

Fabrication and optical evaluation of porous Si particles

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Micrometer-sized porous Si (PS) particles were fabricated in solution by sonicating PS layers. The PS particles were between 0.4 - 2 μm and consisted of Si nanocrystals with average diameters between 2.8 - 10 nm. The PS particles showed strong visible light photoluminescence (PL). Changing the anodization conditions altered the PL color from red to green. The quantum size effect did not explain the PL, which seemed to be associated with recombination via radiative centers that originate in the Si/H/O molecules or defect centers in the partially oxidized PS particles.

Key words: silicon nanoparticles, photoluminescence, porous silicon

1. INTRODUCTION

Since the discovery of strong visible light emission from porous Si (PS) [1], various forms of Si nanomaterials have been extensively studied due to their potential applications in Si light emitting devices. Si nanoparticle films [2-4] and Si-doped glass films [5-8] have attracted wide attention since (1) they form on any substrate, (2) the shapes of these films are easily converted after film formation, and (3) well-defined laminated structures are constructed [9]. Although PS does not have these advantages, it shows a particularly strong luminescence among other Si nanomaterials. One way to mix the advantages of PS and Si nanoparticle films is to fabricate particles made of strongly luminescent PS. By preparing a slurry of PS particles, it is possible to form PS particle films on any substrate after the process of spreading and desiccating the slurry. We fabricated micrometer-sized PS particles by removing the PS layers from the Si substrate in solution and then breaking the PS layers into particles. In this report, the fabrication method and the luminescence properties of the PS particles are presented.

2. EXPERIMENTAL

The PS particles were fabricated by sonicating the PS layers. With the prospect of a large-scale synthesis of PS particles, we used *p*-Si rods that were 2 cm in diameter and 10 cm long as the anode instead of using Si pieces cut from wafers. First, a Si rod with a resistivity of 1 - 10 Ωcm was anodized between 100 - 150 mA/cm^2 for 60 - 120 sec in solutions that consisted of hydrofluoric acid (HF, 46 wt%), methanol (98 wt%) and hydrogen peroxide (H_2O_2 , 30 wt%): the ratio of HF:methanol: H_2O_2 was 1:1:0, 1:1:1, 1:1:2, 1:1:3, 1:1:4, 1:1:5 or 1:1:6. As shown below, the different ratios resulted in the luminescence color variations. Following the anodization, the Si rod was immediately immersed in toluene and sonicated at 30 W for 5 - 10 min to remove the PS layers from the Si rod surface and to break the PS into micrometer-sized particles.

The size of the PS particles was evaluated by laser microscopy (685 nm, 0.45 mW) with a KEYENCE VK-8500. Raman spectroscopy with an Ar^+ laser (514.5 nm, 20 mW) as the incident light was used to estimate the average diameters of the Si nanocrystals that made up the PS particles. Photoluminescence (PL) measurements were conducted with a HITACHI F4500 at an excitation wavelength of 325 nm.

3. RESULTS AND DISCUSSION

The laser microscope image of the PS particles (Fig. 1) shows that sonicating process breaks the PS layers into 0.4 - 2 μm particles. This sample was anodized in a 1:1:0 ratio of HF:methanol:H₂O₂. Changing anodization solutions from 1:1:0 to 1:1:6 of HF:methanol:H₂O₂ did not affect the particle size.

Figure 2 shows the Raman spectra of the PS particles prepared in various anodization solutions. Since there is not a bulk-like sharp Raman peak, it is concluded that the samples do not contain bulk crystalline Si from the Si substrate [10].

Some authors used phonon confinement to derive the Raman line shapes of low dimensional materials. Richer *et al.* [11] developed a qualitative model to estimate the average size of nanocrystals that Campbell and Fauchet later improved [12]. Using this improved model, the first order Raman spectrum of spherical crystals is

$$I(\omega) = \int \frac{\exp(-q^2 L^2 / 4)}{[\omega - \omega(q)]^2 + (\Gamma / 2)^2} d^3 q \quad (1)$$

where q is expressed in the units of $2\pi/a$ with $a = 0.357 \text{ nm}$, which is the lattice constant of c-Si, L is the crystal diameter in the units of a , Γ is the natural linewidth, which is 3.5 cm^{-1} and includes the instrumental contribution in this study, and $\omega(q)$ is the dispersion relation for optical phonons in c-Si. To calculate Eq. 1, an approximate expression for $\omega(q)$ is used: $\omega(q) = A - Bq^2$ with $A = 520.5 \text{ cm}^{-1}$ and $B = 120 \text{ cm}^{-1}$ [10]. As shown in Fig. 2, the experimental spectra fit nicely to the calculated curves by adjusting the diameters. The estimated diameters in the spectra (a), (b), (c), (d), (e) and (f) are 10, 10, 9.0, 6.0, 4.7 and 2.8 nm, respectively.

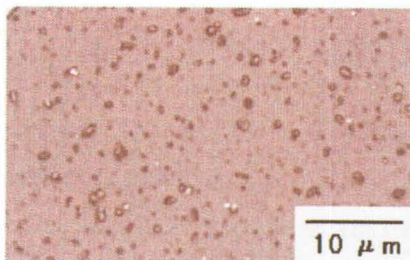


Fig. 1. Laser microscope image of the PS particles. The particles were sparsely deposited on a glass substrate.

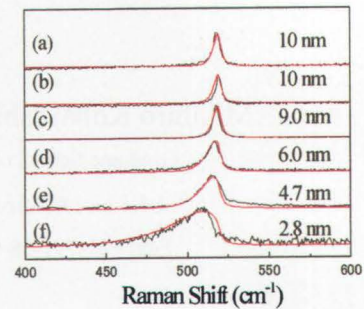


Fig. 2. Raman spectra of the PS particles. The spectra (a), (b), (c), (d), (e) and (f) are for the samples prepared by anodizing in 1:1:1, 1:1:2, 1:1:3, 1:1:4, 1:1:5, and 1:1:6 of HF:methanol:H₂O₂, respectively. The red curves fitted in the spectra are the calculated curves based on the phonon confinement model (Eq. 1). The average diameters estimated from Eq. 1 are also shown.

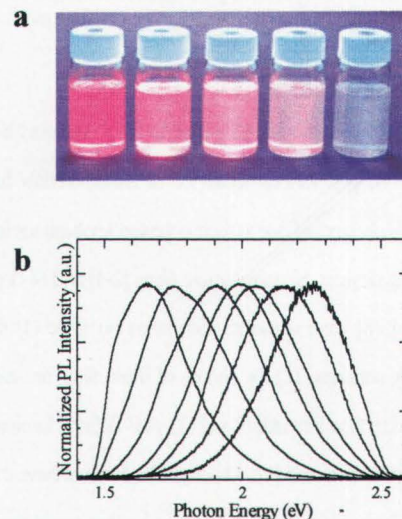


Fig. 3. PL from the PS particles dispersed in toluene: (a) a photograph and (b) PL spectra. The PL peak energy shifts from low to high by increasing the H₂O₂ content in the anodization solution (from 1:1:0 to 1:1:6 of HF:methanol:H₂O₂).

The PS particles show strong visible PL under ultraviolet irradiation (Fig. 3a). As shown in Fig. 3b, changing H₂O₂ content in the anodization solution continuously shifts the PL peak position between 1.6 and 2.3 eV. Since H₂O₂ is an oxidizing reagent, it is natural to assume that the Si nanocrystal

size decreases as H₂O₂ content increases. From the tendency of the PL blue-shift with the increase of H₂O₂ content, the PL shift appears to be due to the quantum size effect. However, the estimated diameters of the Si nanocrystals (Fig. 2) are too large to explain the visible light emission by the quantum size effect [13]. There are at least two other possible mechanisms that explain the PL. The first possibility is recombination via radiative centers that originate in Si/H/O molecules adsorbed on the surface of the PS particles. For instance, the PL peak wavelength of siloxene (Si₆O₃H₆) continuously shifts between 500 and 800 nm after annealing [14]. It is feasible that the different Si/H/O compounds grow on the PS particle surfaces under different anodization conditions, which may result in the various PL colors. The second possibility is radiative recombination via defect centers. Partially oxidized Si nanomaterials contain various types of defects such as nonbridging oxygen hole center (NBOHC), dangling bonds at the Si/SiO₂ interface (P₁ center), and localized states close to the conduction band edge in the Si nanocrystal surface (P_{cc} center) [8,15]. These defect centers have been proposed as radiative centers in Si nanomaterials.

4. SUMMARY

PS particles that consist of Si nanocrystals were prepared in toluene. The PS particles were between 0.4 - 2 μm. The average size of the nanocrystals decreased from 10 to 2.8 nm as the H₂O₂ content in the anodization solution increased. The PS particles showed a strong visible PL under ultraviolet irradiation. The PL peak energy continuously increased from 1.6 to 2.3 eV with the H₂O₂ content. The PL was not simply explained by the quantum size effect and seemed to be due to recombination via radiative centers related to surface Si/O/H compounds or defects in partially oxidized PS particles.

REFERENCES

- [1] L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
- [2] H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki and T. Nakagiri, *Appl. Phys. Lett.* **56**, 2379 (1990).
- [3] H. Morisaki, F. W. Ping, H. Ono and K. Yazawa, *J. Appl. Phys.* **70**, 1869 (1991).
- [4] G. Ledoux, J. Gong, F. Huisken, O. Guillois, C. Reynaud, *Appl. Phys. Lett.* **80**, 4834 (2002).
- [5] D. J. DiMaria, J. R. Kirtley, E. J. Pakulis, D. W. Dong, T. S. Kuan, F. L. Pesavento, T. N. Theis and J. A. Cutro, *J. Appl. Phys.* **56**, 401 (1984).
- [6] Y. Osaka, K. Tsunetomo, F. Toyomura, H. Myoren and K. Kohno, *Jpn. J. Appl. Phys.* **31**, L365 (1992).
- [7] S. Hayashi, T. Nagareda, Y. Kanazawa and K. Yamamoto, *Jpn. J. Appl. Phys.* **32**, 3840 (1993).
- [8] K. Sato, T. Izumi, M. Iwase, Y. Show, H. Morisaki, T. Yaguchi, T. Kamino, *Appl. Surf. Sci.* **216**, 376 (2003).
- [9] T. Ichinohe, D. Kenmochi, H. Morisaki, S. Masaki and K. Kawasaki, *Thin Solid Films* **377-378**, 87 (2000).
- [10] Z. Sui, P. P. Leong, I. P. Herman, G. S. Higashi, H. Temkin, *Appl. Phys. Lett.* **60**, 2086 (1992).
- [11] H. Richter, Z. P. Wang and L. Ley, *Solid State Commun.* **39**, 625 (1981).
- [12] I. H. Campbell and P. M. Fauchet, *Solid State Commun.* **58**, 739 (1986).
- [13] C. Delerue, G. Allan and M. Lannoo, *Phys. Rev. B* **48**, 11024 (1993).
- [14] H. D. Fuchs, M. Stutzmann, M. S. Brandt, M. Rosenbauer, J. Weber, A. Breitschwerdt, P. Deak and M. Cardona, *Phys. Rev. B* **48**, 8172 (1993).
- [15] S. M. Prokes and W. E. Carlos, *J. Appl. Phys.* **78**, 2671 (1995).

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