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Fabrication of Sintered Si Nano-polycrystalline with Reduced Si Nanoparticles and Properties of Photoluminescence in Visible Regime for Sintered Si Nano-polycrystalline by Violet Light Excitation

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Abstract: Si oxide powder is reduced by highly repetitive pulse laser ablation in liquid, and Si nanoparticles are produced efficiently with a low cost in a short time. A Si nanopaste with highly doped Si nanoparticles was sintered by using a hot plate. We succeeded in fabricating a sintered Si nano-polycrystalline for the first time. The structure and components of the fabricated sintered Si nano-polycrystalline were investigated by SEM and EDX analysis. Furthermore, the reduced Si nanoparticles and the sintered Si nano-polycrystalline were excited by violet light and stable photoluminescence (PL), which were observed in the visible regime. The peak wavelengths of the PL were 550 nm and 560 nm. Particularly, the intensity of the observed PL of the sintered Si nano-polycrystalline was five times higher than that of the reduced Si nanoparticles powder. This result is attributed to the PL being amplified inside the sintered Si nano polycrystalline. These experiments show that because the mean diameters of the Si nanocrystals in the reduced Si nanoparticles were below 2 nm, the structure of the Si nanocrystals changed to a direct-transition type; the bandgap energy of the Si nanocrystals changed from 1.1 eV to 2.25 eV, and PL in the visible regime was generated. Moreover, the possibility of Si photonics is discussed. The sintered Si nano-polycrystalline will be applicable to light waveguides, optical switches using a free carrier effect, and light amplifiers.

Keywords: SiO_2, Si, Nanoparticles, Polycrystalline, Optical Waveguide, Optical Switch, Free Carrier Effect, Light Amplification, Photoluminescence, Laser Ablation in Liquids

1. Introduction

Electrons in bulk Si make an indirect transition between bandgaps. The bandgap energy of bulk Si is 1.1 eV. The wavelength is close to near-infrared. Thus, it is difficult for bulk Si to generate photoluminescence. However, due to the quantum effect that occurs when electrons and holes are confined in the area below their wavelength, Si nanoparticles have larger bandgap energy than that of bulk Si, and the bandgap structure changes to a direct transition type. A theory stating that Si nanoparticles can emit photoluminescence in the visible regime has already been proposed [1]. Photoluminescences in both the visible and violet regime have been observed in some experiments [2–9]. The observed experimental results are consistent with the theoretical ones [8–9]. Applications using Si nanoparticles are expected to become alternatives for conventional illumination.

Si nanoparticles are produced by many kinds of methods. The production of Si nanoparticles by pulse laser has been extensively researched. Si nanoparticles work as quantum dots, and they generate photoluminescence in the visible regime [1–6].

Currently, calculations for information processing are mainly performed by using semiconductors. Because of advancements in information technology (IT), the number of calculations has become enormous. Thus, more rapid calculations have been required.

Si photonics, in which arithmetic processing is done for all the information gained by optical signals using light controlling devices based on Si, has been proposed. Calculations by optical signals have also been widely proposed. We are the first to have presented a proposal on a Si optical switch [10] using a free carrier effect [11-12].

Following that proposal, NICT Japan has reported that the Si optical switch was fabricated and that the device actually worked [13]. We have researched Si optical switches to develop an optical computer as shown in reference [10].

Until now, the main focus of research has been on the synthesis of Si nanoparticles. As previously reported, we could produce a sufficient number of Si nanoparticles to work in emission devices. However, Si nanoparticles can barely work as an optical waveguide or device for generating laser light [14]. The nanoparticles should be close to each other to efficiently propagate electromagnetic waves (light) as an optical waveguide. For example, when an electromagnetic wave with a wavelength of 0.5 μm propagates in a nano-polycrystalline with a mean diameter of a few nm, the structure should not negatively influence propagation.

In this study, we used Si oxide powder to synthesize Si nanoparticles. Si oxide powder is reduced by highly repetitive pulse laser ablation in liquid, and Si nanoparticles are produced. A Si nanopaste with highly doped Si nanoparticles was sintered by using a hot plate, and we obtained a Si nano-polycrystalline for the first time. The properties of the photoluminescence in the visible regime of the reduced Si nanoparticles, and the sintered Si nano-polycrystalline are shown. The similar results have not been previously reported as far as we know. The Si nano-polycrystalline has a temporally stable photoluminescence when it is excited by light. If the surface conditions of the Si nanoparticles change with time, and we can not obtain stable photoluminescence. The structure and components of the fabricated sintered Si nano-polycrystalline were investigated by SEM and EDX analysis. We also discuss the possibility of Si photonics.

2. Experimental Setup

2.1. Synthesis of Reduced Si Nanoparticles and Fabrication of Sintered Si Nano-polycrystalline

Si oxide powder (purity 99.9%, mean diameter 4 μm, Kojundo Chemical Co., Ltd.) is reduced by highly repetitive pulse laser ablation in liquid. Here, as shown in reference [7], using the same method, highly repetitive Nd: YAG laser pulses (repetitive rate 18 kHz, wavelength 1064 nm) were focused by a lens. The focused laser pulses were directly irradiated into pure water with the Si oxide powder in a small glass bottle. The water was continuously mixed by a magnetic stirrer, and the Si oxide powder was reduced to Si, and Si nanoparticles were produced at the same time. The irradiating time was ten minutes. The weight of the total Si oxide powder was chosen to be 1 g. The reduced Si nanoparticles were dried, and as many reduced Si nanoparticles as possible were mixed with an Ag paste weighing 5 mg (NAG10, Ag 82 wt.% density, Daiken Chemical Co., Ltd., Japan). Finally, the prepared nanopaste was sintered by using a hot plate.

To compare the sintered Si nanopaste, Si powder (purity 99.9%, mean diameter 5 μm, Kojundo Chemical Co., Ltd.) was mixed with the Ag nanopaste, and the prepared Si nanopaste was sintered.

The Si paste was pasted on a glass plate and sintered using an electrical hot plate (CHP-170AN, ASONE) in an atmosphere of air at 250 deg. for one minute and at 300 deg. for four minutes. When using reduced Si nanoparticles, the prepared Si nanopaste was sintered in an atmosphere of air at 200 deg. for five minutes. Gaps between Si nanoparticles are vanished with keeping the size of Si nanocrystal when the Si pastes are sintered. Also, components except for Ag, Si, and impurity metals are removed from the pastes because they become gas.

The structure of the sintered Si nanopastes was observed by using an S-4700 scanning electron microscope (SEM) (Hitachi High Technologies, Japan). An EMAX7000 energy-dispersive X-ray spectrometer (EDX) (Horiba, Japan) was used for analyzing the distributions of silver, mixed oxides, and impurities.

2.2. Observation of Photoluminescence Excited by Violet Light

In this section, we describe the principles of the PL of the Si nanocrystal line. Si nanoparticles have larger bandgap energy than that of bulk Si by the quantum size effect, and the bandgap structure changes to a direct transition type. The Si nano-crystalline can emit PL in the visible regime (as mentioned in the introduction of this paper). From the results described in references [6, 9], we have considered that the PL is due to the quantum size effect of Si nano-crystalline.

Experimental setup for excitation of the sintered Si nano-polycrystalline is shown in Fig. 1.

LD (NDHV220APAE1, peak wavelength 404 nm, Nichia, Japan) as a source for exciting the sintered Si nano-polycrystalline was used. The emitting image was transferred using a single lens, and the output laser light was focused at a distance of 35 mm from the focusing lens as shown in Fig. 1. The output laser power was 1 mW. The output laser light was focused on the edge of the sintered Si nano-polycrystalline. Here, the intensity of the focused laser light was estimated to be 13 W/cm^2. Moreover, the PL of the reduced Si nanoparticles and the sintered Si nano-polycrystalline were observed and measured using a spectrometer with a fiber light guide (USB4000, Ocean Photonics). The PL of the sintered Si nano-polycrystalline was measured at a distance of 5 cm from the opposite side of the pump surface of the sintered Si nano-polycrystalline.

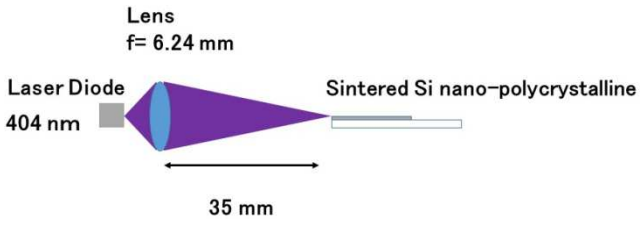


Fig. 1. *Experimental setup for excitation of the sintered Si nano-polycrystalline.*

3. Results and Discussion

3.1. Sintered Si Nanopastes

The color of Si oxide is white. The color of the reduced Si nanoparticles after irradiation with laser pulses in pure water is gray. The color was close to that of Si powder. However, the surface of the reduced Si nanoparticles is oxidized [4, 6–7]. It has been recognized that the mean diameters of the reduced Si nanoparticles were evaluated to be 10 nm using the Scherrer formula and the bandwidth of the X-ray spectrum in XRD analysis.

We have succeeded in fabricating a Si nano-polycrystalline by sintering prepared Si nanopaste. Sintered polycrystallines by using a hot plate are shown in Fig. 2. The Si polycrystalline obtained by sintering a Si paste mixed with Si micro powder is shown in Fig. 2 (a). Also, the Si nano-polycrystalline obtained by sintering a Si nanopaste mixed with the reduced Si nanoparticles is shown in Fig. 2 (b). The size of the Si polycrystalline obtained by sintering a Si paste mixed with Si micro powder is 5 mm x 5 mm. The thickness is around 50 μm. The sintered Si polycrystalline has a clear luster while the sintered nano-polycrystalline has only a slight luster. The size is 6 mm x 13 mm, and the thickness is around 50 μm.

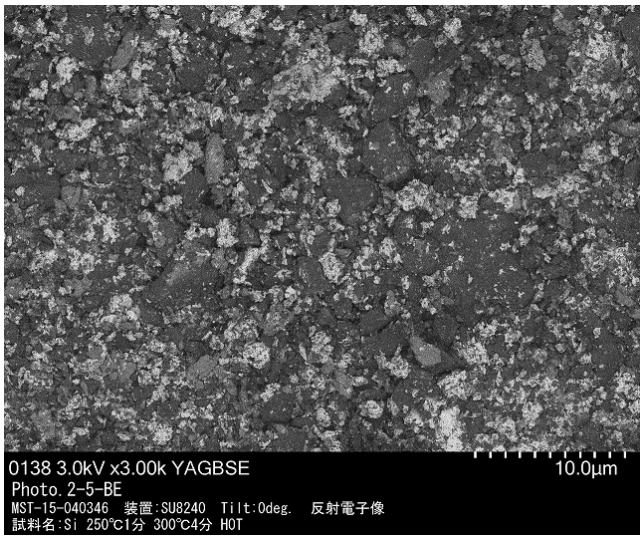
(a)

(b)

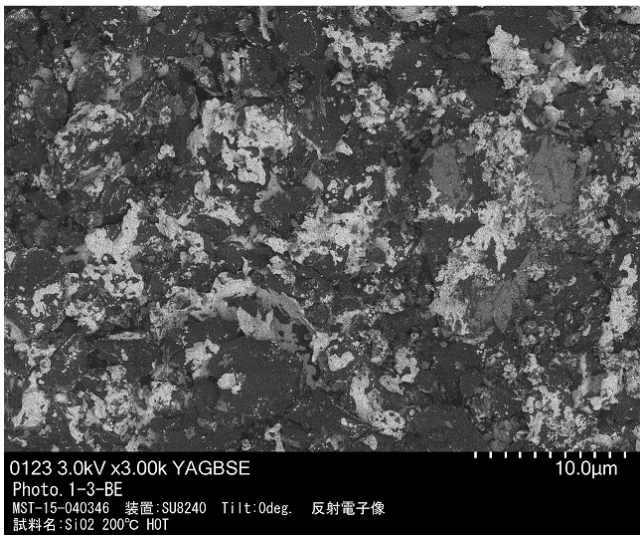
Fig. 2. *Sintered Si polycrystalline. (a) Using Si powder, (b) Using reduced Si nanoparticles.*

The resistances of the sintered Si nano-polycrystalline were evaluated by the four-terminal method, and their volume resistivity was estimated. The volume resistivity of the sintered Si nano-polycrystalline was 4.5 x 10^{-7} (Ω・m). The evaluated resistance of the sintered nano-polycrystalline per 1 cm was 0.01Ω. The value is close to that of metal. The resistance of the Si polycrystalline obtained by sintering a Si paste mixed with Si micro powder is also as low as that of the sintered Si nano-polycrystalline.

3.2. SEM and EDX Analysis



(a)



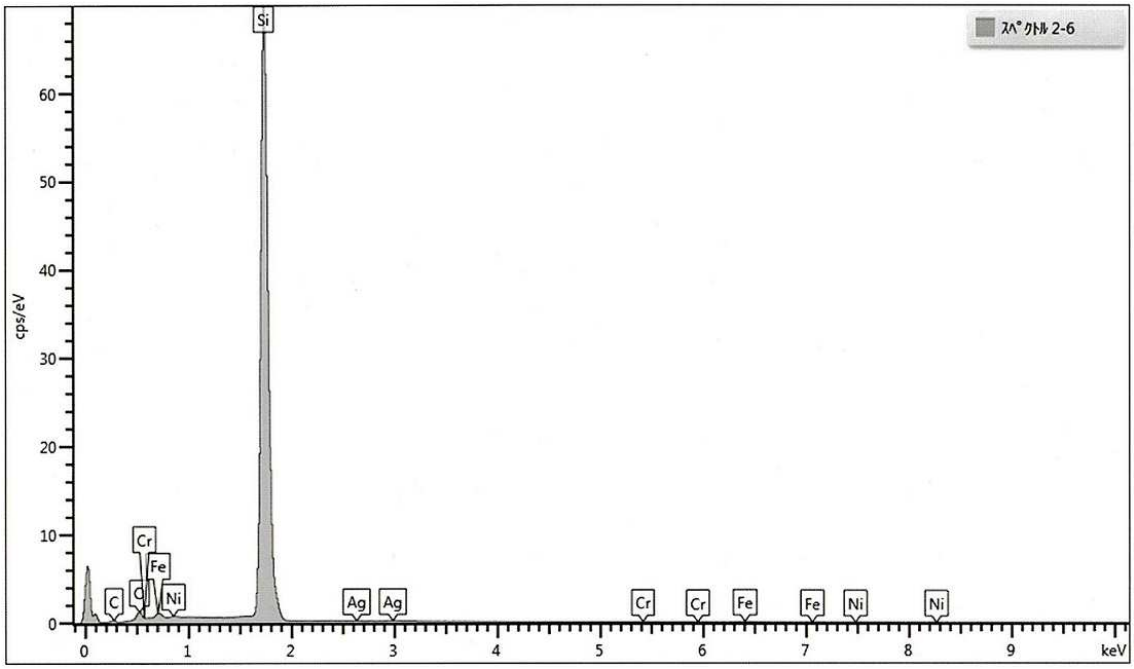
(b)

Fig. 3. *SEM image (Reflection image). (a) Using Si powder. (b) Using reduced Si nanoparticles.*

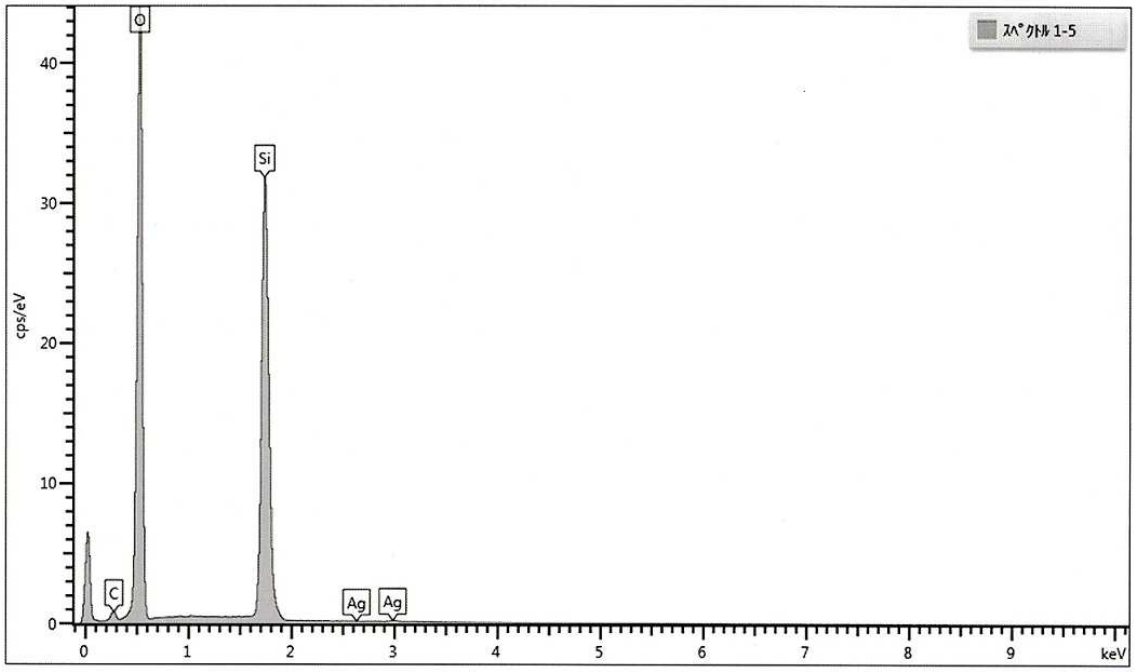
The photo image (reflection image) obtained by SEM analysis is shown in Fig. 3. A photo image (reflection image) obtained by SEM analysis for sintered Si polycrystalline using Si powder is shown in Fig. 3 (a). A photo image (reflection image) obtained by SEM analysis for sintered Si nano-polycrystalline using reduced Si nanoparticles is shown in Fig. 3 (b). Both photo images are results of observing the

surfaces of the sintered Si polycrystalline. It has been proven from the specific X-ray spectrum of EDX analysis that the black parts mainly contain Si. Large Si particles with diameters of 3–5 μm were observed on the surface of the Si polycrystalline as shown in Fig. 3 (a). However, as shown in Fig. 3 (b), fewer large Si particles were observed, and smaller Si particles, whose sizes were below 1 μm, were observed. The sintered Si seemed to be melted, and this melted Si consisted of very small Si nanocrystals with diameters of a few nm.

As for impurities, it has been found that the gray part contains mainly Fe. The gray parts are found as shown in Fig. 3. It has been proven from the specific X-ray spectrum of EDX analysis that the white parts mainly contain Ag. This is because the purity of both the Si powder and the Si oxide powder is 99.9%. The Si and Si oxide are metal grade, and they slightly contain C, Fe, Ni, and Cr.



(a)



(b)

Fig. 4. *Specific X-ray spectral intensity obtained by EDX analysis. (a) Using Si powder. (b) Using reduced Si nanoparticles.*

Specific X-ray spectral intensity obtained by EDX analysis is shown in Fig. 4. Specific X-ray spectral intensity for the sintered Si polycrystalline using Si powder is shown in Fig. 4 (a). Also, specific X-ray spectral intensity for the sintered Si nano-polycrystalline using reduced Si nanoparticles is shown in Fig. 4 (b). As shown in Fig. 4 (a) and (b), strong specific X-ray spectral intensities of the Si were measured. As shown in Fig. 4 (b), the specific X-ray spectral intensity of the oxygen is stronger than that of the Si. Actually, the number of the oxygen atoms should be one hundredth as small as that of the Si atoms. This is because the oxygen should slightly remain when the Si oxide is reduced to Si. The fact that the resistance of the sintered Si nano-polycrystalline is very low should prove that less oxygen remains in the sintered Si nano-polycrystalline.

3.3. Spectrum of Photoluminescence

Fig. 5. *Photo of PL from reduced Si nanoparticles.*

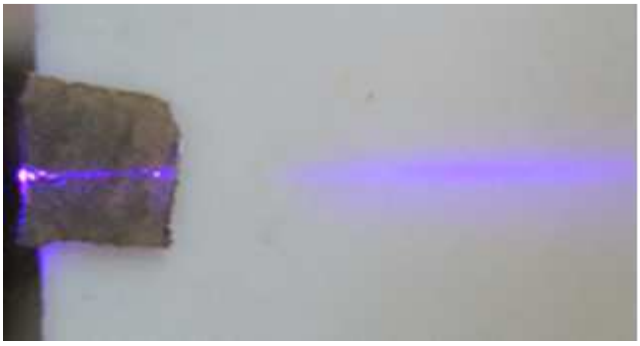


Fig. 6. *Photo of PL from sintered Si nano-polycrystalline. Violet light for excitation was injected from the left side edge of the sintered Si nano-polycrystalline.*

The PL from the reduced Si nanoparticles under the irradiation of weak violet light is shown in Fig. 5. The PL contains a mixture of the colors blue, yellow, and red. When the reduced Si nanoparticles were irradiated with weak violet light, each Si nanoparticle emitted PL uniformly.

Fig. 6 shows a photo of the PL from the sintered Si nano-polycrystalline when the edge of the sintered Si nano-polycrystalline was irradiated with the focused violet light. It has been found that the PL emitted from the surface was below 1 mm. Thus, the absorption coefficient at an excitation wavelength of 404 nm was evaluated to be a few 10 cm^{-1}. Violet light was also focused and irradiated on the sintered Si polycrystalline using Si particles. However, less PL was observed. The observed PL was very weak and could barely be observed. The PL spectrum was broadened from 500 nm to nearly 1000 nm. The intensity was one tenth times lower than that of the sintered Si nano-polycrystalline. The reason is presumed to be because the sintered Si polycrystalline mainly contains Si particles with diameters of around 5 μm and few small Si particles with various diameters below 1 μm. It is prospected that the sintered Si nano-polycrystalline mainly contains small Si nanoparticles with evidently uniform diameters. The diameter of the emitting beam expanded to 2 mm at a distance of 0.8 cm from the end of the sintered Si nano-polycrystalline as shown in Fig. 6. The emission has a certain divergence angle, and the evaluated divergence angle was 0.25 rad.

The refractive index of the sintered Si nano-polycrystalline should be larger than 5.58 [15]; although this is not accurate because the dielectric constant should be changed by the quantum size effect. Thus, the injected excitation light is confined within the sintered Si nano-polycrystalline. Also, the loss due to Fresnel reflection is evaluated to be 48% when the refractive index is 5.58 because the Si nano-polycrystalline has no coating. This value is large.

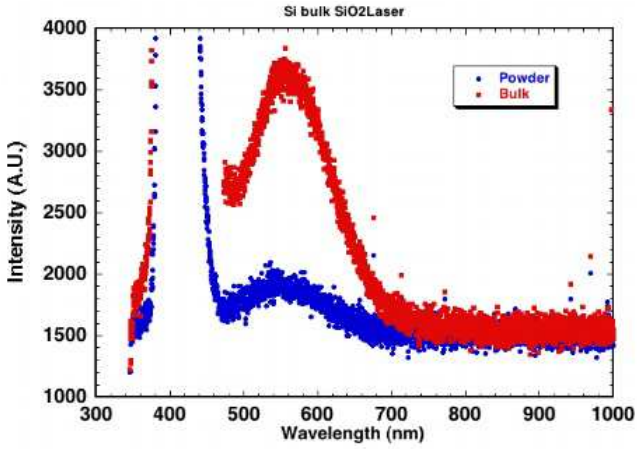


Fig. 7. *Observed spectrum of photoluminescence. Blue dots: Reduced Si nanopowder. Red dots: Sintered Si nano-polycrystalline. PL from the opposite side of the pump surface.*

The measured spectrum of the PL from the reduced Si nanoparticles and the sintered Si nano-polycrystalline by 404 nm violet light excitation is shown in Fig. 7. The peak wavelengths of the PL were 550 nm and 560 nm. The evaluated bandgap energy of the sintered Si

nano-polycrystalline from Fig. 7 was 2.25 eV, and the mean diameter of the sintered Si nano-polycrystalline was below 2 nm. This result shows that the reduced Si nanoparticles with mean diameters of 10 nm prepared by pulse laser ablation are secondary particles. Thus, the secondary Si nanoparticles contain small Si nanocrystals with diameters below 2 nm.

The spectral intensity of PL for sintered Si nano-polycrystalline was five times higher than that of the reduced Si nanopowder when it was observed at the same distance and with the same excitation intensity. To compare the spectra of the PL for the sintered Si nano-polycrystalline with that of the reduced Si nanopowder, the bandwidth for the sintered Si nano-polycrystalline was narrower than that of the reduced Si nanopowder. At this point, we cannot provide a definitive conclusion. However, it may be said from these experimental results that the PL for sintered Si nano-polycrystalline is amplified inside it.

Here, we discuss improvement methods for this sintered Si nano-polycrystalline and a method for tuning the peak wavelength of PL. Basic optical parameters, such as emission efficiency, fluorescence lifetime, and stimulated emission cross-sections, should be obtained by conducting experiments. Improving the transparency of the sintered Si nano-polycrystalline is also required.

The mean diameter of the prepared reduced Si nanoparticles by laser ablation in liquid should be selected to narrow the bandwidth of PL and obtain high optical gain. It has been decided that a stable PL should be obtained from the sintered Si nano-polycrystalline rather than from Si nanoparticles because the surface of the sintered Si nano-polycrystalline is chemically stable.

Highly repetitive pulse laser ablation in liquids makes it possible to produce amount of reduced and emission-capable Si nanoparticles from Si oxide powder. We can also fabricate sintered and emission-capable Si nano-polycrystalline with a low cost in a short time.

The sintered Si nano-polycrystalline will be applicable to optical waveguides, optical switches using a free carrier effect, and optical amplifiers. These results should also indicate that all optical circuits, such as laser light generators and optical signal detectors, can be fabricated on Si substrates.

4. Conclusion

We have succeeded in fabricating a sintered Si nano-polycrystalline for the first time. Si oxide powder is reduced by highly repetitive pulse laser ablation in liquid to produce Si nanoparticles. Si nanopaste with highly doped Si nanoparticles was sintered by using a hot plate, and a Si nano-polycrystalline was obtained. The structure and components of the sintered Si nano-polycrystalline were observed by SEM and EDX analysis. Furthermore, the reduced Si nanoparticles and the sintered Si nano-polycrystalline were excited by violet light, and stable PL in the visible regime was observed. The peak wavelengths of the PL were 550 nm and 560 nm. Strong PL of the sintered Si nano-polycrystalline was observed especially. PL should be amplified in the sintered Si nano-polycrystalline when it is excited by violet light. These experiments show that because the mean diameters of the Si nanocrystals in the reduced Si nanoparticles were below 2 nm, the structure of the Si nanocrystals changed to a direct-transition type; the bandgap energy of the Si nano-crystalline was enlarged to 2.25 eV, and PL in the visible regime was generated. The sintered Si nano-polycrystalline should work as an optical waveguide, an optical switch using a free carrier effect, and an optical amplifier.

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