Synthesis of photoluminescent colloidal silicon nanoparticles 
by pulsed laser ablation in liquids

I Umezu1, 2, H Minami1, H Senoo1 and A Sugimura1, 2
1Department of Physics, Konan University, Kobe 658-8501, Japan
2Quantum Nano-technology Laboratory, Konan University, Kobe 658-8501, Japan
iumezu@um.phys.konan-u.ac.jp

Abstract. We performed pulsed laser ablation (PLA) of a silicon target in liquid environment 
to prepare a silicon colloid solution. The nanoparticles were observed by SEM and TEM 
measurements. The result of Raman scattering indicates that this particle is mainly composed 
of silicon nanocrystallites. The optical gap energies of the colloid solutions varied by changing 
the solvents; 2.9 and 3.5 eV for colloids prepared in water and hexane, respectively. These 
colloid solutions showed efficient PL intensity. Since Si-(CH3)n related bonds were observed 
for the specimen prepared in hexane, surface effects other than the quantum confinement effect 
should be taken into account for the origin of the PL. Our results indicate that new kinds of Si-
based colloid solutions can be prepared by PLA in solvent. Since the PL peak energies were 
sensitive to the surface conditions, these colloid solutions are promising for biological 
applications such as bio-sensors.

1. Introduction
It is well known that silicon is one of the most important semiconductor materials for electronic 
deVICES. Recently, applications for opto elecronic devices have been examined since efficient visible 
photoluminescence was observed in silicon nanocrystallites. [1] Apart from electronic or optical 
deVICES, semiconductor nanocrystallites are possible materials for biological applications. [2] 
Although II-IV semiconductor nanocrystallites such as CdS and CdSe are studied as luminescent 
markers for biological applications, group V semiconductor nanocrystallites such as Si or Ge have not 
been studied for biological applications so far. One of the reasons is that the preparation of colloid 
solutions of silicon is not easy compared with that of II-IV materials. Nanocrystallites embedded in 
solution are promising for biological applications. The Si-based materials are attractive for bio-
materials since they do not include harmful elements such as cadmium or arsenic. Furthermore, a new 
device combined with existing technology based on electronics will be also expected.

In a previous report on preparing Si colloid solution from silane gas [3], aerosol was produced by 
pyrolysis of silane gas and bubbled in ethylene glycol. Laser induced ablation from a solid target is 
known as a good method for nanofabrication. There are many reports on the fabrication of silicon 
nanocrystallites in background gases. [4, 5] Recently preparation of metal nanoparticles in liquid 
environment by PLA of targets immersed in liquid media was reported. [6] Although metal and 
compound semiconductor nanoparticles were obtained by PLA in a solvent, there have been few
attempts to prepare the silicon or germanium nanoparticles. In the present work, we demonstrate that PLA in liquid can be used to produce colloidal solution of silicon.

2. Experiment
The target was a single crystal silicon wafer and the solvents were water, hexane or toluene. A piece of Si target was immersed in solvent which is put into a quartz cell. The second harmonic of a Nd: YAG laser (532 nm) was used to irradiate the target at a fluence of 10 mJ/cm². The laser beam was focused on the target with a lens whose focal length was 25 mm. The target was moved perpendicularly to the laser beam to irradiate fresh surfaces during the process. Ultraviolet-visible (UV-VIS) and photoluminescence (PL) spectra of the colloid solution were measured in the quartz cell. A 325-nm line of a HeCd laser and a CCD camera were used as the excitation source and detector for the PL measurement. The colloid solution was dropped on the single crystal silicon, quartz and carbon mesh and dried to measure IR transmission, Raman scattering and TEM image, respectively.

3. Results and discussion
Figures 1 and 2 show TEM and SEM images of the specimen prepared in hexane and water, respectively. Well dispersed Si nanoparticles whose diameters are less than 3 nm and aggregated particles about 10 nm were measured for TEM and SEM images. Since the aggregation differs depending on the conditions used to dry the specimen, we can not discuss the degree of aggregation. These figures indicate that nanoparticles can be obtained by PLA in liquid environments.

![Figure 1. A TEM image of the specimen prepared in hexane.](image1)

![Figure 2. A SEM image of the specimen prepared in water.](image2)

The Raman scattering of the specimen prepared in hexane was 517 cm⁻¹, which was smaller than that of single crystal Si, 520 cm⁻¹. These results indicate that the nanoparticles observed by TEM and SEM are Si nanocrystallites. The size of the nanocrystallites estimated from Raman shift was about 7 nm. The results of optical absorption measurements are shown in Figure 3. If we assume the obtained material is an indirect bandgap semiconductor, we can define the optical gap from the intersection between the extrapolated plot and the x-axis. The optical gap energies of the colloid prepared in water and hexane are 2.9 and 3.5 eV, respectively. The results of optical bandgap energies indicate that nature of the specimen depends deeply on the solvent. Although the optical bandgap energies roughly correspond to the results of TEM, SEM and Raman scattering that the diameter of nanocrystallites are less than 10 nm, uncertainty in the measurements of the diameter still exist. The optical bandgap energy of the specimen prepared in water shifted from 2.9 to 3.4 eV in six days after the preparation. This may be due to the oxidation of nanocrystallites in the water. On the other hand, optical bandgap energies of the specimens prepared in hexane did not change within six days.
Figure 3. The optical absorption spectra of specimens prepared in various solvents. The dotted lines are extrapolates of the spectra to the x-axis.

These specimens showed efficient PL intensity. The PL spectra are shown in figure 4. The PL efficiency of the colloid was estimated to be more than four orders stronger than that of PLA in background gases. Since the optical bandgap and PL peak energies are similar, one of the possible origins of the PL is the quantum confinement effect. The PL peak energies of the sample prepared in hexane changed from 3.2 to 2.4 eV by drying the colloid solution on the Si substrate. This indicates that surface effect other than the quantum confinement effect should be taken into account. Since PL wavelength is very sensitive to ambient conditions, the PL wave length may be controlled by changing surface condition of the colloid. This character is possible for application to the sensor.

The FTIR spectra is shown in figure 5. The Si-O vibration mode at 1080 cm$^{-1}$ was observed for all samples. The sample prepared in hexane solvent had additional peaks at around 800 and 1260 cm$^{-1}$. These peaks correspond to the vibration frequency of Si-(CH$_3$)$_n$ bonds. These results indicate that the hexane molecule decomposed during the expansion of Si species by a strong laser pulse and CH$_3$ species bond to the surface of the Si nanocrystallites. Therefore, the possible origins of the strong PL intensity other than quantum confinement effect in hexane solution is due to the surface molecule related to Si-(CH$_3$)$_n$ bonds. We previously showed that SiN$_x$ films could be prepared by PLA of Si targets in nitrogen gas, even though the N-N bond of the nitrogen molecule is strong. [7, 8] This is because high temperature and pressure at the shock front area promote reaction between silicon and nitrogen. A similar reaction may take place between ejected Si species and the ambient solvent. The difference in the FTIR spectra shown in figure 5 is due to the difference in the reaction at the shock front area. This result indicates that a new kind of Si-based nanocrystal can be prepared by PLA in solvent. Although the plume dynamics are not observed in the present paper, analysis of the plume expansion and reaction with the ambient solvent is necessary to prepare new kind of materials.

Figure 4. The PL spectra of the specimens prepared in various solvents.

Figure 5. IR absorption spectra of the specimens prepared in various solvents.
4. Conclusion
We performed PLA of silicon targets in liquid environment. The Si nanocrystallites are observed in the solvent by TEM, SEM and Raman scattering. The optical gap energies of the colloids prepared in water and hexane are 2.9 and 3.5 eV, respectively. These materials showed strong PL intensity. Although quantum confinement is one of the possible origins of the PL, we have to consider surface effects since samples prepared in hexane have Si-(CH₃)ₖ related bonds. We could prepare Si-based photoluminescent colloid solutions by a simple PLA technique. These colloid solutions are attractive since they are compatible with bio-materials.

5. Acknowledgement
This work was partially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science, Nippon Sheet Glass Foundation for Materials Science and Engineering, and The Hirao Taro Foundation of the Konan University Association for Academic Research.

References
[1] Canham L T 1990 Appl. Phys. Lett. 57 1046
[2] Bailey R E, Smith A M and Nie S 2004 Physica E 25 1
[3] Littau K A, Szajowski P J, Muller A J, Kortan A R and Brus L E 1993 J. Phys. Chem. 97 1224
[4] Yamada Y, Orii T, Umezui I, Takeyama S and Yoshida T 1996 Jpn. J. Appl. Phys. 35 1361
[5] Movtchan I A, Dreyfus R W, Marine W, Sentis M, Autric M, Lay G L and Merk N 1995 Thin Solid Films 225 286
[6] Mafune F, Kohno J, Takeda Y, Kondow T and Sawabe H 2000 J. Phys. Chem. B 104 9111
[7] Umezu I, Kohno K, Yamaguchi T, Sugimura A and Inada M 2002 J. Vac. Sci. and Technol. A 20 30
[8] Umezu I, Inada M, Kohno K, Yamaguchi T, Makino T and Sugimura A 2003 J. Vac. Sci. Technol. A 21 1680