ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2014, Vol. 59, No. 11, pp. 1328–1332. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © E.N. Abramova, A.A. Gvelesiani, A.M. Khort, A.G. Yakovenko, 2014, published in Zhurnal Neorganicheskoi Khimii, 2014, Vol. 59, No. 11, pp. 1574–1578.

PHYSICAL METHODS OF INVESTIGATION

Effect of the Content of Hydrogen Fluoride in an Etchant on the Formation of Nanopores in Silicon during Electrolytic Etching

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Received April 28, 2014

Abstract—The effect of the HF content on the formation of nanopores in silicon during electrochemical etching was studied. Nanoporous silicon layers were established to be formed only when hydrogen fluoride content in etchants (initial HF content: 49 wt %) was higher than 10–12 vol %. The mass and charge balance of the electrolytic etching of silicon was calculated, and the change in charge number of reaction (effective silicon valence) was determined depending on the HF content. The obtained data were used to propose a silicon etching model with the formation of SiF_4 and nanoporous silicon (where nanopores were formed due to the action of predominantly $(HF_2)^-$ ions).

DOI: 10.1134/S0036023614110023

Nanoporous silicon is a promising material to be used in opto- and microelectronics, chemical sensorics, and some other fields. Nanoporous silicon is usually produced via the electrochemical or chemical etching of single-crystal silicon in strong hydrofluoric acid, which has an initial HF concentration of 48–50 wt % and is diluted by water or ethanol to 20–70 vol % [1–3]. The mechanism of formation of porous silicon in the process of electrochemical etching is described in sufficient details in [1–8], but without detailed consideration of the effect of HF content in the etchant on etching.

Several mechanisms were proposed to explain the formation of nanoporous silicon on the basis of experimental data [1–13].

The most widely known mechanism is the Memming–Sckwandt–Turner mechanism [3, 4], whcih explaims the formation of nanosized pores in the course of electrolytic etching and the conditions for the transition of silicon etching from polishing etching to nanopore-forming etching.

The nanoporous silicon formation mechanism proposed in [3, 4] using the results of calculating the mass-and-charge balance of reaction for electrochemical silicon dissolution, according to which the effective silicon valence Z is determined as

$$Z = n_e/n_{Si} = ((I\tau)/e^-)/n_{Si}, \qquad (1)$$

where n_{Si} is the number of silicon atoms that pass into solution in the process of electrochemical etching, n_e is the number of unit charges transferred in the process of electrolytic etching, I is the etching current, τ is etching time, and e^- is the charge of an electron.

The value $Z \approx 2$ was determined from the calculations for a high (10 N) HF concentration. This made it possible [3, 4] to suppose that single-crystal silicon dissolves to form unstable silicon bifluoride by the reaction

$$\begin{aligned} &Si + 2HF + (2 - Z)e^+ \\ &= SiF_2 + 2H^+ + 2e^- = SiF_2 + H_2, \text{ where } Z = 2, \end{aligned} \qquad (2)$$

followed by the disproportionation reaction

$$2SiF_2 = Si_{amph} + SiF_4. \qquad (3)$$

The silicon atoms formed in reaction (3) precipitate onto the surface of a silicon plate to form a protective amorphous silicon layer with a high electroresistance, which requires that it would undergo point electrical breakdown to generate nanopores.

Hence, the decisive factor of the proposed model is the formation of unstable silicon bifluoride SiF_2. This explains the charge number of reaction (2) equal to $Z = 2$ and the possibility of formation of a protective high-resistance amorphous silicon layer (reaction (3)) to protect the surface of a silicon plate against plane-parallel stripping.

According to this theory, the process occurring on the surface of silicon in the case of its polishing etching with an HF concentration of 1 N in the absence of nanoporous silicon is described by reaction (4) and proceeds with the formation of SiF_4 (effective silicon valence $Z = 4$):

$$\begin{aligned} Si + 4HF + (4 - Z)e^+ = SiF_4 + 4H^+ + Ze^-, \\ \text{where } Z = 4. \end{aligned} \qquad (4)$$

The nanoporous silicon layer formation mechanisms, in which the electrolytic etching of single-crystal silicon was also described by reaction (4), were proposed in [5–7, 9, 13]. The hydrogen fluoride content (HF, 48–50 wt %) in the etchants used in these studies was ~40–75 vol %. The layer of adsorbed hydrogen is considered to be an insulating surface layer preventing the plane-parallel stripping of a plate. The mass-and-charge balance of electrolytic etching was not calculated, and the authors of those studies did not consider the effect of the hydrogen fluoride content in etchants on the character of etching (polishing or porous). The mentioned works emphasized that the F^- ion is an etching agent.

In the later studies [10–12], it was supposed that silicon dissolved to give SiF_2 during the formation of nanoporous silicon layers, and the surface was passivated by hydrogen [10, 11]. The authors thought that hydrogen fluoride solutions can contain different hydrogen fluoride ions and molecules in the form HF, F^-, $(HF_2)^-$, and also its higher-molecular species. agent participating in the formation of nanoporous is the F^- ion Despite the hypothesis about the existence of different groups of atoms in etchants, however, it was assumed that the major etching is F^- ion.

Relying on the aforesaid, it is possible to make the following conclusions: the authors [3, 4] attempted to relate the data of mass-and-charge balance to the electrochemical reactions involved in the formation of nanoporous silicon and the conditions for nucleation and development of pores. However, it is not clear how the effective silicon valence ($Z = 2$) correlates with the tetravalent nature of silicon. At the same time, other authors [5–7, 9, 13] did not confirmed their hypotheses by mass-and-charge balance calculations when developing nanoporous silicon formation mechanisms for tetravalent silicon.

The inconcistencies in the description of the nanoporous silicon layer formation mechanisms seem to be due to the presence of fluoride-containing ions of different compositions in etchants [10–12, 14].

To confirm this supposition, we studied the electrolytic etching of silicon in etchants with different HF contents (different contents of initial hydrofluoric acid (HF, 49 at %)), i.e., with different fluoride-containing ions [14], and calculated mass-and-charge balance.

EXPERIMENTAL

KDB 10 and KEF (0.1, 1, 10) single-crystal silicon was used as a substrate to obtain nanoporous silicon layers. Etching was performed in a conventional horizontal electrolytic cell made of fluoroplast. A platinum plate was used as a cathode.

Strong hydrofluoric acid acid (HF, 49 wt %) of extra chemically pure grade was used in this study. Ethanol or water was used as solvent. The content of initial hydrofluoric acid in etchants was varied from 6 to 90 vol %. Each etchant was used only once. Etching was performed in a galvanostatic mode at a current of 5 and 10 mA for $\tau \le 60$ min. Such etching conditions correspond to the conventional conditions for the formation of nanoporous silicon layers [1–10]. The subsequent stripping of a nanoporous silicon layer from the surface of p-type and n-type silicon plates was performed using the etchant containing ethanol, hydrogen fluoride, and acetic acid at a volumetric ratio of 7 : 3 : 0.5 and the etchant containing hydrogen fluoride, acetic acid, and nitric acid at a volumetric ratio of 5 : 5 : 1, respectively, which allowed nanoporous silicon layers to be stripped without etching the single-crystal substrate. Monitoring was performed via gravimetric measurements of the initial silicon plates before and after the treatment with the mentioned etchants. The completeness of stripping nanoporous silicon layers and their thickness were determined on a POLAM-315 optical microscope. The weight of the obtained nanoporous silicon was determined during gravimetric measurements before and after stripping a nanoporous silicon layer on a SARTORIUS-WERKE balance with a measurement precision of $\pm 5 \times 10^{-6}$ g.

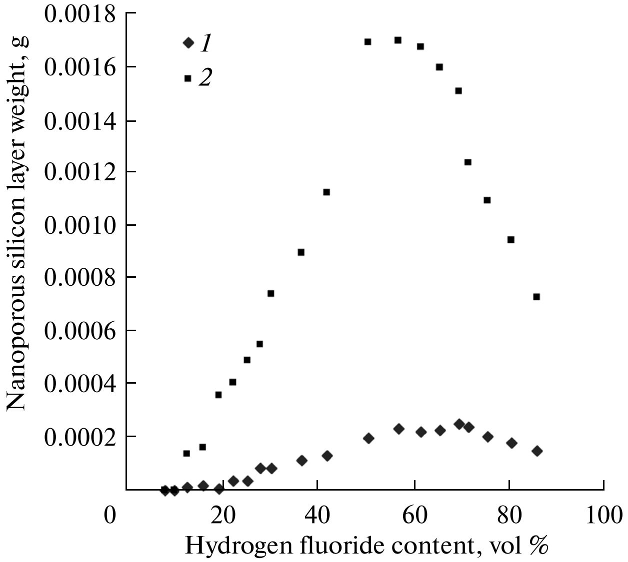

Fig. 1. Nanoporous silicon weight change versus initial strong hydrofluoric acid content in water (KDB-10, τ_{etch} = 30 min, (*1*) I_{etch} = 10 mA, (*2*) I_{etch} = 5 mA).

To solve the formulated problem, the change in the weight of nanoporous silicon layers formed during electrolytic etching was studied depending on the hydrogen fluoride content in etchants. The weight changea nanoporous silicon layers are plotted in Figs. 1 and 2 depending on the initial HF content in etchants, and the relevant scanning electron microscopy (SEM) micrographs are shown in Figs. 3–6.

The obtained data indicate that a nanoporous silicon layer begins to form on the surface of an etched plate when the strong hydrofluoric caid content in etchants exceeds 10–12 vol % and attains a maximum at ~45–60 vol % (Figs. 1, 2). These data are also confirmed by the results of electron microscopy (Figs. 3, 4). The difference sbetween the absolute values in the experiments with different solvents, silicon grades (KDB or KEF), currents (5–50 mA), and etching

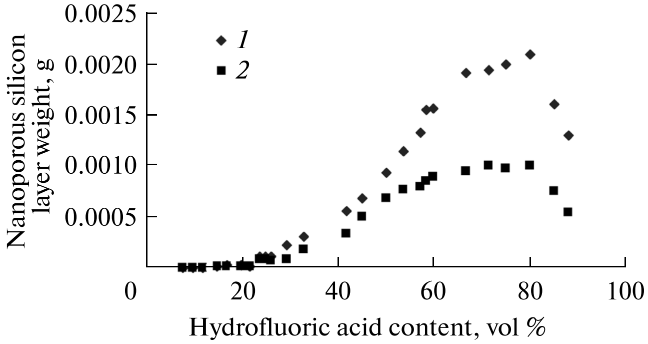

Fig. 2. Nanoporous silicon weight change versus initial strong hydrofluoric acid content in ethanol (KDB-10, $\tau_{\text{etch}} = 30$ min, (*1*) $I_{\text{etch}} = 10$ mA, (*2*) $I_{\text{etch}} = 5$ mA).

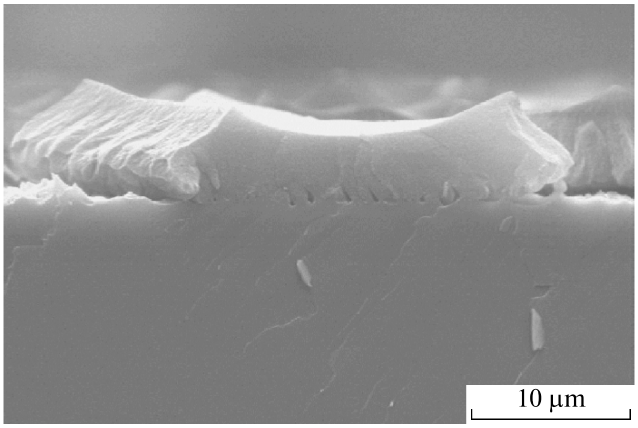

Fig. 3. SEM micrograph of a KDB-1 sample chip. Etchant: water–strong hydrofluoric acid; HF content: 40 vol %; $I_{\text{etch}} = 25$ mA; $\tau_{\text{etch}} = 30$ min.

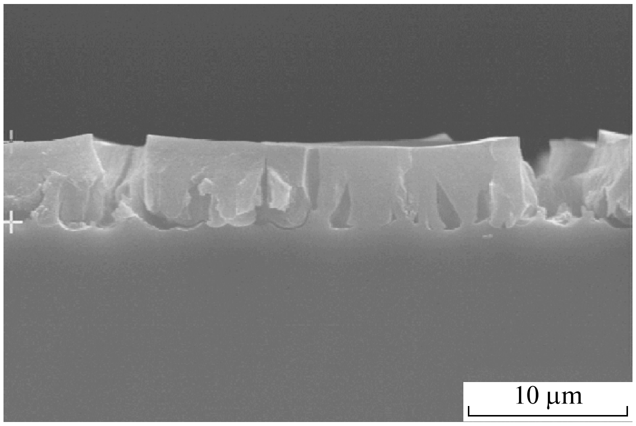

Fig. 4. SEM micrograph of a KDB-10 sample chip. Etchant: water–strong hydrofluoric acid; HF content: 40 vol %; $I_{\text{etch}} = 25$ mA; $\tau_{\text{etch}} = 30$ min.

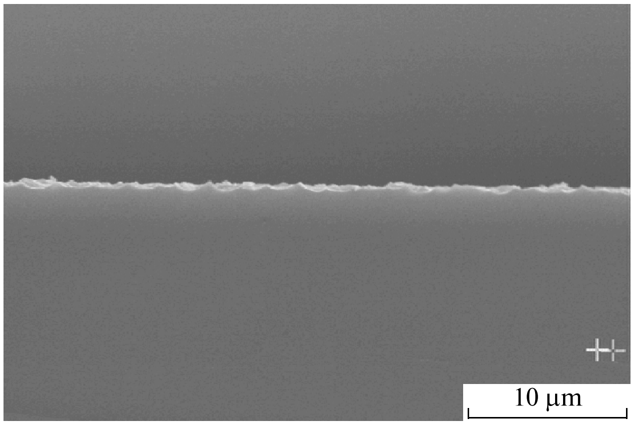

Fig. 5. SEM micrograph of a KDB-1 sample chip. Etchant: water–strong hydrofluoric acid; HF content: 6 vol %; $I_{\text{etch}} = 25$ mA; $\tau_{\text{etch}} = 30$ min.

times (15–60 min) do not have a principal character in this case.

When the initial hydrofluoric acid content in an etchant is less than 10–12 vol %, only polishing etching is observed independently of the silicon grade, the etching current, and other conditions of the experiment (Figs. 5, 6).

The calculation of the mass-and-charge balance of the electrolytic dissolution of silicon depending on the content of initial hydrofluoric acid in etchants is given in the table. From the table it can be seen that $Z = 4$ when the hydrogen fluoride content is less than 10–12 vol %, i.e., in the region where nanoporous silicon is not formed, and the etching of silicon is plane-parallel. When the initial hydrofluoric acid content increases to exceed 10 vol %, the charge number of the reaction decreases and becomes close to $Z \approx 2$ at an acid content of ~35–40 vol %.

The change in the etched off silicon amount during the formation of nanoporous silicon depending on the etching time for KEF silicon with different phosphorous contents is illustrated by Fig. 7. In addition to

Charge number of reaction (*Z*) for the electrolytic etching of silicon depending on the content of initial strong hydrofluoric acid in water and the grade of silicon

Si grade	Content of initial strong HF in water, vol %														
	6	8	10	15	17	23	34	43	50	55	60	67	75	80	88
KDB 10	4.0	4.0	3.8	3.6	3.0	2.7	2.6	2.4	2.2	2.2	2.3	2.2	2.2	2.3	2.7
KEF 0.01	4.0	4.0	3.8	3.5	3.1	2.8	2.6	2.3	2.2	2.2	2.2	2.2	2.1	2.3	2.6
KEF 0.1	4.0	4.0	3.9	3.6	3.2	2.7	2.5	2.2	2.1	2.2	2.2	2.3	2.3	2.2	2.5

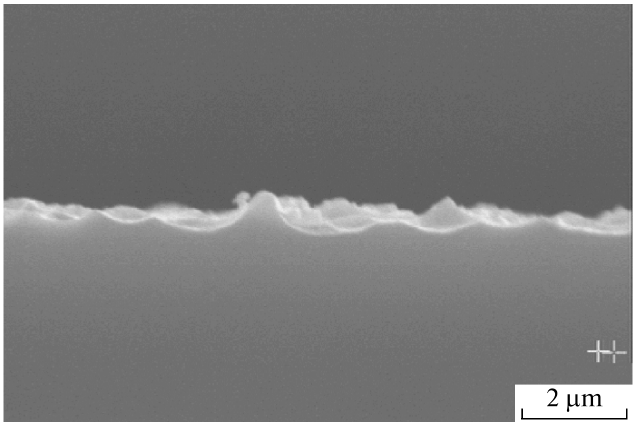

Fig. 6. SEM micrograph of a KDB-10 sample chip. Etchant: water–strong hydrofluoric acid; HF content: 6 vol %; $I_{\text{etch}} = 25$ mA; $\tau_{\text{etch}} = 30$ min.

experimental data, this figure also presents curves *1* and *2*, which show the theoretically calculated change of the removed silicon weight and are fitted by Eq. (1). These curves were obtained at specified etching current (I_{etch}) and etching time (τ_{etch}) for $Z = 2$ and 4. From this figure it can be seen that the experimental data are much closer to the theoretical dependence calculated for $Z = 2$.

RESULTS AND DISCUSSION

The analysis of the studies devoted to the development of nanoporous silicon layer formation mechanisms shows that most of the authors [3–9] suppose the dissociation of an HF molecule in a solution to follows the reaction:

$$\text{HF} \Leftrightarrow \text{H}^+ + \text{F}^-, \quad \text{p}K_\text{a} = 3.2\ [14]. \qquad (5)$$

However, some works [10–12, 14] point to the more complex behavior an HF molecule in a solution depending on the HF concentration. The behavior of HF in a highly dilute solution (the HF content is ≤1 mol/L, which corresponds to ~10–12 vol % of initial strong hydrofluoric acid) is described by Eq. (5). According to [10–12, 14], the dissociation reaction upon an increase in the HF content (>1 mol/L) proceeds as follows:

$$2\text{HF} \Leftrightarrow \text{H}^+ + (\text{HF}_2)^-, \quad \text{p}K_\text{a} = 3.86\ [14]. \qquad (6)$$

Hence, $(\text{HF}_2)^-$ ions will predominate at a high HF content in etchants (the content of initial hydrofluoric acid is higher than 10–12 vol %), although F^- ions can also exist at these HF contents [10–12].

Hence, an etchant can contain both the F^- anion (reaction (5)) and the $(\text{HF}_2)^-$ anion (reaction (6)) with equal negative charges depending on the hydrofluoric acid content. In other words, the same charge (–1) may in fact correspond to two ions with different numbers of fluoride atoms. Consequently, some or another anion appearing in strong hydrofluoric acid solutions of different concentrations has a charge of –1. However, F^- and $(\text{HF}_2)^-$ anions can transport one and two fluoride atom to the surface of silicon, respectively, to provide the process of etching. When $(\text{HF}_2)^-$ participates in the reaction (Eq. (6)), the transfer of

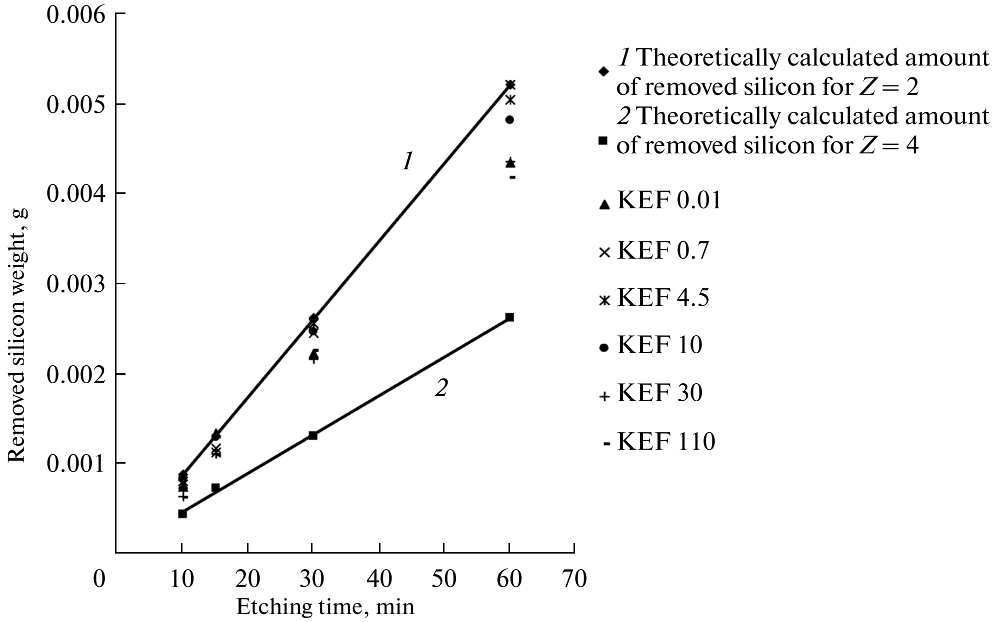

Fig. 7. Removed silicon weight versus etching time in the formation of nanoporous silicon layers. Etchant: water–strong hydrofluoric acid; strong HF content: 50 vol %; $I_{\text{etch}} = 10$ mA.

one silicon atom from a crystal into a solution will be performed by four fluoride atoms in any case despite the fact that the effective silicon valence calculated from the mass-and-charge balance is two. This resolves the inconsistence between the charge number of the electrolytic dissolution of silicon and its valence [3, 4]. Hence, the electrolytic etching of silicon with the formation of nanoporous silicon layers may follows the reaction

$$\mathrm{Si} + 2(\mathrm{HF}_2)^- + (2 - Z)\mathrm{e}^+ = \mathrm{SiF}_4 + \mathrm{H}_2\uparrow + Z\mathrm{e}^-, \quad \text{where } Z = 2. \tag{7}$$

At the same time, the experimentally observed hydrogen evolution at the anode during the formation of nanoporous silicon layers (reaction (7)) can also be explained. This reaction also explains the possible surface passivation of silicon by hydrogen.

Meanwhile, it should be taken into account that F^- ions are also present in solution in addition to $(\mathrm{HF}_2)^-$, but their amount seems to be much lower than that of $(\mathrm{HF}_2)^-$ [14]. This is likely to promote the deviation of the charge number Z from two, especially in prolonged etching (> 30 min) (Fig. 7).

Hence, the formation of nanopores in silicon occurs during its electrolytic etching only when the content of initial strong hydrofluoric acid (HF, 49 wt %) in the solution exceeds 10–12 vol % independently of the other experimental conditions.

The etching of silicon and, correspondingly, the formation of nanopores in it are provided by the action of predominantly $(\mathrm{HF}_2)^-$ ions with the evolution of SiF_4. This allows us to relate the tetravalent nature of silicon to its effective valence and to explain the evolution of hydrogen at the anode during electrolysis.

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Translated by E. Glushachenkova