Review Article

Porous Silicon Formation by Electrochemical Etching

Orest Kuntyi, Galyna Zozulya, and Mariana Shepida

Department of Chemistry and Technology of Inorganic Substances, Lviv Polytechnic National University, Bandery Str. 12, Lviv 79013, Ukraine

Correspondence should be addressed to Mariana Shepida; maryana_shepida@ukr.net

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Porous silicon (PSi) is used as an effective material in biomedicine, sensors, solar cells, electrochemical energy, microelectronics, and nanotechnology. Considering the dependence of PSi functional properties on pore geometry and porous layer architecture, it is important to develop methods for controlled pore formation. After all, in the "procession" the method of obtaining PSi → pore geometry and architecture of PSi → functional properties of PSi, the decisive role belongs to the first participant. Among the most used methods, electrochemical etching is the most suitable for the controllability of the processes of nucleation and growth of pores since it can be controlled using the value of the current density, and the results are easily reproduced. This work analyses the literature on two types of electrochemical formation of PSi by anodic etching of (1) silicon surface and (2) silicon surface, modified with metal nanostructures. A modern explanation of the process of anodic dissolution of silicon with forming a porous surface in solutions containing HF is presented. The influence of such main factors on the process of anodic formation of PSi and its morphology is analyzed: the composition of the electrolyte and the role of each component in it; anode current density and methods of its supply (stationary, pulsed); duration; exposure to lighting; and temperature. Considerable attention is paid to the illustration of the role of alcohols and organic aprotic solvents on the formation of pore geometry. The influence of MNPs and metallic nanostructures on the process of localized metal-activated anodic etching of a semiconductor is analyzed.

1. Introduction

Porous semiconductor materials have attracted special attention during the last decade in scientific and applied aspects due to their unique physical, chemical, optical, and biological properties [1–14]. The most studied is porous silicon, which is effective in such main areas of application (Figure 1): biomedicine [6, 15], sensorsics [2, 6, 15, 16], solar cells [2, 4, 8, 15], nanotechnology [2], electrochemical energetics, and microelectronics [15].

Biomedicine is the preferred choice for porous silicon due to its large surface area (200–800 m²·g⁻¹) that can be loaded with drugs or bioactive species, biocompatible and biodegradable, easy sterilization. Therefore, porous silicon is considered as an effective substrate in drug delivery, tissue engineering, biomolecular screening, biosensing, etc. [1, 2, 5, 6]. A material based on PSi–porous silicon membranes is promising [13–15]. Biocompatibility, large surface area, and open-ended geometry PSiMs allow to be used in biomedical applications in such main fields: small-format hemodialysis with high toxin elimination capabilities, implantable scaffold for cell culture, scaffold for the culture of oral mucosal epithelial cells, tissue scaffold integrated with cell-laden hydrogel biomaterials, and the culture of intestinal epithelial cells.

A sensor is based on the large surface area of PSi [2], pore nanoscale [16], and synergism of 3D semiconductor substrate with metal nanostructures deposited on it [10, 17–21]. In the latter, the gain of the SERS signal is several orders of magnitude higher than on smooth silicon wafers. This provides high sensitivity for detecting amino acids, antibiotics, and amyloid proteins, which are particularly promising in biosensors.

The surface texture of PSi acts as a light trap and improves light absorption in the long-wavelength range. This allows to increase the efficiency of solar cells and reduce the cost of the material during the production of photovoltaic devices [2, 4, 8, 15, 22]. Low thermal conductivity PSi is used
in the manufacture of thermal devices, in particular microheaters. Applications in microelectronics include optoelectronic devices such as wavelength modulators and light-emitting capacitors [15].

Promising in electrochemical power engineering are porous silicon and silicon nanowires obtained by electrochemical etching [15, 23–25]. Thus, the authors of [23, 24] have shown the efficiency of PSi for electrodes of fuel cells, SiNWs as anodes for lithium-ion batteries [25].

The works of recent years indicate the relevance of porous silicon for photocathodes in photoelectrochemical hydrogen production [26–30] and hydrogen storage [29, 31]. Moreover, PSi and 3D silicon nanocomposite are used (PSi/PtNPs [28], PSi/(PtNPs, PdNPs) [30]).

Modern methods make it possible to obtain porous silicon of ultra-small diameter (10 nm or less) and various architecture with its high surface area and tunable pore. Due to the fact that silicon is a semiconductor, PSi has been considered in recent years as a new template for the production of nanomaterials and nanocomposites [32, 33].

The physical, physicochemical, chemical, and electrochemical methods of obtaining nanoporous silicon are known (Figure 2). The most common methods of obtaining porous silicon are stain etching [34], electrochemical etching [2–4, 10, 13–15], metal-assisted electrochemical etching [35–37], and metal-assisted chemical etching [4, 8–10].

In the “procession” of the method of obtaining PSi → pore geometry and architecture of PSi → functional properties of PSi, the decisive role belongs to the first participant. Thus, the choice of the method is based primarily on the controllability of the pore formation process. Electrochemical etching and metal-assisted electrochemical etching are best to meet the requirements for obtaining porous silicon with a given geometry and PSi architecture [2, 13, 22, 37]. After all, among the factors formation of pores, the main one is the value of the controlled anode current density.

Pore formation on silicon surface by electrochemical etching and metal-assisted electrochemical etching takes place in fluoride-containing solutions, which is due to the nature of this semiconductor. Pore formation on the surface of silicon by electrochemical etching and metal-assisted carried out in fluoride-containing solutions [2–4, 13–15, 35–37]. This is due to the chemical nature of the semiconductor, primarily its high affinity for oxygen and a significant negative value of the standard electrode potential ($E^0_{\text{SiO}_2/\text{Si}} = -0.91$ V). Therefore, a dense water-insoluble oxide film is formed on the silicon surface in aqueous solutions at pH ≤ 7 and this oxide film dissolves in alkaline solutions (1) and HF solutions (2). Silicon also exhibits high chemical activity in such solutions (3, 4). So, electrochemical etching of silicon can be performed in two types of solutions. However, in an alkaline medium, in addition to the anodic reaction (3), a side reaction (5) is actively taking place. Therefore, in the aspect of controllability of local dissolution and minimization of the passage of side processes during the anodic formation of a porous surface, the most acceptable are fluoride-containing solutions.

\[
\text{SiO}_2 + 2\text{OH}^- \rightarrow \text{SiO}_2^{2-} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2[\text{SiF}_6] + 2\text{H}_2\text{O} \quad (2)
\]
Advances in Materials Science and Engineering

There were attempts to obtain porous silicon in a nonaqueous chloride medium, particularly organic solvents of the systems of LiCl–MeOH and LiCl–DMF solutions [38, 39]. However, anodization occurs when the values of currents are one or two orders of magnitude lower than in fluoride-containing solutions. However, anodization occurs when the values of currents are one or two orders less than in fluoride-containing solutions. In addition, the pores on the silicon surface are formed inhomogeneously. This is because ionized silicon at the anode hydrolyzes even in the presence of water traces in solutions (6), passivating the surface with a silicon surface are formed inhomogeneously. (Y˙hisis because fluoride-containing solutions. In addition, the pores on the silicon surface are formed inhomogeneously. This is because ionized silicon at the anode hydrolyzes even in the presence of water traces in solutions (6), passivating the surface with an oxide film based on SiO2. So, chloride systems are not used to obtain porous silicon.

\[
\text{Si}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ \quad (6)
\]

The process of pore formation during local anode etching of silicon in F⁻-containing solutions is multistage and complex. It has attracted the attention of many researchers in the last two decades [40–55]. Moreover, the electrochemical etching of the silicon surface [40–49] and Si/MNPs surface, modified with metal nanostructures [8, 50–55], has shown several differences. Therefore, they are preferably considered separately as (1) electrochemical etching method and (2) metal-assisted electrochemical etching method.

In view of the growing interest in electrochemical methods of Psi obtaining, the aim of reviews is a critical analysis of work in this area and proposals for development prospects of electrochemistry of porous silicon and intermediate products (SiNWs, SiNPs).

2. Formation of Porous Silicon by Electrochemical Etching in HF Solution

Localized etching of silicon in solutions of HF + oxidant (H₂O₂, NO₂⁻, VO²⁺, Fe⁵⁺) [34] by the mechanism is identical to electrochemical corrosion. It occurs due to the inhomogeneity of the surface in terms of electrode potential values. The heterogeneity is primarily due to the presence of dopants (D = B, P, Sb, As). So, anodic and cathodic areas appear on the silicon surface in the etching solution. In this case, silicon becomes a microanode, and fragments of silicon compounds with dopants (SiₓDᵧ) become a microcathode (Figure 3).

Electron-generating processes occur in the anode areas, which can be written by the total half-reaction (4). It leads to the local dissolution of silicon with the formation of pores. Oxidation-reduction reactions occur at the cathode areas, for example, NO₂⁻ to NO₂, VO₂⁺ to VO³⁺, Fe⁵⁺ to Fe²⁺, H₂O₂ to H₂O (7), and hydrogen formation (8).

\[
\text{SiO}_2 + 6\text{OH}^- \rightarrow \text{SiO}_2^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- (E^0 = -1.73\text{V}) \quad (3)
\]

\[
\text{Si} + 6\text{F}^- \rightarrow [\text{SiF}_6]^{2-} + 4\text{e}^- (E^0 = -1.2\text{V}) \quad (4)
\]

\[
\text{Si} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_2^{2-} + \text{H}_2 \quad (5)
\]

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (7)
\]

\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (8)
\]

A slight difference between electrode potential values (ΔE) on the surface of doped silicon between Si and SiₓDᵧ fragments in fluoride-containing solutions does not provide a large electromotive force and, accordingly, a high rate of the chemical etching process of a semiconductor substrate. So, this method produces only a thin layer (several microns) of porous silicon and low-aspect ratios between the pore depth and its width. So, only a thin layer (several microns) of porous silicon can be obtained by this method and low-aspect ratios between the pore depth and its width of porous silicon. In addition, chemical etching is spontaneous and does not meet modern requirements for the controllability of pore geometry and porous layer architecture. The electrochemical etching method allows to form PSI thick layers (>60 μm) with a high-aspect ratios of up to >100 (Tables 1 and 2). These advantages of ECE are due to the following. The etching of silicon atoms from the substrate takes place at applied external voltage, which leads to a shift in the potential value to more positive values. Accordingly, the density of the positive charge on the silicon surface increases. This leads to an increase in the concentration of F⁻ ions in the near anode layer. As a result, the rate of electrochemical (9) and chemical (10) reactions and, accordingly, the overall anodic etching process of silicon (4) increases.

\[
\text{Si} + 4\text{F}^- \rightarrow \text{SiF}_4 + 4\text{e}^- \quad (9)
\]

\[
\text{SiF}_4 + 2\text{F}^- \rightarrow [\text{SiF}_6]^{2-} \quad (10)
\]

Due to the anisotropy of doped silicon, there is local etching with the formation of pores. However, at increased iₐₐₜ₀ values, the density of the positive charge on the silicon surface reaches the critical I₁ₚ values (Figure 4), at which the anisotropy is levelled. That is, the difference in the surface inhomogeneity is levelled at the electrode potential values between the SiₓDᵧ fragments and the pure silicon fragments. This leads to uniform etching of the entire surface, i.e., its anodic polishing [2, 44, 62].

It is known that the architecture of pores and the hierarchy of the surface, as factors in the properties of porous materials, determine their main characteristics [85]. So, the controlled formation of pores geometry is a priority issue for...
Electrochemical etching of silicon. Such a method is a multifactorial process, among which the most studied main parameters for the design of the porous structure are (1) values of anode current density; (2) composition of solution; and (3) duration of anodizing. Important parameters also include the type of silicon surface (n-, p-), which is determined by the nature of dopants and doping dose. As already mentioned (Figure 3), the latter causes electrochemical inhomogeneity of the doped silicon surface, affecting pores’ initial formation. However, this issue is insufficiently studied, and individual works [13, 86, 87] do not allow to make generalizations of regularities of pore nucleation.

2.1. Influence of Anode Current Density on the Formation of Porous Silicon. Current density is the main factor of the controlling influence on the formation of porous silicon architecture. However, the nucleation and growth of pores significantly depend on the type of silicon, the HF content in the aqueous solution, the presence of alcohols and their ratio (Table 1), and the medium of organic aprotic solvents (Table 2). So, the \( i_{anode} \) value is considered in conjunction with other anodizing parameters.

Electrochemical etching is carried out mainly by stationary electrolysis [56–58, 60, 61, 63–68, 71–83]. However, attention has also been paid to nonstationary anodizing mode in recent times [59, 62, 69, 70]. But, regardless of the method of supplying current in aqueous or aqueous-alkaline solutions and the medium of organic aprotic solvents, the anode current is the main factor that influences the electrochemical rate of reaction with the formation of SiF\(_4\) (9). The latter forms the \([\text{SiF}_6]^{2–}\) complex anions at high concentrations of fluoride ions, according to reaction (10). The main parameter of influence on the rate of

<table>
<thead>
<tr>
<th>Type of silicon</th>
<th>Electrolyte composition</th>
<th>Anodization parameters</th>
<th>Characteristics of porous silicon</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Si (100)</td>
<td>47% HF:EtOH = 2:1</td>
<td>2–40 mA cm(^{-2}), 3–180 min</td>
<td>Nanoporous and the macroporous layer with thickness 2–10 ( \mu )m and porosity 53–58%</td>
<td>[56]</td>
</tr>
<tr>
<td>n-Si (111)</td>
<td>40% HF:EtOH = 1:1</td>
<td>10, 30, and 50 mA cm(^{-2}), 30 min.</td>
<td>Porous structure with pore size 0.4–0.6 ( \mu )m</td>
<td>[60]</td>
</tr>
<tr>
<td>n-, p-Si (100)</td>
<td>40% HF:EtOH = 1:2</td>
<td>10 mA cm(^{-2}), 30–60 min</td>
<td>Average pore size 20–1900 nm</td>
<td>[61]</td>
</tr>
<tr>
<td>n-, p-Si (100)</td>
<td>40% HF:EtOH = 1:3</td>
<td>20–100 mA cm(^{-2}), 15 min</td>
<td>Pore diameter: 900–1250 nm; porosity: 61–80%; pore depth: 63–69 ( \mu )m</td>
<td>[63]</td>
</tr>
<tr>
<td>n-, p-Si (100)</td>
<td>40% HF:EtOH = 3:7</td>
<td>10–50 mA cm(^{-2}), 30 min</td>
<td>Thin silicon membrane with nanopore ( \varnothing &lt; 40 ) nm</td>
<td>[65]</td>
</tr>
<tr>
<td>n-, p-Si (100)</td>
<td>47% HF:EtOH = 2:3:1</td>
<td>27 mA cm(^{-2}), 90 min; 40 mA cm(^{-2}), 200 min with mechanical stress</td>
<td>Macropore array with thickness up to 300 ( \mu )m on p-Si (100)</td>
<td>[68]</td>
</tr>
<tr>
<td>n-, p-Si (100)</td>
<td>47% HF:EtOH = 4:1:4:1:4</td>
<td>Pulses of peak current density: 10, 20, 50 mA cm(^{-2}); pulse duration ~20 ms</td>
<td>Pore size: 50–100 ( \mu )m; thickness: 54 ( \mu )m; porosity PSI: 70%</td>
<td>[69]</td>
</tr>
<tr>
<td>p-Si (111)</td>
<td>40% HF:EtOH = 3:7</td>
<td>5–110 mA cm(^{-2})</td>
<td>Three different pore morphologies: Macro-, meso-, and micropores with 30–82% ofporosities</td>
<td>[70]</td>
</tr>
</tbody>
</table>
Current density (mA·cm$^{-2}$)

Pore formation

electrochemical etching of silicon is $i_{\text{anode}}$ in conditions when delivery of $\text{F}^-$ ions is provided to the required concentration in the anodic layer and the removal of [SiF$_6$]$^{2-}$ complexes from it. So, with an increase in the value of anodic current density, there is a tendency to increase the pore diameter, their depth, porosity, and a change in the PSi architecture [62, 63, 67, 70, 71]. Thus, in [63], it was shown that arrays of macropores and mesopores are formed by $i_{\text{anode}} < 60$ mA·cm$^{-2}$, with a diameter, pore depth, and porosity of 265–760 nm, 58–63 μm, and 44–61%, respectively. At $i_{\text{anode}} > 60$ mA·cm$^{-2}$, the macropore arrays are formed with a diameter of 900–1250 nm, a depth of 63–69 μm, and a porosity of 61–80%. A similar effect of the anodic current on the main characteristics of PSi was observed in [67, 70]. However, this regularity is observed only in a specific range of $i_{\text{anode}}$ values in other same conditions. After reaching the critical numbers of this value, the depth of the porous layer may decrease (Figure 5). This is primarily due to the diffuse control of reactions (9) and (10). So, in the case of $\text{F}^-$ ions "deficit" in the anodic layer, the silicon surface is passivated by reaction

$$\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4\text{e}$$ (11)

Anodizing in the impulse mode of electrolysis makes it possible to accelerate diffusion processes during the pause period, which prevents the passivation of the silicon surface. It was shown in [62] that the formation rate of a porous layer

Table 2: Conditions for the formation of porous silicon by electrochemical etching in solution with organic aprotic solvents.

<table>
<thead>
<tr>
<th>Type of silicon</th>
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<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si (100), n-Si (111)</td>
<td>2 M HF + 0.25 M TBAP in AN</td>
<td>7 mA·cm$^{-2}$, 15–60 s, 20, 30 min</td>
<td>Microporous structure with triangular pits</td>
<td>[72]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>2–10 M HF + 0.1 M TBAP in DMSO, DMF or AN</td>
<td>2–50 mA·cm$^{-2}$, from 4 min to 3 h</td>
<td>Macropores</td>
<td>[73]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>HF : DMF = 5:1; 7:1; 10:1</td>
<td>2–15 mA·cm$^{-2}$</td>
<td>Macropores</td>
<td>[74]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>49% HF : DMDSO, H$_2$O in 10:30</td>
<td>From 13 to 37 mA·cm$^{-2}$, 15–35°C</td>
<td>Macropores, porosity: 44%; SiNWs</td>
<td>[75]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>HF, DMDSO, and H$_2$O in various volume ratio</td>
<td>Double-step $i_{\text{anode}}$ (11 mA·cm$^{-2}$, 5 min and 17 mA·cm$^{-2}$, 30 min), 25°C</td>
<td>Silicon wires with average length and Ø 16.3 and 0.71 μm, respectively</td>
<td>[76]</td>
</tr>
<tr>
<td>Multicrystalline Si of p-type</td>
<td>HF in DMSO</td>
<td>Galvanostatic mode under 5 mA·cm$^{-2}$, 10 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si (100), p-Si (111)</td>
<td>HF and TBAP in AN, PC, or DMF; H$_2$O was present in the organic solutions</td>
<td>10–500 mA·cm$^{-2}$, 30 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si (100), p-Si (111)</td>
<td>50% HF and TBAP in AN, PC, DMF or DMSO</td>
<td>10 mA·cm$^{-2}$, 10 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>49% HF in DMF or DMSO; HF : DMF = 3:7; 3:4; HF : DMDSO = 4:3; 3:4</td>
<td>10–300 mA·cm$^{-2}$, 18 ± 1°C, 16–30 μm·min$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>HF (49%); AN = 1:14</td>
<td>2.1–10.0 mA·cm$^{-2}$, 10 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Si (100), p-Si (100)</td>
<td>HF (49%): DMF = 1:10</td>
<td>Galvanostatically, 2.5, 5, 7.5, 10 mA·cm$^{-2}$, 15, 30, 45, 60 min, using halogen or LED light</td>
<td>Relatively smooth cylindrical pores with Ø 0.1–1.3 μm, depth = 5–9 μm</td>
<td>[82]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>HF : EtOH : DMF = 1:1:1</td>
<td>Galvanostatically, 100 mA·cm$^{-2}$, 5 min, 18 ± 1°C</td>
<td>Macroporous layer: Ø = 1–2 μm</td>
<td>[83]</td>
</tr>
<tr>
<td>p-Si particles, Ø≈650 μm</td>
<td>10% HF in DMF</td>
<td>Anode etching in the barrel with Ø = 3.5 cm, length = 3 cm, 15–100 mA, 0°C, 0.5–2 h</td>
<td>Thickness of the porous layer ~6.4 μm. Ø &lt; 100 nm</td>
<td>[84]</td>
</tr>
</tbody>
</table>
is two times higher at the pulse current as compared to the stationary one under the same other anodizing conditions.

By depending on pore geometry and porous layer thickness from \( i_{\text{anode}} \), the PSi architecture can be designed. Thus, the authors of [70] showed the possibility of forming different types of bursting multilayer structures with different morphologies (macro-, meso-, and micropores) and propagation from 30 to 82% by changing the anodic current density.

The anodic density factor is not the same for silicon with different crystalline unit cell. Thus, the steric factor for F ions to Si surface atoms is more noticeable for Si (111) than for Si (001) crystalline orientation (Figure 6). So, the pore geometry is different for the same \( i_{\text{anode}} \) values (branched in Si (111) and straight in Si (001)). For Si (001), there is also a higher rate of electrochemical etching [71].

It follows from the literature analysis that the anodic current density, as an extrinsic parameter of pore formation, acts simultaneously with intrinsic parameters, which include, first of all, the nature of the doping type, doping dose, and silicon crystalline orientation. However, the effect of semiconductor crystalline orientation on pore morphology and sizes is actually limited by work [71].

2.2. Influence of Solution Composition on Anodizing Process. The main components of aqueous solutions for PSi obtained by electrochemical etching are fluoric acid and alcohols (Table 1). In a nonaqueous medium, that is, in organic aprotic solvents (Table 2), a conductive application (TBAP) is contained (in addition to HF). Each of these components performs a specific function, so their content affects the anodizing process and, accordingly, the formation of PSi.

2.2.1. Influence of Alcohols. Fluoric acid is the main reagent in electrochemical reaction (9), chemical reactions of the
formation of the $[\text{SiF}_6]^{2-}$ complex (10), and dissolution of $\text{SiO}_2$ on a silicon surface (2). Therefore, HF concentration should ensure the passage of these processes at the appropriate value of $i_{\text{anode}}$. However, fluoric acid is also involved in a side process—the reaction with silicon, which leads to the formation of hydrogen (12). During growth, gas bubbles spontaneously create diffuse limits when they adsorb on the lateral, often rough pore surface. As a result, it is more difficult to control the formation of PSi. The alcohols are added to the anodizing solution, which limits this undesirable process (Table 1). Alcohol molecules, which adsorb on the silicon surface, lead to a decrease in the surface tension of the solution. This reduces the size of hydrogen gas bubbles and facilitates their removal from the pores. As a result, diffuse processes and, in particular, the penetration of HF are intensified. In addition, the adsorption of alcohols weakens the chemical etching of silicon, promoting the formation of a relatively smooth side surface of the pores (Figure 7).

$$\text{Si} + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 4\text{H}^+ + \text{H}_2 + 2e^- \quad (12)$$

The effect of the nature of alcohols on the electrochemical etching process of silicon is little-studied. In separate works [57, 58, 65], a comparative characteristic is given of the dependence of the pores depth and their formation rate on the length of the carbon chain of the single-atom alcohol molecule. Thus, it was shown in [57] that in the series of MeOH–EtOH–PrOH–BuOH, there is a tendency to a slight increase in thickness of the porous layer, while in [58], it is focused on a significant rise of pore depth.

2.2.2. Influence of the Environment of Organic Aprotic Solvents. The study of the influence of organic aprotic solvents on the electrochemical etching of silicon began more than two decades ago using the example of an acetonitrile medium [72]. Subsequently, the electrochemical formation of porous silicon was studied in fluoride-containing solutions based on AN [73, 78, 79, 81], DMF [73, 74, 78–80, 82–84], DMSO [73, 75–77, 79, 80], and PC [78, 79]. A significant influence of organic aprotic solvents on the process of controlled anodizing of silicon with the possibility of obtaining specified pore geometries and PSi morphology is shown. However, the use of solutions of different compositions and concentrations and the difference in the modes of electrochemical etching and the difference in the types of semiconductor surface do not allow a systematic analysis of the influence of such organic solvents on the formation of porous silicon architecture (Table 2). So, we focus on the features of their action in comparison with water and alcohols. Molecules of organic aprotic solvents are characterized by a high donor number in the presence of an N- (AN) or O-donor atom (DMF, DMSO, PC). The presence of a free-electron pair and a partial negative charge promotes the formation of a hydrogen bond with the hydrogen atoms of the HF molecule, for example, $\text{H}_3\text{C}≡\text{N}$: $\rightarrow \text{Si}$; $\text{H}_3\text{C}≡\text{S}$ $\rightarrow \text{Si}$. So, they perform the surfactant function, weakening side chemical processes:

$$\text{(H}_3\text{C)}_2\text{S} = \text{O} \cdots \text{H} \leftrightarrow [\text{(H}_3\text{C)}_2\text{S} = \text{OH}]^+ + \text{F}^- \quad (13)$$

Figure 7: SEM micrographs of macropores formed in HF solutions containing various types of alcohol. Cross-sectional views of silicon anodized in a 10–20 $\Omega$cm prepatterned p-type silicon at 14 mA cm$^{-2}$ for 1 h in HF solutions containing (a) MeOH, (b) EtOH, (c) PrOH, and (d) BuOH [58] under the terms of the creative commons CC BY license.
The aforementioned causes the following features of the effect of organic aprotic solvents on the electrochemical etching of silicon: directional vertical formation of a predominantly smooth and cylindrical pore surface; proportional dependence of the pore depth on the $i_{\text{anode}}$ value; obtaining a thick porous layer and a large ratio of pore depth/diameter; and the possibility of high rate anodizing. (The formation of vertical and smooth pores was observed regardless of the nature of the organic aprotic solvent: AN [73, 78], DMF [73, 74, 78, 80, 82, 83], DMSO [73, 75–77, 80], and PC [78].) The tendency to such pore geometry is observed at the stage of nucleation and at the beginning of growth (Figures 8(a)–8(e)) and during long anodization [74, 75, 77, 78]. The work [73] shows that the pores have almost the same depth and grow parallel to each other.

After nucleation of pores, their growth in time is almost linear (Figure 8(f)). Close to linear is also the dependence of electrochemical etching rate (Figure 9), which is identical to the growth rate of the porous layer, on the $i_{\text{anode}}$ value.

The work [80] shows the high technological prospects of dimethylformamide and dimethylsulfoxide solutions in obtaining PSi by anodizing. So, in HF–DMF and HF–DMSO, the rate of electrochemical etching reaches 16–30 $\mu$m·min$^{-1}$ with the formation of a relatively homogeneous porous layer up to 180 $\mu$m. Moreover, the ratio of pore depth/diameter is controlled and very high—up to 110.

2.3. The Influence of Anodizing Duration and Energy Intensification Factors of the Porous Silicon Formation. The anodizing duration is one of parameters for the controlled PSi formation. However, this value should be considered together with other important factors, primarily the composition of the electrolyte and the anode current density. The pores geometry, the morphology of the porous layer, and the concentration of components in pores are unstable over time. This causes a change in $i_{\text{anode}}$, as the $i_{\text{anode}}$ value is set on the initial area of the silicon surface. The latter increases during anodizing, so the real local $i_{\text{anode}}$ value does not correspond to the set current density. In addition, its distribution on the porous surface is different. The concentration of fluoride ions will also be different due to diffuse restrictions caused by the inhomogeneity factor of the electric field in the pores. As a result, the dynamics of electrochemical etching of silicon changes over time. Therefore, it is advisable to consider in the tendency aspect of the dependence of the etching rate and an increase in the diameter and pores depth on the anodizing duration.

The change in the electrochemical etching rate of silicon and the pore geometry over time has not been systematically studied, which can be explained by the multifactorial nature of the anodizing process. In some works [44, 61, 62, 71, 80, 82], such dependence is fragmentarily considered as one of the characteristics of PSi formation. Thus, [44, 62, 80, 82] show a proportional increase in pore depth over a long time period. Moreover, the increase in pore depth significantly depends on the $i_{\text{anode}}$ value (Figure 8(f)).

The energetic factors influencing the electrochemical etching process of silicon include temperature, light, and mechanical stress. Silicon anodizing is carried out mainly at room temperature (Tables 1 and 2). Higher temperatures are not used because the adsorption of alcohol molecules and organic aprotic solvents is weakened, leading to the
intensification of side processes, including etching with the release of hydrogen gas. As shown in [62, 84], low temperatures are effective for the formation of thick porous layers with a small pore diameter. (Yhus, the PSi obtained at 0°C had a pores depth of one and a half times greater and almost the same pores diameter as compared to room temperature [62].

In [40], the influence of short-wavelength light on the passage of reactions is considered, in particular, on selective and anisotropic etching, which lead to nano- and micro-structuring of the silicon surface. So, illumination of silicon wafers surface is often used to design and intensify the anodizing processes at the nucleation stage and growth of a porous layer [19, 63, 66, 82]. Mechanical action, which leads to the localization of silicon surface defects by scratching [43] or mechanical stresses [68], promotes directional electrochemical etching.

3. Formation of Porous Silicon by Metal-Assisted Electrochemical Etching

One of the conditions for pores nucleation and their subsequent directed growth during chemical or electrochemical etching of a silicon surface is its electrochemical inhomogeneity. As noted earlier, such inhomogeneity is caused by alloying components, which in fluoride-containing solutions lead to the formation of anodic and cathodic regions. However, the ΔE value between them is small, which does not provide silicon’s proper chemical etching rate. Therefore, electrochemical etching is more effective when its rate corresponds to the technological criteria for PSI obtaining. However, the ECE method is very sensitive to the nature of the alloying components, their content, and the orientation of the crystal lattice faces. Accordingly, the geometry of the pores and the architecture of the obtained porous layers depend on these factors. Thus, in the last decade, the method of metal-assisted electrochemical etching of silicon has attracted considerable attention (Table 3).

MAECE is a modification of the widely used metal-assisted chemical etching method of silicon [4, 8, 9, 50, 53, 91–93]. The latter method can be considered as contact electrochemical corrosion of a substrate with the Si/MNPs metals nanostructures deposited on it. Preferably M— are noble metals (Au, Ag, Pd, Pt) for which $E^{0}_{M^{n+}/M} \geq 0.8 \text{V}$. This causes the high value of $\Delta E^{0} (\geq 2 \text{V})$ of galvanic pairs formed in fluoride-containing solutions between metal particles and silicon. Accordingly, a high rate of MACE is provided. In addition, etching is localized, and the pore geometry reproduces the shape and size of metallic nanostructures (nanoparticles and nanoporous films), which provides variety in PSI design. Metal-assisted chemical etching is carried out in similar solutions as chemical etching, i.e., HF + oxidant (mainly $\text{H}_{2}\text{O}_{2}$). Accordingly, the one-type processes take place - (7, 8) at the cathodic and (9, 10) at the anodic areas. At the same time, those processes’ speed and etching direction significantly depend on the concentrations of fluoride and oxidant.

MAECE allows controlling the dissolution rate of silicon by changing the anodic current density. Thus, the etching direction and PSI obtaining of a given architecture is controlled [4, 36, 37, 50–55, 88–90]. Thereby, high values of $i_{\text{anode}}$ lead to the formation of pores in a perpendicular direction to the surface, and small values—along the (100) directions [50]. In this case, silicon etching occurs at the Si/MNPs interface under the MNPs, as shown schematically in Figure 10 (left—during MACE, right—during MAECE).

During MAECE, in contrast to MACE, etching of the pores lateral surface also occurs due to anodic dissolution. As a result, conical pores are formed (Figure 11). So, comparing ECE (Figures 11(a) and 11(b)), MAE

![Figure 9: Macropore etching rate dependence on the current density in the electrolytes containing: (a) (blue triangle) HF: DMF = 3 : 7, (red spot) HF : DMF = 3 : 4, (black square) HF : DMF = 4 : 3; (b) [HF] = 43 vol% and different organic solvents: (red square) DMF; (black spot) DMSO [80] under the terms of the creative commons CC by license.](image)
The authors emphasize that the main difference of the latter method lies in the synergism of the activating action of the metal and the external electric field. This allows the controlled PSI formation with a wide range of pore depth and aperture size.

A feature of MAECE, in addition to the high rate of the process, is the wide design possibilities of PSI due to the geometry of deposited metal nanoparticles on a silicon surface. The nanostructured metal precipitate of the Si/MNPs system is a kind of matrix that predetermines the architecture layers. So, the main thing is to deposit MNPs of a given geometry on a silicon surface. For controlled deposition of nanostructured metals, the method of galvanic replacement [92–95], electrolysis [96–98], and sputtering [54, 90, 91, 99] are used. However, these methods do not yet provide the formation of the given geometry and topography and do not always meet the technological criteria. Yes, the galvanic replacement is technologically simple. But, the electrochemical processes that take place on the Si surface are spontaneous and multifactorial, which makes it difficult to control the deposition of nanostructured metals. Electrodeposition is characterized by effectiveness in the MNPs formation of a given geometry, but technologically it has some disadvantages—the difficulty in ensuring reliable electrical contact of the silicon surface. Sputtering requires complex and expensive equipment, which is not economically and technologically justified today.

### Table 3: Metal-assisted electrochemical anodic etching conditions for the formation of porous silicon.

<table>
<thead>
<tr>
<th>Type of silicon</th>
<th>Metal assisted</th>
<th>Electrolyte composition</th>
<th>Anodization parameters</th>
<th>Characteristics of porous silicon</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Si (100)</td>
<td>AgNPs</td>
<td>HF:H₂O₂:EtOH = 25:10:33</td>
<td>1–40 mA·cm⁻², 30 min, 20°C</td>
<td>Sponge-like PSI layer—at low current density, mosaic layer—at high current densities</td>
<td>[36]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>AgNPs</td>
<td>4.8 M HF</td>
<td>4 and 10 mA·cm⁻²</td>
<td>Nanoporous layer. Ø &lt; 100 nm</td>
<td>[37]</td>
</tr>
<tr>
<td>p-Si (111), p-Si (110), n-Si (111)</td>
<td>AgNPs</td>
<td>3.6 wt % HF</td>
<td>0.2 mA·cm⁻², 90 min; 4 mA·cm⁻², 4 min, 20°C</td>
<td>Nanoporous layer. Ø &lt; 100 nm along &lt;100&gt; directions</td>
<td>[50]</td>
</tr>
<tr>
<td>p-Si (100), p-Si (111)</td>
<td>AgNPs CuNPs</td>
<td>3.4 wt % HF</td>
<td>0.2 mA·cm⁻², 5 mA·cm⁻², 20°C</td>
<td>Nanoporous layer. Ø &lt; 100 nm nanowires Ø &lt; 100 nm</td>
<td>[51]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>AgNPs</td>
<td>HF:H₂O₂:EtOH = 15:10:33; HF-40%, H₂O₂-30%, EtOH-99.7%</td>
<td>1, 5, 10 and 15 mA·cm⁻², 30 min, 20°C</td>
<td>Porous mosaic structure</td>
<td>[52]</td>
</tr>
<tr>
<td>p- c-Si</td>
<td>AgNPs</td>
<td>HF:H₂O₂:H₂O = 3:10:24</td>
<td>5.7 mA·cm⁻² for 60 min</td>
<td>Macropores layer</td>
<td>[53]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>AgNPs</td>
<td>HF:DMSO:H₂O I. 2:5:5 II. 2:5:10 III. 2:5:15</td>
<td>25°C, I. 36 mA·cm⁻², II. 25 mA·cm⁻², III. 22 mA·cm⁻²</td>
<td>Ordered porous silicon and silicon wire arrays</td>
<td>[88]</td>
</tr>
<tr>
<td>p-Si (100)</td>
<td>AgNPs</td>
<td>HF:H₂O₂:EtOH = 25:10:33; HF-40%, H₂O₂ - 30%, EtOH - 99.7%.</td>
<td>1 mA·cm⁻² and 30 mA·cm⁻², 20°C, 30 min</td>
<td>Mosaic porous silicon</td>
<td>[89]</td>
</tr>
<tr>
<td>n-Si (100)</td>
<td>AgNPs AuNPs</td>
<td>6.6 M HF and 0.08 M H₂O₂</td>
<td>20°C, 60 s photoelectrochemical etching irradiance: 17.3 mW·cm⁻²</td>
<td>Mesoporous layers</td>
<td>[55]</td>
</tr>
<tr>
<td>n-Si (100)</td>
<td>PtNPs Porous nanoﬁlms of Ni, Zn, Au</td>
<td>HF:EtOH = 1:2</td>
<td>30 mA·cm⁻², 10 min, back illumination by halogen lamp</td>
<td>Columnar pores with a diameter in the range of several-hundred nanometers</td>
<td>[90]</td>
</tr>
<tr>
<td>p-Si (100), n-Si (100)</td>
<td>Nanoporous 20 nm-thick Au films</td>
<td>4 M HF</td>
<td>8 mA·cm⁻², 10 min; 12.5 mA·cm⁻², 10 min; 23 mA·cm⁻², 5 min; 23 mA·cm⁻², 5 min; 28 mA·cm⁻², 5 min</td>
<td>Si nanowires, porous Si nanowires, a porous Si layer without Si nanowires and porous Si nanowires on a thick porous Si layer</td>
<td>[54]</td>
</tr>
</tbody>
</table>

**Figure 10:** The model illustrates the etching mechanism of the metal–catalyzed electrochemical etching (MCECE) [53] under the terms of the creative commons CC by license.
4. Conclusions

Porous silicon as a semiconductor material with a large surface area and a variety of its architecture is characterized by wide functional properties, which allows its wide usage in biomedicine, sensors, solar cells, electrochemical energy, microelectronic, nanotechnology, etc. In the “cortege”: the method of obtaining PSi → pore geometry and architecture of PSi → functional properties of PSi, the decisive role belongs to the first participant. Therefore, controlled methods of obtaining PSi are one of the priority directions in the last decade of research in this material. Electrochemical etching meets these criteria, and it is technologically promising due to the rapid production of porous silicon.

Anode etching in HF solution is based on localized PSi formation, which is due to electrochemical inhomogeneity of the silicon surface. The latter is due to the anisotropy of doped silicon or metal nanoparticles deposited on silicon. The use of such varieties for the formation of a porous layer of silicon by the methods of (1) electrochemical etching and (2) metal activated electrochemical etching is mostly described in the literature.

Porous silicon formation by electrochemical etching, which is based on the electrochemical inhomogeneity of the doped semiconductor surface, was studied in cases of aqueous solutions and organic solvents. This is a multifactorial process, and regardless of the medium, the main factors influencing the controlled formation of pore geometry and PSi architecture are the following: composition of solution; values of anode current density and methods of its supply (stationary, pulsed); and duration of anodizing, lighting, and temperature. The important parameters include the type of silicon surface, which is due to the nature of dopants, doping dose, and silicon crystalline orientation. However, representation of these issues in the literature is not enough.

The formation of porous silicon by metal-assisted electrochemical etching is a modification of the widely used and widely described in the literature metal-assisted chemical etching method of silicon. An essential feature of MAECE is that the controlling of PSi formation occurs by changing the anodic current density: high \( i_{\text{anode}} \) values lead to the formation of pores in a perpendicular direction to the surface, and small \( i_{\text{anode}} \) values—along the (100) directions. Since silicon etching occurs at the Si/MNPs interface under...
the MNPs, the pore sizes and architecture of PSi are dependent on the topography of the nanostructured metal on the substrate surface. Si/MNPs are obtained mainly by the galvanic replacement method, which does not provide a fully controlled formation of MNPs in the aspect of given geometry and distribution over the surface of silicon. Thus, today this issue is one of the limiting factors for the wide practical usage of MAECE.

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>n-ProOH</td>
<td>n-propanol</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>n-butanol</td>
</tr>
<tr>
<td>n-PeOH</td>
<td>n-pentanol</td>
</tr>
<tr>
<td>2-ProOH</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>Tert-butanol</td>
</tr>
<tr>
<td>CTAC</td>
<td>Hexadecyltrimethylammonium chloride</td>
</tr>
<tr>
<td>TBAP</td>
<td>Tetrabutylammonium perchlorate</td>
</tr>
<tr>
<td>$E$</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>GR</td>
<td>Galvanic replacement</td>
</tr>
<tr>
<td>$i_{\text{anode}}$</td>
<td>Anode current density</td>
</tr>
<tr>
<td>MACE</td>
<td>Metal-assisted chemical etching</td>
</tr>
<tr>
<td>MAECE</td>
<td>Metal-activated electrochemical etching</td>
</tr>
<tr>
<td>ECE</td>
<td>Electrochemical etching</td>
</tr>
<tr>
<td>MNCs</td>
<td>Metal nanoclusters</td>
</tr>
<tr>
<td>MNPs</td>
<td>Metal nanoparticles</td>
</tr>
<tr>
<td>NWs</td>
<td>Nanowires</td>
</tr>
<tr>
<td>PSi</td>
<td>Porous silicon</td>
</tr>
<tr>
<td>PSiMs</td>
<td>Porous silicon membranes</td>
</tr>
<tr>
<td>SERS</td>
<td>Surface-enhanced Raman scattering</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
</tbody>
</table>

**Data Availability**

All related data are mentioned in the manuscript with references.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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**References**


