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Size Regulation of Si Nanoparticles through Photon-enhanced Chemical Etching

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A Si nanoparticle surface was etched in an aqueous HF solution under monochromatic light irradiation in the infrared-to-visible region. The average size of the nanoparticles was controlled by changing the photon energy of the irradiating light. After prolonged photoetching, the size distribution of the nanoparticles was narrowed significantly. The correlation between the photon energy and the final size of the nanoparticles indicated that the band gap energy change due to the quantum size effect played an important role in controlling nanoparticle size.

Electron–hole pair photogeneration in a group IV semiconductor induces a weakening of interatomic bonds,[1] which enhances surface reactions, including oxidation,[2–4] etching,[5] and surface modification.[6–9] The threshold photon energy to induce this enhancement is the band gap energy (E_{gap}), which is inherent in semiconductors. Extending this analogy to nanoparticles, the threshold energy to induce this enhancement should be determined by the nanoparticle core size since E_{gap} depends on size as a result of the quantum size effect. In reactions that induce a core-size decrease, such as surface oxidation and etching, the size-dependent behavior of the threshold energy should play an important role in controlling the size. Although light irradiation accelerates the decrease in core size, this acceleration stops once E_{gap} exceeds the photon energy of the light. This self-limiting property should result in a spontaneous size-uniformalization. Recently, we have confirmed that Ge nanoparticle size was controlled in a range between 3.3 and 6.0 nm in diameter by chemical etching under monochromatic light irradiation with a wavelength between 365 and 940 nm.[10] This process not only decreased the size of the nanoparticles but also narrowed their size distribution.

The present study examines Si. To date, a paper confirming the light-induced change of the Si nanoparticle size has yet to be reported, but some indications have been found in hitherto reported papers. For instance, Ichinohe et al.[5] have irradiated porous Si immersed in a hydrofluoric (HF) solution with various monochromatic lights between 365 and 550 nm. They found that the photoluminescence (PL) peak energy was continuously blue-shifted toward the photon energies of the irradiating light. They concluded that the blue shift was due to the quantum size effect, indicating that the irradiating light controlled the size of the nanocrystals in porous Si. However, this is only speculation because they had no microscopic confirmation of the nanocrystal size, and up to now it has been still obscure whether the light irradiation actually changes the Si nanocrystal size. Herein, we show direct evidence of how the size may be controlled by changing the wavelength of the light irradiation.

The starting Si particles were prepared by grinding Si powders in ethanol with a Retsch PM100 planetary ball mill with 3-mm tungsten carbide balls. Then, the obtained colloidal sample was centrifuged at 22000 × g to remove large fragments. Prior to light irradiation, 0.05 mL of aqueous HF solution (46 wt %) was added to 15 mL of the Si colloid in a PET vial to dissolve the surface oxide on the Si particles and to decrease the Si particle size during the following photoetching process. Then, the sample was irradiated with monochromatic light with a wavelength of 470, 525, 660, 850, or 940 nm. All of the light powers were adjusted to ca. 5 mW m^{-2}. During the light irradiation, the samples were continuously stirred and the vials were kept at 0 °C. At this temperature and HF concentration, the Si particles were etched only when irradiated with light. The irradiation lasted for 45 h, which was sufficient to complete the enhancement effect for all samples. Further light irradiation had a negligible effect on the samples. According to our previous FTIR analysis,[11] the HF-etched Si nanoparticle surface was predominantly terminated with hydrogen. The hydrogen termination effectively protected the particle surface from oxidation in air. Scanning transmission electron microscope (STEM) images of the Si particles were obtained using a Hitachi S4800 scanning electron microscope operating at 13.0 kV.

The obtained samples are shown in Figure 1. A color change, which is attributed to both an increase in E_{gap} and a decrease in particle volume fraction, is observed with decreasing wavelength of the irradiating light. The sample kept in a dark place hardly changed in appearance (Figure 1a).

Figure 2 shows typical STEM images of the Si particles before and after photoetching. The diameters of the starting Si particles ranged from 10 to 30 nm. After photoetching, the particle size was decreased and made uniform. The morphology

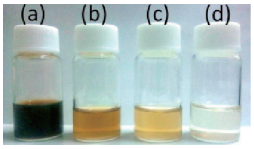

Figure 1. Appearance of the Si nanoparticles after photoetching with different wavelengths: (a) no irradiation, (b) 660, (c) 525, and (d) 470 nm.

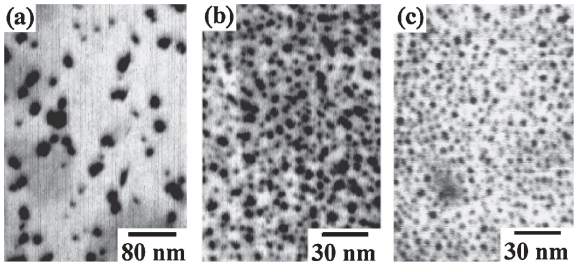

Figure 2. Typical STEM images of the Si nanoparticles (a) before and after photoetching under (b) 850 and (c) 525 nm light.

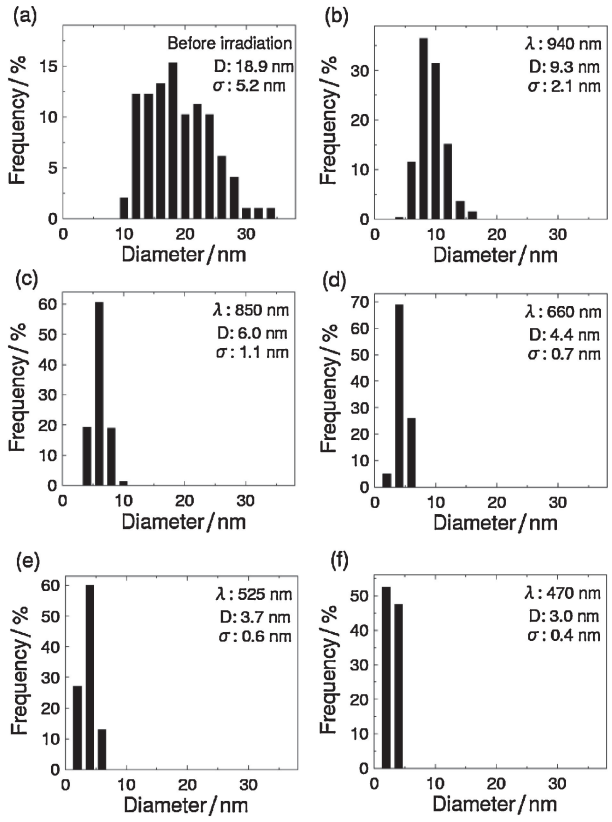

Figure 3. Size distributions of the Si nanoparticles obtained by STEM observation. Wavelength (λ) of the irradiated light for photoetching, obtained average diameter (D) and standard deviation (σ) are shown in each figure.

of the particles changed from irregular to spherical as the etching proceeded. The detailed structures of the particle surfaces are still obscure because of the unclearness of the STEM images.[12] The size distributions obtained from the STEM images are summarized in Figure 3. It clearly shows that the average diameter tends to decrease as the photon energy increases as well as the size distribution narrows by irradiating with light.

Figure 4 shows the correlation between the average diameters obtained in Figure 3 and the photon energy of the irradiated light. As we mentioned earlier, the E_{gap} of the photoetched Si nanoparticles is expected to come close to the photon energy of the irradiating light. If we assume that the E_{gap} of the samples sufficiently approached the photon energy of the irradiated light, the experimental data in Figure 4 can be viewed as the correlation between the nanoparticle size and the E_{gap}. According to the quantum size effect with an effective-mass approximation (EMA),[13] the E_{gap} is written as

$$E_{gap} = E_{bulk} + \frac{h^2}{8\mu D^2} \quad (1)$$

where E_{bulk} is the bulk band gap energy, μ is the reduced mass, and D is the particle diameter. As shown in the black curve in Figure 4, eq 1 gives a good fit to the experimental data by substituting $0.025m_0$ (m_0: electron rest mass in vacuum) for the reduced mass. This size-dependent E_{gap} change resembles the data of Si nanocrystals synthesized in inverse micelles.[14]

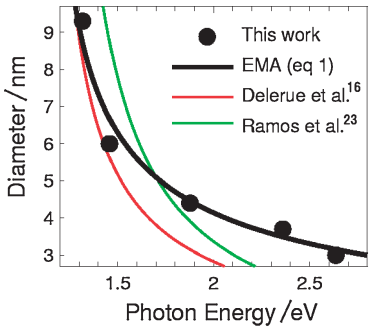

Figure 4. Correlation between the average diameter and the photon energy of the light (dots). The average diameters were obtained from STEM observations (Figure 3). The black curve is eq 1, substituting $0.025m_0$ for μ. The red curve is $E_{gap} = E_{bulk} + 3.73/D^{1.39}$, and the green curve is $E_{gap} = E_{bulk} + 2.96/D$.

As well as EMA, different equations have been frequently used to explain size-dependent E_{gap} changes of Si nanostructures.[15] For instance, Delerue et al.[16] have introduced $E_{gap} = E_{bulk} + 3.73/D^{1.39}$ (where E and D are in units of eV and nm, respectively) as an empirically well-fitted equation[17–22] that has been used especially for porous Si. As the equation for embedded Si nanocrystals, Ramos et al.[23] established $E_{gap} = E_{bulk} + 2.96/D$. These equations are also shown in colored curves in Figure 4. As shown in the figure, these curves do not fit to the experimental data, especially for those in the smaller size range. It seems that our system provides stronger confinement of carriers in the nanoparticles than conventional Si nanostructures.

In summary, Si nanoparticles were produced from ca. 20-nm Si particles using photoetching in an aqueous HF solution. By changing the wavelength of the irradiation light from 470 to 950 nm, nanoparticles with an average diameter from 3.0 to 9.3 nm were obtained. Not only did the average size decrease, but also the size distribution narrowed. There was a linear relationship between the inverse square of the obtained nanoparticle size and the photon energy of the irradiated light. This indicated that the E_{gap} approached the photon energy of the light, and the E_{gap} determined the final size of the photoetching process.

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12 The STEM images (Figure 2) are somewhat blurred. This seems to be due to impurities that are produced in the ball-milling and etching processes. For attempting to obtain clearer images, we removed the impurities and HF by collecting the Si particles on ultrahigh-molecular-weight polyethylene (UPE) membrane filters (pore size 10 nm) and washing with ethanol. The etched Si particles were made less dispersible by adding ultrapure water in advance of the filtration so as not to pass through the UPE filter. However, although the impurities were removed (i.e., the images became clearer), the washed Si particles formed large aggregates that could not be redispersed with sonication. Because of the agglomeration, the size distribution could not be obtained from the images of the washed Si particles. Therefore, in this report we show the images of the Si particles without washing.
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