The Chemistry and Physics of Semiconductor Nanowires

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Abstract

The following article is based on the Outstanding Young Investigator Award presentation given by Peidong Yang of the University of California, Berkeley, on April 14, 2004, at the Materials Research Society Spring Meeting in San Francisco. Yang was cited for “innovative synthesis of a broad range of nanowires and nanowire-heterostructure materials, and the discovery of optically induced lasing in individual nanowire devices.” One-dimensional nanostructures are of both fundamental and technological interest. They not only exhibit interesting electronic and optical properties associated with their low dimensionality and the quantum confinement effect, but they also represent critical components in potential nanoscale devices. In this article, the vapor–liquid–solid crystal growth mechanism will be briefly introduced for the general synthesis of nanowires of different compositions, sizes, and orientation. Unique properties, including light-emission and thermoelectricity, will be discussed. In addition to the recent extensive studies on “single-component” nanowires, of increasing importance is incorporating different interfaces and controlling doping profiles within individual single-crystalline nanowires. Epitaxial growth plays a significant role in fabricating such nanowire heterostructures. Recent research on superlattice nanowires and other nanostructures with horizontal junctions will be presented. The implication of these heterojunction nanowires in light-emission and energy conversion will be discussed. Ways to assemble these one-dimensional nanostructures will also be presented.

Keywords: assembly, heterojunctions, nanowires, semiconductors.

Introduction

Within the context of a “bottom-up” approach, nanoscale science is all about assembling matter at multiple length scales, from atomic and molecular species to individual nanoscale building blocks such as nanocrystals, nanorods, and nanowires. Then, from these individual nanoscale building blocks, higher-level functional assemblies and systems are formed. This hierarchical process covers length scales of several orders, from angstroms to micrometers (or larger).

The past few decades have witnessed great progress in the synthesis of nanocrystals of various compositions, sizes, and shapes. Grand challenges, however, remain in the hierarchical integration of the nanoscale building blocks into functional assemblies and ultimately into systems. Unlike the traditional lithographical process, where precise placement of certain elements or devices is embedded in the design process, the precise placement of nanoscale building blocks—in the right place with the right configuration and with exceedingly high densities—represents a daunting task for researchers in this field. This article will focus on a unique type of one-dimensional (1D) nanoscale building block: inorganic nanowires. These inorganic semiconductor nanowires are being explored as model systems in my laboratory to tackle the aforementioned challenging issues, particularly in the following areas:

- precise growth control,
- complexity and functionality in 1D nanostructures,
- hierarchical assembly, and
- system integration based on these nanowire building blocks.

Nanowire Growth Control

Based on our early study of the mechanism of vapor–liquid–solid (VLS) nanowire growth—a process that starts with the dissolution of gaseous reactants in nanosized liquid droplets of the catalyst metal, followed by nucleation and growth of single-crystalline wires or rods—rationally controlled growth of nanowires is now possible. The diameter of a nanowire is determined by the size of the alloy droplet, which in turn is determined by the size of the starting metal seed. By using monodispersed metal nanoclusters, nanowires with a narrow diameter distribution can be synthesized. Applying the conventional epitaxial crystal growth technique to this VLS process, it is possible to achieve precise orientation control during the nanowire growth. The technique, known as vapor–liquid–solid epitaxy (VLSE), is particularly powerful in the controlled synthesis of nanowire arrays. For example, ZnO prefers to grow along the [001] direction and readily forms a highly oriented array when grown epitaxially on a sapphire (110) substrate (Figure 1a). A similar level of growth control can be achieved for GaN (Figure 1b) and Si/Ge systems. It is possible to use this VLSE technique to grow nanowire arrays with tight control over size (diameter, <20 nm) and diameter uniformity (variation of less than ~10%). This size and monodispersity control is crucial for many proposed applications for these nanowire arrays—light-emission and field-effect transistors, for example.

It is further possible to control the nanowire density in the range of $10^9$-$10^{12}$ cm$^{-2}$ by adjusting the initial nanocluster density on the substrates. In addition, we have also explored various ways to precisely control the location of the nanowire growth. Both direct e-beam lithography and self-organization of the metal nanocrystals have been tested with some success.

Controlling the growth orientation is important for many of the proposed applications of nanowires, including vertical field-effect transistors, for example. We recently developed a simple approach to selectively growing semiconductor nanowires along chosen crystallographic directions (Figure 2). We demonstrated the use of metalorganic chemical vapor deposition (MOCVD) and appropriate substrate selection to control the crystallographic growth.
directions of high-density arrays of gal- 
lium nitride nanowires with distinct geo-
metric and physical properties (for example,
the ability to emit light). Epitaxial growth 
of wurtzite gallium nitride on /H9253 
/LiAlO2(100) and MgO(111) single-crystal substrates 
resulted in the selective growth of nanowires 
in the orthogonal and [001] directions,
exhibiting triangular and hexagonal cross 
sections and drastically different optical 
emission involving an energy shift of 
100 meV. This MOCVD process is entirely 
compatible with current GaN thin-film tech-
nology, which would lead to easy scale-up 
and device integration. Control over the di-
rection of nanowire growth is extremely 
desirable in that anisotropic parameters 
such as thermal and electrical conduc-
tivity, refractive index, piezoelectric polariza-
tion, and bandgap may be used to tune the 
physical properties of nanowires made 
from a given material.

Nanowire Complexity and 
Functionality
The success of semiconductor integrated 
circuits has largely hinged on the capa-
bility of forming heterostructures through 
controlled doping and interfacing, as semi-
conductor heterostructures enable the con-
finement of electrons and holes, the guiding 
of light, and the modulation of phonon 
transport and carrier mobility. Based on our 
fundamental mechanistic understanding of 
nanowire growth, we have explored differ-
ent types of heterostructured nanowires, 
including, for example, coaxial heterostruc-
tured nanowires (COHNs), longitudinal 
heterostructured nanowires (LOHNs), and 
nanotapes (Figure 3).

Coaxial nanowires are an important class 
of heterostructured nanowires that are fun-
damentally interesting and have significant 
technological potential. Coaxial structures 
can be fabricated by coating an array of 
nanowires with a conformal layer of a sec-
ond material. The coating method chosen 
should allow excellent uniformity and con-
trol of the sheath thickness. Cladding 
nanowires with amorphous layers of SiO2 
or carbon is synthetically facile and has been 
routinely demonstrated in the literature. 
A more exciting and difficult task, with 
greater technological importance, is to form 
heterostructures of two single-crystalline 
semiconductor materials. We have reported 
the synthesis of GaN/Al0.75Ga0.25N core– 
sheath structures using a chemical vapor 
transport method (Figure 4a).7 It is important 
to point out that choosing appropriate 
core and sheath materials that have similar 
crystallographic symmetries and lattice 
constants is essential to achieving the depo-
sition of single-crystalline epitaxial thin-film 
sheath structures, thereby producing high-
quality materials. The band structure of the 
different materials used in forming COHNs 
could be chosen to achieve modulation 
doping. For example, the dopant atoms 
would reside in the cladding, while the 
carriers would be located in the core. This 
is the 1D variation of the idea behind modu-
lation doping in two-dimensional (2D) 
semiconductor heterostructures, which have 
achieved very high electron mobilities by 
suppressing charged impurity scattering. 

Similar to the concept of creating a uni-
form sheath around a nanowire is the idea 
of coating 1D nanostructures anisotropically 
(i.e., only along one side of the nanowire 
material). We have developed a versatile 
approach to the synthesis of composite 
nanowire structures in which the compo-
sition limitation is relaxed; the resulting 
nanostructures could readily have multiple 
functionalities such as luminescence, ferro-
magnetism, and ferroelectric or supercon-
ducting properties.8 

In this process, tin dioxide nanoribbons 
were used as substrates for the thin-film 
growth of various oxides (e.g., TiO2,

![Figure 1. Scanning electron microscopy images of (a) ZnO nanowire arrays on a sapphire 
wafer substrate and (b) a GaN nanowire with a hexagonal cross section.](image1)

![Figure 2. Structural models of nanowires with (a) triangular and (b) hexagonal cross 
sections.](image2)

![Figure 3. Three different types of 
heterostructured nanowires: a coaxial 
heterostructured nanowire (COHN), a longitudinal heterostructured nanowire (LOHN), and a nanotape.](image3)
transition-metal-doped TiO2 and ZnO) using pulsed laser deposition (PLD). The energetic nature of the laser ablation process makes the plume highly directional and enables selective film deposition on one side of the nanoribbon substrate by means of the shadow effect (Figure 4b). Electron microscopy and x-ray diffraction studies demonstrate that these functional oxides can grow epitaxially on the side surfaces of the substrate nanoribbons with sharp structural and compositional interfaces.

The creation of epitaxial core–sheath structures imparts the ability to synthesize GaN nanotubes with inner diameters of 30–200 nm and wall thicknesses of 5–50 nm.9 Hexagonal ZnO nanowires have been used as templates for the epitaxial overgrowth of thin GaN layers in a MOCVD system. The ZnO nanowire templates were subsequently removed by simple thermal reduction and evaporation in NH3/H2 mixtures, resulting in ordered arrays of GaN nanotubes on the substrate. This was the first example of single-crystalline GaN nanotubes prepared using the epitaxial casting methodology, and this novel templating process should be applicable to many other semiconductor systems (Figure 4c).

Analogous to the way in which 2D thin-film heterostructures transformed the planar semiconductor industry, superlattice nanowires show potential for use in diverse applications, such as the phonon transport/thermoelectrical application (discussed later). These nanowires also offer great opportunities to explore new physics and phenomena for low-dimensional systems. The growth of longitudinal heterostructured nanowires involves using a single 1D growth mechanism that can be easily switched between different materials in mid-growth. In order to obtain technologically useful heterostructures, the growth mechanism must be compatible with the desired materials and produce well-defined and coherent interfaces. Since the VLS growth mechanism can readily provide such control, most work involving longitudinal heterostructure synthesis has been performed using this approach.

We recently demonstrated the use of a hybrid pulsed laser ablation/chemical vapor deposition process for generating semiconductor nanowires with periodic longitudinal heterostructures. In this process, Si and Ge vapor sources were independently controlled and alternately delivered into the VLS nanowire growth system. As a result, single-crystalline nanowires containing the Si/SiGe superlattice structure were obtained. Figure 4d shows a scanning transmission electron microscopy image of two such nanowires in the bright-field mode. Dark stripes appear periodically along the longitudinal axis of each wire, reflecting the alternating domains of Si and SiGe alloy. Since the supply of vapor sources can be readily programmed, the VLS process with modulated sources is useful for preparing a variety of heterostructures on individual nanowires in a “custom-designed” fashion. The process will also enable the creation of various functional devices (e.g., p–n junctions, coupled quantum-dot structures, and heterostructured unipolar and bipolar transistors) on individual nanowires. These heterostructured nanowires can be further used as important building blocks to construct nanoscale electronic circuits and light-emitting devices.

It must also be emphasized that the elastic boundary conditions of nanowire heteroepitaxial growth offer the possibility to create dislocation-free interfaces in the superlattice nanowires that are otherwise not stable in the conventional 2D configuration achieved by epitaxial film growth on planar substrates. The range of materials that can be grown by coherent epitaxy on a given substrate, and to a required thickness, is greatly limited by the lattice misfit. Our nanowire morphology provides the opportunity to markedly extend the critical thicknesses—or equivalently, the lattice misfit that can be accommodated at a given thickness—due to the change in boundary conditions.

Figure 4. Transmission electron microscopy images of (a) a GaN/AlGaN core–sheath nanowire, (b) a highly crystalline SnO2/TiO2 composite nanoribbon showing the epitaxial growth of TiO2 on the SnO2 nanoribbon surface, (c) a cluster of single-crystalline GaN nanotubes prepared using the epitaxial casting methodology, and (d) two Si/SiGe superlattice nanowires.
Hierarchical Assembly of Nanowires

Putting building blocks into different architectures will surely lead to devices with higher structural complexity and new functionality—to name a few, nanolaser arrays, nanowire arrays as 2D photonic crystals, and light-emitting nanowire/polymer composites. This is a process that will enable the bridging of the nanoscopic world to the macroscopic worlds. The ability to manipulate these nanoscale building blocks is critical for the success of the whole field of nanoscale science and technology.

The key to the future success of 1D nanotechnologies is assembly, or the art of putting nanostructures where one desires with the desired connectivity. Nanostructure assembly is challenging because of the incompatibility of pertinent length scales—"nano" versus "macro." As we have demonstrated, fluidic assembly schemes\(^\text{10}\) offer sufficient control to allow the fabrication of simple networks and the macroscopic patterning of nanowires, but not with the precision, pattern density, or complexity needed for many applications. The research community must develop generalized assembly techniques that go well beyond current capabilities if nanowires, rods, belts, and tubes are to see widespread technological application in optoelectronics and computing. All application areas, including those with little or no direct need for assembly, will benefit from advances made in the spatial manipulation of nanostructures.

Another interesting method for arranging vast numbers of 1D nanostructures on solid surfaces is Langmuir–Blodgett (LB) assembly.\(^\text{11}\) In the LB technique, uniaxial compression of a nanowire–surfactant monolayer floating on an aqueous subphase causes the nanowires to align and pack over a large area (>20 cm\(^2\), Figure 5).\(^\text{12}\) The aligned monolayer can then be transferred to a solid surface en masse. Repeated transfers of different types of nanowires can produce functional nanowire lattices, although the imprecise registry between layers and the difficulties in providing electrical contacts to individual wires are issues that remain to be addressed. The lattices can be patterned using conventional photolithography, yielding arrays of lattice pixels of controlled geometry and pitch. Despite its obvious lack of geometric versatility, Langmuir–Blodgett assembly is the best method available for aligning 1D nanostructures over large areas and with high packing density.

Phonon Transport and Energy Conversion

Phonon transport is expected to be greatly impeded in thin (i.e., \(d < \Lambda\), where \(d\) is the diameter and \(\Lambda\) is the phonon mean free path) 1D nanostructures as a result of increased boundary scattering and reduced phonon group velocities stemming from phonon confinement. Detailed models of phonon heat conduction in semiconducting nanowires that consider modified dispersion relations and all-important scattering processes predict a large decrease (>90%) in the lattice thermal conductivity of wires tens of nanometers in diameter. Size-dependent thermal conductivity in nanostructures presents a major hurdle in the drive toward miniaturization in the semiconductor industry. Yet, poor heat transport is advantageous for thermoelectric materials, which are characterized by a figure of merit,

\[
ZT = \alpha^2 T / \left( \rho \kappa_p + \kappa_e \right)
\]

(1)

(where \(\alpha\) is the Seebeck coefficient, \(T\) is absolute temperature, \(\rho\) is the electronic resistivity, \(\kappa_p\) is the lattice thermal conductivity, and \(\kappa_e\) is the electronic thermal conductivity) that improves as phonon transport worsens.

A decade ago, the Dresselhaus group predicted that \(ZT\) can be increased above bulk values in thin nanowires by carefully tailoring their diameters, compositions, and carrier concentrations.\(^\text{13,14}\) This remains to be experimentally confirmed.

In addition, well-engineered superlattice nanowires may provide better performance by means of a combination of sharp periodic band offsets that offer some amount of quantum confinement, high phonon scattering from the interfaces, and high electrical conductivity. Recent work in our laboratories\(^\text{15,16}\) has focused on understanding the thermal transport properties of Si/SiGe superlattice nanowires as the first step in the experimental verification of enhanced \(ZT\) values in these complex structures.

Measurements of the overall thermal conductivity of Si/SiGe superlattice nanowires\(^\text{15}\) (Figure 6a) have been made as a function of temperature (20 K to 320 K) and nanowire diameter using a suspended microdevice in vacuum. Individual Si/SiGe wires with

Figure 5. (a), (b) Scanning electron microscopy images at different magnifications of a Langmuir–Blodgett silver nanowire monolayer deposited on a silicon wafer.
a superlattice period of 100–150 nm exhibited a thermal conductivity that was substantially lower than that of bulk Si. The broadness of the imbedded Si/SiGe interfaces and the moderate Ge concentration in these wires suggest that alloy (impurity) scattering is the dominant phonon scattering mechanism for short-wavelength phonons, while boundary scattering plays a major role in disrupting phonons of all wavelengths. A comparison of superlattice wires with undoped Si nanowires\(^{16}\) of similar diameter (Figure 6b) shows that the thermoconductivity of the superlattice nanowires is five times smaller at 300 K. Future Seebeck and electronic studies of improved superlattice nanowires are needed to guide the engineering of these materials for thermoelectric applications.

**From Nanowire Lasers to Quantum Wire Lasers**

Nanowires with flat end facets can be exploited as optical resonance cavities to generate coherent light on the nanoscale. Room-temperature UV lasing has been demonstrated in our laboratory for the ZnO and GaN nanowire\(^{17}\) systems with epitaxial arrays, combs, ribbons, and single nanowires (Figure 7). ZnO and GaN are wide-bandgap semiconductors with bandgaps of 3.37 eV and 3.42 eV, respectively, suitable for UV–blue optoelectronic applications. In a series of studies, we have applied far-field imaging and near-field scanning optical microscopy (NSOM) to understand photon confinement in these small cavities

\[
(d \leq \lambda, \text{ where } d \text{ is the nanowire diameter and } \lambda \text{ is the wavelength}).^{18}
\]

Well-faceted nanowires with diameters from 100 nm to 500 nm support predominantly axial Fabry–Perot waveguide modes—separated by \(\Delta \lambda = \lambda^2/(2Ln(\lambda))\), where \(L\) is the cavity length and \(n(\lambda)\) is the group index of refraction—due to the large diffraction losses suffered by transverse trajectories. Diffraction prevents smaller wires from lasing; photoluminescence is lost instead to the surrounding radiation field. ZnO and GaN nanowires produced by VLS growth are cavities with low intrinsic finesse \((F)\) due to the low reflectivity \((R)\) of their end faces\(^{19}\) (~19%) \([F = \pi R^{1/2}/(1 - R)]\), such that the confinement time for photons is short and photons travel a limited number of passes before escaping from the cavity. Far-field imaging indicates that photoluminescence and lasing emission are localized at the ends of nanowires, which suggests strong waveguiding behavior that is consistent with axial Fabry–Perot modes (Figure 7b).

Beyond the nanowire lasers, confined core–sheath nanowire heterostructures provide a unique geometry for applications in optoelectronics. We recently demonstrated UV lasing from optically pumped GaN/Al\(_{1-x}\)Ga\(_x\)N core–sheath quantum wires (Figure 8).\(^7\) Phase separation during the VLS process leads to cylindrical GaN cores with diameters as small as 5 nm clad by a 50–100 nm layer of Al\(_{0.75}\)Ga\(_{0.25}\)N. Normally, GaN nanowires with diameters of less than \(\sim 100 \text{ nm}\) are optically too "leaky" to sustain laser cavity modes. Surrounding the slender GaN wires with a material of a larger bandgap and smaller refractive index creates a structure with simultaneous exciton and photon confinement (waveguiding). The GaN core size is comparable to the Bohr radius of the exciton for GaN (11 nm). The bandgap of the core (GaN, 3.42 eV) is smaller than that of the sheath (Al\(_{0.75}\)Ga\(_{0.25}\)N, 5.25 eV). Both factors would lead to effective carrier/exciton confinement within such unique core–sheath nanostructures. When optically pumped, the core provides a gain medium, while the sheath acts as a Fabry–Perot optical cavity (Figure 8). In the near future, robust assembly methods appropriate to a larger variety of materials will enable the use of injection nanolasers in sensing, optical communications, and probe microscopy applications.

**Figure 7.** (a) Far-field optical image of patterned lasing in ZnO nanowire arrays. Each square pattern unit is 20 \(\mu\text{m} \times 20 \mu\text{m}\). Inset shows a typical emission spectrum below and above the lasing threshold. (b) Lasing spectrum from an individual ZnO nanoribbon. Inset shows a far-field optical image of the waveguiding ZnO nanoribbon (length, 35 \(\mu\text{m}\)).

**Figure 8.** (a) Far-field optical image of a GaN/AlGaN core–sheath-based quantum wire laser (length, 4 \(\mu\text{m}\)). (b) Spectra of light emission from GaN/AlGaN core–sheath nanowires below, near, and above the lasing threshold. The curves are offset for clarity.
Nanoribbon Waveguides for Subwavelength Photonics Integration

The ability to manipulate pulses of light within submicron volumes is vital in order for highly integrated light-based devices, such as optical computers, to be realized. A potentially versatile concept is to assemble photonic circuits from a collection of nanowire elements that assume different functions, such as light creation, routing, and detection. Chemically synthesized nanowires have several features that make them good photonic building blocks, including inherent one-dimensionality, a variety of optical and electrical properties, good size control, low surface roughness, and, in principle, the ability to operate both above and below the diffraction limit. The toolbox of nanowire device elements already includes various types of transistors, light-emitting diodes, lasers, and photodetectors.21 An important step toward integrated nanowire photonics is to develop a nanowire waveguide that can link these various elements and provide the flexibility in interconnection patterns that is needed to carry out complex tasks such as logic operations. We have leveraged the unique diversity of free-standing crystalline nanowires to build prototype multiwire architectures for the manipulation and detection of light.

The nanowires are often of sufficient length and strength to be pushed, bent, and shaped using a commercial micro/micromanipulator21 under an optical microscope. Freestanding wires can be repeatedly and elastically curved into loops with radii as small as 5 μm, which is remarkable for a crystal that is brittle in its bulk form.21 On appropriately chosen surfaces, single wires can be easily fashioned into a variety of shapes with the help of wire–substrate forces to prevent elastic recoil. Such chemically synthesized nanowires represent a unique class of building blocks for the construction of nanoscale electronic and optoelectronic devices. In this regard, we have examined the properties and functions of a key nanowire element for optical integration—a subwavelength optical waveguide—made of individual crystalline oxide nanowires. The extraordinary length, flexibility, and strength of these structures enable their manipulation on surfaces, including the precise positioning and optical linking of nanowire waveguides and other nanowire elements to form optical networks and device components (Figure 9).21 This strategy, although serial, offers an interesting alternative for the possible integration of these nanowire building blocks.

Challenges Ahead

The rapid pace of research in the field of 1D nanostructures is driven by the very exciting scientific challenges and technological potential of mesoscopic systems. Our synthetic capabilities continue to expand quickly, while progress in the difficult tasks of precision property control and assembly inches forward. There are several outstanding scientific challenges in the field that urgently need to be addressed, the most significant of which is the problem of integration and interfacing. The ability to create high-density nanowire arrays is not enough; the questions of how to address individual elements in a high-density array and achieve precise layer-to-layer registration for vertical integration are just two of the many challenges still ahead. To achieve reproducible nanostructured interfaces, semiconductor–semiconductor and metal–semiconductor alike, requires careful examination and understanding of the chemistry and physics occurring at the interface. Equally important is the very precise control of the size uniformity, dimensionality, growth direction, and dopant distribution within semiconductor nanostructures, as these structural parameters will ultimately dictate the functionality of the nanostructures. In particular, the physical significance of the dopant distribution and the interfacial junction, and their implications in device operation and performance, will likely require careful re-examination and/or re-definition at the nanometer length scale. Lastly, accurate theoretical simulations appropriate to the mesoscopic regime are becoming feasible with the enhanced computing power that is now available, and such simulations should assist our understanding of many of these size- and dimensionality-controlled phenomena.

Acknowledgments

I give my sincerest thanks to the talented students and postdoctoral fellows with whom I have had the pleasure to work over the past five years and who have made possible all of the advances described in this article. I would also like to acknowledge very productive collaborations with my colleagues Prof. Richard Saykally and Prof. Arun Majumdar. I wish to acknowledge the very generous financial support from the National Science Foundation and the Office of Basic Science, Department of Energy.
References

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He has received numerous awards and honors in addition to the MRS Outstanding Young Investigator Award for 2004, including the ACS 2005 Pure Chemistry Award, the 2004 Julius Springer Prize for Applied Physics, the 2004 Camille Dreyfus Teacher–Scholar Award, the 2002 Arnold and Mabel Beckman Young Investigator Award, and the 2000 ExxonMobil Solid State Chemistry Award. He was also named among the MIT Technology Review’s TR 100 for 2003 and was an Alfred P. Sloan research fellow in 2001. Yang is the first chair of the nanoscience subdivision of the American Chemical Society and serves on several editorial and advisory boards. He has published more than 90 papers and holds 10 patents. Yang is the scientific co-founder of the nanotechnology company Nanosys Inc.

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