of 0.23 μm per 100 μm. The difference between the two curves for 3.5 V and different depths of the etch pits (0.56 and 0.76 μm) is equal to the difference in the depth of the etch pits. For a voltage of 2.5 V and a size of 0.76 μm for the small pits it is worth noting that finally a region is reached in which the offset remains nearly constant at 0.7 μm (black curve in Fig. 13.9c).

The material used had a resistivity of 1 Ωcm. Comparable experiments were performed with lower doped material of 5 Ωcm resistivity. For the latter one no growth of the small pores could be observed. Only the pores with the large diameter grew. From this result it can be concluded that in the case of the lower doped material no charge carriers were transported to the small pores. Because the SCR extends broader into the lowly doped material, the small pores are shielded from incoming charge carriers, i.e. they cannot grow. In the higher doped material the form of the SCR is more closely adapted to the pore shape. Charge carriers are focused to the large pores as well as to the small ones.

It was also possible to modulate the diameter during the etching process. Applying a strongly modulated current-voltage profile similar to the one discussed in detail in the preceding section leads to a diameter modulation as shown in Fig. 13.9d. The offset is visible in the different positions of the maxima in diameter between small and large pores.

To summarize this section it was shown that not only straight pores with a constant diameter can be grown over large depths. Also pores modulated in diameter can be obtained when the porosity is altered in situ. Generally, smoothly modulated pores are obtained. In extension of this process it was shown that an additional adjustment of theSCR via the applied voltage can lead to pores with a strong modulation and sharp kinks. In the application section, further pore shapes will be presented and their applications will be discussed.

### 13.3 Post Treatment

The range of applications can be significantly expanded by proper post treatment of the etched samples. On one hand the pore surface can be modified to obtain specific surface properties. On the other hand post etching steps can be applied in order to alter the structure itself, i.e. to modify the volume or shape of the macropores.
The treatment of the surface is a very complex topic that is strongly dependent on the desired application. After taking the samples out of the electrolyte and rinsing them in clean water their surface is hydrogen-terminated. In ambient atmosphere this surface coverage is not stable and after some hours a silicon dioxide layer forms. The thickness of this layer is about 3 nm and remains stable. Due to the water in the air the dangling bonds at the surface are saturated with hydroxyl molecules.

When macroporous silicon is used as a template material (see Chapter 5 by Steinhart), in catalysis, chemisorption or in microfluidics, its surface has to be modified with precursors to remove the hydroxyl groups and alter the surface functionality. To give an example, the wettability of the pore walls can be tuned: The hydrogen-terminated silicon surface that is present directly after the etching process is hydrophobic. In contrast, a pure SiO₂ surface and also a surface terminated with Si–OH (silanol) groups is hydrophilic.

### 13.3.1 Isotropic Form Treatment

Beyond the modification of the surface conditions the ease of forming an oxide layer is one of the most valuable properties of silicon. Silicon dioxide, also known as a principal component of glass, is nontoxic and biocompatible. Therefore, it is well suited for interactions with organic molecules. Beside the native oxide on the surface, an oxide layer can also be grown thermally, either in a wet or dry atmosphere. Thermal oxidation of silicon is typically performed at temperatures between 800 and 1,200°C. In a dry oxidation process the environment contains only oxygen. The grown films are very uniform and denser than films grown under wet conditions (i.e. in the presence of hydrogen). The growth rate of a dry oxide, however, is much slower than that for wet oxidation.

About silicon and its oxide numerous publications can be found. In here, only a special feature related to the pore shape will be discussed. The growth rates given in literature are mostly obtained for planar surfaces. The oxidation of pores on the other hand is – dependent on the diameter of the pores – retarded compared to flat interface conditions. The reason is the strain induced during the growth of the oxide layer. The volume of silicon dioxide is 2.25 times larger than that of the original silicon. Inside a pore the grown silicon dioxide layer cannot relax in the same way as on a planar surface. This additional induced strain significantly lowers the diffusion of oxygen through the silicon dioxide layer towards the silicon interface where the oxide growth takes place. Hence, also the growth rate is reduced and the oxidation process – especially for thick silicon dioxide layers of several tens to hundred nanometers – is retarded.

The counterpart of the oxidation – the removal of the oxide layer – is performed in HF-containing acids such as aqueous HF or NH₄F. As shown in Fig. 13.4 the pore walls appear to be rough after the etching. This surface roughness can be decreased by at least one order of magnitude when the macroporous silicon is shortly oxidized followed by a dip in an HF-containing acid to remove the oxide layer.
During the oxidation of silicon not only the surface is affected. With longer oxidation times the amount of silicon that is oxidized increases and the oxide layer grows deeper into the entire structure. Despite the retarded oxidation of macroporous silicon due to the curved surface of the pores it is possible to fully oxidize the silicon [23]. This can be interesting for applications, e.g. in life sciences: While silicon is only transparent for wavelengths larger than 1.1 \( \mu \text{m} \), silicon dioxide is also transparent in the visible spectrum of light.

Beside these two extrema, the surface modification and the complete oxidation of the structure, a partial oxidation can be used to tune the pore diameter after the etching or even to fit a special design as shown in the application section. The dry oxidation in a controlled environment, e.g. in a tube furnace with stabilized heating zones and mass flow controller, gives a very reproducible and homogeneous oxide thickness. In combination with a subsequent etching step in HF or NH\(_4\)F, the structure is widened isotropically. The advantage of this process compared to an isotropic widening in, e.g., a mixture of HF/HNO\(_3\) is the precise thickness control: The amount of silicon removed by this procedure is determined by the thickness of the grown oxide. This allows for tuning of the pore diameter after the etching.

Though this process seems to be straightforward, some restrictions have to be kept in mind. For thin oxide layers (short oxidation times) the oxide growth speed is very high. Hence, statistical fluctuations during the growth can have an undesired effect and the uniform shape of the structure could suffer during this procedure. In the case of thick oxide layers the dominating factor is the induced stress. Therefore, the possibility of damaging the structure has to be taken into account. An oxide layer thickness of 50–100 nm is an optimum value avoiding both, inhomogeneity and cracking. If thicker layers have to be removed a splitting of this procedure into several sequential oxidation and oxide removal steps is recommended.

### 13.3.2 Anisotropic Form Treatment

Another possibility to alter the pore shape after the etching is the treatment in an alkaline solution such as potassium hydroxide (KOH). The \{100\} – and the \{110\} – planes are preferentially etched and the etch rate is one to two orders of magnitude larger than that for the \{111\} – planes [24]. Treating a three-dimensional macroporous silicon structure with this process can result in a variety of different shapes (Fig. 13.10).

Furthermore, it can be useful to have a porous structure with both ends of the pores opened. This means that the remaining silicon from the backside up to the pore bottoms has to be removed. Therefore, a further property of KOH is considered: The etch ratio between silicon and silicon oxide can reach a factor of several thousands. Based on this property the porous structure is first oxidized (a few 10 nm) and afterwards the backside of the silicon is etched in KOH. When the pore bottoms are reached, the silicon oxide protects the porous structure from the KOH for a couple of minutes, giving enough time to stop the process. Subsequently, the oxide is etched away in an HF-containing solution and a porous membrane is obtained (Fig. 13.11).
13.4 Applications

The versatile and complex etching process of macroporous silicon leads to a variety of different pore shapes and surface conditions. This fact is also reflected in numerous applications. In the Chapter 5 by Steinhart several methods are presented in which macroporous silicon is used as a template material. For that purpose the etched samples get a surface treatment well suited for the subsequent filling of the pores. After removal of the silicon an inverted copy of the macroporous silicon sample is obtained. A specific application of this technique is proposed in [26], where diameter-modulated gold microwires are fabricated and their use as microbarcodes is suggested. The utilization as template material is by far not the only application of macroporous silicon. A selection of applications based on macroporous silicon will be presented in the following sections.
13.4.1 Photonic Crystals

A photonic crystal (PC) is a periodic structure with an alternating sequence of materials with different permittivities and a periodicity in the order of the wavelength of the electromagnetic wave. Similar to Bragg-like x-ray scattering at atomic crystal lattices, waves of larger wavelength are scattered at PCs [27, 28]. Macroporous silicon with feature sizes on a micrometer scale and its highly ordered arrangement of pores is an ideal candidate for such applications. A precisely designed PC is capable of guiding light in a specified way or to dramatically reduce the speed of light in the medium. Beyond that, a PC can suppress electromagnetic waves from propagation in a certain energy range. This effect is associated with a photonic band gap and was one of the driving forces in the design of PCs.

Typically, two-dimensional (2D) structures are used as waveguides, or frequency-, direction-, and polarization-filters. More effort is required when PCs are used to control the emission of light. Since a classic dipole emits in all three spatial dimensions also three-dimensionally (3D) modulated structures are required to control and manipulate such a behavior. Furthermore, only 3D PCs can confine light in all spatial dimensions using a complete photonic band gap. Thus the propagation of light is prohibited for certain frequencies in any direction of the PC.

13.4.1.1 Two-Dimensional Photonic Crystals

Although they cannot confine light in all three dimensions, 2D PCs can exhibit large band gaps in two dimensions. The most common types of 2D PCs have a quadratic or hexagonal arrangement of pores. It can be distinguished between two polarization directions of the electromagnetic wave with respect to the pore geometry: While in the transversal-electric (TE) mode the electric field oscillates...
perpendicular to the pores, in the transversal-magnetic (TM) mode the electric field is parallel to the pore axis.

In Fig. 13.12 for both of these lattice types the frequency range of the lowest photonic band gap in dependence on the pore radius is given. For the case of the square lattice (Fig. 13.12a) the photonic band gaps for the TE (blue area) and TM (red area) polarization occur in separated frequency and pore radii ranges. In a hexagonal lattice there is an overlap of both ranges resulting in a 2D complete photonic band gap.

For the experimental characterization of the photonic band gap a 2D PC was grown with a hexagonal lattice and a pore-to-pore distance of $a = 1.5 \, \mu\text{m}$. Thin bars of only a few crystal layers were prepared (Fig. 13.13) using a microstructuring technique [32].

![SEM pictures of 2D macroporous silicon with a hexagonal lattice and a lattice constant of $a = 1.5 \, \mu\text{m}$. The thinner part with its surface along the $\Gamma - M$ direction consists of 13 pore rows. The thicker part is made for reasons of stability. In addition, this structure also features a line defect as can be seen in (c) and (d) [30, 31]](image-url)
Fig. 13.14  (a) Measured (solid line) and calculated (dashed line) transmission spectra of a 2D hexagonal PC for TE (H-polarized) and TM (E-polarized) polarization and the interface cut along the $\Gamma - M$ and $\Gamma - K$ direction. The sample consists of 13 pore rows with a lattice constant of $a = 1.5 \, \mu m$ and a pore radius of $r = 0.46 \, a$. The photonic band gap is centered around $\lambda = 3.2 \, \mu m$ [30]. (b) Measured (points) and calculated (solid lines) transmissivity for samples with a thickness of 1 (■), 2 (●), 3 (▲), and 4 (▼) crystal layers [33]. (c) SEM picture of a single pore row as used for the measurement shown in (b)
The transmission was measured in the vicinity of the photonic band gap for a crystal with its surface along the $\Gamma - M$ and $\Gamma - K$ direction for both polarization modes (Fig. 13.14a). The loss in transmission intensity becomes evident for at least three orders of magnitude around the photonic band gap (centered at $\lambda = 3.2 \mu m$). The comparison of the measured curves with the theoretical calculated ones reveals a very good agreement between theory and experiment.

The photonic band gap is a volume property of a PC. This can be verified by varying the number of crystal rows [33]. Similar to the structures in Fig. 13.13 PCs with one up to four crystal rows were prepared. The transmission measurement of these structures in the mid-infrared revealed clearly a dependence on the thickness and thus on the number of crystal rows (Fig. 13.14b). In fact, an exponential attenuation of 10 dB per crystal layer within the photonic band gap ($3.1 \mu m < \lambda < 5.5 \mu m$) could be observed which is in good agreement with theoretical calculations.

13.4.1.2 Defects in Macroporous Silicon

In extension of the etching process of 2D pore structures the periodicity of the lattice can be perturbed. For instance, single pores can be prevented from being etched or their position or diameter is changed compared to the surrounding ones. This can be realized with a lithographic mask designed accordingly. A missing pore can be thought of as a defect in the etching process. No charge carriers are consumed during the etching at the position of this defect. Since in this self-stabilizing etching process the carrier density is homogeneously dispersed, the pores in the vicinity of this defect have to consume this additional number of charge carriers. As a result, the surrounding pores grow larger in diameter compared to pores further away from this defect. This effect is less developed for small pore diameters than for larger ones since the charge carrier density rises with the square of the pore diameter. Therefore, the pores are preferentially etched with a smaller diameter and afterwards widened isotropically as described in the post treatment section.

As mentioned in the previous section, in a 2D PC a photonic band gap can exist. In the picture of the photonic band structure a defect (for instance a point defect as shown in Fig. 13.15a) breaks the symmetry of the lattice and therefore changes the

Fig. 13.15  SEM pictures of defect structures realized in a 2D PC with an $a = 1.5 \mu m$ hexagonal lattice. (a) A single missing pore. (b) A waveguide that can bend the light sharply around corners and even split one beam in two parts (c) [34, 35]
properties of the PC. With a properly designed defect in a PC it is even possible to generate states inside the photonic band gap. An electromagnetic wave package is localized at this location if it is in resonance with the eigenfrequency of such a defect state [36]. Because of the photonic band gap the wave package cannot escape through the surrounding pores since it is backscattered. Consequently, the light is stored at the location of the defect within the photonic band gap.

Combining several point defects to a line defect, such resonant modes can be guided through a PC. These so called waveguides are as narrow as the wavelength of the transmitted light or even less. Therefore, PC-based waveguides are much narrower than conventional structures used for this purpose based on internal reflections.

The defect structures shown in Fig. 13.15b, c consist of a combination of several missing pores giving a line defect. For example, light can be sharply bent around corners (Fig. 13.15b) or split into two separate beams (Fig. 13.15c). There are no radiation losses in an ideal 2D geometry because of the surrounding material and the band gap. Even in the presence of scattering the radiation losses into the third dimension are low and a high output quality can be reached.

### 13.4.1.3 Three-Dimensional Photonic Crystals

A 3D structure in simple cubic geometry with a complete photonic band gap was proposed by Leonard [37]. In the band structure (Fig. 13.16a) a region can be seen where no propagation of light is possible for any direction in the PC. The model

![Fig. 13.16](image) A 3D simple cubic PC in silicon ($\varepsilon = 11.7$) with a complete photonic band gap as suggested by Leonard [37]. (a) The photonic band structure reveals that there is no propagation possible in any direction for a range of frequencies, i.e. a photonic band gap (grey bar) exists. (b) The reciprocal lattice cell with the points of high symmetry. (c) A model structure of the simple cubic crystal with overlapping air spheres of radius $r = 0.605a$. 
A. Langner et al.

structure for this theoretical prediction is shown in Fig. 13.16c. It is a simple cubic lattice of silicon with inserted overlapping empty spheres. For the highest possible width of the complete photonic band gap the radius of the spheres is \( r = 0.605a \) (\( a \) is the lattice constant). Consequently, the spheres are overlapping each other and thus all pores are connected to each other.

This structure was realized experimentally within the framework of the macro-porous silicon material system. Starting with a square lattice of \( a = 1.5 \, \mu m \) lattice constant a strongly modulated structure was grown (Fig. 13.17a). Thereby, the modulation period equals the lattice constant. The pores are connected in the vertical direction due to the etching process – but not yet in the lateral direction. In order

![Fig. 13.17](image)

**Fig. 13.17** SEM images of a 3D macroporous silicon structure with a square lattice of \( a = 1.5 \, \mu m \) lattice constant. (a) Cross section of the strongly modulated grown structure with a modulation length of 1.5 \( \mu m \). (b) Symmetric pore shape after the homogeneous pore widening. (c, d) Bird’s eye view of this 3D PC structure [21]
to realize the overlapping spheres, the procedure of homogeneous pore widening was applied as described in the post treatment section. All in all four iterations of growing an oxide layer (900°C, 2 h) and removing it in NH₄F (12.5%, 1 h) were carried out. A film of about 70 nm thickness was removed in every step (Fig. 13.17b). In the area of the large pore diameter the walls were opened and neighboring pores became connected to each other. Thus an ordered porous structure was fabricated capable of acting as a PC with a complete photonic band gap in 3D (Fig. 13.17c, d) [21].

The material requirements for applications as PCs are high: The periodicity of the structure has to be on the order of the desired wavelength with a precision in the range of 1/20 of the wavelength. While a couple of preparation techniques are already known for the fabrication of 2D structures, manufacturing 3D structures is still a challenging task. PCs based on macroporous silicon offer this precision. Moreover, they can be fabricated in a large scale process.

13.4.2 Microfluidics

Macroporous silicon cannot only be applied to alter the propagation of light. It can also be used to control the flow of liquids. The material parameters of interest are different from that required for photonic applications. The formation of channels and their shape are the important points to consider. In microfluidics, materials are required with a well defined surface and shape. Macroporous silicon is an excellent candidate for this aim as demonstrated in the following example of a ratchet device.

It was proposed based on theoretical work [38] that a ratchet-shaped pore profile can separate particles of different size – dispensed in a liquid – without a net transport of the liquid itself. An upper and a lower basin are separated by a membrane with asymmetrically shaped pores (Fig. 13.18a). The liquid with the dispersed microparticles is periodically pumped between upper and lower basin with an average net liquid flow of zero.

For the experimental verification of this experiment a macroporous silicon sample with an asymmetric pore profile was grown and afterwards the remaining silicon was removed from the backside with KOH (cf. Fig. 13.11). The pore geometry can be seen in Fig. 13.18c, d: It is a triangular pattern with 6 μm pore-to-pore distance, 150 μm in depth, and the maximum (minimum) diameter of the modulation is 4.8 μm (2.5 μm). Particles of 0.32 μm diameter could be transported to the upper basin with such a membrane when a periodic pressure oscillation was applied.

The density of the spheres in the upper basin was measured via photoluminescence (PL). In Fig. 13.18b some experimental data are shown. The pressure oscillations were toggled on and off every 60 s to exclude long-term drifts. During this period the intensity in the upper basin – and therefore the concentration of particles – starts from a homogeneous particle distribution and increases during the pump-on times (curve U). The effect of the asymmetry of the pore shape can be seen when turning the membrane upside down. Now the intensity decreases (U_reversed). It can be
Fig. 13.18 (a) Schematics of the horizontally mounted and asymmetric diameter-modulated membrane separating two basins. (b) Measured photoluminescence (PL) intensity in the upper basin (U), for the reverse mounted membrane ($U_{\text{reversed}}$), and a cylindrical pore shape for comparison ($U_{\text{cylindrical}}$). (c) SEM picture of a cleaved macroporous silicon membrane used for the experiment. (d) Magnified version with a colloidal sphere of 1 $\mu$m in diameter inside the pore sticking to the pore wall [39]

seen in the curve $U_{\text{cylindrical}}$ that this effect is clearly related to the asymmetric shape of the membrane: The measurement was performed with a sample of cylindrical pore shape (diameter 2.4 $\mu$m) but no significant particle transport could be observed.

13.4.3 Materials Science

This last section will briefly highlight a few additional ideas realized with macroporous silicon. In Fig. 13.19a an area of silicon spikes can be seen. Since silicon is a very hard material it can be used as a micrometer sized structuring tool, e.g. as a stamp for imprint lithography. This structure was prepared using a 2D
macroporous silicon sample in which the pore diameter was strongly increased at the end. Thus neighboring pores got connected to each other and the porous silicon layer can be removed easily. The remaining pore bottom with the spikes has the same lattice geometry as the lithographically defined etch pits.

In Fig. 13.19b a bottom view of a macroporous silicon membrane is shown. The pores were grown in a normal way and afterwards oxidized. With the KOH etching used for the membrane preparation the bulk silicon from the backside was removed. On top of the sample a completely released silicon dioxide microtube can be seen. The bright shining domes are SiO$_2$ tubes with a closed bottom, partly released from the silicon (Fig. 13.19c). A suggested application as a window for electron beams in high vacuum chambers is given in [40].

Also the modulated pore structures can be used as a template. In Fig. 13.19d modulated titanium dioxide tubes are shown: The minimum diameter is 0.4 and
1.6 μm the maximum one. They were fabricated by atomic layer deposition of titanium dioxide in the pores of a modulated macroporous silicon sample. Afterwards, the silicon was selectively removed in KOH. Applications of these biocompatible titanium dioxide spheres may be found in life science, e.g. for drug delivery purposes.

13.5 Summary

A basic introduction to the fabrication as well as applied aspects of macroporous silicon were presented. The enormous adaptability of this material system is based on the fact, that all the common process techniques developed in the silicon industry can be applied. The basic features were presented in this chapter and should give the necessary informations whether a closer look to this material system is worthwhile for the reader. Nevertheless, the most difficult part is still open to the reader: No realization without imagination.

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References


