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Porous silicon preparation by electrochemical etching in ionic liquids

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Abstract: Anodic etching of n-type {111} silicon in ionic liquid (IL) systems ([RMIM][X], R = H, Bu; X = BF_4^- , PF_6^-), realized under galvanostatic conditions and room temperature, allowed the formation of porous silicon surfaces with different pore morphology depending on the etching time, current density and the IL used. The study of the effect of water content in IL on the etching process has shown water content of 1% to be optimal. The role of the anion on the etching process was elucidated using 1-methylimidazolium tetrafluoroborate ([HMIM][BF_4]) and 1-methylimidazolium hexafluorophosphate ([HMIM][PF_6]) IL systems. [HMIM][BF_4] was found to be most efficient for the formation of silicon nanostructured array with a pore size of 30-80 nm. The thus prepared porous silicon samples show fluorescence in blue light (475 nm). The NMR spectra of [HMIM][BF_4] ionic liquid before and after etching does not show

noticeable changes, which makes possible to consider this IL as a potentially recyclable etching agent.

Introduction

Silicon-based materials, in particular porous silicon (PSi), are of high demand in the materials science. Besides dominating solar cells market^[1-4] silicon and its porous form are widely used in various research fields such as optoelectronics,^[5-6] biosensing^[7-9] and biomedical applications.^[10-16]

The primary method of obtaining PSi is oxidative etching of a non-porous silicon precursor in hydrofluoric acid solutions.^[17] In electrochemical version of silicon etching in fluoride solutions the process can be carried out both in potentiostatic and in galvanostatic mode; the latter option is often preferable because of easier control of the process.^[9]

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3 Although the extreme safety hazards of hydrofluoric acid for nature and humans are
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7 well known,^[18] using HF in PSi production seems unavoidable since it is needed for
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10 removal of native oxides on silicon surface and for binding silicon in etching products.
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14 The search for different approaches for replacing HF acid by more environmental-
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17 friendly agents is of great interest in the field of silicon etching^[19,20] and in other areas of
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20 materials science.^[21-23]
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25 A method of silicon etching replacing HF with silicophilic reagents, in particular, salts of
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28 pyridine or N-aromatic bases with tetrafluoroboric acid in an organic solvent was
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31 previously proposed.^[19] It should be noted that for etching silicon in such systems, it is
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34 necessary to use the salts solutions of high concentration. In this regard, etching
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37 systems based on protic ionic liquids,^[24] combining solvent and supporting salt in one
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40 compound^[25-26] that were successfully used in surface electro-chemistry^[27] might be
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Besides entirely merited attention and wide use in almost all chemistry-related areas,^{[28-}

^{31]} ionic liquids permit to address and in many cases to improve very important ecological issues.

In this work, we propose a simple, environment-friendly, and efficient technique for preparing porous silicon by means of an HF-free electrochemical etching in the ionic liquid medium (primarily derivatives of 1-methylimidazolium, [HMIM][BF₄]). This method allows one to prepare a uniformly porous silicon surface with the possibility of controlling the pore size.

Results and discussion

The [HMIM][BF₄] ionic liquid was synthesized by stirring 1-methylimidazole with tetrafluoroboric acid in appr. 1:1 molar ratio with minimal excess of 1-methylimidazole to prevent the presence of HBF₄ in product. After that, the resulting solution was evaporated, washed with ethyl acetate and dried under vacuum according to ^[32].

Several samples of [HMIM][BF₄] were then prepared with a water content of 1%, 5%, and 10%, controlled by Fischer titration.^[33] Synthesized in the similar way [HMIM][PF₆]

was conditioned to water content of 2%. In contrast to dry ILs, such wet ionic liquids (w-IL) remain liquid at room temperature; this enables using them for silicon etching under the ambient conditions without heating which is otherwise needed to liquefy these ILs.

These w-IL were then tested for etching silicon and revealing the influence of current density and etching time on the morphology of the obtained samples.

A polished n-type (111) oriented single-crystal silicon wafer was used (Fig. S1) for this purpose. The etching was carried out at room temperature in a galvanostatic mode, using a specially designed polytetrafluorethylene (PTFE) cell (Fig. 1). The cell was fitted with a PTFE nut with a 4 mm hole protecting the Si sample so that the etching area, limited by the hole, remains constant throughout all experiments. A platinum grid was used as a cathode.

Figure 1. Photograph of a silicon etching setup (A), the scheme of assembling the etching PTFE cell (B), a polished silicon wafer used in the experiments (C), and a PTFE cell (D) for mounting the sample for etching.

We found that etching in 1% [HMIM][BF₄] w-IL system at a current density $j = 8 \text{ mA/cm}^2$ during 30 min results in the development of significant roughness of the surface of silicon wafer (Fig. 2 left). Further increase in etching time leads to the formation of a porous surface.

In particular, a uniform mesoporous surface with the irregularly shaped pores sized of $31 \pm 2 \text{ nm}$ separated by $8 \pm 1 \text{ nm}$ walls was obtained after a 5 hours etching (Fig. 2 right).

Figure 2. Scanning electron microscope (SEM) images of porous silicon obtained by etching in 1% [HMIM][BF₄] w-IL system at a current density 8 mA/cm² during 30 minutes (left) and 5 hours (right).

When etching in HF-based systems, higher current densities are known to increase the pore size and depth.^[34-35] This trend was also observed during the etching of silicon in [HMIM][BF₄]-based w-IL system. Fig. 3 shows an scanning electron microscope (SEM) picture of the sample obtained by etching a silicon wafer at $j = 24 \text{ mA/cm}^2$ for 1 hour.

It can be seen that the pores at thus prepared homogeneous porous surface are larger than those observed after etching for 5 hours at $j = 8 \text{ mA/cm}^2$. Now, the pore size and

the thickness of the separating walls are increased up to 79 ± 6 nm and 21 ± 1 nm, respectively. It is noteworthy that the majority of the cells formed are 4 or 5-faceted.

Figure 3. SEM image of porous silicon obtained by etching in 1% [HMIM][BF₄] w-IL system within 1 hour at a current density of 24 mA/cm².

During etching gas formation is observed, but the change in the amount of water cannot be determined within the measurement accuracy, and after the process the system remains liquid. It contains white amorphous solid.

The increase of water content in the IL significantly affects the nature of etching. So, at 5% water in IL the morphology of the formed layer changed now resembling to a

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3 network of bulges around deeper etching zones of commensurate size (Fig. S2). This
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7 case is intermediate between the cellular structure (Fig. 2, 3) and a spongy surface
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10 when etching is achieved with higher water content (10%) (Fig. S3).

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15 Elucidating the role of anion in the etching process encounters the intrinsic difficulties of
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18 strongly varying electrochemical properties of ILs when changing the anion.

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22 Alkylimidazolium ILs with PF_6^- anion have about ten times higher viscosity and ten-fold
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25 lower conductivity than with BF_4^- ,^[36] which dramatically alters etching efficiency with
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29 $[\text{HMIM}][\text{PF}_6]$. The process becomes non-uniform developing locally (Fig. S5, S6),
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32 though at the bottom of the affected zones the dilution of the IL with etching products
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35 makes the conditions closer to those with less viscous $[\text{HMIM}][\text{BF}_4]$ and leads to the
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38 formation of a similar cellular structure (Fig. S6). Thus, changing the counterion to PF_6^-
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42 has significant impact on the surface structure and the viscosity effects point at a
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51 When the difference in viscosity/conductivity is smaller, ca. 2 times, finer tuning of
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54 etching properties is seen. An isotropic electropolishing occurs (Fig. S4) with
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[BMIM][BF₄] (108.25 cP^[37] and 3.53 mS/cm^[38]), whereas an intermediate regime was observed with [BMIM][PF₆] (284.49 cP^[37] and 1.65 mS/cm^[39]) when mesoporous etching (Fig. 4 a) goes concomitantly with the formation of a sub 100 nm pattern (Fig. 4 c).

It should be noted that the formation of pores occurs without significant oxidation of the silicon surface, as the fraction of silicon oxide in the resulting material is less than 1.5% (according energy dispersive X-ray spectroscopy (EDS) data).

One of the essential qualities of porous silicon is its strong fluorescence.^[40-41] The fluorescence spectrum of a porous silicon sample obtained by etching in 1% [HMIM][BF₄] w-IL system at a current density of 8 mA/cm² for 6 hours (Fig. 5) has a maximum in blue light at 475 nm. A more detailed study of the optical properties of the material is the subject of further study.

Figure 4. SEM images of a silicon samples etched in w-ILs with $[PF_6^-]$ anion: (a) $[HMIM][PF_6]$ (water content 2%) for 1 hour at $j = 24 \text{ mA/cm}^2$, (b) and (c) $[BMIM][PF_6]$ (water content 1%) for 1 hour at $j = 24 \text{ mA/cm}^2$.

Figure 5. The fluorescence spectrum (excitation at 401 nm) of a porous silicon sample obtained by etching in 1% [HMIM][BF₄] w-IL system during 6 hours at $j = 8 \text{ mA/cm}^2$.

Raman spectra of the studied samples (Fig. S19, S20) are quite similar, with the more pronounced 2TO mode of the etched silicon, especially with the 532 nm excitation.

The IL used for preparing the wafer as in Fig. 2 (right) was diluted with CD₃CN, and a comprehensive range of ¹H, ¹³C, ¹¹B, and ¹⁹F NMR spectra were recorded. Comparison of NMR spectra of this IL before and after etching showed that it does not decompose during the etching process (all signals at all nuclei before and after etching are completely identical and only the acidic proton signal shifts to the region of the high fields, which indicates a some decrease in pH ^[42]) and it can be considered as a potentially recyclable etching agent (see Fig. S7-S14). Of course, the interpretation that the ionic liquids will be recyclable because there is no degradation of the IL as determined by NMR spectroscopy is just a preliminary investigation; and, we will need to be examined more closely in the future including examination of the purity of the IL after several uses and using a more sensitive technique.

Experimental

Reagents, solvents, and materials. [BMIM][BF₄] (99 %), used for etching, was supplied by Sigma Aldrich. [BMIM][PF₆] (99%) was supplied by ABCR. [HMIM][BF₄] and [HMIM][PF₆] were prepared from 1-methylimidazol, 99 % (Acros) and fluoroboric acid, 48 wt % (Acros) or hexafluorophosphoric acid, 55 wt % (Sigma Aldrich) respectively.

Ionic liquid systems were washed with ethyl acetate (Acros).

The n-type (111) single-crystalline silicon wafer (d = 5 mm, thickness = 2 mm) was polished to a high gloss with chromium oxide GOI polishing paste and then degreased with isopropyl alcohol (SEM/EDS - see Fig.S1).

Synthesis of ionic liquids. [HMIM][BF₄] was synthesized according to known literary technic.^[32] The synthesis of [HMIM][PF₆] was carried out similarly.

The purity and structure of prepared [HMIM][BF₄], [HMIM][PF₆] were confirmed by ¹H, ¹³C, ¹¹B, ¹⁹F and ³¹P NMR analysis (see SI). The NMR spectra of [HMIM][BF₄] in CD₃CN: ¹H NMR (600 MHz): 3.84 (s, 3H, CH₃), 7.30 (s, H), 7.32 (s, H), 8.26 (s, H),

12.05 (s, N⁺-H). ¹³C NMR (150 MHz): 34.2, 116.9, 121.9, 136.8. ¹¹B NMR (193 MHz): -
1.06 (s). ¹⁹F NMR (565 MHz): - 150.99 (s, ¹⁰BF₄) and -151.04 (s, ¹¹BF₄) in 1:4 intensity
ratio, which corresponding to the natural abundance of ¹⁰B and ¹¹B isotopes in ca. 20%
and ca. 80%, respectively. The NMR spectra of [HMIM][PF₆] in D₂O: ¹H NMR (600
MHz): 3.65 (s, 3H, CH₃), 7.16 (s, 2H), 8.37 (s, H). ¹³C NMR (150 MHz): 35.3, 119.3,
122.8, 134.8. ³¹P NMR (243 MHz): -145.3 (sep, J = 709.17 Hz) ¹⁹F NMR (565 MHz): -
72.85 (d, J = 709.14 Hz)

NMR spectra were recorded on Bruker AV600 spectrometer at ambient temperature.
Standards according to Bruker almanac ^[43] were used. Water content in the ILs was
controlled by Fischer titration using a KAS-01 MD apparatus.

Electrochemical etching. The etching was carried out in a PTFE cell of the original
design (see Fig. 1). It consisted of a PTFE rod fitted with a PTFE nut with a 4 mm hole
that allowed the silicon wafer to be pressed against a stainless steel rod, which served
as a current collector. A PTFE nut also allows us to limit the etching area, so it remains
constant throughout all experiments. In parallel with the silicon wafer, a platinum grid

cathode was fixed above the PTFE cell. The etching agent was placed on the surface of the silicon wafer using a micropipette. The etching process was carried out in galvanostatic mode at current density in the range from 8 mA/cm² to 24 mA/cm² using a PC-piloted digital potentiostat IPC-Pro-MF (Econix). Etching time was varied from 30 minutes to 6 hours. After that, the silicon wafer was washed with ethyl alcohol and stored in a high-purity argon atmosphere in a septum-sealed vial.

SEM/EDS. Morphology of pristine and etched silicon surface was studied using a Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). The images were acquired in secondary electron mode at 20 kV accelerating voltage and the working distance 8-10 mm. Energy-dispersive X-ray spectroscopy (EDS) was carried out using an Oxford Instruments X-max 80 EDS system at 20 kV accelerating voltage and a working distance 15 mm. The samples were studied without metallization in order to avoid metal coating effects.^[44]

Raman spectroscopy. Raman spectra were acquired with a BWS415 spectrometer (BWTEK, Germany) with 785 nm laser, and with EnSpectr532 spectrometer (Enspectr, Russia), integrated with 532 nm laser and CX41 microscope (Olympus, Japan).

Confocal microscopy. Confocal microscopy was performed with Nikon A1 confocal microscope equipped with 401 nm and 514 nm lasers and spectral detector (Nikon, Japan).

Summary

High-purity porous silicon with uniform and size-controlled pores was produced using wet 1-methylimidazolium tetrafluoroborate as the etching solution. Such a non-volatile, non-flammable, and chemically and electrochemically stable system is a good alternative to commonly used aggressive, toxic and dangerous HF.^[45]1-

Methylimidazolium tetrafluoroborate is easily synthesized and does not require special storage conditions. Moreover, it can be considered as a potentially recyclable etching agent. Besides, the etching process is very simple, secure and efficient with no need of additional heating, control of potential or any other special precautions. All this makes

the proposed technique suitable for scaling-up. Application of HF-free solvent-in-salt system for eco-friendly etching is a novel approach with excellent practical opportunities.

Conflicts of interest

There are no conflicts to declare.

ASSOCIATED CONTENT

Supporting Information.

Additional SEM data, NMR and Raman spectra are provided in the Supporting Information.

This file is available free of charge.

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Author Contributions

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ABBREVIATIONS

[BMIM][BF₄], 1-Butyl-3-methylimidazolium tetrafluoroborate; EDS, energy dispersive X-ray spectroscopy; EMIMF·2.3HF, 1-ethyl-3-methylimidazolium oligofluorohydrogenate; IL, ionic liquid; [HMIM][BF₄], 1-Methylimidazolium tetrafluoroborate; [HMIM][PF₆], 1-Methylimidazolium hexafluorophosphate; NMR, nuclear magnetic-resonance; PTFE, polytetrafluorethylene; PSi, porous silicon; SEM, scanning electron microscope; w-IL, wet ionic liquids.

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shifts of all other protons remain the same after etching, ^{11}B and ^{19}F spectra are also identical), can cause a significant high field shift of the acidic proton. In support of this explanation, we have taken a cyclic voltammetry measurement of $[\text{HMIM}][\text{BF}_4]$ under the same conditions as were during etching but in the presence of 1-methylimidazole. It was revealed that its oxidation begins at rather low potentials, namely +0.8 V vs. Ag/AgCl (the wave does not have a pronounced maximum because of high viscosity of the system), which is significantly lower than the real etching potential (> 2 V vs. Ag/AgCl). Also ^1H NMR measurement of $[\text{HMIM}][\text{BF}_4]$ in acetonitrile showed that the presence of 3 mol% HBF_4 (a minimal amount that can be added to a NMR tube with reasonable accuracy) causes a high field shift of the acidic NH-proton signal by 3 ppm.

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48 For Table of Contents
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