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Fabrication and Characterization of Silole and Biotin-functionalized Rugate Porous Silicon

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Abstract

Multi-functionalized rugate porous silicon (PSi) for biosensor was developed by hydrosilylation with silole and its further reaction with biotin groups. PSi was generated by an electrochemical etching of silicon wafer in aqueous ethanolic HF solution PSi prepared by using etching conditions showed that many sharp spectral lines can be obtained in the optical reflectivity spectrum. 1,1-hydrovinyl-2,3,4,5-tetraphenylsilole was obtained from the reaction of 1,1-dilithio-2,3,4,5-tetraphenyl-1,3-butadiene with dichlorovinylsilane. Multi-functionalized PSi with silole and biotin groups was characterized by UV-vis absorption spectroscopy, Ocean optics 2000 spectrometer, and fluorescence spectroscopy. Optical characteristics such as reflectivity and photoluminescence (PL) were observed. An increase of the reflection wavelength in the reflectivity spectrum by 20 nm was observed, indicative of a change in refractive indices induced by hydrosilylation of the silole and biotin groups to the rugate PSi. This red-shift was attributed to the replacement of some of the Si-H group of fresh rugate PSi with silole and biotin group.

Key words : Porous silicon, Functionalization, Silole, Biotin, Hydrosilylation,

1. Introduction

PSi prepared by an electrochemical etching of crystalline silicon wafer has been extensively investigated since the discovery of its luminescence properties in 1990.[1] PSi is basically consisted of silicon nanostructure and presents a high specific surface area, which has shown to be useful for a variety of applications such as chemical and biological sensors,[2,3] switching devices,[4] implantable biomaterials,[5] drug delivery,[6] and in high-throughput screening applications.[7] Multi-structured PSi such as rugate PSi have been recently investigated for use in their possible applications, because they exhibit unique optical properties providing the reflection of a specific wavelength in the optical reflectivity spectrum. Rugate PSi having the photonic structure of a rugate filter can be generated by applying a computer generated sine wave current density waveform.

Siloles, silacyclopentadienes, are well established since the pioneering work of Braye and Hubel in 1959, their optically unique property has stimulated much research in recent years.[8] Silole is a silicon-containing five-membered cyclic diene, that is a silicon analog of cyclopentadiene. There have been extensive studies on the synthesis, reactivities, properties and coordination abilities of such compounds to transition metals, and the aromaticity of their anionic or cationic species. The most notable feature of siloles is their high electron-accepting property, associated with their low-lying LUMOs. Potential applications of silole span a wide range, including photonic and electronic sensors.

In this work, it has demonstrated that a new method for fabrication of multi-functionalized rugate PSi with silole and biotin groups was developed. Optical characteristics such as reflectivity and PL of multi-functionalized rugate PSi were observed.

2. Experimental

2.1. Materials

All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. Solvents were purchased from Aldrich chemical Co. Inc. and distilled from sodium/bezophenone ketyl. Spectroscopy HPLC grade THF and water from Fisher Scientific were used for the flu-

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orescence measurements.

2.2. Preparation of 1,1-hydrochloro-2,3,4,5-tetraphenylsilole

Diphenylacethlene (4.5 g, 25 mmol) and lithium (0.35 g, 50 mmol) were stirred in diethylether (60 mL) at room temperature for 3.5 h. The solution was frozen with a bath of liquid nitrogen. Trichlorosilane (2.5 mL, 25 mmol) was added by a syringe in one portion. The mixture was kept at -197°C for 5 min before the cooling bath was removed, then the solution was allowed to warm up slowly to room temperature and stirred for 4 h to give a yellow solution. The solution was filtered. The product was yellow powder (yields : 3.3 g) Selected data ^{1}H- NMR (300.133 MHz, $CDCl_3$), δ=5.8 (s, H), δ=6.70-7.55 (br m, 20H, Ph)

2.3. Preparation of 1,1-hydrovinyl-2.3.4.5-tetraphenylsilole

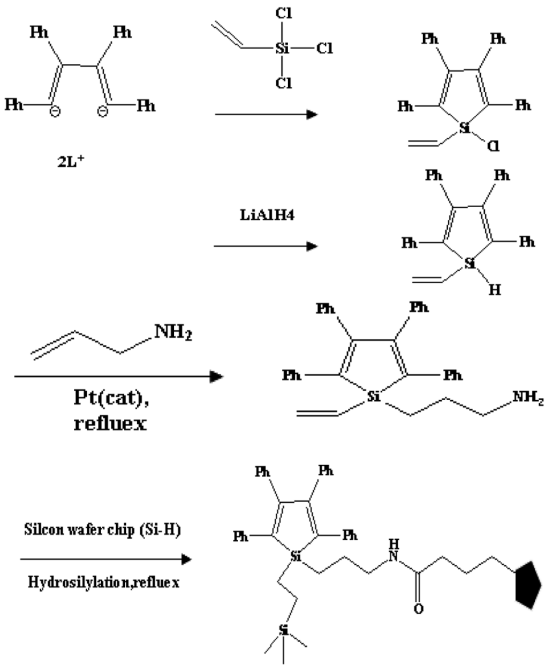
Hydrochlorosilole (0.6 g 1.43 mmol) stirred in THF (60 mL) at room temperature for 0.5 h. 1.0 M vinylmagnesium bromide solution in THF (1.714 mL, 1.72 mmol) was added by syringe in -78°C dropwise. The mixture was kept at -78°C temperature (0.5 h) and stirred for 12 h room temperature and then was give yellow solution. The solution was evaporation, and diethylether add to 60 mL in stirred and filtration made yellow powder. Selected data ^{1}H- NMR (300.133 MHz, $CDCl_3$), d=6.70-7.55 (br m, 20H, Ph), δ=6.05-6.35 (br m, 3H, vinyl H), δ=2.17 (dd, 1H), δ=5.7(s, H)

2.4. Preparation of Rugate Porous Silicon

Rugate PSi samples are prepared by an electrochemical etching of heavily doped p^{++}-type silicon wafers (boron doped, polished on the (100) face, resistivity of 0.08-0.12 mΩ-cm Siltronix, Inc.). The etching solution consisted of a 3:1 volume mixture of aqueous 48% hydrofluoric acid (ACS reagent, Aldrich Chemicals) and absolute ethanol (ACS reagent, Aldrich Chemicals). Prior to etching procedure, the silicon wafer were rinsed throughly with ethanol and dried under a steam of nitrogen. The galvanostatic etch was carried out in a Teflon cell by using a two-electrode configuration with a Pt mesh counter electrode. A sinusoidal current density waveform varying between 124 and 93 mA/cm^2 was applied. The anodization current was supplied by a Keithley 2420 high-precision constant current source controlled by a computer to allow the formation of PSi multilayers. To prevent the photogeneration of carriers, was performed the anodization in the dark. After etching, the samples are rinsed with pure ethanol and dried with nitrogen gas.

2.5. Functionalization of Rugate Porous Silicon

The rugate PSi samples were functionalized by refluxing in a 50 mM solution of hydrovinylsilole for 20 h as described in scheme 1. After functionalization, The sample were rinsed successively with toluene, acetone, and ethanol and subsequently dried under a stream of nitrogen. The 100 mg of biotin (Sigma) was dissolved in a methylene chloride solution (100 mL). The solution was stirrede vigorously for 30 min, and 1-(3-(Dimethyl-amino)propyl)-3-ethylcarbodiimide hydrochloride(EDC) (200 mg, 1 mmol) was added to the solution. The reaction mixture was allowed to stir at room temperature for 1 h. The resulting solution was added to functionalized PSi sample, and sample was incubated overnight. The solution was washed 3 times toluene, methylene chloride, and phosphate-buffered solution (PBS, pH=7.4) and dried the atmosphere.



Scheme 1. synthetic procedure for functionalization of rugate PSi with silole and biotin

2.6. Instrumentation and Data Acquisition

Interferometric reflectance spectra of PSi were recorded by using an Ocean Optics S2000 spectrometer fitted with a bifurcated fiber optic probe. A tungsten light source was focused onto the center of a porous silicon surface with a spot size of approximately 1~2 mm. Spectra were recorded with a CCD detector in the wavelength rang 400~1200 nm. The illumination of the surface as well as the detection of the reflected light was performed along an axis coincident with the surface normal.

3. Results and Discussion

Optical absorption and PL spectroscopy were used to investigate the optical properties of silole-functionalized rugate PSi. An absorption edge appeared at approximately 260 nm for sample as shown in Figure 1 (top). PL spectrum of silole-functionalized rugate PSi was measured at room temperature and the emission spectrum was collected with excitation wavelengths ranging from 260 to 360 nm. The maximum intensity of emission spectrum was centered at 510 nm with an excitation wavelength of 340 nm as shown in Figure 1 (bottom). The PL spectrum of the silole-functionalized rugate PSi showed 90 nm of FWHM.

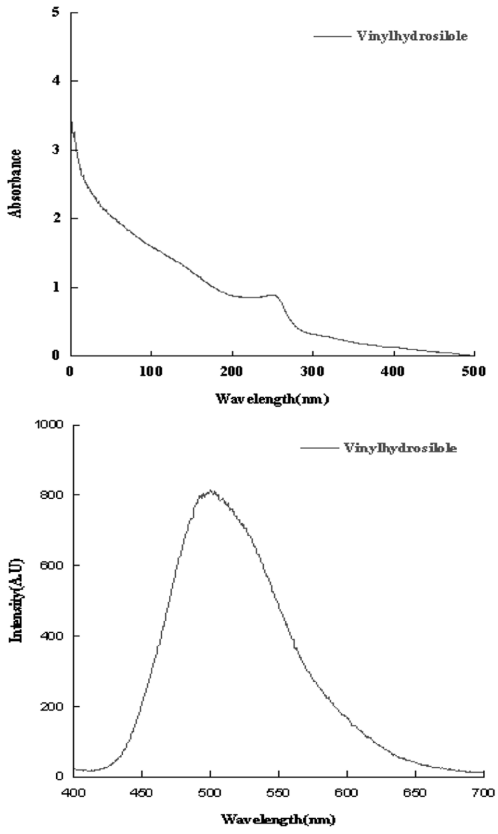


Fig. 1. UV-vis absorption and PL spectra of silole-functionalized rugate PSi.

The rugate PSi exhibited a very sharp line in the optical reflectivity spectrum. This reflectivity can be tuned to appear anywhere in the visible to near-infrared spectral range, depending on the programmed etch waveform. One of the most unique features for multilayer PSi was that its reflective spectral band was much narrower than the fluorescence spectrum obtained from an organic dye or core-shell quantum dot. Thus, more spectral lines can be placed in a narrower spectral window with the photonic structures.

Rugate filters possess a sinusoidally varying porosity gradient in the direction perpendicular to the plane of the filter. The waveform used in the present work involves an individual sine component, which is represented by

$$y_i = A_i \sin(k_i t) + B \quad (1)$$

where y_i represents a temporal sine wave of amplitude A_i, frequency k_i, time t; and an applied current density B. This method of the rugate peak is given by

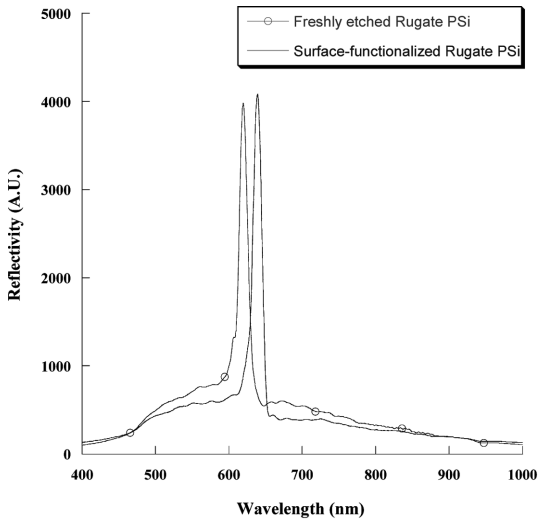


Fig. 2. Reflectivity spectra of freshly etched Rugate PSi and surface-functionalized Rugate PSi with silole and biotin group.

typical etch parameters for the rugate structure involve using a periodic current between 124 and 93 current densities. Its reflection band has a narrow full width at half maximum (FWHM) of 18 nm at 618 nm. Figure 2 showed the change of reflection spectra from freshly etched Rugate PSi to surface-functionalized rugate PSi with silole and biotin group. An increase of the reflection wavelength in the reflectivity spectrum by 20 nm was observed, indicative of a change in refractive indices induced by hydrosilylation of the silole and biotin groups into the rugate PSi. This red-shift was attributed to the replacement of some of the Si-H group with silole and biotin group.

4. Conclusion

A new method for fabrication of surface-functionalized rugate PSi was developed by hydrosilylation with silole group and its further reaction with biotin groups. Optical characteristics such as reflectivity and PL were observed. The reflection band of PSi had a narrow full width at half maximum (FWHM) of 18 nm at 618 nm. Red-shift of 20 nm in reflectivity spectrum was attributed to the replacement of some of the Si-H group of fresh rugate PSi with silole and biotin group.

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