

## Intact sublimation of silicon nanocrystals evidenced via HREM imaging and EELS in a dedicated STEM

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**Abstract.** Silicon nano crystals (NCs) have attracted considerable interest for possible uses in optoelectronics<sup>1</sup> As the particle size decreases the properties of NCs become increasingly sensitive to the surface termination.<sup>2,3</sup> Monolayer chemistries<sup>4-10</sup> have been exploited to control the physicochemical properties. NCs are often prepared by vapour-phase deposition techniques; using these they can be conveniently analysed via gas phase analysis techniques, such as mass spectrometry. This cannot be employed, however, if NCs are not synthesized in the gas phase. Here we present a STEM study of undecyl-capped SiNCs, evaporated intact upon heating in ultrahigh vacuum at 200 °C and collected on a variety of solid substrates, including carbon-coated TEM grids. The BF- and HAADF lattice images confirm that the particles have a crystalline core with Si-lattice spacings. The presence of Si in the core is also confirmed by Si-L edge EELS, which reveals furthermore the presence of a surface oxide.

### 1. Introduction.

The procedure for forming silicon nanocrystals (SiNCs) capped with an Si-C bonded alkyl layer (alkyl-SiNCs) is reported elsewhere.<sup>11,12</sup> Hydrogen-terminated porous silicon films refluxed in toluene or mesitylene solutions of alk-1-enes break into small particles whilst the alkene undergoes hydrosilation at the particle surface. These particles are strongly luminescent and very stable towards oxidation under ambient conditions. Thick films of alkyl-SiNCs on a variety of solid surfaces (graphite, tantalum, gold nitride, silicon wafer, glass slides) can be prepared in a straightforward manner by drop coating from dispersions in apolar solvents, such as toluene and dichloromethane for various characterisation methods: X-ray diffraction (XRD) was used to confirm the crystalline nature of the Si core in these NCs. However, detailed information about the structure and composition of individual NCs can only be obtained by high resolution analytical EM techniques. It is, for example of great importance, to find out how much of the NC constitutes a Si-oxide, and whether the core is truly Si. This challenge is half met through the fact that films of undecyl-capped SiNCs, denoted C<sub>11</sub>-SiNCs, sublime upon heating in ultrahigh vacuum, and the vapour of intact, i.e., undissociated C<sub>11</sub>-

SiNCs can be collected directly on microscopy grids. The evaporated particles were observed to constitute only a small fraction of the total mass deposited as the source from solution, (ca. 0.1 mg). A simple order of magnitude estimate of the mass evaporated, based on the size and number density of the features observed by AFM and the solid angle subtended by the receiving substrate, indicates that heating at 200 °C for 30 min evaporates about 5 ng of C<sub>11</sub>-NCs. This is consistent with the size measurements and the interpretation that smaller particles evaporate preferentially at 200 °C. Proof that the NCs contain indeed crystalline Si-cores can be accomplished by investigation in a scanning transmission electron microscope (STEM) with small probe, where individual atomic columns (or even atoms) in the crystals can be addressed.

The observation of transfer of detectable amounts of C<sub>11</sub>-SiNCs has been published elsewhere,<sup>13</sup> furthermore the thermal stability of similar alkyl monolayers on bulk Si(111) has been studied by other authors.<sup>14,15</sup> Evidence that the transferred material in our case is C<sub>11</sub>-SiNCs comes from X-ray photoemission spectroscopy (XPS), confocal Raman and luminescence microscopy and infrared spectroscopy.<sup>13</sup> XPS confirmed furthermore that the NCs have not undergone marked changes upon evaporation. The main features of the XPS data for evaporated C<sub>11</sub>-SiNCs (C<sub>1s</sub> peak = 284.36 ± 0.05 eV; Si<sub>2p</sub> = 100.8 - 101.6 eV) are consistent with SiNCs capped with a hydrocarbon (undecyl) monolayer and the presence of some Si oxide, though a more detailed analysis is not possible because of the different charging effects.<sup>16</sup> Additionally we have carried out highly spatially resolved core-loss EELS on individual NCs in an aberration corrected STEM, showing similar results (see later); this article concentrates on the latter experiment. Along with the observation of lattice spacings this confirms that these features contain Si-NCs, and more specifically that the particles have a crystalline Si core. We conclude that the transfer of material to the receiving substrate occurs via formation of a vapor of intact C<sub>11</sub>-SiNCs which retain their capping alkyl chains.

## 2. Experimental

TEM samples of Si-NCs were obtained by evaporation of films of undecyl-capped SiNCs, denoted C<sub>11</sub>-SiNCs, at 200 °C in ultrahigh vacuum directly on microscopy grids. Analytical EM was carried out in the Daresbury aberration corrected SuperSTEM1, which is equipped with an Enfina EEL spectrometer. Aside high resolution BF and HAADF lattice images, EEL line scans were obtained across individual particles. The acquisition time per pixel was typically 1 s, in a compromise to achieve reasonable statistics (several 10<sup>3</sup> counts on particles) and to keep radiation damage at minimum.

## 3. Results and Discussion

We have previously characterized the size of the as-prepared C<sub>11</sub>-SiNCs by a combination of absorption, luminescence and Raman spectroscopy, and published calculations of the optical gaps and vibrational modes as a function of particle size.<sup>11,12</sup> Estimates from the height of STM images of tethered C<sub>11</sub>-SiNCs gave a diameter of the Si core of about 2.5 nm.<sup>16</sup> We have now obtained direct size measurements of the solution-deposited C<sub>11</sub>-SiNCs by STM, AFM, XRD and STEM as well as by small angle X-ray scattering (SAXS) experiments on dispersions of C<sub>11</sub>- and C<sub>6</sub>-SiNCs in toluene (supplementary information). Evidence that the sublimed material consists of a fraction of the C<sub>11</sub>-SiNCs comes from STM images of individual islands, assigned to the Si core of the particles, exhibiting a slightly smaller diameter than the solution-deposited counterpart<sup>13</sup>. This is further evidenced by STEM; fig. 1 shows a STEM BF and a HAADF image of evaporated NCs. Lattice structure is clearly visible, and Fourier transforms of individual NCs reveal diffraction patterns that can be assigned to silicon lattice spacings, with the particles presenting themselves in various orientation, mostly 110 (left and right particle), but also in the more unusual 100 orientation (middle particle with Fourier transform) with respect to the electron beam. Isolated particles were found (see right hand HAADF image), but mostly the NCs aggregate into a mass containing other Si, Si-oxide and Ca-rich amorphous phases as well as organic residue.

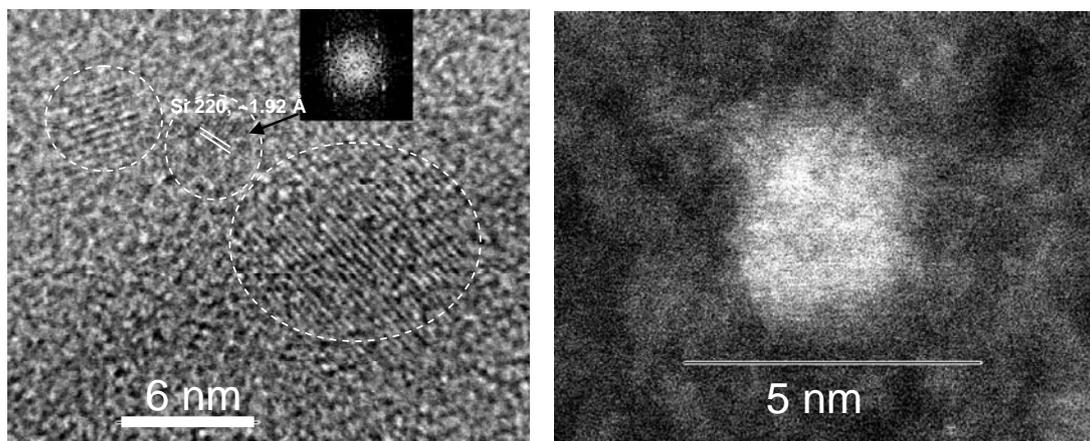


Figure 1: Bright field (left) and high angle annular dark field (right) micrograph of  $C_{11}$ -SiNCs evaporated (at 200 °C) onto a carbon grid, taken in an aberration corrected scanning transmission electron microscope. The beam energy was 100 keV, the resolution  $\sim 0.1$  nm. The inset shows the Fourier transform of a particle in 100 orientation with (220) lattice planes matching those of crystalline Si, the other particles exhibit 111 Si planes in 110 orientation.

Si-core loss EELS with sub-nm probe proved tricky; in many cases the line scan affected the particles. This was witnessed in images taken ‘before’ and ‘after’ the line scan, where the ‘after’ images showed marked differences in the particle structure, from changes in the crystal structure to dissolution of the NC. These results were discarded. In cases, where there were no differences in the images after the EEL measurement, evaluation of the line scans showed a variety of NC compositions, from particles containing silicon oxide cores to such which clearly exhibit a Si core surrounded by silicon oxide (we estimate around 50% of all singular particles, of which successful line scans were obtained). Figure 2 shows such a case. Scan points are equi-spaced along the scan line (arrow). 10 spectra, from which a power-law background was subtracted, are shown; overlaid on spectra 1, 5 and 9 are  $SiO_2$  and Si reference spectra. Spectra 1 and 9, taken at the periphery of the NC, show the Si-L

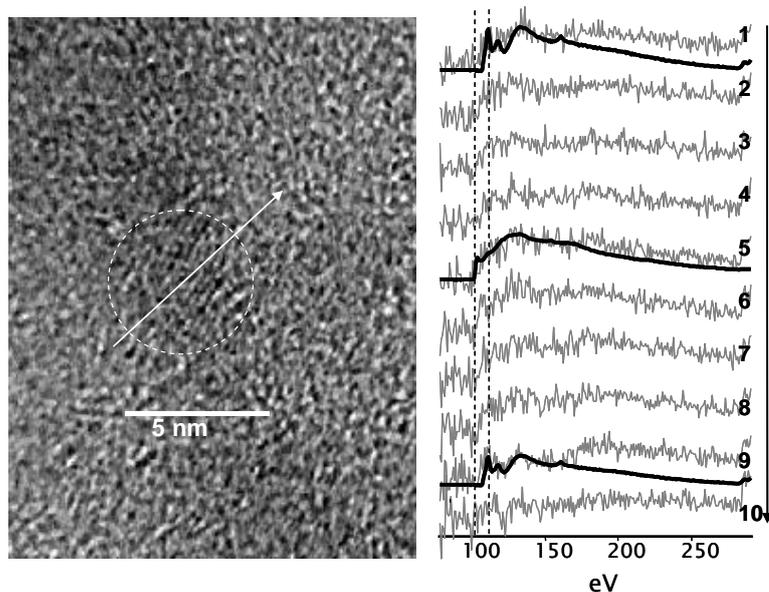


Figure 2, left: BF STEM image of isolated NC on carbon support film with scan line, right: Si L-edge spectra taken in direction of the arrow along the scan line in the left image. All spectra are raw data, from which a pre-edge power-law fitted background was subtracted. The overlaid black spectra are of  $SiO_2$  (1,9) and of Si (5).

edge peak chemically shifted at ~108 eV, concomitant with SiO<sub>2</sub>, whereas spectrum 5 with the probe projecting through the centre of the NC shows the pure Si L-edge peaking at 100 eV. Other spectra (e.g., 6, 7, 8) show intermediate peak positions; the spectrum shape can be fitted well in all cases by summing the pure Si and the SiO<sub>2</sub> spectrum to varying proportions (not shown here). This is to be expected with the probe traversing a varying proportion of Si and oxide.

Combining the STEM results with results of previous characterisation methods we confirm that the deposit contains Si NCs with Si-cores and oxide content towards their surface. The evaporation of nanocrystals of the size reported here is unexpected because large particles or molecules have many possible reaction pathways and tend to decompose before a temperature is reached at which the particle-particle interactions are dominated by thermal motion. We suggest that the phenomenon is observed readily for alkyl-SiNCs for two reasons: (i) the particle-particle interactions are relatively weak dispersion interactions (various alkyl monolayers on Si have been employed for their anti-stiction properties<sup>17</sup>) and (ii) the thermal stability of the alkyl monolayer on Si is substantially higher (340 °C in UHV<sup>15</sup>) than for noncovalently anchored monolayers such as the alkanethiol SAMs which desorb at about 175 °C.<sup>18</sup>

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