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A Low-Temperature Solution Phase Route for the Synthesis of Silicon Nanoclusters

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A solution synthesis, reacting the Zintl compound KSi with $SiCl_4$ to produce crystalline, silicon nanoparticles, is presented. Interest in silicon nanoclusters arose from the suggestion that the visible luminescence seen in porous silicon (PS) results from quantum confinement of electron−hole pairs.[1] The prospect of silicon possessing useful optical properties has generated extensive speculation over the possibilities of new applications for silicon.[2−7] Silicon's wide availability along with its electrical and chemical properties has made this semiconductor the material of choice for many electronic applications. A notable exception to this has been in the fabrication of optoelectronic devices, where low luminescence efficiency, due to silicon's indirect band gap, has resulted in its exclusion from use. However, if the luminescence observed in PS and other silicon nanosystems proves to result from quantum confinement, these particles will be of great technological value to the optoelectronics industry. They may provide an attractive alternative to the III−V binary semiconductors such as gallium arsenide currently used in micro-optoelectronic devices.

Chemical methods for the solution synthesis of II−VI semiconductor nanocrystals along with the techniques for their subsequent surface manipulations are well advanced.[8,9] Chemical methods for III−V semiconductor synthesis are not as highly evolved, but recent work in this area is quickly moving to change this.[10] In contrast, relatively little headway has been made in the solution synthesis of crystalline silicon or germanium nanocrystals. This can be attributed primarily to the difficulty involved in devising a synthetic strategy compatible with the solution chemistry of these elements. Such a strategy would be advantageous because it would provide a better means to control surface passivation/termination of the clusters, as is the case for the II−VI and III−V semiconductor nanoclusters. To date three basic methods have been used to produce silicon nanoclusters. The most successful method is the gas-phase decomposition of silanes.[7,11,12] This produces silicon nanoparticles with a relatively small size distribution but does not lend itself to the easy manipulation of the surface of the particles or to their large-scale manufacture. A second method, investigated by this group and others, is the ultrasonic dispersion of porous silicon in various solvents to produce colloidal suspensions of silicon nanoparticles.[5,13−15] While the initial procedure is straight forward and inexpensive, the effort required for control of size distribution and quantitative characterization is prohibitive for large-scale synthesis, and here also, surface manipulation is limited. The only solution route developed to date to synthesize silicon nanoclusters employs both high temperatures and high pressures.[4] The synthesis is based on reduction of $SiCl_4$ and chloroalkylsilanes by sodium metal. This method provides little control over the particle size and does not result in a surface which is easily manipulated.

We report here a new solution phase synthesis for producing crystalline silicon nanoclusters at significantly lower temperatures than previously required. In addition, it is performed at ambient pressure and yields a particle surface that can be modified by chemical methods. This method has the potential to yield large amounts of silicon nanocrystals in addition to providing reliable control over size distribution and surface termination. In this synthesis we use the Zintl salt KSi as a starting reagent. Zintl salts have been shown to be useful for the synthesis of novel cluster complexes[16,17] and new materials.[18,19] Their unusual bonding, structural configuration, and oxidation states make them ideal candidates for use in synthesizing novel molecular species which incorporate some of the Zintl phase's unique features. Although the ASi (A = Na, K) compounds have been known for some time,[20,21] there are few examples of their use as synthetic reagents.[22] The structure of these salts, in part, consists of an anionic moiety made up of four silicon atoms that form a tetrahedron. This moiety is isoelectronic and isostructural with white phosphorus and is capped on each of its four faces with an accompanying alkali metal cation.[23] A simple metathesis type synthesis of the silicon nanoparticles is achieved using methods similar to those used for solution phase synthesis of III−V and II−VI type semiconductor nanoparticles. Specifically, the KSi salt is refluxed with $SiCl_4$ in a suitable solvent and then passivated with an appropriate capping group. KSi is synthesized by reacting excess K with silicon at 650 °C for 3 days and subliming off the excess K at 275 °C under vacuum. The purity of the air-sensitive, black solid is verified by powder X-ray diffraction. The solution reaction is carried out as follows: dried and degassed glyme, diglyme, or THF (100 mL) is added to 0.1 g KSi followed by the addition of excess $SiCl_4$ (0.2 mL). This is refluxed for 48−96 h under nitrogen at atmospheric pressure.

$$4n\mathrm{KSi} + n\mathrm{SiCl_4} \rightarrow \text{Si nanoparticles} + 4n\mathrm{KCl} \tag{1}$$

The solvent and excess $SiCl_4$ are removed by distillation under vacuum. At this point, the nanoclusters are somewhat air and moisture sensitive and are presumed to be chloride terminated. Methanol (approximately 10 mL) is added to the reaction flask, and the resulting solution is stirred for 1−12 h. This results in

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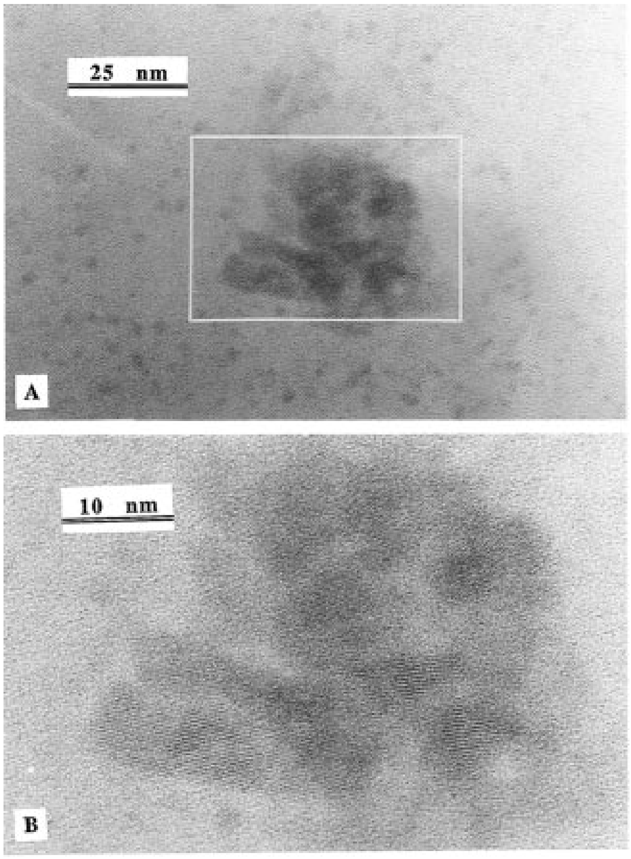

Figure 1. Bright-field HRTEM micrographs of silicon nanoparticles: (A) A single large particle (around 30 nm) of silicon surrounded by many smaller (1.5−2 nm) silicon particles, deposited on an amorphous carbon substrate by evaporation of solvent from the colloid suspension. The larger particles were found to be much less abundant than the smaller ones. The lattice fringes of 3.1 Å (B) on the large particle outlined in (A) correspond to the {111} lattice planes of silicon. The smaller particles do not have observable lattice fringes but are crystalline and of the same material as the larger particles shown by the diffraction pattern they generate.

a stable hydrophobic particle surface which permits easy separation from the KCl salt produced during the initial KSi/$SiCl_4$ reaction. The hydrophobicity of the product is consistent with the reaction.

$$-SiCl + HOCH_3 \rightarrow -SiOCH_3 + HCl \qquad (2)$$

The excess methanol is removed under vacuum, and the resulting powder is washed several times with water until no KCl lines are seen in the X-ray powder diffraction pattern. A colloidal suspension is then made of the silicon particles using hexane or cyclohexane as the solvent. The product consists of gray-black flocculent material which settles out and a colloidal suspension. The particles suspended in the colloid have been shown to be primarily crystalline silicon nanoparticles having the diamond structure. The yield of the colloidal suspension relative to the resulting product is approximately 8% by weight. The flocculent material is amorphous.

Fourier transform infrared (FTIR) spectroscopy and high-resolution transmission electron microscopy (HRTEM) have been used to characterize the resulting product. FTIR data collected for the different colloid samples clearly show only the silicon−oxygen peak near 1100 cm^{-1} and the saturated hydrocarbon peak just below 3000 cm^{-1}. The spectra were collected by depositing several aliquots of the colloid on a CsI salt plate and allowing the solvent to evaporate, leaving the previously suspended particles deposited on the plate. The spectra were similar for all the colloid samples.

HRTEM shows the flocculent precipitate to consist mostly of amorphous material. This is also true of the colloidal suspension obtained from the reaction done in THF. This is not true, however, of the colloidal suspensions obtained from the glyme and diglyme reactions. Figure 1A shows silicon particles obtained from a sample prepared using diglyme as the reaction solvent and having a reflux time of 48 h. The average size of the particles is 2.3(5) nm in diameter, and most are too small for resolution of their lattice fringes. A few larger agglomerates also form as can be seen from the larger particle in the micrograph that is approximately 30 nm in diameter. An enlargement of the agglomerate outlined in Figure 1A is shown in Figure 1B. This enlargement clearly shows lattice fringes that correspond to the {111} planes (∼3.1 Å) in silicon having the diamond structure. Lattice fringes are discernible in the larger agglomerate because interference from the amorphous carbon substrate on which the particle rests does not manifest itself as strongly in the larger particles as it does in the smaller particles. The electron beam diffracted off the agglomerate is much more intense yet only contends with the same substrate interference as that of the beam diffracted from the smaller particles. The electron diffraction pattern of the area shown in Figure 1A confirm the presence of {111} and {220} lattice planes corresponding to diamond structure silicon. Because the diffraction originates from a large number of very small particles rather than from a single crystal, diffuse rings are observed in the diffraction pattern. Small spots are also observed in the {111} ring due to diffraction from the larger silicon agglomerates on the substrate.

The Zintl salt KSi is the important component of this reaction since simple reduction of $SiCl_4$ by sodium metal requires high temperatures and pressures greater than 100 atm in order to produce silicon crystals ranging from 5 to 3000 nm in diameter.[4] The route presented herein provides a small range of particle size which may be further enhanced by the use of other solvents and methods commonly employed in II−VI nanocluster synthesis. We are currently investigating Grignard reagents and alkyllithium as capping reagents. This will provide a stable surface as well as allow for chemical manipulation of the surface with an aim toward attaching these clusters to polymer backbones and to surfaces.

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