Hydrolysis and silanization of the hydrosilicon surface of freshly prepared porous silicon by an amine catalytic reaction

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A novel catalytic reaction using a trace of organic amine as the catalyst enables hydrolysis of the silicon–hydrogen groups on the fresh prepared porous silicon (PS), generating the hydroxyl-terminated surfaces without extensive oxidation of the Si–Si backbonds. The reactivity of the hydroxyl-terminated surfaces with various silanization reagents was investigated, which proceeds by abstraction of the surface –OH to form an organic monolayer of Si–O–Si–C bonds and importantly retains the intrinsic structural properties of the PS layers. Furthermore, an *in situ* silanization modification of the silicon–hydrogen surfaces has been established. Stability testing shows that the resulting organic monolayers are densely packed and are shown to be highly stable under a variety of conditions including hot water, hot organic solvent, acid, and base, but can be removed by a HF rinse.

Introduction

The desirability of constructing silicon-based optoelectronic devices and chemical and biological sensors has prompted considerable developments in the surface chemistry of luminescent porous silicon (PS).[1–7] Hydrogen-terminated PS surfaces, obtained by electrochemical etching in fluoride containing media, oxidize slowly in air, leading to slow degradation of photoluminescence (PL) and concomitant degradation of the electronic properties.[6] Many studies have focused on the formation of silicon oxide species under thermal, electrochemical, or chemical oxidation conditions to stabilize the H-terminated surface.[6,7] Although this approach lowers the reactivity of PS and in some cases can improve the stability of PL, an insulating oxide layer is not desirable for many applications such as electroluminescent devices and sensor applications.[1,7] Recently, there has been increasing interest in the chemical modification of the PS surface by synthetic strategies.[1–5,8–21] These strategies are directed toward the introduction of functional groups on the PS surfaces and the stabilization of the luminescent properties of the PS. A variety of chemical modification reactions have been demonstrated for the preparation of organic monolayers covalently attached through Si–C and Si–O–C bonds to the PS surfaces, most of which involve Si–Si bond cleavage. For example, organic monolayers containing Si–O–C linkages have been fabricated by photoelectrochemical reaction with carboxylic acids and electrochemical and thermal reaction with alcohols of freshly prepared PS surfaces.[8–10] Direct reactions of hydrogen-terminated surfaces with alkyl Grignards and lithium reagents under electrochemical and thermal conditions have been used to modify the PS surface through Si–C linkages.[11–14] Methods for covalent modification of PS through Si–C bonds have been developed by direct hydrosilylation of hydrogen-terminated surfaces with unsaturated hydrocarbons in the presence of a Lewis acid as a catalyst and by a thermal reaction.[15–18] It has been shown that the Si–C linkage modified surfaces are remarkably stable in boiling water and organic solvents or in boiling aqueous KOH (pH = 10–13).[15–17]

Silanization of hydrogen-terminated surfaces with alkoxy- and chlorosilanes is one of the most common methods used for surface derivatization on crystalline silicon.[22,23] Traditionally, this reaction involves chemical oxidation of the Si–H surface to form the Si–OH intermediate.[24] However, for PS, the weaker silicon–silicon bonds have also proven themselves to be reactive during this conventional pretreatment process, resulting in extensive oxidation of the surface.[1,6,25] An alternate strategy used to form hydroxyl-terminated surfaces is hydrolysis of the Si–H groups on the PS surface. It has been shown that the hydrogen-passivated PS surfaces can be derivatized with a monolayer of trimethylsiloxy groups by the vapor phase reaction of hexamethyldisilazane (HMDS, $Me_3SiNHSiMe_3$) in moist air.[19,20] This Me_3SiO species has also been observed to passivate the surface against further oxidation better than the native hydrogen-terminated surface. However, this reaction only proceeds by interaction of the amine on the alkoxy- and chlorosilanes with adsorbed water on the Si surface. Recently, we have reported an *in situ* silanization reaction using a trace of organic amine and water and $Si(OCH_3)_3(CH_2)_3SH$ as reagents to modify the freshly prepared PS surface.[21] The silanization reaction is thought to proceed by catalytic hydrolysis of the silicon–hydrogen groups and then abstraction of the surface –OH with alkylsilane. In this report, we have investigated in more detail the organic amine catalytic hydrolysis of the hydrosilicon surface and have explored the generality of the silanization reaction using a trace of organic amine and water in the first step and alkoxy- and chlorosilanes in the second. Furthermore, characterization of these organic monolayers by FTIR, XPS and PL spectra has been used to evaluate the reactivity and the chemical stability of the modified surfaces in different aqueous and organic media.

Experimental

Sample preparation and treatment

Single side polished p-type (100) silicon wafers with resistivities of 30–50 Ω cm were purchased from General Research

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Institute for Nonferrous Metals (GRINM), China. Thin Al films were evaporated on the back of the wafers to form an ohmic contact. All cleaning and etching reagents were clean room grade. Luminescent PS samples on silicon substrates with resistivities of 30–50 Ω cm were prepared by anodic etching of p-type Si in 1:1 (v/v) pure ethanol and 40% aqueous HF for 10 min at an anodic current density of 80 mA cm^{-2}. After etching, the samples were rinsed with pure ethanol and dried under a stream of dry high-purity nitrogen prior to use.

Catalytic hydrolysis

The functionalization reactions were carried out in standard schlenk flasks. For organic amine catalytic reaction, 2 ml of a 1% n-propylamine toluene solution was injected into the flask using a syringe. Pure water vapor was flowed into the flask by N_2 stream for about 20 min and then the flask was sealed. After 12 h of refluxing in toluene solution, the liquid reagent was removed by syringe and the PS samples were rinsed with toluene and ethanol three times. The samples were then removed from the flask and dried under a stream of high-purity N_2.

Silanization reaction

The fresh hydroxyl-terminated PS samples were placed in the flask and the silanization reagent (2:3 (v/v) alkoxysilane in toluene) was added by syringe. $Si(OC_2H_5)(CH_3)_3$, $Si(OC_2H_5)_2(CH_3)(CH{=}CH_2)$, $Si(OC_2H_5)_2(CH_3)(C_6H_5)$, $Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$, and $Si(OCH_3)_3(CH_2)_3SH$ in toluene were used as silanization reagents (Aldrich Chemicals). For *in situ* liquid phase silanization reaction, the fresh hydrogen-terminated PS samples were placed in the flask and dipped in the liquid reaction solution (0.1/1.0/10 (v/v) organic amine and silane in toluene solution). In a typical *in situ* vapor phase reaction, two uncovered weighing bottles were put into a flask, and the freshly prepared PS layers were placed in one weighing bottle. 5 mL of a solution of 10% $(CH_3O)_3Si(CH_2)_3SH$ in toluene was injected into the bottle containing the PS layers, and 2 mL of a 1% amine solution in toluene was injected into the empty bottle. Then, pure water vapor at room temperature was then injected into the flask in a stream of N_2 for about 20 min. All of the reactions were allowed to proceed for 12 h under refluxing of toluene solution. After removing the liquid by syringe, the samples were rinsed with toluene and ethanol, and then dried under a stream of high-purity N_2.

Stability test

The stability tests of the modified and the unmodified samples were performed using immersion in hot water, hot organic solvent, 1 M HCl and 0.1 M NaOH. After the treatment, both the modified and the unmodified samples were rinsed with pure water and ethanol, and followed by drying with a stream of high-purity N_2.

FTIR analysis

Fourier transform infrared (FTIR) spectra were collected on a Nicolet 550 operating in transmission mode at a 4 cm^{-1} spectral resolution with 32 scans collected. The samples were mounted in a purged sample chamber. Although the FTIR sample chamber was purged with N_2, all of the sample transfers were performed in air.

XPS analysis

X-Ray photoelectron spectra (XPS) were recorded on a VG-ESCALAB 5 multitechnique electron spectrometer equipped with Al Kα as the exciting source. The anode operated at 9 kV and 18.5 mA and the chamber pressure was kept at 10^{-8} Torr.

PL measurements

All of the PL spectra were measured at room temperature in air by a Hitachi FL-4500 fluorescence spectrometer and corrected for the system response. The excitation wavelength used was 350 nm.

Results and discussion

Catalytic hydrolysis of the hydrogen-terminated surfaces

The hydrolysis of the H-terminated PS surfaces to form hydroxyl-terminated surfaces is the most significant accomplishment of the present work. It is found that a trace of organic amine can catalyze the hydrolysis reactions.

Before the hydrolysis reaction, the transmission FTIR spectrum of freshly prepared PS (Fig. 1a) displays absorptions characteristic of a hydride-terminated surface, which consist of ν(Si–H_x) stretching modes at 2088 cm^{-1} for ν(Si–H), 2116 cm^{-1} for ν(Si–H_2), and 2137 cm^{-1} for ν(Si–H_3), and a δ(Si–H_2) scissor mode at 910 cm^{-1}.[26,27] Modes at 626 and 665 cm^{-1} are assigned to Si–H_x vibrations.[26,28] A small signal at 1108 cm^{-1} is assigned to the Si–O–Si stretch mode.[29]

The FTIR spectrum of the sample after exposure to pure water vapor for 50 h is shown in Fig. 1b. It is found that no obvious change in the absorptions related to Si–H_x vibrations is observed in this figure, indicating that the hydrolysis of the Si–H_x on the surface of PS is negligible in the pure water atmosphere. An increase of the intensity of the Si–O–Si stretch mode at about 1108 cm^{-1} and a new Si–H stretching mode band at 2256 cm^{-1} are attributed to an oxide-back-bonded Si–H.[27]

After treatment of the sample with a trace of n-propylamine and water vapor for 12 h, the IR spectrum (Fig. 1c) exhibits bands characteristic of surface –OH (the ν(SiO–H) stretching mode at around 3400 cm^{-1}, the δ(SiO–H) bending mode at 1640 cm^{-1} and the ν(Si–OH) stretching modes at 950 and 887 cm^{-1}).[30] It also shows an intense broad peak at around 1085 cm^{-1}, which may be due to the ν(Si–O) stretching mode for surface silicon–hydroxyl species. Meanwhile, the absorption signals of ν(Si–H_x) and δ(Si–H_2) completely disappear and a relatively weak band assigned to an oxide-back-bonded

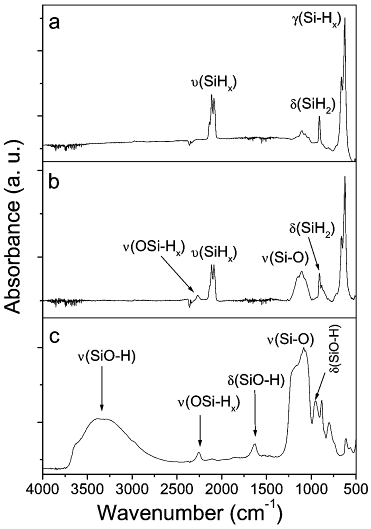

Fig. 1 Transmission infrared spectra of porous silicon: (a) as-prepared; (b) after exposure to pure water vapor for 50 h; (c) after treatment with a trace of n-propylamine and water vapor for 12 h.

Si–H stretching mode appears at 2256 cm^{-1}. The FTIR data suggest that the reaction proceeds by hydrolysis of the surface silicon–hydrogen groups, when a trace of amine and water are present together.

As we know, hydride-terminated silicon surfaces display characteristic absorptions, as shown in Fig. 1(a). These bands of $(Si)_x Si–H_y$ stretching modes, such as peaks at 2088 cm^{-1} for $\nu((Si_3)Si–H)$, 2116 cm^{-1} for $\nu((Si)_2Si–H_2)$, and 2137 cm^{-1} for $\nu(SiSi–H_3)$, are sensitive to the oxide back-bonded on the silicon atom, resulting in a shift of the peak positions of the oxide-back-bonded Si–H stretching mode from about 2100 to 2260 cm^{-1}. At the same time, the absorption intensity of the $(Si)_x Si–H_y$ stretching modes decrease and even disappear. Commonly, the thermally oxidized porous silicon shows an OSi–H stretching mode at 2256 cm^{-1}, which indicates an oxidation of the Si–Si back-bonds ($(Si–O)_x Si–H$). However, it is also possible that the band at 2256 cm^{-1}, as shown in Fig. 1c, originates from (HO)(Si)–Si–H, in which the OH group comes from the hydrolysis of the Si–H group on the surface.

Mechanism of catalytic hydrolysis of hydrosilicon by organoamine

The quenching of porous silicon light emission by organoamine used as Lewis base has been observed by Chun *et al.*[31] and by Chandler-Henderson *et al.*,[32] in which the quenching of the PL are attributed to adduct formation between a Lewis base molecule and a reactive site at the semiconductor surface. But there is no observation of the formation of the Si–OH surface in their works.[31,32] Dubin *et al.* reported that the presence of a trace of water in the reaction system could cause the hydrolysis of the $Si–H_x$ covering the surface of PS in several hours, and then a silanization reaction could take place through the $Si(OH)_x$ intermediates derived from the hydrolysis reaction.[20] However, in our experiment, the hydrolysis of the Si–H groups is negligible within several tens of hours in the saturated water vapor but highly sensitive to traces of amine and water together. As we known, the hydrolysis of the SiH_4 molecule is difficult in pure water, but it is very base sensitive.[33] Similarly, a mechanism of amine-catalyzed hydrolysis of the Si–H groups on the PS surface can be suggested as follows:

$$H_2O + C_3H_8NH_2 \rightarrow OH^- + C_3H_8NH_2H^+ \qquad (1)$$

$$\equiv Si–H + OH^- + C_3H_8NH_2H^+ \rightarrow \equiv Si–OH + H_2\uparrow + C_3H_8NH_2 \qquad (2)$$

This mechanism involves OH^- anions and $C_3H_8NH_2H^+$ cations as intermediates. At first, the amine reacts with water resulting in disassociation of the water molecule and formation of an OH^- anion and $C_3H_8NH_2H^+$ cation (eqn. 1). Subsequently, the OH^- anion attacks the Si–H bond on the surface to generate the Si–OH bond and release a H^- anion. Meanwhile, the H^- anion combines with the H cation in $C_3H_8NH_2H^+$ and produces a H_2 molecule. This proposed mechanism was partly supported by the results reported by Searson *et al.*,[34] in which under the appropriate aqueous conditions, H_2 is liberated from PS surfaces, presumably by coupling of silicon hydrogen with aqueous protons. In our experiment, a lot of small bubbles are clearly observed on the PS surface during the hydrolysis process.

Silanization reaction

To enhance the stability and allow further modification of the reactive Si surface, the reactivity of the hydroxyl-terminated surfaces with silanization reagents was investigated. The general reaction involves replacement of the Si–OH species with a more stable Si–C bonded group (eqn. 3).

$$\equiv Si–OH + R_3SiOR' \rightarrow \equiv SiO–SiR_3 + HOR' \qquad (3)$$

The reaction is carried out by simply exposing a hydroxyl-terminated PS sample to the alkoxysilane or chlorosilane solution (or vapor).

The first example is the PS sample treated with trimethylethoxysilane ($Si(OC_2H_5)(CH_3)_3$). The FTIR spectrum of this product shown in Fig. 2a exhibits bands of a methyl group (aliphatic ν(C–H) stretching modes at 2962 cm^{-1}, deformation modes at 1440 and 1261 cm^{-1} and vibrational stretching mode for Si–C around 750 cm^{-1}).[35] Similar bands were also observed in the infrared spectrum of the sample treated with diethoxymethylphenylsilane ($Si(OC_2H_5)_2(CH_3)(C_6H_5)$) (Fig. 2b). In addition, bands assigned to the surface phenyl species are also shown at 1593, 1547, and 1431 cm^{-1} (aromatic modes) and 3074 and 3050 cm^{-1} (aromatic C–H stretches).[12,31] After treatment with 3-(diethoxymethylsilyl)propylamine ($Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$), the spectrum in Fig. 2c shows alkyl C–H stretching modes between 2850 and 2980 cm^{-1}, C–C stretching modes for alkyl chain at 1574 cm^{-1}, $C–H_x$ bending modes at 1488 and 1454 cm^{-1}, methyl group deformation modes at 1392 and 1261 cm^{-1}.

Furthermore, we have investigated the reactivity of five kinds of silanization reagents with the surface Si–OH, such as $Si(OC_2H_5)(CH_3)_3$, $Si(OC_2H_5)_2(CH_3)(CH{=}CH_2)$, $Si(OC_2H_5)_2(CH_3)(C_6H_5)$, $Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$, and $Si(OCH_3)_3(CH_2)_3SH$, by infrared spectroscopy. The efficiency of the silanization reaction could be determined by the fraction of SiO–H stretch that disappears. Here, it was assumed that the reaction uses Si–OH bonds proportionally to form Si–O–Si–C bonds and there is little surface degradation from the abstraction between the surface –OH groups. Under liquid

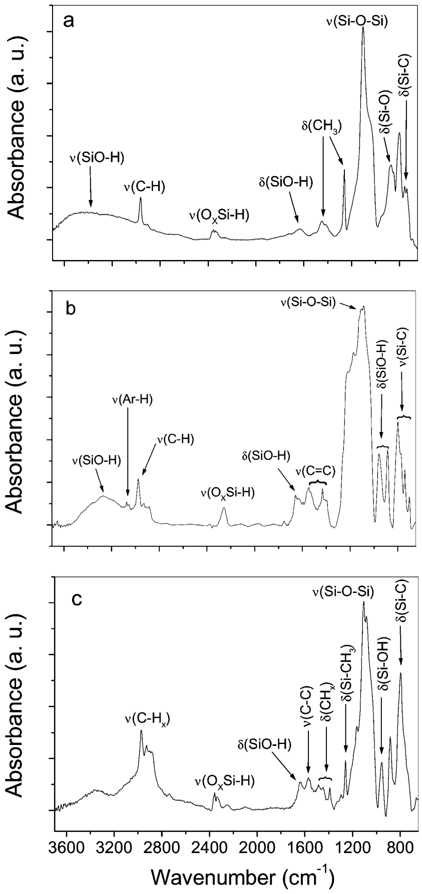

Fig. 2 Transmission infrared spectra of the hydroxyl-terminated porous silicon surfaces derivatized with: (a) trimethylethoxysilane ($Si(OC_2H_5)(CH_3)_3$); (b) diethoxymethylphenylsilane ($Si(OC_2H_5)_2(CH_3)(C_6H_5)$); (c) 3-(diethoxymethylsilyl)propylamine ($Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$).

phase silanization reaction at 60 °C for 12 h, the efficiencies of the reactions are 50–60% for $Si(OC_2H_5)(CH_3)_3$ and $Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$, 40–50% for $Si(OC_2H_5)_2(CH_3)$-$(CH{=}CH_2)$ and 20–40% for $Si(OC_2H_5)_2(CH_3)(C_6H_5)$ and $Si(OCH_3)_3(CH_2)_3SH$. Varying the concentration of the silanization reagent in toluene or increasing the reaction time did not show a consistent response with respect to the silanization reaction efficiency.

In fact, the oxidation of the back Si–Si bonds also existed in the hydrolysis process, due to a trace of oxygen in the atmosphere. Although it is difficult to establish to what extent the surface is back oxidized by oxygen from the IR spectra (Fig. 1(c)), we can give indirect evidence for the formation of the Si–OH surface with less oxidation of the Si–Si back bonds, based on the results of the silanization reactions. In all of the above cases we found that the modifications are accompanied by decreases of the intensities of the surface –OH bands (broad SiO–H stretching mode around 3400 cm^{-1}, SiO–H bending mode at 1640 cm^{-1} and Si–OH bending modes at 950 and 887 cm^{-1}). Meanwhile, a strong sharp band characteristic of the Si–O–Si asymmetric stretching mode is also evident at 1108 cm^{-1} with a full width at half maximum (FWHM) of 95–100 cm^{-1} (Fig. 2a and c), in contrast to a peak position of 1085 cm^{-1} and a FWHM of about 230 cm^{-1} for the hydroxyl-terminated surfaces (Fig. 1c). The FTIR spectral data indicate that functionalization of the hydroxyl-terminated PS surface with silanization reagents proceeds by abstraction of the surface –OH to form a monolayer of Si–O–Si. This assignment is in reasonable agreement with the studies of the vibrational modes of Si–O–Si, in which the absorption signals of the asymmetric stretching of the Si–O–Si bridges were affected by adjacent oxygen atoms in two ways: executing the asymmetric stretching motion in phase with each other and 180° out of phase.[36] It was proposed that the absorption signal of the asymmetric stretching moves to ~1080 cm^{-1} for the former and to ~1200 cm^{-1} for the latter.[36] Commonly, the action of the adjacent oxygen atoms would shift and broaden the signal of the asymmetric Si–O–Si bridges stretching mode.

In situ silanization reaction

The freshly hydrogen-terminated PS surface can not directly react with silanization reagents. For the control sample immersed in a toluene solution of silane (10%, v/v) without amine and water even for 50 h, all of the bands characteristic of Si–H_x and Si–Si were preserved and no bands characteristic of alkyl groups were detected (Fig. 3b). Traditionally, silanization reaction on the hydrogen-terminated crystalline silicon surface requires a pretreatment to form a Si–OH intermediate by chemical oxidation. However, the nanometer c-Si particles have a much higher reactivity than that of the bulk silicon crystal and are very sensitive to oxygen in air and other chemical oxidants. In the present study, it was found that hydrolysis of the silicon–hydrogen groups on the PS surface in the presence of a trace of water and amine is a flexible method to form a hydroxyl-terminated surface without heavy oxidation (Fig. 1c), and then a two-step silanization approach was explored (Fig. 2a–c). Furthermore, we demonstrate that silanization reaction also occurs *in situ* on the surface of the freshly prepared PS when a trace of amine is used as a catalyst. For instance, the FTIR spectrum of the PS samples modified by *in situ* silanization reaction with $Si(OCH_3)_3(CH_2)_3SH$ displays an aliphatic C–H stretching mode at 2974 cm^{-1}, C–H_x bending modes at 1477 and 1446 cm^{-1}, methyl group deformation modes at 1396 and 1261 cm^{-1} and S–H stretching modes at 2604 and 2496 cm^{-1} (Fig. 3c).[37] Meanwhile, the absorption signals of $\nu(Si–H_x)$ and $\delta(Si–H_2)$ completely disappear. The FTIR data suggest that the indirect substitution of the H^- ion on the freshly prepared PS surface by silane has been achieved by *in situ* silanization reaction. This one-step silanization procedure appears to be a general approach. Similar reactivity is observed in the fact that the hydrogen-passivated PS surfaces can be derivatized with a monolayer of trimethylsiloxy groups by the vapor phase reaction of hexamethyldisilazane with amidocyanogen units in moist air.[19,20] In our experimental, several additional silanization reagents have also been successfully used to derivatize silane on the hydrogen-terminated PS surface by this *in situ* silanization procedure.

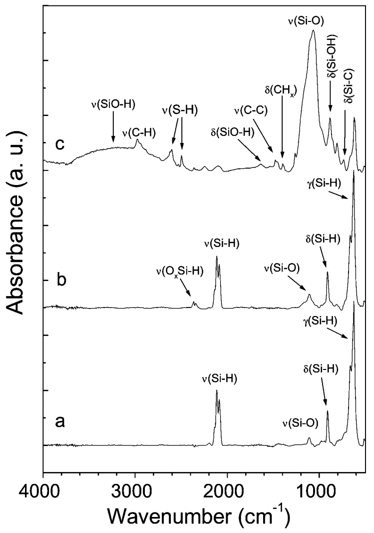

Fig. 3 Transmission infrared spectra for porous silicon (a) as-prepared, and porous silicon immersed in a toluene solution of $Si(OCH_3)_3(CH_2)_3SH$ (10%, v/v) (b) in N_2 atmosphere and (c) in an atmosphere of dilute amine with a trace of water.

X-Ray photoelectron spectroscopy of modified PS surfaces

X-Ray photoelectron spectroscopy (XPS) was used to confirm the elemental and bonding information of FTIR spectroscopy on the PS surfaces. Fig. 4(a) shows the full XPS surveys of the sample modified by the *in situ* silanization reaction with $Si(OCH_3)_3(CH_2)_3SH$ (curve A) and the control sample immersed in toluene under N_2 and dilute amine atmosphere (curve B). In this figure, it is shown that the peak area of the C1s peak at 285 eV in curve A is twice that in curve B, while the Si2s peak at 154 eV, the Si2p peak at 103 eV and the O1s peak at 533 eV in curve A are weaker than those in curve B. The XPS data indicate that the surface of the samples modified by the *in situ* silanization is covered with carbon compounds. The S2p peak of the SH groups, centered at 164 eV,[38] is very prominent in the S2p high-resolution XPS survey of the sample modified, while the control samples do not show such a characteristic peak (Fig. 4(b)). Fig. 4(c) gives the XPS surveys in the Si2p and Si2s regions of the PS before (A) and after (B) exposure to amine/water atmosphere. It is known that the Si2p and Si2s peaks will undergo a high energy shift with increased O content in the SiO_x ($0 \leqslant x \leqslant 2$) compositions.[39] It is observed that both the Si2p and the Si2s peak positions do not change after the exposure, which means that no heavy oxidation took place afterwards. The XPS results further confirm the attachment of the silane-Si–O groups on the surface of the PS.

Steady-state photoluminescence

The emission spectra of the silane-modified PS samples were collected with an excitation wavelength of 350 nm at room temperature. In our experiments, all of the hydroxyl-terminated PS samples exhibit a strong green-yellow PL emission centered between 570 and 600 nm, in which the PL peak

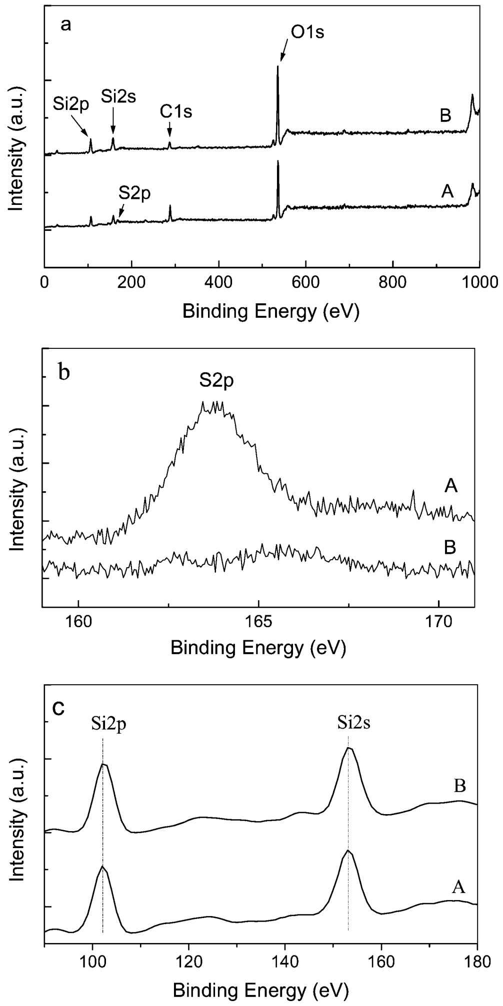

Fig. 4 (a) The full XPS surveys and (b) the high resolution spectra at S2p region for the sample modified by the *in situ* silanization reaction with $Si(OCH_3)_3(CH_2)_3SH$ (curve A) and the control sample immersed in toluene under N_2 and dilute amine atmosphere (curve B). (c) XPS surveys in Si2p and Si2s regions of the PS before (A) and after (B) exposure to amine/water atmosphere.

positions of the freshly hydrogen-terminated PS samples are in the range 800–550 nm.

Fig. 5 shows the PL spectra of the fresh hydroxyl-terminated PS and the functionalized samples. It can be seen that the silane derivatization has a relatively small effect on the PL peak position, but results in a reduction of the PL intensity compared to the hydroxyl-terminated surfaces. The PL intensities of the PS samples derivatized with $Si(OC_2H_5)_2(CH_3)((CH_2)_3NH_2)$, $Si(OC_2H_5)(CH_3)_3$, and $Si(OCH_3)_3(CH_2)_3SH$ are 40%, 60%, and 90% of the hydroxyl-terminated sample, which correspond to the decreases of the absorbance intensities of the –OH stretching vibration in the FTIR spectra. As reported on the Si–C linked PS surfaces, a surface-bound aromatic ring or alkyne or alkene conjugated to an aromatic ring is an extremely effective quenching agent for PL.[12,35] In our experiment, it is also observed that the reduction of the PL from the phenylsilane-modified sample is more than that from the alkylsilane-modified surfaces in which the PL intensity is only 35% of the hydroxyl-terminated surfaces.

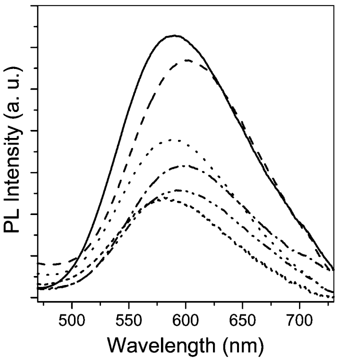

Fig. 5 Photoluminescent spectra of various terminations on the porous silicon, in order of decreasing intensity: Si–OH (—), Si–O–Si–$(CH_2)_3SH$ (---), Si–O–Si–$(CH_3)_3$ (···), Si–O–Si–$(CH_3)(CH{=}CH_2)$ (–·–), Si–O–Si–$(CH_3)((CH_2)_3NH_2)$ (–··–), Si–O–Si–$(CH_3)(C_6H_5)$ (---).

Stability testing of the silane-derivatized surfaces

We have performed stability tests of the silane-derivatized surfaces under a wide variety of conditions which include hot water, hot organic solvent, hot acid, base. For stability testing, PS formed on silicon substrates with resistivities of 1–3 Ω cm were used, which were etched in 2:3 (v/v) pure ethanol and 40% aqueous HF for 10 min at an anodic current density of 30 mA cm^{-2}. The FTIR spectra of the monolayers modified with methyl groups exposed to 0.1 M NaOH for 0, 5, 30, and 120 min are shown in Fig. 6a–d respectively. In this figure, no change in methyl group band (aliphatic ν(C–H) stretching modes at 2962 cm^{-1}, deformation modes at 1440 and 1261 cm^{-1}) are seen, even after immersion in 0.1 M NaOH aqueous solution for 120 min. After 30 min of exposing to base, a strong methyl group deformation mode, which was previously obscured by the Si–O bands, appears at 1261 cm^{-1}. In addition, no obviously stripping or degradation of the PS films is observed during the stability testing in base. In contrast, the freshly prepared PS layer is dissolved rapidly after such treatment for several seconds. This result indicated that the silane-modified PS is significantly more robust than unmodified PS. On the other hand, the intensities of both the O_xSi–H stretching mode at 2240 cm^{-1} and the O_x–SiH bending mode at 887 cm^{-1} decrease when the time of exposure to base increases. Accompanying the loss of intensity shown both in the O_xSi–H bending region and in the O–SiH_x bending region of the FTIR spectra, the band assigned to the O–SiH_x strectching mode around 1200 cm^{-1} is also decreased and a sharp band characteristic of the Si–O–Si asymmetric stretching mode is observed at 1100 cm^{-1}. These FTIR data suggest that the

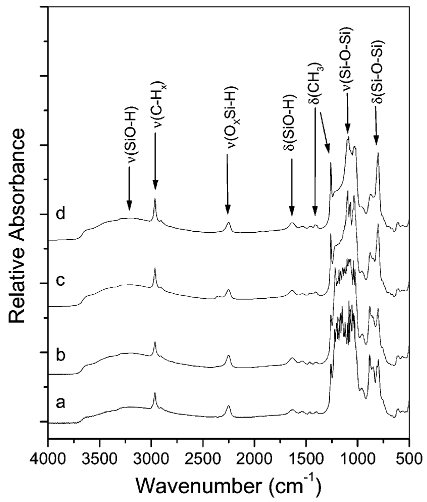

Fig. 6 Transmission infrared spectra of the trimethylsilane-terminated porous silicon surfaces treated with 0.1 M NaOH for (a) 0, (b) 5, (c) 30, and (d) 120 min.

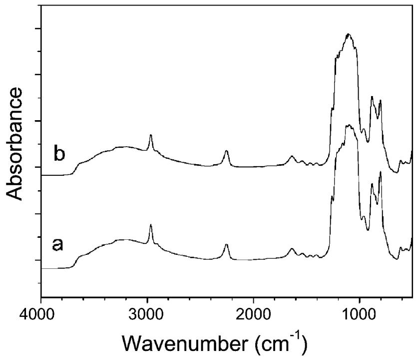

Fig. 7 Transmission infrared spectra of the trimethylsilane-terminated porous silicon surfaces (a) before and (b) after treatment with boiling $CHCl_3$ for 1 h and immersion in a hot 1 M HCl solution for 12 h.

silicon oxide layers back-bonded on the unmodified surfaces are dissolved by aqueous base solution, while the silane layer can protect the PS layer from corrosion.

Additional stability tests were performed to evaluate the resistance of the silane monolayers to the following sequential treatments: boiling in $CHCl_3$ for 1 h and immersion in a hot 1 M HCl solution for 12 h. After these chemical treatments, as shown in Fig. 7, the trimethylsilane-modified surface is found to be extremely robust as evidenced by the unchanged ν(C–H) IR intensity associated with the alkyl group. However, the silane-modified monolayer exhibits poor stability and is easy to remove and the hydrogen-terminated surface is immediately recovered upon exposure to an aqueous 10% HF solution for several seconds.

The PL of the silane-terminated surface is also significantly more stable than that of the nonderivatized surface against chemical attack under such conditions including hot water, hot organic solvent, acid, base, *etc.* Fig. 8(a) shows the PL spectra of the trimethylsilane-modified PS before and after immersion in a 0.1M NaOH solution for 5, 30, and 120 min, in which the PL intensity of the modified samples decreases slightly with increasing of the immersion time. Treatment in this base solution for 2 h results in a decrease in the PL intensity of only 25% compared to the fresh silane-terminated surfaces. By comparison, PL from the nonderivatized PS shown in Fig. 8(b) is quenched by this base solution very rapidly even for several seconds. Furthermore, the PL spectra of the modified sample shown in Fig. 9 indicate no effect on the PL property of the modified PS by immersion in a 1 M HCl solution for 1, 4, and 12 h.

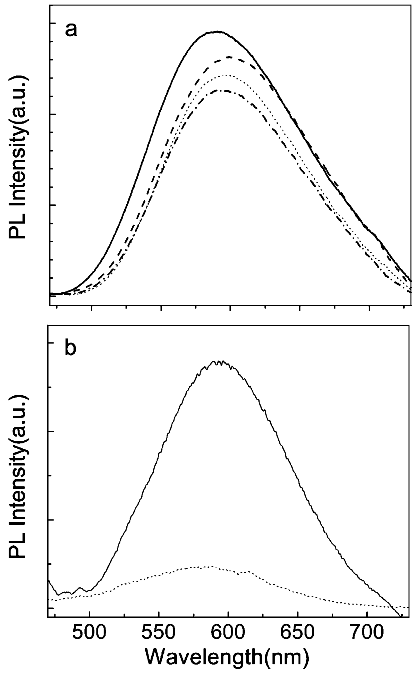

Fig. 8 Photoluminescent spectra for (a) the trimethylsilane-modified PS treated with 0.1 M NaOH for different times: 0 min (—), 5 min (---), 30 min (···), 120 min (–·–). (b) PL from the nonderivatized PS before (—) and after treated with 0.1 M NaOH for 30s (---).

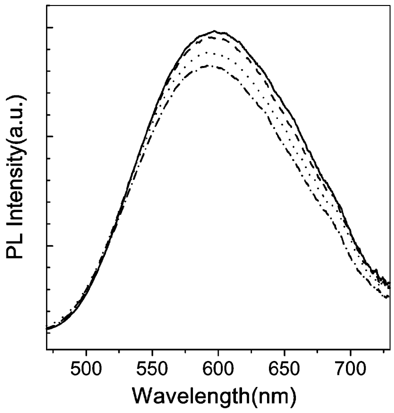

Fig. 9 Photoluminescent spectra for the trimethylsilane-modified PS before (—) and after treated with 1 M HCl solution for 1 (---), 4 (···), and 12 h (–·–).

The PS surfaces covered with Si–O–Si–C bonds have considerable resistance to chemical attack. As we know, the highly electronegative oxygen atom polarizes silicon atoms involved in Si–O linkages, making them susceptible to attack by nucleophiles. In contrast, Si–C is not as highly polarized and so is less susceptible to nucleophilic substitution.[1] For instance, the Si–O bond in alkoxide or ester linkages is readily hydrolyzed[8] and the PS surface modified by Si–C bonds has been shown to provide greater chemical robustness.[15–17] Here, the high stability of the silane-modified surface also appears to be due to the capping of oxidation-susceptible sites on the PS surface. In addition, the hydrophobic character of the alkyl end groups of the alkylsilane chain and the high coverage of the surface prevent the permeation and diffusion of polar molecules.

Conclusion

We have presented a novel and efficient reaction that generated hydroxyl-terminated surfaces from freshly prepared PS. This reaction proceeds by hydrolysis of the surface silicon–hydrogen groups without less oxidation of the back Si–Si bonds, when a trace of amine and water are present together. Following the hydrolysis of the silicon–hydrogen groups, the reactivity of the hydroxyl-terminated surfaces with silanization reagents was investigated. Furthermore, an *in situ* silanization reaction on the surface of the freshly prepared PS has been achieved. The FTIR spectra data indicate that functionalization of the hydroxyl-terminated PS surface with silanization reagents proceeds by abstraction of the surface –OH to form an organic monolayer of Si–O–Si–C bonds and importantly retains the intrinsic structural properties of the PS layers. The resulting monolayers are densely packed and are shown to be highly stable under a variety of conditions including hot water, hot organic solvent, acid, and base, but can be removed by a HF rinse.

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