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Tunable luminescence of nanoporous silicon via electrochemical etching parameters

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ABSTRACT

This paper reports the surface state induces a variation in light emission of nanoporous Si as a function of electrolyte condition, anode–cathode distance and aging in common chemical reagents to achieve strong and stable luminescence of Si semiconductor. The electrochemical derived nano Si was observed to have a nanoporous structure with the pore of about 20 nm in the thickness of 50 μm. The luminescence of nanoporous Si was showed enhancing in the sample with the HF/ethanol of 1:1 and the anode–cathode distance of about 5 cm. As etched specimen, the luminescence of the nanoporous Si was centered at 800 nm; however blue-shift when they were immersed in green chemical reagents. These results suggest that the potential application of electrochemical etching followed by green chemical treatment to tunable luminescence, which was potential application in nanoporous Si based devices and nanomedicine.

1. Introduction

Nano silicon has received a great deal attention in recent years due its ability exhibit to interesting physical properties not observed in bulk silicon [1,2]. Among the various nanostructure, nanoporous silicon is particularly fascinating because of its light emission at room temperature, compatible with electronic devices, large specific capacity for drug loading, as well as excellent biocompatibility [3,4]. Until now, the scientific applications of electrochemical derived nanoporous Si have been investigated for use as optoelectronic [5,6], solar cell [7,8], gas sensor [9], biosensor [10,11], nano carrier [12,13], and substrates for cellular growth [14]. Although, light emission from electrochemical etching derived nanoporous Si has been well documented, but, it is still important to control the surface states and microstructure of nanoporous Si for further improving the luminescence and long term stability of the specimens [15,16], which would be strongly dependent on the electrochemical etching parameters and chemical treatments.

Recently, highly nanoporous Si has been synthesized successfully in our laboratory by electrochemical etching method [17]. In that research, we have investigated the effect of electrochemical etching voltages to the microstructure and luminescence of the nanoporous Si. To expand this research, we herein report the effect of electrolyte concentration, anode–cathode distance and chemical treatment to the luminescence of nanoporous Si. To the best of our knowledge, this is the first time study the effect of anode–cathode distance to the luminescence of nanoporous Si, which would build up more scientific information about nanoporous Si field for designing strong and stable light emission in optoelectronic and nanomedicine. The microstructure of the nanoporous Si was characterized by field emission scanning electron microscopy (FE-SEM). The crystal structure and chemical bonding of the specimen was characterized by infrared spectroscopy. The luminescence was also determined by photoluminescence spectrometer.

2. Experimental procedure

A p type ⟨1 0 0⟩ silicon wafer (Si) with a resistivity of 0.5–2 Ωcm was used as a substrate. Before electrochemical etching, the silicon wafer was dipped into a HF solution of 48% concentration for 10 min to remove the native oxide layer on the wafer. The dipped Si wafer was then electrochemically etched with an electrolyte solution containing various ratios of HF and ethanol, anode–cathode distance in order to control the luminescence. The sample was exposed to the electrolyte solution was approximately 2 cm^2. A platinum grid was used as a counter electrode. The electrochemical etching system was operated under fixed voltages of 10 V at 25 °C in a conventional Teflon bath. To investigate the effect of chemical treatment on the light emission of specimens, the as etched specimen was also immersed in various green chemical solution

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such as distil water, ethanol, and H_2O_2. The microstructure of the nanoporous Si was determined by field emission scanning electron microscopy (JEOL, JSM-7600F, JEOL Techniques, Tokyo, Japan). To investigate the chemical bonding of the nanoporous Si, infrared absorption spectra (IR) were recorded in the wave number range from 4000 to 500 cm^{-1} with a Perkin-Elmer Spectrum BX spectrometer using KBr pellets. Room temperature photoluminescence (PL) tests were performed under excitation wavelength of 276 nm. NANO LOG spectrofluorometer (Horiba, USA) equipped with 450 W Xe arc lamp and double excitation monochromators was used. The PL spectra were recorded automatically during the measurements.

3. Results and discussion

3.1. Microstructure characterization

The microstructure of the nanoporous Si was examined by SEM, as shown in Fig. 1(A) and (B). The nanoporous Si showed a relatively clear nanoporous layer formation with a thickness of ~50 μm (Fig. 1(A). In addition, there was good adhesion between the nanoporous layer Si and the Si substrate, which was attributed to the use of electrochemical etching Si wafer to create the nanoporous Si layer on the same substrate materials. The surface of the nanoporous Si showed a homogenously tiny pore of ~20 nm without noticeable cracks (Fig. 1(B)).

3.2. FT-IR analysis

Fig. 2(A)–(C) shows the typical FTIR spectra of the nanoporous Si processed with the variation of electrolyte concentration. The peak situated at 2090 cm^{-1} and 906 cm^{-1} was attributed, respectively, to the stretching mode of the SiH and the scissor mode of SiH_2 [18,19]. The peak at 1080 cm^{-1} was corresponded to Si—O—Si symmetric stretching mode and was introduced during the electrochemical etching process [20]. The most intense and broad absorption band around 3400 cm^{-1} is attributed to stretching of the O—H bond in SiOH groups and adsorbed water [21]. The SiH stretching mode is centered on 624 cm^{-1} [22,23]. The absorption band around 1630 cm^{-1} is due to C—O bond, probably because of the surface contamination [22]. The intensities of hydride stretching mode, SiH_2 scissor mode and Si—O—Si vibration peak increase on the sample with HF/ethanol of 1:1. These results indicate that the nanoporous Si processed at variation of electrolyte concentration induce a significant change in surface state of the nanoporous Si.

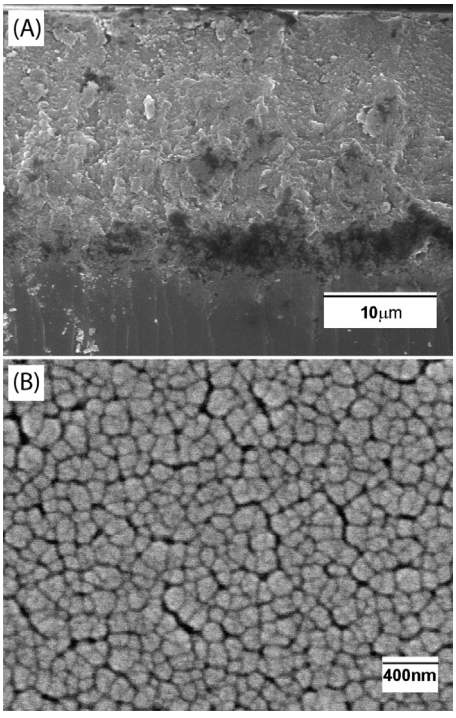

Fig. 1. SEM images showing (A) cross-section and (B) surface morphology of the nanoporous Si.

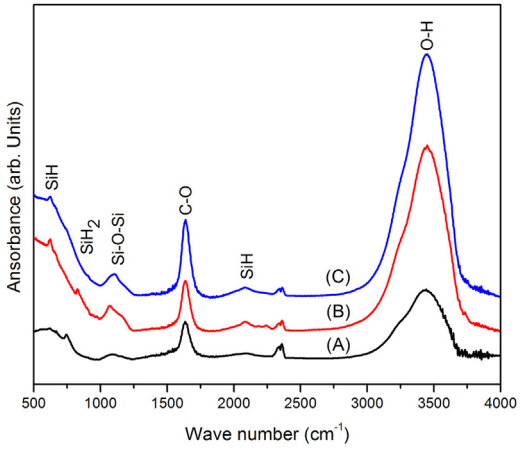

Fig. 2. FT-IR spectra of nanoporous Si with variation of HF/ethanol electrolyte concentration (A) concentrate. (B) HF/EtOH 1:1, and (C) HF/EtOH 1:2.

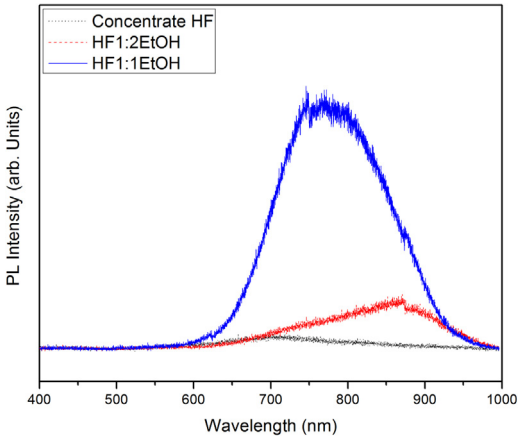

Fig. 3. Photoluminescence spectra of nanoporous Si prepared by electrochemical etching in different electrolyte concentrations

3.3. Effect of electrolyte concentration

Fig. 3 shows the emission spectra of nanoporous Si with different HF/ethanol ratio monitored at 276 nm. All the nanoporous Si showed strong visible luminescence. However, it should be noted that the PL spectra of the nanoporous Si film etched with HF without addition of ethanol showed a signal peak at ~700 nm. As the HF/ethanol ratio of 1:1 and 1:2, the PL signal shifted to longer wavelengths of ~800 nm and 850, respectively and also its intensity increased significantly. It is well documented that the ethanol play important role in the controlling the surface tension or the viscosity of the electrolyte of HF/ethanol mixture in the electrochemical etching, resulting in enhancing the probability of the pore formation and functionalized surface state; that is, the specimens have a variation in luminescence [24]. The observed a higher luminescent emission of nanoporous Si with HF/ethanol of 1:1 is related to the