A Brighter Future From Gallium Nitride Nanowires[1]

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How might gallium nitride semiconductor nanowires change the future of computing? In the spirit of this special issue on how science fiction might become working technology, we offer some speculations and explain the science behind them. This article focuses on what makes nitride semiconductor nanowires unique as technological materials and how those differences could be exploited as the field matures. One major application area is the miniaturization of ultraviolet light sources and detectors for medical devices, forensic and biological analysis tools, ultraviolet-based secure communications, space sensors, mineral identification, and miniature displays. Additional applications include high-power transistors for radar arrays, quantum mechanical devices, and nanoscale mechanical actuators.

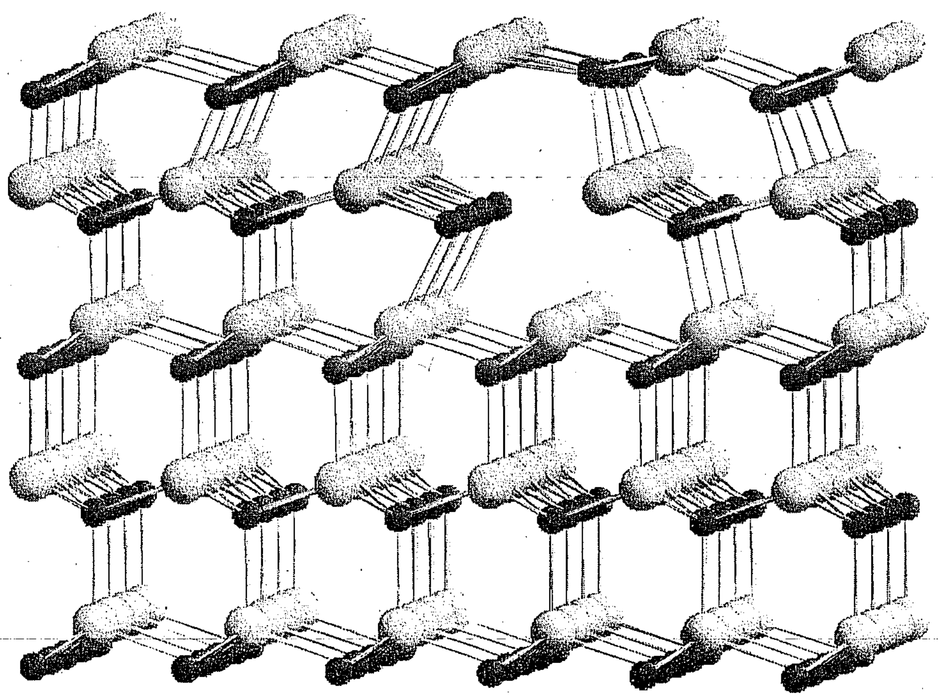
An entire technological revolution began in the 1990s when a series of technological breakthroughs [1, 2] allowed the manufacture of light-emitting diodes (LEDs) and then allowed semiconductor diode lasers that operate at light wavelengths from the ultraviolet to the green. Gallium Nitride (GaN) and Indium Gallium Nitride (InGaN) LEDs are currently a multibillion dollar industry with primary applications in cell phone back lighting, traffic signals, outdoor displays, projection television, and other high-end consumer goods [3]. Nitride LEDs are also poised to displace incandescent and fluorescent lamps for general illumination needs if the manufacturing costs can be reduced. This represents potential worldwide markets of tens of billions of dollars in addition to large reductions in fossil fuel consumption. Blue GaN/InGaN lasers form the technological basis for the higher density DVD storage and playback systems just now being released in select markets and thus impact today's computer technology. Ultraviolet LEDs can also be used for water sterilization and are presently marketed as high-end backpacking equipment. Much of the initial development was funded by the Defense Advanced Research Projects Agency, the Office of Naval Research, and the Department of Energy, with private industry such as Nichia, Nippon Telegraph and Telephone Corp., Samsung, Sumitomo, Cree, Philips/LumiLEDs, Osram, General Electric, Uniroyal, and Agilent all pursuing commercial LED development and manufacture[2].

Limits to Existing Technology

As impressive as these accomplishments and potential markets are, this is only the beginning. Further development is presently limited by cost, yield, and performance issues that are related to the crystal growth process itself. The primary nitride semiconductors are the stable crystalline compounds Aluminum Nitride (AlN), GaN, and Indium Nitride (InN) [4]. In general, it is possible to mix the Al, Ga, and In ratios to make ternary and quaternary alloys such as $Al_{0.5}Ga_{0.5}N$ and $In_{0.2}Ga_{0.4}Al_{0.4}N$. It is, therefore, possible in principle to make semiconductor lasers that emit light from the deep ultraviolet with a photon energy of six electron-volts (6 eV), to the infrared, with a photon energy of 0.8 eV. In practice, only a much narrower range of operation from the near ultraviolet (3.5 eV) to the green (2.4 eV) has been demonstrated. This leaves out a host of applications, including medical and sensor applications where deeper ultraviolet light is essential.

Varying the chemical alloy composition in nitrides induces large changes in the typical atomic spacing in the crystals. Semiconductor devices are generally made by some form of epitaxial growth, which means layer-by-layer growth. In epitaxial growth, deposition starts with a substrate of the same crystal structure desired in the layers. Additional material is deposited under conditions that allow it to copy the substrate crystal structure. If the spacing between atoms in both the substrate and the layer material are equal, this process can go on indefinitely and the growth is said to be *lattice-matched*. If it is not, the layer initially conforms to the spacing of the substrate, but as the layer grows thicker, the strain of maintaining unnatural atomic spacing

Figure 1: *Schematic Diagram of Atoms in a Crystal Structure With a Dislocation Forming to Allow Greater Atomic Spacing on the Top Layers Than on the Bottom Layers. The Larger Light Spheres Represent Ga Atoms, and the Smaller Dark Spheres Represent N Atoms*



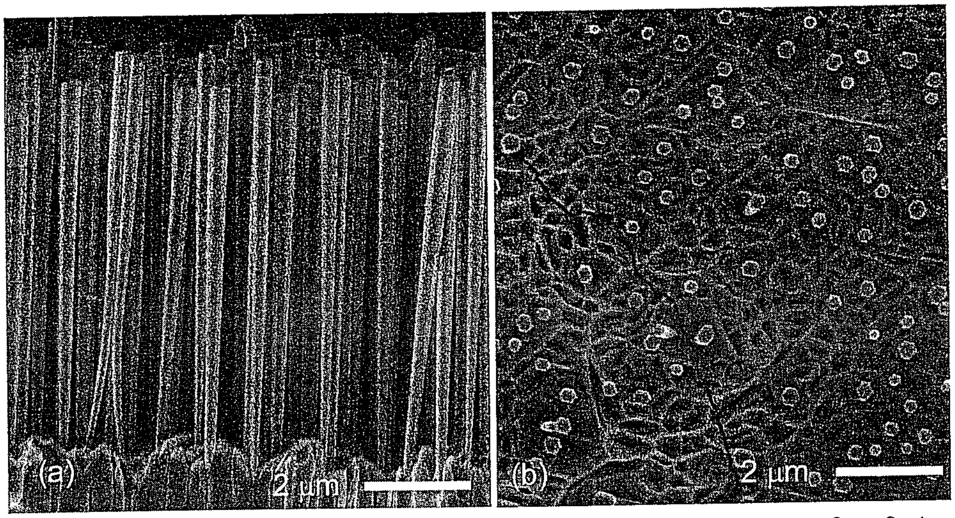


Figure 2: *Field Emission Electron Microscopy Pictures of GaN Nanowires (a) in Cross-Section, Showing the High Aspect Ratio of the Wires, and (b) Top View, Showing the Hexagonal Shape of the Wires*

increases. Finally the layers can no longer tolerate the strain and small atomic-scale defects, called dislocations, form. A schematic diagram of a dislocation is given in Figure 1 (see page 9). Note that the average spacing of the atom rows on the top surface is larger than the spacing at the bottom surface.

These dislocations degrade the optical emission efficiency in LEDs and lead to failure of laser diodes. Dislocations are believed to be the primary factor preventing successful development of ultraviolet lasers, and therefore no diode laser with light emission energy greater than about 3.5 eV has yet been demonstrated. Layer strain can also cause the crystal to separate into regions of different alloy composition, making it difficult or impossible to reach certain alloy combinations. This is a severe design limitation in InGaN devices, where alloys in the middle of the range cannot be grown with conventional technology. Furthermore, there are no lattice-matched substrates upon which to initiate growth in the first place. Unlike silicon wafers, which can be manufactured to high quality with diameters of 300 mm, existing GaN substrates are less than 20 mm across; they are rare, expensive, and high in dislocation density. Commercial GaN devices are typically grown on sapphire or silicon carbide substrates, neither of which have the same atomic spacings as GaN. Even given a successful substrate solution, the variation in atomic spacing within the AlN-GaN-InN alloy system assures that the more interesting combinations of materials will still have to manage strain. This persistent issue for yield and design flexibility is called the *lattice-mismatch* problem.

Nanowires Avoid the Lattice-Mismatch Problem

Enter the nitride nanowire. Nanowires have small cross-sections, allowing them to accommodate much higher levels of strain without formation of dislocations. The wires, furthermore, can rapidly exclude any dislocations that do form to the nearby sidewalls, where they terminate and cease to propagate through the crystal [4]. This defect exclusion mechanism allows the growth of dislocation-free GaN nanowires on the cheapest and highest quality semiconductor substrate around: silicon. Figure 2 shows some typical GaN nanowires grown by the National Institute of Standards and Technology (NIST) by molecular beam epitaxy [5]. The wires range from 50 nanometers (nm) to 400 nm in diameter, depending on growth conditions and can be grown to at least 12 micrometers (µm) in length. The regular hexagonal cross-section arises from the crystal structure of GaN. Although tiny compared with an entire substrate and epitaxial layer used for a conventional semiconductor device, the nanowire volume is still roughly within an order of magnitude of the optically and electrically active region of many such devices. The nanowires can be readily removed from the substrate into solvent solutions and then dispersed onto alternative substrates and processed with photolithography. We have also demonstrated with optical [6] and structural characterization [7, 8] that these nanowires are free of defects and comparable to or better than the best available bulk materials. This high quality persists even when InGaN and AlGaN layers are incorporated within the wires. Other workers in the field have given excellent detailed demonstrations that nitride nanowires can produce higher optical output than conventional materials [9], tolerate large changes in AlGaN alloy composition without defect introduction [10], and reach a broader range of InGaN alloy compositions [11] than is accessible with conventional epitaxial growth technology.

"The nanowire LED and laser will bring new wavelengths and higher energy efficiency to LEDs and diode lasers."

Miniaturization of Ultraviolet Optical Technology: Tricorder, Anyone?

The nanowire LED and laser will bring new wavelengths and higher energy efficiency to LEDs and diode lasers. Nanowires can also be made into wavelength-selective detectors, allowing the miniaturization of spectroscopic analysis. This feature is particularly important in reducing payload size and weight in (real, not fictional) spaceborne sensors and instrumentation. In the future, this technology could conceivably take conventional equipment used for DNA or biological sample laboratory analysis and bring it out into the field. Blue and ultraviolet light are commonly used for fluorescence identification of organic molecules. Current technology relies on power-hungry, high-voltage gas vapor lamps or lasers to produce blue and ultraviolet light and bulky optics to analyze spectra. A handheld, battery-operated (or solar-powered) instrument with functionality such as the *Star Trek* tricorder, then mineral, atmospheric gas, and biological specimen identification could become a reality. Imagine a soldier in remote mountains performing full forensic analysis in real time and uplinking the data via satellite feeds.

Miniature ultraviolet lasers also have a number of medical applications for surgery and diagnostic testing, bringing the hospitals of the future closer to the fictional sick bays on starships. These types of devices will naturally change the way computers interface with sensors, demanding a more portable and specialized interface and database access.

More down-to-earth applications of visible and ultraviolet LEDs and lasers include the following:

- Data storage with higher spatial resolution.
- Compact low-power systems for water purification.
- Higher speed, chip-to-chip, and board-to-board communications within computers.
- Non-line-of-sight secure optical communication via scattered ultraviolet light.

The last application makes use of the fact that ultraviolet light scatters quite efficiently from particulates in the air. This fact is being exploited for the development of secure UV-based, covert urban combat communication systems over short distances.

Power Transistors for Radar Arrays

AlGaN is presently being explored as a new material system for high-power transistors in radar arrays signal processing because it can operate at higher temperatures and withstand sudden power spikes. Unfortunately, the dislocations that degrade laser performance also degrade transistor performance as well. Specifically, the noise in the amplifiers is increased and the gain factors vary with time and usage. Because nanowires can be made dislocation-free, they should be free of these complications.

Quantum Computing and Communication Devices

Another area where nitride nanowires could have far-reaching applications is in the area of quantum computing. Quantum computers are expected to excel at operations that require massive parallel processing of information, including the important cryptography application of factoring products of large prime numbers. Most of the work in quantum computing with semiconductor devices has been done in the technologically more mature semiconductor system of Indium Gallium Arsenide (InGaAs)/Gallium Arsenide (GaAs). Single-photon sources allow secure communications using quantum cryptography, and commercial systems are available on the market today based on these infrared light sources. The operating wavelengths are well matched for long-distance fiber-optic communications, but at the same time these materials are limited to small band gap energy variations. The devices must be cooled to well below room temperature to operate reliably because these energy barriers are smaller than the typical thermal energies of electrons at room temperature. Alloys in the nitride family have much larger band gap differences. Work on GaN quantum dots and quantum wells is just beginning, and there is promise for both single-electron transistors operating at room temperature and single-photon sources and detectors operating at visible or even ultraviolet wavelengths.

Another advantage of semiconductor nanowires for quantum computing is the inherent isolation and interaction control available in the nanowire morphology. Controlled isolation is necessary for the preparation of quantum mechanical initial states and their interaction without loss of phase coherence. Successful single-electron transistors have been demonstrated in nanowire forms of materials that are otherwise too difficult to manipulate in this way [12, 13]. Actual quantum computation operations and devices are still on a rather distant horizon, but bringing the concept demonstrations up to room temperature will speed progress and lower ultimate operating costs.

"Creating control software for these complex machines will be a challenge because of both the large number of control points and the difficulties in communicating instructions."

Nanoscale Actuators

Unlike other common compound semiconductors such as GaAs and Indium Phosphide, the most stable form of the nitride semiconductors is the wurtzite or hexagonal crystal structure. This crystal structure has a significant asymmetry along one axis, and this asymmetry gives the crystals a large piezoelectric coefficient. Piezoelectric materials expand and contract when voltages are applied along certain crystallographic directions.

Nitride nanowires can thus be used as tiny actuators to manipulate particles on a nanometer scale. Fine tuning of positioning would be useful for cellular and molecular probes and possibly for controlling quantum mechanical interactions (tunneling, for example) between nanowires or quantum dots. Realization of these concepts will require additional technological development in order to make electrical contact to the device in a way that is reliable and easily manufactured. The existing state of the art in electron beam lithography is sufficient for making demonstration devices with multiple contacts to a wire lying on a surface; in fact, most nitride nanowires are long enough to process with conventional photolithography. Progress has also been made in placement and manipulation of nanowires with electric fields and optical tweezers. Functional three-dimensional actuators will require truly flexible electrical contacts to free-standing wire sections, which have not yet been demonstrated but may conceivably be realized by other metallic nanowires bonded to the semiconductor nanowires. Breakthroughs in combining nanowires (and other nanostructures) with biologically based assembly methods or polymer technologies might lead to the ability to create very complex machines – the nanobots of the future – with nanowires providing the muscle. Creating control software for these complex machines will be a challenge because of both the large number of control points and the difficulties in communicating instructions.

Summary

We have outlined some of the major areas of technology in which nitride nanowires could have dramatic impact. The miniaturization and efficiency improvement of blue and ultraviolet light sources will lead to greater portability and broader application. The small size of the nanowires contributes to the possibilities of both quantum device designs and very small mechanical devices. The largest potentials for applications are in computer technology, communications, lighting, and health care. This potential has been recognized by *R&D Magazine* editors in selecting our nanowire work as a winner in the 2006 MICRO/NANO 25 competition. All that remains is to *make it so*.◆

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References

1. Amano, H., et al. "P-Type Conduction in Mg-Doped Gan Treated with Low-Energy Electron Beam Irradiation (LEEBI)." Japanese Journal of Applied Physics Part 2-Letters 28 (1989): L2112.
2. Nakamura, Shuji, et al. "Thermal Annealing Effects on P-Type Mg-Doped Gan Films." Japanese Journal of Applied Physics Part 2-Letters and Express Letters 31 (1992): L139.
3. "Gallium Nitride 2005 – Technology Status, Applications, and Market Forecasts." Report Sc-26. Mountain View, CA: Strategies Unlimited, 2005.
4. Trampert, A., et al. "TEM Study of (Ga,Al)N Nanocolumns and Embedded Gan Nanodiscs." Microscopy of Semiconducting Materials 2003. Institute of Physics Conference Series. Bristol: IOP Publishing Ltd. 180 (2003): 167-170.
5. Bertness, K.A., et al. "Spontaneously Grown GaN and AlGaN Nanowires." Journal of Crystal Growth 287.2 (2006): 522-27.
6. Schlager, J.B., et al. "Polarization-Resolved Photoluminescence Study of Individual GaN Nanowires Grown by Catalyst-Free MBE." Applied Physics Letters 88 (2006): 213106.
7. Bertness, K.A., et al. "Catalyst-Free Growth of GaN Nanowires." Journal of Electronic Materials 35.4 (2006): 576-80.
8. M. Kuball, et al, ed. "High Degree of Crystalline Perfection in Spontaneously Grown Gan Nanowires. GaN, AlN, InN and Related Materials in Materials Science." Mater. Res. Soc. Symp. Proc. Boston, MA 892 (2005).
9. Kim, Hwa-Mok, et al. "High-Brightness Light Emitting Diodes Using Dislocation-Free Indium Gallium Nitride/Gallium Nitride Multiquantum-Well Nanorod Arrays." Nano Letters 4.6 (2004): 1059-62.
10. Risti, J., et al. "Carrier-Confinement Effects in Nanocolumnar Gan/Al(X) Ga(1-X)N Quantum Disks Grown by Molecular Beam Epitaxy." Physical Review B 72 (2005): 085330.
11. Kikuchi, A., et al. "Ingan/Gan Multiple Quantum Disk Nanocolumn Light-Emitting Diodes Grown on (111) Si Substrate." Japanese Journal of Applied Physics Part 2-Letters and Express Letters 43.12A (2004): L1524-L26.
12. Thelander, C., et al. "Single-Electron Transistors in Heterostructure Nanowires." Applied Physics Letters 83.10 (2003): 2052-53.
13. Zhong, Zhaohui, et al. "Coherent Single Charge Transport in Molecular-Scale Silicon Nanowires." Nano Letters 5.6 (2005): 1143-46.

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