A Tale of Seemingly “Identical” Silicon Quantum Dot Families: Structural Insight into Silicon Quantum Dot Photoluminescence

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Two quantum dots, both alike in composition, but differing in structure, where we lay our scene. From broader classes, to bring deeper understanding, to the crystalline core that drives the quantum dot's sheen. In this contribution we examine two families of silicon quantum dots (SiQDs) that bring to mind the Capulets and the Montagues in Shakespeare's Romeo and Juliet because of their stark similarities and differences. SiQDs are highly luminescent, heavy-metal-free and based upon earth-abundant elements. As such, they have attracted attention for far reaching applications ranging from biological imaging to luminescent solar concentrators to light-emitting diodes that rely on their size-dependent optical response. Unfortunately, correlating SiQD “size” to their photoluminescence maximum is often challenging. Herein, we provide essential structural insight into the correlation of SiQD dimension and PL maximum through a direct comparison of samples that exhibit statistically identical physical dimensions (d_{TEM}) and chemical compositions, but different crystallite size (d_{XRD}) and PL maxima. We then expand the scope of this investigation and systematically compare groupings of SiQDs: one in which the d_{XRD} and d_{TEM} agree and one where $d_{\text{XRD}} < d_{\text{TEM}}$. This latter comparison clearly shows d_{XRD} better predicts SiQD optical response when using the well-established effective mass approximation.

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1 A Tale of Seemingly “Identical” Silicon Quantum
2 Dot Families: Structural Insight into Silicon
3 Quantum Dot Photoluminescence.

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Abstract

Two quantum dots, both alike in composition, but differing in structure, where we lay our scene. From broader classes, to bring deeper understanding, to the crystalline core that drives the quantum dot's sheen. In this contribution we examine two families of silicon quantum dots (SiQDs) that bring to mind the Capulets and the Montagues in Shakespeare's Romeo and Juliet because of their stark similarities and differences. SiQDs are highly luminescent, heavy-metal-free and based upon earth-abundant elements. As such, they have attracted attention for far reaching applications ranging from biological imaging to luminescent solar concentrators to light-emitting diodes that rely on their size-dependent optical response. Unfortunately, correlating SiQD "size" to their photoluminescence maximum is often challenging. Herein, we provide essential structural insight into the correlation of SiQD dimension and PL maximum through a direct comparison of samples that exhibit statistically identical physical dimensions (d_{TEM}) and chemical compositions, but different crystallite size (d_{XRD}) and PL maxima. We then expand the scope of this investigation and systematically compare groupings of SiQDs: one in which the d_{XRD} and d_{TEM} agree and one where $d_{\text{XRD}} < d_{\text{TEM}}$. This latter comparison clearly shows d_{XRD} better predicts SiQD optical response when using the well-established effective mass approximation.

KEYWORDS: Quantum dots; Silicon nanocrystals; Silicon; Luminescence; Lifetimes

1 Semiconductor nanoparticles (quantum dots; QDs) are fascinating structures that exhibit size- and
2 shape-dependent optoelectronic properties. Prototypical CdSe@ZnSQDs have been widely
3 studied, are generally well understood, and many reports of prototype applications have appeared;
4 in fact, InP-based QDs are revolutionizing consumer electronics as active systems in QLED-TV™
5 displays.^{1,2} Unfortunately, legislation limits use of heavy metals in consumer products and curtails
6 widespread implementation of many QDs;³ furthermore, alternative QD materials such as InP
7 contain costly non-earth abundant elements and exhibit ‘*clear evidence of carcinogenic activity*’
8 in animal models.⁴ In this context, QDs comprised of abundant, non-toxic elements must be
9 prepared, manipulated, understood, and deployed.⁵

10 Silicon-based QDs are attractive for many applications because they are heavy metal-free,
11 comprised of earth-abundant elements, and biologically compatible. In this context, a variety of
12 methods have been developed to prepare and functionalize these promising materials⁶⁻¹¹ and
13 prototype applications including light-emitting diodes,¹² luminescent solar concentrators
14 (LSCs),^{13, 14} biological imaging agents,^{15, 16} sensors,^{17, 18} and lithium ion battery anodes^{19, 20} have
15 appeared. Many of these uses rely on the unique tailorable optical properties of SiQDs; for
16 example, LSCs take advantage of the large Stokes shift (i.e., the energy difference between
17 excitation and photoluminescence maxima) that arises in part because of the indirect nature of the
18 Si band gap.^{13, 14} Despite impressive advances including spectral tuning throughout the full visible
19 region and photoluminescence (PL) quantum yields rivaling that of compound semiconductor
20 QDs, challenges remain;²¹⁻²⁵ paramount among these is the limited predictability of the PL
21 maximum size dependence that appears throughout the literature.²⁶

22 The origin of SiQD PL is clearly complex;²⁷⁻³² for convenience, SiQDs can be categorized into
23 two broad groupings based upon PL properties and associated excited-state lifetimes.²⁸ The first

1 involves SiQDs exhibiting PL characterized by short-lived excited states (i.e., τ = nanoseconds);
2 in these cases the PL maximum that often appears in the blue spectral region (i.e., 390-500 nm), is
3 dependent on excitation wavelength, and largely independent of particle size. Such behavior has
4 previously been attributed to surface-state mediated relaxation processes involving heteroatom
5 containing species (e.g., N, Cl, O, etc.).^{21, 28, 29, 33-35} Other SiQDs show PL throughout the
6 yellow/orange to near-IR regions with long-lived excited states (i.e., τ = microseconds) consistent
7 with the indirect band gap of silicon; the proposal that this luminescence arises from band gap-
8 based processes is further supported as the PL maximum generally *trends* with particle size and is
9 broadly consistent with carrier quantum confinement.^{25, 29, 33, 36}

10 A comprehensive review of SiQDs exhibiting microsecond lifetimes has appeared and a detailed
11 discussion is beyond the scope of the present contribution.³³ However, for context it is useful to
12 consider that while the PL response of these QDs has been attributed to carrier confinement, the
13 PL maximum of seemingly identical particles can vary greatly and its energy frequently does not
14 correlate well with effective mass approximation (EMA) predictions (Figure 1).^{26, 37-39} Numerous
15 explanations for these deviations have appeared; broad particle size distributions,⁴⁰ among
16 others.^{38, 41} As such, alternative strategies (e.g., empirical pseudopotential approximation (linear
17 combination of atomic orbitals),^{42, 43} empirical tight binding band theory,^{44, 45} ab-initio local
18 density approximation)⁴⁶ for correlating PL maximum to SiQD dimensions have been proposed.^{26,}
19 ^{38, 39, 42}

Figure 1: A summary representative literature data showing the relationship between SiQD peak PL emission and particle dimension.^{37, 39, 40, 47-51} Predicted relationships obtained using the effective mass approximation⁵² (solid line; $E_g(r) = 1.12 + 3.77/r^2$) and linear combination of atomic orbitals^{26, 42} (dashed line; $E_g(r) = 1.12 + 3.77/r^{1.39}$) are shown for comparison.

It is well-established that many challenges (as well as intriguing properties) associated with preparing and exploiting SiQDs arise from the extended covalent bonding manifested within the Si diamond-like crystal structure. While amorphous surface layers have been implicated in ultra-fast SiQD photoluminescence,⁵³⁻⁵⁶ the uniformity of the SiQD internal structure has largely been overlooked.⁵⁷ We previously demonstrated the Si core of *large* ($d_{\text{TEM}} \sim 9 - 64$ nm) SiQDs exhibits a radially graded structure consisting of a highly disordered surface that transitions to a crystalline core; in contrast, the structure of *small* SiQDs ($d_{\text{TEM}} \sim 3$ nm) is dominated by disorder and they only possess very small crystallite regions (i.e., $d_{\text{XRD}} \sim 1.2$ nm).⁵⁷ Knowing the electronic structure of bulk silicon strongly depends on crystallinity (e.g., amorphous Si $E_{g,\text{optical}} = 1.6-1.7$ eV; bulk crystalline Si $E_g = 1.1$ eV),⁵⁸ we endeavored to explore the impact of internal structure on SiQD optical response. Herein, we describe an evaluation of the size dependence of SiQD PL maximum

and excited-state lifetime while systematically varying particle and crystallite sizes as determined by transmission electron microscopy (TEM) and X-ray powder diffraction (XRD), respectively.

Results and discussion

To probe the impact of an internally graded crystal structure on SiQD optical properties it was necessary to predictably prepare QDs with the same *particle* (determined using TEM; d_{TEM}) and different *crystallite* (determined using XRD, d_{XRD}) sizes while maintaining all other contributing factors (e.g., surface chemistry/oxidation) the same. Drawing on our intimate knowledge of the hydrogen silsesquioxane (HSQ) -based procedure and the structure of the resulting SiQDs,^{57, 59-61} we prepared two different composites consisting of nanocrystalline silicon domains encased within an SiO₂-like matrix via HSQ reductive thermal processing at 1200 and 1300 °C. Evaluation of the Si domain sizes using TEM was precluded by the oxide matrix however, consistent with expectation,^{37, 60} XRD revealed reflections attributable to nanocrystalline Si domains and that, as expected, larger domains are obtained for products processed at higher-T (i.e., $d_{1200} \sim 3.7$ nm; $d_{1300} \sim 6.1$ nm).

The nanocrystalline domains were liberated as freestanding SiQDs upon etching with alcoholic aqueous hydrofluoric acid. Drawing on the expectation that amorphous/disordered silicon is more susceptible to this etching process, careful definition of the etching time allowed isolation of SiQDs from the two composites that possess statistically identical d_{TEM} but different d_{XRD} dimensions (i.e., different thicknesses of disordered Si shells). Following isolation, the SiQD surfaces were functionalized with dodecyl- moieties (confirmed to be identical at the sensitivity of the FTIR technique; Figure S1) using size independent radical-induced hydrosilylation to render them solution processable and minimize reactions (e.g., oxidation) that are known to impact optical

response.¹¹ For the following discussion, SiQDs resulting from composites prepared at 1200 and 1300 °C will be referred to as 1200-SiQD and 1300-SiQD, respectively.

Prior to evaluating the size and optical properties of the SiQDs, it is essential to confirm the degree and speciation of surface oxidation is consistent across the samples because these factors can also impact SiQD PL response.^{29, 62} To do so, the Si 2p XP spectra of the 1200- and 1300-SiQDs (Figure 2a) were deconvoluted into component spin-orbit couples (Si 2p_{1/2} and 2p_{3/2}) corresponding to Si(0) (i.e., orange), Si(I) (i.e., green), and Si(II) (i.e., blue).⁵⁷ Integrating the total area of the Si (I) and Si(II) components and comparing it to the integrated area of the Si(0) component, provided an estimation of the ratio of oxidized surface silicon species to elemental silicon. For the present samples, the total integrated signal of the Si(I) and Si(II) components corresponds to 21% for 1300-SiQDs and 27% for 1200-SiQDs of the total Si 2p signal intensity. This, combined with the reasonable assumption that the degree of surface functionalization (i.e., surface density of Si-C bonds) is equivalent for both samples indicates 1200- and 1300-SiQDs have similar amounts of oxidation. Furthermore, closer inspection of the O and Si spectral envelopes indicates the speciation of the oxides is near identical. In this context, we expect the influence (if any) of surface oxide species on the optical properties of 1200- and 1300-SiQDs to be equivalent.

Turning to the evaluation of QD particle and crystallite sizes, bright-field TEM analyses of the liberated dodecyl-functionalized particles afforded d_{TEM} of 5.3 ± 1.4 and 5.4 ± 1.1 nm (Figure 2b) for the 1200- and 1300-SiQDs, respectively, and are statistically similar to a 95 % confidence interval. To complement the TEM analyses, crystallite sizes of the identical samples were determined using XRD. Diffraction data were fit to the NIST Si line shape standard (640f) as an “infinite” crystallite reference to account for instrumental broadening and line shape. Having

1 accounted for instrumental factors, Gaussian and Lorentzian peak shape parameters, with the
2 assumption that atomic displacement parameters and crystallographic site deficiencies do not play
3 a role, only size and strain contributions to line broadening remain and can be qualitatively
4 accounted for based on their diffraction angle dependence.^{57, 63} In contrast to the d_{TEM} which were
5 statistically identical, the d_{XRD} (i.e., crystallite sizes) determined from diffraction data (Figures 2e
6 and 2f) were 3.2 ± 1.22 and 4.7 ± 0.4 nm for 1200-SiQDs and 1300-SiQDs, respectively. A
7 straightforward comparison of the d_{TEM} and d_{XRD} clearly shows that, despite having the same
8 physical dimensions, 1200-SiQDs have a smaller crystallite size (and by extension thicker
9 disordered Si shell). This is further supported by high annular angle dark field scanning
10 transmission electron microscopy (HAADF-STEM) that shows thicker disordered layers on 1200-
11 SiQDs (1.7 nm 1200-SiQDs vs. 1.0 nm for 1300-SiQDs; Figure S2 and S3).

Figure 2: a) Si 2p XP spectrum with deconvolution/fitting of the data for 1200-SiQDs and 1300-SiQDs. Fitting peaks are shown as Si 2p_{1/2} and 2p_{3/2} components corresponding to Si(0) (i.e., orange), Si(I) (i.e., green), and Si(II) (i.e., blue). The black trace is the experimental spectrum and the red dashed line represents the overall fitting envelope. b) TEM image of 1200-SiQDs and 1300-SiQDs inset: average shifted histogram with the average size and the distribution width. c) XRD data for 1200-SiQDs and 1300-SiQDs showing experimental powder pattern (black) with fitting (red for 1300-SiQDs and purple for 1200-SiQDs) and residuals (light grey).

Figure 3: Comparing a) the photoluminescence emission of 1300-SiQDs (purple) and 1200-SiQDs (red) as well as b) the luminescence lifetimes of 1300-SiQDs (purple fit) and 1200-SiQDs (red fit). Luminescence lifetimes were fit to a stretched exponential function and the mean lifetimes were then calculated as described in the supplemental information.⁶⁴ The fitting parameters are reported in Table S2.

Having shown 1200-SiQDs and 1300-SiQDs exhibit near-identical physical size (i.e., d_{TEM}) as well as composition (i.e., degree of oxidation, oxidation speciation, surface functionalization) and they only differ in crystallite size (i.e., d_{XRD}), we endeavored to evaluate the impact of the disordered Si shell on the 1200-SiQD optical properties. The PL spectra of SiQD toluene solutions (Fig. 3a) were evaluated using the 351 and 364 nm lines of an Ar ion laser and show maxima of

837 and 955 nm for 1200-SiQDs and 1300-SiQDs, respectively. The marked red-shift in PL maximum with increased d_{XRD} indicates the dimensions of the nanocrystalline domain dominate SiQD PL and band gap; there is little (or no) indication of a contribution from the disordered surface silicon species to these properties. This observation is also consistent with the amorphous silicon shell having a wider band gap than the crystalline core providing a core@shell structure similar to that of more commonly studied CdSe@ZnTe systems (i.e., Type II QDs).⁶⁵ Contrary to the CdSe@ZnTe QD case, in which the ZnTe shell forms epitaxially on the CdSe to reduce interfacial dark defects and increase PL QYs, the interface between the crystalline and amorphous components of the present SiQDs can reasonably be expected to be ill-defined.^{57, 66, 67} As such, there is no obvious trend in the present PL QY data (Figure S5). We also note that 1300-SiQDs exhibit longer PL lifetimes (i.e., 547 μs for 1300-SiQDs vs. 267 μs for 1200-SiQDs), which are often noted for larger SiQDs.⁴⁸

To further explore the broader scope of the relationship between SiQD optical properties with d_{XRD} , SiQD/SiO₂ composites were prepared via reductive thermal processing of HSQ at 1100, 1200, and 1300 °C; it is well-established that larger Si nanodomains form at higher temperatures.^{37, 60} SiQDs were liberated upon alcoholic HF etching for pre-determined times (See: Table S1) and surface functionalized with Si-C tethered 1-dodecyl surface groups via AIBN radical-initiated hydrosilylation. Subsequently, the d_{TEM} , d_{XRD} , as well as PL properties were evaluated/compared. This method yielded SiQDs with varying disordered layer thicknesses, where in all cases the d_{TEM} is larger than d_{XRD} (Figure S6). When examining the lifetimes of all of the SiQDs here studied as a function of PL energy, an obvious trend was observed where $\frac{1}{\tau_{\text{SE}}} = A * e^{E/E_0}$ (Figure S7). This trend is consistent across literature,^{68, 69} is independent of synthetic method and has been implicated with the indirect band gap of silicon.⁷⁰

Figure 4: A comparison of the relationship between PL energy (c and d) and lifetimes (e and f) with d_{TEM} (blue squares) and d_{XRD} (red circles) for SiQDs with a thick amorphous layer (>1 nm; a, c, e) and a thin amorphous layer (<0.4 nm; b, d, f). The solid and dashed black lines in c) and d) represent the EMA and LCAO as in Figure 1. The solid black line in e) and f) is a fitting from all of the d_{XRD} vs. lifetime data according to $(\frac{1}{\tau_{\text{SE}}} = A(\frac{1}{d_{\text{XRD}}})^3 + C)$, with A and C being fit parameters.

To better illustrate/understand the relationship between SiQD dimensions and optical properties, we categorized the present data into two groupings. **1.** Samples in which the d_{TEM} is substantially larger (i.e., $d_{\text{TEM}} - d_{\text{XRD}} > 2$ nm) than d_{XRD} . (These particles possess comparatively thick amorphous/disordered Si layers on their surfaces.) **2.** Samples for which d_{TEM} and d_{XRD} are similar (i.e., $d_{\text{TEM}} - d_{\text{XRD}} < 0.8$ nm). (These particles possess a thin amorphous/disordered Si layer on their

surfaces.) Data were subsequently plotted and compared with the predictions of the effective mass approximation (EMA; Figures 4a and b).

Consistent with our previous observations (see above), there is a clear correlation between d_{XRD} and EMA predictions for the optical properties of SiQDs in Group 1 (i.e., $d_{\text{TEM}} - d_{\text{XRD}} > 2$ nm; Figure 4a) - this is not the case for d_{TEM} . We also note that the EMA consistently overestimates particle size when comparing to d_{XRD} . In contrast, for Group 2 SiQDs that bear a thin amorphous Si layer, the PL emission energy is closely related to d_{XRD} and d_{TEM} (Figure 4b); furthermore, the EMA becomes more representative. We also note similar relationships when evaluating excited-state lifetimes (i.e., τ) in the context of d_{TEM} and d_{XRD} .

Models have shown that the radiative lifetimes of silicon nanocrystals scale very nearly as the inverse cube of their radius.^{71, 72} While there is also a non-radiative contribution whose contribution cannot be unambiguously determined, the dominant non-radiative decay rate has been calculated to also scale inversely with the crystallite volume.⁷³ Thus, the lifetime data was fit to an inverse cubic function $\frac{1}{\tau_{\text{SE}}} = A\left(\frac{1}{d_{\text{XRD}}}\right)^3 + C$ of the XRD radius, which appeared to yield a reasonably good fit to the experimental data (Fig. 4(c,d)).

The direct relationship between theoretical PL energy and lifetimes and the crystallite diameter of the studied SiQDs, especially when they have a thin amorphous layer (Group 2), suggests that the crystalline core controls the optical response. However, the relationships between SiQD luminescence, graded structure, and size presented for Group 1 are similar to those previously noted for $\text{CdSe@CdSe}_x\text{S}_{1-x}\text{@CdS}$ QDs in which the confinement of carriers (i.e., electrons and holes) depends upon a radially varied structure.⁷⁴ A detailed study of the interplay of these factors in the SiQD optical behavior is obviously complicated by the poorly-defined nature of the

transitional region between the crystalline core and amorphous shell, however, one can expect that the confinement should be stronger when the shell is thinner as implied by the results in Fig. 4. This clearly highlights the importance (and promise) of establishing methods for controlling the uniformity of the internal SiQD structure, as well as preparing well-defined core@shell SiQD systems.

Conclusions

In conclusion, the optical properties of functionalized SiQDs have been evaluated in the context of internal crystallinity by examining crystallite and particle dimensions using X-ray diffraction and transmission electron microscopy. For SiQDs prepared via the widely employed “HSQ method”, the d_{XRD} provides a better representation of the optically active QD dimensions, regardless of the presence of an amorphous overlayer. In cases in which a thick Si amorphous layer is present, no obvious correlation between d_{TEM} and optical response is noted. However, EMA estimates derived from d_{TEM} and d_{XRD} dimensions agree when thin amorphous Si layers are present. This fundamental understanding of SiQD structure and its influence on their optical properties illuminates a foundation on which future efforts to better control SiQD optical response can build.

Experimental

Materials:

Reagents:

Hydrofluoric acid (Electronic grade, 48–50%) was purchased from Fischer Scientific. Sulfuric acid (reagent grade, 95–98%) was purchased from Caledon Laboratory Chemicals. Fuming sulfuric acid (reagent grade, 20% free SO_3 bases) and trichlorosilane (99%) were purchased from Sigma (now MilliporeSigma). All reagents were used as received unless otherwise specified. All

solvents were reagent grade and used as received. Toluene was collected from a Pure-Solv purification system immediately prior to use. Benzene was purchased from EMD Millipore (now Millipore Sigma).

Preparation of Hydrogen Silsesquioxane (HSQ):

HSQ was synthesized via known literature procedures where sulfuric acid is used to selectively oxidize trichlorosilane. Dry toluene (45.0 mL) was added to a mixture of concentrated (15.0 mL) and fuming (7.2 mL) sulfuric acid under inert atmosphere. Once the addition was complete, 110 mL of dry toluene was added to 16 mL of trichlorosilane and added drop-wise over a few hours to the sulfuric acid solution. The product dissolved in the organic layer was washed with sulfuric acid solution. After drying the organic layer, most of the toluene was removed via rotary evaporation and the rest was removed *in vacuo*. The resulting white solid was stored under vacuum until use.

Preparation of the SiQDs/SiO₂ composite:

Thermal decomposition of the HSQ, as previously reported, was used to produce the SiQDs used in this study. Six grams of HSQ was annealed in a tube furnace under a 5% H₂/Ar atmosphere at 1100, 1200, and 1300 °C to get various sizes of nanocrystals (the sizes associated with each temperature can be seen in Table S1). The composite was ground using an agate mortar and pestle then shaken for six hours to prepare a fine powder.

Preparation of alkyl passivated SiQDs:

The composite was then etched using a 1:1:1 solution of ethanol:DI water:HF to remove the SiO₂ matrix from the particles using 0.5 g of composite per etch and 15 mL total etching solution. The 1100 °C composite was etched for one hour (one hour and forty-five minutes to two hours and forty-five minutes for 1200 °C composite) and the resulting particles were extracted in toluene. The hydride-terminates SiQDs (H-SiQDs) were centrifuged twice in toluene and redispersed in 10

1 mL dry toluene with 6 mL of dodecene and 300 mg AIBN. The reaction mixture was degassed using three freeze-pump-thaw cycles and placed in an oil bath at 70 °C overnight (~17 hours). The resulting SiQDs were purified via centrifugation using 10 mL of toluene and 20 mL of methanol thrice to remove any unreacted dodecene and AIBN. The purified SiQDs were redispersed in toluene for subsequent characterization.

Characterization:

FTIR

Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo Nicolet Continuum FT-IR microscope by drop casting SiQDs onto a silicon wafer from dry toluene solutions.

XPS

X-ray photoelectron spectroscopy (XPS) was measured using a Kratos Axis 165 Ultra X-ray photoelectron spectrometer. A monochromatic Al K α source operating at 210 W with an energy $h\nu = 1486.6$ eV was used. Survey spectra were collected with an analyzer pass energy of 160 eV and step of 0.3 eV. For high-resolution spectra, the pass energy was 20 eV and the step was 0.1 eV with dwell time of 200 ms. XPS samples were prepared by drop-coating a dispersion of SiQDs in dry toluene onto a copper foil. Spectra were calibrated to the C 1s (284.8 eV) and fit to appropriate spin-orbit pairs using CasaXPS (VAMAS) software with a Shirley-type background. To fit the Si 2p high resolution spectrum the doublet area ratio was fixed at 2:1 and the separation was set at 0.6.

Electron Microscopy

Transmission electron microscopy (TEM) and HR-TEM were performed on a JEOL JEM-ARM200CF S/TEM (Cold Field Emission Gun) electron microscope with an accelerating voltage of 200 kV using SiQDs drop-coated from a toluene solution onto a holey carbon-coated copper

grid. The SiQD size was determined by averaging the size of 300 particles using ImageJ software (version 1.51j8).

XRD

Powder X-ray diffraction was measured on a Rigaku Ultima IV multipurpose X-ray diffraction system using a Cu K α source for most of the samples. The sample was drop cast on a zero-background Si wafer and collected as a thin film. For thin film diffraction, a parallel beam as used with a glancing angle of 0.5°. Some of the data was also collected at the synchrotron, with a wavelength of 0.6892 Å, using transmission mode, to verify the size. These methods gave the same results within the error of the technique and the fitting. This is likely because the line width due to size broadening is significantly larger than the instrument broadening for either of these methods. Pawley fitting of powder pattern was performed on TOPAS was used to determine the crystallite domain size with integral breadth, FWHM and Lorentzian broadening methods. Instrumental effects were accounted for by refining a NIST Si line shape standard (640f) to ensure instrument alignment and line shape. A sample-independent synthetic peak was required at ~22° for all measurements on the laboratory instrument, which is believed to originate from the sample holder imperfections or amorphous products/unreacted materials. The synchrotron data required other small peaks (8, 9, 11, 14, 16, and 19°) due to imperfections in the background subtraction from the Kapton tube (sample holder).

Photoluminescence characterization

Photoluminescence spectroscopy measurements were performed on a solution of silicon nanocrystals dispersed in toluene in a quartz cuvette. Silicon nanoparticles were excited using an argon ion laser with a 351 nm emission wavelength. The resulting photoluminescence was collected by an optic fiber, passed through a 500 nm long-pass filter to eliminate scattered light

from the excitation source, and fed into an Ocean Optics USB2000 spectrometer. The spectral response was calibrated by a blackbody radiator (Ocean Optics LS1). Photoluminescence lifetime measurements were acquired using an argon ion laser (351 nm, ~20 mW) modulated by an acousto-optic modulator (~50 ns response time) operated at a frequency of 200 Hz with a 50% duty cycle. The photoluminescence was fed into an optic fiber and passed through a 500 nm long-pass filter and was then incident on a Hamamatsu H7422P-50 photomultiplier tube (PMT) interfaced with a Becker-Hickl PMS-400A gated photon counter. The photoluminescence data was collected with a total of 10 000 sweeps for good signal-to-noise ratio and using 1 μ s time steps. A log-normal fitting of the data in MatLab was used to calculate the luminescence decay.

Quantum efficiency measurements were performed using a homemade integrating sphere with a 365 nm light emitting diode excitation source. Sample solutions were diluted to have an absorbance between 0.1 and 0.15 at 405 nm, then they were transferred into a cuvette that was lowered into the integrating sphere on a magnetic holder as was a distilled water blank. The photoluminescence and excitation intensities were captured through a fiber attached to the sphere and analyzed with a calibrated Ocean Optics spectrometer. The equation $QE = (I_{PL, sample} - I_{PL, blank}) / (I_{ex, blank} - I_{ex, sample})$ was used to calculate the absolute quantum efficiency, where I_{PL} is integrated photoluminescence intensity and I_{ex} is excitation intensity recorded inside the sphere. The measurements were performed in quintuplicates.

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Supplemental Information

A Tale of Seemingly “Identical” Silicon Quantum Dot Families: Structural Insight into Silicon Quantum Dot Photoluminescence.

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Interpreting luminescence lifetimes:

To understand the luminescence lifetimes, the decays were fit with equation S1.¹

$$(1) \quad I_t = A \exp\left[-(t/\tau_D)^\beta\right] + dc$$

For this function, the mean lifetime is given by equation S2.

$$(2) \quad \tau_{SE} = \tau_D \frac{\Gamma(2/\beta)}{\Gamma(1/\beta)}$$

Figure S1: FTIR of 1200-SiQDs (red) and 1300-SiQDs (purple).

Figure S2: High annular angle dark field STEM images of a) 1200-SiQDs and b) 1300-SiQDs.

Figure S3: Histograms showing the STEM determined non-crystalline shell thicknesses for a) 1200-SiQDs and b) 1300-SiQDs. The numbers represent the average amorphous shell thickness measured over N samples.

Figure S4: Survey XPS scan for a) 1200-SiQDs and b) 1300-SiQDs, showing the presence of only Si, C, O and F.

Figure S5: A comparison of the relationship between quantum efficiency with d_{TEM} (blue squares) and d_{XRD} (red circles) for SiQDs with a thick amorphous layer (>2 nm; a) and a thin amorphous layer (<0.8 nm; b).

Figure S6: Plot showing d_{TEM} vs. d_{XRD} , where the line is $d_{\text{TEM}} = d_{\text{XRD}}$.

Figure S7: A plot of the maximum photoluminescence energy against the lifetimes for all SiQDs in this study. A clear trend is observed that can be fit to the equation $\frac{1}{\tau_{\text{SE}}} = A * e^{E/E_0}$,²⁻⁴ where $A = 62.5 \text{ s}^{-1}$ and $E_0 = 0.34 \text{ eV}$ (the black line).

Figure S8: A comparison of the relationship between PL energy with d_{TEM} (blue squares; standard deviation shown in blue error bars) and d_{XRD} (red circles; fit errors shown in red error bars) for SiQDs with a thick amorphous layer (>2 nm; a) and a thin amorphous layer (<0.8 nm; b). The solid black line in a) and b) represents the EMA as predicted using $E_g(r) = 1.12 + 4.19/r^2$.

Figure S9: Representative FTIR data showing samples 1 (gold), 2 (purple), 3 (green), 4 (blue), 5 (red), 6 (black). Sample numbers refer to numbers in Table S1.

Figure S10: Representative Si 2p XPS data for samples a) 1, b) 2, c) 3, d) 4, e) 5, and f) 6. The oranges peaks represent Si (0); green, Si(I); blue, Si(III); and magenta, Si(IV). The black solid line shows the experimental data and the red dashed line represents the fitting envelope. Sample numbers refer to numbers in Table S1.

Figure S11: Representative bright field TEM a) 1, b) 2, c) 3, d) 4, e) 5, and f) 6. Sample numbers refer to numbers in Table S1.

Figure S12: Average shifted histograms for SiNCs counted from TEM/STEM images for samples a) 1, b) 2, c) 3, d) 4, e) 5, and f) 6. Sample numbers refer to numbers in Table S1.

Figure S13: X-ray diffraction powder patterns for samples a) 1, b) 2, c) 3, d) 4, e) 5, and f) 6. The black trace is the experimental data, the red is the fit and the grey is the difference. Samples a-c were collected at the Canadian Light Source synchrotron facility ($\lambda=0.6891$) and samples d-f was collected on the Rigaku Ultima with a Cu-K α source. Sample numbers refer to numbers in Table S1.

Table S1: A summary of experimental parameters and results for all samples

Sample #	Anneal T ^a (°C)	Etch time ^b (min)	d _{TEM} (nm)	d _{XRD} (nm)	PL Max (nm)	Lifetime ^c (μs)	QE ^d (%)
1300-SiQD^e	1300	240 ^g	5.5	4.69	955	546.8	N/A
1200-SiQD^f	1200	60	5.4	3.24	837	266.6	19.7
1^f	1200	90	4.1	2.07	715	98.8	21.5
2^f	1200	60	4.7	2.62	826	190.4	33.6
3^f	1300	135	5.8	2.99	782	135.7	19.0
4^e	1200	165	3.1	2.33	701	97.0	9.4
5^e	1200	75	3.2	2.64	815	218.7	20
6^e	1300	240	3.3	3.13	800	208.1	14.9
7^e	1100	30	2.8	1.71	659	73.6	8.8
8^e	1200	60	3.4	2.64	823	172.1	33.0
9^e	1200	130	2.5	2.21	675	81.6	7.3
10^e	1200	120	2.8	2.45	700	98.5	10.1
11^e	1100	45	2.8	2.05	684	107.3	4.3
12^f	1300	210	5.3	3.06	819	159.0	15.6
13^f	1200	105	4.8	1.63	641	63.1	10.0
14^f	1200	40	4.7	2.67	860	205.7	24.5

^a Temperature used for annealing HSQ to make the composite^b Time used for HF etching^c Mean lifetimes were calculated as described above.^d Quantum efficiency^e “Thin” amorphous shell samples (Figure 4 b and d).^f “Thick” amorphous shell samples (Figure 4 a and c).^g 5 mL of 49% HF added halfway through etch.**Table S2:** Lifetime fitting parameters for 1200-SiQDs and 1300-QDs

	<i>A</i>	<i>β</i>	<i>Dc</i>
1200-SiQDs	1.031	0.8608	0.00091
1300-SiQDs	1.024	0.8346	0.0053

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