Characterization and Surface-Derivatization of Porous Silicon

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Abstract

Chemical modification of porous silicon surface has been investigated to have different physical surface properties. Porous silicon modified with dodecyl functionality exhibits hydrophobic feature, however the oxidation of porous silicon to modify with hydroxyl group displays hydrophilic properties. Surface characterization for both dodecyl and hydroxyl derivatized porous silicon was investigated by FT-IR spectroscopy. To determine the surface coverage, the amine functionalized surface was reduced by dithiothreitol (DTT) and the released 2-thiopyridone was quantified by UV/vis spectroscopy.

Key words : Porous Silicon, Surface Derivatization, Oxidation, Hydrosilylation

1. Introduction

Since the discovery of porous silicon (PSi)[1], PSi has been intensively investigated for a variety of applications such as chemical[2] and biological sensors[3], medical diagnostics[4], optical band pass filters[5], micro chemical reactors[6], and TNT sensor[7]. Recently, optical devices based on nano-structured PSi attract a great attention of the scientists. From a conceptual point of view, the former is based on optically thin and homogeneous mono-layered PSi. The direction of pores and pore diameters depend on surface orientation, doping level and type, temperature, the current density, and the composition of the etching solution[8,9]. Homogeneous mono-layered PSi has been developed and typically prepared by applying a current waveform to the etch cell. PSi results in a refractive index and exhibits an unique photonic structure[10]. Rugate-structured porous silicon having photonic structure of rugate filter in which refractive index varies sinusoidally has been recently developed by applying a computer-generated pseudo-sinusoidal current waveform[11].

Chemical modification of PSi multilayer exhibits the modification of its physical, chemical, and electronic properties. Chemical or bio molecule can be detected based on changes in the spectral interference pattern[12,13]. Homogeneous PSi with reflection peaks in visible spectral range was recently demonstrated to be applied for the detection of different chemical species[14-16].

For applications in high throughput drug discovery and disease diagnostics, label-free biosensors would be important due to the advantage of easy sample preparation[17,18].

Two main optical transduction methods for label-free biosensors are both optical interferometric methods based on interferometers[19] evanescent wave devices[20], and grating couplers[21] and surface plasmon methods based on metal films[22] and colloids[23]. Biosensor based on porous silicon interferometer has a great advantage due to a large surface area matrix for immobilization of a variety of biomolecules such as enzymes[24], protein[25], and DNA fragments[26]. Sailor et al. recently reported that the electronic or optical properties of mono-layered PSi can also be used as the transducer of biomolecular interaction in biosensor application[27,28]. Therefore, the surface modification of PSi could be one of keys for the application of chemical and biomolecular sensor. In the present work, the surface modifacation and characterization of PSi via oxidation or hydrosilation by using FT-IR spectroscopy were reported.

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2. Experimental Section

2.1. Preparation of PSi

The anodization cell is made of Teflon, which is resistive against attack from the hydrofluoric acid electrolyte. The aluminum foil serves as the anode and it is sandwiched between the top and bottom parts of the Teflon cell. For a better contact, a platinum wire is placed against the silicon wafer where leads can be connected. The cathode is a circular platinum wire that is submerged in the hydrofluoric acid electrolyte. The cathode is held in place, three wing nuts hold the entire anodization cell together during the electrochemical etching process. The hydrofluoric acid electrolyte is placed inside the top part of the Teflon cell. Enough electrolyte must be present to supply the required fluorine ions and to cover the platinum wire cathode. The top part of the Teflon cell has a circular window of area 1.2 cm^2 which exposes the silicon to hydrofluoric acid and forms the PSi. The entire electrochemical process is carried out under constant current supplied by a computer controlled Keithley 2420 power sourcemeter.

2.2. Oxidation of PSi

Surface of a PSi film was predominant hydride-terminated after the etching procedure. This surface was sensitive to oxidation and hydrolysis upon exposure to aqueous solution. Thermally oxidized PSi samples were obtained by heat treatment in a furnace (Thermolyne F6270-26 furnace equipped with controller) using the following parameters: initial ramp rate, 5°C/min to 300°C; hold time, 3 h; and passive cooling to ambient temperature.

2.3. Chemical Modification of PSi Surface

Freshly etched PSi chip was placed in 250 mL of schlenk flask under argon atmosphere. After 20 mL of 1-dodecene was added, the reaction mixture was refluxed for 4 h. Dodecyl-derivatized PSi chip was washed several times with ethanol and dried under argon gas. For the surface modification of (3-aminopropyl)trimethoxysilane terminated PSi with 2-pyridyl-2-carboxyethyl disulfide, 2-pyridyl-2-carboxyethyl disulfide (0.2 g, 94.7 mmol) was quickly dissolved in a 10 mL of methylene chloride solution. 1-(3-(dimethylamino) propyl)-3-ethylcarbodiimide hydrochloride (EDC) (100 mg, 0.6 mmol) was added to the solution. The resulting solution was allowed to stir in dry argon gas for 30 min, before funtionalization of oxidizied rugate PSi was added. The reaction mixture was stirred for 12 h at room temperature. Afterward, the chip was washed by ethanol, methylene chloride, and acetone and then dried under an atmosphere.

2.4. Instrumentation and Data Acquisition

FT-IR spectra were acquired with a Nicolet model 5700 FT-IR instrument in the diffuse reflectance mode (Spectra-Tech diffuse reflectance attachment).The FT-IR sample compartment was purged with nitrogen before each acquisition. 2-Thiopyridone releases were measured by UV-vis spectrometer (UV-2401 PC, Shimazu). The quantity of 2-thiopyridone release from the functionalized rugate PSi was measured at the fixed absorption wavelength of 343 nm on a time scale.

3. Result and Discussion

3.1. Oxidation

Freshly etched PSi is covered by hydrogen atoms that are covalently attached to the silicon surface. The attached hydrogen species are in the form of Si-H, Si-H$_2$, and Si-H$_3$ and can be characterized by fourier transform infrared spectroscopy (FT-IR). FT-IR spectrum of freshly etched PSi immediately after an anodization of the silicon wafer displayed a characteristic band centered at v(Si-H) = 2090, v(Si-H$_2$) = 2115, and v(Si-H$_3$) = 2140 cm^{-1} for the v(Si-H) stretching vibration, and δ(Si-H) = 908 cm^{-1} for the δ(Si-H) bending vibration, respectively.

The hydrogen covered surface provides a good electron passivation layer. After the PSi is exposed to air, a slow oxidation of the surface takes place. Replacing the hydrogen by oxygen (oxidation) is one of the most common ways to passivate the electronic properties of PSi. Oxidation can be occurred by exposing the sample to air, anodic oxidation in a non-fluoride electrolyte[46], chemical oxidation[47], or thermal oxidation[48-51]. Thermal oxidation is the most commonly used because it produces reproducible and controlled oxide layers of good quality. Thermal oxidation is the method used to passivate or oxidize the PSi structure.

Thermal oxidation performed in a furnace at temperatures between 300 ~ 600°C results in the loss of hydrogen and the production of PSi with poor electronic
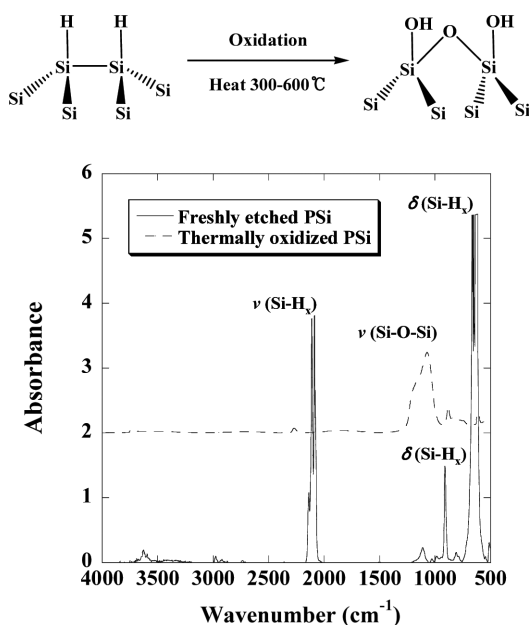
Fig. 1. Chemical scheme for the thermal oxidation (top) and comparison of FT-IR spectra between freshly etched PSi and thermally oxidized PSi (bottom).

properties. The solution is to oxidize at higher temperatures resulting in better passivation, but running the risk of converting the PSi structure into silicon dioxide (SiO_2). Diffuse reflectance FT-IR spectroscopy was used to monitor the oxidation and functionalization reactions of the porous silicon support. Figure 1 shows experimental setup for the thermal oxidation and comparison of FT-IR spectra between freshly etched PSi and thermally oxidized PSi. Thermal oxidation of the PSi layer resulted significant loss of intensity of the v(Si-H) modes in the infrared spectrum at 2085.2150 cm^{-1}, but vibrational bands due to oxygen-back-bonded silicon hydride, v(OSi-H) and δ(OSi-H) modes, grew at 2200 -2250 and 877 cm^{-1}, respectively. Multiple silicon oxide species, Si-O-Si, displayed a strong, very broad absorption band between 1000 and 1200 cm^{-1}.

3.2. Surface-Derivatization (Hydrosilylation)

The hydride-terminated surfaces in general offer many advantages, including their excellent chemical homogeneity (>99% H termination) and strong FT-IR stretching modes (~2100 cm^{-1}) which can provide information as to surface flatness and makeup. The use of the Si-H terminated surface for many applications is
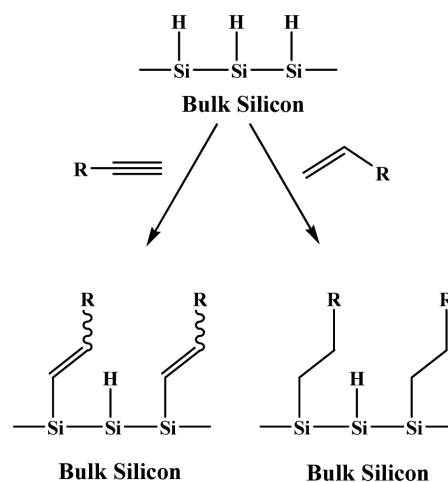

Fig. 2. Schematic hydrosilylation chemistry. Hydrosilylation involves the insertion of an unsaturated bond, alkyne or alkene, into Si-H bond, resulting in Si-C bond formation and formation of alkenyl or alkyl groups, respectively.

precluded due to its propensity to oxidize, but it can be easily handled in air for minutes to tens of minutes without measurable degradation. Rapid and efficient preparation of Si-H hydride-terminated flat surfaces has been known for over 10 years[52-53].

Hydrosilylation involves the insertion of an unsaturated bond onto a silicon-hydride group. Alkene and alkyne hydrosilylation on Si-H-terminated surfaces yield alkyl and alkenyl termination, respectively as shown in Figure 2.

One of the hydrosilylation methods is the thermally induced hydrosilylation. Thermally induced hydrosilylation of alkenes and an alkyne has been applied to Si-H-terminated PSi surface [54-56]. It is initially reported that refluxing PSi for 18-20 h at 110-180°C in an aliphatic alkyne or alkene yields alkyl monolayers[54]. Futher investigation of thermally induced hydrosilylation of 1-dodecene on PSi is examined, and derivaized surfaces are characterized by FT-IR as shown in Figure 3.

Another of the hydrosilylation method is the photochemical hydrosilylation using UV irradiation. The UV irradiation can promote hydrosilylation of unsaturated compounds[57] due to homolytic cleavage of Si-H bonds. UV photoinduction, however, takes place at room temperature and thus a way to avoid thermal input that can be harmful to delicate or small features on a silicon chip.
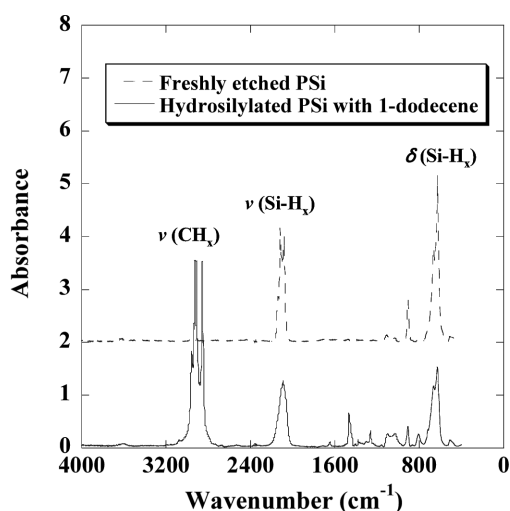
Fig. 3. Comparison of FT-IR spectra between freshly etched PSi and hydrosilylated PSi with 1-dodecene.

Treatment of the porous silicon with ozone results in the oxidation of porous layer. As expected, ozonolysis also leads to complete disappearance of the Si-H vibrational bands. A small band at 887 cm^{-1} assigned to δSi-OH is also observed. Exposure to ozone for longer periods led to complete disappearance of the Si-OH band because the formation of the Si-O-Si bonds is thermodynamically preferred.

3.3. Surface Coverage

To determine the surface coverage, the amine functionalized surface was reduced by dithiothreitol (DTT)
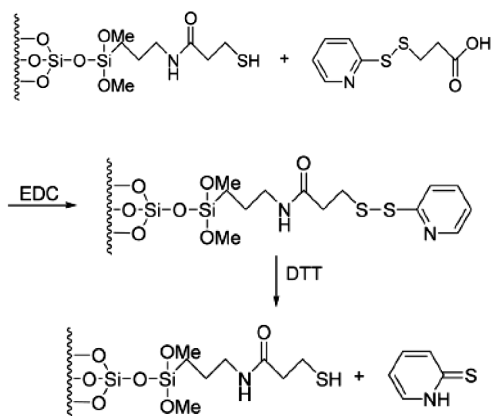

Fig. 4. Schematic diagram to measure the surface coverage of PSi.

as shown in Figure 4. The released 2-thiopyridone was quantified by UV/vis spectroscopy (λ_{max} = 343 nm, ε = 8.08 × 103 M^{-1}cm^{-1}). The number of linker molecules in the case of a silicon chip etched at 250-150 mA/cm^2 was in the range 300 nmol/cm^2, which corresponds to a surface coverage of 30-80% approximately. This calculation is based on the following parameters, assuming cylindrical pores: pore radius, 10 nm; thickness of the porous layer, 90 μm; porosity, 74%; area per molecule of the biotin linker, 0.07 A^2; area of the chip, 1.2 cm^2.

4. Conclusion

The surface modification of porous silicon has been reported to have different physical surface properties such as a hydrophobic property through alkylation of PSi and hydrophilic property through oxidation of PSi. The surface of porous silicon modified with dodecyl functionality and the oxidized porous silicon was characterized by FT-IR spectroscopy. The surface coverage of alkyl group in PSi was quantified by UV/vis spectroscopy.

References

[1] A. Uhlir, "Electrolytic shaping of germanium and silicon", Bell System Tech. J., Vol. 35, p. 333, 1956.

[2] M. W. Hwang and S. D. Cho, "Detection of Organic Vapors Using Change of Fabry-Perot Fringe Pattern of Surface Functionalized Porous Silicon", Journal of the Chosun Natural Science, Vol. 3, No. 3, p. 168, 2010.

[3] D. H. Jung, "Biosensor Based on Distributed Bragg Reflector Photonic Crystals for the Detection of Protein A", Journal of the Chosun Natural Science, Vol. 3, No. 1, p. 33, 2010.

[4] M. Simion, I. Kleps, T. Neghina, A. Angelescu, M. Miu, A. Bragaru, M. Danila, E. Condac, M. Costache, and L. Savu, "Nanoporous silicon matrix used as biomaterial", J. Alloy Compd., Vol. 434, p. 830, 2007.

[5] S. D. Cho, "Preparation of Polystyrene Thin Films Containing Bragg Structure and Investigation of Their Photonic Characteristics", Journal of the Chosun Natural Science, Vol. 3, No. 3, p. 138, 2010.

[6] M. A. Khan, M. S. Haque, H. A. Naseem, W. D. Brown, and A. P. Malshe, "Microwave plasma chemical vapor deposition of diamond films with low residual stress on large area porous silicon sub-

strates", Thin Solid Films, Vol. 332, p. 93, 1998.

[7] S. D. Cho, "Detection of Nitroaromatic Compounds with Functionalized Porous Silicon Using Quenching Photoluminescence", Journal of the Chosun Natural Science, Vol. 3, No. 4, p. 202, 2010.

[8] Y. D. Koh, "Analysis on Oxidation of Porous Silica Obtained from Thermal Oxidation of Porous Silicon", Journal of the Chosun Natural Science, Vol. 3, No. 3, p. 153, 2010.

[9] J. M. Han, "Photoluminescence of Porous Silicon According to Various Etching Times and Various Applied Current Densities", Journal of the Chosun Natural Science, Vol. 3, No. 3, p. 148, 2010.

[10] S. H. Jang, "Study on Thickness of Porous Silicon Layer According to the Various Anodization Times", Journal of the Chosun Natural Science, Vol. 3, No. 4, p. 206, 2010.

[11] K. S. Jung, "Fabrication and Characterization of DBR Porous Silicon Chip for the Detection of Chemical Nerve Agents", Journal of the Chosun Natural Science, Vol. 3, No. 4, p. 237, 2010.

[12] Y. C. Koh, "1-D Photonic Crystals Based on Bragg Structure for Sensing and Drug Delivery Applications", Journal of the Chosun Natural Science, Vol. 4, No. 1, p. 11, 2011.

[13] S. G. Kim, "Optical Characterization of Smart Dust Based on Photonic Crystals and Its Sensing Applications", Journal of the Chosun Natural Science, Vol. 4, No. 1, p. 7, 2011.

[14] S. H. Jang, "Chemical and Physical Properties of Porous Silicon", Journal of the Chosun Natural Science, Vol. 4, No. 1, p. 1, 2011.

[15] T. A. Schmedake, F. Cunin, J. R. Link, and M. J. Sailor, "Standoff Detection of Chemicals Using Porous Silicon "Smart Dust" Particles", Adv. Mater., Vol. 14, p. 1270, 2002.

[16] S. O. Meade, M. S. Yoon, K. H. Ahn, and M. J. Sailor, "Porous Silicon Photonic Crystals as Encoded Microcarriers", Adv. Mater., Vol. 16, p. 2811, 2004.

[17] A. Brecht and G. Gauglitz, "Recent developments in optical transducers for chemical or biochemical applications", Sensor. Actuat. B-Chem., Vol. 38, p. 1, 1997.

[18] J. Janata, M. Josowicz, and D. M. Devaney, "Chemical Sensors", Anal. Chem., Vol. 66, p. 207R, 1994.

[19] J. Piechler, A. Brandenburg, A. Brecht, E. Wagner, and G. Gauglitz, "Characterization of grating couplers for affinity-based pesticide sensing", Appl. Opt., Vol. 36, p. 6554, 1997.

[20] A. P. Abel, M. G. Weller, G. L. Duveneck, M. Ehart, and H. M. Widmer, "Fiber-Optic Evanescent Wave Biosensor for the Detection of Oligonucleotides", Anal. Chem., Vol. 68, p. 2905, 1996.

[21] R. Polzius, E. Diessel, F. F. Bier, and U. Bilitewski, "Real-Time Observation of Affinity Reactions Using Grating Couplers: Determination of the Detection Limit and Calculation of Kinetic Rate Constants", Anal. Biochem., Vol. 248, p. 269, 1997.

[22] J. Homola, S. S. Yee, and G. Gauglitz, "Surface plasmon resonance sensors: review", Sensor. Actuat. B-Chem., Vol. 54, p. 3, 1999.

[23] P. I. Nikitin, A. A. Beloglazov, V. E. Kochregin, M. V. Valeiko, and T. I. Ksenevich, "Surface plasmon resonance interferometry for biological and chemical sensing", Sensor. Actuat. B-Chem., Vol. 54, p. 43, 1999.

[24] J. Drott, K. Lindstrom, L. Rosengren, and T. Laurell, "Porous silicon as the carrier matrix in microstructured enzyme reactors yielding high enzyme activities", J. Micromech. Microeng., Vol. 7, p. 14, 1997.

[25] T. Laurell, J. Drott, L. Rosengern, and K. Lindstrom, "Enhanced enzyme activity in silicon integrated enzyme reactors utilizing porous silicon as the coupling matrix", Sensor. Actuat. B-Chem.. Vol. 31, p. 161, 1996.

[26] K. L. Beattie, W. G. Beattie, L. Mengm, S. L. Turner, R. Coral- Vazquez, D. D. Sith, P. M. Mclntyre, and D. D. Dao, "Advances in genosensor research", Clin. Chem., Vol. 41, p. 700, 1995.

[27] V. S. Y. Lin, K. Motesharei, K. P. S. Dancil, M. J. Sailor, and M. R. Ghadiri, "A Porous Silicon-Based Optical Interferometric Biosensor", Science, Vol. 278, p. 840, 1997.

[28] M. J. Sailor, "Properties of Porous Silicon", Datareview Ser., No. 18, Canham: London, p. 364, 1997.