Silicon Nanocrystals Surface Engineering by Nanosecond Laser Processing in Water

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(Received September 26, 2011)

We report on investigations of silicon nanocrystals (Si-ncs) surface engineering and subsequent integrations into sub-micrometer structures induced by nanosecond laser processing in water. We present that easy and low-cost methods through nanosecond laser processing in water allow of Si-ncs integration self-assemblies ranging several micrometers and sub-micron spherical particles. Room temperature photoluminescent properties were preserved in these particles.

Key Words: Silicon nanocrystals, Surface engineering, Integration, Photoluminescence

1. Introduction

Silicon presents limited environmental concerns. Silicon is abundant in nature and can rely on an existing industrial infrastructure and therefore silicon nanocrystals (Si-ncs) have clear advantages for applications over other nanocrystal materials.1-4 Si-ncs have been intensively studied in the last two decades revealing interesting size-dependent optoelectronic properties with great scientific interest for biology and physics research (e.g. optical gain studies, solar energy conversion).5,6 Recent research showed that colloidal Si-ncs offer the possibility of exploring peculiar Si-nc surface properties and potential technological applications have been demonstrated.7,8,9

Si-ncs that exhibit quantum confinement (less than 10 nm diameter) also imply a high surface-to-volume ratio. It follows that surface engineering can be used efficiently to alter the internal electronic interactions in the confinement states of Si-ncs leading to significant modifications of overall optoelectronic properties.5,10 Pulsed laser ablation in liquid medium has shown the possibility of direct synthesis of Si-ncs; at the same time, the same techniques can be efficient in engineering unique surface properties of the Si-ncs without any surfactants which could prevent the integration of nanocrystals into devices.11,12

In particular, nanosecond laser-induced synthesis and surface engineering in environmentally compatible liquid media could be advantageous for large scale technological applications. On the other hand, the control and understanding of surface changes is crucial to allow the integration. For instance the ability of producing closely packed Si-ncs while preserving their confinement effects will result in enhanced carrier transport through the nanocrystals and simultaneously will improve nonlinear optoelectronic properties (i.e. carrier multiplications) interactions among Si-ncs.12

In this contribution we discuss nanosecond pulsed laser-induced surface engineering in water and how the enhancement of dipole-dipole interactions result in the formation of photoluminescent Si-ncs self-organized assemblies. Next we demonstrate how nanoscale surface engineering by laser processing in water induces bottom-up assemblies of Si-ncs in sub-micrometer spheres.

2. Experimental details

A powder containing single Si-ncs and Si-ncs clustered in micrometer-size aggregates was produced by electrochemical etching of a silicon wafer and subsequent mechanical pulverization.13 The powder was then stored in glass containers in ambient conditions and exposed to air.

For the laser processing, 2.5 mg of the powder was dissolved in 10 mL of water before being processed by the nanosecond laser. The process by nanosecond pulsed laser requires a homogeneous dispersion of the powder in the liquid media.14 Since the Si-ncs are hydrophobic, processing in water required adding a small amount of ethanol (10 drops) to wet the surface of the Si-ncs and aggregates; this allowed producing a homogeneous colloidal dispersion also in water. Surface engineering was conducted by irradiating the solution with a pulsed laser (Kr:F, 245 nm, 20 Hz, 130 mJ/pulse) at room temperature for 35 minutes. In order to induce the formation of larger spheres from the Si-ncs the energy pulsed was 145 mJ/pulse and irradiation was prolonged for 55 min. The laser beam was focused onto a 3 mm diameter spot on the liquid surface by a lens with a focal length of 250 mm. During the irradiation, the glass container was closed and rotated.

To fabricate the Si-ncs by laser ablation we used crystalline silicon wafer as a target. A third harmonic Nd:YAG/KrF laser (Quanta Ray from Spectra-Physics LAB-150-30, 355 nm, 30 Hz, 8 ns) laser was irradiated onto a target immersed in 10 mL of water at room temperature for 30 minutes. After focusing by lens, the laser spot diameter on the target was 1 mm. The laser fluence was about 0.07 mJ/pulse. It has to be noticed that the Si-ncs produced by electrochemical etching and laser ablation were made from the same silicon wafer type (p-type boron doped, <100>, 0.1 Ω cm, thickness 0.525 mm)

The photoluminescence (PL) measurements were performed at room temperature using a fluorophotometer (Shimadzu, RF-5300PC) with excitation by monochromatic light at 325 nm from an Xe lamp. The PL of the colloidal dispersions were checked with a He:Ca laser at 325 nm excitation laser wavelength. A small droplet of the obtained colloidal solution was deposited onto a copper grid with carbon film for
HR-TEM observations. A convergent incident electron beam was sometimes employed in the diffraction measurements to perform more localized analyses of Si nanoparticles. The ns processed samples were drop-cast on a glass substrate for analysis with a Scanning Electron Microscope (SEM; Hitachi S-4300).

3. Results and discussion

3.1 Silicon nanocrystals self-organized assemblies

In addition to synthesis capabilities, nanosecond laser processing (ablation/fragmentation) in water offers unique possibilities for engineering the Si-nC’s surface characteristics.\(^\text{15,16}\) As a result, surface-induced specific interactions of the Si-nCs lead to the organization of Si-nCs into larger structures. Figure 1 demonstrates and summarizes our findings. Figure 1 (a) shows typical SEM image of Si-nCs and Si-nCs aggregates as prepared by electrochemical etching where these are well separated. Nevertheless, after laser processing in aqueous solution, formation of self-organized networks is observed when the colloid is drop-cast on a substrate (Fig. 1 (b)). It has to be noticed that after laser processing, the Si-nCs remain well dispersed in the solution. Due to the Si-nCs quantum confinement effects, bright red-orange PL at room temperature can be seen when the solution is excited by a He-Cd laser beam (indicated by arrow, inset of Fig. 2 (b)). The self-organized patterns generally consist of interconnected and conductive structures\(^\text{15}\) that exceed several hundred micrometres in length (>500 μm). The assembly is the result of surface non-uniformity on the Si-nCs whereby the fragmentation in water has contributed to form surfactant-free Si-nCs. When the Si-nCs de-wet, enhanced dipole–dipole interactions induce long-range self-organized assemblies of connected networks.\(^\text{15}\)

Furthermore, changes in Si-nCs surface characteristics allow a range of new possibilities including easy dispersion of Si-nCs in water in the presence of water-soluble polymers.\(^\text{16}\) An important water-soluble polymer that has been already applied for different organic-based technologies is poly (3,4-ethylenedioxythiophene) (PEDOT). In order to demonstrate the influence of surface functionalization by PEDOT we have produced colloidal dispersions with Si-nCs that were previously laser-processed in water for 35 minutes and we have then added a few drops of PEDOT. As we can observe in Fig. 1 (c) the Si-nCs tend to form networks of closely packed Si-nCs. Investigations showed that the addition of PEDOT in the colloidal dispersion may have an effect in the self-organization mechanism as some minor differences could be observed: the networks seemed to be shorter on average and less dense if compared with networks that did not include PEDOT (Fig. 1 (b)).

The Si-nCs powder before being dispersed in water presents strong FTIR absorption around 626 and 2092 cm\(^{-1}\) which are attributed to Si monohydrides with the second peak influenced by Si–Si dimer bonds. OH-induced cleavage of the Si–Si dimer bonds leads to the formation of one Si-OH and one Si–H termination per dimer. The increased number of Si–H terminations can be related to spectral changes as recorded around 770 cm\(^{-1}\). However, no obvious OH transmission change is observed in the FTIR spectra because adjacent OH terminations tend to progress quickly to condensation and accelerated oxidation producing water as a by-product.\(^\text{16}\) During 35 minutes processing time, a decreased number of reactive sites for the OH radicals and a complete detachment of Si-nCs from larger aggregates is produced. At the same time, a red shift of about 20 nm in PL confirm the replacement of H-terminations with OH-terminations which is also confirmed by FTIR and by a decreased band-gap of the Si-nCs. Due to surface reactions initiated by plasma electrons, radicals have been formed in the liquid dispersion with consequent replacement, at the Si-nCs surface, of the hydrogen bonds with hydroxyl-organic-based bonds. The FTIR transmission of PEDOT is very rich with a number of peaks in the range between 400 and 1300 cm\(^{-1}\). Some of the PEDOT absorption features can be seen replicable in the Si-nC sample with added PEDOT, and specific vibration corresponding to bonds involving Si could be identified (e.g., Si-C or Si-O-C). An absorption peak around 1050 cm\(^{-1}\) that corresponds to Si-O-C bonds is present. The Si-O-C peak is overlapping with the Si-O-Si peak which is clearly broadened in the lower wavenumbers.\(^\text{16}\)

3.2 Bottom-up formation of spherical particles made of Si-nCs

In addition to surface engineering, ns laser processing can be also used to synthesise Si-nCs with strong quantum confinement effects by ablating a silicon targets immersed in water. The specific surface chemistry induced during the Si-nCs growth in direct contact with water leads to the formation of spherical aggregates of sub-micrometre size. Figure 2 shows representative SEM images of Si-nCs aggregated in larger spherical particles. Using this technique we could obtain
well-separated spherical particles with large size distributions ranging from 2 to 100 nm without using any surfactant.

In order to obtain more detailed information about structural properties of spherical particles, TEM investigations have been conducted. A TEM image of a spherical particle with 20 nm in diameter is shown in the inset of Fig. 2 (a). It can be seen that this spherical particle are formed by separate single Si-nanocrystals with quantum confinement size (< 5 nm) (indicated in circles); it can be noted that smaller spherical particles were easier to analyse with the TEM, although we believe that larger spherical particles have a similar composite structure. Electron diffraction spectroscopy and corresponding ring diameters confirmed the crystalline nature and silicon plane orientations: 3.146 Å for <111>, 1.93 Å <220>, 1.64 Å <311>, 1.34 Å <400>, 1.25 Å <331>, and 1.1 Å <422>\(^{11}\). The powder delaminated by XRD measurements revealed three major peaks of crystalline silicon corresponding to the <111>, <220>, and <311>\(^{11}\). Raman spectra of spherical particles confirmed the presence of Si-nanocrystals with the crystalline silicon diamond-like structure. The Raman peak compared to bulk crystalline silicon (~520 cm\(^{-1}\)) is shifted to higher energy and centered at 517.8 cm\(^{-1}\), indicating the presence of nanocrystalline particles.\(^{17}\)

One of the most significant features of Si-nanocrystals is the opening the band-gap of Si due to the strong confinement effects that leads bright photoluminescence at room temperature. Visible PL of Si-nanocrystals prepared by ns laser ablation is shown in the inset of Fig. 2 (b). Due to the opening of the band gap Si-nanocrystals and thanks to a good dispersion of Si-nanocrystals, blue photoluminescence can be seen when the colloids is excited by He:Ne laser.\(^{11,17}\) Figure 2 (b) presents corresponding PL spectra of Si-nanocrystals dispersed in water and excited by 325 nm. A typical broad PL spectrum at room temperature is recorded with a maximum located around 400 nm. It is generally accepted that this visible strong PL could be typically assigned to both surface states and quantum confinement effect (less than 10 nm diameter).\(^{17}\) It might be interesting to notice that synthesis by laser ablation in water and the resulting bottom-up integration of the Si-nanocrystals into the larger spherical particles prevents oxidation of the Si-nanocrystals and optimizes the photoluminescence stability.\(^{17}\)

Further investigations revealed that ns laser processing in water could be used to integrate Si-nanocrystals into larger spherical particles also when Si-nanocrystals where pre-synthesized with other techniques. Here we demonstrate the integration in spherical particles with Si-nanocrystals pre-synthesized by electrochemical etching. Figure 3 shows the SEM images of as-prepared electrochemically etched Si-nanocrystals used in these experiments (Fig. 3 (a)) and the resulting Si-nanocrystals spherical aggregates after laser processing in water (Fig. 3 (b)-(c)). Compared to the self-organized assemblies previously produced by laser processing of electrochemically etched Si-nanocrystals (shown in Fig. 1), in this case we applied longer irradiation time and slightly higher irradiation intensity which induced Si-nanocrystals aggregation in spherical particles as shown in Fig. 3 (b)-(c). Similarly to direct synthesis in water (Fig. 2), the spherical particles are well separated. However spherical particles produced by laser processing of

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Fig. 2 (a) SEM images of silicon nanocrystals (Si-nanocrystals) spherical particles after laser ablation of single-crystalline silicon target in water. (b) Typical photoluminescence (PL) spectra from Si-nanocrystals dispersed in water. Distinct peak represent excitation wavelength (325 nm). Inset shows a photograph of blue light emission from Si-nanocrystals. Si-nanocrystals were excited by a He.Cd laser at 325 nm.

Fig. 3 (a) SEM image of electrochemically etched silicon nanocrystal (Si-nanocrystal) powder before ns laser induced surface engineering. (b) SEM images of Si-nanocrystal spherical particles after laser irradiation of Si-nanocrystal powder in water. (c) Detailed SEM image showing well defined spherical particles.
electrochemically etched Si-ncs seem to have larger diameters (~300 nm on average). It has to be noticed that the liquid medium plays an important role in the Si-ncs integration into spherical particles. We observed for instance that laser processing in ethanol could also form well-separated spherical sub-micrometer particles but this was achieved with shorter processing time and lower irradiation energies.15

Quantum confinement effects and the resulting bright PL suggest the presence of Si-ncs in the colloids. The PL properties of the colloids before and after ns laser processing are shown in Fig. 4. Figure 4 (a) is a photograph of the solution before processing when excited by a laser beam (He:Cd laser, indicated by an arrow). Si-ncs are well dispersed in this case and the colloid shows bright red-orange PL. Si-ncs caused substantial light scattering through the solution and broad PL spectral envelop could be observed. However, after processing, the PL properties of the solution almost completely disappeared and no visible PL was observed when the excitation by the laser was pointed towards the middle of the solution (Fig. 4 (b)). Nevertheless, PL could be clearly observed if the laser was pointed towards the bottom of the glassware (glassware slightly tilted). While small size Si-ncs can easily be suspended in water to form a colloid (Fig. 4 (a)), processed large spherical Si-ncs aggregates (~300 nm diameter) produced a sediment at the bottom of the solution as demonstrated by PL in Fig. 4(c). When the solution of the processed Si-ncs was drop-cast on a substrate brightly luminescent spots could be observed indicating the presence of the highly luminescent spherical Si-ncs aggregates. However a detailed spatial PL analysis would be required to well characterize optical properties of the large spherical particles made of Si-ncs.

Comments should be given on the ns laser irradiation/ablation mechanisms that contributed to the formation of well-separated spherical sub-micrometer particles containing Si-ncs. The specific surface chemistry that was in part discussed in subsection 3.1 together with selective pulsed heating due to laser irradiation are possibly the source of the mechanisms that are responsible for the formation of spherical particles. These conditions would allow for instance Ostwald ripening to take place16 whereby large particles tend to grow at the expense of smaller Si-ncs that are either synthesized by laser ablation or fragmented from electrochemically etched Si-ncs. In Ostwald ripening, it is the surface energy that determines the diffusion of small Si-ncs through the solution and allows their attachment to the surface of larger growing particles. Herein, it should be noted that Ostwald ripening is characterized by the gradual dissolution of small particles. Furthermore, we can get uniform small nanoparticles (with the size smaller than that of raw Si-ncs micrograins, see Fig. 3 (a)-(b)), corresponding to the evaporation of raw nanoparticles as well. A common phenomena observed in pulsed laser irradiation of colloidal nanoparticles.17 This is supported by PL experiments, while after processing the PL of the solution is gone and only large particles sediment and formed on expense of smallest Si-ncs showed PL emission. One another support for it is that the chemistry replacement of H by OH is more effective in case of ethanol. Therefore the spherical particles could be formed even at lower laser fluencies and for shorter time.18

Another mechanism that can concurrently contribute to the formation of spherical particles is the selective pulsed heating of irradiated particles.20 If Si-ncs formed by laser ablation or electrochemical etching diffuse under the beam and absorbs sufficient laser beam energy, could melt or evaporate. The laser fluence used in these experiments is probably sufficient for the temperature to increase dramatically and the Si-ncs dispersed in the solvent might reach the melting point.21 As the irradiation time increases, neighboring Si-ncs could melt into larger spheres and progressively increase in size as other Si-ncs fuse together. After the pulsed heating (within 8 ns), a rapid cooling rate is helpful to inhibit the reorientation of surface atoms retaining the overall spherical morphology. However, for particles with larger diameter (~300 nm), detailed TEM is quite difficult and possibly larger crystalline particles due to re-crystallization might also be formed. However, at this stage of the study, the factor that determines with greater impact the formation of sub-micrometer luminescent particles cannot be identified and both surface chemistry and selective pulsed heating have to be considered.

4. Conclusions

We have shown that ns laser processing can be used effectively for both Si-ncs synthesis and for their surface engineering directly in water. Firstly, we have shown that self-organization of conductive long-range Si-ncs networks can be produced as a result of specific Si-ncs surface characteristics induced by laser processing. Laser processing of Si-ncs facilitate the activation of Si-ncs surface sites for further polymer-based functionalization in water which does not significantly affect the Si-ncs self-organized assemblies. Secondly, surface engineering of Si-ncs allows bottom-up formation of sub-microometer spheres via laser processing, in which induced unique surface chemistry and selective pulsed heating contribute to the formation mechanisms.
Acknowledgments

This work was partially supported by a NEDO Project (Japan). D. M. gratefully acknowledges the support of the JSPS Invitation Fellowship (Japan).

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