Communication

Effects of hydration structure on the femtosecond white light-induced phase transition to crystalline silicon nanocrystal having ultrabright narrowed luminescence

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ABSTRACT: Under the condition of femtosecond impulsive nonlinear optical irradiation, the bright and narrowed blue emission of silicon nanocrystal was observed. This synthetic method produced very small (~ 4 nm) oxide-capped silicon nanocrystal having probably ultra small emitting core (~ 1 nm) inferred from luminescence. By controlling the stirring condition, very high efficiencies of luminescence (4 fold higher) were obtained compared with the other conventional femtosecond laser fragmentation methods, which was attributed to the differences in hydration shell structure during the femtosecond laser induced irreversible phase transition reaction. When we properly adjusted the irradiation times of the white light continuum and stirring condition, very homogeneous luminescent silicon nanocrystal bands having relatively sharp lineshape were obtained, which can be attributable to the luminescent core site isolated and free from the surface defects.

The field of silicon semiconductor nanocrystals is one of the active research areas in which a wide range of industrial applications including solar cells, sensors, secondary battery unit, and PDT sensitizer in nanomedine have been investigated [1-8] and is also expected to have a very promising role in the future informatics like the quantum computing [9]. Especially, silicon is one of the few elements providing nontoxic, earth abundant and environmentally-friendly characters, and has dominated the microelectronics industry due to their unique physicochemical properties. Therefore, in practical applications such as optoelectronics, the fabrication of reliable and functional silicon nanocrystal having homogeneous optical properties is very important future challenge [10-22]. Until recently, considerable synthetic efforts have been placed on the ultrasmall and bright silicon nanocrystals using the femtosecond ablation and fragmentation methods [23-28]. However, the reported luminescence spectra by this method have broad inhomogeneous lineshape which can be attributed to the surface oxide related luminenscent sites [13,18,20]. Also, some theoretical research reported the possible silicon nanocrystal configuration having very isolated and luminous core [9,29]. But, whether conventional luminescent silicon nanocrystal including those obtained by the above femtosecond laser methods have this core structure or not is not determined.

In this study, we adjusted the experimental conditions of the irradiation time of femtosecond laser and stirring condition. By varying these conditions, we observed the luminescence band narrowing and the increased luminescence quantum yields when we increase the femtosecond impulsive nonlinear optical irradiation time

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and stopped the water stirring. The band position and gap were estimated from the UV-VIS absorption. The morphology and crystallanity of the generated silicon nanocrystal were also monitored by high resolution transmission electron microscopy (HR-TEM).

EXPERIMENTAL SECTIONS

Silicon powder used was supplied by Aldrich (60 mesh, 99.999%). The 800 nm femtosecond (spitfire pro 45 fs, Spectra physics) laser light having the energy of ~ 0.35 mJ was focused into the solution in which the silicon powder was dispersed using 10 cm lens. The samples were irradiated with the resulting femtosecond white light continuum for 20 hours, 1 week, 2 weeks, and 3 weeks. Two kinds of solutions were prepared in the stirred and static conditions. After femtosecond laser-induced fragmentation processes, UV-VIS absorption (Hitachi, U-2800), luminescence (Hitachi F-4500) spectra, TEM images of the resulting samples of five conditions (0 hour, 20 hours, 1 week, 2 weeks, and 3 weeks of irradiation time) were taken. HR-TEM analyses on the samples of static condition were conducted on a JEOL, JEM-2100F transmission electron microscope at 300 kV. After 3 months later from the preparation, UV-VIS absorption and luminescence spectra of 0 hour, 20 hours, 1 week, 2 weeks, and 3 weeks samples which were fragmented and prepared in the static solution condition were taken again.
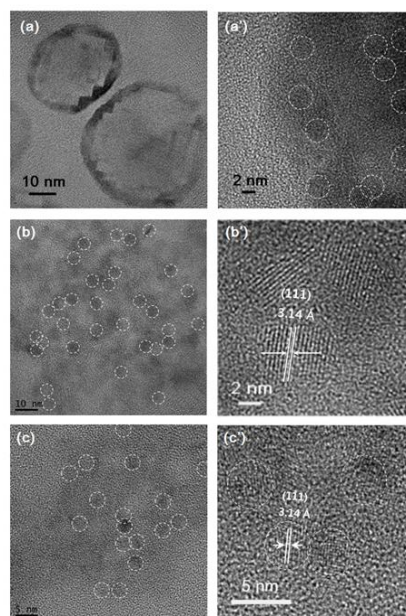

Figure 1. (a) TEM and (a') HR-TEM image of the Si nanoparticles after

the laser fragmentation for 20 h; (b) TEM and (b') HR-TEM image of the Si nanoparticles after the laser fragmentation for one week; (c) TEM and (c') HR-TEM image of the Si nanoparticles after the laser fragmentation for two weeks.

RESULTS AND DISCUSSION

The morphology and crystal structure of Si nanocrystals synthesized in this study were investigated using HR-TEM (Fig. 1). After the fragmentation for 20 h, the purchased silicon particles were broken apart into relatively large fractions having various morphologies such as rectangular and angular shape and relatively small particles indicated by white dotted circles (Figs. 1(a) and 1(a')). After the laser fragmentation for more than one week (Figs. 1(b), 1(b'), 1(c), and 1(c')), the purchased bulk particles seem to be completely broken and to have relatively spherical morphology and good size uniformity with an average particle size of 4 nm (Figs. 1(b), 1(b')). HRTEM analysis of the morphology of these two fragmented particles shows that they have a single crystalline nature. The distance between two neighboring planes is approximately 3.14 Å that is close to those of the (111) planes of a diamond cubic structured Si nanocrystal [30].
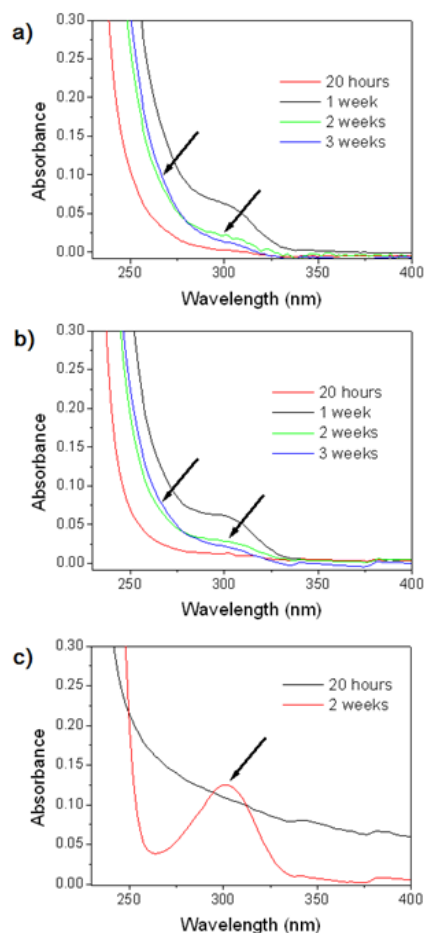

Figure 2. UV-VIS spectra for samples of four irradiation conditions (20 hours, 1 week, 2 weeks, and 3 weeks irradiation times) in the static ((a) immediately after preparation and (b) after 3 months later) and stirred (c) conditions.

In Fig. 2, the UV-VIS spectra for samples of four irradiation conditions (20 hours, 1 week, 2 weeks, and 3 weeks irradiation times) in the static ((a) immediately after preparation and (b) after 3 months later) and stirred (c) conditions are shown. Two peaks seem

to arise and appear in the range of 240 nm – 320 nm) for all four conditions. If we only look at the data of two and three weeks-irradiated samples, the relative absorbance around 266 nm band appears to increase and that of 300 nm to decrease with increasing the irradiation times. The effect of oxidation occurring in water solution during 3 months is not largely manifested in the UV-VIS spectra (Fig. 2(b)). The stirred 2 weeks-irradiated sample exhibits the dominant 300 nm absorption peak whereas the absorption spectrum of stirred 20 hours-irradiated sample is relatively similar to that of static condition.
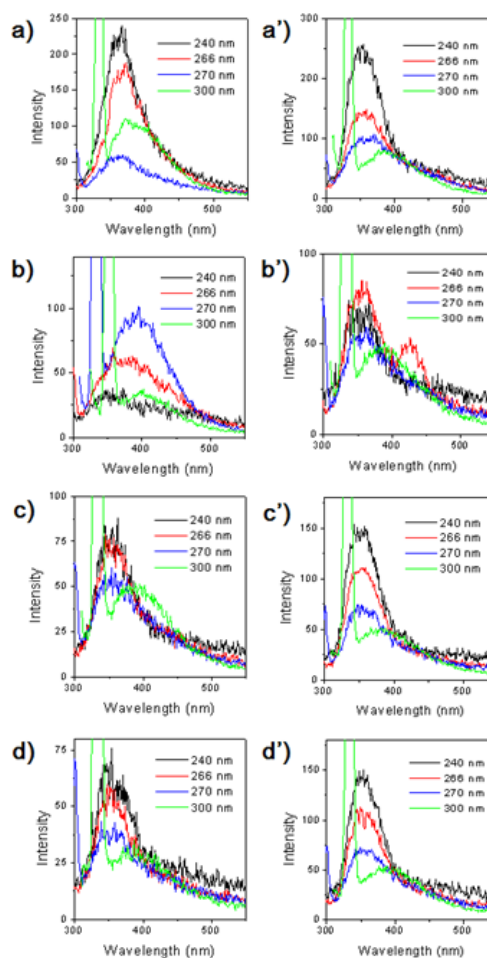

Figure 3. Photoluminescence spectra of the fragmented silicon nanocrystals in static water with the excitation wavelengths ranging from 244 to 300 nm after (a) 20 hours-irradiated (b) 1 week-irradiated (c) 2 weeks-irradiated (d) 3 weeks-irradiated conditions. In (a'), (b'), (c'), and (d'), the luminescence spectra were taken 3 months later after the water oxidation.

Fig. 3 shows the photoluminescence spectra of the fragmented silicon nanocrystals in static water with the excitation wavelengths ranging from 244 to 300 nm. The maximum emission peak is centred at about either 350 nm or 400 nm depending on the excitation conditions. As the irradiation times increase, the bandwidth of 350 nm peak narrows and the lineshape became to be Lorentzian-like and the intensity of 400 nm band increases as shown in Table 1. The overall spectral feature of 20 hours-irradiated sample and 3 weeks-irradiated sample seem to be similar. However, lineshape of 20 hours-irradiated sample looks like more Gaussian compared with that of 3 weeks-irradiated sample as shown in Table 1. The effects of oxidation on the luminescence (Figs. 3(a'), 3(b'), 3(c'), and 3(d')) are more broadened

Gaussian-like lineshapes of 350 nm peak (Table 2) and the decreased intensity of 400 nm peak in every conditions. The overall feature (Fig. 3(b), 3(b')) of 1 week-irradiated sample is substantially changed after the 3 month oxidation processes in water solution. However, as shown in Figure 4 and Table 3, the photoluminescences of silicon nanocrystals fragmented in the stirred condition are quite different from those of particles prepared in the static condition. The overall spectral features are very broad and luminescence quantum yields are estimated to be about 4 times lower than those in the static condition when we determine the values for the 2 weeks-irradiated samples.

Table 1. Fitted band parameters of photoluminescence spectra of the fragmented silicon nanocrystals in static water using Gaussian function regression. (x_c, w, and A mean the center wavenumber, bandwidth, area, respectively.)

Irradiation time	Excitation Wavelength (nm)	x_{c1} (cm^{-1})	w_1 (cm^{-1})	x_{c2} (cm^{-1})	w_2 (cm^{-1})	A_2/A_1
20 hours	244	25,535	6,569	27,600	3,031	0.66
	266	25,498	6,393	27,208	2,627	0.35
	270	25,384	8,880	27,626	3,154	0.21
	300	25,512	5,272			
1 week	244	22,203	3,868	27,793	4,883	1.91
	266	25,464	7,877			
	270	25,003	4,726			
	300	24,592	4,285			
2 weeks	244	22,385	7,853	28,093	3,717	1.23
	266	24,313	9,035	28,189	3,336	0.49
	270	24,752	8,680	28,407	4,039	0.31
	300	25,175	5,569			
3 weeks	244	22,333	4,177	27,973	4,136	3.38
	266	24,504	10,121	28,268	3,405	0.41
	270	24,852	12,090	28,366	3,346	0.13
	300	25,049	5,472			

Table 2. Fitted band parameters of photoluminescence spectra of static samples taken after 3 months water oxidation.

Irradiation time	Excitation Wavelength (nm)	x_{c1} (cm^{-1})	w_1 (cm^{-1})	x_{c2} (cm^{-1})	w_2 (cm^{-1})	x_{c3} (cm^{-1})	w_3 (cm^{-1})	A_2/A_1	A_3/A_1
20 hours	244	22,155	6,978	28,074	3,630			1.77	
	266	23,413	6,723	28,139	3,806			0.93	
	270	24,272	7,855	28,188	4,050			0.35	
	300	25,208	4,750						
1 week	244	22,164	4,378	27,979	4,058			2.52	
	266	21,886	6,305	23,320	1,556	27,927	3,952	0.32	1.62
	270	23,889	7,655	28,300	3,865			0.43	
	300	25,206	5,480						
2 weeks	244	23,301	7,205	28,210	3,520			1.94	
	266	22,534	8,059	28,128	3,658			1.30	
	270	23,790	7,551	28,230	3,791			0.70	
	300	25,370	5,619						
3 weeks	244	21,671	6,413	28,091	3,598			1.68	
	266	22,927	7,662	28,144	3,669			1.09	
	270	23,443	6,290	28,180	4,003			0.89	
	300	25,037	5,282						

Table 3. Fitted band parameters of photoluminescence spectra of the fragmented silicon nanocrystals in stirred water.

Irradiation time	Excitation Wavelength (nm)	x_{c1} (cm^{-1})	w_1 (cm^{-1})	x_{c2} (cm^{-1})	w_2 (cm^{-1})	A_2/A_1
0 hour	244	23,576	6,033	30,035	4,688	0.56
	266	23,969	7,540	30,175	4,524	0.32
	270	24,359	7,479	30,280	4,164	0.29
	300	25,140	5,715			
20 hours	244	21,647	3,795	27,714	5,961	2.65
	266	21,777	4,250	27,146	6,876	3.34
	270	22,255	5,147	27,344	6,593	2.09
	300	25,265	5,833			
2 weeks	244	26,287	9,324			
	266	21,435	3,208	27,243	6,984	11.29
	270	21,483	3,428	26,899	7,040	14.82
	300	25,267	4,152			
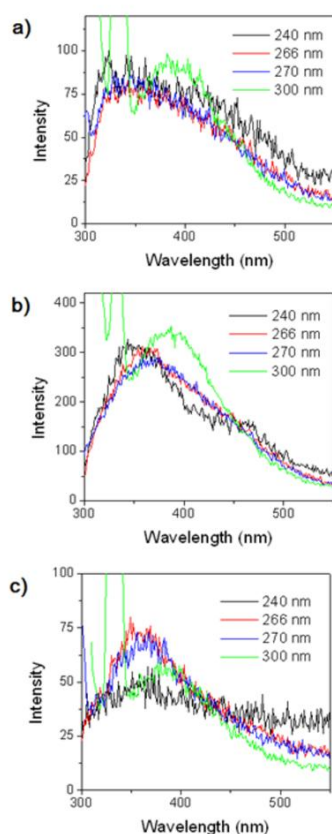
Figure 4. Photoluminescence of (a) silicon powder solution and silicon nanocrystals fragmented and dispersed in the stirred conditions for (b) 20 hours and (c) 2 weeks in water with the excitation wavelengths ranging from 244 to 300nm.

Usually, the conventional silicon nanocrystal generation methods using femtosecond laser ablation and fragmentation have been conducted in the condition of stirring water solution [13,18,20]. In this study, we tried to change and extend the irradiation time of femtosecond laser over several weeks and to alter the hydration structure during the fragmentation processes by stopping the stirring of water solution where the generated nanocrystals were dispersed. When we simply stopped the stirring from starting the irradiation, the quantum yields of luminescence of 2 weeks-irradiated samples were increased at least 4.2 times higher (4.2 times stronger luminescence was obtained when the statically prepared sample was excited at 266 nm compared with the 300 nm excitation of the stirred sample). These small nanocrystals are considered to have very small inner core size (~ 1 nm) inferred from strong 350 nm luminescence band [31,32] and also some surface oxide-related luminescence also to occur at 400 nm [13,18,20]. The crystal having small inner core shows very fast luminescence lifetime (several nanoseconds) whereas those of some surface oxide-related luminescence extend to several hundreds of microseconds [20,31].

As the irradiation time became 1 week, more narrowly distributed small particles having ~ 4 nm were expected from TEM image analysis. Spectral feature gets broadened and inhomogeneous, which can be attributed to more broadly distributed oxide-related energy states generated during the laser irradiation and fragmentation [13,18,20]. However, if we increase and extend the irradiation times of femtosecond whitelight continuum pulse to 2 and 3 weeks, we observe that the 350 nm band gets sharper and narrower and its lineshape looks more Lorentzian-like and the oxide-related luminescence band around 400 nm gets increased. This phenomenon can be expected if the irreversible phase transition to more homogeneous luminous core state and the rearrangement around the surface of oxide-capped nanocrystals occur during the irradiation of femtosecond white light continuum pulse. Although some theoretical research suggested the possible configuration of silicon nanocrystal having very isolated and inert luminous core [9], conventional studies on luminescent silicon nanocrystal including the femtosecond laser methods could not provide direct evidence of such core structures. On the other hand, ultrafast laser-induced phase transitions on other semiconductors have been reported in several cases [33-36] but, mainly fastest processes in the excited states which were reversible were investigated [34].

In this study, we extended the irradiation time to several weeks and checked the overall photo-induced irreversible chemical processes which might follow the femtosecond laser-induced reversible phase

transition in the excited states. By stopping the stirring of water solution, only thermal diffusive processes, which were not related to the photo-induced phase transition, appeared to be affected and the thermalization processes which occurred around 100 ps [37] seemed not to be influenced. Therefore, the non-thermal changes in hydration structure are expected to mainly affect the photo-induced phase transition to the crystalline silicon nanocrytal because the temperature rise which is induced by the thermal energies released after the irradiation is not so high to cause the phase transition. One of the possible reasons is that the impulsive concerted vibrational motions connected with hydrogen-bonded hydration shell which are stimulated by femtosecond whitelight continuum can promote the conformational changes across the excited state potential of silicon core clusters. This reversible phase transition state may have the small cross section of photochemical reaction to more inert crystalline ground nanocrystal structure. However, the stirring of water solution can change the hydration structures around the silicon nanocrystal due to the turbulent motional perturbation and may suppress the possibility of above mechanism [38].

CONCLUSIONS

In summary, we have investigated the effects of laser irradiation times and stirring condition of water solution on the femtosecond laser-induced fragmentation to silicon nanocrystals. As the laser irradiation time increases and the hydration condition changes by stopping stirring of water solution, femtosecond laser-induced irreversible phase transition to nano crystalline phase are expected and silicon nanocrystals having very homogeneous and bright blue-luminescence are generated. These silicon nanocrystals seem to have attractive and novel optical properties which can be applied in fields of quantum computing and optoelectronics.

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