Generation of Silicon Nanoparticles by Line-Focused Laser Irradiation on Waste Silicon Powders

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Recently, silicon nanoparticles are attracting attention as a material for improving the performances of lithium-ion batteries and solar cells. However, conventional methods for producing silicon nanoparticles are expensive and time-consuming. In this study, we proposed a silicon nanoparticle generation method by line-focused laser irradiation on waste silicon powder. The line-focused laser was realized by converting a spot-beam laser through an optical system, which enabled scanning a wide area at once. By reusing waste silicon powder, an industrial waste from semiconductor manufacturing process, as the laser irradiation target, nanomaterials can be generated at low cost. By selecting the processing conditions appropriately, silicon nanoparticles were successfully deposited on the collecting substrate. The effect of laser fluence on nanoparticle deposition morphology and generation amount was investigated. Compared to the spot-focused laser irradiation in the same laser power, about 33 times amount of silicon nanoparticles were generated per unit time. SEM observation showed that the diameter of the nanoparticles ranged between 40 and 100 nm. These results show the possibility of mass production of silicon nanoparticles at a relatively low cost.

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1. Introduction

Silicon nanoparticles have large specific surface area, fluorescence properties, and high solar energy conversion efficiency, which are different from bulk silicon. Due to these useful properties, silicon nanoparticles are recently attracting attention as a high-performance material for lithium-ion batteries and solar cells, and researches on their fabrication have been conducted[1]. One of the conventional methods for silicon nanoparticle fabrications is liquid-phase synthesis[2]. Even though this method is popular in the mass production, it is difficult to collect high-purity silicon nanoparticles, since hydrogen is capped on the nanoparticle surface after the process. Recently, femtosecond pulsed laser irradiation of silicon wafer was proposed to generate high-purity silicon nanoparticles[3]. However, this method is expensive and time-consuming, thus it is inappropriate for mass production.

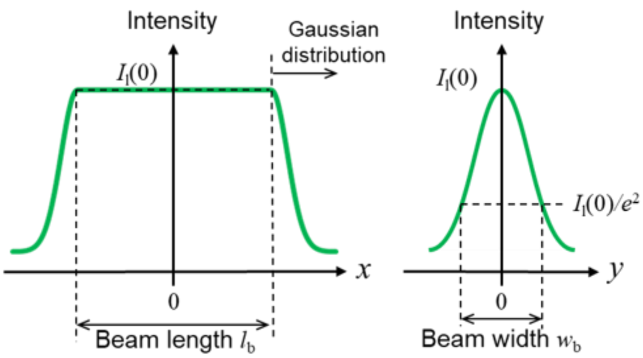
In this study, we propose nanosecond pulsed line-focused laser irradiation of waste silicon powder to generate silicon nanoparticles at low cost and high efficiency. Currently, large quantity of silicon powder is discarded as an industrial waste in the manufacturing process of silicon wafers. By using waste silicon powder, reuse of industrial waste and cost reduction of raw materials can be realized. In a previous study, it was shown that high-purity silicon nanoparticles can be generated by nanosecond pulsed spot-focused laser irradiation of waste silicon powder[4]. However, the overlap rate of spot-focused laser scanning is high due to the round beam shape. Only a small area can be irradiated by laser scanning during a certain period of time, and the generation efficiency of nanoparticles remains low.

A line-focused laser is realized by passing a round laser beam through an optical system that consists of two cylindrical lenses and a focusing lens. The beam length in the long axis direction is more than 100 times larger than the beam width in the short axis direction, and scanning the laser in the short-axis direction enables batch irradiation of a wide area, which is expected to improve the generation efficiency of nanoparticles. The intensity distribution of the spot-focused laser I_s and the line-focused laser I_l can be described using following equations (1) and (2), respectively,

$$I_\mathrm{s}(r) = \frac{2P_0}{\pi b^2}\exp\left(-\frac{2r^2}{b^2}\right) \tag{1}$$

$$I_\mathrm{l}(x) = \frac{P_0}{l_\mathrm{b}} \quad \left(-\frac{l_\mathrm{b}}{2} \leqq x \leqq \frac{l_\mathrm{b}}{2}\right) \tag{2}$$

where r is the radial position, P_0 is the laser power, b is the beam radius of the spot-focused laser, x is the long axis position, and l_b is the beam length of the line-focused laser. The intensity distribution of the line-focused laser in the short axis direction can be described by Eq. (1), by substituting y for r and $w_b/2$ for b, where y is the short axis position and w_b is the beam width of the line-focused laser.



(a) long axis direction (b) short axis direction

Fig. 1 Schematic model of the flat-top intensity distribution of line-focused laser

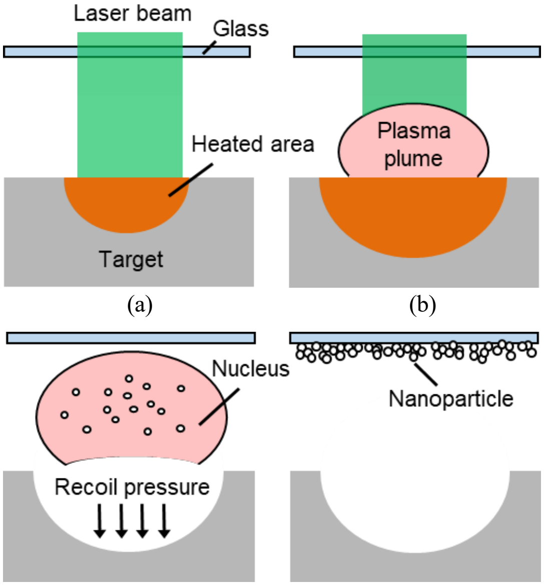


Fig. 2 Mechanism of generation and deposition of silicon nanoparticle by laser irradiation[4]

Fig. 1 shows a schematic diagram of the intensity distribution of the line-focused laser. The intensity is independent of long axis position, enabling uniform laser irradiation when scanned in the short axis direction. Line-focused laser has been used for uniform annealing and recrystallization of a large area[5], but researches on nanoparticle generation have not been conducted, and the effects of process parameters have to be investigated.

In this study, the energy density of the line-focused laser was varied to investigate the morphology and composition of the nanoparticle products, and the effect on the amount produced. The improvement of silicon nanoparticle generation efficiency is expected to contribute to the realization of high-performance battery production.

2. Experimental procedures

2.1 Nanoparticle generation by laser irradiation

The mechanism of nanoparticle generation by laser ablation and deposition on a glass substrate is shown in Fig. 2[4]. When the target is irradiated by laser, the material absorbs the laser and heats up rapidly (Fig. 2 (a)). Soda-lime glass transmits more than 90% of light at a wavelength of 532 nm[6], thus the energy decay can be ignored. The surface of the target melts and evaporates, forming a plume of plasma(Fig. 2 (b)). Due to the rapid expansion of the plume, recoil pressure works in the direction of the target. The plume is cooled by the atmosphere and agglomerates to form nucleus (Fig. 2 (c)). Nucleus grow to nano-size, and are deposited on the glass substrate (Fig. 2 (d)).

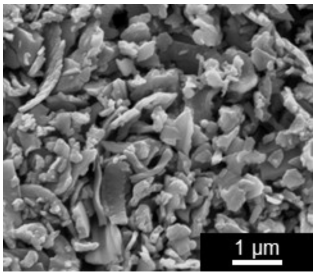


Fig. 3 Irradiation target surface

2.2 Experimental setup

The irradiation target was a silicon wafer coated with waste silicon powder (average particle diameter: 1.6 μm) with a thickness of approximately 100 μm. The surface of the irradiation target is shown in Fig. 3. A nanosecond pulsed laser (EO TECHNICS G200) was used for laser irradiation. The round beam was converted to a line shape by optics. A 1.3 mm thick soda-lime glass substrate was placed at a fixed distance from the target surface, and laser irradiation was applied from the upper surface of the glass to deposit the product on the lower surface of the glass. Table 1 shows the laser irradiation conditions. After the laser irradiation experiments, the glass substrate and irradiated surfaces were observed using a scanning electron microscope (SEM), and the composition of the deposited products was analyzed using X-ray diffraction (XRD). The deposition amount on the glass substrate was measured using an analytical balance.

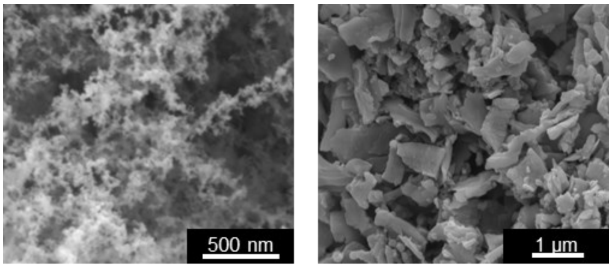
Table 1. Laser irradiation conditions

Parameter	Value
Wavelength (nm)	532
Beam size (mm)	0.025 × 10
Pulse width (ns)	60
Frequency (kHz)	10
Energy density (J/cm^2)	0.50 – 4.0
Scanning speed (mm/s)	15
Substrate-target distance (mm)	2
Environment	In air

3. Results and discussion

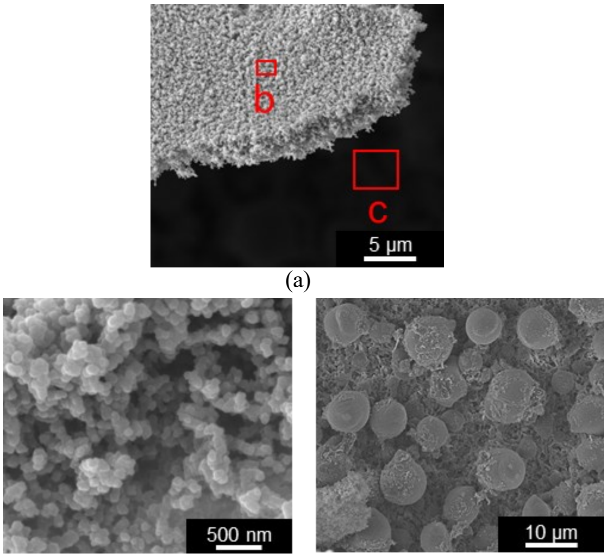
3.1 Deposits on glass substrate

SEM images of the deposition morphology at different energy densities are shown in Fig. 4. When irradiated at 2.0 J/cm^2, nanoparticles formed a reticulate structure (Fig. 4(a)), which is caused by the electrostatic force generated by the friction between silicon nanoparticles and air molecules[7]. Similar morphology was reported in previous studies of nanoparticle generation by spot-focused laser irradiation[3,4], and there was no difference in deposition morphology due to changes in beam shape.



(a) 2.0 J/cm^2 (b) 4.0 J/cm^2

Fig. 4 Deposition morphology of silicon particles at different energy densities



(a)

(b) (c)

Fig. 5 Surface morphology of the target after irradiation at 2.0 J/cm^2

On the other hand, when irradiated at 4.0 J/cm^2 (Fig. 4(b)), polygonal microparticles were deposited. The surface morphology of the target was similar to that before irradiation (Fig. 3). This suggests that the microparticles were deposited on the glass substrate by particles scattering from the target surface due to the recoil pressure generated during ablation process. At high energy densities, the energy absorbed by the material is large, and the amount of material that evaporates increases. The recoil pressure on the material surface also increases at this time, and the pressure is considered to be sufficient for micro-sized particles to reach the glass substrate.

3.2 Irradiated target surface

The target surface after laser irradiation at an energy density of 2.0 J/cm^2 are shown in Fig. 5. An aggregated layer of nanoparticles was observed on the target surface after laser irradiation (Fig. 5(a)). From Fig. 4(a) and Fig. 5(b), the nanoparticles on the target surface are larger in size than those deposited on the glass substrate. After laser irradiation, the plume diffuses around the target surface, and the density of the plume near the target is large, which is thought to facilitate nucleation and growth, resulting in larger particle size[8]. The particles did not reach the glass substrate due to their large mass.

Spherical structures were formed under the nanoparticle layer, on the irradiated surface (Fig. 5(c)). The spherical structure is considered to have been formed by the melting of the silicon particle by laser irradiation, and agglomerating with the surrounding liquid silicon.

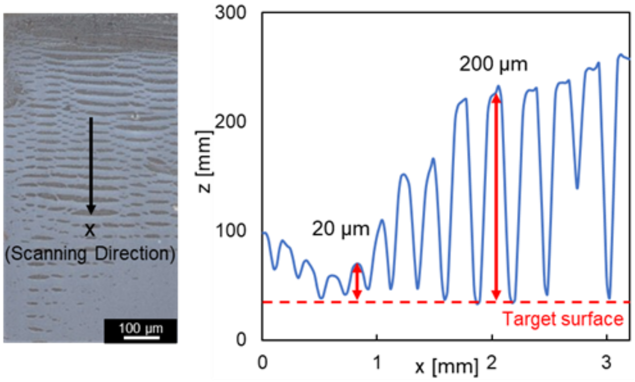


Fig. 6 Cross-sectional profile of the thin layer of silicon nanoparticles

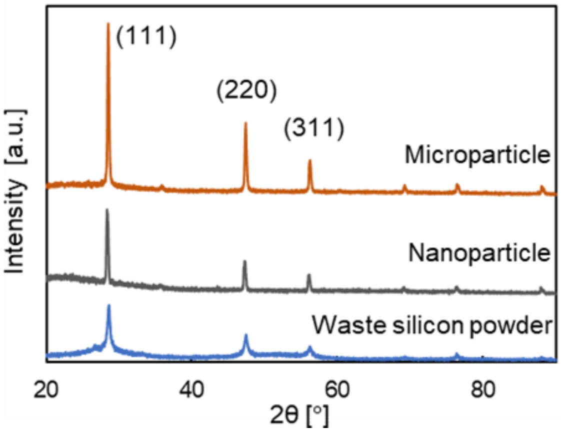


Fig. 7 XRD spectra of microparticle, nanoparticle, and waste silicon powder

Fig. 6 shows the low-magnification image and the cross-sectional profile of the generated thin layer of silicon nanoparticles. It is confirmed that layer is formed at a distance of 20~200 μm from the target surface. The adhesion between the nanoparticles generates tension through the layer, which is assumed to be greater than the gravity, causing the nanoparticles to form at a distance from the target surface. This phenomenon was not observed in the spot-focused laser irradiation, thus it is thought to be unique to line-focused laser irradiation, which has uniform intensity in a wide width.

3.3 Composition analysis

The results of the XRD analysis of the products are shown in Fig. 7. There was no difference in the peak positions of the nanoparticles and microparticles, and silicon, the raw material, was detected in both cases. The larger peak values and smaller FWHM compared to the target before laser irradiation indicate that both deposits are highly crystalline. From this result, it can be inferred that the nucleation from the plume in this experiment is crystal growth. The microparticles are considered to be recrystallized waste silicon powders heated by laser irradiation.

The oxidation of silicon by laser irradiation was insignificant because the SiO_2 peak was not detected. The reason for the low oxidation of the nanoparticles despite laser irradiation in air can be attributed to the short time required for heating and cooling. In addition, the rapid plume generation may have pushed out the air between the glass substrate and the target, reducing the oxygen fraction during the heating process.

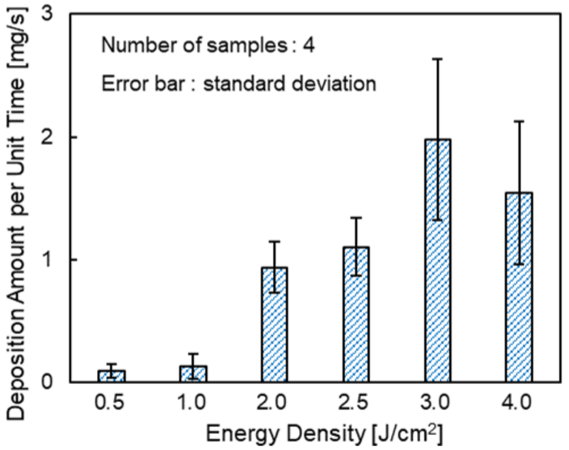


Fig. 8 Deposition amount per unit time at various energy densities

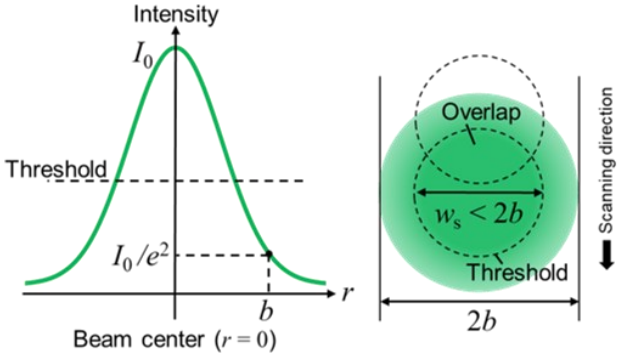


Fig. 9 Nanoparticle generation area in spot-focused laser irradiation

3.4 Effect of energy density on deposition amount

Fig. 8 shows the amount of nanoparticle deposition per unit time at each energy density. The amount of deposition increased with increasing energy density in the range of 0.5 J/cm^2 to 3.0 J/cm^2. As mentioned in 3.1, the amount of material evaporation is thought to have increased as the energy density increases, resulting in this trend.

The silicon nanoparticle generation efficiency was evaluated and compared to the result of spot-focused laser irradiation of waste silicon powders. The generation efficiency is defined as the mass of deposited nanoparticles per unit time. In a previous study, the result of spot-focused laser irradiation of 85μm in diameter at the energy density of 2.0 J/cm^3 showed the nanoparticle deposition amount of 2.08 μm^3/s[10]. To convert from volume to mass, the density of single crystal silicon was substituted, and the generation efficiency was 4.85×10^{-3} mg/s. In this study, the generation efficiency was 9.39×10^{-1} mg/s, which was 193 times higher than that in the previous study[9]. As the laser power used in this study was 5.87 times higher than that in the previous study, the nanoparticle generation efficiency has been improved by a factor of ~33 by using a line-focused laser beam.

This is thought to be due to the difference in the overlap rate and the laser intensity distribution. From Fig. 8, the energy density threshold for high-efficiency nanoparticle generation can be assumed to be between 1.0 J/cm^2 and 2.0 J/cm^2. From Eq. (1), the diameter of the area irradiated by spot-focused laser above 1.0 J/cm^2 is 70 μm, and above 2.0 J/cm^2 is 50 μm. This indicates that the width of the nanoparticles generated w_s is smaller than the spot diameter, as shown in Fig.9. On the other hand, from Eq. (2), the width of the area irradiated by line-focused laser above 1.0 J/cm^2 and 2.0 J/cm^2 is 10 mm, which is equal to the beam length of the laser. This leads to a scanned area 44.1 times larger than that of the spot-focused laser.

4. Conclusions

Nanosecond pulsed line-focused laser irradiation was performed on waste silicon powder which was discharged from the semiconductor manufacturing process. The following conclusions were drawn.

(1) At 2.0 J/cm^2, crystalline nanoparticles with 40 nm diameter were deposited on the glass substrate, and aggregated nanoparticles with 100 nm diameter formed as a thin layer above the irradiated surface.

(2) The nanoparticle production efficiency at the same laser power was ~33 times higher than that of conventional spot-focused laser irradiation.

These results indicate that silicon nanoparticles can be produced from waste silicon powder with high efficiency by using a line-focused laser.

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