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Photodegradation activity and stability of porous silicon wafers with (100) and (111) oriented crystal planes

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ABSTRACT

Hydrogen-terminated porous Si wafers with (100) and (111) oriented crystal planes were fabricated through a photo-electrochemical etching. It is found that the porosity of silicon wafers and their etch rates are determined as a function of crystal orientation. Due to the anisotropic etching behavior of single-crystal silicon, the hydrogen-terminated porous Si (100) wafers exhibit not only more excellent photodegradation activity but also stronger stability for methyl orange degradation than hydrogen-terminated porous Si (111) wafers under visible light irradiation. For the unetched Si wafers, however, the photodegradation activities of methyl orange exhibit a contrary conclusion.

1. Introduction

Silicon (Si) is a very promising material due to its excellent mechanical and thermal properties, its obvious compatibility with silicon-based microelectronics and its low cost. Compared with titanium dioxide (TiO_2) that is the most commonly photocatalyst for the degradation of various pollutants [1–6], silicon is able to utilize visible and/or near UV light, and is photostable (against photocorrosion), inexpensive and nontoxic [7]. For a long time, however, it is not used in pollution control because its valence band is not positive enough to oxidize pollutant species [7].

Recently, some studies have been developed for the application of Si in pollution control. For example, Kong et al. demonstrated that 1–2 nm Si quantum dots (SiQDs) were very sufficient for CO_2 reduction and dye degradation, while 3–4 nm SiQDs were effective photocatalysts for selective oxidation of benzene [8]. Chen et al. used one dimensional hydrogen-terminated silicon nanowires (SiNWs) synthesized by oxide-assisted-growth method for the degradation of methyl red under ultrasonic agitation [9]. Shao et al. investigated the performance of hydrogen-terminated SiNWs and noble metal-modified (Pt, Pd, Au, Rh, Ag) SiNWs for photodegradation of dye. It was found that hydrogen-terminated SiNWs exhibited better photodegradation activity than Pt-, Pd-, Au-, Rh-, and Ag-modified SiNWs in the degradation of dye [10].

Compared with Si nanowires and quantum dots, Si nanopores should belong to negative space materials that may be as important in the development of nanomaterials as it is in creating works of art. Based on such as a realization, some studies have been developed for the application of nanoporous Si in pollution control. For example, Su et al. studied the performance of hierarchically porous silicon, prepared by electro-assisted chemical etching, under visible light irradiation for the degradation of phenol [11]. Duan et al. and Wong et al. fabricated the porous Si wafers from the n- and p-type Si wafers via the metal-assisted chemical etching, respectively, and found that the porous Si wafers had large surface area and displayed good photodegradation activity [12,13]. For porous Si, however, investigations on the facet dependency on photodegradation activity were not carried out in past several years.

In this paper, two kinds of Si pores with (100) and (111) oriented crystal planes have been synthesized by a photo-electrochemical (PEC) etching method in HF solution. Photodegradation activity and recyclability of porous Si materials under visible light irradiation were investigated using methyl orange (MO) as a target. The relative photodegradation and stability mechanisms extrapolated from the experimental results were also discussed.

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2. Experimental

2.1. Preparation of hydrogen-terminated porous silicon and single-crystal silicon

Electrochemical porosification experiments were conducted in a two-electrode cell at room temperature with p-type Si cut into 1×1 cm^2 squares as the anode and a platinum wire as the counter electrode (cathode). The resistivity of p-type Si wafers of 510 μm thickness with (100) and (111) oriented crystal planes was 0.5–1 Ω cm and 0.1–0.9 Ω cm, respectively. The electrolyte was prepared by adding ethanol to HF (49%) with a volume ratio of 1:1. The anodization process was carried out in a constant voltage of 15 V controlled by a (GWINSTEK, GPD-3303S) source meter, while etching current was recorded under room light. After etching, the samples were rinsed with ethanol and dried in N_2. The etched samples with (100) and (111) orientations were named as H-PSi (100) and H-PSi (111) wafers, respectively.

Compared with the photodegradation properties of Si wafers, the Si wafers were treated with the electrolyte for 1 min, producing hydrogen-terminated silicon without pores. Correspondingly, the hydrogen-terminated silicon wafers were called H-Si (100) and H-Si (111) wafers.

2.2. Characterization of the hydrogen-terminated porous silicon

The morphologies and surface chemical states of H-PSi (100) and H-PSi (111) samples, before and after photodegradation experiment, were investigated by scanning electron microscope (SEM) (Zeiss, SUPRA 55) at 5 kV electron acceleration voltage and Fourier transform infrared (FT-IR) spectrometer (Bruker, ALPHA-T), respectively. An X-ray diffraction (XRD) analysis was performed with a D 8 Advance X-ray diffractometer, to study the crystal structure of H-PSi (100) and H-PSi (111) wafers. Mercury intrusion porosimetry (MIP, Quantachrome, PM60GT-18, USA) was used to quantitatively evaluate the pore size distributions of H-PSi (111) and H-PSi (100) wafers. When prepared samples for MIP test, aggregates were avoided from sampling and about 0.15 g sample was used for each measurement. A pressure of more than 400 MPa can be achieved by the machine and this pressure allows the mercury to penetrate pores as fine as 0.003 μm diameter. The surface area of H-PSi (100) and H-PSi (111) wafers were measured by a surface area analyzer (QUADRASORB SI, Quantachrome Corporation, USA) at 77 K. The specific surface area (S_{BET}) was calculated by using the Brunauer–Emmett–Teller (BET) model. A Bruker E500 spectrometer equipped with a Nd:YAG laser (with 532 nm filter) was used for measurements of the electron spin resonance (ESR) signals of radicals by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP). The settings were the following: center field 3510.00 G, microwave frequency 9.86 GHz, and power 10.02 mW.

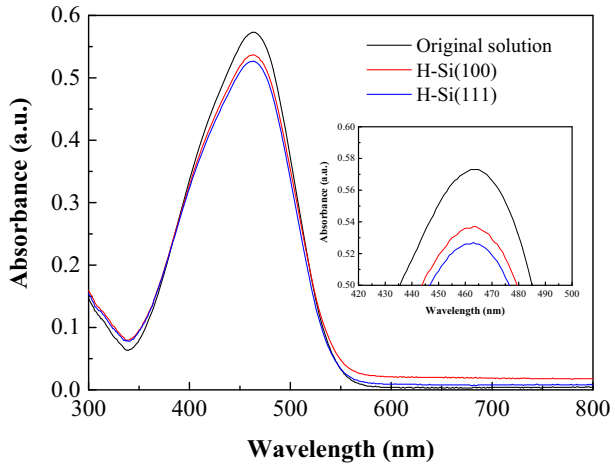

Fig. 1. Absorption spectra of the original MO solution and absorption spectra of the MO solution photodegraded by H-Si (100), H-Si (111) wafers after 1 h of visible light irradiation. The inset is a magnified image.

2.3. Photodegradation ability of hydrogen-terminated porous silicon and hydrogen-terminated silicon

The photodegradation reactions were carried out in a 15 ml quartz tube, containing 4 ml MO solution with initial concentration of 2.5×10^{-5} M under stirring. The reaction system was irradiated under a 30 W fluorescent lamp (light intensity is 3000 lux). The concentration of MO was determined by UV–Vis spectrophotometer (UV-2450, Shimadzu, Japan) by monitoring the adsorption peak at $\lambda_{max} = 463$ nm. All of the photodegradation reactions were carried out under air ambient and at room temperature.

3. Results and discussion

3.1. Photodegradation activity of hydrogen-terminated silicon

Fig. 1 shows the photodegradation properties of H-Si (100) and H-Si (111) wafers for the MO solution. After 60 min of irradiation, H-Si (100) and H-Si (111) wafers with 1×1 cm^2 squares degrade 6.5% and 8.4% of organic dye, indicating that the Si wafers have anisotropy for photodegradation of MO. The anisotropy can be explained by the different densities of surface atoms in the Si (100) and Si (111) wafers, which are 6.78×10^{14} cm^2 and 7.83×10^{14} cm^2, respectively.

3.2. Characterization of H-PSi wafers

To improve the photodegradation activity of signal crystal Si wafers, it is necessary to increase their surface/volume (S/V) ratios. Fig. 2 shows the large-scale top view and cross-sectional images of Si (100) and Si (111) wafers etched for 10 min. From top view images, both samples have uniform surface. By comparing Fig. 2(a) and (c), the density and size of pores on the Si (100) wafers are less and larger than those on the Si (111) wafers, respectively. The etch depth of H-PSi (100) and H-PSi (111) samples is about 45 μm and 11 μm (Fig. 2(b) and (d)), so the etch rate of Si (100) wafers is about 4 times higher than that of Si (111) wafers, indicating that the etching of Si wafers is anisotropic. This result is in good agreement with the previous reports [14,15].

The crystal structures of porous Si can be characterized by X-ray diffraction analyses which were carried out in the 10–80° range of 2θ. Fig. 3 shows the XRD patterns of the Si wafers before and after the etching process. As shown in Fig. 3(a) and (b), the intensity of H-PSi (400) and H-PSi (111) peaks are stronger than that of Si (400) and Si (111) wafers. The increased intensity is, at least partially, due to physical surface roughening which means that diffraction is out-coupled from the crystal more efficiently. Furthermore, the full width at half maximum (FWHM) of the XRD peaks of the etched Si wafers present a slight widening, indicating that the etching can lead to the increase of defect density [16].

To obtain further information about H-PSi (100) and H-PSi (111) wafers, the pore size distributions of the samples were performed. As shown in Fig. 4(a), pore size of the H-PSi (100) wafers ranging from 86.4 to 231 nm is centered at 185 nm, whereas pore size of the H-PSi (111) wafers ranging from 0 to 32.4 nm is centered at 29.1 nm (Fig. 4(b)). The Brunauer–Emmett–Teller (BET)