Synthesis and optical properties of gallium arsenide nanowires

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Gallium arsenide (GaAs) nanowires have been synthesized in bulk quantities and high purity by laser-assisted catalytic growth. Field-emission scanning electron microscopy and transmission electron microscopy investigations show that the GaAs nanowires are produced in >90% yield, are single crystals with ⟨111⟩ growth axes, and have diameters varying from three to tens of nanometers, and lengths extending to tens of micrometers. Photoluminescence (PL) measurements made on individual GaAs nanowires show large blueshifts in the PL peak position compared to bulk GaAs, and are consistent with strong quantum confinement. The implications of these results are discussed. © *2000 American Institute of Physics.* [S0003-6951(00)01509-6]

The growth and elucidation of the properties of well-defined nanoscale materials are critical to efforts directed towards understanding the fundamental physics of nanostructures, creating nanostructured materials, and developing new nanotechnologies.[1–5] In this regard, one-dimensional systems, such as nanowires and carbon nanotubes, have great potential to address basic issues about dimensionality and could play key roles in applications, including photonics,[5,6] nano/molecular electronics,[3,4] and thermoelectrics.[7] To explore these exciting opportunities requires well-defined, crystalline nanowire materials. Over the past several years considerable effort has been placed on the bulk synthesis of nanowires using laser ablation,[8–11] template,[12] solution,[13] and other[14] methods. While these approaches have led to the production of a number of interesting nanowire materials, it has been unclear whether a single method might be used to prepare rationally a wide range of scientifically and technologically interesting materials in the form of single crystal nanowires.

To attack this problem of the rational and general growth of crystalline nanowire materials, we have been developing the laser-assisted catalytic growth (LCG) method,[2,9] which exploits laser ablation to generate nanometer-diameter catalytic clusters that define the size and direct the growth of the crystalline nanowires by a vapor–liquid–solid (VLS) mechanism.[15] A key feature of the VLS growth process and our LCG method is that equilibrium phase diagrams can be used to predict catalysts and growth conditions, and thereby enable rational synthesis of new nanowire materials. Previously, we demonstrated this concept with the growth of elemental Si and Ge nanowires.[2,9] Herein, we extend this method to the high-yield growth of nanowires of the compound semiconductor GaAs. Compound semiconductors, such as GaAs, are especially intriguing targets since their direct band gaps give rise to attractive optical and electrooptical properties. The GaAs nanowires have been prepared as single crystals with diameters as small as 3 nm, which places them in a regime of strong radial quantum confinement, and lengths exceeding 10 μm. In addition, we have used photoluminescence (PL) microscopy to study the luminescence properties of individual GaAs nanowires. These preliminary (PL) studies show large blueshifts in the PL peak position that are consistent with strong quantum confinement.

The apparatus and general procedures for the LCG of nanowires have been described previously.[2,9] The targets used in syntheses consisted of $(GaAs)_{0.95}M_{0.05}$, where M=Au, Ag, or Cu. Typical conditions used for growth were 100–500 Torr Ar:H_2 (95:5), 50–150 sscm gas flow, ablation with a pulsed Nd:YAG laser ($\lambda = 1064$ nm; 10 Hz pulse rate; 2.5 W average power), and furnace growth temperature of 800–1030 °C. The nanowire products were collected at the downstream cold end of the furnace, and were characterized using x-ray diffraction (SCINTAG XDS 2000), field-emission scanning electron microscopy (FE-SEM) (LEO 982), and transmission electron microscopy (TEM) (Philips 420 and JEOL 2010). Convergent beam electron diffraction (ED) and energy dispersive x-ray fluorescence (EDX) measurements were also made with the TEMs. PL measurements were made on a homebuilt instrument of conventional design.[16] Briefly, individual nanowires, which were dispersed on a quartz substrate, were excited through a Plan Fluor 60× objective (Nikon) using an Ar-ion laser and the resulting PL was collected through the same objective, focused, and either imaged or spectrally dispersed onto a liquid nitrogen cooled charge-coupled device.

The predictable growth of GaAs nanowires using the LCG method is more challenging than previous studies of elemental Si and Ge nanowires[2,9] due to the complexity of ternary phase diagrams. This complexity can be greatly reduced by using pseudobinary phase diagrams for GaAs and potential metal catalysts such as Cu, Ag, and Au.[17] For example, the pseudobinary phase diagram of Au–GaAs shows that Au–Ga–As liquid and GaAs solid are the principle phases above 630 °C in the GaAs rich region;[17] that is, Au can serve as a VLS catalyst in this region of the phase diagram. FE-SEM studies of the material obtained by LCG using a $(GaAs)_{0.95}Au_{0.05}$ target [Fig. 1(a)] demonstrate that the product consists almost exclusively of wire-like structures with diameters on the order of 10 nm and lengths up to and exceeding 10 μm. The high-resolution FE-SEM images show that few particles are produced by LCG, and we estimate that >90% of the product consists of nanowires. X-ray

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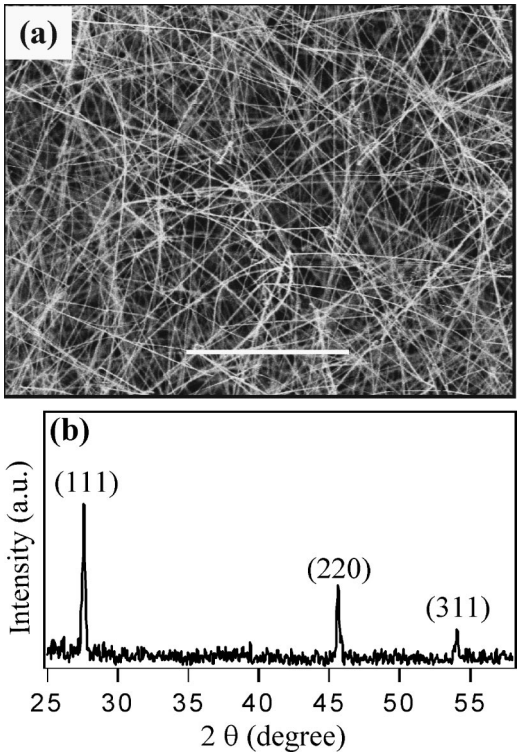

FIG. 1. (a) FE-SEM image of GaAs nanowires obtained from a $(GaAs)_{0.95}Au_{0.05}$ target by LCG. The scale bar corresponds to 5 μm. (b) XRD pattern obtained from a bulk sample of GaAs nanowires.

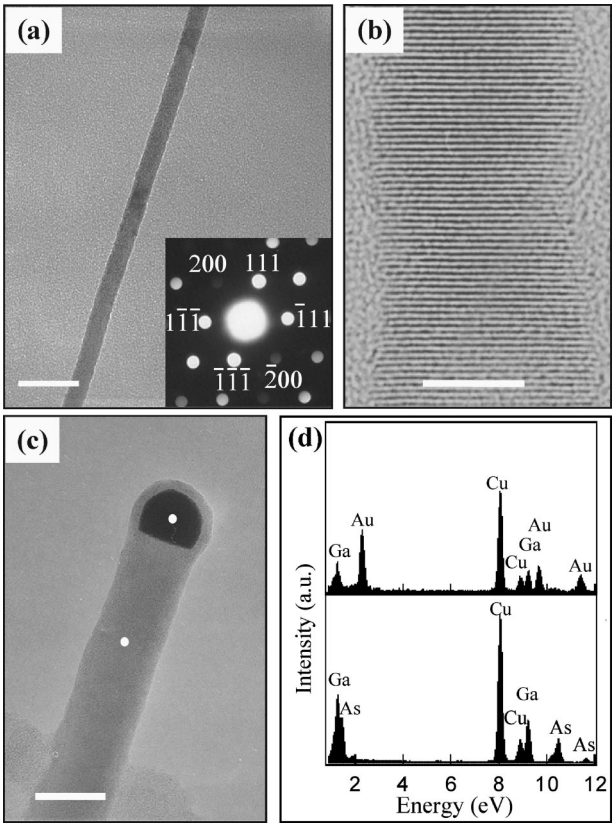

FIG. 2. (a) Diffraction contrast TEM image of a ~16 nm diameter GaAs nanowire. The scale bar corresponds to 50 nm. The inset shows a convergent beam ED pattern recorded along the [0–11] zone axis. (b) High-resolution TEM image of a ~10 nm diameter nanowire. The (111) lattice planes (separation=0.32±0.01 nm) are clearly visible and perpendicular to the wire axis. The scale bar corresponds to 5 nm. (c) TEM image of the end of a nanowire. The dark flattened sphere at the nanowire end is the catalyst nanoparticle. The scale bar corresponds to 20 nm. (d) EDX spectra recorded at the positions of the white dots in (c). The upper spectrum corresponds to the white dot on the (dark) nanoparticle at the end of the nanowire, and the lower spectrum to the dot on the nanowire. The Cu peaks in these spectra are due to background from the copper TEM grid.

diffraction (XRD) measurements were made on the bulk nanowire samples to assess the overall structure and phase purity. The three major diffraction peaks shown in Fig. 1(b) can be indexed to the GaAs zinc-blended structure with a lattice constant ($\mathbf{a}=0.563$ nm) consistent with bulk GaAs ($\mathbf{a}=0.565$ nm). The diffraction data also show that the material is pure GaAs to the 1% level. In addition, high yields of GaAs nanowires were obtained using Ag and Cu catalysts. These results are consistent with the fact that these metals exhibit psuedobinary phase diagrams similar to that of Au.[17]

The detailed structure and composition of individual GaAs nanowires have been characterized using TEM, ED, and EDX. TEM studies show that the nanowires have diameters ranging from 3 to ~30 nm. Figure 2(a) shows a representative diffraction contrast image of a 16 nm diameter wire. The uniform contrast of the nanowire indicates that it is single crystal without, for example, planar defects. These TEM images also show that the nanowires produced by LCG have uniform diameters. EDX measurements show a 1:1 Ga:As composition within experimental error and are consistent with stoichiometric GaAs. ED recorded perpendicular to the axis of this nanowire [inset, Fig. 2(a)] can be indexed for the [0–11] zone axis of GaAs and shows that growth occurs along the [111] direction. Figure 2(b) shows a high-resolution image of the (111) lattice planes, $d=0.32\pm0.01$ nm, oriented perpendicular to the wire axis, and thus confirms the [111] growth direction of the nanowires. This image also exhibits a very thin amorphous coat at the nanowire exterior and shows that some small variations in diameter may be present. We believe that the amorphous layer can be attributed to the oxide layer that forms when GaAs is exposed to air.

TEM studies also reveal that most of the GaAs nanowires terminate in a nanoparticle at one end as shown in Fig. 2(c). EDX measurements made on the nanoparticle and ~30 nm away on the nanowire indicate that the nanoparticle is composed primarily of Au, while the nanowire is GaAs with no detectable Au contamination. The Ga observed in the EDX recorded at the nanowire end is believed to correspond to an amorphous Ga(O) layer coating the high contrast nanoparticle, although additional studies are needed to resolve this point in detail. The presence of Au nanoparticles at the ends of the nanowires is consistent with the pseudobinary phase diagram,[17] and represents strong evidence for a VLS growth mechanism proposed for LCG. Gold has been used in the past for the VLS growth of surface supported GaAs nanowires by metalorganic chemical vapor deposition (MOCVD).[18] The nanowires produced by MOCVD are distinct from our materials in several ways, including (1) MOCVD nanowires are produced on surfaces and not in the bulk quantities, (2) the MOCVD nanowires taper from the base to their ends (i.e., they do not have uniform diameters), and (3) the smallest nanowire diameters, 10–15 nm, are larger than the 3–5 nm diameters achieved in our work. More generally, the LCG method can be easily extended to

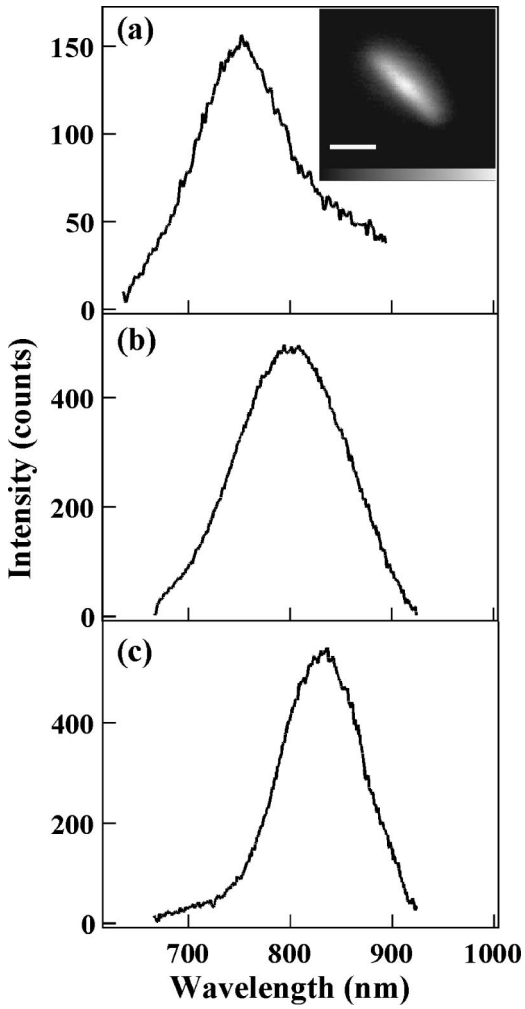

FIG. 3. PL spectra recorded on three individual GaAs nanowires at room temperature. PL peak maxima in (a), (b), and (c) are 752, 794, and 836 nm, respectively. The spectra were recorded by dispersing single wire luminescence with a 150 lines/mm grating in a 300 mm spectrometer. The dispersed PL signal was integrated for 60 s to obtain each spectra. The inset in (a) corresponds to an image of the total PL integrated for 10 s. The white scale bar corresponds to 2 μm, and the intensity scale ranges from 120 counts (dark) to 340 counts (white).

nanowires of III–V and II–VI materials simply by producing solid targets of the material of interest and catalyst.[19]

Last, we have carried out studies of the optical properties of these new GaAs nanowires. Semiconductor quantum wires can confine excitons as in quantum dots and also show other interesting phenomena, such as exciton diffusion (along the wire), not seen in quantum dots.[5,18,20] Previous optical studies of one-dimensional semiconductors have been restricted to studies of quantum wires produced on substrates.[18,20] We believe that our investigations are complementary to this work, since they will enable optical properties to be investigated in (i) systems in which the electron and hole confining potentials are similar and radially symmetric and (ii) two- and three-dimensional arrays assembled from the bulk GaAs nanowires. Figure 3 summarizes preliminary room-temperature PL measurements made on three individual GaAs nanowires. We find that the individual nanowires, which exhibit strong luminescence, can be readily imaged [inset, Fig. 3(a)]. In addition, the PL spectra are strongly blueshifted relative to bulk GaAs. In Fig. 3, the nanowire PL peak maxima occur at 752, 794, and 836 nm versus the 870 nm value for bulk GaAs. These data show clearly strong radial confinement of excitons in the nanowires. We also note that the PL line widths are relatively broad for these individual nanowires, and may be indicative of exciton diffusion along the wire axes. Studies of the PL diameter and temperature dependences are now in progress to address this and other issues.

In summary, we have synthesized GaAs nanowires in bulk quantities by LCG. FE-SEM and TEM investigations have shown that the GaAs nanowires are obtained in >90% yield as single crystals with diameters as small as 3–5 nm and lengths exceeding 10 μm. PL measurements made on individual nanowires show large blueshifts that are consistent with strong quantum confinement. The availability of these semiconductor nanowires is expected to enable fascinating opportunities such as probing confinement, dynamics and transport of excitons in one dimension, and creating optically active nanostructured materials.

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[1] L. E. Brus, J. Phys. Chem. **98**, 3575 (1994); A. P. Alivisatos, *ibid.* **271**, 933 (1996).
[2] J. Hu, T. W. Odom, and C. M. Lieber, Acc. Chem. Res. **32**, 435 (1999).
[3] C. Dekker, Phys. Today **52**, 22 (1999).
[4] J. R. Heath, P. J. Kuekes, G. Synder, and R. S. Williams, Science **280**, 1717 (1998).
[5] D. Snoke, Science **273**, 1351 (1996).
[6] J. D. Joannopoulos, P. R. Villeneuve, and S. Fan, Nature (London) **386**, 143 (1997).
[7] L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 16 631 (1993); D. A. Broido and T. L. Reinecke, Appl. Phys. Lett. **67**, 100 (1995).
[8] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, Science **271**, 483 (1996).
[9] A. M. Morales and C. M. Lieber, Science **279**, 208 (1998).
[10] D. P. Yu, C. S. Lee, I. Bello, X. S. Sun, Y. H. Tang, G. W. Zhou, Z. G. Bai, Z. Zhang, and S. Q. Feng, Solid State Commun. **105**, 403 (1998).
[11] Y. F. Zhang, Y. H. Tang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Appl. Phys. Lett. **72**, 1835 (1998).
[12] C. R. Martin, Science **266**, 1961 (1994); H. Dai, E. W. Wong, Y. Z. Lu, S. Fan, and C. M. Lieber, Nature (London) **375**, 769 (1995).
[13] T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, and W. E. Buhro, Science **270**, 1791 (1995); S.-S. Chang, C.-W. Shih, C.-D. Chen, W.-C. Lai, and C. R. C. Wang, Langmuir **15**, 701 (1999).
[14] P. Yang and C. M. Lieber, Science **273**, 1836 (1996); A. M. Cassell, J. A. Raymakers, J. Kong, and H. Dai, J. Phys. Chem. B **103**, 6484 (1999).
[15] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[16] S. A. Empedocles, D. J. Norris, and M. G. Bawendi, Phys. Rev. Lett. **77**, 3873 (1996).
[17] M. B. Panish, J. Electrochem. Soc. **114**, 517 (1969).
[18] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, and H. Kakibayashi, J. Appl. Phys. **77**, 447 (1995).
[19] X. Duan and C. M. Lieber, Adv. Mater. (to be published).
[20] Y. Nagamune, H. Watabe, F. Sogawa, and Y. Arakawa, Appl. Phys. Lett. **67**, 1535 (1995).