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Photo-modification and synthesis of semiconductor nanocrystals

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Abstract

Both photo-oxidation and photosynthesis manifest a strong interaction between nanoparticles and photons due to the large surface area-to-volume ratio. The final sizes of the semiconductor nanocrystals are determined by the photon energy during these phenomena. The photosynthesis is demonstrated in a Si-rich oxide and is similar to thermal synthesis, which involves the decomposition of SiO_x into Si and SiO_2 , that is well known and often employed to form Si or Ge nanocrystals embedded in SiO_2 by annealing SiO_x at high temperature. However, photosynthesis is much faster, and allows the low-temperature growth of Si nanocrystals and is found to be pronounced in the SiO nanopowder, which is made by thermal CVD using SiH_4 and O_2 . The minimum laser power required for the photosynthesis in the SiO nanopowder is much lower than in the Si-rich oxide formed by the co-sputtering of Si and SiO_2 . This is attributed to the weak bond strength of Si–Si and Si–O in the SiO nanopowder. Photosynthesis, which can control the size and position of Si nanocrystals, is a novel nanofabrication technique making the best use of the strong interaction between photons and nanoparticles. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

The ultimate goal of nanofabrication is to control the size and position. Because of its large surface area-tovolume ratio and carrier confinement in a nanoparticle, the semiconductor nanoparticle can be easily modified or synthesized by light irradiation. We earlier reported a phenomenon unique to semiconductor nanocrystals, called photo-oxidation [1], which results from the photon-nanoparticle interaction. When Ge nanocrystals were exposed to UV light in an air or oxygen atmosphere at room temperature, they become oxidized, and the nanocrystals surrounded by the oxide shell became smaller.

The electron-active model, in which the rate-determining step of the oxidation was to break up the molecular oxygen into its smaller atomic components with the assist of electrons, was modified to physically understand the photo-oxidation of the Ge nanocrystals. When the nanocrystal was exposed to UV light, the light was absorbed

* Corresponding author. *E-mail address:* nozaki@ee.uec.ac.jp (S. Nozaki). by the Ge nanocrystal, and electron-hole pairs were generated. The electrons injected into the oxide shell met the molecular oxygen and assisted its breakup into smaller atomic components according to the electron active model. On the other hand, the remaining holes made it easier for the Ge atoms to bond to the oxygen atoms. As a result, the Ge nanocrystal was photo-oxidized.

According to this model, the size distribution of the Ge nanocrystals becomes smaller with the irradiation time, and the final size is determined by the photon energy of the incident photons. The photo-oxidation ceases when the apparent band gap energy reaches the photon energy, and a further increase in the apparent band gap would result in the transmission of the incident light. Therefore, for a prolonged photo-oxidation, the sizes of the Ge nanocrystals surrounded by the oxide shell would become uniform. The higher the incident photon energy, the smaller the final size of the Ge nanocrystals is. These hypotheses were well supported by our experimental results for the Ge and Si nanocrystals, and the photo-oxidation, which was photomodification of semiconductor nanocrystals, was proved to be a self-limiting process to obtain Ge or Si nanocrystals with a high size-uniformity.

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Besides the size control, it is also important to control the position of the nanostructure in the nanotechnology. Although the nanocrystals can be formed by epitaxial growth or lithography, the most popular and "simple" techniques to form semiconductor nanocrystals are electrochemical etching, the cosputtering of a semiconductor and SiO₂, and gas evaporation [2]. Nevertheless, none of these techniques forms nanocrystals with good control of the positions. Recently, we discovered the photosynthesis of Si nanocrystals resulting from a photon-nanoparticle interaction [3]. When the Si-rich oxide SiO_x was exposed to laser light, Si nanocrystals were formed only in the irradiated region. Since the photosynthesis is highly selective, it could well control the positions of the semiconductor nanocrystals. In this paper, we present the photosynthesis as a new technique to fabricate semiconductor nanocrystals and discuss its features and future prospects.

2. Si-rich oxide

We studied two types of Si-rich oxide, which consisted of Si and O atoms, but macroscopically had more Si atoms than the stoichiometric oxide SiO₂, for the photosynthesis of Si nanocrystals; the SiO_x thin film made by the cosputtering of Si and SiO₂ [4] (hereafter called the sputter-deposited SiO_x film) and SiO nanopowder made by thermal CVD using SiH₄ and O₂. Since the latter is unique and more suitable for the photosynthesis, it will be described more in detail.

The SiO nanopowder is similar to the commercially available SiO powder in regard to the chemical composition, and macroscopically contains the same number of Si and oxygen atoms. It should be noted that the Si and O atoms do not need to be uniformly distributed. Fig. 1 compares the Si2p XPS (X-ray photoelectron spectroscopy) spectra of the commercial SiO powder and the SiO nanopowder. The binding energies of the Si2p for Si and SiO_2 are 99.3 and 103.3 eV, respectively, as shown in the figure. Although both SiO powders consist of an equal number of Si and O atoms, there is a significant difference in their spectra. Both show two distinct peaks corresponding to Si and SiO₂. The intensity of the SiO₂ peak is much higher than that of the Si peak in the commercial SiO powder, while the intensities of the SiO₂ and Si peaks are about the same in the nanopowder. The difference in the XPS spectra suggests that the commercial powder contains a smaller "total" volume of Si-Si bonding regions than the nanopowder.

Since the XPS spectrum of the nanopowder shows a higher "total" volume of Si–Si bonding regions, we expect to see a Raman peak associated with either the amorphous Si or crystalline Si. As shown later, the nanopowder did not show any peak associated with the amorphous or crystalline Si. Instead, the commercial powder clearly showed a peak at about 515 cm^{-1} , indicating presence of Si nanocrystals. as shown in Fig. 2. The average size is estimated to be about 6 nm from the quantitative model developed



Fig. 1. Si2p XPS spectra of the SiO powders: (a) commercial SiO powder, and (b) SiO nanopowder.

by Campbell and Fauchet [5], which will be described in the next section.

It is concluded from the XPS and Raman measurement results that Si nanocrystals are present in the commercial SiO powder and contribute to the Si-like peak in the XPS specrum, while the amorphous or nanocrystal Si is absent in the SiO nanopowder. The Si–Si bonding regions contributing to the Si peak in the XPS spectrum of the SiO nanopowder must contain two- or one-dimensional Si networks or extremely small Si clusters. The high intensity of the Si peak in the XPS spectrum suggests that such Si networks are more homogeneously distributed in the SiO₂ so that the "total" volume of the Si–Si bonding regions can increase.



Fig. 2. Raman spectrum of the commercial SiO powder.

Since the commercial SiO powder is made from Si and SiO_2 vaporized at high temperature, Si nanocrystals are present as residues in the formed SiO powder. Unlike the commercial SiO powder, the SiO nanopowder is made by thermal CVD using SiH₄ and O₂ and does not contain any Si nanocrystals, but two- or one-dimensional Si networks or Si clusters. The bond strength of the Si–Si and Si–O bonds in such structures is expected to be weaker.

Fig. 3 shows TEM micrographs of the SiO powders. The nanopowder consists of spherical particles with sizes less 50 nm, while the commercial powder consists of irregular-shaped flakes of submicron sizes. This difference is also attributed to a difference in the fabrication methods of the SiO powders. A large surface area-to-volume ratio

and weak bond strength of the Si–Si and Si–O in the nanopowder enhance the interaction with photons and produce a unique phenomenon called photosynthesis, as discussed in the rest of this paper.

3. Experimental procedures of Raman and photosynthesis

A continuous-wave (cw) Nd:YVO₄ laser with the wavelength of 532 nm was employed in both the photosynthesis and Raman scattering measurements unless the wavelength is specified. The laser operates in the TEM₀₀ mode, and its beam intensity has a Gaussian distribution in the spot. Raman scattering measurements were carried out in the right-angle scattering geometry with the incident laser beam focused onto the sample surface. The beam diameter was about 1 mm on the sample in both the photosynthesis experiments and Raman scattering measurements. The laser power was set to 20 mW, which was large enough to obtain a significant Raman peak for the Si nanocrystals, but small enough not to modify the sample during the Raman scattering measurements.

The sequence in the experiments for the Raman scattering measurement and photosynthesis is as follows. First, the Raman spectrum of the sample was obtained with a laser power of 20 mW to confirm no clear Si-associated peak, and then the laser power was adjusted to a specified value higher than 20 mW for the photosynthesis experiment. Second, the same spot on the sample was exposed to the laser beam for a specified period of time. Finally, the laser power was again set back to 20 mW for the Raman scattering measurement. Since the laser irradiation with a power of 20 mW even for extremely longer periods of time did not synthesize Si nanocrystals, this sequence



Fig. 3. TEM micrographs of the SiO powders: (a) commercial SiO powder, and (b) SiO nanopowder.

of Raman measurement and photosynthesis experiments could determine whether or not Si nanocrystals were formed by the laser irradiation. The beam position was fixed throughout the sequence of experiments, which were the Raman measurement, photosynthesis and then the Raman measurement, so that the same sample area could be characterized for the photosynthesis of the Si nanocrystals.

The average size L of the Si nanocrystals in the laser-irradiated area was estimated from the Raman peak position and lineshape in the Raman spectrum using the quantitative model developed by Campbell and Fauchet [5]. For a spherical nanocrystal, L is the diameter. Using this model, the first-order Raman spectrum $I(\omega)$ is

$$I(\omega) \propto \int \exp(-q^2 L^2/4) \frac{d^3 q}{\left[\omega - \omega(q)\right]^2 + \left(\Gamma/2\right)^2},\tag{1}$$

where q is expressed in $2\pi/a$ and L is in units of a, with a = 0.54 nm being the lattice constant of silicon. Γ is the natural linewidth (~4 cm⁻¹ for c-Si at room temperature including the instrumental contributions) and $\omega(q)$ is the dispersion relation for the optical phonons in c-Si. To calculate the lineshape, the analytic form $\omega(q) = A - Bq^2$, with A = 520.5 cm⁻¹ and B = 120 cm⁻¹ is used. This model has been frequently employed to estimate the average size of semiconductor nanocrystals [2,6]. The sizes estimated from the Raman spectrum using the above equation and the X-ray diffraction pattern using the Scherrer formula agreed quite well [6]. In each Raman spectrum shown in this paper, the light-colored curve fitted in the spectrum is the calculated curve based on the phonon confinement model (Eq. (1)).

4. Results and discussion

Fig. 4 shows the Raman spectra of the sputter-deposited SiO_x film before and after the laser irradiation. The film



Fig. 4. Raman spectra of the sputter-deposited SiO_x film before and after the laser irradiation. The sample was exposed to the laser wavelength of 532.4 nm and power of 500 mW in air for 1 min at room temperature.

was exposed to the laser having a 500 mW power for 1 min. As formed by the thermal annealing at 1000 °C for 30 min, the Si nanocrystals were formed, and the average size was estimated to be 8 nm, similar to that by the thermal synthesis. The laser power of 500 mW was the minimum required for the photosynthesis of the Si nanocrystals from the sputter-deposited SiO_x film. The photosynthesis is similar to the thermal synthesis of Si nanocrystals from SiO_x, involving the decomposition of SiO_x into Si and SiO₂, but it is much faster, and allows the low-temperature growth of Si nanocrystals from SiO_x.

The photosynthesis of Si nanocrystals was also observed in the SiO nanopowder, as shown in Fig. 5. The disc cut from the pellet formed by pressing the SiO nanopowder was exposed to the laser with a 50 mW power for 1 min. Note that the wavelength used for the photosynthesis was 670 nm in Fig. 5 and different from that in Fig. 4. Unlike the SiO nanopowder, the nanocrystals already present in the commercial SiO powder do not show any further growth or modification by the laser irradiation. Fig. 6 shows the average size of the formed Si nanocrystals for various laser-exposure periods. The laser power was 100 mW. An average size of 7 nm was obtained during the 1 sec exposure, and the size remained the same for the longer exposures. The laser power-dependent growth of Si nanocrystals for 1-min exposure is shown in Fig. 7. Although the peak is not significant, the minimum power required for the photosynthesis of Si nanocrystals appears to be 18 mW for the SiO nanopowder, much lower than 500 mW for the sputter-deposited SiO_{x} film. Since the intensity of the Si-associated peak for laser power of 18 mW was extremely low, as seen in Fig. 7, all of the Raman spectra in this study were obtained using a laser power of 20 mW after we confirmed that the laser power of 20 mW was still low enough not to significantly modify



Fig. 5. Raman spectra of the SiO-nanopowder disc before and after the laser irradiation. The disc was cut from the pellet made by pressing the SiO nanopowder. The sample was exposed to a laser wavelength of 670 nm and power of 60 mW in air for 1 min at room temperature.



Fig. 6. Raman spectra of the SiO-nanopowder disc after laser irradiation for various periods. The sample was exposed to the laser wavelength of 532.4 nm and power of 100 mW in air at room temperature.

the sample during the photosynthesis, as mentioned earlier. The temperature required for the thermal synthesis for the SiO nanopowder was 600 °C, also much lower than 900 °C for the sputter-deposited SiO_x film. The lower power required for the photosynthesis is attributed to the lower bond strength of Si–Si and Si–O in the SiO nanopowder, as discussed earlier.

It is clear from Figs. 6 and 7 that the growth of the Si nanocrystals is self-limited to the laser irradiation time or laser power. After the average size reaches a certain value, a further increase in the irradiation time or laser power does not increase the average size. Fig. 8 shows the photosynthesis using lasers of various wavelengths. The laser power for each wavelength was adjusted to provide the same photon flux. The photosynthesis for any wavelength studied here shows the self-limited growth. The final average sizes for the wavelengths of 325, 532, 670 and 1064 nm are 9, 7, 6.5 and 5 nm, respectively. The final size increases with the increasing photon energy of the laser. The final average sizes are reached within 1 sec for the wavelengths of 325, 532 and 670 nm, while the growth is slow, and it takes more time to reach the final average size when using the wavelength of 1064 nm.

These results provide some clues to clarification of the photosynthesis mechanism. One may argue that the growth is merely thermal due to the increased temperature resulting



Fig. 7. (a) Raman spectra of the SiO-nanopowder disc after the laser irradiation using various laser powers. (b) Sizes of the Si nanocrystals formed by the photosynthesis at various laser powers. The sample was exposed to the laser wavelength of 532.4 nm for 1 min in air at room temperature.

from the laser exposure. It should be mentioned that the photosynthesis was observed only in the laser-irradiated area. The area right next to the irradiated area did not show the presence of Si nanocrystals. This suggests that the photosynthesis is not a thermal process, because the temperature in the area next to the irradiated area should not be much different from that in the irradiated area. The thermal synthesis of Si nanocrystals from a pellet of the SiO_x nanoparticles requires a temperature higher than 600 °C, and it is unlikely that the unirradiated area with a center only 1 mm from the center of the irradiated area is unheated by heat transfer from the irradiated area. Therefore, the photosynthesis can be regarded as selective low-temperature formation of Si nanocrystals by laser irradiation.

The photosynthesis is similar to the thermal synthesis of Si nanocrystals from SiO_x , involving the decomposition of



Fig. 8. Sizes of Si nanocrystals formed by the photosynthesis for various exposure periods at different wavelengths of the laser. The laser power was adjusted to provide an equal number of photons (about 10^{17}) per second over the beam area. The sample was exposed to the laser in air at room temperature.

 SiO_x into Si and SiO_2 , but it is much faster, and allows the low-temperature growth of Si nanocrystals from SiO_x . Although the photosynthesis was observed in the sputterdeposited Si-rich oxide thin film, it required a much lower laser power in the SiO nanopowder due to weak bond strength of the Si-Si and Si-O, which was attributed to a two- or one-dimensional Si network or Si clusters present in the SiO nanopowder. It is speculated that the photosynthesis has three stages, similar to the thermal synthesis: breaking of Si-Si and Si-O bonds, diffusion of the Si atoms and nucleation of Si nanocrystals. The photon energy in the photosynthesis mainly affects the diffusion length of Si atoms, and the number of Si atoms available for nucleation at each nucleation site is greater for a longer diffusion length resulting from irradiation using high-energy photons. As a result, larger nanocrystals are formed using a shorter wavelength. However, the details of the photosynthesis mechanism are under study and will be reported elsewhere.

5. Conclusions

Both photo-oxidation and photosynthesis are unique phenomena resulting from a strong interaction between photons and nanoparticles. They can be employed to precisely control the sizes by photon energy, because the oxidation and growth of nanoparticles are self-limiting. The photosynthesis, which has been discussed in detail in this paper, is similar to the thermal synthesis of Si nanocrystals from Si-rich oxide, but it is much faster and allows the lowtemperature growth of Si nanocrystals from SiO_x. Because of its selective formation of the Si nanocrystals, the positions of Si nanocrystals are well controlled. We have demonstrated the photosynthesis of Si nanocrystals in two types of Si-rich oxides, i.e., the sputter-deposited film and the SiO nanopowder. The SiO nanopowder is unique and contains two- or one-dimensional Si networks or Si clusters. Since the bond strength of Si-Si and Si-O in such networks is weak, photons can easily decompose SiO_x into Si and SiO₂. Therefore, the minimum power required for the photosynthesis of Si nanocrystals in the SiO nanopowder is much lower than in the sputter-deposited film. If one develops a technique to form the thin film made of the SiO nanopowder, a two-dimensional array of Si nanocrystals can be embedded in SiO_x with the position-controlled formation of Si nanocrystals by the photosynthesis. Such a structure is attractive in a wide variety of device applications.

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