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Fourier Transform Infrared Spectroscopy and Temperature-Programmed Desorption Mass Spectrometry Study of Surface Chemistry of Porous 6H-SiC

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Porous SiC (PSC) freestanding layers were prepared via UV light-assisted electrochemical etching of an n-type 6H-SiC wafer. Fourier transform infrared (FTIR) spectroscopy and temperature-programmed desorption mass spectrometry (TPD-MS) were applied to characterize functional groups on the PSC surface and their chemical reactivity. It was shown that as-prepared PSC contains silanol groups, carboxylic acid groups, minor amounts of SiH and CH_x groups, and also a carbon-rich surface phase. Annealing of PSC in air at 673 K resulted in the oxidation of the carbon-containing surface species and the formation of a hydrated silicon oxide surface layer. Using $-Si(CH_3)_3$ groups as a model, it was demonstrated that organic functional groups can easily be grafted on oxidized PSC via common silanization chemistry. Treatment of oxidized PSC with HF resulted in the formation of a surface terminated with methyl groups. It confirms that the walls of the PSC pores are constituted of the (0001) "silicon" crystal face of SiC and faces with similar atomic structure.

I. Introduction

In recent years, porous semiconductors such as porous silicon,[1,2] porous SiC (PSC),[3,4] and porous GaAs[5] attract a lot of attention from researchers because of their photoluminescent and unusual electrical properties as well as their compatibility with existing semiconductor technology. In fact, such materials possess the electrical properties of semiconductors and the textural parameters (large surface area, adjustable porosity, and pore size) of porous adsorbents. That is why porous semiconductors are studied intensively as materials for optoelectronic devices,[6] chemical and biological sensors,[7−9] chromatography chips,[10,11] size-selective nanoporous membranes for protein separation,[12] or fuel cells.[13] Porous silicon is in fact the most frequently studied material for the above-mentioned applications. However, its chemical stability is not perfect: Porous silicon is easily oxidized and interacts with water in a weakly alkaline medium.[14] This problem can be solved by replacing of this material by silicon carbide with its well-known ability to withstand harsh chemical environments.

Photoluminescent, sensing, capillary, and other properties of porous semiconductors are determined substantially by the composition of their surface layer and can be tuned by its appropriate chemical modification. That is why it is important to know which chemical groups are located on the internal surface of porous semiconductors. In contrast to porous silicon with the surface covered by silane groups (SiH_x with $x = 1, 2,$ or 3),[1] porous silicon carbide has more complicated and less studied surface chemistry. Different chemical species, such as C−H and Si−H fragments, were detected on the PSC surface mainly by infrared spectroscopy.[15,16] Great attention was focused on the study of surface-

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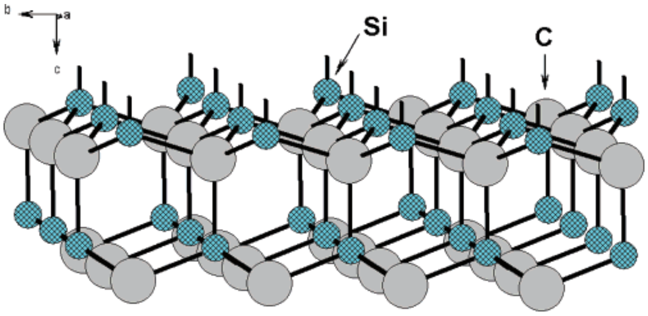


Figure 1. Ball and stick representation of the (0001) surface of hexagonal SiC.

related electronic defects in the PSC, a possible origin of the PSC photoluminescence.[17] However, a detailed study of the PSC surface chemistry has not been performed up to now.

To understand the chemical properties of the PSC surface we should consider its atomic structure. Usually, the PSC possesses the crystalline structure of the bulk SiC wafer from which it originates. Any silicon atom in the SiC structure is bonded to four carbon atoms, and any carbon atom is bonded to four silicon atoms. Most often the pores of PSC can be represented as the rows of tetrahedrons.[3,4] The walls of the tetrahedron are constituted by the (0001) plane (Si plane) and inclined planes with similar atomic structure: $(1\bar{1}0\bar{2})$ for 4H SiC polytype and $(1\bar{1}0\bar{3})$ for 6H-SiC (Figure 1).[18] Such a structure of the pore walls is originated from the highest chemical stability of "Si-terminated" SiC surface to oxidative treatments.[19]

In this work, we examine which chemical fragments terminate the PSC surface to study their reactivity and to establish the reactions appropriate for the PSC chemical modifications. Fourier transform infrared (FTIR) spectroscopy and temperature-programmed desorption mass spectrometry (TPD-MS), applied previously for the characterization of porous silicon[20] and chemically modified silica gel,[21] were used to characterize the composition of the PSC surface layer after different chemical treatments.

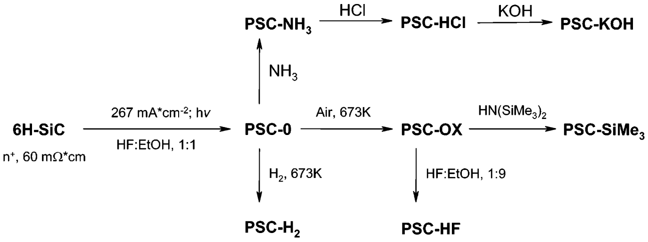
II. Experimental Section

II.1. Porous Silicon Carbide Preparation and Chemical Modification. Porous silicon carbide was prepared by anodic etching of the C-side $(000\bar{1})$ of n^+-doped ($\rho = 60$ mΩ·cm) 6H-SiC wafer polished on its Si side. Anodization was achieved in a Teflon cell with a copper electrode as backside contact. The counter electrode was made of gold. Samples were etched in an HF (49%) and ethanol mixture (1:1 by volume) with a 267 mA·cm^{-2} anodic current density under UV light irradiation. At the end of the anodization process, PSC layers were detached from the bulk SiC by switching to the electropolishing regime (pulse at 0.9 A·cm^{-2} during 30 s), rinsed with deionized water and ethanol then dried in ambient air. As-prepared samples, referred to as PSC-0, displayed a yellow-brown color, a 75 μm thickness, and a 50% gravimetric porosity.

The PSC-NH_3 sample was prepared by exposure of the PSC-0 to saturated vapors of 28% ammonia aqueous solution for 20 min. PSC-HCl and PSC-KOH were obtained from PSC-NH_3 after the following treatment: the sample was dipped into 5% water solution of the corresponding chemical (HCl or KOH) for 10 min, then rinsed with H_2O followed by ethanol, and afterward dried in air. PSC-OX and PSC-H_2 samples were obtained by annealing of the PSC-0 at 673 K for 1.5 h in air or in H_2, respectively. PSC-$SiMe_3$ was obtained by refluxing of PSC-OX sample (2 mg) in a 15% solution of $HN(SiMe_3)_2$ in toluene (2 mL) for 15 h, followed by rinsing with boiling toluene and ethanol. PSC-OX was treated by 5% HF in ethanol to give the PSC-HF sample.

Processes of the PSC preparation and the following chemical treatments are summarized in Scheme 1:

Scheme 1



II.2. Characterization Methods. FTIR spectra of free-standing PSC samples were recorded in the 370−4000 cm^{-1} range in transmission mode in ambient conditions using a Perkin-Elmer GSX-2 spectrometer. To make possible the comparison of the peak intensities, the area of the free space used as a background was always kept the same as the area of the sample measured. The intensity of the bands of surface-related species was found to be much weaker than the intensity of the SiC bands in the 1000−1800 cm^{-1} interval. To monitor the changes of these weak bands, the differential spectra were calculated: the spectrum of the sample of interest was subtracted by the spectrum of the initial SiC (or PSC) sample multiplied by a correcting factor eliminating the two-phonon SiC bands from the resulting spectrum. Positive bands in the differential spectrum correspond to the species arising in the sample as a result of the initial sample treatment, while negative bands relate to the species eliminated from the sample.

TPD-MS measurements were carried out by heating of the sample under high vacuum ($p < 10^{-3}$ Pa) at a heating rate of 0.167 K/s. The evolving products were analyzed by mass spectrometry (EI, −70 eV) on a MX7304A instrument (Selmi, Ukraine).[22] Before TPD-MS measurements, samples were pre-evacuated to 10^{-3} Pa for 20 min.

III. Results and Discussion

III.1. Surface Species of Porous 6H-SiC. To interpret the FTIR spectra of PSC samples, the spectrum of the nonporous 6H-SiC wafer should be analyzed first. As a lattice constructed by polar chemical bonds, SiC has nondegenerate longitudinal optical (LO) and transverse optical (TO) phonons at the frequencies of 970 cm^{-1} (LO) and 794 cm^{-1} (TO).[23,24] That is why the SiC wafers as well as PSC samples strongly

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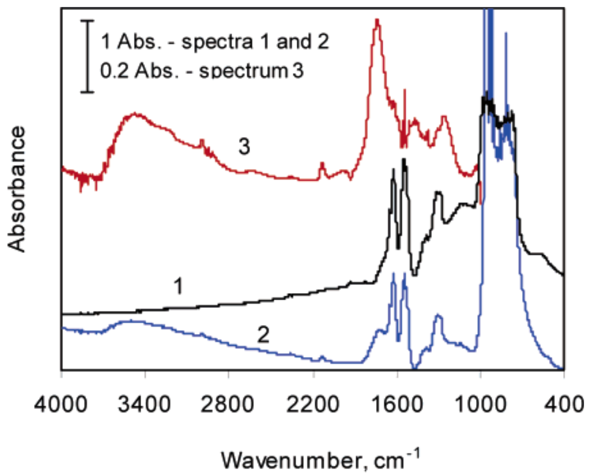


Figure 2. FTIR spectra: (1) 6H-SiC wafer; (2) porous 6H-SiC (PSC-0 sample), and (3) baseline corrected differential spectrum of porous 6H-SiC relative to the 6H-SiC wafer.

absorb light in the spectrum region between the TO and the LO phonon frequencies. Additionally, several strong absorption bands in the range of 1000−1800 cm^{-1} are observed in the FTIR spectra of 6H-SiC wafer and PSC samples (Figure 2). These bands are attributed to the two-phonon combination modes: 2 × LO at 1700 cm^{-1} (shoulder), TO + LO at 1622 cm^{-1}, 2 × TO at 1542 cm^{-1}, LO + longitudinal acoustic (LA) at 1388 cm^{-1}, TO + LA at 1307 cm^{-1}, and TO + transverse acoustic (TA) at 1135 cm^{-1}.[23] The presence of weak bands at 1530, 1650 cm^{-1}, and so forth can be attributed to the splitting of the main modes as a result of the presence of six formula units in the unit cell of 6H-SiC.[25]

In addition to the bands described above, the FTIR spectrum of PSC-0 possesses some extra bands (Figure 2). The broad band at 3500 cm^{-1} can be assigned to the combination of stretching modes of hydrogen-bonded −OH groups attached to Si or C atoms, as well as to the adsorbed H_2O molecules. The weak band at 2850−3000 cm^{-1} relates to CH stretching, and the band at 2130 cm^{-1} relates to SiH stretching of $C_3Si{-}H$ surface species.[26] The intense band at 1735 cm^{-1} will be interpreted below. Above-described bands and the bands at 1380 cm^{-1} (CH scissors) and 1250 cm^{-1} can be seen much more clearly in the differential spectrum of the PSC-0 relative to the SiC wafer (Figure 2).

It is important that the PSC-0 sample has no detectable amount of SiC oxidation products, such as SiO_2, SiOC, or silicon suboxides: the band of Si−O asymmetric stretching at 1100 cm^{-1} cannot be clearly identified in the FTIR spectra of PSC-0. Fluorine-containing species were also not detected in PSC-0: no fluorine-containing ions, which are usually observed during thermal decomposition of solids with fluorinated surface,[27] were found in the TPD-MS spectrum of PSC-0 (Figure 3). Absence of significant amounts of Si−O and Si−F species in the PSC-0 agrees well with X-ray photoelectron spectroscopy (XPS) results of earlier works.[28,29]

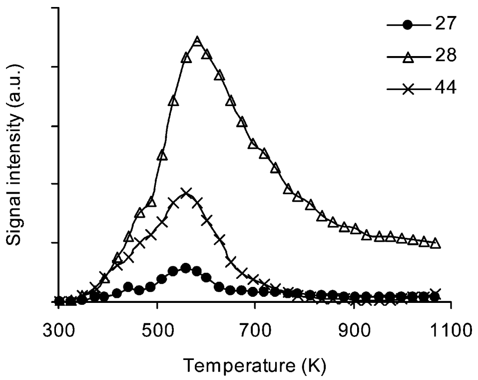
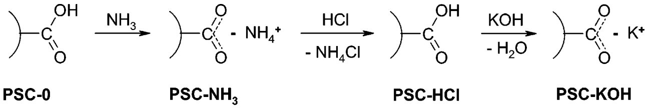


Figure 3. TPD-MS profiles of porous 6H-SiC (PSC-0) for the ions with *m/z* 27 ($C_2H_3^+$), 28 (CO^+ and/or $C_2H_4^+$), and 44 (CO_2^+).

Thermal decomposition of PSC-0 in a vacuum, monitored by TPD-MS, resulted in intense CO_2 (ions with *m/z* 44 (CO_2^+), 28 (CO^+)), ethylene (ions with *m/z* 28 ($C_2H_4^+$), 27 ($C_2H_3^+$), 26 ($C_2H_2^+$)), and probably CO (ion with *m/z* 28 (CO^+)) evolution (Figure 3). The temperature of this process (560 K) is too low to assign it to the decomposition of silicon oxocarbide or to the reduction of silicon oxide by carbon. It is more likely that CO_2 and CO, observed in the TPD-MS spectrum of PSC-0**,** have been generated by decomposition of C−O-containing surface species, particularly carbonyl (>C═O) and/or carboxylic acid (−CO_2H) functionalities. This assumption is proved by the FTIR spectrum of PSC-0 sample, where the band observed at 1735 cm^{-1} can be clearly assigned to C═O stretching.

The presence of carboxylic acid groups on the PSC-0 surface gives a rational explanation of the ability of PSC to be an effective ammonia sensor.[7] We have used ammonia as a probe molecule to study PSC surface sites by FTIR. Bands at 3320 and 3100 cm^{-1} (NH stretching) and 1429 cm^{-1} (NH bending), which can be attributed to the NH_4^+ ion rather than to the coordinated NH_3 molecule[30] and negative bands at 1735 cm^{-1} and 1250 cm^{-1} as well as the positive band at 1610 cm^{-1} were found in the differential FTIR spectrum of PSC-NH_3 (Figure 4). These spectral features can easily be explained by the reaction of NH_3 with carboxylic acid groups (Scheme 2). NH_3 is protonated while the −CO_2H groups (ν(C═O) at 1735 cm^{-1} and ν(C−O) at 1250 cm^{-1}) transform into carboxylate anions (ν_{as}(−CO_2^-) at 1610 cm^{-1} and ν_s(−CO_2^-) at 1400 cm^{-1}).

Scheme 2



Additional proof for the presence of −CO_2H groups on the PSC surface was obtained from the following chemical experiment: the PSC-NH_3 sample was treated with HCl to transform ammonium carboxylate fragments into carboxylic acid groups (Scheme 2). The FTIR spectrum of the product

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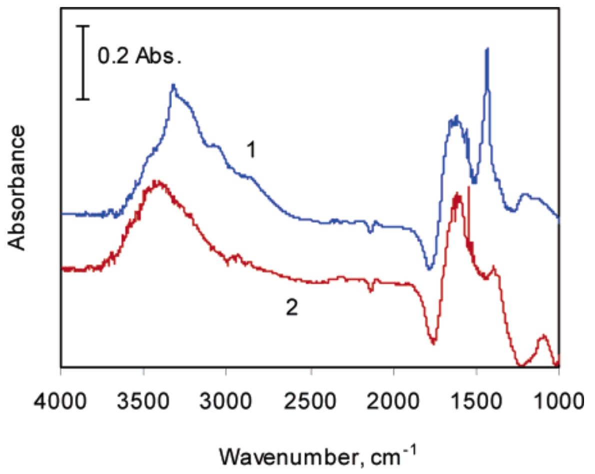
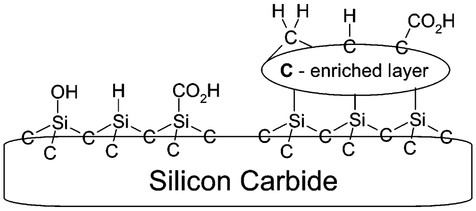


Figure 4. Differential FTIR spectra relative to PSC-0: (1) PSC-NH_3 and (2) PSC-KOH.

(PSC-HCl) coincides with the spectrum of PSC-0: the bands of $-CO_2H$ are observed while the bands of NH_4^+ and $-CO_2^-$ are not. Subsequent treatment of PSC-HCl with KOH resulted in deprotonation of $-CO_2H$ groups (Scheme 2). In the differential spectrum it was indicated by the appearance of positive $-CO_2^-$ and negative $-CO_2H$ bands (Figure 4).

Thus, a wide variety of different functionalities is present on the surface of as-prepared PSC: carboxylic acid groups, silane groups, hydrocarbon fragments, and hydroxyl groups (Scheme 3).

Scheme 3



Moreover, as it was shown by Shin et al.[28] by means of the XPS method, the internal surface of as-prepared PSC is enriched in carbon and so the formation of carbon-rich surface layer can be considered (Scheme 3).

III.2. Thermal Transformations of PSC Surface Species in Air and H_2 Atmosphere. The chemical reactivity of the PSC was studied with respect to thermal treatment in oxidative (air) and reductive (hydrogen) atmosphere. The visual result of such a treatment was a change of sample color: PSC-0 is yellow-brown, PSC-OX is white, and PSC-H_2 is black, which is in accordance with the data of Shin et al.[28] Probably, annealing in air resulted in oxidation of the carbon-rich surface layer (the color turns white), while annealing in H_2 (also in vacuum or in inert atmosphere, as it is studied in the works in refs 28 and 31) resulted in sample graphitization (the color turns black).

More detailed study of PSC-OX and PSC-H_2 surface groups was performed by means of FTIR (see the differential spectra in Figure 5). Negative bands of $\nu(CH_x)$ at 2800−3000 cm^{-1}, $\delta(CH_x)$ at 1380 cm^{-1}, $\nu(C{=}O)$ at 1735 cm^{-1}, and $\nu(C{-}O)$ at 1250 cm^{-1} in both spectra indicate the destruction of CH_x and $-CO_2H$ surface fragments under oxidation as well as graphitization. The SiH stretching band lost its intensity compared to that of PSC-0 and shifted to 2115 cm^{-1} for PSC-OX and to 2120 cm^{-1} for the PSC-H_2 sample. Changes in the frequency of $C_3Si{-}H$ stretching under thermal treatment of the PSC can be related to the change in the far coordination environment of the SiH group as well as to the changes of the properties of SiC as an ensemble. We supposed that O_3SiH groups, which are typically formed under oxidation of porous silicon,[1] should also appear under the oxidation of PSC-0. However, their FTIR signal (ν(SiH) at 2260 cm^{-1}) was not detected in the PSC-OX spectrum. A possible explanation for this is the higher stability of Si−C bond (370 kJ/mol) as compared to that of the Si−Si bond (210 kJ/mol).[32] This difference can play a crucial role in determining the stability of PSC to oxidation in comparison with porous silicon.

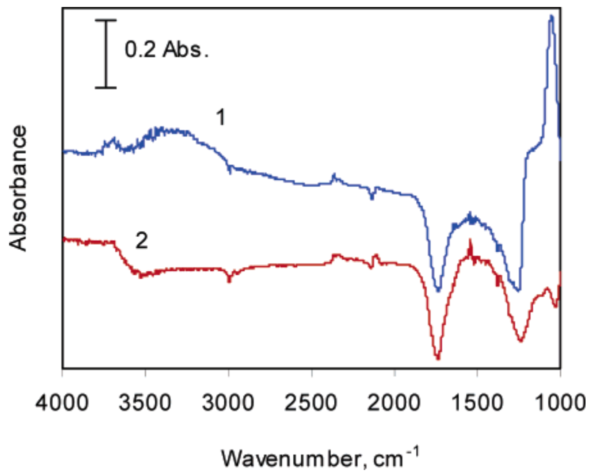


Figure 5. Differential FTIR spectra relative to PSC-0: (1) PSC-OX and (2) PSC-H_2.

Positive bands of O−H stretching (3000−3700 cm^{-1}) and Si−O asymmetric stretching (1000−1230 cm^{-1}) observed in the spectrum of PSC-OX (Figure 5) indicate the formation of a hydrated silicon oxide layer on the surface of the sample. The shape of the Si−O band (main peak at 1050 cm^{-1} and a shoulder at 1175 cm^{-1}) is similar to the shape of the Si−O band in the spectrum of amorphous silica,[33] but the latter is situated at a higher frequency (1110 and 1200 cm^{-1}, correspondingly). It indicates that the oxide layer formed on PSC at 673 K, similarly to amorphous silica, is constituted by trigonally distorted SiO_4 units.[34]

Both PSC-OX and PSC-H_2 were not active in ammonia adsorption. FTIR bands related to the NH_3 molecule were not found in the spectra of the samples after ammonia treatment. We can assume that adsorption of ammonia on the PSC is facilitated mainly by carboxylic acid groups which were identified in PSC-0 but are absent in PSC-OX and PSC-H_2. The presence of other acidic adsorption sites such as

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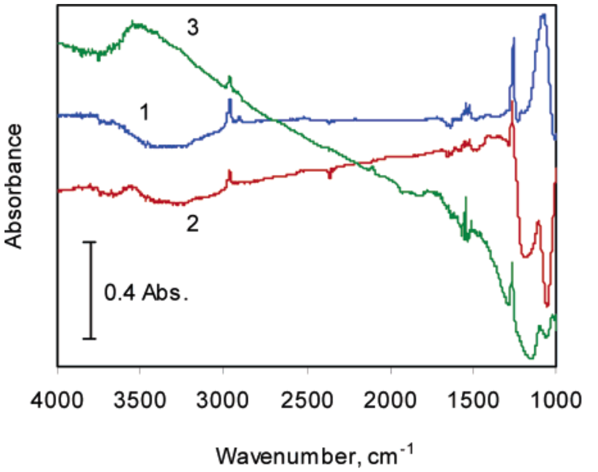
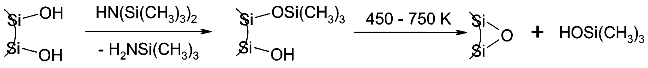


Figure 6. Differential FTIR spectra: (1) PSC-SiMe$_3$, (2) PSC-HF (both relative to PSC-OX), and (3) PSC-HF relative to the 6H-SiC wafer.

surface defects, Lewis acid sites, acidic silanols, and so forth in the PSC is not evident from our experiments.

III.3. Chemical Functionalization of Oxidized PSC Surface with Trimethylsilyl Groups. To check the appropriateness of oxidized PSC surface for the functionalization with organic groups via the silanization reaction,[35] the sample of PSC-OX was treated with HN(SiMe$_3$)$_2$ to give the PSC-SiMe$_3$ sample. Characteristic bands of the CH$_3$ groups bonded to the Si atom (ν_{as}(CH$_3$) at 2964 cm^{-1}; ν_s(CH$_3$) at 2912 cm^{-1}; and δ_s(CH$_3$) at 1257 cm^{-1}), positive Si−O band (1080 cm^{-1}), and negative O−H stretching band (3700−3000 cm^{-1}) in the differential FTIR spectrum of PSC-SiMe$_3$ (Figure 6) indicate the covalent grafting of the −SiMe$_3$ groups (the first step in Scheme 4).

Scheme 4



The intensities of the Si−O asymmetric stretching bands (1000−1200 cm^{-1}) are of the same order of magnitude in the differential spectra of PSC-SiMe$_3$ (Figure 6) and PSC-OX (Figure 5). Thus, we can state that the number of trigonally distorted SiO$_4$ units on the surface of PSC-OX is close to the number of Si−O−SiMe$_3$ groups in PSC-SiMe$_3$. Therefore, SiO$_4$ units constitute just a monolayer or a few layers on the PSC-OX surface. No thick layer of silicon oxide is formed under applied oxidation conditions.

Thermal decomposition of PSC-SiMe$_3$ (the second step, Scheme 4) resulted in the desorption of HOSi(CH$_3$)$_3$ (ion with *m*/*z* 75, (HOSi(CH$_3$)$_2$$^+$)) with a maximum at 575 K (see TPD-MS curves, Figure 7). As it was shown previously for trimethylsilylated silica gel,[21] HOSi(CH$_3$)$_3$ is produced by the reaction of the grafted −Si(CH$_3$)$_3$ group with neighboring silanol group. If the concentration of residual silanols is low, the reaction between −Si(CH$_3$)$_3$ groups with formation of Si(CH$_3$)$_4$ occurs. The relative low temperature of HOSi(CH$_3$)$_3$ formation and absence of Si(CH$_3$)$_4$ among PSC-SiMe$_3$ decomposition products indicate that residual silanols are present in PSC-SiMe$_3$ in a higher amount and closer to trimethylsilyl groups than in modified silica gel. Hence, the density of silanol groups on the surface of the initial PSC-OX is also higher than on the surface of amorphous SiO$_2$.

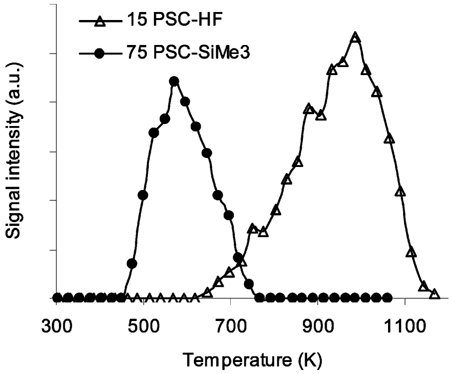


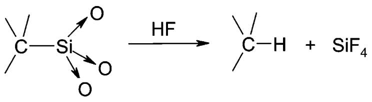
Figure 7. TPD-MS profiles of PSC-HF for the ion with *m*/*z* 15 (CH$_3$$^+$) and PSC-SiMe$_3$ for the ion with *m*/*z* 75 (HOSi(CH$_3$)$_2$$^+$).

III.4. Oxidized PSC under HF Treatment. One of the most important reactions in the surface chemistry of silicon (bulk as well as porous) is the dissolution of the surface oxide in HF, producing a surface terminated with SiH$_x$ groups.[36] We investigate similar reaction with respect to the PSC. Presence of negative Si−O and O−H bands in the differential FTIR spectrum of PSC-HF relative to PSC-OX (Figure 6) confirms the dissolution of the PSC-OX surface oxide in HF. At the same time, a weak positive band at 1100 cm^{-1} and a wide band at 3000−3700 cm^{-1} are observed in the differential spectrum of PSC-HF relative to the SiC wafer (Figure 6). These bands can be attributed to Si−O and O−H stretching of C$_3$Si−OH surface fragments, respectively. In addition, characteristic bands of Si−CH$_3$ groups (ν_{as}(CH$_3$) at 2965 cm^{-1}; ν_s(CH$_3$) at 2915 cm^{-1}; and δ_s(CH$_3$) at 1266 cm^{-1}) can be clearly seen. The presence of −CH$_3$ groups terminating the surface of PSC-HF is also confirmed by the intense process of methane desorption at 750−1150 K observed by TPD-MS (Figure 7). Surface species containing fluorine were not detected in PSC-HF either by FTIR or by TPD-MS similar to the PSC-0 sample. Thus, ≡Si−OH, ≡Si−CH$_3$, and a minor amount of ≡Si−H groups indicated by a weak FTIR band at 2110 cm^{-1} (SiH stretching) are the only species we have detected on the surface of PSC-HF.

To understand chemical transformations taking place under HF treatment of PSC-OX, the properties of the Si−C bond with different substituents at the Si atom should be considered. If the silicon atom is bonded to three C and one O atom, the Si−C bond is not polarized enough to be cleaved by HF. Furthermore, the hydroxyls of the C$_3$Si−OH surface fragments are not substituted by fluorine probably because the silicon atom on the surface of SiC carries a smaller positive charge than in silicon−organic compounds or in SiO$_2$.

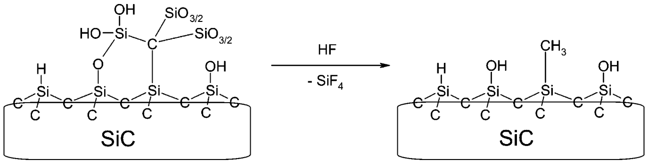
If a silicon atom is bonded to three O and one C atom, the Si−C bond is polarized and easily cleaved under HF treatment (Scheme 5):

Scheme 5



This process is similar to the formation of SiH species on the surface of oxidized silicon (or porous silicon) exposed to HF.[36] Methyl groups can be formed via reaction, described in Scheme 5, if the carbon atom is bonded to three SiO_3 units and one Si atom belonging to SiC bulk. This situation takes place on the surface of PSC, when its atomic structure is similar to the (0001) SiC plane: the near-surface carbon atom possesses one bond directed toward the surface and three bonds directed away from the surface while the bonds of silicon atoms are positioned in the reverse order (see Figure 1). Therefore, the formation of methyl groups under the HF treatment confirms the presence of the described structure units on the surface of PSC. Processes of dissolution of the PSC-OX surface oxide layer in HF can be summarized by Scheme 6.

Scheme 6



As it can be seen from the Scheme 6, the surface of the PSC-HF sample contains ≡Si–OH, ≡Si–CH_3, and ≡Si–H groups.

V. Conclusions

The surface chemistry of PSC was found to be more complicated than that of porous silicon. Functional groups, namely, Si–OH, –CO_2H, C_3Si–H, and CH_x, and also the carbon-enriched surface phase were found on the surface of as-prepared PSC. The presence of carboxylic acid groups in PSC results in its ammonia sensing properties.

Thermal treatment (673 K) of PSC in the hydrogen atmosphere resulted in graphitization of carbon-containing surface species; on the other hand, annealing in air resulted in the oxidation of these species and the formation of a hydrated silicon oxide layer. This layer can be used for functionalization with organic groups using common silanization chemistry. It seems that thermal oxidation of PSC is much different from the similar process for porous Si. For SiC samples, surface C–H and Si–H groups are the main reactive sites, while for porous silicon, the Si–Si bonds of the matrix are oxidized rather than the Si–H surface bonds.

Under HF treatment, the oxide layer on oxidized PSC dissolves, producing a surface terminated with C_3Si–CH_3 groups, C_3Si–OH groups, and C_3Si–H groups. The formation of methyl groups confirms that the pore walls of PSC are constituted by the (0001) plane (Si plane) and inclined planes with similar atomic structure (plane $(1\bar{1}0\bar{3})$ for the 6H-SiC polytype). Similar to Si–OH groups of oxidized PSC, –CH_3, C_3Si–OH, and C_3Si–H groups remaining after the oxide dissolution can be used for future chemical functionalization.

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