Supporting Information

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I. Plasma-synthesized Si Nanocrystals:

a) Preparation

Silicon NCs are prepared using a custom-built RF-enhanced plasma reactor, the

mL for larger NCs, 30 mL for smaller NCs) and then centrifuged at 12,000 x *g* for 5 min. The supernatant is decanted, and the Si particles are dissolved in additional dry toluene (10 mL) and precipitated and isolated as before. Excess solvent is removed in vacuo, leaving dry material with the appearance of wafer Si shards (for 7.8 and 6.3 nm samples) or a waxy solid (for 3.8 and 3.2 nm samples).

b) Measurements

Transmission electron microscopy (TEM) samples are prepared inside an inert-atmosphere glove box by drop-casting a solution of dodecyl-capped Si NCs in dry hexane onto lacey-carbon-coated copper grids. Imaging is performed on a FEI Tecnai T30 microscope operating at 300 kV.

Photoluminescence measurements are made from solutions of dodecyl-capped Si NCs in 1-cm cuvettes. Emission spectra are recorded in tetrachloroethylene solutions with an optical density at the excitation wavelengt

X-ray diffraction (XRD) measurements are conducted on dry, unfunctionalized Si NCs packed into 0.5 mm glass capillary tubes and sealed with wax in an inert-atmosphere glove box (to prevent oxidation). XRD is performed using CuKα radiation (40 kV, 35 mA) from a Bruker D8 Discovery system equipped with a beryllium area CCD detector.

Raman spectra are recorded for dodecyl-capped NCs in cyclohexane solvent, in a backscattering configuration with excitation at 532 nm from a frequency-doubled YAG laser.

Inductively-coupled plasma optical emission spectroscopy (ICP-OES) is performed by Columbia Analytical Services, Inc., Tucson, AZ, USA.

UV-vis-NIR absorption measurements are conducted in cuvettes with 1-cm path length filled with solutions containing ~10 mg/mL of Si NCs in trichloroethylene (TCE). The cuvettes are sealed so there is no exposure to air. Optical transmission measurements are performed using a Varian Cary 5000i spectrophotometer equipped with an integrating sphere. Samples are placed in the path of the light beam, at the entrance of the integrating sphere.

II. Si Nanocrystals in Oxide Matrix:

a) Preparation

Size-selected Si NCs embedded in SiO_2 are deposited by the superlattice (SL)

determined by TEM analysis, is approximately 5 nm. The SiO_2 spacing layer thickness is 3 nm.

We prepare 3 different samples: one piece is annea

control samples is made with identical superlattice layers as the experimental samples, but not subjected to the high-temperature anneals that cause the segregation of excess Si into NCs. These suboxide superlattice control samples also have an order of magnitude lower absorption. This confirms that the observed absorption features are due to the Si NC superlattice stack, and specifically from the NCs rather than any remaining suboxide.

At higher energy, the absorption is sufficiently strong for standard spectrophotometer transmission/reflection measurements; we use a Cary 6000i system. The sample absorption data obtained by PDS is first corrected for the system response and then scaled to match the absolute sample absorption at 3 eV from spectrophotometer measurements.

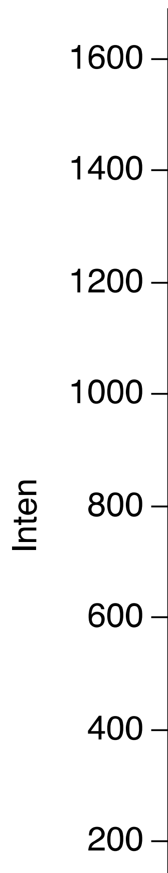
Elemental analysis is done by elastic recoil detection analysis (ERDA) as described in [5].

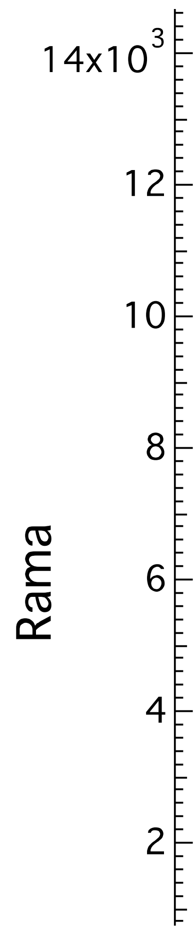
Having determined the Si content of the superlattice NC stack, we can calculate

Table S1. Conditions used to prepare Si nanocrystals using a RF-enhanced plasma reactor.

Si Nanocrystal Size (nm)	7.8	6.3	3.8	3.2
Emission Wavelength (nm)	1000	960	840	780
Argon Flow (sccm)	30	80	60	60
10% SiH_4/He Flow (sccm)	30	30	30	30
Hydrogen Flow (sccm)	0	0	60	60
Forward RF Power Applied (W)	75	75	100	75
RF Power Delivered to Plasma (W)	9.2	8.3	17.7	10.6
Pressure (Torr)	3.0	3.0	3.0	2.5
Residence Time (ms)	2.3	1.2	0.9	0.8

Fig. S1: a) XRD of the plasma-synthesized Si NCs, showing peaks indicative of nanocrystalline phase in nanoparticles with diameters of 3.2, 3.8, 6.3, and 7.8 nm. b) Raman spectra of the NCs. The sharp peak near 520 cm^{-1} is a signature of nanocrystalline phase. We note that our separate, recent extensive study obtained better quality Raman spectra and found evidence for crystalline phase even in the smallest NCs [6].

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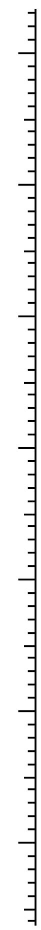
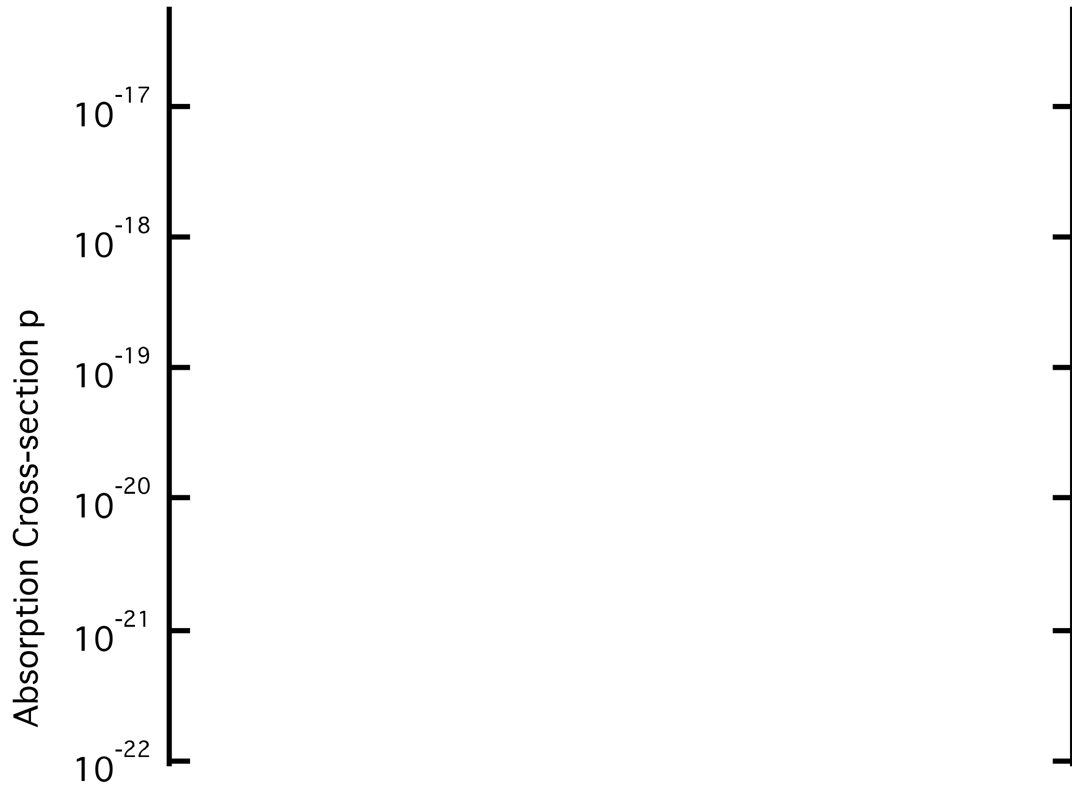


Fig. S2: Absorption cross-section per Si atom of 5 nm size Si NCs in oxide matrix with different annealing treatments, as compared to the absorption of bulk c-Si scaled to account for the local field factor correction in small particles.



References:

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