Effects of Surface Passivation on Silicon Nanoparticle Photoluminescence

David E. Harwell, John C. Croney,[†] Wenjie Qin, John T. Thornton,[††] Jason H. Day, Evan K. Hajime, and David M. Jameson*[†]
Department of Chemistry, University of Hawaii, 2545 The Mall, Honolulu, HI 96822, U.S.A.
[†]*Department of Cell and Molecular Biology, University of Hawaii, 1960 East-West Road A209, Honolulu, HI 96822, U.S.A.*
[††]*Digital Instruments, Veeco Metrology Group, 223 Wilmington-West Chester Pike, Suite 114, Chadds Ford, PA 19317, U.S.A.*

(Received September 8, 2003; CL-030824)

Silicon nanoparticles were produced by a relatively low temperature (164 °C), solution-phase synthesis. The particles exhibit UV to blue photoluminescence (PL) which varied with excitation wavelength. The average lifetimes, excited at 300 nm, ranged from 4.4 to 5.9 ns. The mean particle diameter, determined by atomic force microscopy, was ≈1.08 nm. The PL spectra of particles passivated with methoxy or butyl groups were blue-shifted with respect to those passivated with hydroxy groups.

Since the discovery of room-temperature photoluminescence (PL) from porous silicon in 1990,[1] a great deal of creative energy has been devoted to elucidating the origins of PL emissions in semiconductor nanoparticle materials. Theories explaining the PL emissions of quantum dots, comprised of silicon or other semiconductors, have traditionally fallen into one of two camps: quantum confinement,[1–6] or surface state emissions.[7–9] The present work is concerned primarily with the effect and modification of surface states.

The silicon nanoparticles reported herein, were synthesized by simple reduction of silicon tetrachloride using sodium metal in the moderately high-boiling, coordinating solvent, diglyme (Figure 1).

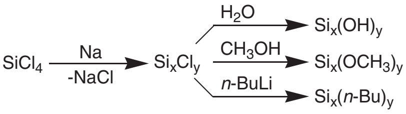

Figure 1. Scheme for silicon nanoparticle production.

Reflux of the reaction mixture with constant stirring for 24 h followed by immediate reaction with water, methanol, or *n*-butyl lithium produced silicon nanoparticles which were passivated with hydroxy, methoxy, or *n*-butyl groups, respectively. Unless noted otherwise, reagents were purchased from Acros or Aldrich and used without further purification. Diglyme was distilled from sodium under nitrogen prior to use, and silicon tetrachloride was triply distilled. Methanol was distilled from calcium hydride to minimize hydrolysis side-reactions. All procedures up to the addition of water, methanol, or *n*-butyl lithium were done under nitrogen using standard Schlenk line techniques. In addition to the silicon nanoparticles, this procedure produces an amorphous silicon precipitate, which was separated from the solution using a 0.45-μM filter. A fluorescent by-product was produced by the partial polymerization of diglyme by sodium at reflux. This by-product was separated by adding water to the reaction solution after the initial filtration, and then removing the solvent in vacuo while gently heating (80 °C). This simple procedure causes further polymerization of the by-product into an insoluble red, amorphous glass. The remaining purified residue was then redissolved in water (hydroxy-coated particles), or hexanes (methoxy- and *n*-butyl-coated particles). Absence of the by-product was confirmed by UV–vis absorption and fluorescence spectroscopy measurements.

PL spectra were obtained using an ISS PC photon-counting spectrofluorometer (ISS, Inc., Champaign, IL). Lifetime measurements were performed using an ISS K2 multifrequency phase and modulation spectrofluorometer (ISS Inc., Champaign, IL) equipped with a Spectra-Physics model 2045 Argon ion laser (Spectra-Physics, Mountain View, CA) as the excitation source.[10] Samples were excited at 300 nm and emissions were viewed through a Schott WG 320 filter.

The sizes of the Si$_x$(OH)$_y$ nanoparticles were analyzed using an atomic force microscope (AFM) in tapping mode. Measurements were acquired with a NanoScope© Dimension™ 3100 Scanning Probe Microscope. The AFM used was equipped with a silicon tip, which had a nominal radius of 5 to 10 nm to scan the surface topography.

The PL spectra for the hydroxy and methoxy-coated silicon nanoparticles are shown in Figure 2. The PL spectra for the Butyl coated particles were similar to the methoxy spectra and not presented. Although reaction conditions prior to the addition of a passivating reagent were identical, there is a significant difference in the PL. In all cases, the emission maxima demonstrate a strong dependence upon the excitation wavelength, but the methoxy and butyl-coated nanoparticles are blue-shifted with respect to the hydroxy-coated nanoparticles by more than 20 nm on average indicating a significant surface-state contribution to the nanoparticle PL.

The butyl derivative, Si$_x$(n-Bu)$_y$, was chosen as a control in the experiment. Since it lacks hydroxy group, it could not easily generate a silanone surface species. Any PL emissions observed from Si$_x$(n-Bu)$_y$ could therefore be attributed to a different mechanism. The methoxy derivative, Si$_x$(OCH$_3$)$_y$, was chosen as an intermediate between the hydroxy and butyl derivatives. Because it contains an Si–O bond, but not an O–H, it can be used in combination with Si$_x$(OH)$_y$ and Si$_x$(n-Bu)$_y$ to probe the contributions of Si–O and O–H bonds to the PL emissions of silicon nanoparticles. For reasons of solubility, the Si$_x$(OH)$_y$ nanoparticles were dissolved in water while the Si$_x$(CH$_3$)$_y$ and Si$_x$(n-Bu)$_y$ nanoparticles were dissolved in hexanes. Although a solvent effect could account for the observed differences between the PL emission spectra of Si$_x$(OH)$_y$ and the other two species, we have found no other reports in the literature for such a phenomenon with respect to silicon nanoparticles.

The major components contributing to the average PL lifetimes of the nanoparticles are quite short on the order of 0.3–7.3 ns, and the average lifetimes for the three species were different: 5.9 ns for Si$_x$(OH)$_y$, 6.4 ns for Si$_x$(OCH$_3$)$_y$, and 4.4 ns for

$Si_x(n\text{-}Bu)_y$. The short PL emission lifetimes of these species set them apart from porous silicon samples, and the differences in average lifetimes is indicative of surface state contributions. All of the samples were found to exhibit 2–4% of a long lifetime component of ~60 ns.

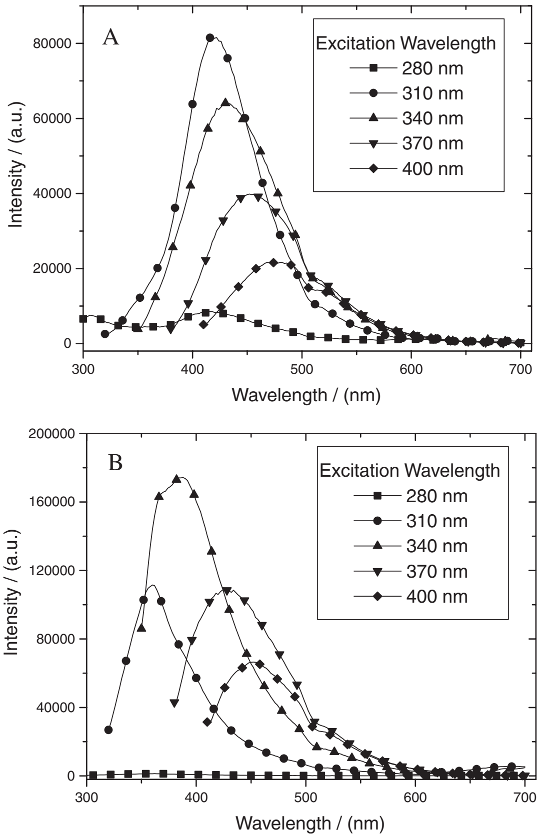

Figure 2. Fluorescence emission spectra for hydoxy (A) and methoxy (B) passivated silicon nanoparticles with varying excitation wavelength. Butyl passivated particles exhibit similar spectra as the methoxy (B) and were not presented.

Cross-sectional measurements and particle analysis were used to measure the size of the $Si_x(OH)_y$ nanoparticles yielding an average particle height of 1.08 nm (standard deviation 2.17 nm). Height was used for particle size determination since the diameter of the probe tip can widen the apparent width of the features to include the feature width plus the tip diameter.

Wilcoxon, et al.[11,12] have indicated that the blue emissions observed in silicon nanoparticles are solely due to direct electron-hole recombination, i.e., quantum confinement. If this were the case, however, we would not observe a blue-shift in the PL spectra of $Si_x(OCH_3)_y$ and $Si_x(n\text{-}Bu)_y$ with respect to $Si_x(OH)_y$. Tamura et al.[13] have also described a green/blue PL attributed to OH groups adsorbed on structural defects in the SiO_2 network and Kimura and Iwasaki[14,15] have also considered surface effects on the PL of silicon nanocolloids.

Based on our data (PL spectra, and the PL emission lifetimes of $Si_x(OH)_y$, $Si_x(OCH_3)_y$, and $Si_x(n\text{-}Bu)_y$), we conclude that there is a contribution to PL emissions from surface states. It can also be surmised that the differences in the PL spectra of species studied are due to surface modification, since the silicon cores are identical. The products formed in this reaction are similar to those produced by Kauzlarich[16–20] and Heath[21]; however, we were able to avoid highly exotic reagents and high pressures. In addition, our particles differ from those produced by Kauzlarich, in that they exhibit blue PL, while Kauzlarich reported red emissions similar to porous silicon.

Wilcoxon, et al.[11,12] reported a method for the synthesis of Si nanoparticles using micelles as reaction vessels. However, their method produces particles that are typically larger (2–10 nm) than those produced by our method. Their particles are also reported to be hydrogen-passivated. Nevertheless, similarities exist in the PL spectra.

Wolkin, et al.[8] have suggested that the PL emissions of small silicon nanoparticles ($d < 3$ nm) are dominated by surface states. In a comparison of passivated Si nanoparticles, the PL emissions of those exposed to oxygen were red-shifted with respect to hydrogen-passivated silicon nanoparticles. The shift occurred in a matter of minutes with the most extreme examples shifting from blue (400 nm) to red (650 nm) in a matter of seconds. This correlates well with the observations of Wilcoxon, but it cannot explain the blue photoluminescence observed from our particles.

This work was supported by the Research Council of the University of Hawaii. JHD thanks the NSF/REU program (Grant No. 651112). Mahalo to John Head and Randy Larsen.

References

1 L. T. Canham, *Appl. Phys. Lett.*, **57**, 1046 (1990).
2 M. Nirmal and L. Brus, *Acc. Chem. Res.*, **32**, 407 (1999).
3 W. L. Wilson, P. F. Szajowski, and L. E. Brus, *Science*, **262**, 1242 (1993).
4 L. E. Brus, *Abstr. Pap.-Am. Chem. Soc.*, **211**, 1 (1996).
5 L. Brus, *Jpn. J. Appl. Phys., Part 2*, **34**, 3 (1994).
6 J. P. Proot, C. Delerue, and G. Allan, *Appl. Phys. Lett.*, **61**, 1948 (1992).
7 F. Zhou and J. D. Head, *J. Phys. Chem. B*, **104**, 9981 (2000).
8 M. V. Wolkin, J. Jorne, and C. Delerue, *Phys. Rev. Lett.*, **82**, 197 (1999).
9 F. Koch, V. Petrova-Koch, and T. Muschlik, *J. Lumin.*, **57**, 271 (1993).
10 J. C. Croney, M. K. Helms, D. M. Jameson, and R. W. Larsen, *Biophys. J.*, **84**, 4135 (2003).
11 J. P. Wilcoxon and G. A. Samara, *Appl. Phys. Lett.*, **74**, 3164 (1999).
12 J. P. Wilcoxon, G. A. Samara, and P. N. Provencio, *Phys. Rev. B*, **60**, 2704 (1999).
13 H. Tamura, M. Ruckschleoss, T. Wirschem, and S. Veprek, *Appl. Phys. Lett.*, **65**, 1537 (1994).
14 K. Kimura and S. Iwasaki, *J. Appl. Phys.*, **83**, 1345 (1998).
15 S. Iwasaki and K. Kimura, *Mater. Res. Soc. Symp. Proc.*, **452**, 165 (1997).
16 C. S. Yang, S. M. Kauzlarich, H. W. H. Lee, and G. R. Delgado, *Abstr. Pap.-Am. Chem. Soc.*, **216**, 2 (1998).
17 R. A. Bley and S. M. Kauzlarich, *J. Am. Chem. Soc.*, **118**, 12461 (1996).
18 Nanoclusters: R. A. Bley and S. M. Kauzlarich, *NATO ASI Ser., High Technology*, **18**, 467 (1996).
19 Nanocrystals: G. R. Delgado, H. W. H. Lee, S. M. Kauzlarich, and R. A. Bley, *Mater. Res. Soc. Symp. Proc.*, **452**, 177 (1997).
20 B. R. Taylor, S. M. Kauzlarich, G. R. Delgado, and H. W. H. Lee, *Chem. Mater.*, **11**, 2493 (1999).
21 J. R. Heath, *Science*, **258**, 1131 (1992).