Supercritical Fluid−Liquid−Solid Synthesis of Gallium Phosphide Nanowires

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Rapid advances in the study of semiconductor nanowires have pressed the need for general synthetic methods applicable to a broad range of materials. In addition to serving as experimental models with the potential for quantum confinement in one-dimension, nanowires have been proposed as the materials basis for a variety of self-assembled nanoscale electronic and optical devices. Semiconductor nanowires can be produced by both vapor-phase and solution-phase routes using a metal particle-seeded approach.[1] The primary requirement for metal particle-seeded growth of semiconductor nanowires is a reaction temperature that exceeds a metal/semiconductor eutectic temperature. Using gas-phase reactants for metal particle-seeded nanowire growth, as in the case of chemical vapor deposition (CVD) and laser ablation, the process is called vapor−liquid−solid (VLS) growth.[1−3] Metal-seeded nanowire growth in solution has been called solution−liquid−solid (SLS) or liquid−liquid−solid (LLS) growth.[4−7] Since most semiconductor/metal eutectic temperatures exceed the boiling point of conventional solvents, we have explored the use of pressurized solvents at temperatures exceeding their critical points to produce a wider range of materials, and have referred to this approach as supercritical fluid−liquid−solid (SFLS) growth.[8−12]

Reaction temperatures exceeding most metal/semiconductor eutectic temperatures are accessible in high-temperature supercritical fluids, which can be heated to ∼600 °C without significant degradation for some solvents (i.e., toluene). For example, the eutectic temperatures of Au:Si and Au:Ge are both approximately 350 °C, which is easily accessible using supercritical fluids. Other semiconductors, such as Group III−V materials such as GaAs are more challenging, as the eutectic temperatures with Au are in excess of 500 °C. In our laboratory, we have previously demonstrated SFLS synthesis of Si,[8−10] Ge,[10,11] and most recently GaAs,[12] nanowires in supercritical hexane. Yet it remains to be seen how general the SFLS approach will be for semiconductor nanowire synthesis. There is a delicate balance between precursor reactivity and nanowire growth: if the precursors are too reactive, or the temperatures are too high, then homogeneous nucleation and precipitation of particles occurs. Here we demonstrate the successful SFLS synthesis of the Group III−V semiconductor, gallium phosphide (GaP).

GaP nanowires were synthesized in hexane at 500 °C and 37 MPa ($T_c = 507.5$ K; $P_c = 3.01$ MPa)[13] by reacting $P(SiMe_3)_3$ (STREM Chemical Co.) and $(t\mathrm{Bu})_3\mathrm{Ga}$[14] in the presence of 7.5-nm-diameter dodecanethiol-stabilized gold nanocrystals[15] using a reaction setup like that described by Hanrath et al.,[11] modified to include two 200-μL, in series, 6-way HPLC injection loops. A 1-mL titanium reaction cell with a Si/SiO_2 deposition substrate was heated to 500 °C and pressurized to 7 MPa. The Au nanocrystal dispersion and a stock solution containing both precursors were injected into the reactor sequentially using an HPLC pump set at 2.75 mL/min and a maximum pressure of 37 MPa. For this semibatch process, the concentration of each precursor reached 10 mM with a 100:1 precursor/gold mole ratio. The resulting product was a light yellow mesh of tangled wires, as shown in the scanning electron microscope (SEM) image in Figure 1a. The highest quality GaP nanowires produced by SFLS ranged in diameter from 6 to 50 nm with an average diameter of approximately 20 nm and lengths up to tens of micrometers.

X-ray diffraction (XRD) patterns obtained from the nanowire product (Figure 2a) match that of zinc blende GaP (JCPDS Card 32-0397). EDS of individual nanowires (Figure 2b) show predominantly Ga and P with trace amounts of Si. The carbon and oxygen signals can be attributed to surface contamination, and copper from the support grid also appears in the spectra. The Si detected by EDS is most likely present in the GaP nanowires as a result of unintentional doping from the phosphorus precursor. In the case of the GaAs nanowires described in ref 12, electrical measurements and compositional analysis indicated that Si served as a n-type dopant in GaAs nanowires synthesized using $As(SiMe_3)_3$ as the Group V precursor.[12] Figure 3 shows an HRTEM image of a typical GaP nanowire. The wire is a single crystal with a lattice

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(1) For a recent review, see Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.
(2) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(3) See for example, Duan, X.; Lieber, C. M. *Adv. Mater.* **2000**, *12*, 298 and references contained therein.
(4) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1791.
(5) Dingman, S. D.; Rath, N. P.; Markowitz, P. D.; Gibbons, P. C.; Buhro, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1470.
(6) Yu, H.; Buhro, W. E. *Adv. Mater.* **2003**, *15*, 416.
(7) Grebinski, J. W.; Richter, K. L.; Zhang, J.; Kosel, T. H.; Kuno, M. *J. Phys. Chem. B*, **2004**, *108*, 9745.
(8) Holmes, J. D.; Johnston, K. P.; Doty, R. C.; Korgel, B. A. *Science* **2000**, *287*, 1471.
(9) Lu, X.; Hanrath, T.; Johnston, K. P.; Korgel, B. A. *Nano Lett.* **2003**, *3*, 93.
(10) Hanrath, T.; Korgel, B. A. *Adv. Mater.* **2003**, *15*, 437.
(11) Hanrath, T.; Korgel, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 1424.
(12) Davidson, F. M., III; Schricker, A. D.; Wiacek, R. J.; Korgel, B. A. *Adv. Mater.* **2004**, *7*, 646.
(13) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987; p 703.
(14) $(t\mathrm{Bu})_3\mathrm{Ga}$ was synthesized as described by Kovar, R. A.; Derr, H.; Brandau, D.; Callaway, J. O. *Inorg. Chem.* **1975**, *14*, 2809.
(15) Dodecanethiol nanocrystals were synthesized using procedures described by Saunders, A. E.; Sigman, M. B.; Korgel, B. A. *J. Phys. Chem. B* **2004**, *108*, 193−199.

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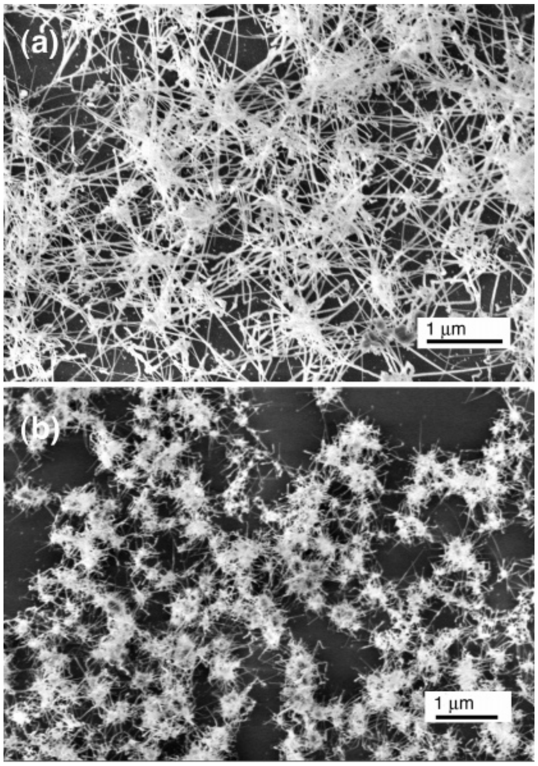

Figure 1. HRSEM images of GaP nanowires formed in hexane at 500 °C and 37 MPa by reacting (tBu)$_3$Ga and P(SiMe$_3$)$_3$ in the presence of (a) 7.5-nm Au nanocrystals and (b) 4-nm Au nanocrystals.

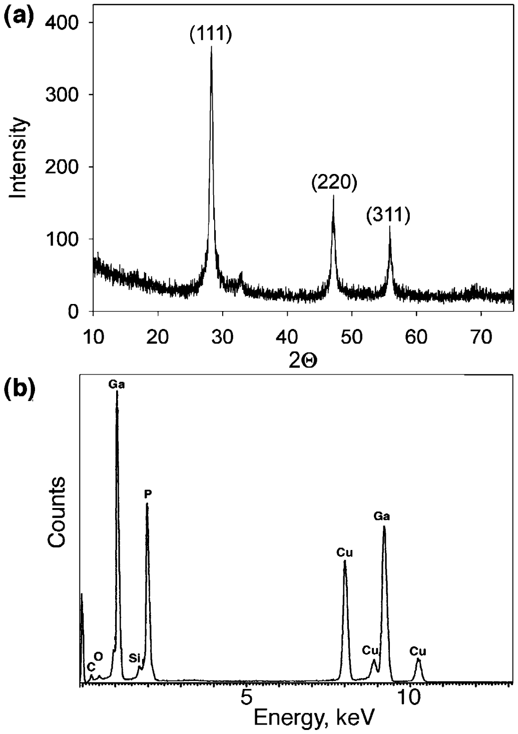

Figure 2. (a) XRD pattern (Bruker-Nonius D8 Advance theta-2theta powder diffractometer, Cu Kα radiation with a wavelength of 1.54 Å) of GaP nanowires produced at 500 °C and 37 MPa from (tBu)$_3$Ga, P(SiMe$_3$)$_3$ and 7.5-nm Au nanocrystals. (b) Nanobeam EDS of a wire indicates the predominant presence of Ga and P with trace amounts of Si. The Cu signal appears from background scatter from the copper TEM grid.

spacing of 0.316 nm, in good agreement with the expected (111) lattice spacing of bulk GaP (0.314 nm). All nanowires imaged by HRTEM (20 of 20 wires examined with visible lattice fringes) were observed to grow in the [111] direction.

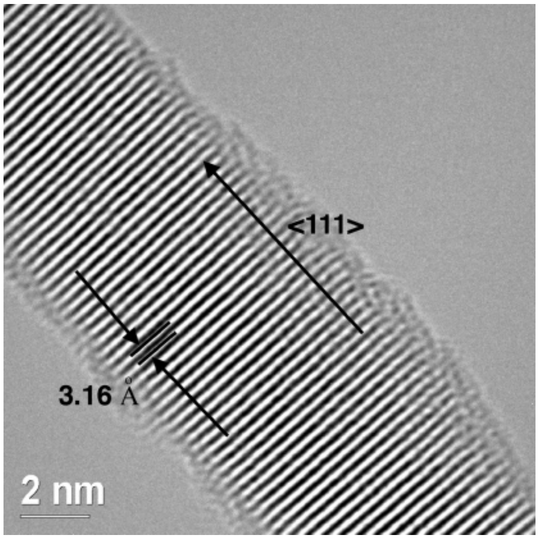

Figure 3. HRTEM image of a GaP nanowire.

In comparison to SFLS GaAs nanowire synthesis as in ref 12, a slower precursor injection rate was needed to reduce excessive particulate formation. To avoid homogeneous particle nucleation and growth, the precursor degradation kinetics must balance with the rate of heterogeneous precursor consumption by the seed particles. Apparently, the nanowire growth rate is slower for GaP nanowires compared to GaAs, most likely due to a greater crystallization energy requirement for GaP. Furthermore, there appears to be a seed particle size dependence on the nanowire growth rate, as smaller (~4 nm) Au nanocrystals produced poor quality short nanowires (as shown in Figure 1b) with low yield, most likely as a result of slower nanowire growth. This is consistent with observations in VLS nanowire synthesis by CVD of decreasing growth rate with decreasing seed particle size.[16]

The most significant challenge to producing GaP nanowires by SFLS results from a difference in decomposition kinetics between the phosphorus and gallium precursors. Comparing the GaP system to the GaAs system, the precursor P(SiMe$_3$)$_3$ is more stable than its arsenic corollary, and free Ga metal accumulates during the GaP reaction when the precursors are fed into the reactor stoichiometrically. Excess Ga generated in the reactor accumulates at the tips of growing nanowires and can even seed new nanowires. This fact was discovered after performing nanobeam energy dispersive X-ray spectroscopy (EDS) on particle tips at the end of several wires, which revealed only trace amounts of gold and predominantly Ga for reactions performed with 1:100 Au/precursor mole ratios—the conditions that gave the highest quality nanowires. Ga metal is a well-known SLS seed for Group III−V nanowires,[17] and so the role of the Ga and the Au nanocrystals in the SFLS process was unclear. To determine their respective roles, a series of reactions were carried out under three different conditions: one used no Au nanocrystals, one was performed at 550 °C with a 3:1 P(SiMe$_3$)$_3$/(tBu)$_3$Ga mole ratio, and a third used a very high gold/precursor mole ratio of 1:10.

In the absence of gold nanocrystal seeds, GaP nanowires are indeed still produced. Ga metal accumulates from

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(16) Yu, Y.; Fan, R.; Yang, P. *Nano. Lett.* **2002**, *2*, 83.
(17) Pan, Z. W.; Dai, S.; Beach, D. B. *Appl. Phys. Lett.* **2003**, *83*, 3159.

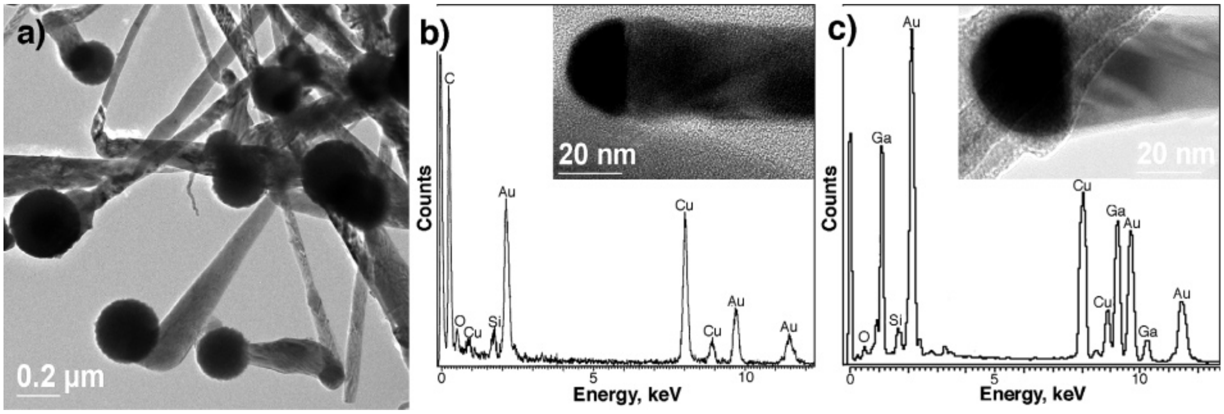

Figure 4. (a) TEM image of GaP nanowires with large Ga seed particles attached, formed in absence of Au nanocrystals. (b) HRTEM image of a Au seed particle attached to a GaP nanowire that was formed with a 3:1 P/Ga precursor ratio at 550 °C. The inset shows an EDS spectrum of the Au tip. Note the absence of Ga and P. (c) HRTEM image of an alloy seed particle consisting of both Au and Ga attached to a GaP nanowire synthesized with a 10:1 precursor/gold ratio. The inset EDS confirms the presence of both Au and Ga in the wire tip.

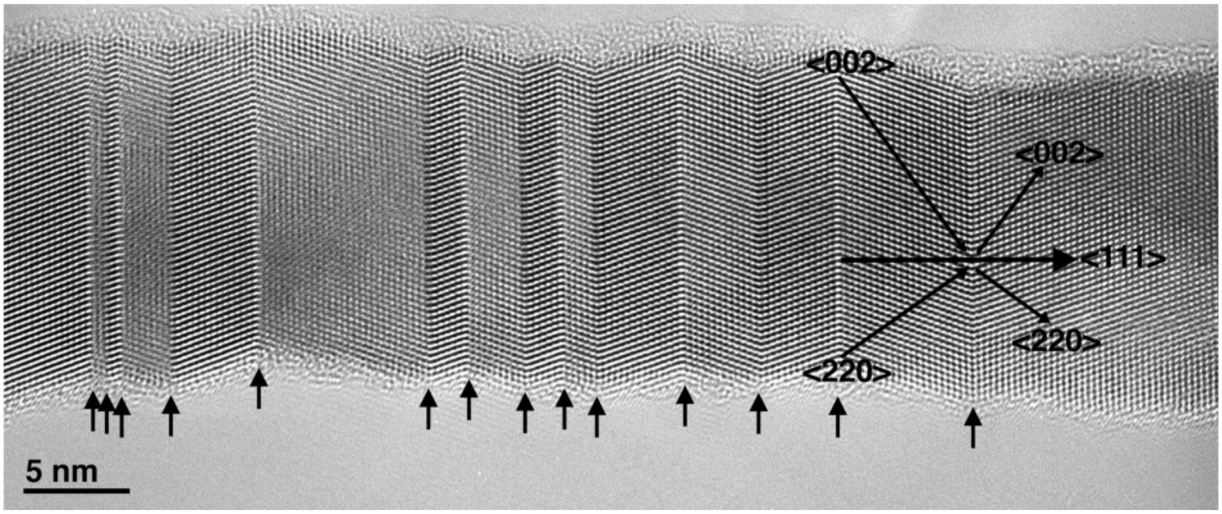

Figure 5. HRTEM image of a GaP nanowire exhibiting twinning faults perpendicular to the growth direction.

the faster decomposition of $(t\mathrm{Bu})_3\mathrm{Ga}$ relative to $\mathrm{P(SiMe_3)_3}$ seeds GaP nanowires. However, as shown in Figure 4a, the "self-seeded" GaP nanowires are of relatively poor quality, with diameters that vary greatly along their lengths as a result of rapidly increasing Ga accumulation as the reaction proceeds. With the addition of excess $\mathrm{P(SiMe_3)_3}$ to the reaction with gold nanocrystals as seeds, the nanowire diameters are consistent along their lengths and Ga buildup at the tips does not occur (Figure 4b). With stoichiometric amounts of Ga and P precursor, the use of high mole ratios of gold/precursor (i.e., 1:10) results in GaP nanowires with alloyed Ga and Au at their tips (Figure 4c). Under the best reaction conditions (1:100 gold/precursor), only trace amounts of Au is found on the tips of the nanowires. Most certainly, Ga accumulates at the nanowire tips during the process and may play a role in promoting nanowire growth; however, Au nanocrystals serve as the primary metal seeds and are required to obtain high quality nanowires with consistent diameters. Nonetheless, as nanowire growth proceeds in the reactor it appears that Au is consumed by the nanowires, most likely ending up as an impurity dopant in the nanowires.

Wires larger than 10 nm in diameter exhibited twinning faults identical to those observed in GaAs nanowires.[12,19] The faults appear in the TEM images as discrete dark lines stretching orthogonally to the length of the wire, or as planes separating segments of alternating wire contrast. Figure 5 shows a 50-nm GaP nanowire segment containing 14 twinning faults. The twins are confined to a single (111) plane and result from a reflection in order across an fcc close-packed atomic layer: in essence, the ABCABCABC stacking of close-packed layers becomes ABCA*B*ACBA, where the reflection in symmetry occurs in the italicized plane, *B*. A reflection in symmetry is also revealed in the way that the secondary [002] and [220] directions reflect off the [111] direction at the twin boundary. A matter of interest is the increased frequency of twins in GaP versus GaAs nanowires produced under the same reaction conditions. We believe that the twins form during wire growth due to localized fluctuations in conditions within the reactor, such as precursor concentration and temperature. Subtle changes in precursor reactivity during wire growth, or small GaP crystallizations at some instant within the metal seed itself, could lead to the formation of the twin. The fact that the nanowire stretches for micrometers as essentially a single crystal is itself quite remarkable.

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(18) Shah, P. S.; Hanrath, T.; Johnston, K. P.; Korgel, B. A.; *J. Phys. Chem. B* **2004**, *108*, 9574.

(19) Mikkelsen, A.; Sköld, N.; Ouattaraa, L.; Borgstrom, M.; Andersen, J. N.; Samuelson, L.; Seifert, W.; Lundgren, E.; *Nat. Mater.* **2004**, *3*, 519.

The SFLS method represents a general strategy for the production of binary semiconductor nanowires. A suitable metal/semiconductor pair must be identified with a eutectic temperature in the appropriate range. And as with GaAs,[12] and Si and Ge for that matter,[8−11] the precursor decomposition kinetics must not be too fast relative to the wire growth rate for high-quality GaP nanowires. In addition, the degradation rates of each individual precursor must be well matched to avoid secondary reactions and other complications. Finally, the reactor design itself must be considered, as the broad distribution of GaP wire diameters produced in the semibatch reactor that results from significant amounts of seed particle aggregation during the reaction could perhaps be reduced by changing to a continuous SFLS process, as has been demonstrated for Ge nanowires.[18] Given the convincing demonstrations of solution-phase VLS-type growth of Si,[8−10] Ge,[10,11] AlAs,[20] InN,[5] GaAs,[6,12] InAs,[21] and InP,[22] solution-based methods for nanowire synthesis clearly offer a great flexibility in materials and structures, with the additional potential for in situ doping and surface derivitization.[23] Many of the remaining challenges facing the metal particle-seeded growth of semiconductor nanowires in solution relate to processing challenges, such as scale-up and the ability to tightly control the nanowire diameter in large (i.e., gram-scale) preparations of nanowires.

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(20) Markowitz, P. D.; Zach, M. P.; Gibbons, P. C.; Penner, R. M.; Buhro, W. E. *J. Am. Chem. Soc.* **2001**, *123*, 4502.

(21) Kan, S.; Mokari, T.; Rothenberg, E.; Banin, U. *Nat. Mater.* **2003**, *2*, 155.

(22) Yu, H.; Li, J.; Loomis, R. A.; Wang, L. W.; Buhro, W. E. *Nat. Mater.* **2003**, *2*, 517.

(23) Hanrath, T.; Korgel, B. A. *J. Am. Chem. Soc.* **2004**, *126* (47), 15466−15472.