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Stability improvement of porous silicon surface structures by grafting polydimethylsiloxane polymer monolayers

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Abstract

Organic silicone, polydimethylsiloxane (PDMS), was covalently grafted onto the porous silicon (PS) surface to improve its stability to oxidation. Transmission Fourier-transform infrared (FTIR), photoluminescence (PL) and interferometric reflectance spectra have been recorded to evaluate the surface modification and the passivation effect. After modification, the porous nanostructure retained, the stability against oxidation was significantly improved and the PL still kept.

Keywords: Porous silicon; Polydimethylsiloxane; Nanostructure; Photoluminescence

1. Introduction

Much attention has been attracted in the field of porous silicon (PS) for its diverse applications in bio- and chemical sensing [1–3]. Unique properties for theses applications include the significantly increased surface interaction area, simplicity and repeatability of fabrication, and compatibility with the well-established silicon microfabrication technology. But the major barrier preventing commercial applications of PS is the instability of its native interface with a metastable Si–H_x termination. The metastable hydrosilicon can undergo spontaneous oxidation in ambient atmosphere and results in the degradation of surface structures. Therefore, surface passivation is crucial for the technological success of this material. Many organic molecules such as alkenes or alkynes had been covalently grafted onto the PS surface by wet chemical approaches to passivate its surface [4,5]. Recently, polymer films, instead of hydrocarbon monomer monolayers, on PS are of special interest because they provide a strong armature to protect the surface nanostructure. To our knowledge, the well-known and successful product of hydrosilylation is polydimethylsiloxane (PDMS) by the reaction of hydrosilicone with vinyl silicone. With this in mind, we grafted the vinyl silicone on porous silicon surfaces. The grafted PDMS was characterized with the transmission Fourier-transform infrared spectroscopy (FTIR) and the contact angle goniometer. The retention of the surface nanostructure is characterized by an interferometric reflectance spectrometer. The stability and photoluminescence (PL) of PS were tested under stringent conditions to present the advantage of using PDMS for preventing PS from oxidation and degradation.

2. Experimental

Silicon wafers were purchased from Huajing Microelectronics (China). Sylgard 184 Silicone Elastomer Base (B) was purchased from Dow Corning (USA). Single side polished (100) oriented p-type silicon wafers (7.3–9.0 Ω cm resistivity) were cleaned in 3:1 (v/v) concentrated H_2SO_4/30% H_2O_2 for 30 min at room temperature and then rinsed copiously with deionized water (resistance >18 MΩ cm). The cleaned wafers were immersed in 40%

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aqueous HF solution for 1 min at room temperature to remove the native oxide. The hydrogen-terminated surfaces were electrochemically etched in a 1:1 (v/v) pure ethanol and 40% aqueous HF for 30 min at a current density of 6 mA/cm^2. After etching, the samples were rinsed with pure ethanol and dried under a stream of dry nitrogen prior to use. The freshly prepared PS surface (1.54 cm^2) was covered with 20 μl a vinyl-PDMS (Sylgard184 B) and incubated in an oven at 80 °C for 2 h. The excess of unreacted and physisorbed reagent was rinsed three times with toluene at room temperature and dried under a stream of dry N_2.

Transmission FTIR spectra were recorded using a Bruker IFS66/S spectrometer at 0.25 cm^{-1} resolution. Typically, 128 interferograms were acquired per spectrum. The samples were mounted in a purged sample chamber. Background spectra (except those for alkaline solution measurements) were obtained using a flat untreated Si(100) wafer.

Contact angle measurements of the hydride-terminated and PDMS-grafted surfaces with deionized water were carried in air by the sessile-drop method with a contact angle goniometry (Rame-Hart, USA). Readings were taken after the angles were observed to be stable with time. Reported data are an average of the readings taken at three different spots for each sample.

Interferometric reflectance spectra of PS were recorded by using an HR2000CG-UV-MR spectrometer (Ocean Optics, USA) fitted with a bifurcated fiber optic probe. A Xe 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 charge-coupled-device detector in the wavelength range 400–1000 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. The optical thickness of the porous silicon was determined by Eq. (1) [6].

$$nd = \frac{\Delta k \lambda_1 \lambda_2}{2(\lambda_1 - \lambda_2)} \quad (1)$$

where n is the average refractive index of the porous silicon film, d the film thickness, λ_1 and λ_2 the wavelengths of two adjacent minima or maxima, respectively, and for two adjacent minima or maxima the difference in order (Δk) is 1.0.

All of the PL spectra were measured at room temperature in air by a SLM 4800 DSCF/AB$_2$ fluorescence photospectrometer (SLM, USA) using 450-W Xe laser, excited by a 366-nm line.

A Si(100) wafer and a modified PS sample were put into the boiling 0.01 M NaOH aqueous solution. The FTIR spectra of the modified PS samples were recorded after 0, 5,10, 20, 40, 60 and 120 min treatment in the base solution and thorough washing with water. Background spectra were obtained by using a flat Si(100) wafer by the same treatment with the base solution.

3. Results

The grafting of PDMS on the PS surface is confirmed by the transmission FTIR. The spectrum of the freshly prepared PS (Fig. 1) is similar to that reported by Buriak [4]. The spectrum of a freshly hydride-terminated PS (Fig. 1a) exhibits a typical tripartite band for Si–H$_x$ (x=1–3) stretching modes (2087 cm^{-1} for υ_{Si-H}, 2114 cm^{-1} for υ_{Si-H_2} and 2138 cm^{-1} for υ_{Si-H_3}). The Si–H$_x$ bending modes are observed at 916, 669 and 630 cm^{-1}. Fig. 1b is the spectrum of PDMS-grafted PS. In the spectra, vibrations of CH_3 in PDMS are characterized by the aliphatic υ_{C-H} stretching modes at 2961 cm^{-1} and deformation modes at 1440 cm^{-1}. The absorption peaks at 1260 cm^{-1} is attributed to the stretching bands of Si–O. The unit Si–O constructs the backbone of PDMS. Therefore, functionalization of porous silicon with PDMS is successful from the FTIR measurement. All bands of Si–H$_x$ from PS after modification are still observable but exhibit a significant decrease. The average conversion efficiency E is related to the change in the integrated intensity A of the Si–H$_x$ region (2000–2200 cm^{-1}) after modification:

$$E = (A_0 - A_1)/A_0$$

where A_0 and A_1 are the integrated peak areas of the freshly etched and the modified samples in the Si–H$_x$ region (2000–2200 cm^{-1}), respectively. According to this equation the value E is 13.4%, which corresponds well to the reported average value 15% for organic monomer molecules [7].

Another evidence for the PDMS attachment is the contact angle measurement. The measurement revealed that the PS surfaces had an advancing contact angle of 120°, while the value for PDMS-grafted PS surfaces was found to be 107° [8].

The well-established method to analyze the surface nanostructure of PS is the interferometric reflectance spectra. The freshly etched and the modified PS samples show well-resolved Frabry-Pérot fringes in their reflection spectra (Fig. 2). The spectra confirm the retaining of the

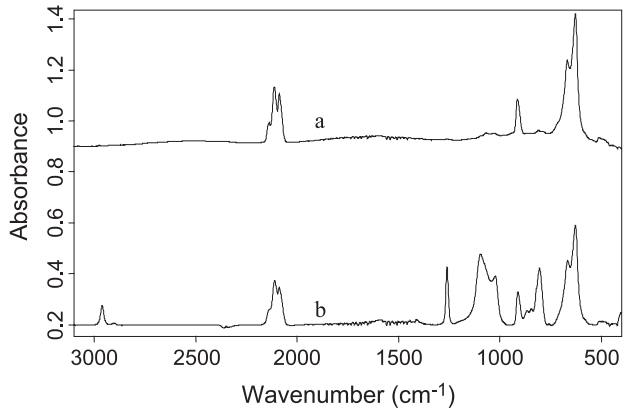

Fig. 1. Transmission FTIR spectra for PS (a) freshly hydride-terminated samples and (b) grafted with PDMS.