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Stability Enhancement of Partially-Oxidized Porous Silicon Nanostructures Modified with Ethyl Undecylenate[1]

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ABSTRACT

The thermal reaction of ethyl undecylenate with a hydrogen-terminated porous silicon surface takes place at 85 °C to yield an organic monolayer covalently attached to the surface through Si–C bonds. The presence of traces of water in ethyl undecylenate induces a partial oxidation of the surface and leads to a surface that is composed of alkylated and oxidized regions. A PSi surface with a comparable chemical composition was prepared by the direct reaction of an electrochemically anodized PSi surface (in 1 M H_2SO_4) with anhydrous ethyl undecylenate. The physical and chemical properties of the functionalized surfaces have been characterized using photoluminescence, transmission infrared, and X-ray photoelectron spectroscopies. The derivatized surfaces proved to be very stable in boiling CCl_4 and water, and against corrosion when exposed to 100% humidity in air.

Organic derivatization of semiconductor surfaces is a very active field of research because of the role of these materials in modern technology. Controlling the electronic properties and understanding the reactions at the surface of silicon is crucial for developing new devices. Several methods have been proposed in the literature for chemical modification of both single-crystal silicon (c-Si) and porous silicon (PSi) surfaces under various conditions.[2−6] Porous silicon is of particular interest following the first report on its bright photoluminescence (PL) at room temperature, as a result of quantum confinement within the nanostructures composing this material.[7] A significant volume of work has been devoted to studying its properties ranging from fundamental aspects of its formation to device applications.[8,9] The most sought after applications so far are based on using the PSi layers for integration into optoelectronic devices. Potential applications based on electrical and/or optical measurements for sensing chemical and biochemical species have been demonstrated using PSi.[10] More recently, an important step toward utilization of PSi for biomedical applications has been achieved. Canham et al. have shown that PSi layers of low porosity are active in vivo and that hydroxyapatite could be grown on the PSi matrix.[11−13]

PSi surfaces are prepared in HF-based solutions by electrochemical or chemical etching.[8] The as-prepared PSi surface is terminated by Si−H_x bonds. This monolayer reacts slowly in air to form an oxide submonolayer. For some applications, the PSi matrix is deliberately oxidized in order to achieve a higher stability and better passivation. Oxidation either under thermal, chemical or electrochemical conditions is the most studied route for surface passivation.[14] The oxidation reaction offers some advantages regarding the electronic and chemical stability, but presents some disadvantages associated with exploitation in devices. The electrochemical oxidation retains the integrity of the porous layer, but it is self-limited and thus leaves oxidized (O−SiH_x) and non-oxidized (Si−H_x) domains.[15] The native Si−H_x bonds oxidize slowly in air and introduce surface defects, which are responsible for the PL quenching. In the case of samples oxidized thermally, the nanostructure matrix is consumed by the process and only some crystallites remain in the oxide layer, which can affect the PL yield.

Recently, chemical strategies have been developed for covalent attachment of organic monolayers on PSi surfaces based on the chemical reactivity of the silicon−hydrogen bonds of the PSi layers.[2] It has been demonstrated that

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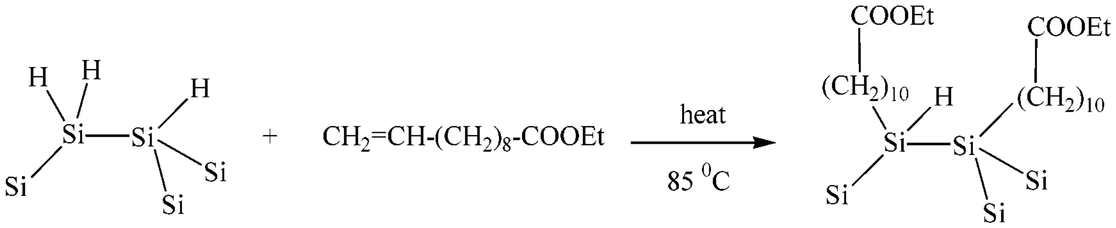
Scheme 1



organic derivatization of PSi surfaces passivates effectively the surface and retains the intrinsic structural and physical properties of the surface. Replacing the $Si-H_x$ bonds by Si−C and Si−O−C bonds under thermal conditions preserves the PL and enhances the stability of the PSi surface in aqueous solutions of HF and KOH. Thermal reaction of hydrogen-terminated PSi surfaces with alkenes, alkynes, and aldehydes has been achieved at elevated temperatures.[5,6,16]

This paper describes a chemical route for organic functionalization of PSi layers using ethyl undecylenate.[17−19] The presence of traces of water in the chemical reagent induces, in a competitive process with the hydrosilylation reaction, a partial oxidation of the PSi surface. If the traces of water were removed by adding 5% volume of chlorotrimethylsilane (TMSCl), an oxide free surface can be prepared. A deliberate partial oxidation of the PSi surface using a post-anodization of the freshly prepared PSi surface in 1 M sulfuric acid produces after derivatization a surface with oxidized and alkylated regions. The presence of oxidized regions on the surface along with organic molecules offers novel properties to the surface. The chemical properties of the surfaces have been characterized using transmission Fourier transform infrared (FT-IR)[20] and X-ray photoelectron spectroscopies. The derivatized PSi surfaces were stable in boiling CCl_4 and water. The effect of the surface composition on the photoluminescence was examined, and the stability against corrosion in 100% humidity was studied using chemography.

Thermal reaction of the hydrogen-terminated PSi surface with ethyl undecylenate at 85 °C offers a surface bearing an ester function at the end of the organic layer (Scheme 1). As shown by FT-IR spectroscopy, a freshly prepared PSi surface exhibits peaks due to $Si-H_x$ stretching at 2112 cm^{-1} (ν_{Si-H_x}) and $Si-H_2$ scissor at 908 cm^{-1} (δ_{Si-H_2}) (Figure 1a). A small peak at 1066 cm^{-1} is present in the freshly prepared sample, due to interstitial oxygen in the original silicon substrate lattice. After reaction with ethyl undecylenate, new absorption peaks appear between 2850 and 2960 cm^{-1} associated with $C-H_x$ stretching, and features at 1464 and 1373 cm^{-1} due to methylene and methyl bending of the alkyl chain. Intense bands due to the carbonyl function at 1740 cm^{-1} accompanied by C−O and Si−O−Si stretching near 1050 cm^{-1} were observed. The silicon−hydrogen band intensity decreased substantially, and a new band centered at 2243 cm^{-1} was obtained. The shift to higher energy of the $Si-H_x$ stretch and the intense band observed at 1050 cm^{-1} are due to partial oxidation of the surface (Figure 1b).[15] A control experiment was carried out by reacting hydrogen-terminated PSi with deoxygenated ethyl acetate for 18 h at 90 °C. There was no change in the IR absorption, which implies that the ester function does not react with either the Si−Si or $Si-H_x$ bonds. This is in agreement with previous observations on the thermal reaction of Si(100)−H with ethyl undecylenate.[18] The same observation applies when a freshly prepared PSi sample was heated in deoxygenated decane at 100 °C for 22 h.[6] When the reaction was carried out in the presence of TMSCl a similar infrared spectrum (Figure 1c) was obtained, but this time the intensity of the peak centered at 1050 cm^{-1} is smaller and the peak at 2243 cm^{-1} is absent. This is consistent with a chemical process taking place without any surface oxidation. The silicon−hydrogen peak becomes broad and featureless. This is due to electronic effects and steric interactions between the remaining $Si-H_x$ on the surface and the adjacent alkyl chain attached to the surface. The absorption intensity of ν_{Si-H_x} and δ_{Si-H_2} decreases substantially after the reaction, indicating that a significant fraction of the silicon−hydrogen bonds has reacted with the unsaturated C=C bond. This makes the thermal route very suitable for surface passivation and the introduction of functional groups (ester group) onto the surface.

X-ray photoelectron spectroscopy (XPS) was used as a tool to analyze the composition of the surface before and after derivatization. An XPS survey of the as-anodized PSi surface shows signals due to silicon Si 2p and Si 2s at 99 and 151 eV, respectively, and small peaks due to carbon, oxygen, and fluorine. The latter signals could result either from hydrocarbon contamination or from small amounts of fluorine and ethanol attached to the surface during the electrochemical preparation of the PSi sample (Figure 2a). After reaction with ethyl undecylenate, an increase of the carbon and oxygen signals was observed (Figure 2b). The oxygen signal was more intense than expected in comparison with the elemental composition of the organic molecules composing the monolayer. In fact, the XPS high-resolution spectrum of silicon showed a silicon peak at 103 eV attributed to the oxidized surface. Part of the oxygen signal is associated with oxide formation on the surface during the thermal reaction. When the surface was prepared under conditions that scavenge the traces of water present in the chemical reagent, a similar spectrum (Figure 2c) was obtained but with a much reduced signal of oxygen. In addition, the complete absence of a peak at 103 eV confirms that the hydrosilylation reaction occurred in this case without any apparent oxidation of the surface.

Steady-state room-temperature PL of the hydrogen-terminated surface (Figure 3a) shows a peak centered at 1.8 eV, which is consistent with 70% porosity PSi.[21] The surface modified with ethyl undecylenate (in the presence of TMSCl)

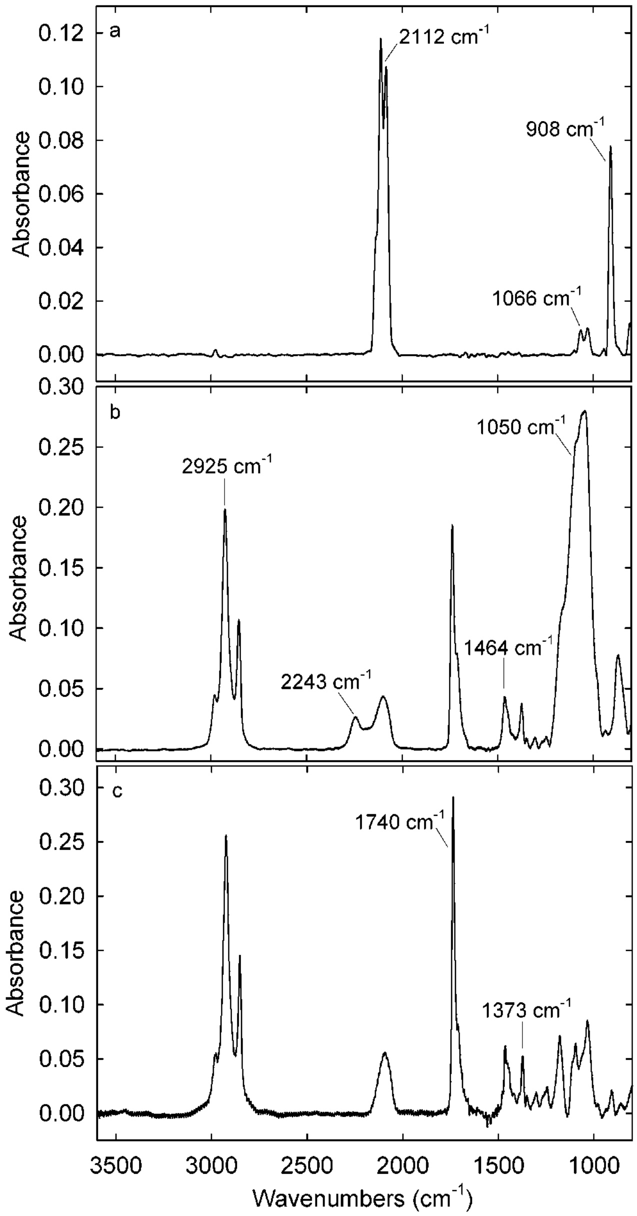


Figure 1. Transmission infrared Fourier transform spectra of the (a) as-anodized PSi before derivatization and PSi functionalization with (b) ethyl undecylenate, and (c) ethyl undecylenate in the presence of TMSCl.

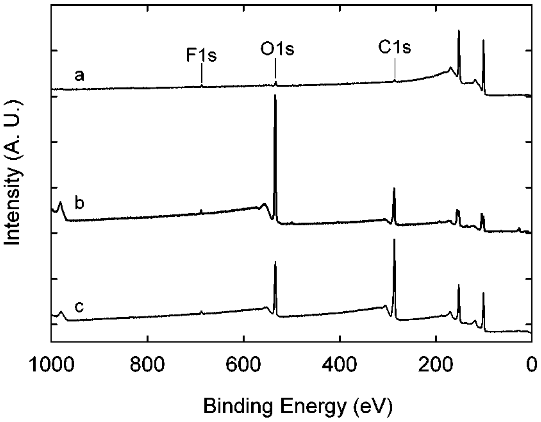


Figure 2. XPS survey of (a) a freshly prepared PSi surface, and PSi samples thermally modified with (b) ethyl undecylenate, and (c) ethyl undecylenate in the presence of TMSCl.

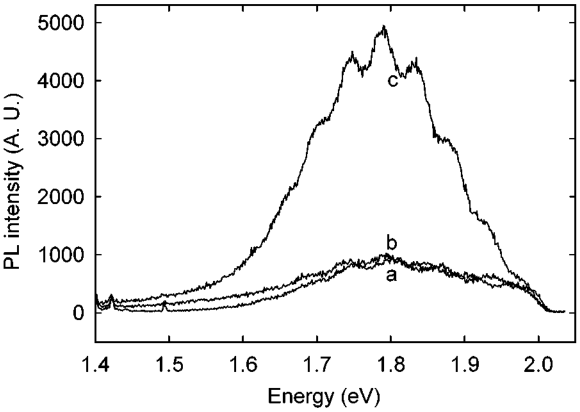


Figure 3. Steady-state room-temperature PL spectra of (a) as-anodized PSi, (b) modified with ethyl undecylenate in the presence of TMSCl, and (c) derivatized sample with ethyl undecylenate.

exhibits a similar peak in shape, intensity and energy maximum (Figure 3b). Since there was neither a shift of the PL maximum nor a PL quenching after chemical modification of the surface, this implies that the structural integrity and the physical properties of the PSi layer are unaffected and thus makes this process highly efficient for PL preservation. The partially oxidized PSi surface produces a PL at the same peak position with an intensity 10 times higher than the intensity of the freshly prepared surface (Figure 3c). This effect has been observed when a decyl terminated PSi surface was subjected to a steam treatment and was attibuted to partial oxidation of the surface.[6] A similar effect has been reported by Campbell et al. when the PSi surface was oxidized at high temperatures using dry oxygen.[22]

When stored in air for several weeks, the treated surfaces did not show any apparent degradation. They are stable to 2.4 N HCl at 70 °C for several hours, and only the ester hydrolysis was observed. An organic monolayer with acid terminal groups was formed during this treatment. Surfaces that contain alkylated and oxidized regions are stable in boiling CCl_4 and water (there was no decrease of the Si$-$H$_x$ IR-intensity after boiling in CCl_4 and water for 1 h). For comparison, under the same conditions, the native silicon$-$hydrogen (Si$-$H$_x$) bonds of a freshly prepared PSi surface were completely transformed to Si$-$Cl bonds.[23] However, in our samples the silicon$-$hydrogen bonds with oxidized back-bonds (OSi$-$H$_x$) were not converted, in the similar way, to Si$-$Cl bonds. The lack of reactivity is thought to result from the lower reactivity of siloxanes versus silanes and/or a high passivation of the organic monolayer. We believe that the density of organic molecules on the surface is high enough to protect the remaining unreacted Si$-$H$_x$, as seen in the case of derivatized samples without any oxide film present on the surface.

When a surface that had been partially oxidized was immersed in 15% HF aqueous solution for 15 min, the oxidized regions were completely dissolved (shown by the disappearance of the Si$-$H$_x$ stretching at 2243 cm^{-1} and the strong Si$-$O$-$Si stretching at 1050 cm^{-1}) and new Si$-$H$_x$ bonds were formed. The modified regions with the alkyl

Scheme 2

$$\equiv \mathrm{Si\text{-}SiH_xR_{(3-x)}} + \mathrm{H_2O} \longrightarrow \equiv \mathrm{Si\text{-}OH} + \mathrm{SiH_{(x+1)}R_{(3-x)}}$$

chain remained, however, unchanged. This is in agreement with a surface that is composed of patches of separate alkylated and oxidized regions rather than a random distribution of the oxide on the surface. The treated surface in HF was chemically derivatized using 1-decene to yield a surface that is covered with an organic monolayer with different end groups (methyl and ester). This step is very important to control the wetting properties of the surface and also the distribution of functional groups on the PSi surface.

Finally, we have used electrochemical post-anodization of the freshly prepared PSi surface in 1 M H_2SO_4 to produce a surface that contains native silicon−hydrogen bonds (Si−H_x) and silicon−hydrogen bonds with oxidized back bonds (OSi−H_x).[15] This method is known to induce a selective oxidation of the walls of the PSi layers. Figure 4a displays an IR spectrum of a PSi sample that has been electrochemically oxidized in 1 M H_2SO_4 for 5 min at 3 mA/cm^2. Two peaks are visible in the region of the silicon−hydrogen bonds: 2127 cm^{-1} (Si−H_x stretching) and 2250 cm^{-1} (OSi−H_x stretching). A very intense peak at 1065 cm^{-1} was also present (not shown on the spectrum) due to Si−O−Si stretching resulting from the electrochemical oxidation of Si−Si back-bonds. Further reaction of the anodized PSi sample with ethyl undecylenate in the presence of TMSCl at 120 °C for 21 h gives a surface bearing an organic monolayer with an ester terminal group (Figure 4b). A net decrease of the intensity of the non-oxidized Si−H_x was observed, which is consistent with a thermal hydrosilylation that consumes preferentially the native Si−H_x bonds rather than the oxidized ones (OSi−H_x). The modified PSi surface showed a comparable stability in 15% HF solution and in boiling CCl_4 and water, as the one prepared from the freshly anodized (without electrochemical oxidation) PSi surface that had been derivatized with ethyl undecylenate in the absence of TMSCl. Again this proves that the oxidized silicon−hydrogen bonds (OSi−H_x) are less reactive than the native Si−H_x, and the surface produced during this process is comparable to the one formed during the thermal functionalization of the PSi surface (without post-anodization) with ethyl undecylenate in the presence of traces of water. The chemical nature and the electronic properties of the two regions are different. It is, however, difficult to explain this observation, and to propose a rational mechanism, at this stage of the research.

Recently, Canham et al. have developed a new method to monitor the degree of oxidation of the porous surface based on silver halide (present in photographic emulsion) reduction by gaseous silane, SiH_4, resulting from the chemical hydrolysis of the silicon−silicon back bonds.[24,25] This same method was used to previously monitor the behavior of modified PSi surfaces (formed through a catalytic route using $EtAlCl_2$ as a catalyst) in air at 100% humidity[26] (Scheme 2). The chemography reveals the extent to which the organic monolayer protects the surface against corrosion. The degree of oxidation is related to the optical density of the corresponding spots formed on the photographic plates. Our samples were exposed to 100% humidity in air. After a 1 h exposure, the functionalized surface with ethyl undecylenate in the presence of TMSCl shows a light circular spot, whereas the hydrogen-terminated surface has been heavily reduced (Figure 5a). The optical density of the spot corresponding to the modified surface with ethyl undecylenate (without TMSCl) increases after a 4 h exposure to 100% humidity in air, but the oxidation rate is much slower when compared to the as-anodized surface under the same conditions (Figure 5b). This implies that the alkyl chains of the monolayers prevent hydrolysis of the Si−Si bonds. The high density of organic molecules attached to the surface through the hydrosilylation reaction and the hydrophobic character of these chains protect well the surface from oxidation in ambient air. Amazingly, the surface modified with ethyl undecylenate containing oxidized domains on its surface did not show any changes after a 4 h exposure, and even after 16 h only a slightly darkened spot is noticeable (Figure 5c). This is an unprecedented effect, since even when the surfaces are heavily oxidized by extended storage in ambient air they did not show such a strong prevention against corrosion.[25] This result is in accordance with a high stability of the alkylated regions and a low reactivity of the oxidized domains. The chemographs in Figure 5 show that the edges of the PSi sample in the case of the hydrogen-terminated surface (comprising c-Si) are completely corroded, whereas in the case of the modified samples with ethyl undecylenate, the edges were not affected by the treatment. The hydrolysis reaction occurs only in the porous area. To understand this behavior, we have used XPS to evaluate the elemental composition of the c-Si edges. The XPS survey showed a similar surface composition of the porous area and the c-Si edge of the sample, indicating a similar chemical modification. The difference in the behavior may result from a higher density of organic molecules at the sample surrounds due to the physical structural differences in the surfaces of the c-Si and the porous regions.

In conclusion, we have shown that organic functionalization of PSi surfaces under thermal conditions offers an excellent method for the surface passivation and PL preservation of PSi. This route is easy to carry out and is tolerant of different functional groups, which allow further chemical manipulations to achieve more complex structures on the surface. The surface is protected against corrosion when exposed to 100% humidity in air. The presence of small amounts of oxide formed during the chemical process, when no special precautions were taken in order to eliminate the traces of water present in the chemical reagent, increases remarkably the surface resistance against corrosion. A surface with a similar composition was obtained when a PSi surface electrochemically anodized in 1 M H_2SO_4 was thermally modified with ethyl undecylenate in the presence of TMSCl.

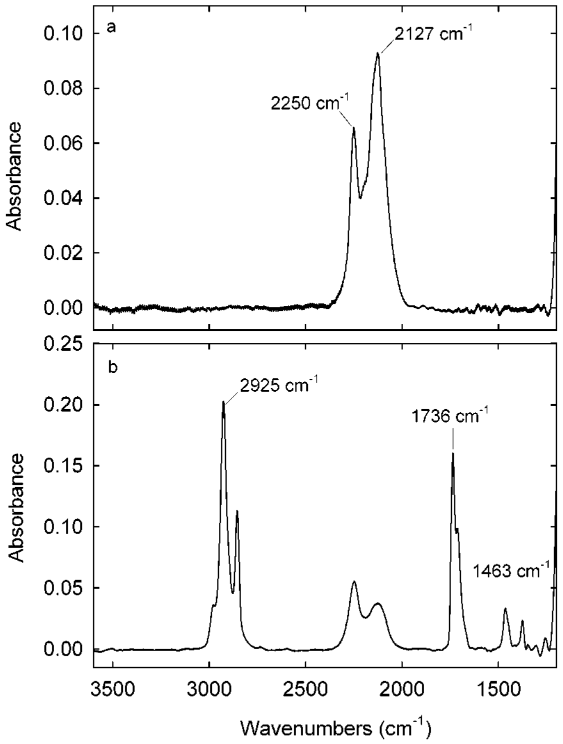


Figure 4. Transmission FT-IR spectra of (a) a freshly prepared PSi sample anodically oxidized in 1 M H_2SO_4 for 5 min at 3 mA/cm^2 and (b) the same sample functionalized with ethyl undecylenate in the presence of TMSCl.

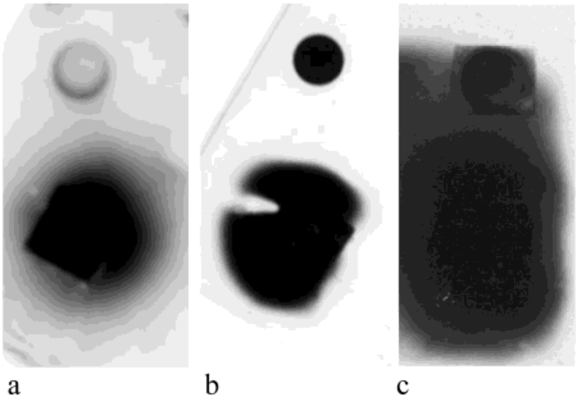


Figure 5. Chemography studies of H-terminated (lower spots) and modified PSi surfaces (upper spots) with ethyl undecylenate in the presence of TMSCl after exposure to 100% humidity for (a) 1 h and (b) 4 h, and (c) PSi modified with ethyl undecylenate after 16 h exposition to 100% humidity.

The oxidized regions can be selectively dissolved in 15% HF solution to form new Si$-$H$_x$ bonds and thus allow a further chemical transformation of these new Si$-$H$_x$ bonds. The stability of the surface to hydrolysis is, in this case, comparable to that of heavily oxidized PSi surfaces in which the semiconducting nature is heavily degraded. Such a high surface stability augurs well for in vivo sensing. Finally, the presence of regions of different chemical composition (oxidized regions and organic modified regions or organic regions with different terminal functional groups) on the surface is of interest for controlling the wetting properties of the surface. This is an important step toward applications of the PSi matrix for DNA and protein microarray processing.

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(21) Porous silicon samples used in this report were etched at curent densities of 5 mA/cm^2 in HF/EtOH = 1/1 (v/v) for 8 min. Under these conditions, the porosity was estimated to be ca. 70% by an X-ray reflectivity technique, the porous layer thickness was evaluated using atomic force and scanning electron microscopy (cross section) and found to be 2 μm, and the pore diameter is smaller than 10 nm.[6]
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(24) The chemographs were taken using 25 μm thick Ilford L4 nuclear tracking emulsion plates. Porous silicon samples were placed in direct contact with the plate in air of 100% relative humidity at room temperature for times ranging from 1 to 16 h in complete darkness. The plates were then presoaked in deionized water, developed using 3:1 diluted Kodak D19 developer for 5 min 30 s, and fixed in 7:1 diluted G333C AGFA for 30 min. All of these operations were conducted at 5 °C. Subsequent washing in water for 1 h was carried out at room temperature. The plates were then printed out onto photographic paper using a Fuji Pictostat 300 running in transmission mode so that the black features shown here correspond to high exposure in the original plate.
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