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Room Temperature Solution Synthesis of Alkyl-Capped Tetrahedral Shaped Silicon Nanocrystals

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Received September 26, 2001

Elemental silicon is of great technological importance. Single-crystal silicon is the basis of the computer revolution while polycrystalline silicon has applications in photovoltaic devices.¹ Recently, nanocrystalline silicon has received a great deal of attention due to its particle size dependent optical and electronic properties.^{2,3} Several different routes are now available for the preparation of such nanoparticles, including both gas-phase and solution decomposition of silanes,^{4–7} the reactions of silicon Zintl salts with silicon halides^{8–12} as well as the solution reduction of silicon halides by sodium,¹³ lithium naphthalenide¹⁴ or hydride reagents,^{15,16} or reduction of $\text{Si}(\text{OEt})_4$ with sodium.¹⁷ Although there has been significant progress in size and shape control of II–VI and III–V semiconductors,¹⁸ there has been very little in the pursuit of Si nanoparticles. A degree of control has been claimed through the use of inverse micelles;¹⁹ however, the size of silicon particles produced ranges from 1 to 10 nm in diameter.^{15,16} Control may be possible through the use of coordinating ligands and supercritical fluids to produce a smaller size distribution of nanoparticles.⁷ The use of lithium naphthalenide to reduce SiCl_4 has been reported to produce amorphous silicon nanoparticles, although details were not provided.¹⁴ While solution reduction routes to silicon nanoparticles have been reported, it has been suggested that both high temperatures and high pressures are necessary to obtain crystalline silicon. These conditions are usually obtained by bomb reactions or ultrasonication.^{13,17} We now report a room temperature solution synthesis of crystalline silicon nanoparticles with well-defined crystal facets.

Tetrahedral shaped silicon nanocrystals were produced by sodium naphthalenide reduction of silicon tetrachloride in 1,2-dimethoxyethane followed by surface termination with an excess of *n*-butyllithium.²⁰ The stoichiometry of the reaction was calculated such that after complete consumption of the sodium the silicon:chlorine ratio would be 4:1. The rationale behind this stoichiometry is that an active Si–Cl surface should be left on the particles formed, which allows surface termination with *n*-butyllithium. The use of sodium naphthalenide rather than bulk sodium ensures homogeneity of the reaction mixture. Both the ^1H and ^{13}C NMR spectra displayed broad resonances in a region consistent with the presence of *n*-butyl groups as well as aromatic resonances due to surface naphthalene moieties.²¹

The bright-field transmission electron microscope (TEM) image of a number of the silicon nanoparticles on a holey carbon grid, along with the selected area electron diffraction pattern (SAED), is given in Figure 1. To prepare the TEM grids the sample was diluted approximately 100-fold in hexane and sonicated to resuspend the nanoparticles. A 20 μL aliquot of this solution was dropped on a holey carbon grid which was then dried in an oven at 120 °C for 1 h. The dark triangular shapes are the silicon nanoparticles.

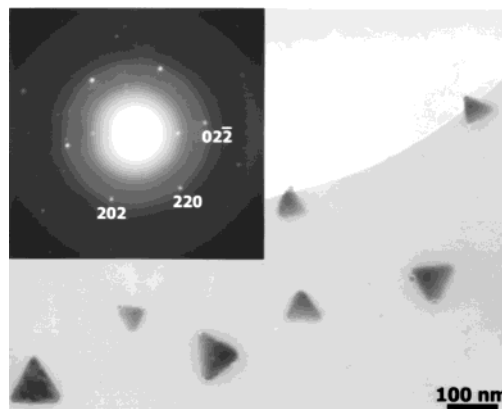


Figure 1. Bright-field TEM²² image of a holey carbon grid on which the silicon nanocrystals (dark triangles) have been precipitated. Darkness is relative to electron beam opacity of the sample. The inset in the top left is the SAED spot pattern for the particles, consistent with diamond crystalline silicon.

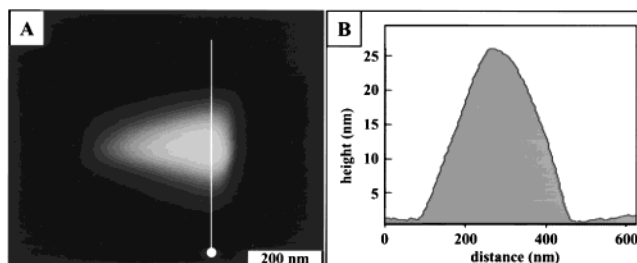


Figure 2. (A) An AFM topograph of a typical silicon nanocrystal on a mica(0001) surface. (B) The corresponding cursor profile across the top of the tetrahedral particle, which reveals a height of 26 nm.

The three-dimensional geometry of the silicon nanocrystals can be directly observed by using atomic force microscopy (AFM). Figure 2A is an AFM topograph of a typical nanoparticle, which reveals the tetrahedral geometry of the nanoparticle. The height of the nanocrystal, read from the corresponding cursor profile in Figure 2B, is 26 nm. The height of most nanoparticles ranges from 20 to 40 nm. The actual width and slope are sharper than the cursor profile in Figure 2B as the tip geometry is convoluted into the lateral direction of the AFM topograph.

The SAED pattern is from several of the particles shown in the TEM image and thus multiple zone axis patterns are observed. The [111] zone axis pattern for diamond cubic is the most prevalent, along with the [112] zone. The [111] zone axis pattern is indicated. The diffuse rings arise from the amorphous carbon of the holey carbon grid.

A survey of 55 particles from several different areas on the grid gave edge lengths between 40 and 130 nm with 95% of the particles

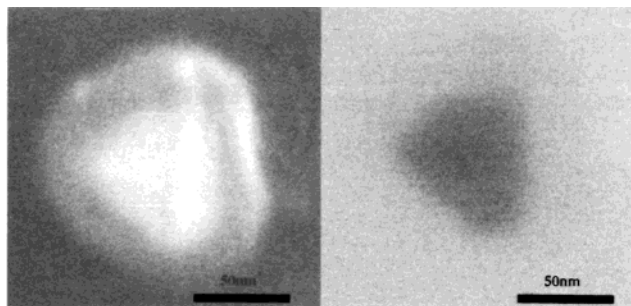


Figure 3. The left image is a SEM²³ image of a silicon nanocrystal while the right image is the TEM image of the same nanocrystal at the same magnification. It can be seen that the TEM image is much smaller than the SEM image. This is consistent with the nanocrystals being covered with an organic layer.

falling within the 40–80 nm range and 80% falling within the 50–70 nm range.

Hexane solutions of these particles showed no evidence of photoluminescence attributable to silicon nanoparticle quantum confinement. For such effects to be observed the particles need to be substantially smaller.²⁴

A Wurtz-type coupling mechanism can be used to explain the oligomerization of silicon chloride precursors into a nanoparticle. Sodium naphthalenide acts as a soluble and active source of sodium metal. It can exchange alkali metal for halide on silicon. The resulting species can then react with another silicon halide to give a silicon–silicon bond. This can explain both the intermolecular formation of Si–Si bonds needed to add an atom to the growing cluster and the intramolecular bond formation required to close the six-membered rings of the silicon diamond structure.

Comparison of scanning electron microscope (SEM) to TEM images in Figure 3 shows a TEM image of the particle that is smaller than that in the SEM. The SEM shows an obvious core triangle with a less well-defined surface coating. This is consistent with a layer of organic material covering the nanocrystals, which is visible in the SEM but not the TEM. The surface material appears to be beam sensitive, consistent with an organic rather than SiO₂ coating.

The particles obtained are of interest for several reasons. While relatively large, they are of a limited size distribution, without the need for complicated separation techniques. They are also all of the same morphology.

The crystal shape is of interest. For tetrahedral crystals of a diamond cubic crystal type the (111) plane must give rise to the facets. For a given single crystal the most prevalent faces will be those with the slowest growth. The face with the greatest surface roughness and largest number of dangling bonds will give rise to the fastest growth, while the smoothest with the least number of dangling bonds will have the slowest face growth and thus be the most prevalent face. In the case of diamond crystalline silicon, the choice of facet greatly changes the number of dangling bonds. Cleavage through the (111) plane gives rise to surface silicon atoms with only one dangling bond whereas through other planes surface silicon atoms with more dangling bonds are observed. The slow growth of the (111) plane is consistent with this. He ion implantation/annealing experiments also suggest that the (111) face has the lowest surface free energy and is the most stable surface.²⁵

While the same reaction in solvents other than 1,2-dimethoxyethane gave rise to crystalline silicon (as determined by TEM), the particles obtained were significantly smaller and contaminated with large amounts of organic byproducts.

In conclusion, the reduction of silicon tetrachloride with sodium naphthalenide in 1,2-dimethoxyethane at ambient temperature and pressure, followed by termination with *n*-butyllithium, gives rise to faceted tetrahedral silicon crystallites. Further investigations on the effects of conditions on the nature of the nanoparticles formed and the extension of the technique to other members of the silicon group are in hand.

Acknowledgment. The authors thank Mike Dunlap for help with the SEM and TEM. This work was supported by the Petroleum Research Foundation, administered by the ACS, the National Science Foundation DMR-9803074, LLNL (Materials Research Institute), and Evergreen Solar by means of a NIST, ATP grant. K.A.P. received support from an NSF IGERT “Nanomaterials in the Environment, Agriculture and Technology”. J.C.G. received support from an NSF IGERT “Smart Sensor and Integrated Devices” at WSU.

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- (19) It was claimed that since the “ionic salts” (SiCl₄) are completely insoluble in the hydrocarbon used (eg. octane), nucleation and growth are restricted to the micelle interior and size control is then achieved. In fact silicon tetrachloride is extremely soluble in hydrocarbons such as octane. This suggests that the limited size control obtained (1–10 nm, an order of magnitude) does not arise from containment of the silicon halide within the micelles.
- (20) A tetrahydrofuran solution of sodium naphthalenide (0.9 g (39 mmol) of Na and 3.23 g (25 mmol) of naphthalene in 30 cm³ tetrahydrofuran stirred for 3 h) was added rapidly at room temperature via cannula to a 500 cm³ Schlenk flask containing 300 cm³ of 1,2-dimethoxyethane and 1.14 g (6.7 mmol) of SiCl₄ with rapid stirring. On completion of the naphthalenide addition a large excess of *n*-butyllithium (10 cm³, 1.6 M in hexane) was added immediately. The solvent was removed in vacuo from the resulting yellow brown suspension. The residue was extracted with hexane and washed with water to remove sodium and lithium salts. Evaporation of the hexane layer followed by heating under vacuum to remove residual naphthalene gave 0.7 g of a viscous yellow oil.
- (21) ¹H NMR (C₆D₆, 400 MHz) δ 0.4–1.8 (br multiplet, butyl CH₂ and CH₃), 7.0–7.8 ppm (br multiplets, aromatic CH), ¹³C{¹H} NMR (C₆D₆, 100.53 MHz) δ 10–16 (br multiplet, CH₃ and SiCH₂), 25–28 (br multiplet, butyl CH₂), 125–130 ppm (br multiplet, aromatic CH).
- (22) Phillips CM12 operating at 100 keV.
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JA017170B