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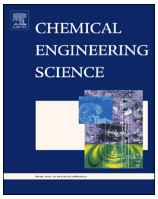

Measurement and kinetic modeling on photoluminescence stability from “trenched” silicon microparticles under continuous excitation

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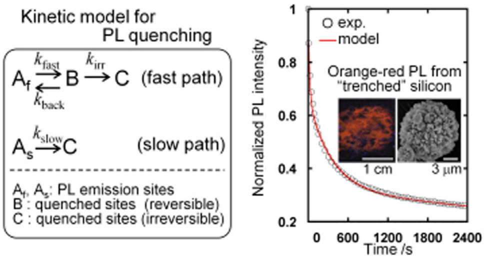
HIGHLIGHTS

- PL quenching by both reversible and irreversible processes.
- Adsorption/desorption of O_2 followed by oxidation as fast quenching path.
- Retarded transport of O_2 by narrow trenches as slow quenching path.
- Good agreement between experiments and our kinetic model.
- Discussion on the kinetics and possible strategy to improve PL stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The stability of photoluminescence (PL) intensity from chemically etched silicon microparticles is studied. Etched microparticles have many narrow and deep trenches on surface. They show visible orange–red PL, which decreases in intensity during continuous excitation by ultraviolet light. The intensity of PL partially recovers when the surrounding gas is changed from air to nitrogen. Thus PL quenching consists of both reversible and irreversible processes and we propose a kinetic model that consists of two quenching paths. Adsorption and desorption of oxygen followed by irreversible oxidation of emission sites are considered in the fast quenching pathway, while the slow pathway involves transport of oxygen molecules to emission sites in trenches with poor access. Our model agrees well with experimental data and rate constants of involved processes are determined, with which we discuss kinetics in PL quenching. Possible strategy to increase PL stability is also discussed.

1. Introduction

While bulk silicon does not show visible photoluminescence (PL), some types of silicon materials, such as nanosized silicon particles and porous silicon, show visible PL. Since the discovery of visible red emission from porous silicon by Canham (1990), considerable attention has been paid to preparing photoluminescent silicon materials. The low toxicity of silicon compared to other heavy metals makes photoluminescent silicon materials suitable for practical application in bio-imaging both *in vitro* (Erogbogbo et al., 2008; Shen et al. 2011; Ohta et al., 2012a, 2012b; Warner et al., 2005) and *in vivo* (Erogbogbo et al., 2010, 2011; Park et al., 2009). In addition, formation of singlet oxygen from photoirradiated porous silicon has been explored for silicon-based phototherapy (Kovalev et al., 2004; Kovalev and Fujii, 2005; Balaguer and Matveeva, 2010; Xiao et al., 2011; Kotkovskiy et al., 2012). Thus, although bulk silicon has been widely used in industry and its bulk properties are well known, silicon materials can still show interesting features when they have nanometer-sized structures.

The stability of PL is important in applications. PL from porous silicon is sensitive to the surrounding environment and surface

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conditions (Sailor and Lee, 1997; Geil et al., 2012). Porous silicon shows PL quenching upon exposure to oxygen (Tischler et al., 1992; Harper and Sailor, 1997; Salonen and Laine, 1996) and other organic molecules such as methanol (Lauerhaas et al., 1992; Rehm et al., 1995), tetrahydrofuran (Lauerhaas et al., 1992) and anthracene (Ko and Meyer, 1995; Song and Sailor, 1997). The degree of PL quenching can be manipulated by surface modification (Lauerhaas and Sailor, 1993). PL lifetime measurements revealed that the formation of rapid nonradiative decay pathways caused by photoirradiation or adsorption of chemical species was one of the main reasons for PL quenching (Mihalcescu et al., 1996; Gardelis et al., 2008; Sailor and Wu, 2009). Photoinduced loss of hydrogen from the silicon surface also decreases PL efficiency (Collins et al., 1992). Thereby, a microscopic physical picture of the mechanism of PL quenching is now well understood. However, we consider that there is still a necessity to study kinetics in PL quenching, especially, caused by oxygen. This is simply because stability of PL emission in air is a practical issue when we use porous silicon as luminescent materials. The number of available data on PL quenching itself is rather limited and thus some important issues, such as the rate of PL quenching, the effect of excitation light intensity on quenching rate or reversibility in PL emission to gas change under continuous excitation of light, are not well understood yet. In addition, although efforts have been made to describe PL quenching data with a kinetic model, they generally used an empirical model (Singh and Lakshmikumar, 2002; Tamura and Adachi, 2009), and therefore discussion on quenching kinetics is not sufficient. This is our main concern in this work. We used chemically etched silicon microparticles formed *via* the zinc reduction reaction of silicon tetrachloride ($SiCl_4$) as a sample material.

The zinc reduction reaction of $SiCl_4$ has been known for several decades as a reaction pathway to produce silicon. The overall reaction is:

$$SiCl_4(g) + 2Zn(g) \rightarrow Si(s) + 2ZnCl_2(g). \quad (1)$$

In this reaction, $SiCl_4$ is reduced into solid silicon with zinc vapor. We have reported that silicon materials with a variety of morphologies can be formed in this reaction, such as nanowires (Uesawa et al., 2010), microparticles (Shen et al., 2010) and needle-like wires (Yamaguchi et al., 2012; Inasawa, 2015). Detailed reaction pathways and the overall activation energy for this reaction have also been studied (Uesawa et al., 2011). Among them, silicon microparticles formed by zinc reduction show an interesting feature. After etching with a simple mixture of hydrofluoric acid (HF) and nitric acid, their morphology changes dramatically into trenched particles, which show visible red PL under irradiation with ultraviolet (UV) light (Shen et al. 2010). We expect that such narrow trenches could contribute to decrease the rate of PL quenching, because transport of oxygen by diffusion could be retarded by such trenches.

In this work, we measured the PL stability of trenched silicon microparticles under continuous irradiation of UV light. The effects of excitation light intensity and surrounding gas, air or nitrogen, are examined. Then we propose a kinetic model to describe PL quenching behavior on the basis of the results. Our model shows good agreement with PL data and we discuss kinetic aspects of PL quenching using the proposed model.

2. Experimental

2.1. Chemicals

$SiCl_4$ (99.9999%) was purchased from Tri Chemical Laboratories Inc. (Yamanashi, Japan). Zinc metal (99.995%) was purchased from Mitsui Kinzoku, Tokyo, Japan. Argon (Ar) carrier gas was G1 grade, and was purchased from Tokyo Kouatsu Yamazaki Inc., Tokyo, Japan along with nitrogen. HF (47 wt% in water) was purchased from Wako Pure Chemicals Industries, Osaka, Japan. Nitric acid (63 wt% in water) was purchased from Kanto Chemical, Tokyo, Japan. All chemicals were used as received.

2.2. Synthesis and chemical etching of silicon microparticles

We used a quartz tube with a diameter of 50 mm and length of 1000 mm. Zinc metal (ca. 20 g) was placed in a quartz boat with a length of 200 mm, and then the boat was placed in the middle of the reactor tube. A gas line was connected to one open end of the reactor tube, from which we introduced source gas. The other end was connected to a gas line to a water scrubber to treat unreacted gas. Source gas consisting of Ar and $SiCl_4$ was obtained by bubbling of the Ar carrier gas through a liquid $SiCl_4$ in a bubbler. The temperature of the bubbler was set at 18 °C, which was controlled by a water bath. The total flow rate of the mixed gas was 150 sccm. We used an electric tubular furnace (ARF3-500-60KC, Asahi Rika, Chiba, Japan) to heat the reactor. We placed the reactor tube so that its middle was heated. Prior to heating, the reactor was flushed with Ar. The total pressure inside the reactor was 1 atm, and the reaction temperature was typically 850 °C. The vapor pressure of zinc at the reaction temperature was ca. 420 mmHg. The reaction time was typically 1 h, and ~0.5 g of silicon solids was obtained. After washing the solid silicon with hydrochloric acid to remove zinc metal, silicon particles smaller than 50 μm in diameter were isolated using a sieve. The silicon microparticles (1 g) were etched with a mixture of water (37.5 mL), HF (25 mL) and nitric acid (5 mL) for several minutes. Etched particles were collected by vacuum filtration through a hydrophilic polytetrafluoroethylene membrane and washed carefully with pure water to remove residual acid. Collected particles were dried in air. Samples were stored in air in the dark for at least 2 months prior to PL measurement to allow sufficient natural surface oxidation so that no further change upon further storage was expected.

2.3. Measurements

The morphology of the silicon microparticles was observed using scanning electron microscopy (SEM; TM1000, Hitachi High-Technologies, Tokyo, Japan). We also used another SEM with higher resolution (S-900, Hitachi, Tokyo, Japan) to observe the surface morphology of particles in greater detail. Visible PL color was visually recorded by a digital camera (EX-FH20, CASIO, Tokyo, Japan) under a hand-held UV illuminator. PL spectra and time lapse spectra of PL intensity were measured by a spectrofluorophotometer (FP-6300, JASCO, Tokyo, Japan). Excitation light with a wavelength of 360 nm was used for all PL measurements. Five different light intensities, 4%, 12%, 50%, 80% and 100%, relative to the original intensity of excitation light were used for excitation. The original intensity of excitation light was $\sim 14\ \mathrm{mW\ cm^{-2}}$. We used a hand-made quartz chamber with a rubber spacer for PL measurements, which is schematically shown in Fig. 1. Part of a rubber sheet (30 mm × 40 mm × 3 mm) cut so that it contained an open space of 15 mm × 25 mm × 3 mm in its center was used as a spacer. We pierced one side of the spacer with two thin needles, which were used as the gas inlet and outlet. We also prepared a set of transparent quartz plates (30 mm × 40 mm × 1 mm). Etched silicon microparticles were placed on one of the quartz plates. The rubber spacer was then clipped to the quartz plates so that the silicon powder was inside the chamber. We positioned a sharp-cut filter in front of the detector to cut excitation light. PL intensity was measured under nitrogen at a flow rate of $50\ \mathrm{mL\ min^{-1}}$, or under air without gas exchange. For measurements performed in air, we removed the quartz plate without powder to ensure enough air was exposed to the samples. Humid nitrogen was prepared by bubbling it through milli-Q water. Nitrogen was bubbled through the water