

Crystal Orientation Dependence and Anisotropic Properties of Macropore Formation of p- and n-Type Silicon

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The dependence of macropore morphology on the orientation of p- and n-type silicon samples was studied for various organic and aqueous electrolytes containing hydrofluoric acid. Scanning electron microscopy was used studying the morphology of the macropores. The results show that the macropore formation in p- and n-type silicon is a strongly anisotropic process. Depending on the substrate orientation $\langle 100 \rangle$ and $\langle 113 \rangle$ preferred growth directions could be observed. The microstructure of macropores was studied by analytical and high-resolution transmission electron microscopy. The surface of macropores in n- and p-type Si(001) shows {111} facets indicating that {111} planes are stabilized against further dissolution. Breakthrough pores show very specific anisotropic properties independent of the electrolyte. These pores consist of periodic arrangements of truncated octahedral voids with {111} walls strung up in $\langle 100 \rangle$ directions. The crystal orientation dependence of pore formation reflects specific properties of the pore formation mechanism and one of the important electrolyte parameters is the ability to form an anodic oxide. Macropores formed in more strongly oxidizing electrolytes tend to have smoother macropore walls. © 2001 The Electrochemical Society. [DOI: 10.1149/1.1369378] All rights reserved.

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In 1990 Lehmann and Föll discovered that very regular arrays of macropores with extremely large aspect ratios could be obtained in the n-Si/HF system.¹ They explained the formation of these pores on the base of a so-called space-charge region model, assuming that the current (photogenerated at the back side of the specimen) is focused on pore tips because of the bending of the space-charge region around the pore tip. The model has some merit for the formation of macropores in n-type Si, especially for the regular pore arrays as shown in Ref. 2. Based on this model and additional empirical results, it is possible, within limits,³ to produce pore structures as desired.⁴

In 1994 macropores on p-type silicon were found by Propst and Kohl by anodic etching in a HF-containing organic electrolyte (HF in water-free acetonitrile).⁵ The authors explained the macropore formation in a mostly chemical way; the silicon dissolution was assumed to be a strong function of the crystal planes. A subsequent model for macropore formation on p-type silicon assumed chemical passivation of the macropore walls via selective solvent molecules⁶ or employed special effects due to the high resistance of the electrolyte and the substrate in the experiments performed so far.⁷ Lehmann argued that the space-charge region model used for n-type Si, if coupled with general diffusion properties, could also explain macropore formation on p-type silicon.⁸ In the following years, many papers were published dealing with macropores on p-type Si (cf. Ref. 9 and 10) and their possible formation mechanism, but the dependence of pore morphologies on crystal orientation was neither studied very much nor well understood.¹¹

Another model relevant to macropore formation is the "fieldinduced breakthrough" model,¹² which assumes that at some pore tips the electrical field strength is sufficient to allow avalanche breakthrough which then generates the necessary carriers for further macropore growth. Combinations of the space-charge region model and the breakdown mechanisms were used to explain the transition from macro- to mesopore formation.¹³ Models referring to, *e.g.*, pore wall passivation,^{14,15} diffusion-limited random walk,¹⁶ or surface instabilities give general scales for the pore morphology under certain conditions.¹⁷⁻¹⁹

Lehmann already found that macropores tend to grow in $\langle 100 \rangle$ directions.⁴ With increasing etching voltage the $\langle 100 \rangle$ directions become more dominating for the side pores as well. Rönnebeck *et al.*¹¹ investigated the orientation dependence of macropore and break-

through pore formation on n-type silicon under back-side illumination. The main macropore growth direction, either $\langle 100 \rangle$ or $\langle 113 \rangle$, depends on the surface orientation, while breakthrough pores grow always in (100) directions independent of the surface orientation. Propst and Kohl found that the nucleation of the p-type macropores formed in hydrofluoric acetonitrile (MeCN) takes place at (111)faceted pyramid-shaped pits in a generally rough surface.³ A certain indirect orientation dependence for p-type was also found for macropores in p-type Si obtained in water-free MeCN, because no pores could be obtained on {111} -oriented surfaces in contrast to {100} surfaces. Ponomarev et al. etched p-type macropores on both surface orientations with different organic electrolytes.⁶ Christophersen et al. could produce macropores for the first time on 0.020- $0.060 \ \Omega \ \text{cm} \ \text{n-type} \ \text{silicon},^{20} \ \text{too}.$ The nucleation of the macropores takes place at (111)-faceted pyramid-shaped pits in a generally rough surface; the pores grow in the $\langle 100\rangle$ directions defined by the substrate ortientation, and the pore tips are strongly faceted on (111).

In the present paper we extend our previous investigations regarding the crystal orientation dependence of macropores on n-type silicon¹¹ to macropores obtainable with organic electrolytes in pand n-type Si. Besides results on the orientation dependence, new kinds of pore morphologies were obtained. In addition to the orientation dependence, a direct comparison of macropore formation in strongly and weakly oxidizing HF-containing electrolytes was made. Results on the influence of different organic electrolytes and of additives in the electrolyte on macropore morphology and orientation dependence are presented, too. Transmission electron microscopy (TEM) investigations provide additional information on the microscopic anisotropic nature of the macropore formation.

Experimental

Since p- or n-type-Si specimens with orientations other than {100} and {111} are hard to obtain, samples for experiments were produced by cutting slices from Si crystal heads and tails at predetermined orientations (p-type wafer: 10-20 Ω cm, n-type wafer: ~5 and 0.5 Ω cm). For n-type Si samples with substrate orientations near {100}, {10 1 1}, {411},{311}, {322}, and {111} were produced, while for p-type Si samples with {100}, {511}, {5 5 12}, and {111} orientations were made. The crystal orientations of these specimens were controlled by Laue diffraction patterns using a modified STOE precession camera. Furthermore, {100} and {111} oriented p- and n-type standard wafers (supplier: MEMC) with comparable doping levels were included in the experiments. After polishing the resulting slices with diamond paste of 3 µm grain size, specimens with

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Figure 1. (a) Typical *I-U* curve of an n-Si electrode in contact with aqueous HF. (b) Important features of the etching apparatus.

lateral dimensions of 2×2 cm were cut using a modified ID saw. In the present investigation no prestructured nuclei were used.

The specimens were cleaned by a HF dip. Fig. 1a shows the relevant features of the etching cell and a typical *I-U* characteristic (Fig. 1b) for n-type Si anodized in an aqueous HF-containing electrolyte.

The electrolyte consisted of 4-10 wt % HF, adding a tenside to the aqueous electrolytes to ensure wetting of the sample surface. The electrolyte was pumped through the cell. The temperature was kept constant by running it through a heat exchanger controlled by a thermostat.

All experimental parameters (current, voltage, and electrolyte temperature) were computer controlled, and the specimens were subjected to anodic etching under the following conditions.

1. p-Type silicon samples: Constant (galvanostatic) current density between 0.5 and 2 mA/cm², stabilized electrolyte temperature of 20°C without back-side illumination. The following organic electrolytes were used (which have already been described as an organic solvent for HF for p-type macropore formation^{6,9,10}): acetonitrile (MeCN), dimethylformamide (DMF), and dimethylsulfoxide (DMSO). In the case of MeCN, diethyleneglycol (DG) for supplying hydrogen has been added on occasion. For aqueous HF-containing electrolytes the etching conditions described in Ref. 8 were used.

2. n-Type silicon samples: Constant external bias (4 V) and constant current density of 4 mA/cm² achieved by PC-controlled backside illumination adjustment. The electrolyte temperature was stabilized at 20°C. Hydrofluoric DMF and aqueous solutions were applied for the n-type macropore formation.

All electrolytes were prepared from a 48% HF solution; therefore a certain amount of water (\sim 4 wt %) was always present even in the organic solutions.

The etching conditions of all measurements are summarized in Table I. The corresponding number of each etch condition is marked in the text with round brackets in the figure captions.

The valence of the etching process was measured via the mass loss (Δm) according to the formula

п

$$=\frac{ItA_{\rm r}}{eN_{\rm A}\Delta m}$$
[1]

with *I* the etching current, *t* the etching time, $A_r = 28.08 \text{ g/mol}$, and $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$.

The pore morphologies were investigated by scanning electron microscopy (SEM) using a Philips XL30 microscope. Cross section specimens were prepared using cleavage technique and polishing. The microstructure and the interfaces of the macropores were investigated in cross section and plain-view samples by TEM at 300 kV using a Philips CM30 transmission electron microscope. The electron-transparent specimens for TEM were prepared using ion milling at 2.5 kV.

Results

Macropores in p-type silicon.—The observations of n-type micropores³ show that the temporal evolution of macropore formation can be subdivided into three stages: (i) "homogeneous" etching with an etch rate in the range of 0.14 μ m min⁻¹, (*ii*) surface roughening ("redistribution phase of the macropores" ³), and (*iii*) formation of the macropores (stable macropore growth). This general behavior has also been observed in these experiments. In hydrofluoric DMF (with 4 wt % H_2O) and DMSO (with 4 wt % H_2O) we found etch rates of $\sim 0.1 \ \mu m \ min^{-1}$ for the "homogeneous" etch craters. The stable growth rates are $\sim 0.5 \ \mu m \ min^{-1}$ for DMF (with 4 wt % H_2O) (n = 2.2) and DMSO (with 4 wt % H_2O) (n = 2.4). Figure 2 shows a TEM image of p-type macropore tips etched in hydrofluoric DMF. The pore walls are very smooth and the diameter is constant over the pore depth. In contrast, using MeCN (with 4 wt % H₂O) we found no etch craters but a dense layer of mesoporous silicon (structure size about 10 nm, cf. the TEM image in Fig. 5).

Organic and aqueous electrolytes^{6,8,9} were used for p-type Si samples with orientations of {100}, {511}, {5 5 12}, and {111}. Generally the macropores grow preferentially in the $\langle 100 \rangle$ directions, only on {111} samples $\langle 100 \rangle$ and $\langle 113 \rangle$ oriented macropores were found-reminiscent of the results in n-type-Si¹¹. In contrast to n-type silicon in aqueous electrolytes, the switch over from $\langle 100 \rangle$ to $\langle 113 \rangle$ is not as well defined. The specific morphology and orientation dependence of the p-type macropores depends strongly on the choice of the electrolyte (Fig. 3, Fig. 4).

DMF (with 4 wt % H_2O) and DMSO (with 4 wt % H_2O) lead to very small and regular pores with constant diameters between 700 and 1000 nm (Fig. 4). In contrast to these pores the macropores in the HF-H₂O system are very wavy with strongly changing diameters. It is not easy to define their main growth direction. Macropores etched in hydrofluoric acetonitrile have larger pore diameters than in DMF (with 4 wt % H_2O) and DMSO (with 4 wt % H_2O) and the growth directions are not as well defined.

The nucleation layer as well as the filling in some macropores consists of mesoporous silicon as ascertained by TEM (Fig. 5). This mesoporous silicon has a preferential orientation along $\langle 100 \rangle$ near the macropore center; this orientation changes to almost normal incidence near the pore walls. High-resolution TEM images taken along the $\langle 110 \rangle$ zone axes prove the remaining silicon to be crystal-line, with diameters on the scale up to a few nanometers. The crys-

Sample number	Substrate orientation	Doping N: n-type silicon P: p-type silicon Substrate resistance (Ω cm)	Etch voltage (V) (for back-side illumination)	Etch current (mA/cm ²)	Electrolyte 4 or 10 wt % hydrofluoric acid
1	(100)	P 10-20		2	DMF (4) ^b
2	{511}	P 10-20		2	$DMF(4)^{b}$
3	{5 5 12}	P 10-20		2	$DMF(4)^{b}$
4	{111}	P 10-20		2	$DMF(4)^{b}$
5	{100}	P 10-20		2	$DMSO(4)^{b}$
6	{5 5 12}	P 10-20		2	DMSO $(4)^{b}$
7	{511}	P 10-20		2	DMSO $(4)^{b}$
8	{111}	P 10-20			DMSO $(4)^{b}$
9	{100}	P 10-20		2	MeCN $(4)^{b}$
10	{100}	P 10-20		0.5	Aqueous (10)
11	{100}	P 10-20		2	$MeCN+H_2O$ (4 wt %) ^c
12	{111}	P 10-20		2	$MeCN+H_2O$ (4 wt %) ^c
13	{100}	P 10-20		2	MeCN+DG (4 wt %) ^c
14	{111}	P 10-20		2	MeCN $(4)^{b}$
15	{111}	P 10-20		2	MeCN+DG (4 wt %) ^c
16	{100}	N 5	4	4	Aqueous (4)
17	{100}	N 5	4	4	$DMF(4)^{b}$
18	{10 1 1}	N 5	4	4	$DMF(4)^{b}$
19	{411}	N 5	4	4	DMF $(4)^{b}$
20	{311}	N 5	4	4	DMF $(4)^{b}$
21	{211}	N 5	4	4	DMF $(4)^{b}$
22	{322}	N 5	4	4	DMF $(4)^{b}$
23	{111}	N 5	4	4	DMF $(4)^{b}$
24	{100}	N 0.5	2	4	DMF $(4)^{b}$
25	{5 5 12}	P 10-20		0.5	Aqueous (10)
26	{322}	N 5	4	4	Aqueous (4)

^a Electrolyte temperature: 20°C. All n-type Si samples were etched potentiostatic under back-side illumination and all p-type Si samples galvanostatic. The j_{ps} peaks for the aqueous solutions after Ref. 4 are: 4 wt % HF, 38 mA/cm²; and 10 wt % HF, 150 mA/cm². For the organic solutions (with ~4 wt % water) we find a new characteristic peak in the iv curves.

 b With 4 wt % $H_{2}O.$

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^c With 4 wt % HF.

talline nature of the filling of the macropores could also be confirmed by the presence of distinct diffraction spots in selected areas (see Fig. 7 in Ref. 21).



Figure 2. A TEM micrograph of a macropore tip etched in hydrofluoric DMF (with 4 wt % H₂O). (sample 1) Very smooth pore walls are visible.

Influence of oxygen and hydrogen availability.--Acetonitrile is known as an organic solvent remaining inert,²¹ in contrast to DMSO²² and DMF. The role of the availability of oxygen and hydrogen for the electrochemical reactions was studied in the MeCN system by adding H₂O. Most prominent is the observation that pores in pure hydrofluoric MeCN (containing only the amount of water form the 48% HF solution for preparing the etch solutions) are filled with mesoporous silicon. The valence of the electrochemical reaction in hydrofluoric MeCN (with 4 wt % H₂O) is n = 4.5 Upon increasing the amount of water in the electrolyte to 8 wt % the pore filling disappears. The gravimetric measurements then yield n = 3. Instead of a porous nucleation layer, now an etch crater with the same depth as the mesoporous nucleation layer is formed. The macropores with MeCN (with 8 wt % H₂O) tend to grow more uniformly in comparison with the pores etched in HF-MeCN (with 4 wt % H₂O).

Adding 5 wt % DG to MeCN (with 4 wt % H_2O) does not change the pore morphology much: the pores remain filled and a (thinner) mesoporous nucleation layer is still present. However, the pores are much more regular than in the standard HF MeCN system (cf. Fig. 6) and the reaction valence drops strongly to n = 2.5.

The valence n has been measured in all experiments with p-Si, and the results are shown in Fig. 7. In increasing the concentration of water in MeCN a significant reduction of the valance is found (cf. Fig. 7b). For different electrolytes correspondingly strong changes in the valance occur (Fig. 7a). In contrast, the surface orientation of



Figure 3. The orientation dependence of macropores on p-type Si on {100}, {511}, {5 5 12}, and {111} oriented samples for two organic electrolytes. Samples (a) 5, (c) 6, (e) 7, and (g) 8 were etched in HF containing DMSO (with 4 wt % H₂O); Samples (b) 1, (d) 2, (f) 3, and (h) 4 were etched in HF containing DMF (with 4 wt % H₂O). Both electrolytes show the same orientation dependence; the $\langle 100 \rangle$ direction is the main growth direction. On (111) samples $\langle 113 \rangle$ and $\langle 100 \rangle$ growth directions exist.

the samples has almost no influence on the valence of the chemical reactions (cf. Fig. 7a).

Macropore surfaces.—TEM investigation of the macropore walls in cross-sectional specimens show that the pore surfaces or pore walls at some distance to the pore tips are faceted on a small scale on {111} planes for n-and p-type silicon (Fig. 5 and 8). The



Figure 4. Macropores in p-type silicon etched in different hydrofluoriccontaining electrolytes: (a) p-type Si DMF (with 4 wt % H_2O) (sample 1); (b) DMSO (with 4 wt % H_2O) (sample 5); (c) MeCN (with 4 wt % H_2O) (sample 9); (d) H_2O (sample 10).

dimensions of the facets are between 20 and 100 nm depending on the etch solution. For example, the facets etched with a DMF (with 4 wt % H₂O) solution measure about 100 nm, while approximately 40 nm facets result for macropores etched with MeCN (with 4 wt % H₂O) solution. However, near the macropore tips in n-and p-type Si the faceting is not observed.

Propst and Kohl found a {111} faceting of the surface during the nucleation of p-type macropores etched in hydrofluoric MeCN,⁵ while Christophersen *et al.* found a similar kind of pore nucleation for macropores on highly doped n-type silicon.²⁰ These are earlier indications that a {111} faceted surface plays an important role in the formation mechanism of macropores in p-and n-type silicon.

Orientation dependence of macropores obtained in n-type silicon with organic electrolytes.—In a second series of experiments n-type silicon was etched in organic electrolytes using back-side illumination. A typical example for a {100}-oriented n-type silicon is shown in Fig. 9. Under all conditions (including those where perfectly straight and unbranched macropores were obtained in p-type Si) the macropores formed were strong and showed "rough" pore walls, an effect otherwise only observed in aqueous electrolytes at much higher voltages. Figure 9 shows that the branches form symmetrically around the main pore in a regular fashion. Quite remarkable pore morphologies emerged from the n-type Si samples of {10 1 1}, {114}, {113}, {211}, {223}, and {111} orientations (Fig. 10). In all samples pores with these distinctly different features can be found.

1. Many "breakthrough" pores with diameters of approximately 250 nm (in Ref. 23 dubbed "dendritic pores") are found between the macropores.

2. While the $\langle 100 \rangle$ direction is the main growth direction, in some cases a preferential growth in $\langle 113 \rangle$ is also visible (cf. Fig. 10a and 10f).

3. The directions of the branches (and of some main pores), however, are not always easily identified; a naive interpretation of the SEM pictures can be misleading. In Fig. 10f, for example, the pores seem to grow in the $\langle 111 \rangle$ direction perpendicular to the surface, which would be in blatant contrast to the general observation that $\{111\}$ planes are the most stable ones. In higher magnifications (Fig. 11) the nature of the "disturbing" $\langle 111 \rangle$ branches can be identified as a new feature of pore etching not reported before.

Upon close inspection of the micrographs (bearing in mind that the cleavage surface is no longer necessarily a {110} surface), it can be seen that there is still a main pore growth in a $\langle 100 \rangle$ direction, or, on occasion, in a $\langle 113 \rangle$ direction. While these pores usually emit clearly defined side pores (in $\langle 110 \rangle$ or $\langle 113 \rangle$ directions), these branches are the starting points for new pores. They may alternatively grow two-dimensional cavities which branch out from a main pore and are bounded by {111} planes on one side, whereas more regular $\langle 100 \rangle$ pores emerge from the underside. Figure 12e gives a schematic comparison between these branches and regular side pores, and Fig. 11a-d show relevant micrographs.

Anisotropic properties of breakthrough pores.—In all experiments on n-type silicon under back-side illumination, breakthrough pores (defined in Ref. 3 and 4) were produced simultaneously with the heavily branched macropores. In contrast to the n-type macropores etched in organic electrolytes, they show a well-defined orientation dependence (see Fig. 13). The main direction is always $\langle 100 \rangle$ as in aqueous electrolytes, and it is independent of the substrate orientation. Growth of breakthrough pores etched in aqueous electrolytes along $\langle 100 \rangle$ has been reported by Osaka *et al.*;²³ however, no detailed analysis of the pore structure has been published.

Our investigation of the breakthrough pores (see Fig. 8 and 14, and Ref. 21) showed that the pores always consist of connected octahedral voids. The quasi-periodic arrangement of octahedral voids with {111} facets is shown schematically in Fig. 15. This general form of the breakthrough pores is independent of the choice of the electrolyte. In Fig. 16 breakthrough pores are shown which



Figure 5. TEM bright-field micrographs of macropores in p-type silicon etched in hydrofluoric MeCN (sample 9). The left side shows an overview. The pores are filled with silicon fibers. The inlay shows a macropore wall which is covered with {111} facets. The right side shows the mesoporous nucleation layer. The pores grow preferentially perpendicular to the surface in the $\langle 100 \rangle$ direction.

were etched in hydrofluoric DMF (with 4 wt % H_2O). Such breakthrough pores etched in organic electrolytes tend to show sharper structures compared to breakthrough pores etched in aqueous electrolytes as shown in Ref. 20. Obviously the {111} planes are the most stable planes against the electrochemical dissolution. Even in apparently straight $\langle 100 \rangle$ oriented pores, the pore walls are faceted in {111} if viewed at high magnification.

The high-resolution SEM micrographs in Fig. 13 confirm this finding for breakthrough pores in n-type silicon etched in hydrofluoric DMF (with 4 wt % H_2O) using back-side illumination. As mentioned previously, macropores (with branches) and breakthrough pores were etched simultaneously. The breakthrough pores grow strictly anisotropically in $\langle 100 \rangle$ directions, and $\{111\}$ planes always form the edges of the individual octahedral voids. This is remark-



Figure 6. The influence of oxidizing and protonizing additives to hydrofluoric MeCN electrolytes was studied: (a) MeCN (4 wt % H₂O) (100) (sample 9), n = 4, nucleation layer thickness 2 µm; (b) MeCN + DG (100) (sample 13), n = 2.5, nucleation layer thickness 1 µm, (c) MeCN + H₂O (100) (sample 11), n = 3, no nucleation layer; (d) MeCN (with 4 wt % H₂O) (111) (sample 14), n = 3.5; (e) MeCN + DG (111) (sample 15), n = 2.25; (f) MeCN + H₂O (111) (sample 12), n = 1.8.

able considering that n-type macropores etched in an organic electrolyte show a quite irregular orientation dependence in comparison to breakthrough pores.

Discussion

The results obtained show that the crystal orientation influences pore growth in Si in many ways, some rather surprising, and most



Figure 7. (a) The valence for all tested electrolytes is only a weak function of the surface orientation, but it depends strongly on the electrolyte. (b) The dependence on the choice of the electrolyte is most pronounced for the H_2O -MeCN system.



Figure 8. TEM micrograph of macropores in n-type silicon etched in aqueous electrolyte with back-side illumination (sample 16). Macropores start to grow in the $\langle 100 \rangle$ direction. The inlay shows a high magnification of a pore wall; {111} facets can be identified. At the tips of the macropores break-through pores are formed.

not easily predicted. This can be taken as direct evidence that the orientation dependence of pore formation in Si is not well understood. Among the models for explaining pore formation in silicon, there is a general agreement that the electrochemical dissolution occurs preferentially at the pore tip, and this was explained by more physical mechanisms (focusing on the semiconductor properties) or more chemical mechanisms (focusing on the electrolyte properties and their interactions with the bonds at the interface).

It is generally accepted that silicon dissolution in general is triggered by at least one hole.¹⁹ This provides the basis for the "physical theories," concentrating on the hole supply at the silicon electrolyte interface. In order to obtain pore formation, physical models must explain why the hole capture occurs preferentially at the pore tips. Possible mechanisms are, *e.g.*, enhanced diffusion to the pore tip or a locally enhanced generation of holes at the pore tips. Focusing the hole current on the pore tip by an appropriate shaping of the electric field inside the space-charge region is generally possible and has been used to explain the formation of pores^{24,25} in several distinct ways.



Figure 9. Macropores in n-type Si (with back-side illumination) obtained with the optimized electrolytes used for macropores in p-type Si (sample 17). The pores show pronounced branching. The pore walls are very rough as a consequence of this branching.



Figure 10. n-Type silicon samples with {10 1 1} (sample 18), {114} (19), {113} (20), {112} (22), {223} (23), and {111} (24) surface orientations were etched in hydrofluoric acid containing DMF (with 4 wt % H_2O). The pores show complex growth shapes and growth directions. The main growth direction is still $\langle 100 \rangle$, but also macropores growing in $\langle 113 \rangle$ are found.

For n-type macropores (on low-doped substrates) a depletion layer is formed surrounding each pore. Using back-side illumination, the holes diffuse from the back side to the pore. When the holes reach the depletion layer they are accelerated by the electric field toward the macropore tip. This was the model proposed by Lehmann and $F\ddot{o}ll$.¹

Beale and co-workers²⁵ proposed that there is a barrier (of the space-charge regime) thinning at the pore tip, to explain even the microsporous silicon formation.



Figure 11. (a,b) Details of the branches on $\{112\}$ (sample 22) and $\{100\}$ (sample 17) oriented samples. (c) Details of the main pore for the $\{10 \ 1 \ 1\}$ oriented sample (18) and (d) for the $\{322\}$ sample (23). The fundamental difference between branch and main pore is the symmetry: The main pores grow in a preferential direction with symmetric branches in different directions. The branch systems can be very complex, but all branches and subbranches stop on (111) planes as visible in (b). Some smooth macropores with a diameter around 200 nm exist as well as shown in (c).



Figure 12. (a) The schematic illustration compares the branches and the sidepores of macropores. (b) An overview picture of the $(10\ 1\ 1)$ sample (18) shows all three structures: (*i*) breakthrough pores, (*ii*) branches, and (*iii*) macropores.

Lehmann and Gösele²⁶ explain the micropore formation by a quantum wire effect. Due to the quantum confinement, the bandgap is larger in the pore walls and holes again are focused by the resulting electrical fields on the pore tips.

Some other models solve the Laplacian problem, *i.e.*, general diffusion instabilities emerging even from homogeneous starting



Figure 13. Breakthrough pores in n-type silicon [{100} (sample 17), {113} (20), {211} (21), and {322} (22) orientations; HF containing DMF (with 4 wt % H₂O)]. The pores are always (111) octahedra connected along a $\langle 100 \rangle$ direction.



Figure 14. High-resolution TEM image in [110] zone axis of a break-through pore etched in aqueous electrolyte (sample 16).

conditions¹⁷⁻¹⁹ for the pore formation. This approach focuses on the diffusion (or migration within an electric field) of all reactants participating in the dissolution reaction.

While it appears that the physical effects, generally associated with the space-charge regime, do play a major role in pore formation, they do not easily explain the anisotropy of pore formation since all these models are inherently isotropic. Lehmann considers the anisotropy of macropore formation in n-type silicon in aqueous electrolytes under back-side illumination to be correlated with the anisotropy of j_{ps}^4 (first peak in the *I-U* curve⁴), while Chazalviel and co-workers include the anisotropy into their linear stability analysis of pore formation as a modulated "surface tension." ¹⁹



Figure 15. Schematic illustration of breakthrough pores based on the high-resolution TEM images of Fig. 14.





The more chemically oriented models focus on the chemistry of the dissolution reactions. The dissolution at the pore tip is obviously easier than at the pore walls, demanding an effective passivation of the walls or an autocatalytically enhanced reaction at the pore tip. Unagami²⁷ proposed a passivation of the walls by a coating of silicic acid. Parkhutik and Shershilsky¹⁵ suggest a similar model of a "virtual passivation layer" which protects the walls against further electrochemical attack. This layer is assumed to be a kind of oxide layer. Kooij and Vanmaekelbergh²⁸ based their model on surface intermediates leading to an autocatalytically enhanced dissolution reaction at the pore tip. Allougue *et al.*²⁹ and others (*e.g.*, Parkhutik³⁰ and dos Santos and Teschke¹⁴) assume that hydrogen is formed at the pore tip and diffuses into the silicon substrate. The acceptor atoms are then passivated by H, causing an increase in the resistivity of the p-type material which then leads to pore formation. Rieger and Kohl³¹ proposed that the chemical reactivity of the H-terminated silicon surface depends on the kind of bonds pointing into the electrolyte.

While all these models based on chemical reaction kinetics are inherently anisotropic and thus have no principal difficulty with anisotropic pore growth, their predictive power is very limited in general and not very specific (beyond the well-known fact that {111} planes are always very stable), in particular when details of the pore anisotropies are involved.

Based on our results, we consider it very likely that the passivation degree and kinetics of the dangling bonds on the Si surface, which differ for different orientations and solvents, play a major role in the pore formation, but no predictions of the actual behavior seem to be possible at present. As shown by Yablonovitch,³² the degree of H-passivation on {111} surfaces (as measured in the physical quantity "surface recombination velocity") is much better than on {100} surfaces. In addition, there is evidence that the kinetics of H passivation is faster on a {111} surface than on a {100} surface. A chemical attack leading to silicon dissolution is therefore more likely on $\{100\}$ surfaces. Thus, $\langle 100 \rangle$ directions are a preferred growth direction for macropores (pore tips). As shown by the experiments, the {113} planes are also preferentially dissolved and, following this reasoning, it might be predicted that {113} planes are the second least perfect and/or slowest in H passivation. A more detailed consideration of the causes of the pore growth anisotropy within this general frame of reasoning can be found in Ref. 33. In this context cyclavoltammograms,^{5,6,34} capacitance measurements of the interface,³⁵ or impedance measurements,³⁶ if done for different sample orientations, may be suitable tools to investigate the peculiarities of H passivation.

The prevalence of the $\{113\}$ surface in addition to the $\{100\}$ surface in macropore formation is not understood, but not a total surprise either. Several phenomena exist where $\{113\}$ planes play a special role in the silicon crystal. The so-called $\{113\}$ defect or

stacking fault often observed after irradiation of Si (the nature of which, after much investigation, is still not understood) should be mentioned,³⁷ or the unique 3×2 and 3×1 reorganization of the (113) surface under ultrahigh-violet (UHV) conditions.^{38,39} Dislocations have been seen aligned in (113) directions, and other {113} phenomena are occasionally mentioned in gatherings of silicon experts, but rarely published because of their obscurity.

Since interface states in the bandgap must be expected to be charged to some extent, the space-charge regime collapses due to Fermi level pinning for badly passivated surfaces retaining their interface states. That part of the voltage that formerly dropped in the space-charge regime now increases the electrochemical etching potential at the surface, which leads to an increased electrochemical dissolution. This effect is stronger in low-doped material normally used for macropore formation in p- and n-type silicon than in highly doped Si.

Besides differences in surface passivation, back-side illumination must be considered to influence the anisotropies observed. Since the back side is the source of the holes and the pores must grow toward the source of the holes, they have a tendency to grow perpendicular to the surface and thus favor only the $\langle 100 \rangle$ or $\langle 113 \rangle$ directions extending in this direction. While the general orientation dependence for p-type macropores is the same as for n-type pores, the switch from $\langle 100 \rangle$ to $\langle 113 \rangle$ in p-type silicon is not as well defined as in n-type silicon and branching, *i.e.*, growth in all other preferred directions is easier.

While arguments based on surface passivation and back-side illumination apply to all situations, the experiments demonstrate, as certainly expected, that the type of electrolyte used also influences the anisotropy and other pore parameters. While the detailed influence of the electrolyte (solvent molecules and additives) is not clear at the moment, these experiments together with observations reported in Ref. 9 and 40 suggest that properties of the organic solvent molecule, such as protic or aprotic, play a role in the silicon dissolution. The electrochemical parameters of the Helmholtz doublelayer, the space-charge region at the silicon/electrolyte interface, the number of surface states, and the solubility of silicon hexafluoride ions play a major role (and are significantly different between different aqueous and organic electrolytes).

This pronounced influence of the electrolyte is most obvious when comparing macropores in n-type silicon growing in organic and aqueous electrolytes: well-formed pores with smooth walls and almost without branches are obtained in aqueous electrolytes. Much smaller, rough, and highly branched macropores are found in organic electrolytes under comparable etching conditions. This is quite unexpected because back-side illumination should, by the current focusing effect, stabilize macropore growth rather than destabilize it. One conclusion possible from the experimental result is that the electrolyte strongly influences the diameter of the macropores (additionally to known etch parameters such as, *e.g.*, current density,⁴ fluoride concentration,⁴¹ and pH value of the solution⁴²). The roughness and the tendency for branching in organic electrolytes may then be viewed as the result of a competition between different length scales impressed on the system by the diameter of the pores and the space-charge region width, which perfectly coincide for the aqueous electrolytes under certain conditions. Increasing the doping level and correspondingly decreasing the space-charge region of the silicon, may then allow the formation of very narrow macropores in organic electrolytes, a feat extremely difficult to achieve with n-type Si. Such macropores, with diameters smaller than 500 nm, would be of considerable interest for many applications.⁴³

It is remarkable that all properties of breakthrough pores do not depend strongly on the electrolytes used. Breakthrough pores occur if the available supply of holes is extremely small compared to the current the system could carry.^{4,13,19,20} Holes then are generated by avalanche breakthrough in the silicon if the field strength is large enough, and this leads to almost the same etching structures independent of the electrolytes (aqueous or organic). While avalanche breakthrough may have some anisotropy, the maximum field strength must be expected to be perpendicular to the surface, and it appears unlikely that the observed anisotropy can be explained by avalanche breakthrough alone.

While the detailed mechanism for the formation of the very pronounced octahedra often seen in breakthrough pores is open to discussion, it is clear that the growth of a new octahedron start will with higher probability at its tips (pointing in a $\langle 100 \rangle$ direction) and not on the {111} planes of its sides. Without any secondary parameters inducing a second preferential direction, all tips are equivalent and a breakthrough pore with branches in all $\langle 100 \rangle$ directions forms.

Conclusions

While the results obtained may induce more questions than answers with respect to pore formation in Si, some hard new facts about macropore formation emerged: $\langle 100 \rangle$ and $\langle 113 \rangle$ directions are generally the major growth directions, and $\{111\}$ planes are the main stopping planes for almost all macropores under all kinds of etching conditions. The detailed dominance of crystallographic directions strongly depends on the choice of electrolyte. Breakthrough pores, in contrast, show a pronounced anisotropic pore growth independent of the electrolyte; they are quasi-periodic arrangements of octahedral voids in $\langle 100 \rangle$ directions with $\{111\}$ walls. Pore morphologies in n-type silicon etched in organic electrolytes under back-side illumination are quite different from those observed in aqueous electrolytes or in p-type Si under comparable conditions.

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