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Author	Hiroki Kobayashi, Pattarin Chewchinda, Hiroyuki Ohtani, Osamu Odawara, Hiroyuki Wada
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# Effects of Laser Energy Density on Silicon Nanoparticles Produced Using Laser Ablation in Liquid

**Hiroki Kobayashi, Pattarin Chewchinda, Hiroyuki Ohtani, Osamu Odawara, Hiroyuki Wada**

Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503  
Japan

E-mail: kobayashi.h.aw@m.titech.ac.jp

**Abstract.** We investigated the morphology of silicon nanoparticles prepared using laser ablation in liquid through varying the energy density and laser irradiation time. Silicon nanoparticles were prepared using laser ablation in liquid. A silicon wafer was irradiated in ethanol using a laser beam (Nd: YAG/second harmonic generation, 532 nm). Crystalline silicon nanoparticles approximately 6 nm in size were observed by TEM observation. The quantity of silicon nanoparticles proportionally increased with an increase in energy density greater than the laser ablation threshold. This quantity also increased with an increase in laser irradiation time without saturation due to absorption of the nanoparticles in liquid in the light path.

## 1. Introduction

Silicon nanoparticles are important for applications such as optoelectronics [1], [2] and bioimaging [3], [4]. Silicon nanoparticles have been researched to synthesize or to apply to applications. Silicon is used as the raw material for a semiconductor chip and is easily acquired. Small nanoparticles less than the de Broglie wave of an electron and the hole or Bohr radius of exciton produce a quantum effect. Such particles are “quantum-dots”. A quantum-dot has discrete bands instead of continuous bands and notably produces impact ionization [5]. Impact ionization is also “multiple exciton generation” (MEG). In general, one photon generates an exciton (a pair of electron and hole). However, this phenomenon generates more than 2 exciton pairs from one photon. Silicon can produce 2.6 exciton pairs from one photon (3.4 eV) [6]. The maximum size of a silicon quantum-dot can be estimated using the Bohr radius of an exciton in silicon. The diameter is 8.6 nm [7]. Therefore, silicon nanoparticles with a diameter 8.6 nm or lower are necessary for certain applications, especially MEG-based applications. Laser ablation in liquid is one method for synthesizing nanoparticles. This method produces nanoparticles by irradiating a target in solution using a laser with high energy density. Laser ablation in the gas phase or under vacuum has been studied since the 1960s [8], while the study of laser ablation in liquid was started recently [9] ~ [11]. In the case of laser ablation in liquid, the target material was metal usually. Later, organic material [12] and ceramics [13] ~ [17] were used as a target. Laser ablation in liquid is advantageous for producing silicon nanoparticles because silicon nanoparticles can be stably maintained on a particle surface by using ethanol as solvent [18]. Moreover, laser ablation in liquid has other advantages: the simplicity of the process and the possible creation of small nanoparticles with relatively small spatial dispersion [19].

Silicon nanoparticles have attracted attention, but it is difficult to produce high quantities by laser ablation in liquid. This study explores fabrication of silicon nanoparticles using laser ablation in liquid for applications such as a quantum-dot-sensitized solar cell. Therefore, production of silicon nanoparticles with a diameter less than 8.6 nm at a certain quantity is the objective for the study herein. Thus, the laser energy density and irradiation time were investigated for their dependence on nanoparticle size and quantity.

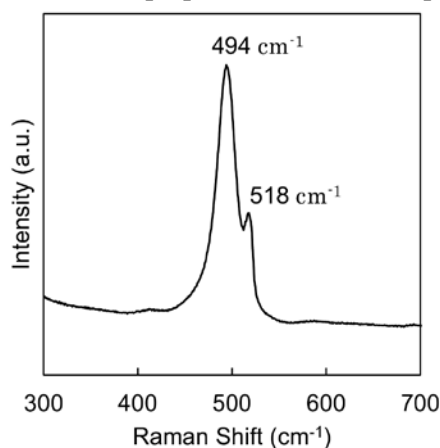
## 2. Experimental

A <100> p-type silicon wafer 600  $\mu\text{m}$  thick with a 11.5 ~ 15.5  $\Omega\text{ cm}$  resistance was used as the raw material. The silicon wafer was cut 2 cm by 2 cm. Before laser ablation, the silicon wafer was cleaned in ethanol using ultrasonication twice for 10 minutes and then dried. The silicon wafer was irradiated with a laser beam, which was not focused with a lens. The unpolished side of the silicon wafer was placed 7 mm beneath the top surface of the ethanol. Ethanol was used as the solvent for laser ablation to prevent oxidation of the silicon during laser ablation. The ethanol was stirred using a magnetic stirrer during laser ablation. The laser beam was a second harmonic generation of a Nd:YAG laser (wavelength: 532 nm; pulse duration: 13 ns; and repetition rate: 10 Hz). The diameter of the irradiated laser beam on the silicon wafer was 14 mm (1.54  $\text{cm}^2$ ). The energy density varied from 0.17 to 0.63  $\text{J}/\text{cm}^2$  (laser energy: 2.6 - 9.7 J/pulse). Irradiation time varied from 30 minutes to 3 hours.

The prepared nanoparticles were identified using Raman spectroscopy. The solution containing silicon nanoparticles was dropped in an Al pan under  $\text{N}_2$  atmosphere and then dried. This solution drying procedure was repeated 4 times. After this procedure, black powder was confirmed on the Al pan. To measure the Raman spectrum, the black powder was irradiated with a laser under the atmosphere to measure Raman spectrum. The particle size of the prepared silicon nanoparticles was measured using a transmission electron microscope (TEM). After laser ablation, the solutions were filtered with a Teflon filter (pore size: 100 nm). The solutions were then dropped onto a Cu grid, and the grid was then dried overnight at 70  $^\circ\text{C}$  in a vacuum. The quantity of silicon nanoparticles was measured using inductively-coupled plasma mass spectrometry (ICP-MS). Absorption spectra were measured by spectrometer with an integrating sphere.

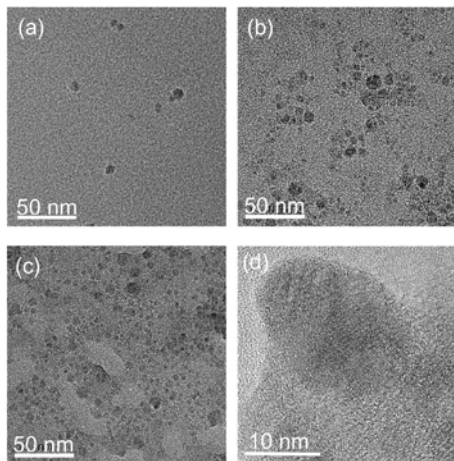
## 3. Results and discussion

Figure 1 shows a Raman spectrum of the silicon nanoparticles produced by ablating a silicon wafer in ethanol under an Ar atmosphere. The energy density was 0.17  $\text{J}/\text{cm}^2$ , and the ablation was performed for 2 hours. Two peaks were observed at 494  $\text{cm}^{-1}$  and 518  $\text{cm}^{-1}$ . The peak wavelength of the silicon crystal is at 520  $\text{cm}^{-1}$ . The particle size of silicon estimated by the value of Raman shift is 4 nm [20]. This peak was slightly shifted as an effect of nanosize silicon, whereas the sample peak at 494  $\text{cm}^{-1}$  indicates silicon dioxide [21]. The Raman peak for silicon dioxide is attributed to the silicon wafer native oxide layer or oxidation of the prepared silicon nanoparticles during Raman spectra

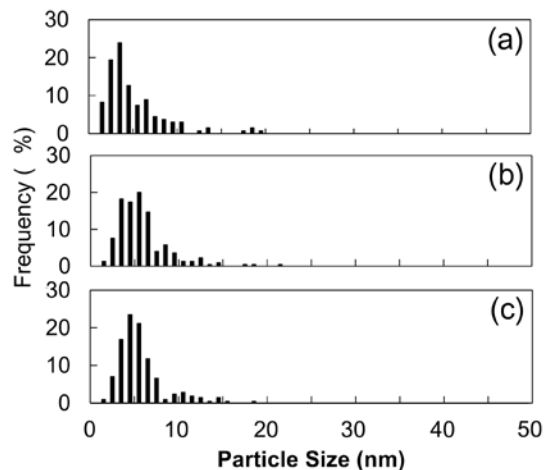


**Figure 1.** Raman spectrum of the silicon nanoparticles.

measurement. Therefore, the powder in the solution, which was prepared using an irradiating green laser at  $0.17 \text{ J/cm}^2$  on a silicon wafer in ethanol, comprises silicon nanoparticles with silicon dioxide. We investigated the effect of energy density from the irradiating laser on the morphology of the silicon nanoparticles. The irradiation time was 1 hour. Figure 2 shows TEM images of silicon nanoparticles. These images indicate that we produced silicon nanoparticles at approximately 6 nm. Moreover, the nanoparticle shapes are almost spherical. Lattice fringes were confirmed through a high magnification image. These observations indicate that the silicon nanoparticles are crystallized.



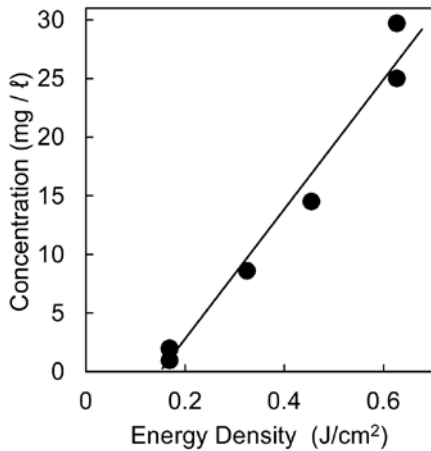
**Figure 2.** TEM images of the silicon nanoparticles. (Energy density: (a)  $0.17 \text{ J/cm}^2$ , (b)  $0.32 \text{ J/cm}^2$ , (c)  $0.45 \text{ J/cm}^2$  and (d) high magnification image of  $0.45 \text{ J/cm}^2$ . Irradiation time: 1 hour.)



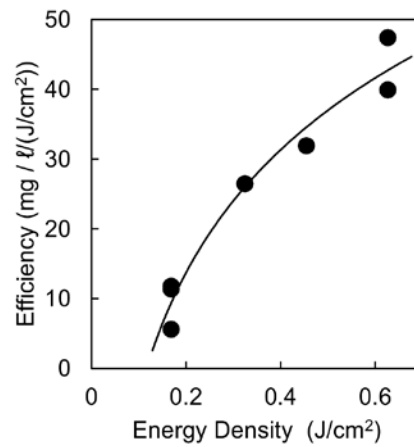
**Figure 3.** Particle size distributions for the silicon nanoparticles. (Energy density: (a)  $0.17 \text{ J/cm}^2$ , (b)  $0.32 \text{ J/cm}^2$ , and (c)  $0.45 \text{ J/cm}^2$ . Irradiation time: 1 hour.)

Figure 3 shows the particle size distribution of the silicon nanoparticles measured through TEM images. The average sizes were 5.6 nm, 6.3 nm and 6.2 nm at energy densities of  $0.17 \text{ J/cm}^2$ ,  $0.32 \text{ J/cm}^2$  and  $0.45 \text{ J/cm}^2$ , respectively. Silicon nanoparticles were produced with the desired size, less than the Bohr radius of exciton. Given these results, the energy density of the irradiating laser does not significantly influence the silicon nanoparticle size under such experimental conditions.

Mechanism of fabrication of crystalline Si nanoparticles in liquid might be recrystallization of liquid or vapor of silicon in cavitation bubble, which would be created by heating target using laser light. Indeed there are many reports of the relation between cavitation bubble and nanoparticle formation [22-25]. In our experiment, the particle size of silicon nanoparticles was approximately 6 nm. This particle size might be related to lifetime of bubbles, which might restrict the growth of silicon nanoparticles. The lifetime of bubbles would not be changed under our experimental conditions because pressure and temperature of ethanol were almost constant. Therefore, the particle size of silicon nanoparticles was not changed. At the same time, the recrystallization in ethanol might be possible, too. We investigated the effect of the irradiating laser energy density on the quantity of silicon nanoparticles. Figure 4 shows an estimate of the silicon nanoparticle quantity through ICP. The threshold was approximately  $0.15 \text{ J/cm}^2$ . In general, the penetration depth as a function of energy density is saturated at a high energy density. If ablation is consistent with this rule, the ablated depth of a silicon wafer per unit energy density decreases with an increase in energy density. However, the experimental results indicate that an increase in laser energy density proportionally increases the quantity of silicon nanoparticles. This result is likely related to the ablated area of the silicon wafer as an element. The ablated area increased with an increase in energy density even in the same irradiated area. To consider the preparation efficiency of silicon nanoparticles as a function of laser power, Figure 4 was deformed. Figure 5 shows an estimate for the quantity of silicon nanoparticles per unit energy density.



**Figure 4.** Silicon nanoparticle quantity as a function of energy density.

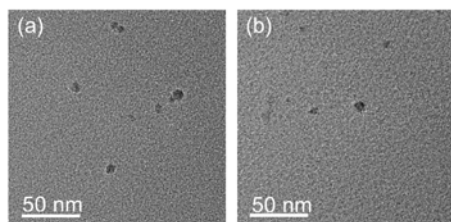


**Figure 5.** Silicon nanoparticle production efficiency as a function of energy density.

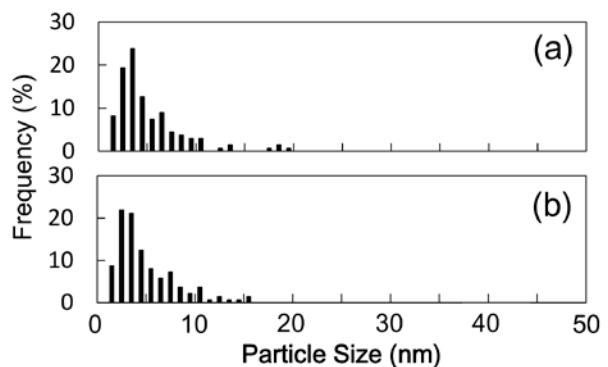
These concentrations in Figure 5 were calculated by dividing the original concentration with energy densities. Efficiency, which is vertical axis value in Figure 5, increased at a low energy density but was saturated at a high energy density. The monotonic increase in Figure 5 indicates that higher energy density effectively increase the quantity of silicon nanoparticles. The tendency toward saturation at a high energy density is likely due to the threshold. When the threshold was subtracted from the energy density, and the concentration was divided by this difference, these values were approximately the same at each energy density. The threshold effect was high at low energy densities and low at high energy densities.

The effect of laser ablation irradiation time on silicon nanoparticle morphology was investigated. In previous study [26], long irradiation times reduced the quantity of silicon nanoparticles because silicon nanoparticles prepared in liquid absorb and scatter the laser, which decreases the energy density at the target and efficiency of silicon nanoparticle production. To confirm the irradiation time dependency, irradiation time was varied. The laser energy density on a silicon wafer was fixed at 0.17 J/cm<sup>2</sup>. Figure 6 shows TEM images for the silicon nanoparticles. The particle sizes of the silicon nanoparticles were desirable particle size. The nanoparticle shapes were almost spherical. Figure 7 shows the particle size distribution for the silicon nanoparticles. The average particle size was approximately 6 nm, which is desirable for quantum confinement. These results were similar under each set of experimental conditions. Therefore, irradiation time does not affect silicon nanoparticle morphology under such experimental conditions.

The effect of laser ablation irradiation time on the quantity of silicon nanoparticles was investigated. The quantity of silicon nanoparticles was estimated using ICP. This result is shown in Figure 8. The

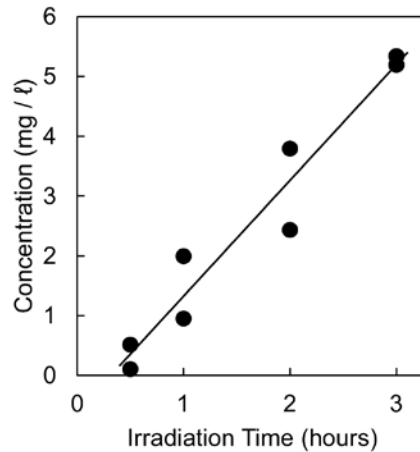


**Figure 6.** TEM images of silicon nanoparticles. (Irradiation time: (a) 1 hour and (b) 3 hours. Energy density: 0.17 J/cm<sup>2</sup>.)



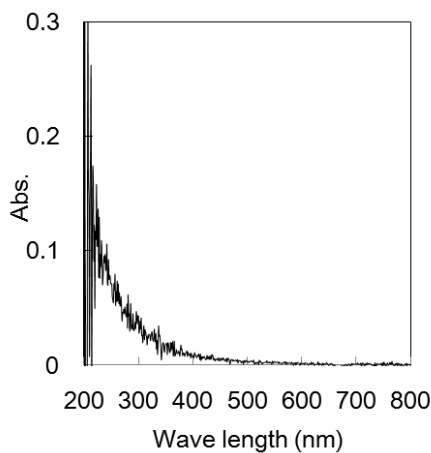
**Figure 7.** Particle size distributions of silicon nanoparticles. (Irradiation time: (a) 1 hour and (b) 3 hours. Energy density: 0.17 J/cm<sup>2</sup>.)

quantity of silicon nanoparticles increased linearly with irradiation time. We observed a small threshold, which is likely related to native silicon dioxide on a target bare silicon wafer. Silicon dioxide has a higher band gap than silicon; therefore, silicon dioxide has a lower absorbance with the green laser. Further, the silicon dioxide melting point is higher than for silicon. The lower absorbance likely decreases laser ablation efficiency. In this experiment, saturation of the quantity of silicon nanoparticles prepared was not observed. Therefore, a longer irradiation time can increase the quantity of silicon nanoparticles.

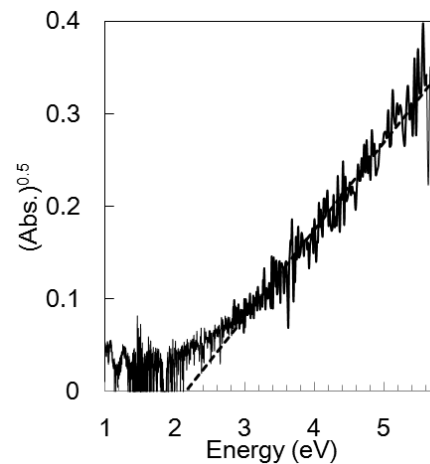


**Figure 8.** Silicon nanoparticle quantity as a function of irradiation time.

Figure 9 shows an absorbance spectrum for the silicon nanoparticles dispersed in the solution. Although absorption was observed at 532 nm, it has only small influence on particle generation. Therefore, the quantity of silicon nanoparticles increased linearly even at a high energy density. Figure 10 shows the square root of absorbance as a function of photon energy because silicon is indirect transition material. The intercept of horizontal axis which means bandgap  $E_g$  is 2.2 eV. Increase in bandgap by quantum confinement was observed as a result of nanosize effect.



**Figure 9.** Absorbance spectrum for silicon nanoparticles dispersed in a solution.



**Figure 10.** Absorbance spectrum for silicon nanoparticles dispersed in a solution.

#### 4. Conclusion

Silicon nanoparticles were prepared using laser ablation in liquid. In general, the quantity of nanoparticles produced from laser ablation in liquid is low. To increase this quantity, the effect of energy density from the irradiating laser on a silicon wafer was investigated. An increase in energy density proportionally increased the quantity of silicon nanoparticles. The preparation efficiency for

the silicon nanoparticles per unit laser power gradually decreased with a decrease in energy density from the laser ablation threshold. Particle size was not influenced by changing the energy density under such experimental conditions. Therefore, higher energy density compared with the laser ablation threshold is necessary for higher nanoparticle preparation efficiency. The effect of irradiation time was also studied. The quantity of silicon as a function of irradiation time was linear. The effect of silicon nanoparticle absorption in liquid was not observed under such experimental conditions. Conditions for increasing silicon nanoparticle production were determined herein. Such conditions will likely contribute to silicon nanoparticle applications, such as solar cells.

## 5. Acknowledgements

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