

Quantum Confinement in Size-Selected, Surface-Oxidized Silicon Nanocrystals

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The dynamics and spectroscopy of silicon nanocrystals that emit at visible wavelengths were analyzed. Size-selective precipitation and size-exclusion chromatography cleanly separate the silicon nanocrystals from larger crystallites and aggregates and provide direct evidence for quantum confinement in luminescence. Measured quantum yields are as high as 50 percent at low temperature, principally as a result of efficient oxide passivation. Despite a 0.9-eV shift of the band gap to higher energy, the nanocrystals behave fundamentally as indirect gap materials with low oscillator strength.

The study of nanometer-size effects in direct gap semiconductor crystallites (for example, CdSe) is an active field (1). In this size range, three-dimensional quantum confinement completely changes the optical and electronic properties of these nanocrystals compared to those of the bulk. The band gap increases with decreasing diameter, and the excited electronic states become discrete with high oscillator strength. However, there is little experimental understanding of the basic nature of confinement for indirect gap materials such as silicon (2), despite strong theoretical interest. Silicon confinement contains new physics as well as possible technological importance. Confinement could enhance band gap luminescence (3–5), which is forbidden in bulk material, possibly enough to enable laser or display applications. However, a quantitative characterization of this enhancement in real nanocrystals has not been explored.

To investigate how quantum confinement plays a role in the visible luminescence of porous Si (PS) films (6–11), it is necessary to understand confinement in well-characterized, size-separated, isolated nanocrystals. Data on this phenomenon will be key to correlating the effect of porosity on Si oscillator strength. An understanding of the quantum mechanics of carriers moving in nanocrystal Si within a few nanometers of an oxide interface is important to define the ultimate performance and possible limitations of very large scale integrated circuits.

Here we describe the analysis of the optical spectra and photophysics of size-selected Si nanocrystals and uncover clear evidence for quantum confinement. The data indicate that although these nanocrystals have high luminescence yields, they behave fundamentally as indirect band gap materials with low oscillator strengths.

We previously described an aerosol apparatus that makes an ethylene glycol (EG) colloid of 1- to 10-nm, surface-oxidized Si

single crystallites (12). The nanocrystal structure as shown by transmission electron microscopy (TEM), powder x-ray Bragg scattering, and infrared spectroscopy consists of a 12 to 15 Å oxide surface layer over an interior Si crystallite with a lattice constant unchanged within 0.25% of the bulk. These high-quality passivated nanocrystals exhibit visible luminescence, similar in spectrum, quantum yield, and 293 K lifetime to that observed for PS. The broad width of the emission presumably reflects the size distribution in these colloids as well as in PS.

Two methods to separate sizes physically are used: size-selective precipitation (SSP) and size-exclusion chromatography [high-performance liquid chromatography (HPLC)]. In SSP, as developed for organically capped CdSe nanocrystals (13), the ability of a solvent to dissolve particles is decreased, by the addition of a miscible "nonsolvent," to the point of particle agglomeration. The larger particles agglomerate first, and with each other, apparently as a result of their greater van der Waals attraction for each other. An agglomerated fraction rich in the larger particles is precipitated under centrifugation, leaving smaller solvated particles. The process is reversible, in that the physisorbed agglomeration can be redissolved in the initial solvent.

The addition of tetrahydrofuran (THF) to the EG colloid gives such reversible SSP. The broad emission and corresponding HPLC spectrum for an initial colloid are shown in Fig. 1. The HPLC spectrum shows a peak due to single crystallites at 8.9 min, a dimer peak at 8.1 min, and a tail of larger aggregates to smaller times. (The dimer and aggregates here are permanently attached by surface bonding at high temperature in the aerosol.) The solution was precipitated with 15-fold added THF. Nanocrystals in the supernatant, eluting as monomers at 9.1 min in HPLC, exhibit the higher energy part of the original luminescence. The precipitate, redissolved in EG, shows a lower energy emission and an HPLC spectrum depleted in smaller mono-

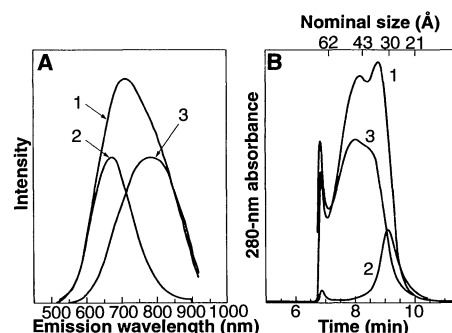


Fig. 1. (A) Spectrally corrected luminescence spectra (350-nm excitation) in organic glass (20 K), made with 5% glycerol in EG. Traces: 1, initial colloid complete distribution; 2, supernatant; 3, redissolved agglomerate. (B) Corresponding HPLC on Hypersil SAS (London) columns. The spike at 6.7 min is the column large-size exclusion limit and does not indicate a specific nanocrystal size. The approximate logarithmic size calibration is made by comparison with equivalent hard sphere diameters of sulfonated polystyrene standards on a Zorbex 300 (Mac-Mod) column. Trace numbers as in (A).

mers. Its luminescence survives the precipitation-redissolution procedure. Precipitation with THF is a practical method to separate cleanly only small monomers, a tiny fraction of the total mass, from a large distribution.

Direct HPLC fraction collection from the initial colloid, albeit more tedious and yielding less mass than the precipitation method, separates larger HPLC fractions from each other more cleanly. The smaller two HPLC fractions do produce the higher energy emission, with narrow widths, in the lumines-

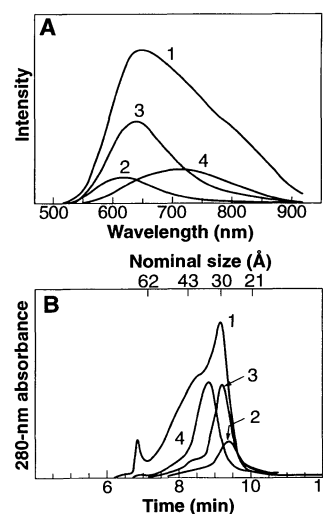


Fig. 2. (A) Luminescence and (B) HPLC comparison for the complete distribution (1) and for collected fractions (2 to 4). A tailing contribution of molecular luminescence peaking in the blue, made by oxidation of the EG solvent, has been subtracted from the HPLC fraction luminescence.

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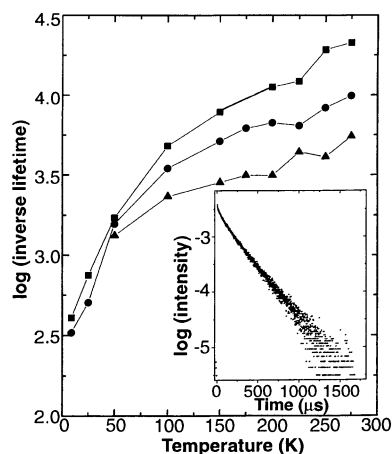


Fig. 3. Plot of the log of the inverse of the best single exponential lifetime versus temperature. Emission wavelengths: squares, 630 nm; circles, 730 nm; triangles, 830 nm. The sample was excited at 355 nm at 540 Hz with a 5-ps pulse, and the emission was recorded and averaged in analog fashion with a photomultiplier. Inset: typical luminescence decay at 730 nm and 150 K.

cence of the initial colloid (Fig. 2). The next fraction is shifted to lower energy and has a larger width because, as with larger HPLC fractions, it has both large monomers and aggregates of smaller particles.

These two separation experiments directly prove a basic tenet of the Si quantum confinement hypothesis: smaller particles show a greater luminescence shift to higher energy. This result is often inferred in PS because of the luminescence dependence on porosity and progressive oxidation.

The absolute emission quantum yields (QY) of initial colloids at 300 K are typi-

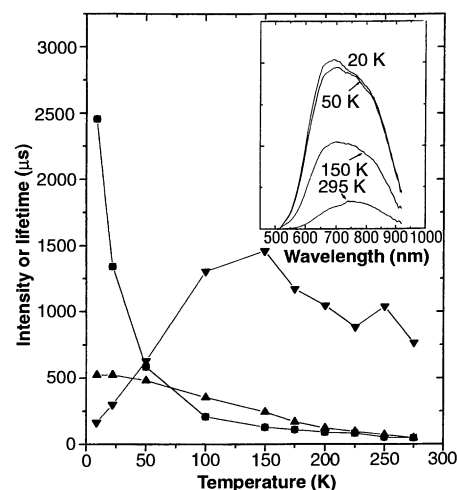


Fig. 4. Average lifetime at 630 nm (squares), continuous wave luminescence intensity (triangles), and intensity or lifetime (inverted triangles) versus temperature. The intensity is scaled to the lifetime to give coincident 275 K points. Inset: luminescence.

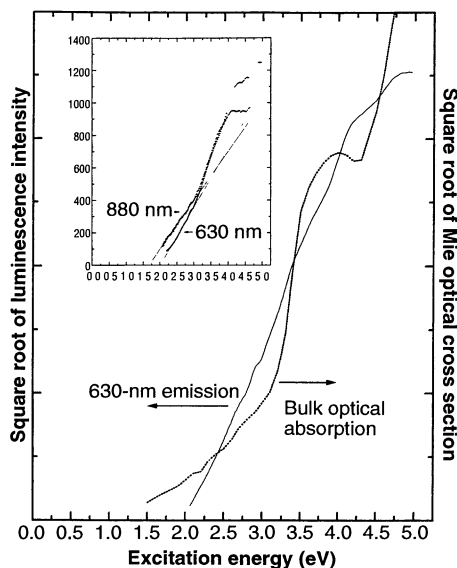


Fig. 5. Left scale: square root of 630-nm emission (20 K) intensity versus excitation energy, both at a 2-nm resolution, for an organic glass sample optically thin and clear. (Above 4.5 eV, the curve begins to saturate as the optical density approaches 1.0.) Right scale: square root of Mie optical extinction cross section for a sphere of bulk Si. Inset: comparison of 630- and 880-nm excitation spectra.

cally 4 to 5% (14). In Fig. 1, the supernatant has a QY of 5.6% (293 K), increasing to 50% below 50 K. For the redissolved precipitate, the values are 4.6% (293 K) and 20% below 50 K. It is generally observed that the net increase in emission at low temperature is greater for smaller crystallites. Time-resolved emission data appear in Fig. 3. At one emission wavelength, the decay is moderately multiexponential. We attribute this range to the distributions of shapes and decay dynamics for a given "size" and emission wavelength. Best single exponential fits have been made to provide a simple measure of unimolecular decay. Individual average lifetimes τ at a given wavelength and temperature are insensitive to the sample's size distribution and emission spectrum.

The 630-nm average lifetime increases from 50 μ s (293 K) to about 2.5 ms (20 K). The luminescence intensity I also increases monotonically to lower temperature but not in the same proportion as the lifetime τ (Fig. 4). If the nanocrystal electron hole pair decays unimolecularly with competing radiative Γ_r and nonradiative Γ_{nr} rates, then $\tau^{-1} = \Gamma_r + \Gamma_{nr}$ and $QY = \Gamma_r / (\Gamma_r + \Gamma_{nr})$. Below 50 K, the intensity is essentially constant while the lifetime continues to lengthen. This relation can be explained if the radiative decay dominates the nonradiative decay and is temperature dependent. That is, below 50 K the lifetime is purely radiative, with $QY = 100\%$ for emission. The ratio I/τ in Fig. 4 gives the temper-

ature dependence of Γ_r , which increases from about $4 \times 10^2 \text{ s}^{-1}$ at 20 K to a broad maximum of $2 \times 10^3 \text{ s}^{-1}$ near 200 K. The high, but less than 1.0, measured absolute QY below 50 K suggests that a fraction of the crystallites are "dark"—that is, have a QY of 0. This difference in QY values can occur, for example, if that fraction has some nonradiative structural defect, whereas the emitting fraction is structurally perfect.

Figure 5 shows photoluminescence excitation spectra compared to the expected absorption spectrum of bulk Si, in small particle form as given by Mie theory (15). The bulk curve shows indirect gap, square-root extrapolation to the bulk 1.1-eV band gap. The 630-nm emission curve at low energy shows indirect gap, square-root extrapolation to a $2.0 \pm 0.03 \text{ eV}$ gap, corresponding to the 630-nm emission energy (16). In addition, the 630-nm spectrum shows extensively broadened absorption—essentially indirect gap behavior—in the 3- to 4-eV region of the bulk Si 3.4-eV direct gap (16). This latter behavior is different from the appearance of discrete, quantized states as observed in direct gap, II-VI nanocrystals (1). In the 880-nm excitation spectra (inset, Fig. 5), the direct gap 3.4-eV feature is partially developed.

The extremely small value of Γ_r for the 630-nm emitter and the 2- to 3-eV excitation spectra show that Si nanocrystals emitting at 630 nm simply behave as an indirect gap material with a band gap 0.9 eV larger than that of the bulk (17). At the present resolution, there is no Stokes shift between band gap and luminescence; the particle appears to luminesce from the quantized band gap state. The observed Γ_r temperature dependence has been predicted in models of spin (18) or valley-orbit (17) fine structure. Emission quantum yields are high principally because the nanocrystal oxide passivation is extremely efficient.

The similarity of our lifetime and spectroscopic data to those reported for high-quality PS films is strong evidence that single crystallite quantum confinement is an important contributor to the PS emission mechanism. Porous Si luminescence excitation spectra show momentum-conserving transverse optical (TO) phonon structure, suggesting that the emitting species is an indirect gap, crystalline Si fragment (18).

In both PS (9) and nanocrystals, radiationless deactivation shortens the lifetime and lowers the QY value at 293 K. Our Γ_{nr} Arrhenius plots at 630 and 730 nm show similar, small activation energies of about 27 meV, with the preexponential factor being two times larger at 630 nm than at 730 nm. The excitation energy and temperature dependence do not agree with those calculated for multi-phonon radiationless

trapping of the photoexcited electron on a localized Si dangling bond in the band gap (17). However, these data are consistent with simple models of carrier escape by tunneling, as proposed by Vial *et al.* for PS (9). Our observation of similar lifetimes in isolated nanocrystals and in aggregates reveals that tunneling to larger crystallites does not control the dynamics. Surface silanol groups and adsorbed water may affect the dynamics, because, the luminescence of both nanocrystals (12) and PS (19) is strong at acid pH and quenched at neutral and basic pH.

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Real-Time Observation of the Vibration of a Single Adsorbed Molecule

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The newly developed femtosecond field emission camera was used to observe the time dependence of field emission through a single copper phthalocyanine molecule adsorbed on a tungsten tip. In many of the individual 212-picosecond-long recordings, the field emission was found to oscillate with a frequency between 5×10^{10} and 20×10^{10} hertz. The oscillations, which were not observed from a bare tip, are believed to arise from the vibration of a single molecule with respect to the surface. Numerical simulations confirmed the statistical significance of the data.

For the investigation of the atomic and molecular motions that govern chemical and physical processes, the ideal measurement would observe continuously a single molecule or collision on the time scale of atomic motion. Such a measurement would, however, require both the sensitivity to observe a single molecule without strongly perturbing its motion and a time resolution on the time scale of a molecular vibration, between 10^{-14} and 10^{-11} s. Although single atoms and molecules may now be routinely imaged, the fast laser

techniques used for probing molecular dynamics (1) are, generally, too insensitive for the observation of individual molecules. Repeated pumping techniques may be used, however (2). Because optical transitions strongly perturb a molecule by changing its electronic state, laser methods cannot give continuous measurements on a single molecule. These problems can be overcome by the femtosecond field emission camera (FFEC) (3, 4), an instrument we have developed to continuously record the motion of individual atoms and molecules with a temporal resolution as fast as 10^{-14} s. Here, we report the continuous observation of the dynamics of a single molecule, with the recording of the vibrational motion of single copper phthalocyanine (CuPc) mol-

ecules adsorbed on a tungsten tip.

In a strong electric field, the width of the potential barrier that normally traps electrons in a metal can be reduced sufficiently to allow field emission (FE), the quantum mechanical tunneling of electrons into vacuum (Fig. 1). In the FFEC, FE is induced by the application of ≈ -1000 V to a metal tip, which concentrates the electric field (F) at the tip surface to $\approx 1 \text{ V } \text{\AA}^{-1}$ (3). If the tip is very sharp, the FE can be confined to a subnanometer high-field region at the apex and may be as large as 10^{-5} A (5) or $10^{14} \text{ e}^- \text{ s}^{-1}$. Thus, many electrons will be emitted during the vibrational period of heavier atoms and molecules that may be present on the surface. The intensity of the FE depends strongly on the position of any adsorbates, which change the barrier height and contribute localized electronic states. Thus, a molecular vibrational motion on the tip will cause an FE oscillation, which we resolve by focusing the emitted electrons into a beam that is electrostatically swept across an efficient detector (Fig. 2). The spatial variation of the detected electron intensity records the temporal variation of the FE. Because the metal tip is an ideal point source for focusing and the time-of-flight spread of the electrons in the strong tip field is very small, a resolution of 10^{-14} s is achievable (3). Unlike laser techniques, the FFEC is limited to observing dynamics on sharp tips.

For our initial study of single-molecule dynamics, we chose the vibration of a large rigid molecule, CuPc (Fig. 3A), expecting that its large mass and vibrational amplitude would give a slow vibration with respect to the surface. The components of the electric polarizability of CuPc parallel ($\alpha_{\parallel}$) and perpendicular ($\alpha_{\perp}$) to the molecular plane are ≈ 100 and $\approx 45 \text{ \AA}^3$ (6), respectively. In a strong field (F), the polarization potential for the molecule's pivoting down by an angle θ (Fig. 3B) from perpendicular toward parallel to the surface is $\frac{1}{2}F^2(\alpha_{\parallel} - \alpha_{\perp})\sin^2\theta$, which at $F = 1 \text{ V } \text{\AA}^{-1}$ favors, by 2 eV, the perpendicular over the parallel orientation. For this pivoting motion, the moment of inertia (I_L) is ≈ 5600 atomic mass units $\cdot \text{\AA}^2$, giving a vibrational frequency of 15×10^{10} Hz. If this vibration were excited to an energy of kT (where T is the temperature and k is the Boltzmann constant), at $T = 1000$ K the end of the molecule would move $7 \text{ \AA}$, large enough to give a sizable change in the FE. The field-free adsorption potential of the molecule would ordinarily favor θ near $\pi/2$, which counteracts the polarizability potential and thereby reduces the frequency. These estimates show that of the many vibrational modes, at least one should be resolvable within our present 1- to 2-ps resolution. Other adsorption geometries might have

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