

Synthesis and Spectroscopic study of Alkyl-Terminated Silicon Nanoparticles

Ryo Saito* **, Tadafumi Kamikake**, Akinori Tanaka** and Hidehiro Yasuda**

*Department of Physics, Graduate School of Science, Tohoku University,
Aoba-ku, Sendai 980-8578, Japan

FAX: +81-78-803-6155, e-mail: ryo-s@mail.tains.tohoku.ac.jp

**Department of Mechanical Engineering, Faculty of Engineering, Kobe University,
Nada-ku, Kobe 657-8501, Japan

FAX: +81-78-803-6123, e-mail: a-tanaka@mech.kobe-u.ac.jp

FAX: +81-78-803-6129, e-mail: yasuda@mech.kobe-u.ac.jp

Silicon nanoparticles (Si NPs) with ethyl-terminated surface have been synthesized by a room temperature solution route. Transmission electron micrographs show no aggregation of nanoparticles, and Fourier transform infrared spectrum shows a well alkyl-terminated surface of Si NPs. Optical extinction spectrum in the photon energy range from visible to ultraviolet shows an absorption edge considerably blue-shifted from the band gap in bulk Si crystalline (1.17 eV). The photoluminescence spectrum of present Si NPs exhibit the excited photon energy dependence, and similar feature to those of the previous hydrogen-terminated Si nanoclusters with a size of 1-2 nm. From these results, we discuss the optical properties of alkyl-terminated Si nanoparticles.

Key words: silicon nanoparticles, spectroscopy

1. INTRODUCTION

Semiconductor nanoparticles or nanoclusters have a great interest in the field of physical science and also application to future nanoelectronic and nanophotonic devices. Especially, since the luminescence from the porous Si has been reported,¹ Si nanocrystallines have attracted much interest. Photoluminescence from the silicon nanocrystallines is a key feature to advance in science and utility to optical devices. Though the bulk Si crystalline shows low efficient luminescence in the infrared region only at low temperature due to the indirect energy gap, the distinguished luminescence is observed in the visible region with decreasing the crystalline size. Up to now, numerous research focused on the photoluminescence from silicon nanoparticles (Si NPs) prepared by the various methods such as chemical etching,² ion sputtering,³ chemical vapor deposition,⁴ ion implantation,⁵ laser ablation,⁶ and inverse micelle method⁷ etc. Moreover, in order to explain the luminescence from Si NPs, a number of model related to the electron and hole quantized state, surface states originated Si-O bond, or impurity state^{8,9} etc. have been proposed. However, the details of luminescence from Si NPs are still controversial because the optical spectra in Si NPs are strongly depends on the samples that is prepared by different methods. It is because that the Si NPs prepared by different methods have different chemical state of surface. Therefore, Si NPs with well-defined surface without any contaminations have been strongly desired. Recently, the remarkable preparation methods of Si NPs passivated with organic molecules and the intense photoluminescence from these passivated Si NPs have been reported.¹⁰⁻¹⁵ Among the Si NPs passivated with organic molecules, alkyl-terminated Si NPs synthesized from the Zintl salt phase silicide are most stable and show a little evidence of oxidation.^{10,13} In this paper, we have synthesized the alkyl-terminated Si NPs with well-defined surface using solution route,

and discuss the optical properties of alkyl-terminated Si NPs.

2. EXPERIMENT

Alkyl-terminated Si nanoparticles were prepared by two-step termination route.¹³ Firstly, bromine-terminated Si NPs were formed by metathesis reactions of magnesium silicide (Mg_2Si) with bromine. And then, alkyl-terminated Si NPs were obtained by alkyl substitution reaction with grignard reagent or alkyllithium reagent. Manipulations of chemicals and reactions were carried out in a glove bag or Schlenck line using standard anaerobic and anhydrous techniques, and all glassware was silanated and dried prior to use. 200 mg of Mg_2Si and 0.8 mL of bromine were added to 200 mL of octane (dried with potassium, distilled, and degassed by several freeze-pump-thaw cycles) with stirring for two hours. In this process, the color of solution was changed from deep reddish brown to colorless. The mixture was heated slowly to reflux and color disappeared after heating for 30 min. Solvent mixture was refluxed over 60 hours, and the color of solution changes to a black suspension in this process. After the mixture was cooled down to room temperature, the remaining unreacted bromine was removed by evaporation. Excess ethyllithium was added to reaction mixture and then this mixture was stirred for 24 hours. After removal of solvent by evaporation, colorless oily residue was obtained. Hexane was added to the residue and then this mixture was transferred to a separatory funnel. Si NPs was extracted into hexane, and washed with acidic water several times for neutralization of salts and removal of other byproducts. Finally, colloidal hexane was centrifuged to improve the nanoparticle size distribution. The particle size and shapes of the synthesized ethyl-terminated Si NPs were characterized by *ex situ* observations with a H-800 (HITACHI Co.) transmission electron microscopy (TEM). The samples

for TEM observations were prepared by drying the hexane dispersions of ethyl-terminated Si NPs on the amorphous carbon-coated copper TEM grids. The terminal moieties on the centrifuged Si NPs surface were characterized with a NEXUS-470 (Nicolet Co.) Fourier transform infrared (FTIR) spectrophotometer FTIR spectra for nanoparticles were measured at room temperature by pipetting the samples on a ZnSe flat plate. As a further characterization, optical extinction and photoluminescence spectra of the centrifuged sample in a quartz cell were measured with a V-570 (JASCO Co.) and V-750 (JASCO Co.) spectrometer, respectively. These spectra were measured at room temperature.

3. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the transmission electron micrographs for the as-prepared ethyl-terminated Si NPs and the centrifuged ethyl-terminated Si NPs, respectively. As shown in Fig. 1, the present ethyl-terminated Si NPs have spherical shape. An important point to note is that each nanoparticles is well separated from its neighboring nanoparticles, indicating that the present Si nanoparticles are well passivated by the ethyl groups. Furthermore, while the as-prepared sample has a large size distribution, there is no large particle in the centrifuged sample and the nanoparticle

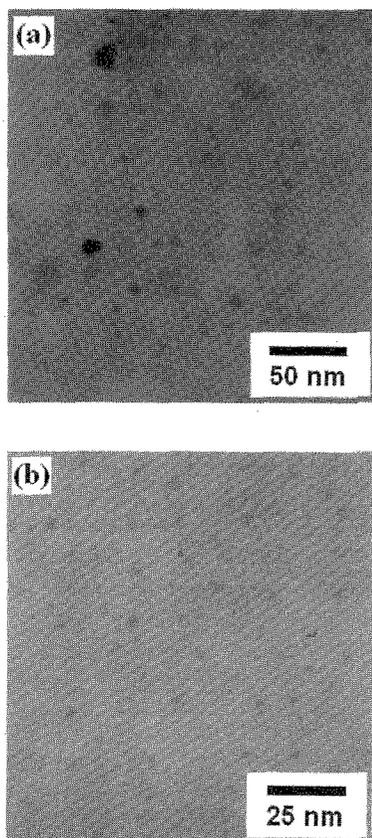


Figure 1. Bright field transmission electron micrographs for (a) the as-prepared ethyl-terminated Si NPs, and (b) the centrifuged ethyl-terminated Si NPs, respectively.

diameter of 1-2 nm is dominant. This result suggests that the present centrifuging process after the synthesis is in particular effective to improve the nanoparticle size distribution. According to colloidal chemistry, equilibrium system in synthesis is basically needed for preparation of monodispersed nanoparticles. However, in our method, the synthesis is based on metathesis reactions between solid phase Mg_2Si and bromine radicals in the organic solvent. Therefore, only the surface of Mg_2Si can react directly with the radical species. It is considered that such a nonequilibrium system of synthesis leads a large size distribution for as-prepared sample as shown in Fig. 1(a).

Figure 2 shows the FTIR absorption spectrum of the ethyl-terminated Si NPs. The strong peaks in the stretch region between $2980-2850\text{ cm}^{-1}$ and $1450-1350\text{ cm}^{-1}$ are observed. These absorptions are assigned to C-H stretching mode (2855 and 2922 cm^{-1}), terminal CH_3 stretching mode (2955 cm^{-1}), and C-H bending/scissoring mode (1464 and 1377 cm^{-1}), respectively. Additionally, a slight weak absorption at 1256 cm^{-1} is assigned to Si- CH_2 symmetric bending mode. These absorptions originated from the presence of methylene or methyl groups attributed to the alkyl chain in the passivant. This result is closely similar to alkyl-terminated Si NPs produced by other preparation methods in the previous works.^{10, 14} However, in addition to the absorptions related to alkyl-termination, the previous works have also shown the additional absorptions due to Si-O-C linkage ($1070-1100\text{ cm}^{-1}$) assigned to the alkoxy-termination¹⁰ and Si-H stretching mode ($2100-2150\text{ cm}^{-1}$).¹⁴ On the other hand, the present ethyl-terminated Si NPs show no such evidences. This result suggests the homogeneous ethyl-terminated surface of Si NPs in our sample. Furthermore, there are no evidence of Si-O-Si anti-symmetric and symmetric stretches mode absorptions ($1020-1080\text{ cm}^{-1}$) in our sample. This result shows no oxidation that observed for other Si NPs terminated with hydrogen or nitrogen etc. Thus, the present FTIR spectrum indicates well-controlled surfaces and complete passivation with ethyl groups for the synthesized Si NPs.

Figure 3 shows optical extinction spectrum of the ethyl-terminated Si NPs. As shown in Fig. 3, an absorption edge around at 3.8 eV in photon energy,

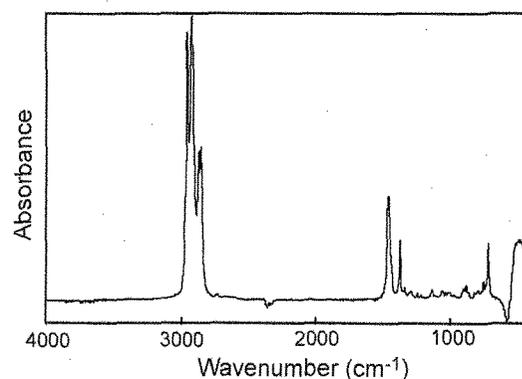


Figure 2. Fourier transform infrared spectrum of the ethyl-terminated silicon nanoparticles.

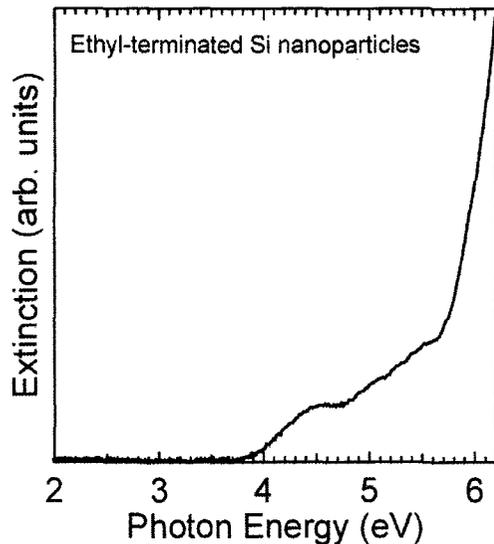


Figure 3. Optical extinction spectrum for the ethyl-terminated silicon nanoparticles.

which is considerably blue-shifted from the band gap of the bulk Si crystalline (1.17 eV), has been observed. In the bulk Si crystalline, the long absorption tail is observed between 1.2-3 eV related to the indirect gap, however our result shows no such evidence. The present absorption edge is located above 0.3 eV than that of the alkyl-terminated Si NPs with the size of 3-6 nm in the previous works.¹⁰⁻¹⁵ Figure 4 shows the photoluminescence spectra of the present ethyl-terminated Si NPs. In Fig. 4, the excitation energy was varied between 5.64 eV and 4.96 eV in photon energy, and each emission spectra was normalized at the maximum photoluminescence intensity. As shown in Fig. 4, the photoluminescence in the ultra-violet region were observed. Such a intensive ultraviolet photoluminescence can not be observed for the bulk Si crystalline due to the indirect energy gap of 1.17 eV. Wolkin *et al.*¹⁶ have reported that Si NPs with a size less than 3 nm can not exhibit the photoluminescence due to the trap state associated to the silicon-oxygen bonds at higher photon energy than 2.1 eV. Since the energy position of the present photoluminescence is inconsistent with this energy position, the present photoluminescence in the ultraviolet region can not be attributed to the trap state related to the oxygen. Furthermore, as shown in Fig. 4, it found that photoluminescence spectra of the present sample depend on the excitation energy. This dependence suggests that the origin of the photoluminescence is less likely to be from the organic molecules in the passivants or trap states related impurity and surface. As shown in Fig. 1(b), the present ethyl-terminated Si NPs show a size distribution. If each nanoparticle have the different band gaps depending on their individual sizes due to the quantum confinement, these nanoparticles can be selectively excited at the energies corresponding to its band gaps. Considering that the optical extinction spectra contains the contributions of the ensemble of nanoparticles with the various sizes, the observed photoluminescence spectra in Fig. 4 correspond to the

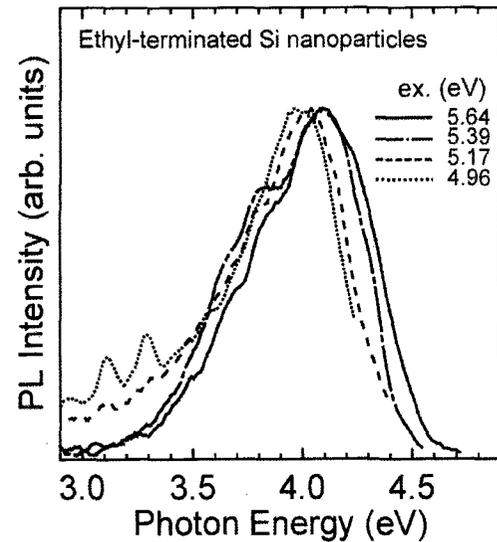


Figure 4. Photoluminescence spectra for the ethyl-terminated silicon nanoparticles. Each spectrum was excited at 5.64 (solid line), 5.39 (dashed dotted line), 5.17 (dashed line), and 4.96 (dotted line) eV, respectively.

absorption edge shown in Fig. 3. However, the photoluminescence spectra shown in Fig. 4 are blue-shifted comparing to that of the alkyl-modified porous silicon¹⁷ and other Si NPs of size above 2 nm in the previous works.^{10-13,18,19} On the other hand, Rao *et al.*²⁰ have reported the hydrogen-terminated Si nanoclusters with size of approximately 1 nm, which exhibit the photoluminescence spectra at almost same energy as the present result. Mitas *et al.*^{21,22} have calculated using the functional theory and Monte Carlo approach that the size and band gap of $\text{Si}_{29}\text{H}_{24}$ cluster are 0.9 nm and 3.5 eV, respectively. In addition, Draeger *et al.*²³ have reported other two types $\text{Si}_{29}\text{H}_{24}$ configurations which the surface Si atoms connect to an interior tetrahedral Si core in the different two ways and have also calculated using Monte Carlo simulation, that band gaps are estimated to 4.5 and 4.1 eV, respectively. From comparison with these calculations, Rao *et al.* have concluded that the observed photoluminescence originates from the $\text{Si}_{29}\text{H}_{24}$ with heterogeneous configurations noted above. That is, they have concluded that the hydrogen-terminated Si nanoclusters with size of 1 nm exhibit the photoluminescence centered at approximately 4.0 eV. Moreover, Reboredo *et al.* have calculated the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) among the alkyl-terminated and hydrogen-terminated Si nanoclusters with size of approximately 1-1.5 nm (Si_{20} , Si_{29} , Si_{66} , and Si_{142}), using density functional theory. In their works, the calculated HOMO-LUMO gaps for these Si nanoclusters are independent on the surface passivants. Since the hydrogen-terminated Si nanoclusters with size 1 nm exhibits the photoluminescence centered at approximately 4.0 eV and the HOMO-LUMO gaps among the surface-passivated Si NPs is reported to be independent of surface passivants, it is expected that the photoluminescence from ethyl-terminated Si nano-

clusters with size of approximately 1 nm is observed at the same energy region. Therefore, we can conclude that the observed photoluminescence around at 4.0 eV originates from the recombination of electron and hole in the quantized electronic state of the ethyl-terminated Si NPs with size of 1-2 nm due to the quantum confinement.

4. SUMMARY

We have synthesized the ethyl-terminated Si NPs by a room temperature solution route. TEM micrographs show the isolated and spherical nanoparticles, and the particles with the size in the range 1-2 nm are observed for the sample centrifuged after the synthesis. FTIR spectrum shows the alkylated surface of Si NPs and no evidence of oxygen and other contaminations. Optical extinction spectra show an absorption edge considerably blue-shifted from the band gap of bulk Si crystalline. Additionally, the photoluminescence spectra in the ultraviolet region are observed and exhibit the dependence on the excitation energy. This dependence suggests that the origin of luminescence is less likely to be from the organic molecules in passivants or trap states related to impurity and surface. On the other hand, the present photoluminescence spectra are closely similar in photon energy to that of previous hydrogen-terminated Si nanoclusters with size about 1 nm ($\text{Si}_{29}\text{H}_{24}$). Furthermore, the previous theoretical calculation has shown that the HOMO-LUMO gaps of the Si nanoclusters with size of 1-1.5 nm are independent on the surface passivants. Therefore, we conclude that the observed ultraviolet photoluminescence originates from the recombination of electron and hole in the quantized electronic state of the ethyl-terminated Si NPs with size of 1-2 nm due to the quantum confinement.

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