Integrated Nanoscale Electronics and Optoelectronics: Exploring Nanoscale Science and Technology through Semiconductor Nanowires

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Semiconductor nanowires (NW) represent an ideal system for investigating low dimensional physics and are expected to play an important role as both interconnects and functional device elements in nanoscale electronic and optoelectronic devices. To explore the diverse and exciting opportunities in 1D system requires materials for which the chemical composition, physical dimension, and electronic/optical properties can be controlled and systematically varied. This thesis presents a series of key advances towards integrated nano-systems from the bottom-up approach using chemically synthesized semiconductor NW building blocks.

Semiconductor Nanowire Building Blocks

Rational design and synthesis of nanoscale materials is critical to work directed towards understanding fundamental properties, creating nanostructured materials, and developing nanotechnologies [1-2]. In this thesis, we first introduce a general approach to controlled synthesis of a broad range of semiconductor NWs via a metal cluster-catalyzed vapor-liquid-solid (VLS) growth mechanism.[3-4] Here the catalyst is envisioned as a nanocluster or nanodroplet that defines the diameter of the NWs and serves as the site that directs preferentially the addition of reactant to the end of a growing NW much like a living polymerization catalyst directs the addition of monomers to a growing polymer chain.(Fig.1a) Within this framework, semiconductor NWs, typically with diameters of on the order of 10 nm, and lengths extending up to tens of micrometers (Fig. 1b), can be rationally and predictably synthesized in single crystal form with all key parameters, including chemical composition, diameter and length, and physical properties controlled.[4-5] Semiconductor NWs thus represent best-defined class of nanoscale building blocks, and correspondingly has enabled a wide-range of devices and integration strategies to be pursued.

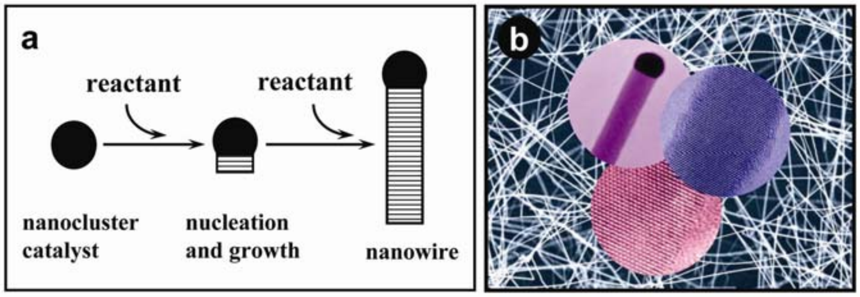

Figure 1. Semiconductor NW building blocks. (**a**) Schematics illustrating the underlying concept for catalytic growth of NWs. Liquid catalytic clusters act as the energetically favored site for localized chemical reaction, absorption of vapor phase reactant and crystallization of crystalline NWs. (**b**) The figure shows a scanning electron microscope (SEM) image of as-synthesized semiconductor NWs. The circular insets show transmission electron microscope (TEM) images of the NWs.

Assembly of Nanowires

In order to fully achieve the potential of such materials, it is essential to assemble them into well-ordered structures-- another key concept in bottom-up technology known as self- or directed assembly, a process by which building blocks come together to form ordered functioning systems.

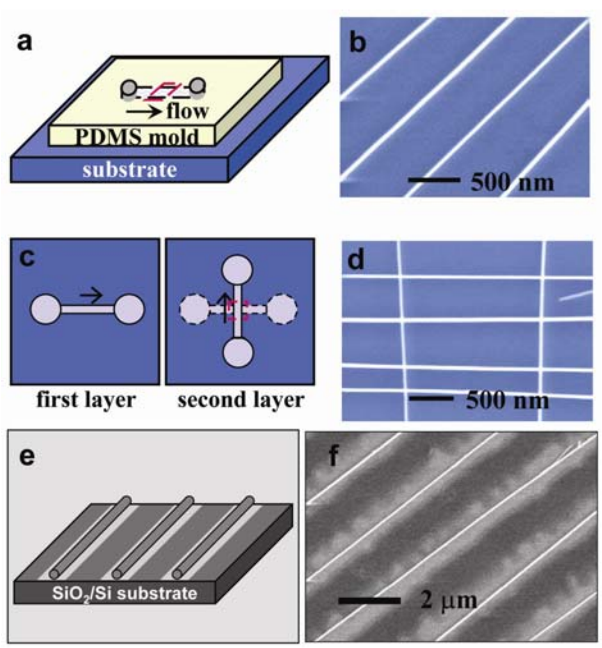

Figure 2. Assembly of nanowires. (**a-b**) Schematic (a) and SEM image (b) of parallel NW arrays obtained by passing a NW solution through a channel on a substrate; (**c-d**) Schematic(c) and SEM image(d) of crossed NW matrix obtained by orthogonally changing the flow direction in a sequential flow alignment process. (**e-f**) Schematic (e) and SEM image (f) of regular NW arrays obtained by flowing NW solution over a chemically patterned surface.

To this end we demonstrate the development of hierarchical assembly methods used to organize NW building blocks into functional devices and complex architectures.[6-7] In particular, microfluidic flows have been explored for the assembly of NWs with controlled spatial location and directionality.[7] In this approach, NWs can be readily aligned into one direction over millimeter area by flowing a NW suspension inside a micro-channel on a substrate (Fig.2a-b). The space between such NW arrays can be controlled by using chemically patterned surface as the substrate (Fig.2e-f). Crossed NW arrays can also be obtained by changing the flow direction in a sequential assembly process (Fig.2c-d). The crossed NW matrix represents an important geometrical configuration for nanocircuits, where each crossing point can function as an independently addressable device element. [7]

Integration of Nanowire Electronics

Next, we will discuss a variety of conceptually new nanoscale electronic and photonic devices, and device integrations enabled by high quality NWs and flexible assembly methods.

A p-n diode can be obtained by simply crossing a p- and an n-type NWs [6,8,9]. Transport measurement of such p-n diode shows clear current rectification (Fig 3a). In addition, such p-n diode can be assembled in >95% yield, and multiple crossed NW p-n diode arrays can be easily assembled use the approach described above (Fig. 3b). [9]

A FET-like device can be achieved by slightly varying the bias configuration in a crossed NW device [9]. Specifically, a nanoscale FET can be constructed by using one NW as the conducting channel and the other crossed NW as the gate electrode (Fig.3c). Transport measurement of such FET shows typical characteristics of a conventional FET (Fig.3d). Notably, the conductance modulation (5 orders of magnitude) is much more significant with the NW gate than that with a global back gate (inset in Fig. 3d).

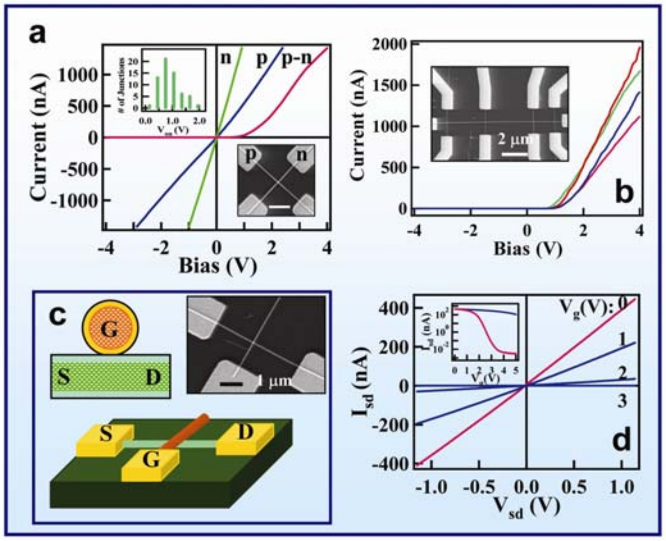

Figure 3. Crossed nanowire devices. (**a**) Top, Current-voltage (I-V) relation of the crossed p-n diode. Linear or nearly linear I-V behavior of the p- (blue) and n-type (green) NWs indicates good contact between NWs and metal electrodes. I-V curves across the junction (red) show clear current rectification. The top-left inset shows histogram of turn-on voltage for over 70 as-assembled junctions showing a narrow distribution around 1 volt. The bottom right inset shows a typical SEM image of a crossed NW p-n diode. Scale bar: 1 μm. (**b**) I-V behavior for a 4(p)x1(n) multiple junction array. Inset shows a SEM image of a NW p-n diode array. (**c**) Schematics and illustrating the crossed NW FET concept, and a SEM image of a real device. (**d**) Gate dependent I-V characteristics of a cNW-FET formed using a p-NW as the conducting channel and n-NW as the local gate. The red and blue curves in the inset show I_{sd} vs. V_{gate} for n-NW (red) and global back (blue) gates when the V_{sd} is set at 1 volt. The conductance modulation ($>10^5$) of the FET is much more significant with the NW gate than that with a global back gate (<10).

In these crossed NW-based devices, all critical device dimensions are defined by the diameter of cross point of the NWs. For example in cNW-FETs, (1) a nanoscale channel width determined by the diameter of the active NW (~2-20 nm depending on chosen NW); (2) a nanoscale channel length defined by the crossed gate NW diameter (~10 nm); and (3) a nanoscale gate dielectric thickness determined by the NW surface oxide (~1 nm). These distinct nanoscale metrics could lead to greatly improved device characteristics such as high gain, high speed and low power dissipation. Significantly, the local NW gate enable independently addressable FET arrays and thus enable highly , integrated nanocircuits, including logic gates(Fig.4a-f)[9], computational circuits (Fig.g-h) [9], and memory device arrays[10].

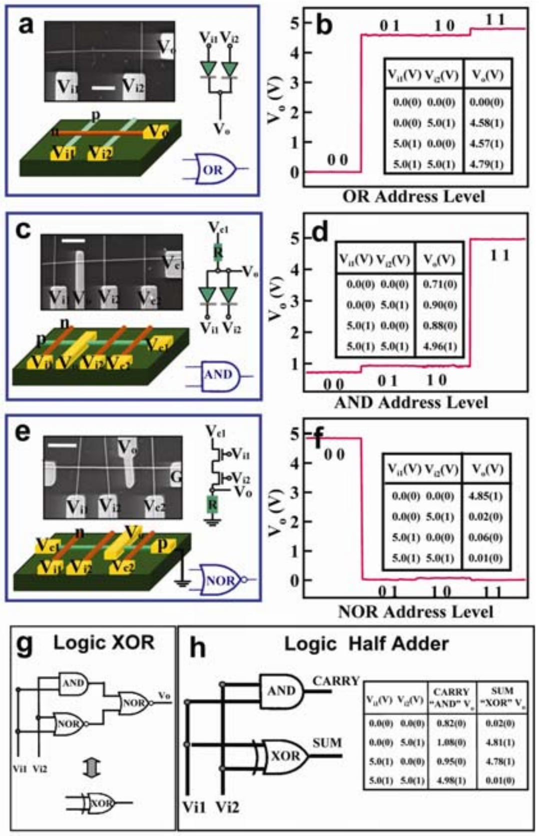

Figure 4. Nanoscale logic gates. (**a,b**) Schematic and measured output vs. address level relation for a logic OR gate assembled from two crossed NW p-n diode. The insets in (a) show the SEM image and equivalent electronic circuit of the device. The bar is 1 μm. The inset in (b) shows the experimental truth table for nano-OR gate. (**c,d**) Schematic and measured output vs. address level relation for a logic AND gate assembled from two diode and one crossed NW FET. The inset in (d) shows the experimental truth table for the nano-AND gate. (**e,f**) Schematic and measured output vs. address level relation for a logic NOR gate assembled from three crossed NW FET. The inset in (f) shows the experimental truth table for the nano-NOR gate. (**g,h**) Schematics for a logic XOR gate and logic half adder realized by interconnecting individual logic gate elements. Significantly, the logic half adder assembled this way can be used to do digital computation just as conventional electronics do (experimental truth table shown in (h)).

Nanowire Optoelectronics

As electronic circuits become ever smaller and faster, photonics and optoelectronics could play an increasingly important role in future computing systems, including smart displays, information storage and communication. [11, 12] In the last section of the thesis we present a number of optoelectronic devices and device arrays.

The availability of a broad range of NW materials readily allows us to choose materials with different properties to tailor device functions in a manner that is unique to the bottom-up assembly approach. In direct band gap semiconductors like InP, the p-n diode also forms the basis for the critical optoelectronics devices, including light emitting diode (LED) and laser diode (LD). To assess whether our nanoscale devices might behave similarly, we have studied the electroluminescence (EL) from crossed NW p-n junctions. Significantly, EL can be readily observed from these nanoscale junctions in forward bias [6]. A 3D plot of the EL intensity taken from a typical NW p-n diode at forward bias (Fig. 5a) shows the emitted light comes from a point-like source, and moreover, comparison of EL and PL (inset, Fig.5a) images recorded on the same sample show that the position of the EL maximum corresponds to the crossing point in the PL image. These data thus demonstrate that the emitted light indeed comes from the crossed NW p-n junction. NanoLEDs with emission spectra covering UV to near IR wavelength were easily assembled by using different NW materials.[13] In addition, integrated multi-color nanoLED arrays were assembled by crossing three different n-type NWs (e.g. GaN, CdS and CdSe) over a p-type Si NW (Fig. 5b). In this device, the p-Si NW acts as a universal hole injector and the n-type NWs function as the emitters. Spectra measurement shows three distinct emissions peaked at 365 nm (UV), 510 nm (green) and 700 nm (red) respectively (Fig.5c). [13]

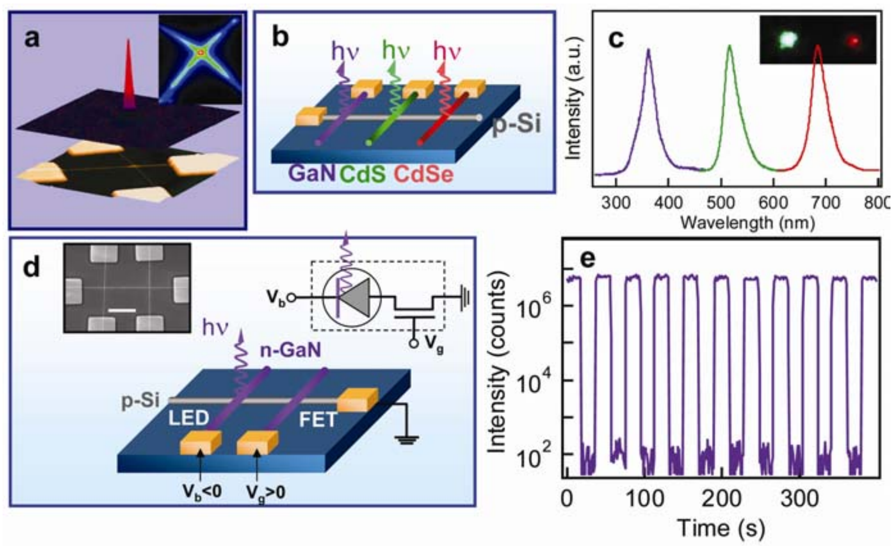

Figure 5. (**a**) **Crossed nanowire LED** (top) Three-dimensional (3D) plot of light intensity of the electroluminescence from a crossed NW LED. Light is only observed around the crossing region. (bottom) 3D atomic force microscope image of a crossed NW LED. (inset) Photoluminescence image of a crossed NW junction. **Multi-color nanoLED array.** (**b**) Schematic view of a integrated triple color nanoLED array. The array was obtained by first fluidic flow aligning a layer of p-Si NW, which was then cover with PMMA, and patterned with electron beam lithography followed fluidic flow aligning n-GaN NW in the perpendicular direction. The process was repeated for another two times to align CdS and CdSe NWs in parallel to GaN NW with a lateral shift of 5 μm. (**c**) The normalized EL spectra obtained from the triple color LED array. **Integrated smart pixel consisting of a nanoFET-nanoLED array** (**d**) Schematic view and SEM image (inset, top left) of an integrated crossed NW FET and crossed NW LED formed by a 1 by 2 cross junction. The inset on the top right shows the equivalent electronic circuit. (**e**) Reversible switching of nanoLED emission with alternative 0 and +4 V pulses applied to the NW gate and a constant load of -6V.

The assembly of a variety of devices (p-n diode, FET, and LED) based on similar crossed NW configuration was also exploited to create integrated devices combining electronic and photonic functions. For example, an integrated smart pixel was assembled by incorporating a crossed NW FET and LED together (Fig. 5d) In this device, the current passing through the LED and the light output from the LED can be modulated in a controlled way by varying the gate voltage applied to the FET (Fig.5e). In this smart pixel, a single nanoFET drives a nanoLED, and thus facilitates addressing, simplifies drive circuitry and reduces cross talk between pixels in a display matrix. [13]

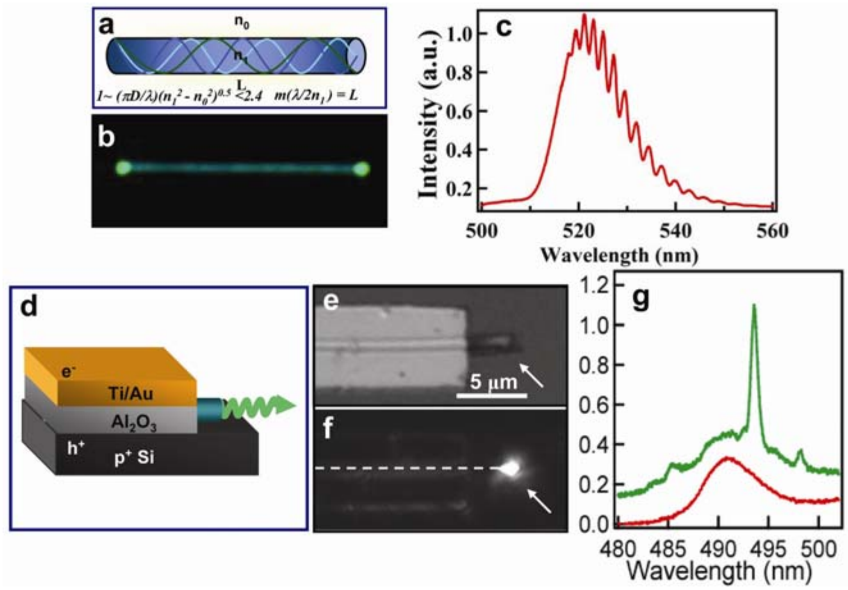

Figure 6. Nanowire as optical waveguide and optical cavity. (**a**) Schematic view of a NW functions as a single mode optical waveguide and optical cavity (see text). (**b**) Fluorescence image of a NW end shows enhanced emission near the NW end. (**c**) Spectrum from the NW exhibits periodic intensity modulation which corresponds to the Fabry-Perot modes of the NW. **Nanowire electrical injection laser**. (**d**) Schematic showing the device structure. In this structure, electrons and holes can be injected into the CdS nanowire cavity along the whole length from the top metal layer and the bottom p-Si layer, respectively. (**e**) Optical image of a device described in (d). The arrow highlights the exposed CdS NW end. Scale bar, 5 μm. (**f**) Electroluminescence image recorded from this device at room-temperature with an injection current of ca. 80 μA. The arrow highlights emission from the CdS NW end. The dashed line highlights the NW position. (**g**) Emission spectra from a CdS nanowire device with injection currents of 200 μA (red) and 280 μA (green) recorded at 8 K. These spectra offset by 0.10 intensity units for clarity.

Free-standing semiconductor nanowires can also function as a stand-alone optical cavity and gain medium and support lasing. [14] In general, a NW will function as a single mode optical waveguide [15] when $1\sim(\pi D/\lambda)(n_1^2-n_0^2)^{0.5}<2.4$, where $\boldsymbol{D}$ is the NW diameter, λ is the wavelength, and $\boldsymbol{n_1}$ and $\boldsymbol{n_0}$ are the refractive indices of the NW and surrounding medium, respectively. If the ends of the NW are cleaved, they can function as two reflecting mirrors that define a Fabry-Perot optical cavity with modes $m(\lambda/2n_1) = L$, where **m** is an integer and $\boldsymbol{L}$ is the length of the cavity (Fig.6a-b). Optical studies revealed that emissions from NW ends show prominent periodic modulation in intensity, suggestive of the Fabry-Perot characteristic of the NW cavity. [14] (Fig. 6c)

At high enough injection current we have achieved lasing action from the ends of the NWs and made a nanoscale laser diode. [14] (Fig.6d-g)

Conclusion

In conclusion, this thesis demonstrates powerful assembly strategies, novel nanodevice concepts and integrated nanoscale device arrays, which represent critical steps towards highly integrated nanoscale electronics and optoelectronics. While electronic and photonic devices based on semiconductor materials are plentiful, the relevance of the work presented in this thesis lies in the fact that these nanoscale devices are synthesized by chemical means and subsequently integrated by assembly methods, rather than the established physical ones, which in the long run may promise cheaper, faster, more versatile fabrication of semiconductor devices, arrays, and related applications.

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Publication List

1. **Y. Huang**, X. Duan and C. M. Lieber "Integrated Multi-color Optoelectronics Assembled from Nanowire Building Blocks", in preparation (2003).
2. X. Duan, **Y. Huang**, R. Agarwal and C. M. Lieber "Single Nanowires as Fabry-Perot Optical Cavity under Electrical Injection" in preparation. (2003).
3. X. Duan, **Y. Huang**, R. Agarwal and C. M. Lieber "Single Nanowire Injection Lasers" *Nature* **421**, 241-245 (2003).
4. X. Duan**,** **Y. Huang**, and C. M. Lieber "Nonvolatile Memory and Programmable Logic from Molecule-Gated Nanowires", *Nano Letters*, **2**, 487-490 (2002).
5. **Y. Huang**, X. Duan**,** Y. Cui, and C. M. Lieber "Gallium Nitride Nanowire Nanodevices," *Nano Letters*, **2**, 101-104 (2002).
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Awards

Top 100 Young Innovators by Technology Review, MIT	2003
Grand Prize Winner of Collegiate Inventors Competition	2002
Materials Research Society Graduate Student Award	2002