Dependence of Macropore Formation in n-Si on Potential, Temperature, and Doping

M. Hejjo Al Rifai, M. Christophersen, S. Ottow, J. Carstensen, and H. Föll^{*,z}

Faculty of Engineering, Christian-Albrechts-Universität, 24143 Kiel, Germany

Subjecting illuminated n-type silicon wafers to anodic bias in an HF containing electrolyte results in the formation of macropores under certain conditions. In this paper the formation of randomly nucleated macropores is studied as a function of the applied potential, the temperature, and the doping levels of the samples. A large number of micrographs was evaluated by computerized image processing and the data obtained are compared to predictions of pore formation models. It was found that the formation of randomly nucleated macropores involves a prolonged nucleation phase. Starting from a polished surface, first macropores occur after a certain amount of Si has been homogeneously dissolved. In this nucleation phase the thickness of the homogeneously dissolved Si depends strongly on the doping level and the temperature, but only weakly on the applied bias. In a second phase of stable pore growth, the density of pores is investigated as a function of temperature and anodic potential. For low-doped material a strong influence of the space-charge region on the average macropore density is observed in accordance with existing models; an increases the pore density, in contrast to predictions. The pore growth in this region is not very sensitive to the space-charge region but seems to be dominated by the chemical-transfer rate.

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Electrochemical etching of silicon in suitable electrolytes may produce pores in a bewildering multitude of sizes and shapes, cf. the reviews.¹⁻³ Among the many different kinds of pores, the "nanopores" (also called "micropores") with typical dimensions in the 1 nm range and obtained on moderately doped p-Si or n-Si in electrolytes containing HF and at current densities below the so-called PS peak (see Fig. 1a), received overwhelming attention since Canham⁴ and Lehmann and Gösele⁵ discovered the quantum wire nature of the remaining skeleton of these pores, and Canham showed that nanoporous Si layers exhibit strong photoluminescence. The advent of Si optoelectronics seemed to be at hand, cf. Ref. 6. However, after 8 years of concentrated research, the detailed mechanism of the photoluminescence is still debated, optoelectronic devices based on nanoporous Si are elusive, and not overly much is known about the formation mechanisms of the nanopores.⁷

Nanopores are but one of many manifestations of pores in Si. Around the time of the discovery of the quantum wire aspects of nanoporous Si, other types of pores were known and discussed in the literature.⁸⁻¹¹ For the sake of clarity and to avoid excessive use of quotation marks, we first shall define and use specific denominations for different types of pores. Besides the term "nanopores" which is already sufficiently clear, we use the term "bsi-macropores" whenever addressing the pronounced pores with diameters in the 1 μ m region obtained in back-side illuminated (bsi) n-type Si at medium potentials (see Fig. 9 in Ref. 9 as an example for typical bsi-macropores or Fig. 2 in this paper), while "breakthrough pores" denote the narrow (diam < 100 nm) pores often obtained in n-type Si in the dark at high potentials.^{8,12} Also known in 1991,¹ but rarely published, were the "fsi-macropores," *i.e.*, macropores obtained in n-Si under front-side illumination (fsi) conditions.^{13,14}

In the meantime, formerly unknown types of pores and surprising properties of known pores were discovered. Most exciting, perhaps, is the discovery of rather large pores in p-type Si (diameters in the micrometer range), first described by Propst and Kohl¹⁵ and subsequently in Ref. 16 and 17, which are termed "p-macropores." But also "mesopores" (with typical dimensions in the 10 nm region), obtained in heavily doped p^+ -Si or n^+ -Si, under conditions that would produce nanopores in moderately doped Si, ¹¹ must be added to the list. Finally, the recently discovered specific dependence of bsi-macropores and breakthrough pores on crystal orientation¹⁸ must be considered when addressing pore formation in Si. It should be noted that the six kinds of pores defined do not cover all archetypical manifestations of pores in Si (bsi-macropores on $\{111\}$ substrates, for example, have morphologies totally different from those on $\{100\}$ substrates^{9,18}) and that mixtures of two pore types are possible (bsi-macropores, *e.g.*, may contain nanoporous layers).

There is a general lack of quantitative models that explain the formation mechanisms of the various kinds of pores enumerated, not to mention the total lack of a unified model that explains all pore formation (for recent review see Ref. 2). Whereas several qualitatively different kinds of formation models may be distinguished, they all suffer from shortcomings with respect to old and emerging experimental findings. In short, the "quantum wire model,"¹⁹ while possibly explaining the formation of nanoporous Si, has nothing to say about the formation of all other pores. The "space-charge region model," first invoked by Lehmann and Föll,9 while explaining some of the features of bsi-macropores, does not seem to work at extreme (e.g., high doping or high potentials) parameters, as shown in this paper, and does not directly address nanopores, mesopores, or pmacropores. Beale et al.²⁰ invokes space-charge region effects by Fermi level pinning at the electrolyte-silicon contact for nanopores in p-type Si in a purely phenomenological approach. The "passivated surface model" presented by Parkhutik²¹ and Santos and Teschke²² and the "hole diffusion model" of Smith *et al.*,²³ while reproducing some observed properties of macropores or mesopores in computer simulations, operate under assumptions that are not yet backed up by detailed physical mechanisms at the solid-liquid interface. The "breakthrough model" of Theunissen,⁸ by its nature, applies only to breakthrough pores. Finally, diffusion models, based on general interface instability analysis,^{24,25} may have some bearing on bsi- and fsi n-macropores for the special case of random nucleation, but so far without much predictive power. To summarize from the point of view of the experimentalist: Few quantitative predictions exist for the outcome of experiments which are performed in hitherto unvisited areas of the parameter space.

Essentially only Lehmann and $Föll^9$ and Lehmann *et al.*^{26,27} make quantitative and measurable predictions for bsi-macropores in n-Si which are based on the space-charge region model and can be checked against experimental data. These predictions are

1. The average wall thickness a between bsi-macropores in equilibrium should equal about twice the depth w of the space-charge region width, *i.e.*

^{*} Electrochemical Society Active Member.

^z E-mail: hf@techfak.uni-kiel.de

2. The relation of the pore cross-sectional area $A_{\text{pore}} = \pi d^2/4$ (with d = pore diameter of an individual pore) to the pore generation area A_{gen} from which it draws current equals the current density in the external circuit *j* divided by the current density of the porous silicon layer (PSL) peak, j_{PSL} , *i.e.*

$$A_{\text{pore}}/A_{\text{gen}} = j/j_{\text{PSL}}$$
 [2]

Equation 2 also holds if the two areas are interpreted as the averages over many individual pores.

The fundamental assumption of Eq. 2 is that in a stable growth mode every pore consumes a constant part of the available current and that the current density at a pore tip then is constant. Since the current density could adjust itself to any value because the pore diameter is not fixed, it is reasonable to assume that the current density adjusts to the one specific value, j_{PSL} , that stands out in the current-voltage characteristics of the system.

The first equation is essentially a synonym for the space-charge region model per se, as already noted by Lehmann and Föll,⁹ because the space-charge region model only works if the space-charge regions between pores overlap, demanding $a \le 2w$. However, since most work on bsi-macropores has been done with prestructured nuclei aiming for a regular and predetermined array of bsi-pores, Eq. 1 so far has not been checked quantitatively. This is so because with prestructured nuclei, the distance between pores is not a free parameter. All that can be expected if the distance between pores chosen by the prestructured nuclei is too large or too small, is a branching of pores into two pores, or pores that cease to grow.²⁷

To get average values one can neglect the diameter of the pores in comparison to the wall thickness *a* of the pores (at least for the experimental data given in this paper) leading to $A_{\text{gen}} \approx a^2$. Feeding this into Eq. 1 and 2 we obtain for the average diameter *d*, and the average distance *a* between pores

$$d = 4w(j/\pi j_{\rm PSL})^{1/2}$$
[3]

$$a = 2w = d/2(\pi j_{\text{PSL}}/j)^{1/2}$$
 [4]

The space-charge region width w can be obtained in a sufficiently good approximation from the Schottky contact theory

$$w \approx (2\epsilon\epsilon_0 U/eN_{\rm D})^{1/2}$$
 [5]

with U the junction voltage, ϵ and ϵ_0 dielectric constants of Si and vacuum permittivity, respectively, e elementary charge, and N_D the concentration of donors. The measurable quantities d and a as functions of the primary etching parameters j, j_{PSL} , U, and N_D finally are obtained as

$$d = (8\epsilon\epsilon_0 jU/\pi eN_{\rm D}j_{\rm PSL})^{1/2}$$
[6]

$$u = 2w \approx (8\epsilon\epsilon_0 U/eN_{\rm D})^{1/2}$$

In order to gain more insight into the bsi-pore formation processes, a number of experiments were carried out with the aim to obtain reliable data on the formation and growth dependence of randomly nucleated or unstructured bsi-macropores on the applied potential, temperature, and the doping level. The term "unstructured bsimacropores" refers to the simple fact that in contrast to most work on bsi-pores, the nuclei for the pores were not lithographically prestructured in this work.

Experiments and Data Processing

Specimens were taken from standard {100}-oriented, 150 mm diam, n-type Si wafers with four different doping levels corresponding to specific resistivities of 0.5, 2, 5, and 20 Ω cm by cutting the wafer into 20 \times 20 mm parts. In some cases the nominal resistance proved not to be accurate enough; in these cases the actual resistance was measured with a four-point probe.

The specimens were cleaned by HF dips and introduced into the electrochemical cell for etching experiments. Figure 1b shows the relevant features of the etching apparatus together with a typical I-U characteristic (Fig. 1a). A simple pseudoreference electrode (Pt wire

close to the specimen surface) was used in all cases to ensure reproducible results and quantitative control of the junction potential. Figure 2 shows examples of the macropores obtained under random nucleation conditions.

The electrolyte was typically 4% HF with a drop of a commercially available wetting agent. The electrolyte was pumped through the cell and its temperature was kept constant by running it through a heat exchanger controlled by a thermostat.

The current density was set at $j = 5 \text{ mA/cm}^2$, which is ~20% of the peak value j_{PSL} for the chosen setting (cf. Fig. 1a).

The intensity of the light illuminating the back side of the sample was determined by relating the induced photocurrent to that of a previously calibrated light source.

Essentially two series of experiments were performed for all doping levels. The first series was taken at a constant applied voltage U_{an} and temperatures *T* varying between $T = 5^{\circ}$ C and $T = 30^{\circ}$ C; the second series varied the anodic potential between $U_{an} = 1$ V and $U_{an} = 6$ V at constant temperature.

All parameters were controlled by a PC running on customized software (developed by Lehmann and Grüning^{12,27}) that allows preprogramming of the system with respect to the desired pore depth and, in the case of prestructured bsi-pores, the pore diameters. The program essentially compensates for two effects: (*i*) With increasing pore depth the distance of the pore tip to the illuminated back side decreases, which leads to an increase in current depending on the minority carrier diffusion length of the sample in question, because an increasing percentage of the minority carriers generated at the



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



Figure 2. A typical SEM cross-sectional micrograph of random bsi-macropores. Bottlenecks (marked) are frequently observed formed at the top of the macropores.

back side can diffuse to the pore tip. (*ii*) The diffusion of electrolyte into deep pores is more difficult with increasing pore depth, which leads to a (temperature-dependent) reduction of the HF concentration at the pore tip and to a concomitant lowering of j_{PSL} . Both effects lead to an increase in the pore diameters with increasing depth, if the illumination is kept constant. The software, using Eq. 2 and empirical relations, compensates for these effects if the temperature is given as an input variable by adjusting the illumination intensity and thus the current in such a way that the pore diameter stays constant. For pore depths of several 100 μ m the variation of the current density *j* is typically a few percent of the starting current. The software usually works very well, and this is nicely demonstrated in the extremely uniform prestructured bsi-pores shown, *e.g.*, in Ref. 9, 12, 26, and 27.

In our experiments the pores were not prestructured; the software thus runs on expectations of average values. In essence, however, for the pore depths used in our experiments, the corrective effect of the control unit on the etching current *j*, while still insuring controlled conditions, is negligible in comparison to the effects of nucleation and reorganization of the "random" bsi-pores in our case.

The control unit in our case thus keeps the current nearly constant at the preselected value. However, in contrast to prestructured bsipores, this task can only be achieved if the intensity of the backside illumination is varied to a considerable degree. This intensity can be recorded and used as an indication for changes in the valence n of the electrochemical process as a function of the etching time or pore depth, respectively. Since the compensation for the temperature-dependent diffusion of electrolyte in and out of the pores is still working (on average), any strong temperature effects observed in our experiments must result from nondiffusional effects.

The etched samples were investigated with respect to (i) the step height between the original surface and the etched surface (which, in contrast to what seems to be known from prestructured bsi-pores, is not zero), (ii) the average distance between pores, (iii) the average diameters of pores, and (iv) the depth distribution of pores, *i.e.*, their appearance in cross section. Step heights between the original surface and the etched surface were determined by a Dektak 800 from VEECO.

Average pore diameters and distances were obtained in two ways: The surface of the samples was either left as etched if the nucleation phase of macropore growth was to be examined, thus showing all pores. If the phase of stable pore growth was of interest, typically 20 μ m was polished off by mechanical polishing with a diamond suspension with an average grain size of 6 μ m in order to remove pores that did not grow into the depth of the sample. Second, scanning electron microscopy (SEM) micrographs were taken at typically 1000-3000 times magnification. The resulting micrographs could be grouped into three categories

1. Pore distribution patterns which were clearly irregular and most likely linked to preferred nucleation at surface irregularities, *e.g.*, contamination rings from evaporated water droplets or other chemicals. Figure 3a shows an example. Micrographs of this kind were discarded and not used for data acquisition.

2. Random arrays of clearly visible macropores. Micrographs of the as-etched surface then generally show well-developed pores (strong dark contrast) intermixed with smaller and less pronounced (gray contrast) pores. An example is given in Fig. 3b. Cross-sectional images of these samples indicate that this image is due to a mixture of fully developed pores (mostly with "bottlenecks") showing strong contrast and shallow depressions or short pore nuclei causing the weak contrast. Samples where parts of the surface layer (and thus the bottleneck part) was removed result in clear micrographs, of fully developed macropores as shown in Fig. 3c.

3. Macropores intermixed with breakthrough pores appear at higher voltages. A typical picture is given in Fig. 3d. Micrographs belonging to categories illustrated in Fig. 3b, c, and d were selected for an automatic evaluation of the pore density *N* and the pore diameters. After digitizing the micrographs, a program written for this particular purpose identified pores (including breakthrough pores) and determined the pore generation area A_{gen} belonging to an individual pore by constructing the individual Wigner-Seitz cell of the pore. The pore generation areas determined in this way could be visualized in color for a quick optical check of the performance of the program. The essential results obtained in this way were the distributions of the pore generation areas, the average distance between pores, $a = (A_{gen})^{1/2}$, or the pore densities $N = 1/A_{gen}$, respectively. Figure 4 illustrates the procedure and gives an idea of the results that could be obtained.

Pore areas (A_{pore}) could be obtained in nearly the same way, yielding a pore diameter distribution. They have to be used with caution, however, because the SEM micrographs do not always show the true size of a pore due to secondary electrons which were backscattered from the inside of pores.

Results

Nucleation phase of the macropores.—From the work on prestructured pores,⁹ it is known that small etch pits or any other kind of damage on an otherwise-polished Si surface lead to the immediate nucleation and growth of a stable macropore at the damage site; no pores are nucleated at unintended sites. This observation holds even in the case where the spacing between nucleation sites is larger than twice the space-charge width.²⁷ From this it might be concluded that nucleation of macropores on polished surfaces is not an easy process. The present investigation supports this view. Stable macropore growth on surfaces without prestructured nucleation sites is preceded by a prolonged nucleation and redistribution phase of pores.

In a first step, Si dissolves homogeneously resulting in a step of height h from the original surface to the surface of the etched Si. We refer to this first process as nucleation phase. At the end of this nucleation phase, shallow macropores in a relatively high density are formed. As soon as bulk dissolution stops they grow into the depth of the sample.

In a second step a redistribution process starts, because the density of the macropores growing in this phase is not yet the equilibrium density. During the redistribution process some pores stop growing and terminate, whereas other pores continue to grow with increased diameters. As soon as this redistribution process is finished, the phase of stable pore growth starts yielding an arrangement of pores that is stable and does not change very much anymore. Figure 5 shows the three steps schematically.

SEM analysis of many specimens showed that during the larger part of the nucleation phase only a roughening of the surface is visible, macropore nuclei are rarely observed. Toward the end of the nucleation phase more macropores start to develop, and with increasing time their density increases rapidly. The time interval during which first macropores occur is longer for more heavily doped Si in comparison to lightly doped samples.

The thickness h of the dissolved nucleation layer was measured with a DEKTAK 800 as a function of doping, voltage, temperature, and time, parameters that were found to strongly influence h. Figures 6-8 show the measured relationships.

Figure 6 illustrates that *h* eventually saturates at a saturation thickness h_{sat} which depends on the doping level (for the sake of clarity only the curves for the extreme doping levels are shown); h_{sat}

increases considerably with decreasing doping. That this effect is not due to the different voltages used for the two doping levels shown is demonstrated in Fig. 7, where it can be seen that the influence of the junction voltage (as measured via the reference electrode) on $h_{\rm sat}$ is rather weak. In contrast, the temperature *T* has a pronounced effect on $h_{\rm sat}$, as shown in Fig. 8.

Redistribution phase of the macropores.—The density and the size of the macropores in the beginning of the redistribution phase was measured as a function of doping, temperature, and junction voltage using the aforementioned technique. Typical results are shown in Fig. 9 and 10. Whereas the more lightly doped material does not show a pronounced dependence of the pore density on voltage or temperature, the situation is different for the highly doped material. As mentioned before, the effect of the temperature on the pore density is not caused by the diffusion of the reactants in the liquid and thus must be due to some kinetic effect at the interface.

Stable growth phase of the macropores.—Systematic investigation of the pore density as a function of junction voltage, doping, and









d.)

Figure 3. SEM micrographs of various macropore arrays at 1000-3000 times magnification: (a) irregular pore distribution not suitable for automatic evaluation, and (b) "good" random pore distribution. Only micrographs of this kind were used for the data acquisition. (c) and (d) "Good" arrays after polishing off about 20 µm. (d) Mixtures of macropores and breakthrough pores at larger voltages (breakthrough pores are cross-shaped).



Figure 4. Digitizing and data acquisition. (Ia–d) shows the process for the nucleation phase, (IIa-d) for the stable pore growth phase, (a) SEM image, (b) pore definition by software, (c) construction of the Wigner-Seitz cells, (d) resulting histograms for the pore area (equals the size of Wigner-Seitz cells). Histograms for the pore sizes and densities were obtained by the same procedure.

temperature were made. Only samples with well developed "random" pore patterns (excluding the ones shown in Fig. 3a) were used for analysis after the redistribution layer has been removed. The results obtained are shown in Fig. 11 and 12.



Figure 5. SEM micrograph and schematic drawing of the pore nucleation and growth phases: (a) the "crater" formed before macropores are nucleated, (b) redistribution phase, and (c) stable pore growth.

Figure 11 shows the density of pores Nvs. the applied voltage. For sake of clarity the theoretical curves from Eq. 1 are not included, but it is clear that the density of pores should decrease as U increases and that this is clearly not the case for the samples with higher doping levels. Since the space-charge region model predicts unambiguously that the pore density must decrease with increasing voltage, the results for the more highly doped material are definitely not within the scope of that model.

This analysis has been done twice, including and neglecting the breakthrough pores as shown in Fig. 3d. The second approach yielded much better results, since smooth curves as a function of potential could be found. This may indicate that breakthrough pores are not really different from macropores and constitute just a different manifestation of the same underlying phenomena. Neglecting the breakthrough pores reduces the density of pores and thus even increases the discrepancy between the theoretical value according to Eq. 1 and our experimental results.

Figure 12 shows the temperature dependence of the pore density. As already pointed out, the temperature dependence of the diffusion of the reactants into and out of the pore is compensated by the software of the controller. Accordingly, within the space-charge region model, no temperature dependence would be expected. Again, as in the redistribution phase, pronounced deviations from this expectation are evident for the more highly doped samples.

The time-dependent valence of the macropore etching process.—As mentioned previously, the illumination intensity needed to obtain a nearly constant etching current density was recorded as a



Figure 6. Depth of the "crater" as a function of time, doping, and bias. The different bias values were used because they correspond to comparative junction conditions; the bias, however, is not important for $h_{\rm sat}$, as shown in Fig. 7.

function of the etching time, a typical result (log of the back-side illumination intensity is plotted) is shown in Fig. 13. The number of holes generated per second is directly proportional to the light intensity. Only a part of the photogenerated holes reaches the front side and allows the pore formation. Taking into account the diffusion and recombination processes in the silicon bulk, the ratio of the illumination-induced current $I_{\rm Ph}$ and the current reaching the pore tips $I_{\rm etch}$ is approximately given by Ref. 29



Figure 7. The saturation thickness $h_{\rm sat}$ of the etch crater as a function of the doping level and etching potential U.



Figure 8. The saturation thickness $h_{\rm sat}$ of the etch crater as a function of temperature and doping.

$$\frac{I_{\rm Ph}}{I_{\rm etch}} \approx \cosh\left(\frac{d_{\rm W}-1}{L}\right) \approx \exp\left(\frac{d_{\rm W}}{L}\right) \exp\left(\frac{-l}{L}\right)$$
[7]

where *L* is the diffusion length, $d_{\rm W}$ the thickness of the wafer, and *l* the length of the pores. According to Eq. 7, an exponential reduction of $I_{\rm Ph}$ as a function of time is expected for a constant etching current $I_{\rm etch}$, provided that the valence *n* of the reaction at the pore tips is constant. This prediction agrees well with the result in Fig. 13 in the phase of stable pore growth, *i.e.*, after a time of pore nucleation, a exponential fall in the curve can be observed.



Figure 9. Density of pores in the redistribution phase as a function of etching potential U and the doping level of the material.



Figure 10. Density of pores in the redistribution phase as a function of temperature and doping level.

However, during the nucleation phase of the pores, a nearly constant light intensity is found which allows determination of exactly the time when stable pore growth starts. It may also indicate that the valence of the processes in this regime is different from the valence during stable pore growth, but this would need additional consideration.

Discussion

The most intriguing results needing discussion can be summarized as follows

1. Nucleation of macropores is not an easy process and depends strongly on doping and temperature.



Figure 11. Density of pores in the stable growth phase as a function of etching potential and doping. The number of pores, as expected, decreases with potential for low-doped material but increases unexpectedly for high-doped material.



Figure 12. The density of stable pores as a function of temperature and doping.

2. After some time of homogeneous dissolution, first macropores form. Their diameter may increase for some time (bottleneck effect). Their density is generally larger than the density during the stable growth phase and depends on the applied voltage and temperature. In a redistribution phase the equilibrium concentration is achieved because some pores stop growing. The sinks for the current in this starting phase are the tips of nascent pores, but also the surface at large, dissolving homogeneously.

3. The relation between macroscopic current density and the average pore spacing as given in Eq. 6 is at best correct for low-doped Si but not for high-doped Si.

4. The (stable) macropore density generally increases with increasing temperature; this effect is not due to the temperature dependence of diffusion processes of reactants to the pore tips.



Figure 13. Typical curve of the logarithm of back-side illumination intensity *vs.* etching time (for a 5 Ω cm sample etched at 3 V bias). A process with a constant valence leads to a straight line. In the crater formation phase (first 30 min) the curve deviates from the constant valence curve of the stable growth phase; the valence in this area is smaller.

5. The average distance between pores in highly doped samples is always larger than predicted; it increases with increasing junction voltage (Fig. 14).

6. The relation between pore areas and current densities according to Eq. 2 holds within the uncertainties of the evaluation of the mean pore area in our method.

We discuss these results only briefly, because we are not yet able to explain them in a coherent model. As far as the nucleation is concerned, it is clear that nucleation pits are etched before pores were formed. The time before stable pore growth occurs can be quite long (for low-doped material up to 30 min) and is a function of the etching parameters.

Lévy-Clement *et al.*¹³ reported on the formation of nucleation pits preceding fsi-macropores, which depends on the amount of transferred charge. The formation of the nucleation pits was discussed in terms of an electropolishing reaction with a valence *n* smaller than 4 and associated with a collapsed nanoporous silicon layer. This leads to a multilayer structure starting with a "crater," a nanoporous layer, and a macroporous layer, beneath. In contrast to these results we did not find a nanoporous layer, which may result from the differences for front-side and back-side illumination. Such a nanoporous layer, however, was found in the nucleation phase of macropores on p-type silicon in organic electrolytes.³⁰

The results of Lévy-Clement *et al.* concerning nucleation of macropores, however, are generally consistent with our results; taken together and taking into account the experimental results which demonstrate a strong crystal anisotropy for macropore nucleation and formation,¹⁸ as well as the existence of macropores in p-Si,¹⁵ they indicate that the electrochemical reactions at the silicon-electrolyte interface are still not well understood.

The growth phase of stable bsi-macropores is discussed next. First we compare the data of Fig. 10 against the predictions of Eq. 1 and 2. This is most easily done by replotting Fig. 11 in a form where comparison is straightforward. We use the theoretical average distance a_{theory} between pores (= 2w) divided by the measured average distance $\langle a \rangle = 1/\langle N \rangle^{1/2}$ (calculated from the density of pores N) as a function of the applied voltage U. According to the space-charge region model, this should be a straight line at $a_{\text{theory}}/\langle a \rangle = 1$. The result is shown in Fig. 14. It is clear that the expectation of the space-



Figure 14. Replotting the pore distance *vs.* the etching potential normalized to the predictions of the space-charge model. The data demonstrate unambiguously that this model does not apply to highly doped material.

charge model is met for doping levels corresponding to 5 Ω cm or smaller but that for increasing doping levels or decreasing voltage levels, Eq. 1 does not hold anymore. The average distance between pores is considerably larger than expected for small voltages and higher doping levels. This is a clear indication that the space-charge region model does not fully explain bsi-macropore etching at high doping and/or low voltage conditions.

The same result is obtained from the temperature dependence of the average pore density. The expected (residual) independence on T is only seen for the low-doped samples; for the high-doped samples, the average density increases with increasing temperature, meaning that the average distance decreases.

The observation that the average distance between pores for high-doped Si is by far larger than expected is a rather unwelcome finding because it implies that the growth of prestructured bsimacropores with sub-micrometer dimensions for applications in, *e.g.*, photonic crystal research^{27,28} may be much more difficult than envisaged.

The space-charge region model implies that holes cannot penetrate the areas between the pores. All holes diffusing from the back side to the front side of the samples should be focused on the pore tip; pores, therefore, could only grow into the depth but not laterally.

In high-doped samples pores still do not grow laterally, but there is now no reason why holes could not diffuse into the area between pores. There are thus only two possibilities to explain the experimental findings: (*i*) Holes are still not present between pores due to some other mechanism than the bent space charge region and consequently they are all consumed at the pore tip; and (*ii*) holes are present between the pores but the sidewalls of the pores are "passivated," *i.e.*, holes reaching the sidewall cannot react with the electrolyte and diffuse back into the Si until they either recombine in the bulk or reach a reactive pore tip.

The first possibility could be an outcome of general diffusion models.²³ Essentially, an existing sink for diffusion minority carriers, e.g., the pore tip, would, via Ficks law, induce a concentration gradient of the minority carriers, which at a much larger scale than the (bent) space-charge region would produce nearly the same result: carriers are focused on the tip of existing pores. Whereas this could be true for minority carriers, it cannot be true for majority carriers which always are present at the equilibrium concentration, because even small concentration gradients would induce very large currents; the currents used for pore etching are caused by tiny variations of the local concentrations. The fact that pores very similar to the macropores in n-Si are observed in p-type Si 15,30 thus may indicate that concentration gradients of holes due to carrier diffusion is not decisive for the growth of the pore tip. However, at present, this mechanism cannot be ruled out with certainty because the average distance between p-macropores so far seems to be consistent with the space-charge region model. Additional experiments where gradients in the hole concentration on a scale much larger than the spacecharge region cannot exist could help to decide which explanation holds. Macropores in p-type or n⁺-type silicon (obtained without illumination) with separations much larger than w could, e.g., not be easily explained by diffusion models but would point to a passivation mechanism. Similar considerations would pertain to experiments employing front-side illumination. Considering all results, we favor the viewpoint that some passivation mechanism is operative during pore etching, similar to the view of Parkhutik.²¹ Whereas it is too early at the present stage of the investigation to discuss detailed models of the underlying passivation mechanism, hydrogen passivation, as suggested in Ref. 31 may be a likely candidate. However, as stated before, no clear decision between models seems to be possible at present.

Since we find a strong reorganization of pores in the nucleation phase, especially in the case when macropore growth is not very stable, *i.e.*, at high doping levels, we have to discuss an additional feature: Not every pore which can grow under the experimental conditions will grow in the stable phase. There is a certain possibility that although sufficient minority carriers are present (otherwise no pore tip would have been formed), some pores cease to grow, thus allowing neighboring pores to increase their diameter. In consequence, not each minority carrier which reaches a pore tip will lead the chemical reaction at this tip; there must be a possibility for a carrier to leave the pore tip again and to diffuse to another pore. This may be an independent indication for some kind of (time-dependent) chemical passivation mechanism, *e.g.*, hydrogen passivation as discussed previously.

Conclusions

Statistical evaluation of many pore etching experiments performed with Si specimens of various doping levels and as a function of temperature and bias provided some hard new facts about macropore formation and nucleation. The nucleation of macropores was found to be a relatively difficult process, depending on all parameters mentioned. Macropores finally result from nucleation pits, which form after a specific time of homogeneously dissolving Si. After a redistribution phase, stable pore growth commences with some of the nucleated macropores. All processes are generally dependent on doping, temperature, and voltage. Whereas some of the data obtained are consistent with the space-charge model, others clearly are not. Macropore formation in high-doped Si seems to be a more complicated process than in low-doped Si and most likely calls for a kind of passivation mechanism of the macropore walls.

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