Room temperature photoluminescence of the freestanding silicon nanocrystals

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This paper presents a comparison study of photoluminescence (PL) properties of freestanding silicon nanocrystals (Si-ncs) prepared by electrochemical etching and nanosecond pulsed laser ablation in two liquid solutions i.e. de-ionized water and spin on glass. The Si-ncs fabricated by electrochemical etching show visible room temperature PL with peak maximum at 680 nm. The PL peak of Si-ncs synthesized by pulsed laser ablation is significantly blue shifted with maximum centered at 420 nm after aging for at least 8 weeks. Laser ablation process in electronically compatible liquid spin on glass accelerated Si-ncs surface passivation. As a result the aging process was shortened to 24 hours with the same PL peak position. PL intensity of Si-ncs embedded in SOG increased with the laser fluence for ablation. A Si-ncs formation scheme during the nanosecond pulsed laser ablation in both liquids is proposed to explain obtained results and discussed in detail.
Key words: colloidal silicon nanocrystals, laser ablation

1. INTRODUCTION

Up to date high quality semiconductor nanocrystals can be prepared routinely by simple wet chemistry colloidal techniques [1.2] Nevertheless, this way is impossible for synthesizing of colloidal silicon nanocrystals (Si-ncs). Therefore, substantial interest has been devoted to the development of numerous synthesis techniques to produce luminescent colloidal silicon nanocrystals (Si-ncs) by physical ways [3, 4, 5]. It has been demonstrated that freestanding nontoxic Si-ncs prepared by electrochemical etching reflected to be one of the possibility to produce highly luminescent Si-ncs at room temperature [5]. On the other hand, an ultra fine blue luminescent Si-ncs can be fabricated by nanosecond pulsed laser ablation in water [6]. Advantage of both techniques is surfactant-free process during synthesis, which can particularly be interesting for various biological applications.

In this paper we compare photoluminescence (PL) properties of colloidal Si-ncs prepared by two independent methods; (1) the red luminescent Si-ncs prepared by electrochemical etching, and (2) blue luminescent Si-ncs by nanosecond laser ablation in liquid media. We studied elaboration and laser processing of Si-ncs in de-ionized water and silicon technology compatible spin on glass (SOG). In the case of laser ablation in water, aging in water for 8 weeks is necessary to obtain visible blue luminescence. We show that a processing of Si-ncs in the SOG accelerated nanocrystals surface oxidation and led to a considerable increase of visible room temperature PL within 24 hours.

2. EXPERIMENTAL DETAILS

As reported elsewhere [5], the freestanding Si-ncs by electrochemical etching were prepared by following way. Silicon wafer (p-type boron doped, <100>, 0.1 ohm·cm) was etched for 2 h at 1.6 mA/cm^2 in HF/ethanol solution and then mechanically pulverized. Si-ncs powder was dispersed to prepare aqueous colloidal solutions of 0.1 wt%.

To fabricate the Si-ncs by laser ablation, we used same crystalline silicon wafer as a target immersed either in de-ionized water or SOG. The SOG (Si-59000) was commercially purchased from Tokyo Ohka Kogyo Co., ltd. Then a third harmonic Nd:YAG laser (Spectra Physics LAB-150-30, 355 nm, 30 Hz, pulse width 8 ns) was irradiated on the Si-ncs target immersed in 5 ml of liquid at room temperature for 2 h. The laser spot on the target was 1 mm in diameter after focused by a lens. A series of samples at different laser fluences ranging from 0.008 – 085 J·cm^{-2} was prepared to investigate the fluence effect on the PL. The colloidal suspension prepared by laser ablation in SOG was sonicated for 10 min and solidified in air atmosphere at 323 K for 24 h, resulting in the formation of self-supporting samples [5]. Si-ncs were also prepared by laser ablation of the Si target in deionized water for comparison, and the obtained colloidal solution was aged in deionized water at ambient temperature, as reported previously [6].

In the case of the solidified Si-ncs/SOG, the crushed pieces were dispersed in deionized water, and a droplet of the aqueous colloidal solution was similarly deposited onto a copper grid to enable transmission

electron microscopy (TEM) observations. The PL of colloidal solutions was measured at room temperature using a fluorospectrophotometer (Shimadzu, RF–5300PC) with excitation by monochromatic light at 300 nm from a Xe lamp. The PL of solid self-supporting films was measured at room temperature with the excitation of a He-Cd cw laser at 325 nm. The emission spectra were recorded by a spectrometer (JASCO, CT-10) using a photomultiplier as a detector.

3. EXPERIMENTAL RESULTS AND DISCUSION

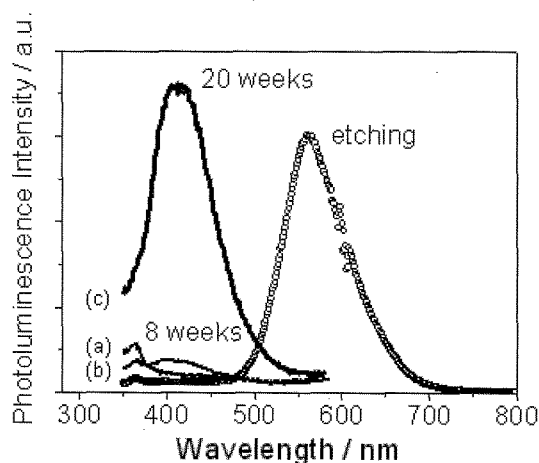### 3.1 Luminescent Si-ncs in de-ionized water

Figure 1: Photoluminescence (PL) spectra of silicon nanocrystals in de-ionized water. Open circles represent the PL of Si-ncs prepared by electrochemical etching. Curve (a) is from Si-ncs freshly obtained by laser ablation of silicon wafer in deionized water at the laser fluence of 0.63 J·cm^{-2}. Curves (b) and (c) show PL spectra after 8 and 20 weeks of subsequent aging in deionized water.

Figure 1 shows room temperature PL spectra of Si-ncs in de-ionized water prepared two different methods. The Si-ncs fabricated by electrochemical etching revealed red luminescence immediately after the preparation and dispersion in deionized water (open circles). A typical broad PL spectrum at room temperature was recorded with a maximum at 560 nm. It is well accepted that tiny Si-ncs exhibits unique room temperature PL properties resulting from quantum confinement size effect surface states, and silicon oxide related defects [5, 7] that is the same in our case. The TEM microscopy for Si-ncs prepared by electrochemical etching [5] and by laser ablation [6] showed the presence of Si-nc below quantum size confinement limit less than 10 nm with broad size distributions. In both

cases it is observed that the Si-ncs size vary from 1 to 6 nm and is rather the similar. However, in average the typical size of Si-ncs prepared by electrochemical etching is slightly larger (3.3 nm) compare to laser ablation (2.4 nm). The laser ablation surface chemistry induces through the electronegative oxygen wider band gap, which is more pronounced for smaller Si-ncs in diameter [6].
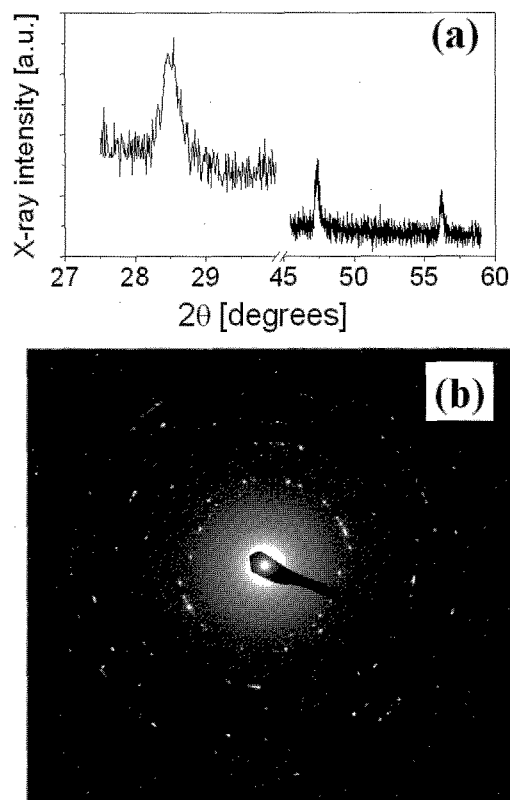

Figure 2: (a) XRD spectra of silicon nanocrystals aged for 24 weeks in de-ionized water. Three major peaks of crystalline silicon were clearly detected at $2\theta=28.50°$, $47.33°$, and $56.17°$, corresponding to the <111>, <220>, and <311>. (b) Corresponding transmission electron diffraction patterns of Si-ncs with diamond structure.

One can speculate that the laser ablation process could be advantageous since the Si-ncs can be directly prepared in water without any additional post-treatment and surfactant that could be a sources for the potential contaminations [6]. The drawback of this approach is that the Si-ncs immediately after preparation do not show visible PL. It has to be noted that the increased PL intensity in the region (350 – 380 nm) is due the Raman scattering effect in the water. Curve (c) in Figure 1 represents intense PL spectrum from Si-ncs prepared by laser ablation of silicon wafer in de-ionized water at 0.63 J·cm^{-2}, followed by 20-week aging in de-ionized water. In our experience the first PL intensity increase started

after aging for 8 weeks (curve (b)) in water at room temperature. Continuous aging in de-ionized water leads to further PL improvement.

The question is whether such Si-ncs after long aging for several weeks still keep their crystalline structure. Figure 2 (a) shows XRD spectra of silicon nanocrystals aged for 24 weeks in de-ionized water without exposure to air. The three major peaks of crystalline silicon were clearly detected at $2\theta=28.50°$, 47.33°, and 56.17°, corresponding to the <111>, <220>, and <311>. It has to be noted that also slight lines broadening by 5% of XRD peaks compared to that from bulk silicon was observed.

As depicted in Figure 2(b) the crystalline structure of Si-ncs after aging was further confirmed by TEM structural analysis. Diffraction patterns were observed and corresponding ring positions to the lattice spacing of crystalline silicon with diamond structure, 0.31 nm for <111>, 0.20 nm for <220>, 0.169 nm for <311>, 0.120 nm for <331>, and 0.109 nm for <422> could be assigned..

In contrast to the electrochemically etched Si-ncs, those prepared by nanosecond laser ablation and aging for several weeks showed a blue PL with a maximum located around 420 nm. It is believed that the PL origin is similar to the case of Si-ncs prepared by electrochemical etching [5, 6, 7], namely, due to the surface states and quantum confinement effect. Laser ablation in de-ionized leads to the generation of smaller Si-ncs in diameter. Furthermore the oxidation in water leads to Si-ncs size decrease, local stress, opening of bandgap, and subsequent blue PL observation [6]. However, oxide passivation of Si-ncs surface states and defects in oxide layer effectively possibly increase the PL intensity. Aging and oxidation might also influence the quantum size effect, surface states and SiO_2 defect relaxation that act together and improve the observed PL properties.

3.2 Si-ncs in spin on glass

The Si-ncs prepared by common techniques have red PL (Fig. 1, open circles) [7, 8]. The Si-ncs prepared by laser ablation in de-ionized showed a blue PL after aging that can be useful for certain applications. In this section we discuss the possibilities for direct formation of blue luminescent Si-ncs in electronically compatible SOG by nanosecond laser ablation. Si-ncs fabrication in transparent SOG glasses is advantageous to utilize optical properties of Si-ncs [5]. Therefore one can expect that it could improve PL properties of ultra fine blue luminescent Si-ncs prepared laser ablation and solve some associated problems. Figure 3 compares PL spectra of colloidal silicon Si-ncs prepared. Curve (a)

presents PL spectrum of Si-ncs in the SOG solution immediately after the preparation by pulsed laser ablation (0.85 $J·cm^{-2}$) of the silicon crystalline target. However, the PL intensity is very weak and slightly more intensive than the PL spectrum of pure liquid SOG (curve (d)). The SOG during the solidification process for 24 h accelerated Si-ncs surface oxidation and passivation. As a result, visible room temperature PL of stabilized Si-ncs in solid SOG is achieved with a maximum located at 430 nm. This PL spectrum is very similar to that from the Si-ncs colloidal solution obtained by laser ablation of the Si target and subsequent aging in de-ionized water (curve (c)). Other advantage compared to the de-ionized water is that the laser ablation in the silicon-dioxide-based SOG inhibited aggregation through the hydrophobic methyl groups that also at the same facilitate the termination of silicon free bonds of Si-ncs [9].
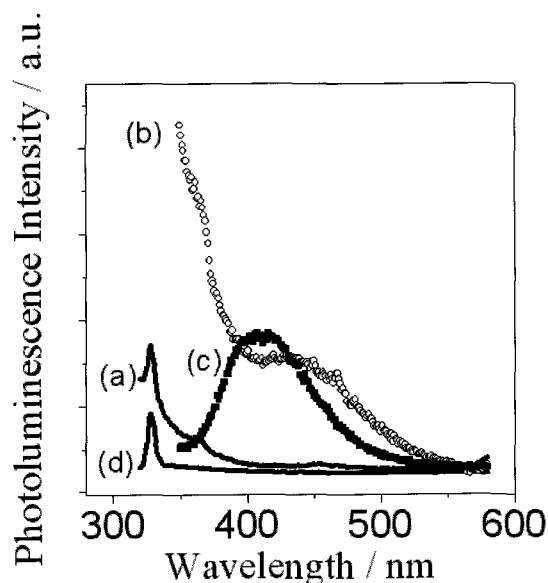

Figure 3: Photoluminescence spectra of colloidal silicon nanocrystals (Si-ncs). Curve (a) is from SOG solution of Si-ncs immediately after preparation by pulsed laser ablation (0.85 $J·cm^{-2}$) of the silicon crystalline target. Curve (b) is the PL spectrum of the Si-ncs/SOG in aqueous solution that was obtained by dispersing in water the crushed powder of dried Si-ncs prepared for curve (a) by laser ablation of Si in SOG. Curve (c) is from Si-ncs prepared by laser ablation of the Si target in water under the same conditions as for (a) and subsequent aging in deionized water. Curve (d) presents the PL spectrum of pure liquid SOG for comparison.

Further we demonstrate that the blue luminescent Si-ncs properties could improve not only by solidifying SOG but also with increasing of the laser fluence. The

preparation of Si-ncs in liquid SOG allowed formation of self-supporting films several millimeters square with high concentration of stabilized Si-ncs [5]. Figure 4 shows the typical PL spectra of such samples (3 mm × 3 mm) fabricated with different laser fluences. The PL intensity increased with increasing laser fluence. The PL maximum was also blue-shifted from 446 nm at 0.008 J·cm^{-2} to 420 nm at 0.76 J·cm^{-2}. The self-supporting Si-ncs/SOG with a flat surface efficiently suppressed the light-scattering effect on the surface, compared with the case dispersed in water (curve (b) in Fig. 3). A blue shift of PL peak accompanied by the narrowing of the spectra can be tuned by varying the laser fluence. The quantum confinement size effect and surface/defect states in the surrounding silicon oxide are responsible for efficient blue PL. The controllability of blue luminescent intensity from a film by laser fluence during laser ablation is of significance for optoelectronic applications.
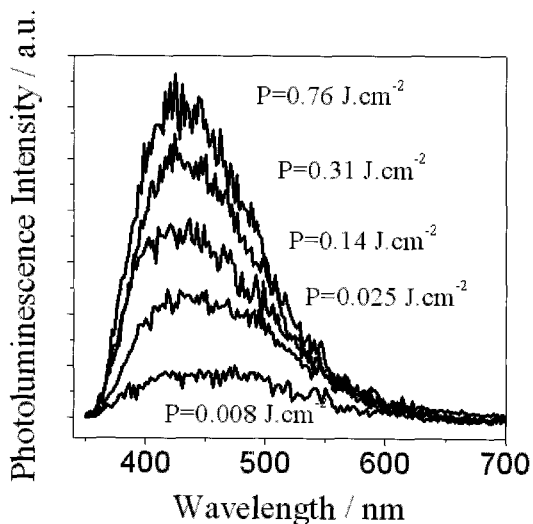

Figure 4: Photoluminescence spectra of silicon nanocrystals (Si-ncs) embedded in solid SOG films obtained by laser ablation of the Si target under different fluences ranging from 0.008 to 0.76 J·cm^{-2}.

We have verified the presence of Si-ncs in SOG by TEM analysis. A precise evaluation of the electron diffraction angle allow us to assign corresponding lattice planes. Five rings corresponding to silicon in the cubic phase were identified; 3.19 Å for <111>, 1.96 Å for <220>, 1.25 Å for <331>, 1.06 Å for <422>, and 0.92 Å for <531>. In addition we observed four peaks at 2.11 Å, 1.10 Å, 0.83 Å, and 0.81 Å. The origin of these peaks is not yet clear. The formation of silicon carbide could be expected by the reaction between Si and carbon content in SOG induced by the laser ablation process. However, the corresponding values did not match any SiC peaks. Considering the elemental analysis results, the peaks could possibly be assigned to a monoclinic silicon

dioxide. It must also be noted that no diffraction spots were recorded from solidified SOG without Si-ncs.

It should also be noted that Si-ncs with the crystalline cubic phase were observed in water and SOG. One can expect that light emission from Si-ncs depends not only on the intrinsic properties of the material (quantum confinement effect) but also on the properties of the surrounding media. It is well known that oxygen passivation of the Si-ncs surface strongly influences the optical properties [10]. Electronegative elements such as oxygen possess a special ability to widen the silicon band gap [11]. Si-ncs growth is suppressed when as-formed particles escape from the plume and reach the liquid SOG. The Si-nc surface begins to oxidize and SiO$_x$ surface can be formed. The blue shift was accompanied by PL intensity increase (Fig. 2) with laser fluence increase. We believe that this result was due to the increased concentration of Si-ncs and a specific surface area having an Si/SiO$_2$ interface. Contributions from quantum confinement and surface states led to the observed findings.

3.3. Nanosecond laser ablation Si-ncs formation

It is clear that understanding Si-ncs formation in de-ionized water and liquid SOG by nanosecond laser ablation is crucial to determine the nature of the surface states, and therefore the properties of Si-ncs. Hence, the dynamic formation mechanisms of Si-ncs in the laser plasma confined by liquid are quantitatively discussed to describe the obtained results.

The presented studies revealed the possibility of forming blue luminescent crystalline Si-ncs in water and SOG. The confinement of nanosecond laser-generated plasma in liquid allowed the Si-ncs formation. The Gibbs free energy can describe particle formation [12, 13]. The Gibbs free energy (G) for Si-ncs formation as a function of pressure (P) within the plume and the plume temperature T can then be expressed as

$$G(P) = kT \ln\left(\frac{P(I)}{P_0}\right) \qquad (1)$$

where k is the Boltzmann constant and P_0 is ambient pressure. Let us consider the formation process of Si-ncs in liquids (SOG, water) as follows. Absorption of nanosecond laser pulses in an Si wafer led to rapid heat generation. Immediately after the laser beam hit the silicon wafer, a dense cloud of Si atoms spread over the plume. Embryotic particles are also formed in such a cloud. The initial rapid attachment of silicon atoms to ejected embryotic particle continued until all silicon

atoms in the confined area were completely consumed. The dissipated kinetic energy of the material ejected by pulsed laser ablation is assumed to be proportional to the Gibbs energy of as-formed crystallites. When particles escaped from the plume into the liquid the SiO_x present in water and SOG that stacks on the Si-nc surface and suppress the growth [13].

Ultra fine Si-ncs prepared by laser ablation induce the quantum confinement size effect of excitons, resulting in a blue shift of PL maxima (circles in Fig. 5). Since the blue shift is related to the change in the Si-ncs size and the Gibbs free energy describes initial particle formation that finally determines the Si-ncs size. Figure 5 reveals quantitatively relationship between the Si-ncs formation in liquid-confined laser-generated plasma and blue shift of PL maxima. The calculated Gibbs free energy by Eq. (1) (line in Fig. 5) follows the blue shift of PL maxima. It is assumed that smaller amount of Si atoms is attached on embryotic particle and smaller Si-ncs in diameter are formed when Gibbs energy is saturated with the laser fluence increase.

Figure 5: Photoluminescence (PL) maxima position (solid circles) and Gibbs free energy of as-formed Si-ncs
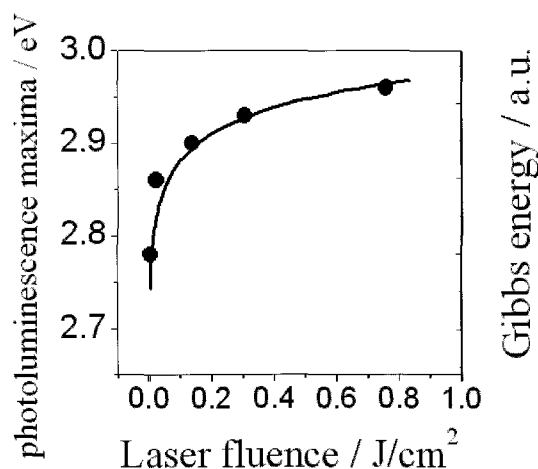
(full line) as a function of laser fluence.

4. CONCLUSIONS

In conclusion, the electrochemical etching and nanosecond laser ablation of silicon wafer would be promising techniques to prepare nontoxic colloidal Si-ncs without assistance of surfactant. Si-ncs in de-ionized water show an efficient red and blue PL at room temperature, respectively. However, an aging process of Si-ncs for several weeks is required to obtain bright blue PL after pulsed laser ablation in water.

We demonstrated that laser processing of Si-ncs in spin on glass (SOG) could overcome this drawback. The hydrophobic methyl groups present in SOG, facilitating the termination of silicon free bonds during solidification with electronegative oxygen. The oxygen passivation of Si-ncs promotes the localization of excitons and improves the Si-ncs photoluminescence properties. Even more, the PL intensity of Si-ncs colloidal solution can be increased by laser ablation fluences.

The pulsed laser Si-ncs formation could be described as serial processes of embryotic Si particle growth and consecutive quick oxidation in the SOG or de-ionized water. It is assumed that the size reduction of Si-ncs below the quantum confinement limit and surface oxygen passivation is essential for visible PL at room temperature.

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