Novel Nano-Engineered Semiconductors for Possible Photon Sources and Detectors

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1. Nanotechnology & nanomaterials
   -- Functional nanomaterials enabled by nanotechnologies.

2. Semiconducting nanowires
   -- Why semiconducting nanowires? (Physics, applications & fabrication)
   -- Fabrication of NWs.
   -- Novel properties of strained silicon nano-pillar arrays (2 ~ 5 nm diameters) & FET’s and quantum dots based on Si nano-pillars.

3. Graphene nanoribbons & related nanostructures
   -- The rise of graphene.
   -- Physics of graphene.
   -- Novel phenomena of graphene & related structures.
   -- Potential applications to light emission & photodetection.
* **In collaboration with**

Prof. A. Scherer & group members  --------------------------------------------  *(Caltech)*  
Prof. M.W. Bockrath & Prof. C.-N. Lau  ----------------------  *(UC Riverside)*

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1. **Nanotechnology & nanomaterials**
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2. **Semiconducting nanowires (NWs)**

3. **Graphene nanoribbons & other related nanostructures**
1. Nanotechnologies & Nanomaterials

- Nanotechnologies have enabled uniquely functionalized or structured nano-materials (“meta-materials”) for:
  - studies of low-dimensional physics in quantum confinement;
  - applications “from A to B” (astronomy, biology, beyond CMOS, etc.)

- Reduced dimensionalities:
  - **Two-dimensional** (graphene, 2DEG)
  - **One-dimensional** (nanowires, nanotubes)
  - **Zero-dimensional** (quantum dots, nanocrystals)

![Graphene Image](http://www.ece.mcgill.ca/~ts7k_op/images/graphene.xyz.jpg)

V. G. Dubrovskia et al., Semiconductors 43, (2009)

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2. Semiconducting Nanowires (NWs)

2.1. Why semiconducting NWs?

- Semiconducting nanowires (NWs) have been demonstrated to be highly versatile optoelectronic components for a wide variety of applications, including:
  - polarization-sensitive photodetectors & arrays with sub-wavelength resolution;
  - polarization-sensitive nano-APD (with gains up to $10^5$);
  - optical modulators & nano-waveguides;
  - nano-LEDs and nano-lasers;
  - solar cells, biomedical sensors, etc.

L. Y. Cao et al. (2009)
Polarization-sensitive & spatially resolved nano-APDs

- p-type Si-NW & n-type CdS-NW
- Gain up to $10^5$
- Spatial resolution better than 250nm

2.2. Fabrication of NWs

- Mechanism of the growth vapor-liquid-crystal:

V. G. Dubrovskii et al., Semiconductors 43, (2009)

An ensemble of GaAs-NWs grown by MBE

An individual GaAs-NW
• Formation of NWs by selective epitaxy on treated surfaces w/o a catalyst:

V. G. Dubrovskii et al., Semiconductors 43, (2009)

GaAs-NWs grown on the GaAs (111) surface for $d_0 = 200$ nm

GaAs-NWs grown on the GaAs (111) surface for $d_0 = 50$ nm

• Other growth mechanisms such as self-assembly, etc.
2.3. **Strained silicon nano-pillars**  

When small silicon pillars are oxidized, the silicon lattice expands by approximately 40%, which leaves the adjacent un-oxidized silicon under tremendous tensile strain. In nanowires, this strain can increase to the point where the silicon oxidation process is self-limited, leaving stable 2 ~ 10 nm wide tensile-strained silicon cores within a silicon dioxide shells.

The nano-pillar diameter is controlled by the oxidization temperature.

![Diagram of Silicon Nano-rods]

Silicon Nano-rods can be further decreased in size by thermal oxidation

Si → SiO₂ is accompanied by a 40% volume expansion
Atomically resolved imaging & spectroscopy using scanning tunneling microscopy (STM)

**STM operation is based on:**

1) **Quantum tunneling of electrons**
   -- Tunneling current (I) depends strongly on the surface work function (\(\phi\)), the separation (s) and the biased voltage (V) between the tip & sample.

2) **Piezoelectric control**
   -- Enables atomic scale resolution for surface topography and lateral scanning capabilities.

**Two primary modes of operation:**

1) **Three-dimensional imaging**
   -- Under feedback control, the “constant current map”.

2) **Spectroscopy**
   -- Fixed location differential conductance (dI/dV)-vs.-V map, under constant \(\phi\).
Strain-enhanced energy gap in silicon nano-pillars

Spatially resolved spectroscopy of HF-etched silicon nano-pillars

Surface topography from STM after HF chemical etching

The energy gap increases from \(~ 1.1\) eV for crystalline silicon to \(~ 3.0\) eV for the strained silicon nano-pillars.

Further quantum confinement is expected for a finite magnetic field parallel to the silicon nano-pillars, because the diameter of the nano-pillars is typically smaller than the cyclotron orbit.

(Our preliminary STM results)
Making a transistor out of a strained silicon nano-pillar:

1. oxidize

2. gate metal

3. planarize

Deposit metal and oxide

Deposit contacts

4. Source and drain

5. Litho & metallize

Mechanically push over pillars

Quasi-1D short silicon channels can be gated from all sides to form a self-aligned FET structure where mechanical cleaving of pillars defines the source-drain path.

(Courtesy of Axel Scherer)
Similar transistor structures have been demonstrated in InAs nanowires with larger diameters and separations:

V. G. Dubrovskiia et al., Semiconductors 43, (2009)
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3.1. The Rise of Graphene

Carbon structures in different dimensions:

- Graphene consists of carbon atoms in honeycomb lattice.
- Unique Dispersion Relations: massless Dirac Fermions.
- First experimental isolation by Geim’s group in 2004.
  [Novoselov et al, Science (2005).]

Two sublattices in the honeycomb lattice:

(Courtesy of M.W. Bockrath)
3.2. **Physics of graphene**

Electronic bandstructures of graphene:

- Tight binding approximation, assuming a perfectly ordered infinite system, 3 covalently bonded $sp^2$ and 1 $2p_z$ conduction electrons.

- The resulting $E_{2D}(k)$ band structure is

$$E_{2D}(k_x, k_y) = \pm 3 \sqrt{1 + 4 \cos \frac{\sqrt{3} k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}} (eV) \approx \pm v_f \hbar |\vec{k}|$$

Near the “Dirac points” $K$ & $K'$

Graphene bipolar field effect transistors (FETs)

- Conductivity ($\sigma$) increases linearly with charge density ($n$): $\sigma \propto V_g \propto n$
- Extremely high mobility: ~15,000 cm²/Vs in as-prepared, non-optimized samples, compared to ~2,000 cm²/Vs for silicon.
- Conductivity $\sigma$ remains finite at Dirac point $\rightarrow \sigma_{\text{min}}$
Applications of Graphene

**Demonstrated applications:**

- Transparent electrodes for solar cells, LCD, etc.
- Robust, non-volatile, atomic switches.
- Chemical and biological sensors based on graphene.
- Electronics, Spintronics, and Valley-tronics.

**Post silicon electronic materials:**

- With advantages of carbon nanotubes.
  - high thermal conductivity (~5000 W/mK)
  - high current density (~ mA/µm width)
  - high mobility (~20,000 cm²/Vs in as-prepared samples, 300,000 if suspended)
  - supports ballistic transport over large distances
- 2D → compatible with lithographic techniques.
- Potential for large scale synthesis.
**Challenges & Current Research Directions**

- **Large-scale & high-quality production**
  - → MBE or CVD growth.

- **Device and bandgap engineering**
  - → graphane (*i.e.* hydrogenated graphene)
  - → nanoribbons
  - → atomic switches
  - → local strain

- **Novel devices**
  - → ballistic transistors
  - → supercollimators & electronic lensing
  - → Schottky diodes & light emitting diodes
  - → photodectors

*Graphene is a semi-metal, or zero-gap semiconductor. How does one engineer an energy gap in graphene-based systems?*

*Graphene nanoribbon (0 ~ 200 meV)*
3.3. **Novel properties of graphene & related structures**

- **Energy gap engineering of graphene nanoribbons (GNR):**
  - Band gap induced by quantum confinement.
  - GNR field effect transistors (FETs).
  - Lithographically or chemically defined nanoribbons.

\[
E_g = \frac{0.2}{(W - W^*)} \text{ eV/nm}
\]

- On/Off ratio ~ $10^6$.
- Mobility ~ 200 cm$^2$/Vs.
• Strain-induced modifications to the electronic properties of graphene:

1. Mechanically exfoliated graphene on SiO$_2$.
2. CVD-grown graphene on Cu.
STM calibration on graphite

- We tested on graphite to calibrate STM and verify tip quality.

- STM topography scan over graphite manifests the A-B-A-B stacking of graphene hexagon sheets, known as the Bernal stacking.
STM studies of graphene on SiO₂

- STM topographic image of graphene reveals a distorted honeycomb lattice, showing surface corrugations (~ 0.7 nm z-axis modulations over ~ 20 nm distance) correlated with the underlying SiO₂ substrate.
• Fourier transform of the topographic image of graphene reveals a strained-induced distorted reciprocal lattice.

• Local electronic properties are also modified by the strain fields.
Strained-induced conductance modulations

- Constant-$V_B$ conductance maps at small $V_B$ values correlate with overall surface corrugation and the resulting strain fields.

- Maps of strain tensor components:

\[
S_{xx}(x,y) = \frac{\partial u_x(x,y)}{\partial x} \\
S_{yy}(x,y) = \frac{\partial u_y(x,y)}{\partial y} \\
S_{xy}(x,y) = S_{yx}(x,y) = \frac{\partial u_x(x,y)}{\partial y} + \frac{\partial u_y(x,y)}{\partial x}/2
\]

Displacement field:

\[
u(x,y) = [u_x(x,y) e_x + u_y(x,y) e_y]
\]
Strain-induced modifications in the out-of-plane phonon-assisted tunneling gaps & conductance

This work:
M.L. Teague et al, Nano Letters 9, 2542 (2009)

References:

ωph varies from 21 meV to 44 meV.
The out-of-plane phonon frequencies increase with increasing strain, suggesting coupling of $\pi$-electrons to the underlying phonons of the dielectric $\text{SiO}_2$.

Strain-induced structural & conductance modifications in large-scale CVD grown graphene on copper

- CVD growth of graphene on copper foils at ~ 1000°C under hydrogen gas with CH₄ partial pressure.

- Large differences in the thermal contraction coefficients of graphene and copper lead to ripple structures.  
  [N.-C. Yeh et al, (2010)]
Modifications to electronic properties due to structural changes

Topography (distorted structure)

Fourier-transformed structure

N.-C. Yeh et al., (2010).

Conductance spectra of representative regions

Conductance spectra along the dashed line in the upper left figure.
3.4. Potential applications to light emission & photodetection

- **Graphene nanoribbons**: semiconducting energy gaps may be engineered by the controlling the width, from 0 ~ 200 meV.

- **Graphane**: semiconducting energy gaps may be engineered by controlling the hydrogen coverage, from 0 ~ 3.5 eV.

**Device concept**

The light emitting process may be reversed for the detection of photocurrents.

**Future work**: measurements of the I-V characteristics & photocurrents.
Summary

- Novel nanostructures such as strained silicon nano-pillars, semiconducting nanowires and graphene-based nano-devices may be interesting candidates for new types of ultra-high-density ultra-compact sensitive photodetectors, possibly even single-photon-counting detectors.