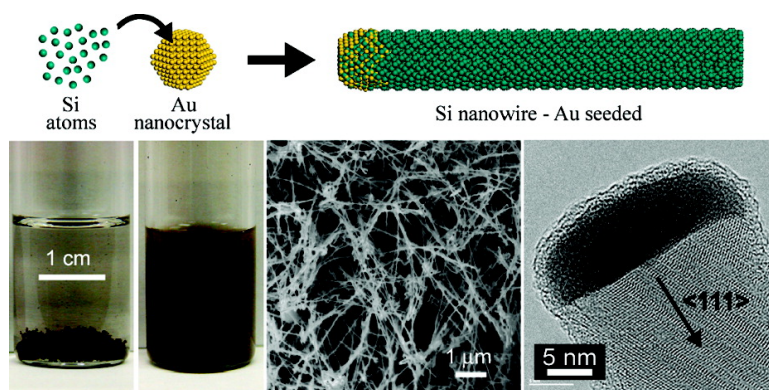


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Solution–Liquid–Solid (SLS) Growth of Silicon Nanowires

Andrew T. Heitsch, Dayne D. Fanfair, Hsing-Yu Tuan,[†] and Brian A. Korgel*

Contribution from Department of Chemical Engineering, Texas Materials Institute, and Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712-1062

Received February 14, 2008; E-mail: korgel@che.utexas.edu

It is not by chance that the integrated circuits found in every home computer are made from Si. The first transistor used germanium,¹ but Si was later identified as a better material—Si is stable over a wider range of processing temperatures and conditions, and it forms a chemically and electrically stable oxide with the appropriate conduction and valence band offsets. Si can be either *p*- or *n*-doped with impurities at a wide range of concentrations, and for optical sensing and photovoltaics it has a useful band gap energy (at 1.1 eV or \sim 1100 nm) near the red edge of the visible spectrum.² One of the drawbacks of Si for some optoelectronic applications is that its indirect band gap makes it a very poor light emitter. Nanoscale Si, however, can exhibit efficient, visible photoluminescence and might be useful for applications like light-emitting diodes and as emitter materials for displays, lighting, and medical imaging.³ Narrow diameter Si nanowires should also have higher carrier mobilities than bulk Si, which would be useful for making faster, more powerful computers.^{4,5}

Colloidal approaches have been used to make a variety of semiconductor nanowires—of group II–VI,^{6,7} III–V^{8–10} and IV^{11–13} semiconductors—by using metal nanocrystals to promote nanowire formation.¹⁴ Of these materials, Si has been one of the most challenging to make in solution, and currently the only solution-phase route that can produce large quantities of crystalline Si nanowires requires extreme temperatures and pressures that exceed the critical point of the solvent, i.e., by supercritical fluid–liquid–solid (SFLS) growth in organic solvents at \sim 450 °C and \sim 100 bar in pressure.^{11,15,16} The need for these extreme conditions arises partly from the fact that Si reactants are generally very stable. SiH₄ decomposes at temperatures greater than \sim 400 °C, and halogenated silanes and organosilanes require a higher temperature.^{17,18} Si nanowire synthesis requires a silicon reactant that decomposes below the boiling temperature of the solvent, as well as metal seed nanocrystals with a eutectic that forms at the reaction temperature.^{19,20}

Here, we demonstrate the first example of Si nanowire growth by the SLS mechanism at atmospheric pressure using trisilane (Si₃H₈) as a reactant in octacosane (C₂₈H₅₈) or squalane (C₃₀H₆₂) and either gold (Au) or bismuth (Bi) nanocrystals as seeds. Au forms a eutectic with Si at 363 °C, and Bi forms a eutectic with Si at 264 °C (see Supporting Information for phase diagrams),¹⁷ and the boiling temperatures of octacosane (C₂₈H₅₈, *T*_b = 430 °C) and squalane (C₃₀H₆₂, *T*_b = 423 °C) both exceed these eutectic temperatures. Figure 1 illustrates the process.

Figures 2 and 3 show TEM and SEM images of Si nanowires synthesized by injecting either Au or Bi nanocrystals along with

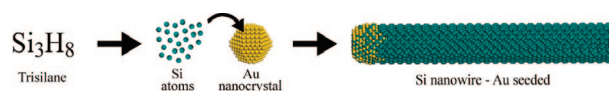


Figure 1. SLS growth of a Si nanowire: trisilane (Si₃H₈) decomposes to generate Si atoms, which are consumed by the Au seed to form a Au/Si eutectic that promotes wire growth. Bi nanocrystal seeded nanowire growth proceeds via a similar reaction pathway.

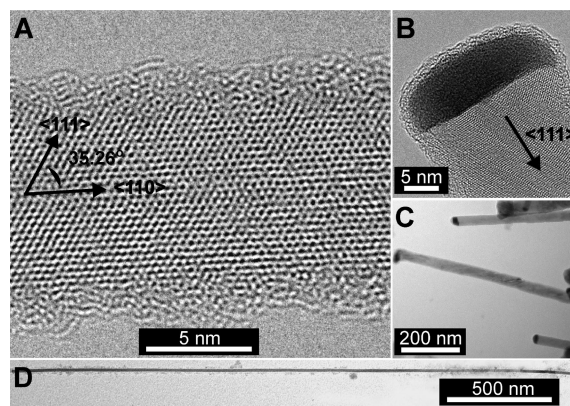


Figure 2. TEM images of Si nanowires synthesized in hot octacosane at ambient pressure by Si₃H₈ decomposition in the presence of either Au or Bi nanocrystals: (A) A Si nanowire synthesized at 410 °C with Au nanocrystal seeds; (B) one Si nanowire with an Au seed at the tip; (C) Si nanowires grown using Bi nanocrystals as seeds (EDS confirmed that the dark particles at the tips of the wires are composed of Bi, confirming that the nanowires grow by the SLS mechanism); (D) a Si nanowire (Bi seeded) longer than 3 μ m.

Si₃H₈ into octacosane heated near reflux (see Supporting Information for Experimental Details). Using this approach, approximately 5 mg of Si nanowires are produced in a reaction carried out in 5 mL of solvent (see Figure 3). The nanowires are crystalline with a diamond cubic structure (Figure 4). They are also relatively clean with no significant amounts of amorphous or particulate byproduct and predominantly straight with diameters typically ranging between 20 and 30 nm (see Figure 3 for example) and lengths greater than 1 μ m (Figure 2C and 3). Figure 2D shows an example of one Si nanowire that is longer than 3 μ m.

EDS data acquired from the tips of nanowires with visible seed particles confirmed that nanowires synthesized in the presence of both Au and Bi nanocrystals form by the SLS mechanism (see Supporting Information). The principle growth direction was \langle 111 \rangle (Figure 2B), but \sim 20% of the nanowires (like the one in Figure 2A) had a \langle 110 \rangle growth direction.

At similar reaction temperatures, equivalent Si nanowire quality and yield were obtained from reactions carried out in either octacosane or squalane and using either Au or Bi

[†] Present address: Department of Chemical Engineering - National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China.

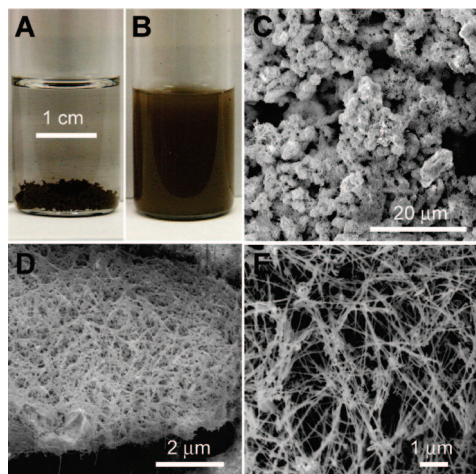


Figure 3. (A,B) Photographs of 4 mg of Si nanowires (synthesized by adding Si_3H_8 and Bi nanocrystals to octacosane at reflux) dispersed in chloroform. The nanowires settle from solution after ~ 10 min, as in (A), but readily redispense with light sonication as shown in (B). (C–E) SEM images of the Si nanowires obtained by adding Si_3H_8 and Bi nanocrystals to octacosane at 430°C . (The reactions were carried out for 10 min with a Si/Bi atomic ratio of 1600:1. The average nanowire diameter and length are 25.8 ± 5.3 nm and 2.0 ± 0.9 μm , respectively.)

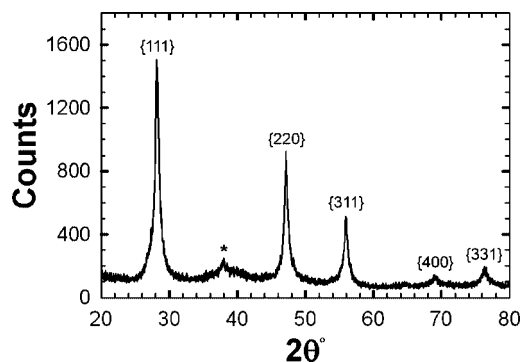


Figure 4. XRD from 2 mg of Si nanowires made by Si_3H_8 decomposition under ambient pressure in refluxing squalane in the presence of Au nanocrystals. The diffraction pattern indexes to diamond cubic Si [pdf # 027-1402]. The peak labeled with * corresponds to the {111} diffraction peak of Au (see Supporting Information for XRD of Bi-seeded Si nanowires).

nanocrystals as seeds (see Supporting Information). The nanowire growth process was found to be insensitive to the metal/Si eutectic temperature, and therefore it appears that Si_3H_8 decomposition is the limiting process in nanowire growth. This is similar to the Au-seeded SFSL growth of Si nanowires using phenylsilanes as reactants, in which reactant decomposition kinetics set the growth temperature near 450°C .^{15,16}

Si_3H_8 decomposition proceeds through the formation of various polysilane ($\text{Si}_n\text{H}_{2n+2}$) intermediates, silylene (SiH_2), and silyl radicals.²¹ All of these reaction intermediates eventually reduce to silane (SiH_4) via the 1,2-hydrogen shift reaction mechanism,²¹ which then decomposes to Si. Si_3H_8 (~ 300 – 310°C) and other polysilanes decompose at lower temperature than

SiH_4 , which requires temperatures exceeding 400°C .^{17,21–24} A significant yield of crystalline nanowires was observed only when reactions were carried out at temperatures higher than 410°C , which is consistent with *in situ* SiH_4 decomposition being the limiting step in the nanowire growth process.

In conclusion, large quantities of crystalline Si nanowires can be obtained by SLS growth using trisilane as a reactant with either Au or Bi nanocrystals as seeds in high boiling point solvents, octacosane or squalane. In contrast to the use of organosilanes for Si nanowire growth in solution, Si_3H_8 is sufficiently reactive to yield nanowire growth in a solvent under ambient pressures and provides a reactant that gives no carbonaceous byproduct. The reaction scheme outlined here provides many future possibilities for exploring Si nanowire doping, diameter and length control, surface passivation, and scaleup using solution-based processes.

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Supporting Information Available: Au/Si and Bi/Si phase diagrams, experimental details, and EDS, TEM, and SEM of wires synthesized under various reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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