Importance of Solvent-Mediated Phenylsilane Decompositon Kinetics for High-Yield Solution-Phase Silicon Nanowire Synthesis

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The colloidal synthesis of silicon (Si) nanomaterials in solution is challenging because Si is difficult to crystallize and Si atoms are not easily generated from silane reactants at the relatively low temperatures afforded by solvents; nonetheless, significant progress has been made in this regard in recent years.[1–7] One relatively successful approach for producing crystalline Si nanowires in organic solvents has been supercritical fluid-liquid–solid (SFLS) growth.[8–13] In this process, gold nanocrystals are fed with a silane reactant into a hot, pressurized supercritical solvent that can be heated above the Au:Si eutectic temperature of ~360 °C; the silane decomposes to Si, which dissolves in the Au seed particles and crystallizes into nanowires.[8] The silane decomposition kinetics are of central importance to the yield and quality of nanowires.[12,14]

Recently, we studied several silane reactants for SFLS nanowire growth, including alkylsilanes, arylsilanes and polysilanes, and determined that monophenylsilane (MPS) is the best organosilane reactant for Au-seeded SFLS Si nanowires.[12] MPS gives very high quality Si nanowires; however, the MPS conversion to Si in a typical reaction has thus far been relatively low, with product yields of only 1−5%. Thus, we have sought ways to enhance reactant decomposition while maintaining high quality nanowire growth. This is not straightforward because reactant decomposition must balance with nanowire growth, otherwise homogeneous particle nucleation can occur. For example, we have found that trisilane decomposes much faster than MPS, but its decomposition is so rapid that it leads to amorphous Si particles instead of nanowires.[12,14,15] We have also explored catalysts like metal halides that are known to accelerate MPS decomposition;[16] but have found that these additives in general disrupt nanowire growth. In the course of these studies, we have discovered that MPS decomposition is dramatically influenced by the solvent. We report here our findings: changing the solvent from hexane to toluene and benzene increases the yield of Si nanowires from milligram quantities to tens-of-milligrams in a 10 mL reactor, with over 50% atomic conversion of silane to Si nanowires.

Figure 1 shows a photograph of 40 mg of Si nanowires obtained from MPS decomposition in supercritical benzene at 460 °C and 6.9 MPa in the presence of dodecanethiol-capped Au nanocrystals (see the Supporting Information for experimental details). Scanning electron microscopy (SEM) (Figure 1b) shows that the product is composed of nanowires with very little particulate byproduct. The nanowires are more than 20 μm long with aspect ratios greater than 1000 (Figure 1c−e). X-ray diffraction (XRD) (Figure 1g) and lattice imaging by TEM (Figure 1f) confirm that the nanowires are crystalline diamond cubic Si with few extended defects and little variation in diameter along their length. <111> was the predominant growth direction of most of the nanowires (~90%), with the remainder (10%) growing in either the <110> or <211> directions, as we have found previously for Au-seeded Si nanowires.[12,14]

The nanowire product ranges from a dark green appearance to a yellow color. For example, the Si nanowire product in Figure 1 has a yellow color near the edges of the substrate. Reactions at higher temperature tend to produce more yellow product, like the nanowires in Figure 2a that were produced at 500 °C. In SEM images, the dark green and yellow products look similar with no noticeable difference in quality; however, TEM reveals that the yellow nanowires have thicker sidewall coatings of amorphous material (about 5 to 18 nm thick) composed of Si and small amounts of carbon and oxygen (see Figures S3 and S4 in the Supporting Information for compositional mapping of the surface layer by nanobeam EDS). TEM imaging of the green product reveals that these wires have only a very thin (<2 nm) rough surface layer (Figure 1f). The total yield of nanowires increases with increasing reaction temperature, with reactions at 460 °C giving a conversion of ~50% and reactions at 500 °C giving ~63%; however, nanowires produced at 500 °C had significantly thicker side-wall deposition of the amorphous layer and were much more yellow in color (Figure 2a).

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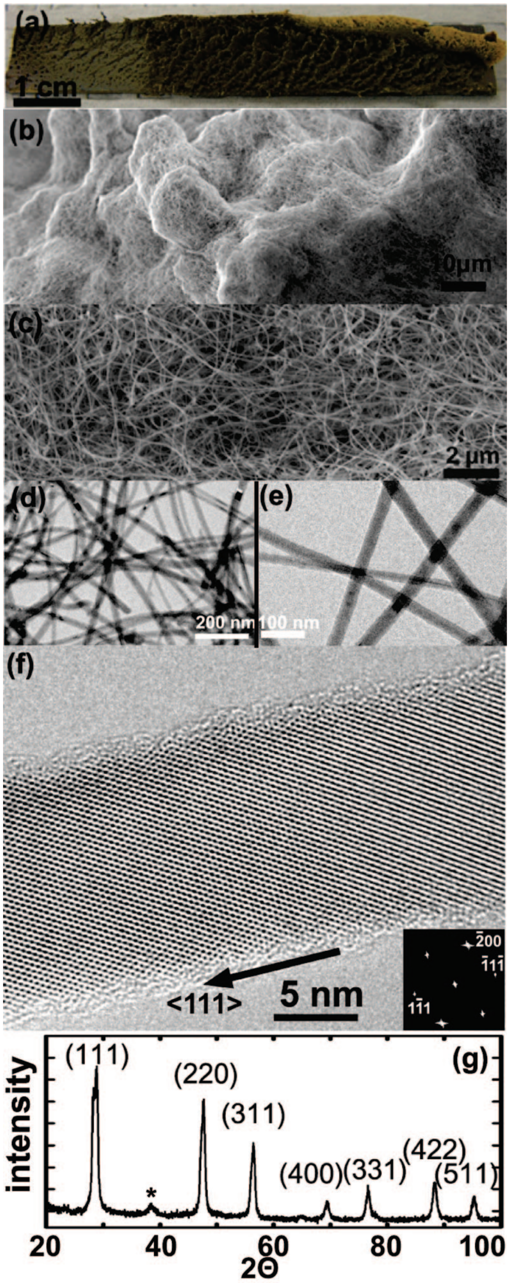


Figure 1. SFLS-grown silicon nanowires produced with Au nanocrystals, MPS in benzene: (a)photograph; (b, c) SEM; (d−f) TEM; (g) XRD. In (g), the peak labeled "*" corresponds to Au.

Figure 2 shows SFLS-grown Si nanowires generated from MPS in either benzene, toluene or hexane at 500 °C. There is a large difference in the amount of product obtained, with benzene giving the largest quantity of nanowires and hexane giving the lowest. In benzene, 63% of the Si converted from MPS to nanowires; in toluene, 38.4% was converted and in hexane, only 1.4% was converted (see Table S1 in the Supporting Information for yield calculations).

Our findings show that MPS decomposition and Si nanowire growth depend strongly on the solvent. Coutant and Levy[17] determined from gas-phase decomposition reactions of phenylsilanes that monophenylsilane undergoes homogeneous bimolecular disproportionation, involving hydrogen and phenyl exchange via a four-center activated complex to produce silane and diphenylsilane:

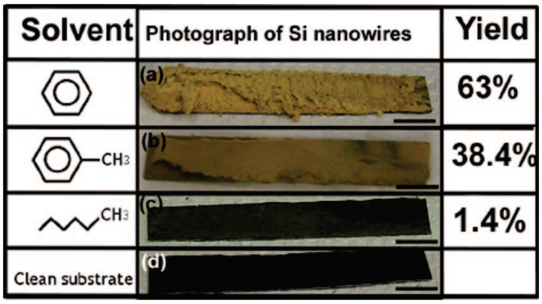
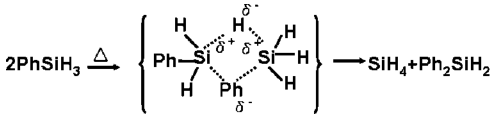


Figure 2. Photographs of silicon nanowires obtained by Au nanocrystal-seeded SFLS growth in different solvents. Nanowires were collected on a silicon substrate placed in the reactor. The yields are given as atomic conversions of Si from MPS to crystalline Si. Complete conversion MPS to Si is limited to 75%.[10,11] The scale bar is 1 cm.



Phenylsilane disproportionation reactions have also been observed many years ago in solution in both the presence and absence of catalyst.[18–20] In the SFLS nanowire growth reactions, monophenylsilane decomposition most likely occurs via disproportionation to silane.[12] If disproportionation proceeds via a similar four-center transition state (which is most likely), then it would not be surprising that benzene and toluene more effectively stabilize this transition state than hexane, thus leading to accelerated reactions in these solvents. This is similar to what occurs in many organic reactions in which the solvent plays an influential role.[21] It is also worth noting that alkylsilanes can disproportionate,[20] but in the absence of catalyst these reactions are too slow to generate significant quantities of nanowires.[12]

There is also a noticeable difference in the quality of the nanowires produced in benzene versus toluene. The yield is lower in toluene and the reactions are not as clean, with more particulate byproduct; XRD patterns from the product obtained in toluene also have a broad peak at $2\theta \approx 52°$ because of amorphous byproducts (see Figure S5 in the Supporting Information for example). Of the solvents tested, benzene gives the highest yield, the least particulate byproduct and the highest quality crystalline Si nanowires.

In conclusion, high conversions of MPS to Si nanowires (>50%) were achieved in solution-phase reactions, giving tens-of-mg quantities of nanowires in a single reaction. The decomposition kinetics of MPS depend strongly on the solvent, with benzene giving much higher yields than hexane. We propose that benzene better stabilizes the intermediate species involved in the homogeneous bimolecular disproportionation of phenylsilane to enhance MPS decomposition

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relative to hexane. This study demonstrates that the SFLS approach to Si nanowires has the potential to be scaled up for kg/day production.

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Supporting Information Available: Experimental details, SEM, TEM, elemental mapping by nanoprobe EDS, XRD, and nanowire yield calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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