

Bulk synthesis of silicon nanowires using a low-temperature vapor–liquid–solid method

M. K. Sunkara,^{a)} S. Sharma, and R. Miranda

Department of Chemical Engineering, University of Louisville, Louisville, Kentucky 40292

G. Lian and E. C. Dickey

Department of Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky 40506

(Received 16 May 2001; accepted for publication 10 July 2001)

Silicon nanowires will find applications in nanoscale electronics and optoelectronics both as active and passive components. Here, we demonstrate a low-temperature vapor–liquid–solid synthesis method that uses liquid-metal solvents with low solubility for silicon and other elemental semiconductor materials. This method eliminates the usual requirement of quantum-sized droplets in order to obtain quantum-scale one-dimensional structures. Specifically, we synthesized silicon nanowires with uniform diameters distributed around 6 nm using gallium as the molten solvent, at temperatures less than 400 °C in hydrogen plasma. The potential exists for bulk synthesis of silicon nanowires at temperatures significantly lower than 400 °C. Gallium forms a eutectic with silicon near room temperature and offers a wide temperature range for bulk synthesis of nanowires. These properties are important for creating monodispersed one-dimensional structures capable of yielding sharp hetero- or homointerfaces. © 2001 American Institute of Physics.

[DOI: 10.1063/1.1401089]

Nanorods of semiconductors and metals will find both passive and active applications in electronics and optoelectronics.^{1–3} Silicon at nanoscale dimensions becomes a direct-band-gap semiconductor due to quantum-confinement effects.⁴ This property enables silicon nanowires to exhibit visible photoluminescence at room temperature. Similarly, the electrical conduction and optoelectronic properties of other elemental semiconductor and metallic wires of nanoscale dimensions are of fundamental interest.^{5–8} For these reasons, nanowire synthesis methods that allow direct generation of sharp homo- and heterointerfaces are of great importance, yet unavailable.

Nanowires have been obtained with methods such as step-edge templating⁹ and nanotube-confined reactions.^{10,11} Using the well-known vapor–liquid–solid (VLS) mechanism,¹² several researchers exploited different techniques to create the necessary nanometer-scale metastable droplets of transition-metal catalysts in order to synthesize nanowires.^{13–18} However, the required synthesis temperatures when using these metals range from 500 °C for gold to 950–1150 °C for other transition metals. In addition, all these metals exhibit high eutectic compositions, for example, 31 at.% Si for Au–Si at 371 °C. Other variations of VLS techniques such as solution–liquid–solid¹⁹ and vapor–solid–solid²⁰ methods have also been reported. All these techniques require the creation of nanometer-scale catalyst particles, which in itself is a nontrivial task. In some cases, it may be impossible to create 1–3-nm-size droplets without the help of stabilizing surfaces or templates. In addition, the high eutectic composition would make it impossible to generate abrupt heterointerfaces in a nanowire by simply switching the gas-phase precursor for the dissolved

component. One would predict the precipitation of a ternary phase instead of a pure second component when a second component is dissolved into these eutectics. Here, we report a VLS technique that does not require either nanometer-scale droplets or catalyst metals at high temperatures for the bulk synthesis of silicon nanowires. Our technique utilizes atomic-hydrogen-mediated gas-phase chemistry to synthesize silicon nanowires using low-melting-point metals as the solvent. These low-melting-point metals form eutectics with silicon at low temperature and with extremely low content of the elemental semiconductors. This is illustrated in Fig. 1 with a Ga–Si phase diagram.²¹ Gallium forms a eutectic with small quantities of 5×10^{-8} at. % Si at 29.8 °C and exists as a perfectly mixed liquid over a broad temperature and composition range.

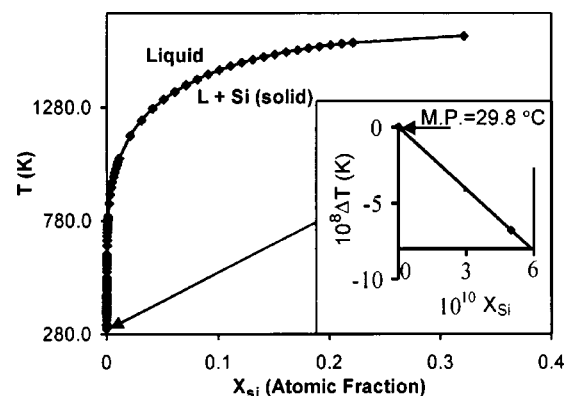
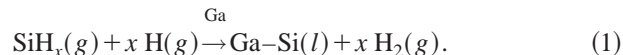


FIG. 1. Phase diagram of the Ga–Si system showing the liquidus line for silicon precipitation from the Ga–Si molten alloy (see Ref. 21). Inset shows the magnified version of the solubility diagram for the Ga–Si system near the eutectic point. ΔT denotes the difference between the melting point of gallium and the eutectic temperature. The eutectic temperature is approximately 7×10^{-8} K less than the melting point for gallium metal.

^{a)}Electronic mail: mahendra@louisville.edu

This gallium-mediated VLS growth of Si wires represents a broad class of VLS techniques using low-melting-point metals such as Ga, In, and Bi. The significant difference of this technique with respect to others that rely on catalytic decomposition of silane by transition metals is that silane or silyl decomposition is mediated by atomic hydrogen:



Gallium is not known for its catalytic activity for dehydrogenation. Nevertheless, reaction (1) is thermodynamically feasible, although its kinetics and mechanism are not known and currently being studied.

The Ga-Si liquidus line, shown in Fig. 1, indicates that Si precipitation from a Ga-Si alloy is possible at temperatures as low as 100 °C. Because of the low equilibrium composition of Si in the liquid alloy, the critical nucleus size for silicon crystallization from the Ga-Si melt tends to be in the nanometer range, according to classical nucleation theory for solute precipitation from dissolved solutions:²²

$$d_c = \frac{4\Omega\alpha}{RT \ln\left(\frac{C}{C_\infty}\right)}, \quad (2)$$

where, d_c , Ω , α , C , and C_∞ represent the critical nucleus diameter, molar volume, surface free energy, concentration of silicon within a liquid alloy, and equilibrium concentration, respectively. At a temperature of 400 °C, using typical values for surface free energy²³ of 1610 erg/cm² and a molar volume of 1.2×10^{-5} m³/mol, the critical nucleus diameter is estimated to be around 6 nm with a modest dissolved Si concentration of 1 at.%. In comparison, other systems involving transition metals or noble metals as liquid media exhibit equilibrium compositions in excess of 20–30 at.%, and thus the critical nuclei sizes exceed the equilibrium sizes of droplets, which are around 0.2 μm .²³ Low miscibility and high surface tension in the Ga-Si system influence the nuclei to surface out and ensure that further growth of these nuclei is one-dimensional. The diameter of these nanowires depends upon the supersaturation of Si in the Ga-Si liquid alloy, which then controls the crystallization rate and diameter distribution. However, the supersaturation in liquid gallium would depend upon several variables such as substrate temperature, gas-phase composition, and plasma kinetics. These factors allow control of the size and size distribution of nanowires and eliminate the problems associated with the creation of quantum-sized droplets.

The experiments were conducted in a microwave plasma reactor (ASTEX 5010) using a H₂/N₂ gas mixture. Silicon substrates covered with a thin film of Ga were exposed to 1:100 sccm of H₂ in N₂ plasma at 700 W microwave power. The hydrogen plasma etches exposed silicon regions to provide silyl radicals in the vapor phase. The substrate temperature was measured using an infrared pyrometer (a Raytek model RAYMA2SCCF) to be around 400 °C. The experiments were conducted for durations ranging from 1 to 9 h. The length of the wires was directly proportional to the duration of the experiment. A 3 h growth experiment produced nanowires hundreds of microns long with diameters ranging

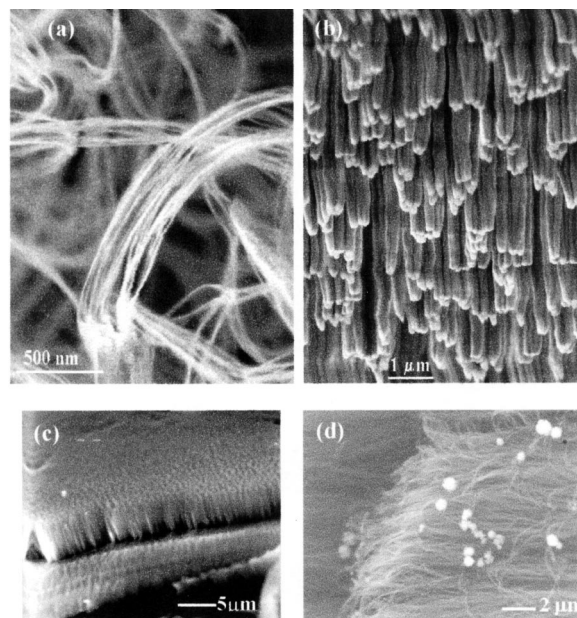


FIG. 2. Silicon nanowires grown using our Ga VLS process: (a) silicon nanowires (~10 nm size) growing as a bunch of filaments; (b), (c), and (d) oriented growth of silicon nanowires using pools of gallium melt (approximate sizes of 90, 90, and 50 nm). The range of experimental conditions: microwave power of 700–1000 W, pressure of 30–60 Torr, growth duration of 4–8 h, and H₂/N₂ of 0.5%–1%.

from 6 to 50 nm. The size distribution of the resulting nanowires from an individual pool of gallium was uniform. Figure 2 shows scanning electron microscopy (SEM) images of silicon nanowires synthesized using pools of gallium. The different wire diameters observed resulted from different amounts of atomic hydrogen in the gas phase. The SEM images in Fig. 3 illustrate how silicon nanowires nucleate and grow as one-dimensional crystals. Figure 3(a) shows submicron-sized silicon rods growing out of a larger-size gallium droplet and Fig. 3(b) shows growth of nanowires with 20 nm mean diameter from a larger-sized gallium droplet. Silicon nanowires were also obtained using gallium-covered pyrolytic boron-nitride substrates, surrounded by small silicon pieces exposed to a microwave plasma. These results suggest that one can supply silane directly in the gas phase and control the substrate temperature independently.

Nanowires were analyzed for crystallinity and composition by high-resolution transmission electron microscopy (HRTEM) (200kV JEOL 2010F model) and energy-dispersive x-ray spectroscopy (EDS) (see Fig. 4). The bright-field image in Fig. 4(a) shows 6-nm diam nanowires with gallium droplets at their tips. The EDS spectrum shown in Fig. 4(b) confirms the existence of silicon in the bulk of the wire. The signal for Cu resulted from the transmission electron microscopy (TEM) grid and O resulted from the surface oxide. The HRTEM images in Figs. 4(d) and 4(e) show lattice images of two crystalline silicon nanowires. The lattice spacings indicated in Figs. 4(d) and 4(e) match that of bulk silicon in the diamond cubic structure. The wires are found to be polycrystalline with no obvious preferred growth direction.

Results confirm that bulk synthesis of silicon nanowires can be achieved with a noncatalytic, low-melting-point metal solvent, gallium. Because of its low miscibility with several

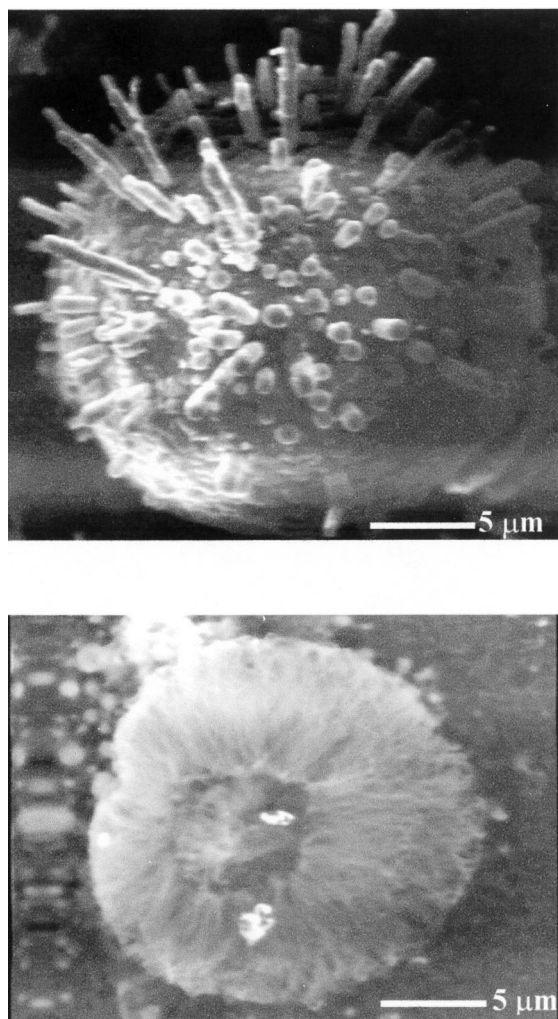


FIG. 3. SEM images showing evidence for nucleation of multiple sub-micron and nanoscale silicon wires from a single gallium droplet in two different experiments: (a) 1000 W power, 30 Torr, 3 h duration, and H_2/N_2 : 0.25%; (b) 950 W power, 50 Torr pressure, 7 h duration, and H_2/N_2 of 0.95%.

other elemental semiconductors and metals, the processing method can be extended to many different materials. For example, Ge forms a eutectic with gallium at 30 °C at a composition of 5×10^{-5} at. % Ge.²¹ However, the main advance is that it is not necessary to create quantum-sized droplets for bulk synthesis of quantum wires. This becomes more important when one considers the synthesis of 1–3-nm-size wires or rods. The structure of Si nanowires with sizes in the 1–3 nm range could differ from the bulk silicon structure by having Si_{24} -type clusters in the core.²⁴ These 1–3 nm silicon nanowire structures made of cage compounds are predicted to be optimum for atomically controlled doping, which is important for molecular electronics (one dopant atom per cage).²⁵ The VLS method reported here can be generalized to other low-melting metals, such as indium, bismuth, and tin, to grow a variety of elemental semiconductor and metallic nanowires using appropriate precursors in the vapor phase. Moreover, this method affords the generation of compositionally modulated nanowires and sharp interfaces by means

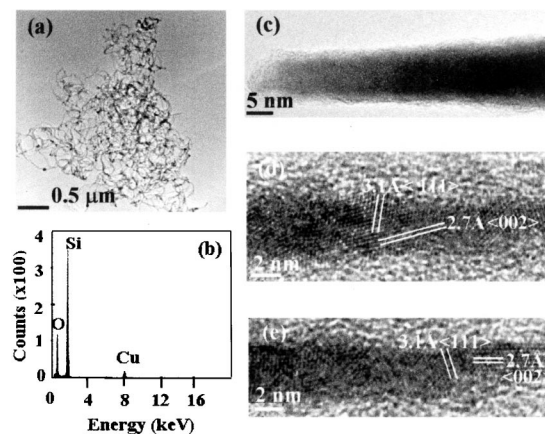


FIG. 4. (a) Bright-field TEM image of a cluster of Si nanowires. The samples were prepared by ultrasonicated the nanowires in ethanol and placing a drop of the suspension on a TEM carbon support film. (b) EDS spectrum from an individual nanowire confirms the presence of Si with no detectable Ga. The O peak results from the surface oxide on the nanowire and the Cu is an artifact from the Cu TEM grid. (c) TEM image of a 10 nm Si rod with an amorphous- SiO_x surface layer. (d) and (e) additional HRTEM images of 6 nm Si nanowires showing the crystalline structure.

of dynamic switching of vapor-phase precursors during synthesis. This is the subject of on-going research.

Partial financial support from National Science Foundation through CAREER Grant No. 9876251 and infrastructure Grant No. 0083103 is gratefully appreciated.

¹C. Wu, *Prism* **10**, 21 (2000).

²Y. Cui and C. M. Lieber, *Science* **291**, 851 (2001).

³A. P. Alivisatos, *Science* **271**, 933 (1996).

⁴D. P. Yu, Z. G. Bai, J. J. Wang, Y. H. Zou, W. Qian, J. S. Fu, H. Z. Zhang, Y. Ding, G. C. Xiong, L. P. You, J. Xu, and S. Q. Feng, *Phys. Rev. B* **59**, R2498 (1999).

⁵S.-W. Chung, J.-Y. Yu, and J. R. Heath, *Appl. Phys. Lett.* **76**, 2068 (2000).

⁶F. C. K. Au, K. W. Wong, Y. H. Tang, Y. F. Zhang, I. Bello, and S. T. Lee, *Appl. Phys. Lett.* **75**, 1700 (1999).

⁷A. Zunger and L.-W. Wang, *Appl. Surf. Sci.* **102**, 350 (1996).

⁸A. M. Saitta, F. Buda, G. Fiumara, and P. V. Giaquinta, *Phys. Rev. B* **53**, 1446 (1996).

⁹P. Scheier, B. Marsen, M. Lonfat, W.-D. Schneider, and K. Sattler, *Surf. Sci.* **458**, 113 (2000).

¹⁰W. Han, S. Fan, Q. Li, and Y. Hu, *Science* **277**, 1287 (1997).

¹¹C.-H. Kiang, J.-S. Choi, Todd T. Tran, and A. D. Bacher, *J. Phys. Chem. B* **103**, 7449 (1999).

¹²R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).

¹³J. Westwater, D. P. Gosain, S. Tomiya, S. Usui, and H. Ruda, *J. Vac. Sci. Technol. B* **15**, 554 (1997).

¹⁴A. M. Morales and C. M. Lieber, *Science* **279**, 208 (1998).

¹⁵X. Duan and C. M. Lieber, *Adv. Mater.* **12**, 298 (2000).

¹⁶X. Duan and C. M. Lieber, *J. Am. Chem. Soc.* **122**, 188 (2000).

¹⁷S. Q. Feng, D. P. Yu, H. Z. Zhang, Z. G. Bai, and Y. Ding, *J. Cryst. Growth* **209**, 513 (2000).

¹⁸Y. F. Zhang, Y. H. Tang, N. Wang, C. S. Lee, I. Bello, and S. T. Lee, *J. Cryst. Growth* **197**, 136 (1999).

¹⁹J. D. Holmes, K. P. Johnston, R. C. Doty, and B. A. Korgel, *Science* **287**, 1471 (2000).

²⁰J. L. Gole, J. D. Stout, W. L. Rauch, and Z. L. Wang, *Appl. Phys. Lett.* **76**, 2346 (2000).

²¹C. D. Thurmond and M. Kowalchik, *Bell Syst. Tech. J.* **39**, 169 (1960).

²²W. A. Tiller, *The Science of Crystallization: Microscopic Interfacial Phenomena* (Cambridge University Press, New York, 1991), p. 346.

²³E. I. Givargizov, *J. Cryst. Growth* **31**, 20 (1975).

²⁴M. Menon and E. Richter, *Phys. Rev. Lett.* **83**, 792 (1999).

²⁵U. Landman, R. N. Barnett, A. G. Scherbakov, and P. Avouris, *Phys. Rev. Lett.* **85**, 1958 (2000).