Introduction to Nanowires

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(Credit and citation: Prof. Charles Lieber & Lieber Research Group at Harvard)
Why Nanowires?

- Central importance of nanoscale wires in integrated nanosystems
- Fundamental scientific questions in 1-dimensional systems
- Synthetic challenge of controlling structure and composition on many length scales
- New/novel materials can make revolutionary vs. evolutionary changes in science and technology!
Nanowires: A General & Predictable Approach

- **Breaking symmetry for 1D growth.** Nanoscale wires can be prepared rationally by exploiting a catalyst to direct preferentially the addition of reactant.

- The key issue for controlled nanowire growth is the generation of nanometer scale ‘catalyst’ clusters.

- The growth process begins when the catalyst becomes supersaturated with reactant, and terminates when the nanowires pass out of the hot reaction zone.

Functional Nanowires: A Beginning

+ Designed synthesis yields materials with diverse & predictable physical properties beyond that achievable with template
  - Requires template & limited in classes of materials

<table>
<thead>
<tr>
<th>Carbide Nanowire</th>
<th>Metal Reactants</th>
<th>Nanowire Structure</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>TiO or Ti + I₂</td>
<td>Single crystal</td>
<td>Metal</td>
</tr>
<tr>
<td>NbC</td>
<td>Nb + I₂</td>
<td>Polycrystalline</td>
<td>Superconductor</td>
</tr>
<tr>
<td>Fe₃C</td>
<td>FeCl₃</td>
<td>Amorphous</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>SiC</td>
<td>SiO or Si + I₂</td>
<td>Single crystal</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>BCₓ</td>
<td>B₂O₂</td>
<td>Polycrystalline</td>
<td>Insulator</td>
</tr>
</tbody>
</table>

## Nanocluster-Catalyzed Nanowire Growth: An Early Summary

<table>
<thead>
<tr>
<th>Material</th>
<th>Group IV</th>
<th>Group IV Alloys:</th>
<th>III-V</th>
<th>III-V Alloys</th>
<th>II-VI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si, Ge</td>
<td>Si(<em>x)Ge(</em>{1-x})</td>
<td>GaAs</td>
<td>GaAs(<em>x)P(</em>{1-x})</td>
<td>ZnS, ZnSe, CdS, CdSe</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>GaP</td>
<td>InAs(<em>x)P(</em>{1-x})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>GaN</td>
<td>InP</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Growth Conditions</td>
<td>330-1200 Fe, Ni, Au</td>
<td>850-950 Fe, Au</td>
<td>700-1000 Cu, Ag, Au</td>
<td>800-950 Au, Ag</td>
<td>700-1000 Au</td>
</tr>
<tr>
<td>Composition</td>
<td>pure</td>
<td>1:1</td>
<td>defined by starting composition</td>
<td>1:1</td>
<td></td>
</tr>
</tbody>
</table>

- Minimum diameters ~2 nm with single crystal structure
- Controlled nucleation yields monodisperse diameters with controlled lengths
- Surface properties tailored for assembly and device properties

Nanowire growth

ZnO nanostructures

VLS: the pre-history

VLS: Vapor-Liquid-Solid growth of nanowires

Nanowire growth

R.S. Wagner and W.C. Ellis,
App. Phys. Lett. 4, 89 (1964)
History: Key Growth Concepts

\[ r_{\text{min}} = 2\sigma_{LV}V_L/RT\ln\sigma \]
\[ \sim 100 \text{ nm} \]

\( \sigma_{LV} \) is liquid-vapor interfacial free energy
\( V_L \) is the liquid molar volume
\( \sigma \) is the vapor phase supersaturation

Wagner & Ellis, *Appl. Phys. Lett.* 4, 89 (1964)
VLS growth

- surface
- temperature
- gas pressure
- catalyst particle

VLS-growth

gold particle

eutect

gas pressure

Time

liquid Au-GaP vapor
Nanowire growth: epitaxial growth

GaP nanowires on GaP

(111) substrate

1 μm
Nanowire growth: Epitaxial growth

InP nanowires

Nanowire growth: Hetero-epitaxial growth

InP on Ge(111) 3.7% mismatch

Integration of III-V semiconductors with Si

Nanowire growth

VLS-growth

lateral growth

Time

gold particle

liquid Au-GaP eutect

vapor
Nanowire Heterostructures & Superlattices

1-d growth nucleation

axial growth

axial heterojunction/superlattice

radial growth

radial heterostructures

Nanowire growth: Lateral growth

No lateral growth

950 sec. lateral growth

\( \bar{d} \sim 22 \text{nm} \)

\( \bar{d} \sim 90 \text{nm} \)
Nanowire growth: Tapered nanowires
Coaxial nanowire: InP core/ GaP shell

Hetero-junctions:
Germanium/Silicon Core/Shell Nanostructures

- Designed core/shell nanowire structure enables investigations of electron and hole gases confined in uniform 1D potential.
- Reduced scattering can yield higher mobility transistors and open up studies of fundamental quantum phenomena at low-temperatures!

Lu, Xiang, Timko, Wu & Lieber, PNAS 102, 10046 (2005)
Pushing Nanowire Transistor Limits

Transconductance = 26 μS/V
Max $I_{on} = 35$ μA
Scaled values ($V_{dd}=1V$; 70/30 on/off):  
  $G_m = 1.4$ mS/μm  
  $I_{on} = 0.78$ mA/μm

Transconductance = 60 μS/V
Max $I_{on} = 91$ μA.
Scaled values ($V_{dd}=1V$; 70/30 on/off):  
  $G_m = 3.3$ mS/μm  
  $I_{on} = 2.1$ mA/μm

First demonstration that a nanowire transistor could exceed limits of top-down devices!!

Nanowire FETs: How Good Are They?

- $L = 40\, \text{nm}, 8x$ faster than Si p-MOSFET, and shows fundamental limit $> 2\, \text{THz}$
- $I_{on}$ is $\sim 100\%$ of the ballistic limit at low bias

Double Quantum Dot with Integrated Charge Sensor Based on Ge/Si Nanowires

- Fully control of interdot coupling and barrier height by local top gates
- Plunger gates control charge number
- Double dot capacitively coupled to sensor dot on adjacent nanowire
- Charge sensing critical for single-electron double dots and spin control

Core/Shell Architecture is Rich in Function: Photovoltaics

\textbf{p-i-n Core/Shell Nanowire Properties}

- Dark current-voltage (\(I-V\)) data demonstrate (i) ohmic contacts and (ii) good rectifying/diode behavior with quality factors, \(n\), of \(~2\).

- Under 1-sun illumination, yield an open circuit voltage of 0.260 V, a short circuit current (density) of 0.503 nA (24 mA/cm\(^2\)), and stable operation of at least 8-months!

- 1-sun efficiency, \(~3.5\%\), and current density exceed values achieved with nanoparticle & nanorod composite systems, although open circuit voltage is lower.

- Power output is \(~1\) nW (ca. 100 W/m\(^2\))

Axial $p$-$i$-$n$ Nanowire Photovoltaics

- Optical absorption and transport characteristics are unique compared to radial core/shell nanowires.
- Important point of comparison for studies of carrier generation, recombination and collection at the nanometer scale.
Axial \( p-i-n \) Nanowires: Synthesis & Properties

- Controlled modulation of \( p-, i-, \) and \( n \)-type diode regions
- Etching delineates different doped Si regions

- Good quality diodes (not Schottky) with quality factors for \( i = 4 \) \( \mu \text{m} \) of 1.2-1.3.
- \( \Delta I_{sc} \) is proportional to \( \Delta i_{\text{length}} \) implies that photocurrent is predominantly from i-region

Kempa, Tian, Zheng, Lieber & coworkers
Axial p-i-n Nanowires: Tandem Cells

- Controlled nanowire synthesis enables integration of 2 (or more) p-i-n diodes in series with independent control of all junctions.
- Substantial increase in open circuit voltage realized in ‘tandem’ single nanowire photovoltaic elements!

Kempa, Tian, Zheng, Lieber & coworkers
Assembly of Multi-Functional Structures: NW-Photovoltaic Powered Nanodevices

- Individual coaxial nanowires function as robust photovoltaic devices with sufficient power output to drive nanoelectronic devices ‘on chip’.
- A single photovoltaic nanowire integrated with a nanowire sensors is capable of powering the nanowire sensor device without external input.

Interfaces between nanoelectronic & biological systems

- Natural length-scale for electronic interfaces
- Create new tools for biophysics to healthcare
- Hybrid materials that enable new opportunities in science & technology
A Bio-Nanowire Device Interface

Because the sizes of biological macromolecules are comparable to nanowire building blocks, these structures represent natural transducers for ultra-sensitive detection.

Nanowire Nanosensors: Beginning

A nanotransistor is transformed into a nanosensor by modifying the surface with a receptor.

Changes in the surface charge ‘gate’ the device and yield a conductance change.

Detection of Proteins

- Real-time label-free
- High-sensitivity and specificity

Cui, Wei, Park & Lieber, Science 293, 1289 (2001)
Nanosensor Chip for Real-Time, Label-Free Multiplexed Detection

- **Bottom-up/top-down hybrid fabrication yields large number of addressable nanowire elements**
- **Assemble distinct types of nanowires on single chip**
- **Personalize sensor elements with distinct receptors**

Multiplexed Cancer Marker Detection

- Multiplexed, real-time monitoring of cancer marker proteins.
- Quantitative & selective detection of protein concentration to femtomolar level.
- General platform for multiplexed, ultrasensitive, real-time detection of proteins and other species!

Undiluted Blood Serum Analysis

- Serum samples are characterized after single step ‘desalting’ purification.
- (1) buffer; (2) Donkey Serum (DS), 59 mg/ml total protein; (3) DS + 2.5 pM PSA; (4) DS + 25 pM PSA
- (1) DS + 0.9 pg/ml; (2) DS

Marker proteins are detected selectively in presence of ca. 100-billion-fold excess of serum proteins!

Making Good on the Promise: Commercialization

- Vista combines nanowire devices and biotechnology to provide all the tools needed to measure **biomarkers over time**.
- Revolutionize monitoring of biomarkers of therapeutic response and toxicity in the clinic and lab for drug development through patient care.

Vista Therapeutics, Inc.
[www.vistatherapeutics.org](http://www.vistatherapeutics.org)
Ultimate Sensor: Single-Particle Detection

Can nanoscience enable detection at ultimate limit of a single biological entity?

Can the sensitivity of nanowire sensors be pushed to enable true single molecule detection?

Consider the case of small oligonucleotides:

*Fang, Zheng, Tian, Yan, Zhou & Lieber*
Nanoelectronic-Cell Interfaces

An example:

Nanowire nanoelectronic devices can enable:

- Interface to cells at natural scale of biological communication
- Input/output of electrical signals
- Input/output of chemical/biological signals
Nanowire/Neuron Junctions

- Nanowire (NW) response correlated with conventional measurements
- Multiplexed recording with flexible arrays is straightforward
- Nanowire/neuron junctions can be localized at the level of individual neurites

Nondestructive, Real-time Neurotransmitter Detection

Selective detection of neurotransmitter dopamine to at least 100 fM sensitivity

Reversible & nondestructive

Potential for high spatial and temporal resolution

Potential for simultaneous neurotransmitter & action potential recording

X. Jiang, L. Wang, S. Zou & Lieber
Better Approaches for Building & Using These Tools?
Interfacing to Brain Slices

S. Pal & V. Murthy
Q. Qing, B. Tian, G. Yu & Lieber
Vision for Life Sciences

Nanoelectronic-Biological Interfaces Enable:

- Diagnostic devices for disease detection
- General detection & kinetics platform
- New tool for single-molecule detection/biophysics
- Powerful devices for electronic and chem/bio recording from cells, tissue & organs
- Potential implants for highly functional & powerful prosthetics, as well as hybrid biomaterials enabling new opportunities
Evaluating Research Motivation: Progress?

- Synthetic challenge of controlling structure and composition on many length scales
- Fundamental scientific questions in 1-dimensional systems
- Central importance of nanoscale wires in integrated nanosystems
- New/novel materials can make revolutionary vs. evolutionary changes in science and technology!

⇒ Many fundamental scientific questions remain, and will require bold researchers to address.
⇒ Pushing ourselves to identify and tackle these ‘big’ challenges, while difficult, offers the best opportunity to make revolutionary advances and benefit society!
Motivation

Box 1 Hot topics in nanophotonics

**Photonics–electronics convergence:**
- Integrating photonic functions with electronics may aid progress in several application fields (for example datacoms and telecoms, imaging and displays, and sensors).
- A generic, high-volume fabrication process (for example, one that is CMOS-compatible) is mandatory for rapid progress in the field and competitive prices.

**Semiconductor nanostructures for emission and detection of light:**
- Compound semiconductor nanowires and quantum dots for lasers and LEDs (for example, III–V nanowire laser sources grown on silicon, quantum-dot lasers, II–VI or III–V nanowire-based LEDs and quantum-dot nanophosphors)

- All-silicon lasers
- Solar cells

**Plasmonics and metamaterials:**
- Nanostructured materials open up new possibilities (for example strong light confinement, and light filtering, guiding and extracting). Applications lie in sensing, optical interconnects, data storage, displays, lighting, imaging and photovoltaics.
- Left-handed metamaterials could potentially provide optical cloaking and superlensing, as well as other applications.

Source: Nature Photonics (May 2008), based on the roadmap developed by the EU consortium MONA (merging optics and nanotechnologies)
**optical properties of nanowires**

individual (polarization anisotropy, directional emission) and ensembles (birefringence, scattering)

**Goal:** understand light emission by nanowires and light propagation through ensembles. Identify potential applications of nanowires.

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**light emission and close to metals**

nanoantennas, plasmonic crystals

**Goal:** improve efficiency of emitters, control emission (directionality, polarization)
Introduction

InP nanowire

- diameter, \( d = 10-100 \text{ nm} \)
- length, \( h \gg d \)
- \( d \ll \lambda \ll h \Rightarrow \text{optical anisotropy} \)

- hetero-epitaxial growth \( \Rightarrow \) aligned structures
- can be doped \( \Rightarrow \) p-n, band-gap engineering
- easy to contact \( \Rightarrow \) electrical devices
- large surface to volume ratio \( \Rightarrow \) sensors
The past (the 1990’s)

Nanowire LEDs

Himura et al., Hitachi Ltd.

The present (>2000)

Applications:

• waveguides
• lasers
• photodetectors
• sensors
• photovoltaics
• quantum optics
• ...

Waveguides

715 μm long SnO₂ nanowire

M. Law, ..., P. Yang,
Lasers

Optically pumped
GaN nanowires

Electrically pumped
CdS nanowires

X. Duan, ..., C.M. Lieber,

Johnson et al.,
Photodetectors

InP nanowire

J. Wang,..., C.M. Lieber,
Science 293, 1455 (2001)
Antireflection coatings

![Antireflection coatings images](a) (b) (c) (d)

Graph showing Total Reflection vs. Energy (eV) for different Wavelengths (nm).
Sensors

Quantum Optics: single photon sources

M.T. Borgstrom, V. Zwiller, E. Muller, and A. Imamoglu, Nano Lett. 5, 1439 (2005)
Mie scattering

\[ d = 2r \]

Scattering efficiency

<table>
<thead>
<tr>
<th>Size parameter, ( k_0r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scattering efficiency</td>
</tr>
<tr>
<td>( Q_{\text{scat}</td>
</tr>
<tr>
<td>( Q_{\text{scat}}_\perp ) perpendicular to nanowire</td>
</tr>
</tbody>
</table>

\( n = 3.3 \)
scattering contrast GaP nanowire in air
n = 3.3 at $\lambda = 660$ nm
Anisotropic scattering

Darkfield imaging of InP nanowires:

scattered light out

white light in

microscope objective

sample

$\uparrow$ polarization

Anisotropic scattering $\Leftrightarrow$ birefringence
Birefringence

- **Natural birefringence**
  - Quartz $\Delta n = 0.009$
  - Calcite $\Delta n = 0.17$
  - Rutile $\Delta n = 0.29$

- **Form birefringence**
  - 2D photonic crystal: $\Delta n = 0.36$
  - F. Genereux et al., PRB 63, 161101 (2001)
Birefringence of nanowire ensembles

Effective refractive index:

\[ n = \begin{pmatrix} n_⊥ & n_⊥ \\ n_⊥ & n_∥ \end{pmatrix} \]
Birefringence of nanowire ensembles

Nanowire photonic material:
- high refractive index
- filling fraction $\sim 50\%$
- low absorption
- thin nanowires $d \ll \lambda$
- high alignment

GaP:
$E_g = 2.26$ eV, $\lambda_g = 550$ nm , $n = 3.3$
Angle-dependent reflection & transmission
Transmission measurements

Transfer matrix fits:
\[ n_{\parallel} = 1.1 \]
\[ n_{\perp} = 1.045 \]

Retardation over \( \pi \) at \( \theta_{\text{in}} = 72^\circ \)
Semiconductor filling fraction dependence

- GaP substrate
- No shell (<d>=22 nm)
- 200 s shell (<d>=35 nm)
- 400 s shell (<d>=45 nm)

Graph showing contrast as a function of angle \( \theta_{in} \) for different shell thicknesses.
Giant birefringence

$\Delta n = 0.8$

O Muskens, ..., JGR APL 89, 233117 (2006)

F. Genereux et al., PRB 63, 161101 (2001)
In-plane birefringence

Non vertical GaP nanowires on a (100) GaP substrate

Anisotropic luminescence

**InP nanowire:** $\langle d \rangle = 30$ nm, $\lambda_{\text{pump}} = 460$ nm
Control of nanowire polarization anisotropy

InP nanowires on a gold grating
Control of nanowire polarization anisotropy

Surface plasmon polarization excited by the nanowire and coupled out by the grating
Control of polarization anisotropy

NWs $\parallel$ grooves  NWs on flat Au  NWs $\perp$ grooves

$\langle \rangle = 3.8 \pm 1.5$

$\langle \rangle = 5.9 \pm 1.5$

$\langle \rangle = 11.4 \pm 2.5$

Conclusion

Semiconductor nanowires are novel nanostructures with promising applications and extreme optical properties.

Phd and postdoc positions available
www.nanawirephotonics.com