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# Tailorable, Visible Light Emission From Silicon Nanocrystals

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**Abstract**

Crystalline, size-selected Si nanocrystals in the size range 1.8 - 10 nm grown in inverse micellar cages exhibit highly structured optical absorption and photoluminescence (PL) across the visible range of the spectrum. The most intense PL for the smallest nanocrystals produced (~2 nm) was in the blue (~365 nm) with a radiative lifetime of ~1 ns and is attributed to direct recombination at zone center.

## DISCLAIMER

There is presently a large research effort aimed at exploring physical and chemical means to induce a useful level of visible photoluminescence (PL) from silicon (Si). The approaches include[1] porous silicon and quantum wires and dots. These two approaches, which may be mechanistically related via quantum confinement, have considerable potential but are poorly understood. Visible PL has been observed[1] from Si nanocrystals, or quantum dots, produced by a variety of techniques including aerosols,[2] colloids,[3] and ion implantation.[4] However, all of these techniques produce large distributions of cluster sizes resulting in broad, unstructured optical absorption and PL features which limit usefulness and make definitive interpretation of results difficult.

We have used inverse micelles as reaction vessels[5] to produce useful quantities of Si nanocrystals which have been remarkable in their size monodispersity, the sharpness and richness of their spectral features and tailorability of their properties. In what follows we describe the synthesis and some of the properties. Details of the work will be published elsewhere.[6] An anhydrous ionic salt (e.g., $SiX_4$, where X = Cl, Br, or I) is dissolved in the hydrophilic interior of a solution of micelles in octane with complete absence of water. The surfactants used, nonionic aliphatic polyethers or quaternary ammonium cationic surfactants, are dissolved in anhydrous tetrahydro furan (THF) and dried over Na metal. We next reduce Si(IV) to Si(0) using an anhydrous metal hydride, (usually 1M $LiAlH_4$ in THF). The reduction is rapid with vigorous bubbling of $H_2$ gas. One can determine the progress of the reaction by following the disappearance of the Si(IV) charge transfer absorption from the precursor solution. Nanocrystals with diameters between 1.8 and ~10 nm were produced. Spectroscopy and high pressure liquid chromatography (HPLC) with on-line absorbance, conductivity and refractive index detectors were used to demonstrate 100% reduction of the Si(IV) to the final Si(0)

nanocrystal form. The nanocrystals were characterized by high-resolution transmission electron microscopy.

The optical absorption spectra of our nanocrystals are much richer in spectral features than earlier nanocrystal spectra making it possible to assess the role of quantum confinement in Si. An example is shown in Fig. 1 for a sample of 2 nm nanocrystals. The figure also shows the spectrum of bulk Si where the spectral features reflect the details of the band structure shown in the inset in Fig. 2. Specifically, the long absorption tail between 1.2 and ~ 3 eV reflects the indirect nature of the bandgap. The sharp rise in absorption with increasing photon energy starting around 3.2 eV (380 nm) is associated with the direct transition at the $\Gamma$ point [$\Gamma_{25} \rightarrow \Gamma_{15}$] whose energy is 3.4 eV (365 nm), and the second sharp rise starting around 4 eV (320 nm) is associated with a second direct transition, most likely the $\Gamma_{25}$ - $\Gamma_{2'}$ transition whose energy is 4.2 eV (295 nm) or possibly the direct transition at X.

The close resemblance in the shape of the two spectra in Fig. 1 is remarkable indicating that the bulk-like character of the band structure of Si is preserved down to the $d \approx 2$ nm size (i.e. ~ 200 atoms or less). The results show clear evidence for quantum confinement; specifically, both direct transitions of the nanocrystals are blue shifted by about 0.4 eV compared to the bulk. This is larger than is predicted by model calculations.[9] The indirect absorption tail is also blue-shifted, and the gap appears to remain indirect. Because our samples are very dilute (~$10^{-4}$ molar) the signal-to-noise ratio for the sample in Fig. 1 is low for the low absorbances associated with the indirect transition. For other samples, however, the signal-to-noise was considerably higher and the spectrum less noisy in this region allowing meaningful analysis of the data. Analysis of results on 1.8 nm nanocrystals yielded an indirect bandgap of 2.2 ± 0.3 eV.[6] This result is in close agreement with the 2.06 eV obtained by Brus et al[2] on $SiO_2$-capped Si

nanocrystals estimated to have a Si core diameter of 1-2 nm. These measured quantum confinement effects are smaller than those predicted by effective mass theory but are comparable to results of some model calculations.[9,10]

Figure 2 shows the absorption spectrum of larger nanocrystals. In this case, an as-grown sample of 8-10 nm nanocrystals was used without size separation/purification through the HPLC column. The spectrum reveals a shoulder at ~370 nm (~3.4 eV) associated with the $\Gamma_{25}$ -$\Gamma_{15}$ direct transition followed by a relatively sharp increase in absorbance and double peaks at ~270 nm (4.6 eV) and 230 nm (5.4 eV). The resemblance of these features and closeness in energy to those in the spectrum of bulk Si in Fig. 1 are striking indicating that nanocrystals of this size (8-10 nm), which is comparable to the size of the excitonic diameter in the bulk, retain much of the character of bulk Si with little evidence for quantum confinement effects.

Room temperature PL results on an HPLC size-selected, purified 2 nm nanocrystals sample are shown in Fig. 3 which also shows the corresponding absorption spectrum. As noted in Fig. 1, the first absorption peak at 325 nm (3.81 eV) is attributed to the $\Gamma_{25}$ - $\Gamma_{15}$ direct gap, but blue shifted by ~0.4 eV due to quantum confinement. Excitation at 245 nm yields the PL spectrum shown. The major PL peak is centered at 365 nm (= 3.40 eV). We attributed this peak to direct *e* - *h* recombination at $\Gamma$. Consistent with this assignment we find that the radiative lifetime for these nanocrystals is ~1 ns, comparable to that for direct recombination in bulk GaAs. We have estimated the quantum efficiency (Q.E.) of the PL. The largest room Q.E. measured was 4% in acetonitrile solvent with no special surface treatment or annealing of the samples.

Figure 3 also shows the PL spectrum for a similar sample excited at 490 nm (2.53 eV) i.e., just above the indirect gap for this size. This PL peak is centered at 580 nm (2.14 eV), and it is tempting to attribute it to indirect bandgap recombination. However, we note that this PL is

identical to that observed on the much larger (d ≅ 8-10 nm) nanocrystals as shown in Fig. 2. We are thus led to conjecture that this PL is due to surface or defect recombination. The independence of this luminescence of crystal size may be relevant to semiempirical tight-binding and ab initio local density calculations by Allan et al[11] which demonstrated the stability of self-trapped excitons at the surface of Si nanocrystals. The excitons are obtained for dimer bonds passivated by, e.g., hydrogen or silicon oxide. Light emission from these trapped excitons is essentially independent of size. In this regard it is noted that since we use anhydrous metal hydrides as reducing agents in the synthesis, it is quite likely that our nanocrystals are terminated by hydrogen.

In summary, we have grown highly crystalline, size-selected Si crystals in the size range 1.8 - 10 nm. These nanocrystals retain bulk-like optical absorption and an indirect bandgap down to the smallest sizes produced (~1.8 nm containing about 150 Si atoms). The various electronic transitions are blue shifted by different amounts by quantum confinement. Room temperature PL from these nanocrystals was observed in the range 700 - 350 nm (1.8 - 3.5 eV), i.e., across the visible range. The most intense PL for the smallest (~2 nm) crystals was in the blue region of the spectrum (~365 nm) and is attributed to direct electron-hole recombination at Γ. The short radiative lifetime for this PL (~1 ns) is consistent with this assignment.

**Acknowledgement**

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## References


1. See, e.g, S. S. Iyer and Y. H. Xie, Science 260, 40 (1993) and references therein.
2. L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, S. Schuppler and P. H. Citrin, J. Am. Chem. Soc. 117, 2915 (1995).
3. S. Iwasaki, T. Ida and K. Kimura, Jap. J. Appl. Phys. 35, L551 (1996).
4. J. G. Zhu, C. W. White, J. D. Budai, S. P. Withrow, and Y. Chen, J. Appl. Phys. 78, 4386 (1995).
5. J. P. Wilcoxon, U.S. Patent #5, 147, 841, issued September 15, 1992.
6. J. P. Wilcoxon, G. A. Samara and P. N. Provencio, unpublished.
7. S. M. Sze, Physics of Semiconductor Devices, Wiley-Inferscience (New York, 1969) p. 54.
8. M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).
9. M. V. Rama Krishna and R. A. Friesner, J. Chem. Phys. 96, 873 (1992).
10. A. Zunger and L. W. Wang, Appl. Surf. Science 102, 350 (1996).
11. G. Allan, C. Delerue and M. Lannoo, Phys. Rev. Lett. 76, 2961 (1996).

## Figure Captions

Figure 1. The absorption spectrum of $d$ = 2 nm Si nanocrystals compared to that of bulk[7] Si. The inset shows a lattice fringe image of one of the crystals.

Figure 2. The extinction and PL (excitation at 490 nm) spectra for $d$ = 8-10 nm Si nanocrystals. The inset shows the band structure of bulk[8] Si.

Figure 3. Co-plot of the extinction and PL spectra (for two excitation wavelengths) for $d$ = 2 nm Si nanocrystals.

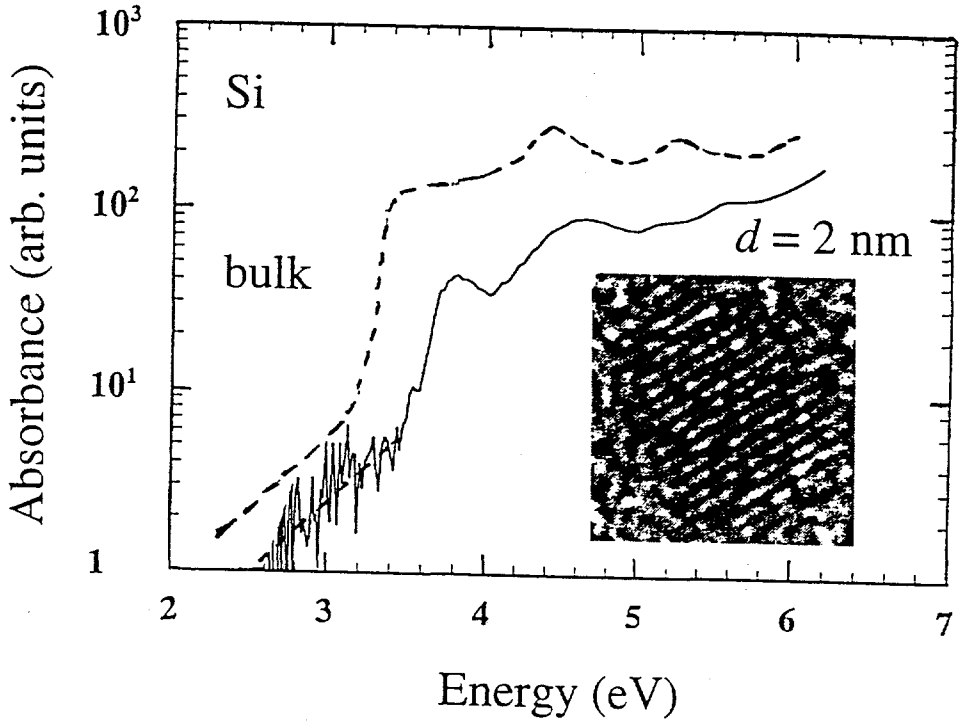


Figure 1
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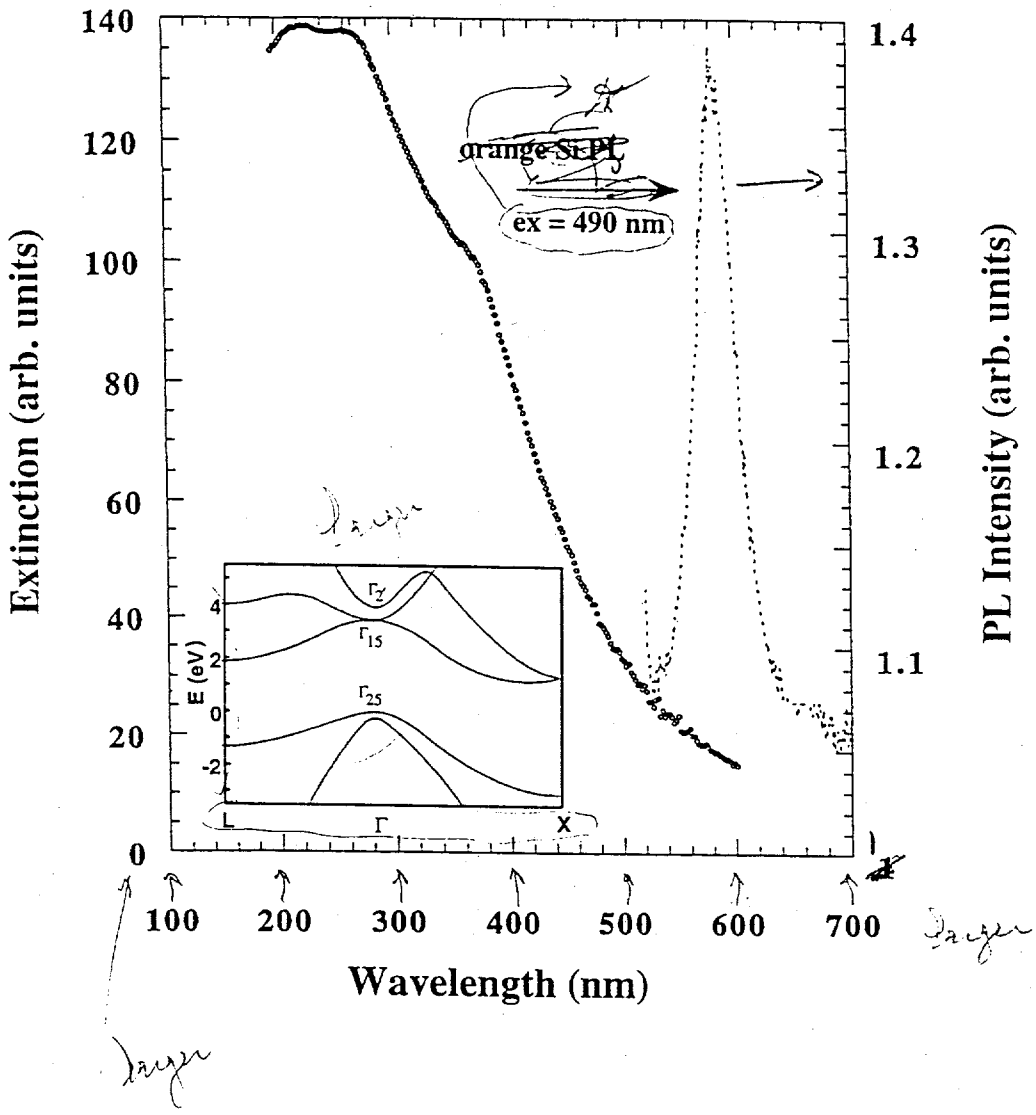


Figure 2
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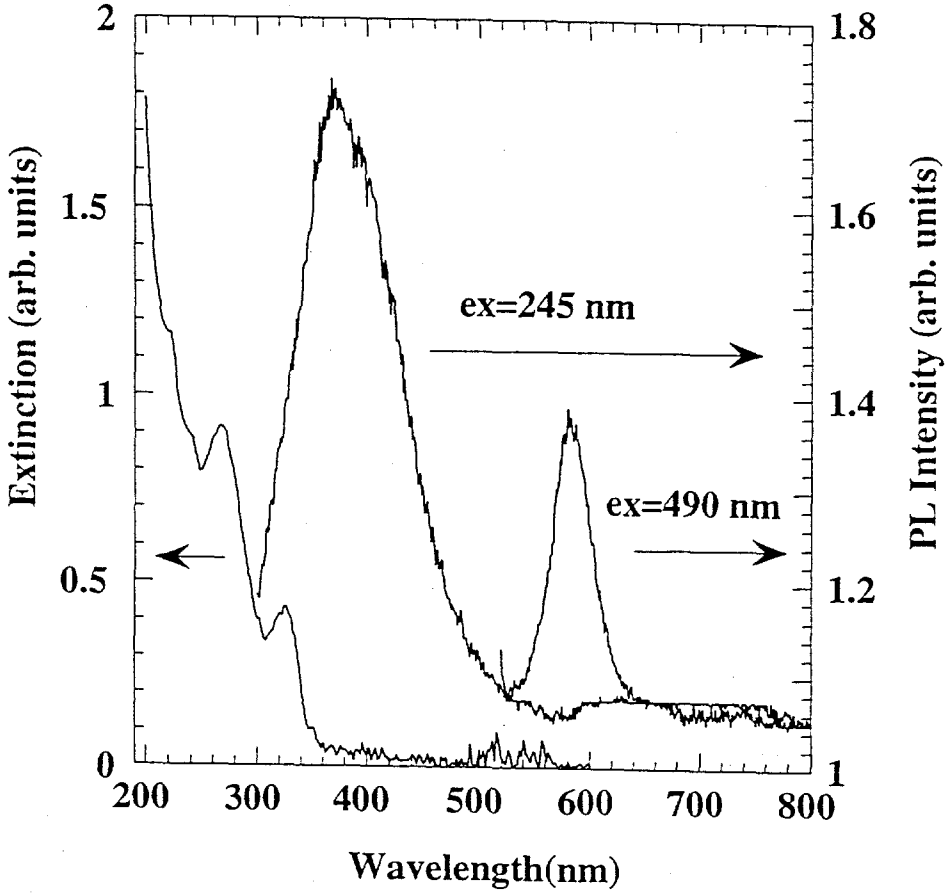


Figure 3
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