Functional Nanowires

Also in This Issue:
The Mechanics and Physics of Defect Nucleation
Functional Nanowires

Charles M. Lieber and Zhong Lin Wang, Guest Editors

Abstract
Nanotechnology offers the promise of enabling revolutionary advances in diverse areas ranging from electronics, optoelectronics, and energy to healthcare. Underpinning the realization of such advances are the nanoscale materials and corresponding nanodevices central to these application areas. Semiconductor nanowires and nanobelts are emerging as one of the most powerful and diverse classes of functional nanomaterials that are having an impact on science and technology. In this issue of MRS Bulletin, several leaders in this vibrant field of research present brief reviews that highlight key aspects of the underlying materials science of nanowires, basic device functions achievable with these materials, and developing applications in electronics and at the interface with biology. This article introduces the controlled synthesis, patterned and designed self-assembly, and unique applications of nanowires in nanoelectronics, nano-optoelectronics, nanosensors, nanobiotechnology, and energy harvesting.

Nanowires As Building Blocks for Bottom-Up Nanotechnology

The field of nanotechnology represents an exciting and rapidly expanding research area that crosses the borders between the physical, life, and engineering sciences. Much of the excitement in this area of research has arisen from recognition that new phenomena, multifunctionality, and unprecedented integration density are possible with nanometer-scale structures. In general, there are two philosophically distinct approaches for creating small objects: top-down and bottom-up.

In the top-down approach, small features are patterned in bulk materials by a combination of lithography, etching, and deposition to form functional devices and their integrated systems. The top-down approach has been exceedingly successful in many venues, with microelectronics being perhaps the best example today. While developments continue to push the resolution limits of the top-down approach, these improvements in resolution are associated with a near-exponential increase in cost associated with each new level of manufacturing facility. This economic limitation and other scientific challenges with the top-down approach, such as making nanostructures with near-atomic perfection and incorporating materials with distinct chemical and functional properties, have motivated efforts worldwide to search for new strategies to meet the demand for nanoscale structures today and in the future.2–4

The bottom-up approach, in which functional structures are assembled from well-defined chemically and/or physically synthesized nanoscale building blocks, much like the way nature uses proteins and other macromolecules to construct complex biological systems, represents a powerful alternative approach to conventional top-down methods.5,6 The bottom-up approach has the potential to go far beyond the limits and functionality of top-down technology by defining key parameters controlled during growth, including chemical composition, diameter, length, doping, growth direction, and possibly surface properties.5,6 NWs and NBs thus represent one of best-defined and controlled classes of nanoscale building blocks compared to, for example, carbon nanotubes. The unique control over the microstructure of NW building blocks arises from an excellent understanding of their growth mechanisms and the broad range of chemical compositions achievable (versus simply carbon)6–14. Such control has enabled a wide range of devices and integration strategies to be pursued in a rational manner. For example, semiconductor NWs have been assembled into nanometer-scale field-effect transistors (FETs),5,11–13 NWs thus represent one of best-defined and controlled classes of nanoscale building blocks compared to, for example, nanoscale lasers, complex logic gates, and even computational circuits that have been used as basic digital calculators.16 Gas sensors,17 nanoelectronics,18,19 and nanogenerators.20 Polar-surface-dominated NBs spontaneously self-assemble into nanosprings,21,22 nanobows,23 nanorings,24 and nanohelices,25 which are candidates for nanoscale transducers, actuators, and their corresponding physical properties. To meet this goal requires developing methods that enable rational design and predictable synthesis of building blocks. Second, it is critical to develop and explore the limits of functional devices based on these building blocks. Nanoscale structures may behave in ways similar to current electronic and optoelectronic devices, although it is also expected that new and potentially revolutionary concepts will emerge from these building blocks, for example, due to quantum properties. Third and central to the bottom-up concept will be the development of architectures that enable high-density integration with predictable function, and the development of hierarchical assembly methods that can organize building blocks into these architectures.

Nanowires (NWs)3,6 and nanobelts (NBs)7,8 represent an important and broad class of one-dimensional (1D) nanostructures at the forefront of nanoscience and nanotechnology. NWs and NBs are typically single-crystalline, highly anisotropic, semiconducting, insulating, and/or metallic nanostructures that result from rapid growth along one direction. The cross section of NWs and NBs is uniform and much smaller than the length. NWs are typically cylindrical, hexagonal, square, or triangular in cross section; NBs are typically rectangular in cross section, with a large anisotropy in dimensions. NWs and NBs can be rationally and predictably synthesized in single-crystal form with all key parameters controlled during growth, including chemical composition, diameter, length, doping, growth direction, and possibly surface properties.5,6 NWs and NBs thus represent one of best-defined and controlled classes of nanoscale building blocks compared to, for example, carbon nanotubes. The unique control over the microstructure of NW building blocks arises from an excellent understanding of their growth mechanisms and the broad range of chemical compositions achievable (versus simply carbon)6–14. Such control has enabled a wide range of devices and integration strategies to be pursued in a rational manner. For example, semiconductor NWs have been assembled into nanometer-scale field-effect transistors (FETs),5,11–13 NWs thus represent one of best-defined and controlled classes of nanoscale building blocks compared to, for example, nanoscale lasers, complex logic gates, and even computational circuits that have been used as basic digital calculators.16 Gas sensors,17 nanoelectronics,18,19 and nanogenerators.20 Polar-surface-dominated NBs spontaneously self-assemble into nanosprings,21,22 nanobows,23 nanorings,24 and nanohelices,25 which are candidates for nanoscale transducers, actuators, and...
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sensors. These advances and the growing interest in NWs and NBs can be quantified in terms of the rapidly increasing number of publications per year since the early 1990s (Figure 1).

Nanowires and Carbon Nanotubes

Another class of 1D nanostructures that have received considerable attention is carbon nanotubes (NTs). In contrast to NTs, whose electronic properties are largely determined by the chirality of the graphene layers, NWs offer several unique merits. First, NW devices can be assembled in a rational and predictable manner because the size, interfacial properties, and electronic properties of the NWs can be precisely controlled during synthesis. Moreover, reliable methods exist for their parallel assembly. The growth direction and side surfaces of nanowires can be precisely controlled during synthesis. Second, it is possible to combine distinct NW building blocks in ways not possible in conventional electronics and to leverage the knowledge base that exists for the chemical modification of inorganic surfaces to produce desired properties. Second, it is possible to combine distinct NW building blocks in ways not possible in conventional electronics and to leverage the knowledge base that exists for the chemical modification of inorganic surfaces to produce desired properties. Second, it is possible to combine distinct NW building blocks in ways not possible in conventional electronics and to leverage the knowledge base that exists for the chemical modification of inorganic surfaces to produce desired properties.

Designed Synthesis of Nanowires and Nanowire Heterostructures

The rational design and synthesis of nanoscale materials is critical to work directed toward understanding fundamental properties, creating nanstructured materials, and developing nanotechnology. Strategies have been developed to design and rationally synthesize NWs and NBs with predictable control over the key structural, chemical, and physical properties. Among the numerous methods that have been explored, a strategy that has received increased focus in the past several years involves exploiting a “catalyst” to confine growth in 1D. Depending on the phases involved in the reaction, this approach is typically defined as vapor–liquid–solid (VLS), solution–liquid–solid (SLS), or vapor–solid (VS) growth. In VLS growth, the catalyst is envisioned as a nanodroplet that defines the diameter of and serves as the site that preferentially directs the addition of reactant to the end of a growing NW, as indicated in Figure 2a by the yellow region at the left-hand end of the NW.

Modulated nanostructures in which the composition and/or doping are varied on the nanometer scale represent important targets of synthesis since they could enable new and unique function and potential for integration in functional nanosystems. The approach to axial NW heterostructure growth (Figure 2b) exploits metal-catalyzed nanowire synthesis. To create a single junction within the NW, the addition of the first reactant is stopped during growth, and a second reactant is introduced for the remainder of the synthesis; repeated modulation of the reactants during growth produces NW superlattices. In principle, this approach can be successfully implemented if a nanocluster catalyst suitable for growth of the different superlattice components under similar conditions is found. Gold nanoclusters meet this requirement for a wide range of Group III–V and Group IV materials. This methodology for the growth of superlattice structures can be generalized in many materials systems. Structures have been fabricated for $p$–$n$ junctions within individual Si NWs by Au-nanocluster-catalyzed chemical vapor deposition (CVD) and dopant modulation. Similar structures have also been demonstrated for Si-Ge and InAs-InP. These superlattice structures greatly increase the versatility and power of NW building blocks for nanoscale electronic and photonic applications such as nanobarcodes, injection lasers, and engineered 1D waveguides.

Designed Synthesis of Radial Nanowire Homo- and Heterostructures

The growth of crystalline overlayers on nanostructure surfaces is important for controlling surface properties and enabling new function. This concept has been proved by the synthesis of silicon and germanium core–shell and multishell NW homo- and heterostructures using the CVD method applicable to a variety of nanoscale materials. Axial growth is achieved when reactant activation and addition occurs at the catalyst site and not on the NW surface through epitaxial growth (Figure 2b). Correspondingly, it is possible to drive conformal shell growth by altering conditions to favor homogeneous vapor-phase deposition on the NW surface. Subsequent introduction of different reactants and/or dopants produces multishell structures of designed composition, although epitaxial growth of these shells requires consideration of lattice structures.

Designed Synthesis of Hierarchical Structured Nanowire Networks

In VLS growth, the location at which the NW grows is defined by the site of the catalyst particle, and the orientation of the NW is determined by the surface lattice of the substrate on which an epitaxial relationship can be built. Based on such a principle, by decorating a grown radial/axial NW heterostructure with catalyst particles, side branches can be grown along the...
Figure 2. Schematic illustration of the evolution of nanowire structural and compositional complexity enabled today by controlled synthesis, from (a) homogeneous materials to (b) axial and radial heterostructures and (c) branched heterostructures. The colors indicate regions with distinct chemical composition and/or doping.

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Nanowires of Functional and Smart Materials

Complex oxides with structures such as perovskite, spinel, and garnet have many important properties and applications in science and engineering including ferroelectricity, ferromagnetism, colossal magnetoresistance, luminescence, optoelectronics, and semiconductors. These properties are crucial for applications such as data storage, data retrieval, and sensing. Besides the synthesis of conventional binary oxides (discussed by J. Wang et al. in this issue), methods have been developed to synthesize NWs of functional and smart materials. Liu et al.42 have demonstrated a generic approach for the synthesis of single-crystal complex oxide nanostuctures of perovskites, spinels, and various hydroxides, including monoclinic, corundum, CaF$_2$-structured, tetragonal, and metal hydroxides.42,43 The method is based on a reaction between a metallic salt and a metallic oxide including monoclinic, corundum, CaF$_2$-rovskites, spinels, and various hydroxides, allowing the integration of high-performance III–V semiconductors monolithically with silicon technology, since fundamental issues of III–V integration on Si, such as lattice and thermal expansion mismatch, can be overcome.

Simple, convenient, and innovative strategy for synthesizing nanostructures of complex oxides with important scientific and technological applications in ferroelectricity, ferromagnetism, colossal magnetoresistance, fuel cells, optics, and more.

Organization and Assembly of Nanowires

The organization and/or directed assembly of NWs into designed hierarchical structures is a key goal necessary for creating arrays of devices. Using a patterned catalyst, NWs can be directly grown on a solid substrate in a designed configuration. This strategy enables nanoscale structures to be produced directly on a 2D substrate without extensive lithography, but it still faces many of the traditional constraints of planar growth and device fabrication. Alternatively, NW materials produced under synthetic conditions optimized for their growth can be organized into arrays by several techniques including (1) electric-field-directed, (2) fluidic-flow-directed, (3) Langmuir–Blodgett, and (4) patterned chemical assembly.

Applied electric fields (E-fields) can be used effectively to attract and align NWs due to their highly anisotropic structures and large polarization.11 E-field–directed assembly not only can organize NWs along the electric field, but also can be used to position individual NWs at specific positions with controlled directionality.44 Another powerful approach called fluidic-flow-directed assembly allows alignment of NWs (or NTs) by passing a suspension of NWs through microfluidic channel structures. Fluidic-flow-directed assembly can also be used to organize NWs into more complex crossed structures, which are critical for building dense nanodevice arrays, using a layer-by-layer deposition process. The microfluidic method enables the alignment of NWs up to about the millimeter scale.

Assembly on larger scales with precise spacing down to the nanometer level requires alternative strategies. The Langmuir–Blodgett (LB) technique, in which an ordered monolayer is formed on water and transferred to a substrate, represents an alternative method that is beginning to achieve this goal. For example, parallel and crossed NW structures have been assembled by single and sequential transfers over centimeter length scales; moreover, these large-area arrays have been efficiently patterned into repeating arrays of controlled dimensions and pitch to yield hierarchical structures with order defined from the nanometer through the centimeter length scales.45 In addition, patterned chemical modification of a substrate can be an effective approach for directed- or self-assembly of NWs and NTs.16,46

Nanoelectronic Devices

Homogeneous doped NWs represent key building blocks for a variety of electronic devices.46–51 A prototypical example of such a device with broad potential for applications is the NW field-effect transistor (NWFET). For example, studies of NWFETs fabricated from boron-46 and phosphorus-doped Si NWs have shown that the devices can exhibit performance comparable to the best reported for planar devices made from the same materials. Studies have also demonstrated the high electron mobility of epitaxial InAs NWFETs with a wrap-around cylindrical gate structure surrounding a nanowire.48

More generally, controlled bottom-up assembly and synthetic elaboration of NWs offers unique opportunities. The crossed NW architecture enables device properties to be defined by the assembly of the NW components and not by lithography, and has been utilized to demonstrate logic gate structures, basic computation, and selective addressing.47,48 Synthesis of axial modulation-doped NW heterostructures has enabled the creation of address decoders and coupled quantum structures without a critical use of lithography,50 while the design of radial Ge/Si core–shell NW heterostructures demonstrated a true performance benefit of NWFETs compared with state-of-the-art planar devices.51

Nanowire Nanosensors

Field-effect transistors fabricated using individual NWs are ultrasensitive nanosensors for detecting a wide range of gases, chemicals, and biomedical species in both commercial and research applications.52,53 The high-performance characteristics of NWFETs, such as high surface-to-volume ratio and specially designed surface structures, are key factors that lead to very high...
sensitivity. More important to overcoming the sensitivity limitations of previous planar FET sensors is the 1D morphology of these nanoscale structures. Specifically, binding to the surface of a nanowire leads to depletion or accumulation of carriers in the “bulk” of the nanometer-diameter structure versus only the surface region of a planar device. NW-FETs can be configured as highly selective and highly sensitive detectors by linking recognition or receptor groups to detector blocks and is approaching the performance of TFTs, but is also significantly better than solution-processed organic semiconductors. Most recently, Group III–V or II–VI nanowire single-crystal silicon-based devices and glass, providing a new approach for the assembly of these NW TFTs not only greatly surpasses that of solution-processed organic TFTs, but is also significantly better than that of conventional amorphous Si TFTs, and is approaching the performance of single-crystal silicon-based devices. Furthermore, Group III–V or II–VI nanowire or nanobelt materials of high intrinsic carrier mobility or optical functionality can be assembled into thin films on flexible substrates to enable new multifunctional electronics and optoelectronics that are not possible with traditional macroelectronics, in which electronic components are distributed over substrates with surface areas on the order of square meters. This can have an impact on a broad range of existing applications, from flat-panel displays to image sensor arrays, and enable a whole new generation of flexible, wearable, or disposable electronics for computing, storage, and wireless communication.

**Nanophotonics**

Nanowires represent attractive building blocks for active nanophotonic devices, including light-emitting diodes (LEDs), lasers, and detectors. Significantly, the ability to assemble and electrically drive nanoscale sources and detector blocks could allow for fully integrated nanophotonic systems for use in applications ranging from biodetection through information processing. The crossed NW approach was the first to demonstrate true nanoscale LEDs, or nanoLEDs (Figure 3a). In this work, nanoscale p–n diodes were created by crossing well-defined p-type and n-type InP NWs, and subsequent device measurements showed that band-edge emission is observed at the nanoscale cross-points in forward bias. This concept has enabled the assembly of a wide-range of nanoLEDs on a single chip, with emission ranging from ultraviolet through near-infrared in a manner not possible with conventional planar technology. The crossed NW architecture can be further generalized to hybrid devices consisting of n-type direct-bandgap NWs assembled onto p-Si electrodes defined in heavily p-doped planar substrates. Significantly, using n-type CdS NWs in this type of nanostructure has led to the demonstration of the first nanoscale electronic injection laser (Figure 3b). In addition to nanoscale light sources, crossed NW p–n junctions can also be configured as photodetectors critical for integrated photonics. For example, avalanche multiplication of the photocurrent in nanoscale p–n diodes...
has recently been shown in crossed Si-CdS NWs (Figure 3c).37 These NW avalanche photodiodes, or nanoAPDs, exhibit ultrahigh sensitivity with detection limits of less than 100 photons and subwavelength spatial resolution of 250 nm. Moreover, the elements in nanoAPD arrays can be addressed independently without electrical crosstalk. These characteristics exceed the capabilities of any known detector and could open up unique opportunities, for example, for integrated lab-on-a-chip devices and imaging of biological systems.

The controlled synthesis of radial NW structures also offers substantial opportunities for nanophotonics, since the required n- and p-type active materials can be incorporated directly as the core and shells in the NW. This general approach was first demonstrated with the growth of well-defined doped III-nitride–based core–multishell NW heterostructures (Figure 4a).58,59 In these nanostructures, an n-type GaN core and p-type GaN outer shell serve as electron and hole injection layers, and an In$_x$Ga$_{1-x}$N shell provides a tunable-bandgap quantum well for efficient radiative recombination of injected carriers.

Nanophotonic devices with separate contacts to the n-type core and p-type outer shell show expected p–n diode current rectification (Figure 4b). In forward bias, the devices yield strong light emission with the LED color dependent on the indium composition. Significantly, nanophotodiode and nanophototransistor spectra collected from such radial NW heterostructure devices have shown a systematic redshift from 367 nm to 577 nm (Figure 4c), covering the short-wavelength region of the visible spectrum, and moreover, they indicate that very high quantum efficiencies will be possible in such defect-free structures. The efficient injection and radiative recombination of carriers, as well as the synthetically tunable emission wavelength of radial NW devices, represent a clear advance in nanophotodiode and nanophototransistor sources and thus a promising pathway to multicolor NW injection lasers in the future.

**Nanobiotechnology**

Integration of nanosystems and biosystems is a multidisciplinary field that has the potential for tremendous impact on biology, chemistry, physics, biotechnology, and medicine. The combination of these diverse areas of research promises to yield revolutionary advances in healthcare, medicine, and the life sciences through, for example, the creation of new and powerful tools that enable direct, sensitive, and rapid analysis of biological and chemical species. Patolsky et al.60 have demonstrated the first application of NW nanosensors for ultrasensitive detection of proteins down to individual virus particles as well as multiplexed recording of these species using distinct NW elements within a sensor device. In addition, Patolsky et al.60 have demonstrated an unprecedented approach for investigating the electrical properties of hybrid structures consisting of arrays of NWFETs integrated with the individual axes and dendrites of live mammalian neurons, where each nanoscale junction can be used for spatially resolved, highly sensitive detection, stimulation, and/or inhibition of neuronal signal propagation. Details are described by Patolsky et al. in this issue. Arrays of nanowire–neuron junctions enable simultaneous measurement of the rate, amplitude, and shape of signals propagating along individual axons and dendrites. The configuration of nanowire–axon junctions in arrays, as both inputs and outputs, makes possible controlled studies of partial to complete inhibition of signal propagation by both local electrical and chemical stimuli. This revolutionary development opens a new field in integrated nano-biotechnology.

**Nanoelectromechanical Systems**

The development of novel technologies for wireless nanodevices and nanosystems is critically important for *in situ*, real-time, and implantable biosensing and biomedical monitoring. Nanosensors are currently undergoing intense development for ultrasensitive and real-time detection of biomolecules. This research demonstrates the feasibility of harvesting energy from the environment, such as converting mechanical energy (e.g., body motion or muscle stretching), vibrational energy (e.g., acoustic or ultrasonic waves), and hydraulic energy (e.g., body fluid and blood flow) into electric energy for self-powered nanosensors and nanosystems. It also has a huge impact on miniaturizing the size of integrated nanosystems by reducing the size of the power source and improving its efficiency and power density. Piezoelectric FETs and diodes as well as force sensors have also been demonstrated using NWs.
Conclusions

The development of nanowire- and nanobelt-based materials represents breakthrough achievements with rapid expanding impact in all areas of nanotechnology. The remarkable level of synthetic control of the performance properties of NWs and NBs is leading to revolutionary technologies in electronics, optoelectronics, sensors, the life sciences, and defense and will continue to broadly impact the fields of physics, chemistry, biology, medicine, environmental science, and engineering. The articles in this issue of MRS Bulletin make it clear that NWs are truly powerful building blocks for achieving the bottom-up paradigm of nanotechnology with demonstrated impacts on both fundamental science at the nanoscale and on applications. Looking forward, we believe that the future is remarkably bright, with likely revolutionary technologies from NW-based nanosystems that will impact in many ways such areas as the life sciences, healthcare, information technology, and energy science, to name just a few.

References

1. For an introduction, see Sci. Am. (September 2001).


28. See detailed issues on carbon nanotubes in MRS Bull. 29 (April 2004) and MRS Bull. 31 (April 2006).


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**Charles M. Lieber,** Guest Editor for this issue of *MRS Bulletin,* is the Mark Hyman Professor in the Department of Chemistry and Chemical Biology at Harvard University and holds a joint appointment in Harvard’s Division of Engineering and Applied Sciences.

Lieber’s research focuses on the chemistry and physics of materials, with an emphasis on low-dimensional and nanoscale materials; rational synthesis of new nanoscale and nanostructured solids; development of methodologies for hierarchical assembly of nanomaterials into complex and functional systems; investigation of fundamental electronic, optical, and optoelectronic properties of nanoscale materials; and design and development of nanoelectronics and nanophotonic systems with an emphasis on biological detection; electrical and optical-based computing; and interfaces between nanoelectronic and biological systems.

Lieber can be reached at Harvard University, 12 Oxford St., Cambridge, MA 02138 USA; tel. 617-496-3169, fax 617-496-5442, and e-mail cml@cmliris.harvard.edu.

**Zhong Lin Wang,** Guest Editor for this issue of *MRS Bulletin,* is a Regents’ Professor, COE Distinguished Professor, and director of the Center for Nanostructure Characterization and Fabrication at the Georgia Institute of Technology. He has more than 15 years of research experience in nanotechnology. His group’s discovery of the nanobalance in 1999 was selected as a breakthrough in nanotechnology by the American Physical Society. In 2001, Wang and his colleagues discovered the nanobelts, considered to be a groundbreaking work.

Wang’s most recent research focuses on oxide nanobelts and nanowires, *in situ* techniques for nanoscale measurements, self-assembly of nanostructures, the fabrication of nanodevices and nanosensors for biomedical applications, and nanogenerators for self-powered nanosystems.

Wang was elected as fellow of the American Physical Society in 2005. He has received numerous awards and prizes for his research work and has authored or co-authored four textbooks and more than 500 peer-reviewed journal articles, review papers, or book chapters. He has edited or co-edited 14 volumes of books on nanotechnology and holds 20 patents or provisional patents.

Wang can be reached at the Georgia Institute of Technology, School of MSE, 771 Ferst Dr., E.J. Love Bldg., Atlanta, GA 30332 USA; tel. 404-894-8008, fax 404-894-8008, and e-mail zlwang@gatech.edu.

**Erik P.A.M. Bakkers** is a senior scientist and project manager at Philips Research Laboratories in Eindhoven, the Netherlands. He received his MS and PhD degrees in 1996 and 2000, respectively, in physical chemistry from Utrecht University. During his PhD work, he studied electron tunneling between nanocrystals and metals by low-temperature scanning tunneling microscopy and time-resolved photoelectrochemical techniques.

Bakkers has been at Philips since 2000, working on semiconductor nanocrystals and nanowires for electronic and photonic applications. His research interests include the synthesis, structural characterization, electronic transport, and optical properties of nanostructures.

Bakkers can be reached at Philips Research Laboratories, High Tech Campus 4, 5656 AE Eindhoven, the Netherlands; and by e-mail at erik.bakkers@philips.com.

**Magnus T. Borgström** is a Marie Curie postdoctoral fellow at Philips Research Laboratories in Eindhoven, the Netherlands, where he works on epitaxial growth and characterization of semiconductor nanowires.

He received his MSc in 1999 and his PhD degree in physics in 2003 from Lund University in Sweden. He spent a year as a postdoctoral researcher at ETH Zurich in Switzerland, working on optical properties of semiconductor nanowires, before joining Philips.

Borgström can be reached by e-mail at magnus.borgstrom@philips.com.

**Knut Deppert** is a professor at Lund University in Sweden. He studied crystallography at Humboldt University in Berlin, where he obtained his PhD degree in 1985. As a postdoctoral researcher, he worked on growth of crystal structures for optoelectronic devices.

Deppert can be reached at Lund University, his research centers on the application of aerosol methods to generate novel nanomaterials and nanodevices, in particular, size-selected semiconductor nanoparticles; tailored patterning with nanoparticles; and the creation of one-dimensional semiconductor structures such as nanowires and nanotrees. He is also director of the university’s education program on nanoscience and nanotechnology.

Deppert can be reached at Solid State Physics, Lund University, Box 118, SE 221 00 Lund, Sweden; tel. 46-46-222-9520, fax 46-46-222-3637, and e-mail knut.deppert@ffl.lth.se.

**Kimberly A. Dick** is a PhD student in solid-state physics at Lund University in Sweden. She completed her undergraduate studies in chemical physics in Canada and the United States before moving to Sweden in 2003.

Her research focuses on the production and characterization of III–V nanowires and branched nanowire structures. Her particular interests are growth mechanisms involved in nanowire formation, materials interactions during vapor-phase
epitaxial growth, and applications of complex branched structures. She received an MRS Graduate Student Silver Award in 2005.

Dick can be reached at Solid State Physics, Lund University, Box 118, SE 221 00 Lund, Sweden; tel. 46-46-222-9586, fax 46-46-222-3637, and e-mail kimberly.dick@ftf.lth.se.

Xiangfeng Duan is principal scientist and manager of advanced technology at Nanosys Inc. in Palo Alto, California. He received a BS degree from the University of Science and Technology of China in 1997, an MA degree in chemistry from Harvard University in 2002, and a PhD degree in physical chemistry from Harvard University in 2002.

Duan joined Nanosys Inc. in 2002, leading the effort in expanding the company's core nanotechnology platform and identifying new commercial applications. He has carried out pioneering work in developing methods for the synthesis and assembly of semiconductor nanostructures into increasingly complex architectures, and investigating new electronic and optoelectronic device concepts based on these assembled nanostructures.

He has published numerous papers in leading scientific journals and holds a number of nanotechnology patents. Duan is the recipient of several awards for his work in nanoscience and nanotechnology, including an MIT Technology Review TR100 Award, an ACS Regional Industrial Innovation Award, and Nanotech Briefs' "Nano 50" Award.

Duan can be reached at Nanosys Inc., 2625 Hanover St., Palo Alto, CA 94304 USA; tel. 617-448-0983, fax 650-331-2101, and e-mail xduan@nanosysinc.com.

Lisa S. Karlsson is a PhD student in the Division of Polymer and Materials Chemistry at Lund University, Sweden, and is active at the National Center for High-Resolution Electron Microscopy (nCHREM).

Karlsson’s work is centered on the characterization of nanoparticles and nanowire structures by transmission electron microscopy, in collaboration with the Solid State Physics research group at Lund University. Karlsson has been involved in characterization of metal, alloy, and core-shell aerosol nanoparticles produced by an evaporation/condensation technique. Recently, her focus has been on the crystallography of III-V nanowires and nanotrees with detailed characterization on the atomic scale.

Karlsson can be reached at Polymer and Materials Chemistry, Lund University, Box 124, SE 221 00 Lund, Sweden; tel. 46-46-222-8232, fax 46-46-222-4112, and e-mail lisa.karlsson@polymat.lth.se.

Magnus W. Larsson is a final-year PhD student in the Division of Polymer and Materials Chemistry at Lund University, Sweden, and is active at the National Center for High-Resolution Electron Microscopy (nCHREM). He holds an MSc degree in chemical engineering from Lund University.

Larsson’s research is focused on transmission electron microscopy of semiconductor nanowires, working with high-resolution HAADF-STEM imaging and in situ techniques such as TEM-STM and high-temperature microscopy. His other research interests include photovoltaics and electrochemical solar cells, fuel cells, and hydrogen energy systems.

Larsson can be reached at Polymer and Materials Chemistry, Lund University, Box 124, SE 221 00 Lund, Sweden; tel. 46-46-222-8112, fax 46-46-222-4112, and e-mail magnus.larsson@polymat.lth.se.

Fernando Patolsky is a postdoctoral fellow in the Department of Chemistry and Chemical Biology at Harvard University. He received BS and PhD degrees in chemistry from Hebrew University of Jerusalem in Israel.

His research at Harvard focuses on the development of high-performance nanowire field-effect transistors and their applications as a general means for label-free, real-time, ultrasensitive, and multiplexed detection of biological and chemical species. His interests also include the design of electrical interfaces between nanowire-based devices and living neurons.

Patolsky can be reached at Harvard University, 12 Oxford St., Cambridge, MA 02138 USA; tel. 617-496-3169, fax 617-496-5442, and e-mail fernando@cmliiris.harvard.edu.

Lars Samuelson is a professor of solid-state physics at Lund University in Sweden. He is also the director of the Nanometer Structure Consortium, started in 1988, which is today the primary center for nanoscience in Sweden. Samuelson is the leader of a major European R&D project called NODE (Nanowire-Based One-Dimensional Electronics), with participation by leading European electronics industries, research institutes, and academic research teams.

Samuelson is internationally recognized for his research on low-dimensional structures and the physics and applications made possible by these structures. In recent years, his research has been directed toward the formation of ideal 1D heterostructured nanowires through self-assembly; investigation of their physical properties; and applications of semiconductor nanowires in electronics, photonics, and the life sciences.

He is a fellow of the Institute of Physics in the United Kingdom and a member of the Royal Swedish Academy of Sciences. He has authored more than 300 articles in refereed journals and has given approximately 150 plenary/invited talks at international conferences and workshops. Samuelson can be reached at Solid State Physics, Lund University,
Functional Nanowires

Marcel A. Verheijen

L. Reine Wallenberg

Box 118, SE 221 00
Lund, Sweden; tel. 46-46-222-7679, fax 46-46-222-3637, and e-mail
m.a.verheijen@polymat.lth.se.

Werner Seifert is a professor of solid-state physics at Lund University, Sweden. He holds Dr. rer. nat. and Dr. sc. nat. degrees from the University of Leipzig, Germany.

Seifert worked on the optimization of CVD for LED applications at Werk für Fernsehelektronik, Berlin. He was a docent for solid-state chemistry in 1985 and has been at Lund University since 1991.

In 1997, Seifert briefly headed an epitaxy group at the University of California, Santa Barbara. The group focused on the growth and characterization of GaN nanostructures. His current research interests are epitaxy of semiconductor compounds and in situ growth and self-organization of nanostructures.

Seifert can be reached at Solid State Physics, Lund University, Box 118, SE 221 00 Lund, Sweden; tel. 46-46-222-7671, fax 46-46-222-3637, and e-mail werner.seifert@ftf.lth.se.

Brian P. Timko is a graduate student in the Department of Chemistry and Chemical Biology at Harvard University, where he is pursuing his PhD degree in physical chemistry under the direction of Charles M. Lieber.

Timko received BS degrees in chemistry and chemical engineering from Lehigh University in 2002.

His research interests include nanowire synthesis along with structural and electrical characterization, the design of electrical interfaces between nanowires and cells, and the properties of neural networks and computation. He was an NSF Graduate Research Fellow from 2002 to 2005 and a recipient of a Best Poster Award at the MRS 2006 Spring Meeting.

Timko can be reached at Harvard University, 12 Oxford St., Cambridge, MA 02138 USA; tel. 617-496-3169, fax 617-496-5442, and e-mail brian@cmi.harvard.edu.

Marcel A. Verheijen is a senior scientist at Philips Research Laboratories in Eindhoven, the Netherlands. He received his MS degree in 1991 and his PhD degree in 1995, both in solid-state chemistry, from Radboud University in Nijmegen, the Netherlands. During his PhD studies, he researched single-crystal growth of incommensurately modulated crystals and fullerene crystals using optical microscopy and AFM. Since 1996, he has been a TEM application specialist, studying nanowire microstructure, rewritable optical storage discs, and various semiconductor device issues using TEM and related techniques such as electron holography.

Verheijen can be reached at Philips Research Laboratories, High Tech Campus 11, 5656 AE Eindhoven, the Netherlands; e-mail m.a.verheijen@philips.com.

L. Reine Wallenberg is a professor of solid-state chemistry at Lund University in Sweden, where he has been since 2000. He also is the director of the National Center for High-Resolution Electron Microscopy (nCHREM) and one of the founders of Lund’s Nanometer Structure Consortium.

He received his PhD degree from Lund in 1987 on the subject of nanoparticles and electron microscopy. After research visits at Arizona State University, Australian National University, and the Institute for Scientific and Industrial Research in Osaka, he joined the faculty of Lund.

His research interests include nanowires and nanoparticles, catalysts, mesoporous materials, and electron microscopy techniques for inorganic and biological materials.

Wallenberg can be reached at Polymer and Materials Chemistry, Lund University, Box 124, SE 221 00 Lund, Sweden; tel. 46-46-222-8233, fax 46-46-222-4112, and e-mail reine.wallenberg@polymat.lth.se.

Jianxiong Wang works in the Institute of Physics at the Chinese Academy of Sciences (CAS) in Beijing. He received his PhD degree at Beijing National Laboratory for Condensed Matter Physics.

His current research interests focus on controllable synthesis, structure, and physical properties of semiconducting oxide nanostructures; fabrication of oxide nanowire-based devices; and the application of oxide nanostructures in nanocomposites, biomedical devices, and sensors. He has authored or co-authored approximately 30 research papers in international journals.

Wang can be reached at the Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, P.R. China; tel. 86-10-82649081, fax 86-10-82640215, and e-mail jxwang@nthu.edu.sg.

Gengfeng Zheng is working towards his PhD in the National Center for Nanoscience and Nanotechnology at CAS and features a Japanese author in the text.

Sishen Xie is a physicist and an academician at the Chinese Academy of Sciences (CAS) and a fellow of the Third World Academy of Sciences.

He graduated with a degree in physics from Peking University in 1965 and earned his PhD degree in 1983 from the Institute of Physics at CAS. He is the director of Center for Nanoscience and Nanotechnology at CAS and chief scientist at the National Center for Nanoscience and Technology of China.

His research interests are mainly in solid-state and materials physics, including high-Tc superconductivity of oxides, phase diagrams and relations of inorganic systems, fullerenes, and nanomaterials. He has published more than 200 research papers in international journals.

Also, Xie was awarded the Ho Leung Ho Lee Foundation Prize for Scientific and Technological Progress in 2000.

Xie can be reached at the Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, P.R. China; tel. 86-10-82649081, fax 86-10-82640215, and e-mail sxs@aphy.iphy.ac.cn.
Zheng received an MRS Graduate Student Gold Award and the American Academy of Nanomedicine’s Young Investigator Award in 2006.

Zheng can be reached at Harvard University, 12 Oxford St., Cambridge, MA 02138 USA; tel. 617-496-3169, fax 617-496-5442, and e-mail gzheng@cmliris.harvard.edu.

Weiya Zhou is a research scientist at Beijing National Laboratory for Condensed Matter Physics within the Institute of Physics, Chinese Academy of Sciences. She received her PhD degree in physical chemistry from Jilin University in 1990. Her current research interests focus on growth, structure, and properties of fullerene single crystals; the preparation and properties of doped fullerene-related nanomaterials; the synthesis, structure, and physical properties of carbon nanotubes; and the fabrication, nanostructure, and properties of one-dimensional semiconductors. She has authored or co-authored more than 100 research papers in international journals.

Zhou can be reached at the Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, PR China; tel. 86-10-82649381, fax 86-10-82640215, and e-mail wyzhou@aphy.iphy.ac.cn.