Synthesizing silicon and germanium quantum dots and nanowires

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Nanocrystals and nanowires for use as active elements in electronic and optical applications can be created using novel, solution-based synthetic methods.

Semiconductor nanostructures exhibit unique size-dependent properties. These include energy-level quantization, single-electron charging, blue-shifted optical absorption, and enhanced luminescence and photocatalytic activity. Simply by changing structure size, one can tune material properties for specific applications.

Nanostructure fabrication methods are of two types. ‘Top-down’ approaches use patterning followed by etching or deposition, while ‘bottom-up’ synthesis converts chemical reactants to nanomaterials. Although both approaches provide control over size, shape, composition, and surface chemistry, the bottom-up approach has more advantages. It facilitates the large-scale, low-cost manufacturing of dispersible nanomaterials for low-temperature processing, deposition on plastic substrates, mixing with molecular and polymeric materials in coatings and composites, and even interfacing with living organisms for medical applications.

Solution-based (colloidal) synthetic methods can produce narrow size and shape distributions of many kinds of nanometer-size crystalline particles with coated surfaces and useful optical and electronic properties. Moving away from the trial-and-error development of ‘recipes,’ the field of nanomaterials chemistry has evolved a fundamental understanding of synthesis with control of size, shape, and properties. For the last several years, my research group has focused on the challenges of controlling nanocrystal shapes—which include nanorods, nanodisks, and nanowires—and solution-grown nanostructures made from crystalline Group IV elements, including carbon (C), silicon (Si), and germanium (Ge).

Crystalline Si nanostructures are extremely challenging to synthesize in solution, because they require relatively high temperatures to crystallize. For example, chemical-vapor deposition processes are carried out at temperatures exceeding ~400°C, but silane (SiH₄), which is relatively inert, does not thermally decompose below ~350°C. The problem, then, is how to carry out reactions in a solvent at temperatures between...
In supercritical fluid-liquid-solid (SFLS) nanowire synthesis, solutions of organic monolayer-coated metal nanocrystals such as the gold (Au) at the upper left, are fed with organometallic reactants, such as diphenylgermane \((\text{Ph})_2\text{GeH}_2\), into a reactor at a temperature and pressure exceeding the solvent critical point. The precursor thermally decomposes to the semiconductor, which crystallizes into nanowires, as shown in the scanning electron micrograph in the lower right. (The Au nanocrystal TEM is courtesy of Aaron Saunders, and the SEM of the germanium nanowires is courtesy of Tobias Hanrath.)

350°C and 500°C. In 1999, we began to explore high-temperature, high-pressure (i.e., supercritical) organic solvents as reaction media to produce Si and Ge nanocrystals.\(^{12}\) Our first attempts used diphenylsilane as a Si reactant in hexane at \(~450°C\) and \(~200\) bar,\(^6,10,13\) and capping reagents such as octanol and dodecanethiol that were added to the system. The results were Si nanocrystals less than 5nm in diameter with relatively stable photoluminescence similar to porous silicon.\(^{10}\) Such crystals are sufficient for single-particle spectroscopy,\(^{14}\) electrogenerated chemiluminescence,\(^{15}\) and electroluminescence in LEDs (see Figure 1). Still, this synthetic route faces problems. Significant amounts of oligomeric byproducts form, which greatly limits the reaction yield, and the particle-passivation chemistry is poorly understood. These challenges must be resolved before Si nanocrystals can be produced in commercial quantities.

In contrast, Si nanowires can be made with very high yields in solution by adding metal seed-particles to promote Si crystallization.\(^{13}\) Gold (Au) forms a liquid Au:Si alloy at \(~360°C\) in equilibrium with solid, crystalline Si—a eutectic—that promotes Si crystallization at low temperature.\(^{16}\) Au nanocrystals, injected as crystallization seeds into supercritical hexane at 450°C with diphenylsilane, produce crystalline nanowires with a diameter close to that of the seed particle.\(^5\) This synthetic process is called ‘supercritical fluid-liquid-solid’ (SFLS) growth (see Figure 2). Reactants are fed into a supercritical fluid to produce Si that dissolves into a liquid Au:Si alloy and crystallizes into solid Si nanowires.\(^{16}\) The SFLS process is quite general, and we have grown Si,\(^6,13,16,17\) Ge,\(^{18,19}\) gallium arsenide (GaAs),\(^{20}\) and gallium phosphorous (GaP)\(^{21}\) nanowires (see Figure 3). We have also produced up to 1g of wires in a single reaction.\(^{22}\)

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Nanowires are being explored for applications such as chemical sensing, photovoltaics, and computation, where the nanowires serve as conductive channels between electrodes (see Figure 4). We have begun to assess the electronic properties of SFLS-synthesized nanowires.\textsuperscript{20, 22–24} Surface chemistry is very important in this regard, and chemical-surface passivation strongly influences the carrier mobility and field response of the nanowires.\textsuperscript{22–24}

The metal seed can also influence properties. Au, for instance, traps carriers in Si and is probably not a good choice for electronics applications. We recently showed that cobalt (Co) and nickel (Ni) nanocrystals work well as seeds for Si and Ge nanowires.\textsuperscript{25, 26} This is encouraging since both materials are commonly used in the semiconductor industry to make source/drain contacts. Interestingly, Co- and Ni-seeded nanowires grow at temperatures (\(~\sim 450{^\circ}\)C) hundreds of degrees lower than the bulk Ni:Si and Co:Si eutectic temperatures, indicating that these nanowires grow by a solid-phase seeding process from a silicide.\textsuperscript{25, 26}

Furthermore, Ni and Co induce nanowire formation, presumably by catalyzing precursor decomposition, from reactants like octylsilane and trisilane that do not form nanowires in the presence of Au.\textsuperscript{25, 26} We recently applied the concept of solid-phase seeded catalytic growth to multiwall carbon nanotubes made in supercritical toluene at \(~\sim 640{^\circ}\)C using metallocene catalysts.\textsuperscript{7} The metallocene degrades in situ to metal particles, which then catalyze toluene decomposition to C and promote graphitization and nanotube formation. Without the catalyst, toluene does not decompose and therefore serves as both solvent and carbon source.

High-pressure and -temperature reactors, although very useful, have safety concerns. One of our long-term goals has been to synthesize Si and Ge nanowires under milder conditions on the bench in high-boiling solvents like long-chain ethers. Low-melting metals, such as bismuth (Bi), form eutectics with Si and Ge at a relatively low temperature. For example Bi:Si and Bi:Ge exhibit eutectics at \(~\sim 280{^\circ}\)C. We recently demonstrated Bi nanocrystal-seeded nanowire growth at relatively low temperatures (300–350°C) using Ge\textsuperscript{27} nanowires in trietylphosphine, as well as with Group III-V compounds\textsuperscript{28} such as GaAs, indium arsenide (InAs), GaP, and InP. We are currently working on Si nanowires.

Challenges remain for the synthesis process, including high-yield solution methods for Si nanocrystals, a benchtop colloidal synthesis of Si nanowires, and a solution route to single-wall carbon nanotubes. \textit{Commercialization} is also one important goal for the nanomaterials field. High-payoff opportunities exist, such as Si nanowire electronics for memory, logic, photovoltaics, and display driver electronics, but these have very high development costs and risks.

There are also smaller, short-term opportunities with lower costs. For instance, we are developing Si nanowires to serve as the critical dimension metrology standards for the Si-CMOS industry that will be needed to support next-generation chips. Commercialization requires robust and scalable synthetic processes. It also needs broad intellectual property that covers processes, applications, device structures, and even composition of matter, applications, or devices that are reliable and cheap to implement. There must also be realistic business opportunities. There are several relatively mature (founded less than 4 years ago) start-up companies—including Nanomix, Nanosys, Qdot (which was recently acquired by Invitrogen), and Innolight. They are trying to exploit the synthetic advances made during the last decade. Nonetheless, these companies are still searching for the right combination of business, innovation, and functional nanotechnology needed to break into the marketplace.

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\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4.png}
\caption{The Ge nanowire at top connects to four electrodes on a substrate. Below, a Si nanowire is shown suspended between scanning tunneling microscopy tips. (The Ge nanowire image is courtesy of Tobias Hanrath, and the Si nanowire image is courtesy of Damon Smith.)}
\end{figure}
of germanium nanocrystals in high temperature supercritical fluid solvents

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References


