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Study on surface chemistry and particle size of porous silicon prepared by electrochemical etching

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ABSTRACT

In the present study, surface chemistry of porous silicon was tailored by thermal oxidation and thermal hydrosilylation method. Porous silicon nanoparticles were prepared by applying ultrasound to freestanding porous silicon films. The results showed a mesoporous silicon layer with an average pore diameter of 28.26 nm, porosity of 70.7% and thickness of 4660 nm. Porous silicon surface was modified and compared with native surface by Fourier transform infrared spectroscopy. Ultrasonic fracture of porous silicon films for 8 h resulted in nanoparticles with average particle size of 149 nm. Zeta potential measurements of nanoparticles at varying pH reveal presence of different surface chemistry of particles.

1. Introduction

Porous silicon (PSi) was discovered over 50 years ago by Uhlir [1] during experiments on silicon wafers to produce smooth polish surfaces. Since then, PSi has been intensively investigated for numerous applications including optoelectronic devices [2], optical biosensing [3], biomolecular screening [4], tissue engineering [5] and drug delivery [6]. The PSi is prepared by electrochemical etching of single-crystalline silicon wafers in ethanolic HF based electrolytes [7]. PSi fabrication by this method allows tuning of several physical and optical properties for the design of drug delivery platforms such as; controllable pore size, high surface area [8], convenient surface chemistry [9], biocompatibility [10] and very low toxicity [11]. PSi degrades completely to orthosilicic acid in physiological fluids which is readily excreted by the kidneys. Additionally optical properties of the PSi can be tuned for self reporting drug delivery system [12].

The as-prepared PSi surface has Si–H, Si–H_2 and Si–H_3 hydrides and observes aging owing to the oxidation when stored at ambient air. In addition to that hydrogen terminated surface of PSi is found to be reactive with many drugs [7]. Therefore, several stabilization treatments are used to produce specific surface chemistry for drug attachment and controlled drug delivery. The important treatments of PSi for drug loading and drug delivery are; thermal oxidation, thermal hydrosilylation and thermal carbonization. Many studies have already been carried out on the PSi for loading and sustained release of poorly water-soluble drug molecules [13], peptides, proteins [14] and small interfering RNA [15]. Thermal oxidation is generally carried out at mild conditions (i.e. 300 °C) or at higher temperature (i.e. 800–1000 °C) to obtain partially or completely oxidized PSi, respectively. On the other hand thermal hydrosilylation involves reaction of an alkene or alkyne with Si–H species. Thermal hydrosilylation provides more stable Si–C chemistry than Si–O chemistry of thermal oxidation which results in a slow release of drug molecules attached via covalent bonding to the PSi surface [12,16].

PSi nanoparticles are generating more interest as the drug delivery carriers owing to their size and porosity in comparison with microparticles [17,18]. The porous structure helps in loading of drug molecules into the pores and nano sized particles provide the benefit of administration in the circulatory system through injections. Furthermore, PSi nanoparticles with specific pharmacokinetic behaviour can be obtained to target a certain tissue or cell [19]. Zeta potential measurements of the PSi nanoparticles help in monitoring the surface chemistry of nanoparticles in suspension. Different surface treatments such as; thermal oxidation, thermal hydrosilylation, changes the zeta potential of PSi particles. This change affects drug loading of particles from the solution. PSi nanoparticles with native and oxidized surfaces are negatively charged which can be exploited for loading of positively charged drug molecules [7].

In this study, the PSi was fabricated by electrochemical etching of single-crystalline silicon wafer in order to tailor the surface

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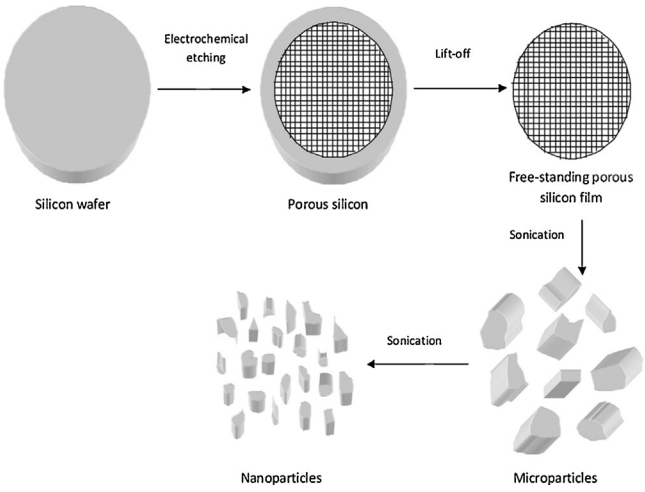

Fig. 1. Schematic representation of formation of PSi nanoparticles by ultrasonic fracture of freestanding films.

chemistry and particle size formation. PSi was characterized by UV–vis spectrometry and scanning electron microscopy. PSi surface was stabilized by thermal oxidation and thermal hydrosilylation treatments and resulted surface chemistry was studied using Fourier transform infrared (FTIR) spectroscopy. PSi film was removed from the silicon substrate by "lift-off" process and particles were prepared by ultrasonic fracture of freestanding films in ethanol (Fig. 1). Particle size of PSi was engineered by varying ultrasonication time and measured using dynamic light scattering (DLS). Furthermore, the impact of different stabilization treatments on surface potential of PSi at varying pH was studied using zeta potential measurements.

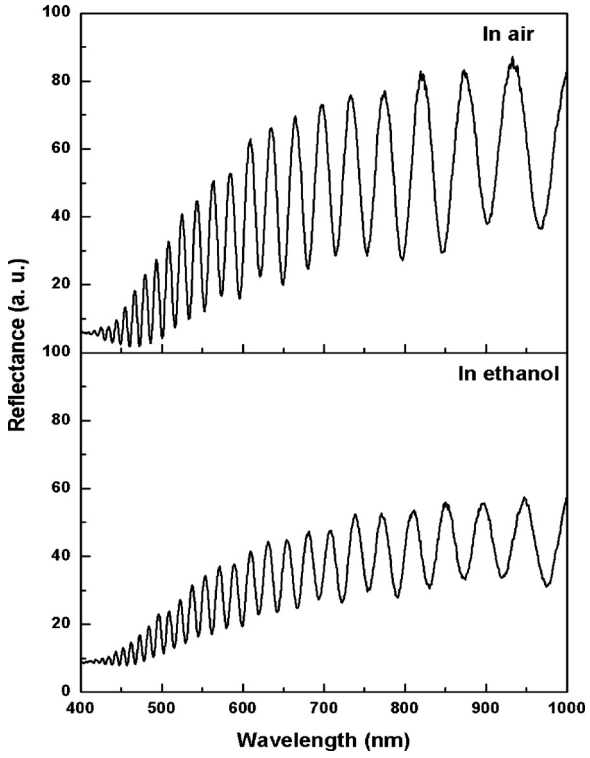

Fig. 2. Relative reflectance spectra of a PSi film prepared at a current density of 50 mA cm^{-2} for 180 s. Spectra are measured in air (top) and immersed in ethanol (bottom).

2. Experimental

2.1. Fabrication of PSi

PSi was anodized from a highly boron-doped p$^+$ type (1 0 0) silicon wafers (Siltronix corp., France) with a resistivity of 0.01–0.02 Ω cm. An aqueous hydrofluoric acid (40%, Finar Chemicals, Ahmedabad, India) and ethanol (99.9%, Changshu Yangyuan, China) in a volumetric ratio of 1:2 was used for the electrochemical etching of a silicon substrate. Silicon wafers with an exposed area of 2 cm^2 were contacted on the back side with a strip of aluminium foil and top with a platinum loop in Teflon etching cell [20]. Electrochemical etching of silicon substrate was carried out by applying current density of 50 mA cm^{-2} for 180 s. After anodization, PSi film was thoroughly rinsed using ethanol. The resulting PSi film was then removed from the crystalline silicon substrate by applying current density of 6 mA cm^{-2} for 120 s in hydrofluoric acid based electrolytes. The etching and electropolishing procedure was repeated 15 times per wafer and the resulting freestanding films were then placed in ethanol till further use.

2.2. Measurement of interferometric reflectance spectra

Fiber optic spectrometer (Ocean Optics, Maya2000 Pro, FL, USA) was used for the measurement of reflectance spectra of the prepared PSi films. Reflectivity data were recorded in the wavelength range of 400–1000 nm with a spectral integration time of 10 ms. Thickness and porosity of PSi film was determined using a program based on the spectroscopic liquid infiltration method (SLIM) [21].

2.3. Preparation of PSi nanoparticles

PSi nanoparticles were prepared by ultrasonic fracture of freestanding PSi films placed in ethanol. Ultrasonic cleaner (Elma Transsonic TI-H5 MF2, USA) with a frequency of 45 kHz

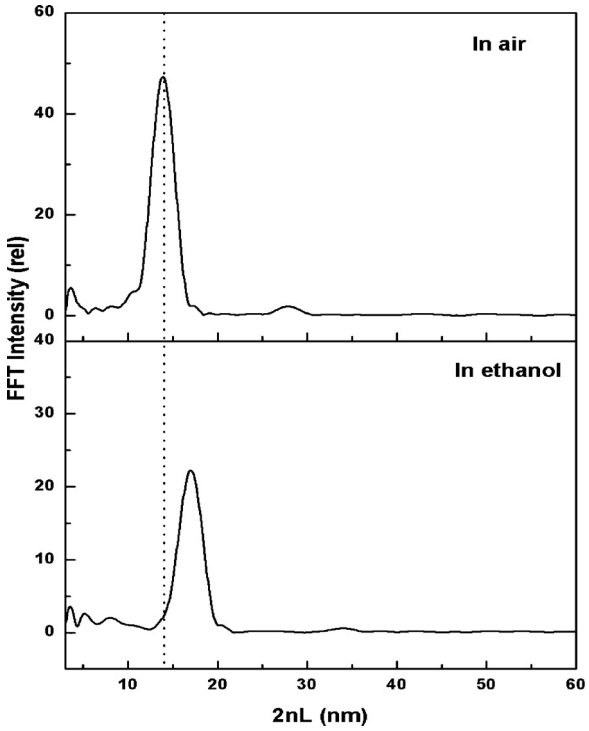

Fig. 3. Fourier transformations of a PSi film in air (top) and immersed in ethanol (bottom). The 2 nL values are given in nm (×10^3).