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Fast pore etching on high resistivity n-type silicon via photoelectrochemistry*

Bao Xiao-Qing(包晓清)[a)b)], Ge Dao-Han(葛道晗)[a)b)],
Zhang Sheng(张 圣)[a)b)], Li Jin-Peng(李金鹏)[a)b)],
Zhou Ping(周 萍)[a)], Jiao Ji-Wei(焦继伟)[a)†], and Wang Yue-Lin(王跃林)[a)]

[a)] *State Key Laboratories of Transducer Technology, National Key Laboratories of Microsystem Technology, Shanghai Institute of Microsystem and Information, Chinese Academy of Sciences, Shanghai* 200050, *China*

[b)] *Graduate School of Chinese Academy of Sciences, Beijing* 100049, *China*

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In this paper, five factors, namely the HF (hydrofluoric acid) concentration, field strength, illumination intensity as well as the oxidizing-power and conductivity of electrolytes were found to strongly affect the fast pore etching. The oxidizing power of aqueous HF electrolyte of different concentrations was especially measured and analysed. A positive correlation between optimal bias and HF concentration was generally observed and the relationship was semi-quantitatively interpreted. Pore density notably increased with enhanced HF-concentration or bias even on patterned substrates where 2D (two-dimensional) nuclei were densely pre-textured. The etch rate can reach 400 μm/h and the aspect ratio of pores can be readily driven up to 250.

Keywords: pore density, SCR width, H-passivation, current-burst-model, breakdown mechanism
PACC: 6140G, 8100

1. Introduction

Concerning pore formation, numerous works with respect to SCR (space charge region) effects, electrochemical oxidation, etc., were advanced.[1−14] Other reports established a general framework for the pore-morphology under varied conditions.[15−28]

To our knowledge, so far no works have been concentrated on fast pore etching via photo-assisted electrochemical. Compared with the conventional technique (where the etch rate, based on SCR model, was around 1 μm/min and hence a little slow),[22] fast pore etching, due to its high etching speed, has an obvious advantage in mass production.[29] However, fast pore formation in existing works were only limited to the etching in the dark (without back side illumination (bsi for short hereafter)):[22,30] no perfect macropores have been rapidly produced on low-doped n-Si since the etched pore-walls could be quite rough,[30] although the results achieved on moderately-doped n-Si were quite exciting.[22] It is known that a rather high HF concentration ([HF]) is a must for fast pore etching. However, as shown in this work and in a report,[4] if exclusively in light of SCR principles, no 'good' pores of large aspect ratios (> 50) can form with a high [HF] (> 15 wt.%). Nevertheless, it has been found[30,31] that even by etching n-Si with a [HF]> 15 wt.% via a high bias (12–25 V) (rather than a low one (1–3 V) as applied in Ref.[4]), it is still possible to rapidly yield good pores of an aspect ratio up to 250.

Additionally, as shown in the previous works,[27,31] the density of one-dimensional (1D) pores increases markedly with enhanced HF-concentration or voltage despite an unchanged or increased SCR width. However, such a phenomenon, deviating quite a bit from SCR principles, has only been observed on linear nuclei (where 1D pores form). On samples predefined with densely-arrayed point nuclei (where 2D pores form), what will occur still remains unknown.

This work thus aims at fast growing pores (of good quality) from prestructured point defects on n-Si with bsi technique. The potential drop in the Helmholtz layer, current-burst-model (CBM) as well as breakdown mechanism was employed to justify the observed results. Most importantly, a positive correlation between optimal bias and HF concentration was

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†Corresponding author. E-mail: jiaojw@mail.sim.ac.cn

discovered and interpreted.

2. Experiment

N-type silicon (3–8 Ω cm, 450 μm-thick, CZ (Czochralski)-grown, [100]-oriented and polished) was used. A 500 nm-thick silicon-nitride film was employed as a mask via PECVD (plasma enhanced chemical vapour deposition). By standard photolithography, the specimen was textured with a hexagonal point-lattice of 3 μm lattice constant: the predefined points are of a square shape with 1.5 μm side-length. After the removal (via ion beam bombardment) of silicon nitride in the predefined area, point defects with an inverted pyramidal shape were formed by TMAH (tetramethylammonium hydroxide) etching. Finally, the remaining silicon-nitride film was removed by BOE (buffered oxide etchant) to generate a maskless and stable etching.

All specimens were anodized on an electrochemical etching platform in a decontamination chamber at room temperature. Constant-voltage conditions were applied. A power-controlled halogen lamp (0–150 W) was placed 12 cm away from the back-side of the specimen to generate illumination to obtain the electronic holes required for silicon dissolution;[1] a platinum grid (as cathode) was placed 5 mm away from the front side of specimen. An Au/Cr (300 nm/20 nm) film was sputtered on the backside of the specimen to establish a good ohmic contact, while an illumination window was formed via the removal of the corresponding Au/Cr layer by wet etching. Aqueous electrolytes based on a mixture of HF acid (48%) and deionized water were used; here the HF concentration was expressed by weight percentage of HF acid (not pure HF). The pores produced were investigated with a field-emission scanning electron microscope (FESEM: Hitachi S-4700). Plan views show (100) plane, whereas after cleaving the samples, cross-sections show the pores in (110) cleavage planes.

3. Results

The pore morphology dependence on HF concentration and etching bias was investigated (see Figs.1–4 for details), whereas the anodization with HF of 20% concentration (Figs.2 and 3) was focused on. With a 5% [HF] and a 1.5 V (determined by the predefined pitch of pores based on SCR model[2]) bias, regular array of macropores can be obtained via backside illumination. However, if etched with [HF] $>$ 10% and a 1–3 V bias (based on SCR model), no good pores of large aspect ratios ($>$ 40) can be produced, as shown in Fig.3(b). Rather, a 10–15 V voltage was found to be suitable for stable pore growth with 12% [HF] (Fig.1) and a larger bias (15–25 V) is needed to grow stable pores with higher [HF] (20–40%, see Figs.2–4). Although for the etching with a 20% [HF], numerous experiments were conducted with a voltage between 0.5 and 3 V, merely pores of rather bad quality can be produced at a low speed ($<$ 2 μm/min) (see Fig.3(b)); note that if based on the predictions of SCR model, the bias applied should be ∼1.5 V in our cases and the etch rate should reach 4–5 μm/min under a 20% [HF].[3]

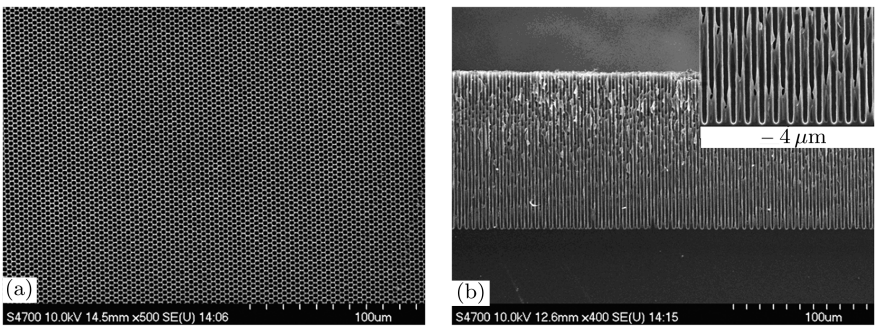


Fig.1. 12% HF, 140 W illumination, 12 V for 45 min. (a) Plan-view: Top-diameters (around 2 μm) of pores show little variation over the anodized surface. The pore density was calculated as 0.13 μm^{-2}. (b) Cross-section: Stable pores with 115 μm depth and 2 μm diameter (and aspect ratio of approx. 60) are obtained. No degeneration of pore shape occurred (see the inlay). The pores are straight, cylindrical and rather smooth. Owing to different rows of pores present in cross-section, the artefacts induced by cleavage operation cannot be avoided. The etch rate is around 150 μm/h.

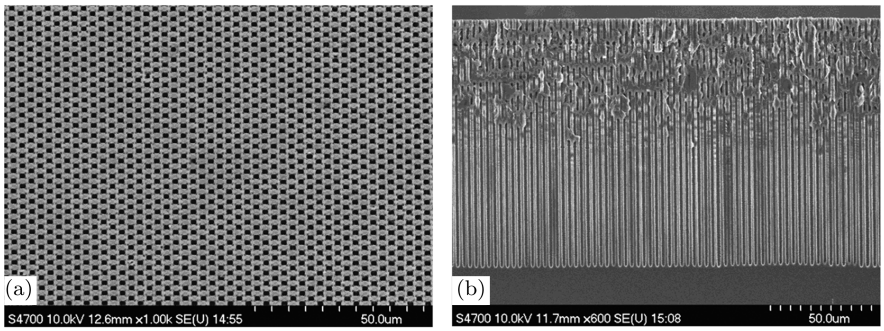


Fig.2. 20% HF, 140 W illumination, 25 V for 30 min. (a) Plan-view: Top-diameter (around 1.5 μm) of pores show little variation over the anodized surface. For the convenience of comparison (with Fig.4), a 25 V bias is applied. Owing to the large bias, a trace of branching tendency on (but not beneath) the etching surface emerges; better pores (without branches) can be obtained with a little lower bias, e.g., 22 V. (b) Cross-section: Stable pores with 120 μm depth and 1.5 μm diameter (and an aspect ratio of 80) are obtained. The pores are generally good; the etch rate is around 240 μm/h.

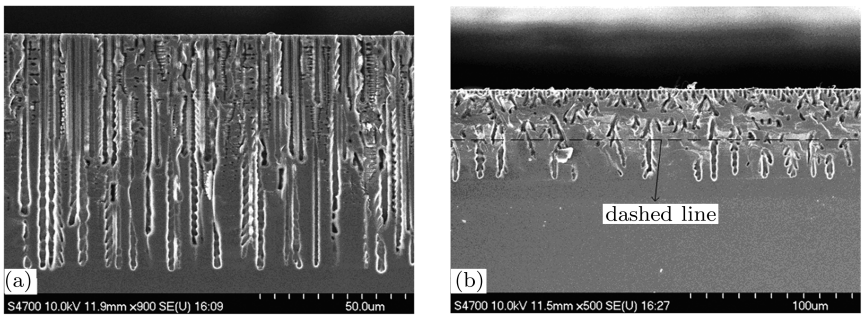


Fig.3. 20% HF, 140 W illumination, (a) 8 V and (b) 2 V for 30 min. (a) Cross-section: Rather bad pores propagate to a depth of 80 μm. Compared with Fig.2, only the bias was reduced here and the quality of pores obviously worsened. The pore sizes are about 2 μm. Some pores apparently cease growing; the density of pores (with a 80 μm depth) is reduced from 0.13 μm^{-2} (Fig.2) to $\sim$ 0.07 μm^{-2}. The etch rate is 160 μm/h. (b) Cross-section: Bad pores propagate to a depth of approx. 50 μm. After a re-nucleation phase (the porous area beyond the dashed line), stable pores (beneath the dashed line) start to grow. The diameters of stable pores are around 5 μm. The pores are extremely 'bad' (not straight and rather rough). The density of stable pores is estimated at 0.01 μm^{-2}; the etch rate is 100 μm/h.

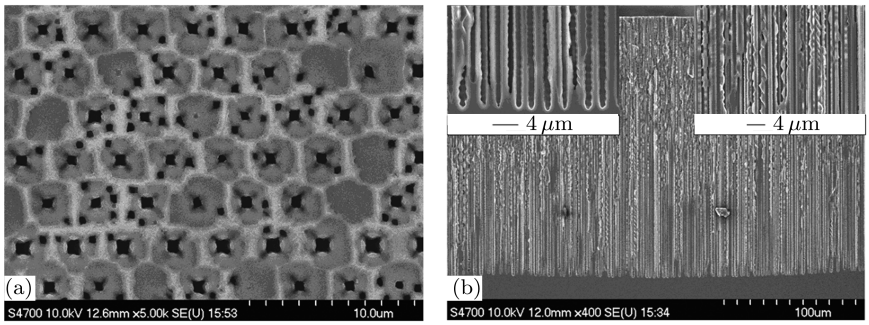


Fig.4. 40% HF, 140 W illumination, 25 V for 30min. (a) Plan-view: An increase of pore density can be clearly observed, simply due to a marked enhancement of [HF] (compared with Figs.1 and 2). A random re-nucleation of pores occurred: via self-organization some pores do not grow at the predefined point nuclei (while the others do); the pores no longer array themselves hexagonally. (b) Cross-section with the right inlay showing the centre part of (b) and the left inlay the pore-tip region: Stable pores with $\sim$200 μm depth and $\sim$0.8 μm diameter are obtained: the aspect ratio can be up to 250. The etch rate is $\sim$400 μm/h. A thin uniform microporous layer on pore walls can be discerned in the inlay. No obvious degeneration effects happened in the porous region close to pore-tips (see the left inlay). The pore density is estimated at 0.25 μm^{-2} (see (a)).

In general, fast pore etching with a speed up to 400 μm/h can be realized with a high [HF] (> 10%) and with a conventional bsi approach on low-doped n-Si.

4. Discussion

In all cases (except Fig.3(b)), breakdown around pore-tips occurred.[15,28] In order to evaluate the ratio of photo-current to breakdown-current, the I–V characteristics were measured (Fig.5). Since the scan range of bias is quite wide (0–35 V) and our chosen electrolytes have a high [HF] (12–40%), the potential sweep rate was set as a quick one of 0.25 V/s.[10] No clear current peak J_{PS} could be observed on I–V curves perhaps due to either the rough scan method or the perturbations caused by the evolution of numerous hydrogen bubbles at high current densities (originating from a high [HF]> 10%).[10,32] In Fig.5, for a given [HF] and bias, the current density with 140 W illumination was found to be at least 8 times greater than the results obtained in the dark across the whole spectrum of scanned biases (0–35 V). Considering the actual biases applied in our cases were no greater than 25 V, the photo-current can be at least 1 order of magnitude larger than the breakdown-current: an enhanced bias will generally lead to a decreased ratio of photo-current/breakdown-current for a given electrolyte and illumination. The measurement of I–V curves was also conducted on unpatterned samples: the overwhelming role of photo-generated currents in the total currents was evidenced as well. Generally, these measurements revealed that the photo-currents (rather than breakdown-currents) preponderate in the pore formation in our shown cases (Figs.1–4).

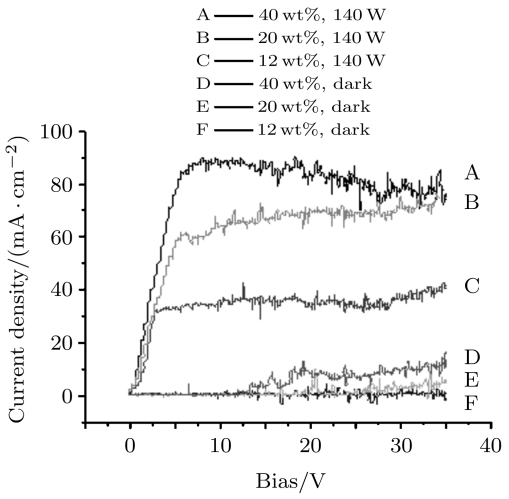


Fig.5. I–V characteristics corresponding to 12%, 20% and 40% HF concentrations were measured on patterned samples with and without a 140 W illumination. No reference electrode was employed. For 40% [HF] and for any given bias between 0 and 35 V, the current density with a 140 W illumination (curve A) is at least 8 times greater than the result obtained in the dark (curve D); for a 12% or 20% [HF], similar trends can be clearly visible (see curves B, C, E and F).

A rather high speed of etching (150–400 μm/h) was reached: five factors pertaining to fast etching should be considered. The first one is the high HF concentration (12–40%): a high [HF], according to CBM,[7,31] will accelerate the direct removal of silicon and the dissolution of the oxides electrochemically generated by oxidants [the O_2 (dissolved in water) for our case], compared with a lower [HF]. However, the enhancement of [HF] does not necessarily mean a higher etch rate: for example, in comparison with Fig.3(b), due to a higher field strength around pore-tips (originating from a greater bias and a smaller radius of pore-tips) in Fig.1, the etch rate of 12% [HF] (Fig.1) can be markedly higher than that of 20% [HF] (Fig.3(b)). Hence, the second critical factor is the field strength (determined by both applied biases and pore-tip radii) around pore-tips, which can influence the etch rate for a fixed HF concentration. That is, if a lower field strength comes into play, the etching speed will be suppressed correspondingly. As addressed in our previous work,[31] the correlation between etch rate and field strength is markedly positive for an electrolyte of identical composition. As clearly shown in Figs.2 and 3, where the one and only variable is the bias applied, etch rates of 240, 160 and 100 μm/h was reached under biases of 25 (Fig.2), 8 (Fig.3(a)) and 2 (Fig.3(b)) V, respectively: usually, for a given electrolyte, a higher voltage leads to a stronger field strength (if neglecting the little variation in pore-tip radii).

Thirdly, the illumination intensity can effectively influence the etch rate. For a given bias and electrolyte, damping the illumination can hasten the etching, since a reduced illumination leads naturally to a smaller pore-tip radius and thus a stronger field strength (around pore-tips): for a given electrolyte, a stronger electrical field can accelerate the etching (as addressed in the second factor). However, on the other side, a decreased pore-size resulting from a reduced illumination can act as a diffusion barrier for HF species and thus can lower the [HF] in the pores: therefore, a damped illumination can exert a negative

influence upon fast pore etching. This effect can be more pronounced especially when the pores propagate to a certain depth where an effective diffusion barrier comes into play.[22]

With respect to fast etching, the fourth factor concerns the oxidizing power of electrolytes. If the oxidizing power of an electrolyte is higher, a stronger oxidation will occur in a single current burst and thus lessen the etching speed on a macroscopic scale (since oxide dissolution is the most time-consuming part in a current burst).[13,21] In this experiment, the aqueous electrolytes are mildly oxidizing,[13] thus to some extent benefiting fast pore formation: the rate of etching can be easily driven up to 400 μm/h. If etching with a less oxidizing electrolyte, e.g., a mixture of HF acid and MeCN (methyl cyanide),[22] a faster etch rate can be expected. Figure 6 further supports our conclusion: for a given kind of electrolyte, a higher HF concentration demonstrates a weaker oxidizing power, thus leading to a faster etching. For example, compared with Fig.2, Fig.4 (where a higher HF was used while the other conditions remain the same) showed a faster etching rate (see the captions of Figs.2 and 4). Note that for Fig.6, at the start of such an experiment, due to the oxide formed (but not yet dissolved), the voltage has to rise in order to keep the current density constant: at the beginning of the anodization the $U(t)$-curves are always linear and the slope $\mathrm{d}U/\mathrm{d}t$ can be used as a measure of the oxidizing power.[13]

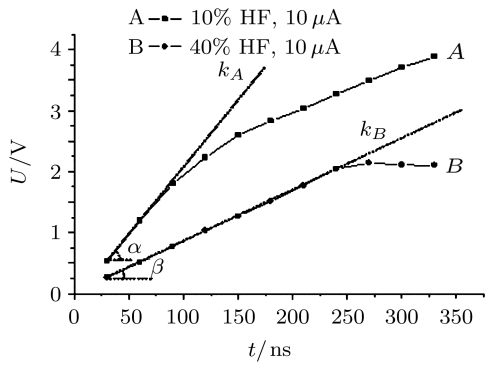


Fig.6. The oxidizing power was measured by the method as mentioned in Ref.[13]. Under the same galvanostatic condition ($10\,\mu\mathrm{A}\cdot\mathrm{cm}^{-2}$), the slope k_A of the initial part of curve A is apparently larger than that (k_B) of curve B, indirectly signifying a greater oxidizing power of the 10% HF (compared with 40% HF). Notice that $k_A = \mathrm{tg}\,\alpha$ and $k_B = \mathrm{tg}\,\beta$, while $\alpha > \beta$.

The last factor for fast pore etching lies in the conductivity of electrolytes: if the resistivity of electrolyte is rather high, the ohmic and hence potential losses in the pores will be significant, inevitably resulting in a negative influence upon fast etching. As shown in Figs.1, 2 and 4, the porous layers of considerable depths are rather uniform and no puff pastry-like structures[17] were observed: this indicates that aqueous electrolytes with a [HF] $> 10\%$ are of good conductivity.

Note that the results achieved here (Figs.1, 2 and 4) were not in light of SCR model: the biases applied (12–25 V) was approximately 1 order of magnitude above and thus significantly greater than the voltage ($\sim$1.5 V) determined by SCR model. As addressed above, a high [HF] is a first choice for fast pore etching. In our experience, however, it appears that the relation between a high [HF] and an optimal etching bias could not be as simple as predicted in SCR model.[2,3] In Fig.7, based on empirical data (with which nice pores of high aspect ratios can form), optimal biases were given as a function of [HF]. For a given [HF], if etching with a bias beyond the upper limit, conventional branching of pores will come into play;[13] if below the lower limit, no good pores of high aspect ratios can be produced due to a premature degeneration effect[4] as shown in Fig.3. Usually, due to a stronger hydrogen termination closely related to what occurs in the Helmholtz double layer [ihp (inner Helmholtz plane) and ohp (outer Helmholtz plane)], a greater [HF] leads to a stronger passivation which in turn necessitates a higher bias needed for passivation breakdown (through Helmholtz layer round pore-tips).[12,14,29,32] Note that H-passivation, as stressed

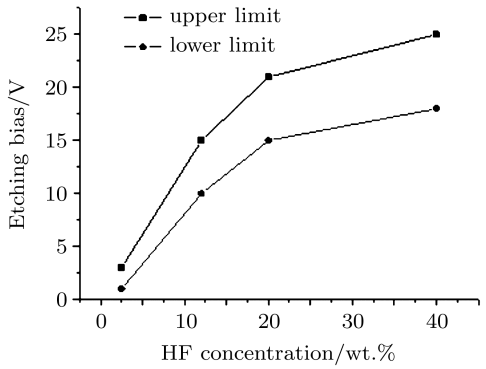


Fig.7. Based on experiential data for our patterned samples, this graph exhibits the upper and lower limit of biases suitable for stable pore formation; the optimal biases fall into the regime in between where good pores of high aspect ratios can form. A positive correlation between optimal etching bias and HF concentration is clearly visible. Note that such results are repeatable.

in CBM,[9,13] is omnipresent in our cases, since aqueous HF electrolytes are protic and they can donate dissociable H^+.[13,32] Therefore, if etching with a higher [HF], a larger bias should be firstly considered (Fig.7). To a certain degree, this could also be corroborated by the I–V curves measured: (Fig.5) due to a stronger hydrogen passivation, a higher [HF] leads to a later appearance of the plateau region (for an equal illumination). Note that the optimal bias should fall into the plateau regime, or no good pores can form, as evidenced in Figs.2 and 3.

In addition, the dependence of pore degeneration depth on [HF] in the bulk electrolyte has been reported in Ref.[4]. A negative correlation between maximum pore-depth (without degeneration) and [HF] was given there: e.g., for a 20% [HF], the maximum pore-depth achieved without a degeneration effect at the pore-tips can only be about 50 μm, quite shorter than the stable pore length (120 μm) realized in Fig.2. For a 40% [HF], the pore-depth without degeneration can be actually driven up to 200 μm (Fig.4): it even deviates much more from the implications of Ref.[4]. The results of this work and Ref.[4] seem controversial, but in fact are compatible: they are two aspects of the same thing. As mentioned in the previous paragraph, a stronger H-passivation resulting from a higher [HF] necessitates a greater etching bias [see Figs.2 and 3]. But, if etching with an equal bias of 2 or 3 V (this is exactly the case in Ref.[4]), a higher [HF] can lead only to an earlier degeneration of pores due to a stronger hydrogen termination, as implied in Fig.3(b). Therefore, with respect to the degeneration effects, our results are well consistent with those of Ref.[4]. However, no explanation was given there,[4] while here for a fixed bias we contribute an earlier deformation of pore-shapes to a stronger and faster H-termination correlated to a higher [HF].

Therefore, if [HF] is rather high (e.g.> 15%), it is likely that the contribution from Helmholtz layer should be considered:[14,29,32]

$$eV_H = B + kT[\mathrm{H_3O^+}] = B - 0.059pH \qquad (1)$$

with e being the elementary charge, V_H the potential drop in the Helmholtz layer, B a constant, k the Boltzmann constant, T the absolute temperature, $[\mathrm{H_3O^+}]$ the concentration of hydrated hydrogen ion and pH the measure of acidity. Since $pH = -\log[H^+]$, V_H can thus be calculated from Eq.(1). SCR does exist: it is known that SCR model applies well under low [HF] and low bias conditions.[1−3] Under the circumstance of high [HF], the potential drop across the Helmholtz layer V_H could probably be influential as addressed above and as supposed in a review article[14] (where the authors concluded that the contribution from SCR and Helmholtz layer is equally important). For n-Si, if not considering V_H,

$$d_{\mathrm{SCR}} = \sqrt{2\left(V_{\mathrm{bias}} + V_{\mathrm{BI}}\right)\varepsilon_{\mathrm{Si}}\varepsilon_0\mu_n\rho}, \qquad (2)$$

and if considering V_H,

$$d_{\mathrm{SCR}} = \sqrt{2\left(V_{\mathrm{bias}} + V_{\mathrm{BI}} - V_H\right)\varepsilon_{\mathrm{Si}}\varepsilon_0\mu_n\rho} \qquad (3)$$

with V_{bias} and $V_{\mathrm{BI}}(\approx 0.5\,\mathrm{V}$ for our case) being the absolute value of the applied and built-in biases, respectively, $\varepsilon_{\mathrm{Si}}$ and ε_0 the dielectric constants of Si and vacuum permittivity, respectively, μ_n the mobility of carriers, and ρ the resistivity of Si.

Hence, compared with the widely employed 3–5% [HF], a stronger hydrogen passivation originating from a higher [HF] (12–40%) could come into play in our cases: a larger potential drop in the Helmholtz layer may exert a considerable influence over our results. As implied in Eq.(3), due to the negative contribution of V_H to the SCR width d_{SCR}, for a higher [HF] (and thus a higher V_H as indicated in Eq.(1)), the etching bias V_{bias} has to rise in order to keep a fixed d_{SCR}. It should be noted that, to maintain a stable pore growth, the optimal value of d_{SCR} has to be fixed by the predefined pore-pitch, or the pores will not grow downwards in accordance with the pre-structured point nuclei. Therefore, in its revised form (Eq.(3), SCR model can justify the results obtained in this work. For example, in the case of Fig.2, the SCR width (corresponding to a 4 Ω cm resistivity and a 25 V bias) calculated from Eq.(2) (without the term V_H) equals about 3.7 μm, quite larger than the pore pitch of 3 μm, but if considering a marked contribution from V_H, equation (3) (with the term V_H) can reduce the SCR width from above 3.7 μm to about 3 μm (the value of actual pore pitch) or even much smaller, thus rendering our observations rather reasonable.[1] Unfortunately, V_H can hardly be quantitatively retrieved by experimental methods due to limited instrumentation in our lab:[12] thus, concerning the positive correlation between [HF] and optimal etching bias, equations (1)–(3) can only give a semi-quantitative interpretation here.

Additionally, in the case of Figs.2 and 4, the pore density can increase with an enhanced [HF] despite the presence of pre-textured 2D nuclei. Moreover, figures

2 and 3 indicate strongly that the pore-density can act as a function of bias, apart from [HF]: for a given [HF], the density of stable pores apparently decreases with reduced bias, as shown in Figs.2 and 3 (cf. their captions). This accords well with our previous finding,[30] where an interpretation has been given. Hence, this work can reveal that the conclusions obtained from 1D pores[27,28,31] also remain effective for 2D pores, simply due to one important nature, self-organization, possessed by both 1D and 2D pores. However, the correlation between optimal etching bias and [HF] was not investigated in our previous works (concerning 1D pores):[27,28,31] this work, with a focus on fast 2D pore formation, thus exhibits some new and critical results. For the same reason as addressed in the previous paragraphs, for 1D pores, a positive correlation between [HF] and optimal etching-bias can also be expected, though not experimentally confirmed yet. Therefore, similar investigation of 1D pores is still under way.

5. Conclusions

The etch rate can reach 400 μm/h and the aspect ratio of pores can be driven up to 250, while pore sizes span 0.5 to 2 μm. Fast pore formation depends sensitively on the anodization conditions concerning [HF], bias, illumination as well as the oxidizing-power and conductivity of electrolytes. A positive correlation between optimal bias and HF concentration was frequently evidenced and semi-quantitatively interpreted. Generally, the results deviate quite a bit from SCR principles. The formation of such 2D pores corresponds well with our previous findings where 1D pores were addressed.

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