Novel Nano-Engineered Semiconductors for Possible Photon Sources and Detectors

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Department of Physics, California Institute of Technology

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

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

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National Science Foundation ------------------------------ **(UC Riverside)**

1. **Nanotechnology & nanomaterials**

   -- Functional nanomaterials enabled by nanotechnologies.

2. **Semiconducting nanowires (NWs)**

3. **Graphene nanoribbons & other related nanostructures**

1. Nanotechnologies & Nanomaterials

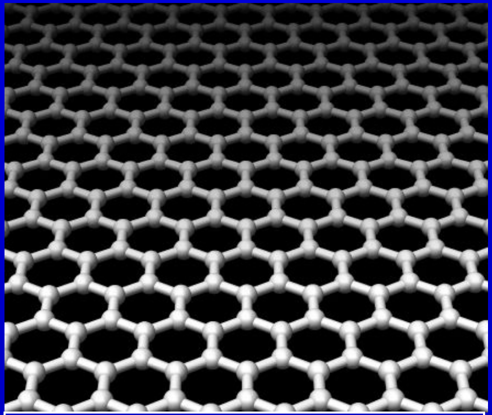
- Nanotechnologies have enabled uniquely functionalized or structured nano-materials (“meta-materials”) for:

→ studies of low-dimensional physics in quantum confinement;
→ applications “from A to B” (astronomy, biology, beyond CMOS, etc.)

- Reduced dimensionalities:

Two-dimensional

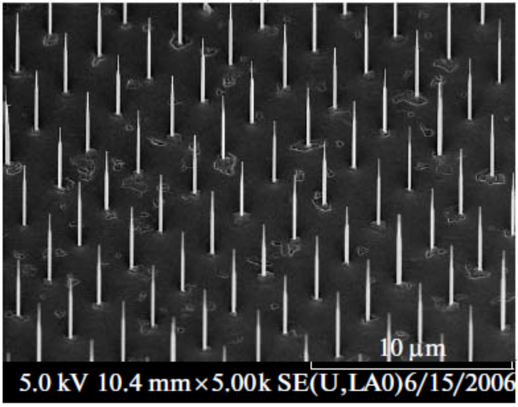
(graphene, 2DEG)



http://www.ece.mcgill.ca/~ts7kop/images/graphene_xyz.jpg

One-dimensional

(nanowires, nanotubes)



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

Zero-dimensional

(quantum dots, nanocrystals)

L. Kouwenhoven et al.,
Phys. World (2001)

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3. **Graphene nanoribbons & related nanostructures**

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:

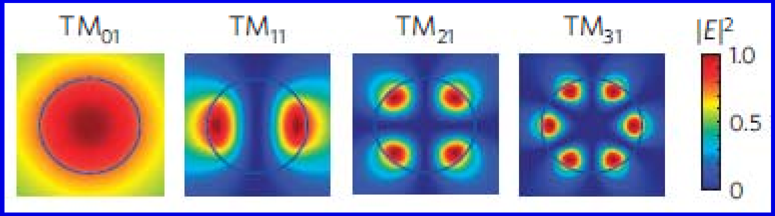
* polarization-sensitive photodetectors & arrays with sub-wavelength resolution;

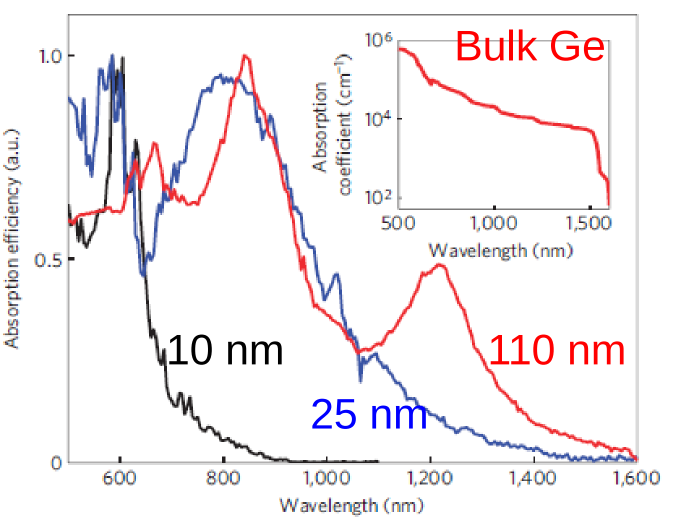
* polarization-sensitive nano-APD (with gains up to 10^5);

* optical modulators & nano-waveguides;

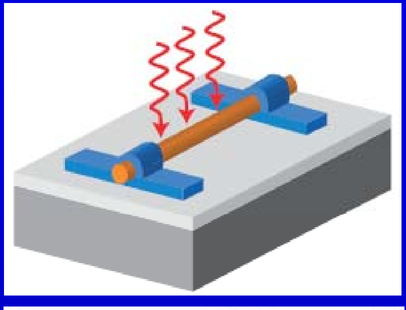
* nano-LEDs and nano-lasers ;

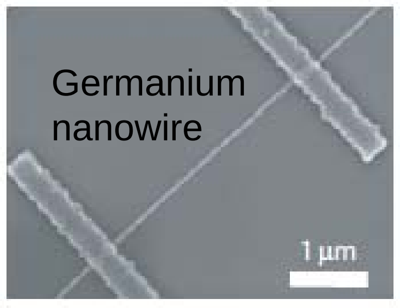
* solar cells, biomedical sensors, etc.

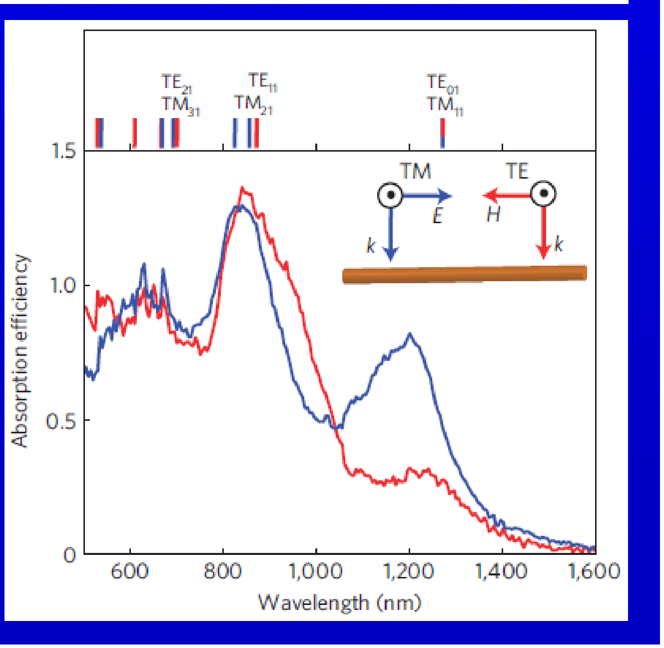




L. Y. Cao et al. (2009)





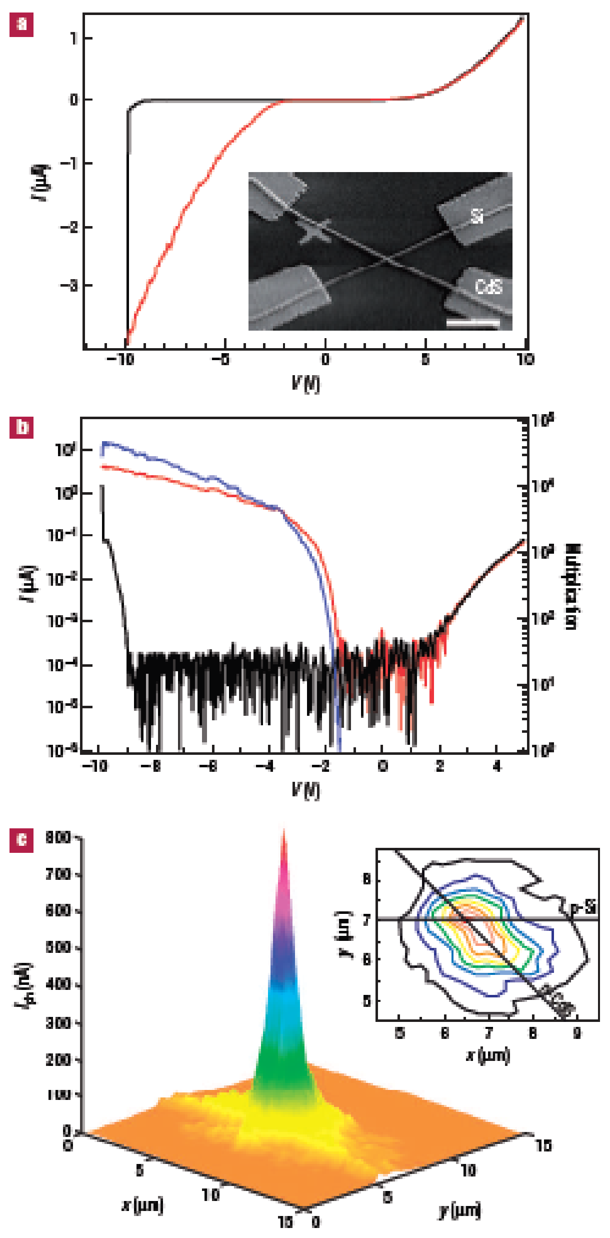


Polarization-sensitive & spatially resolved nano-APDs

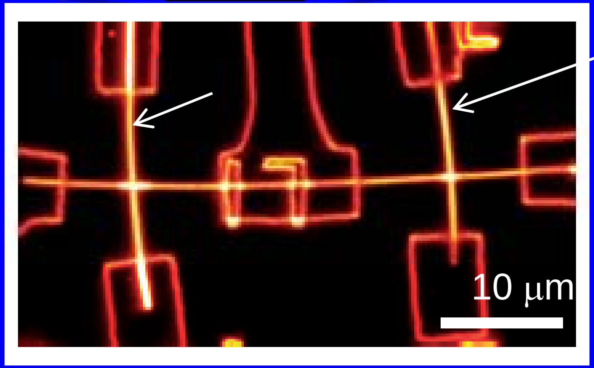
p-type Si-NW
&
n-type CdS-NW

Gain up to 10^5

Spatial resolution better than 250nm

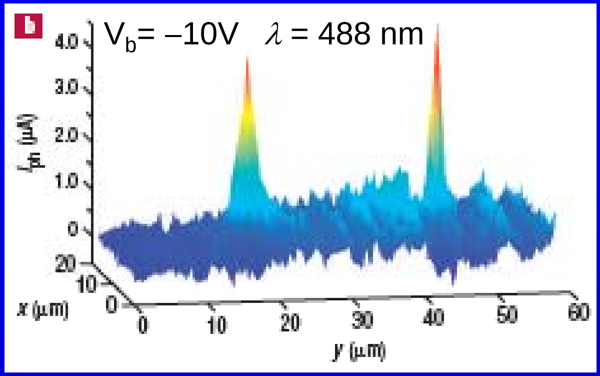


Hayden et al.
Nature Mat.
5, 352 (2006)

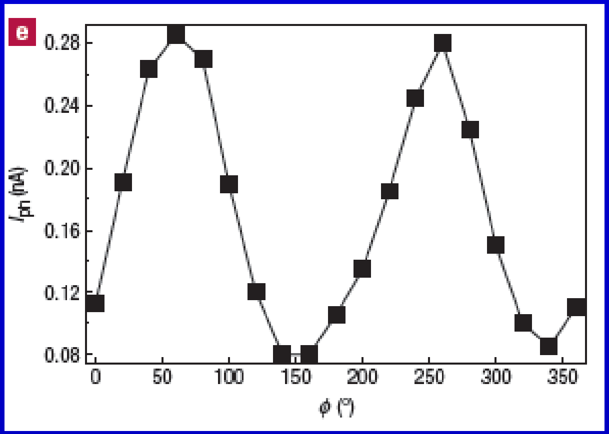


p-Si

n-CdS



No cross talk

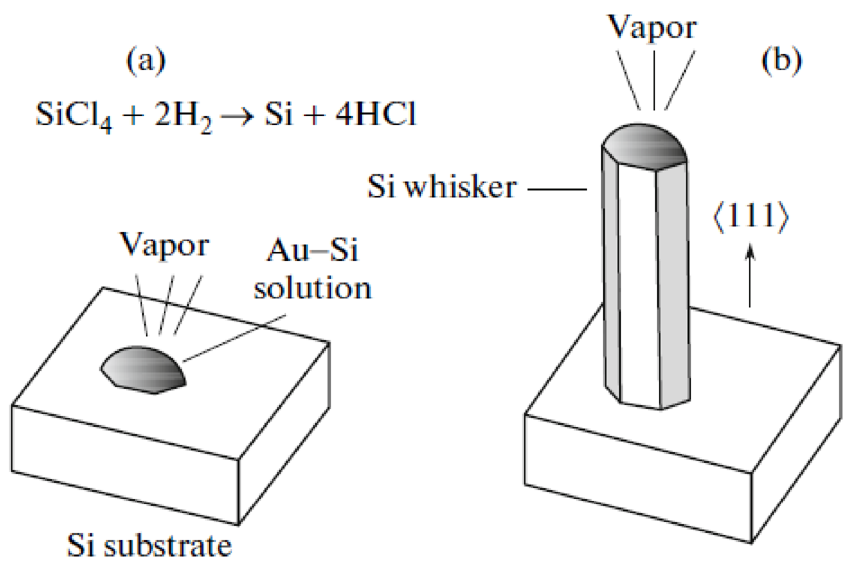


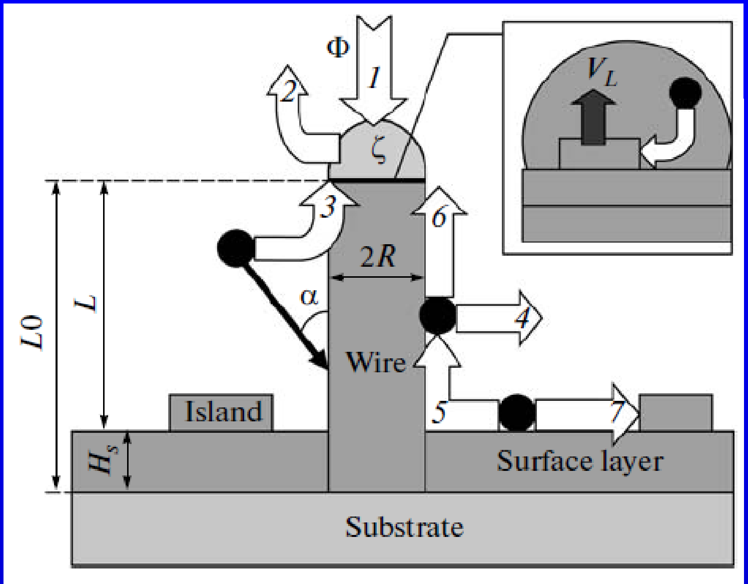
Polarization -sensitive

2.2. Fabrication of NWs

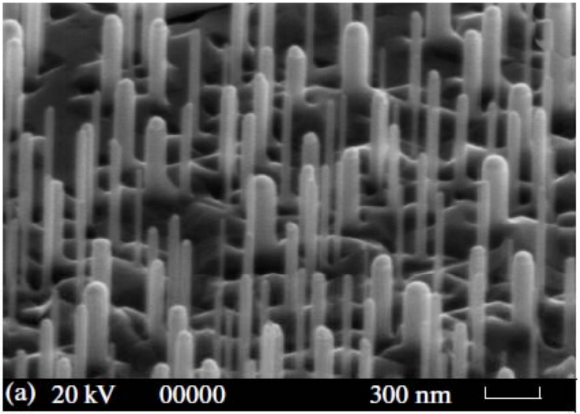
- Mechanism of the growth vapor-liquid-crystal:

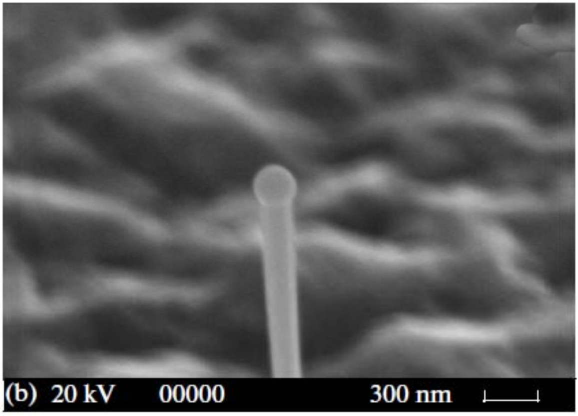
V. G. Dubrovskiia et al.,
Semiconductors 43, (2009)





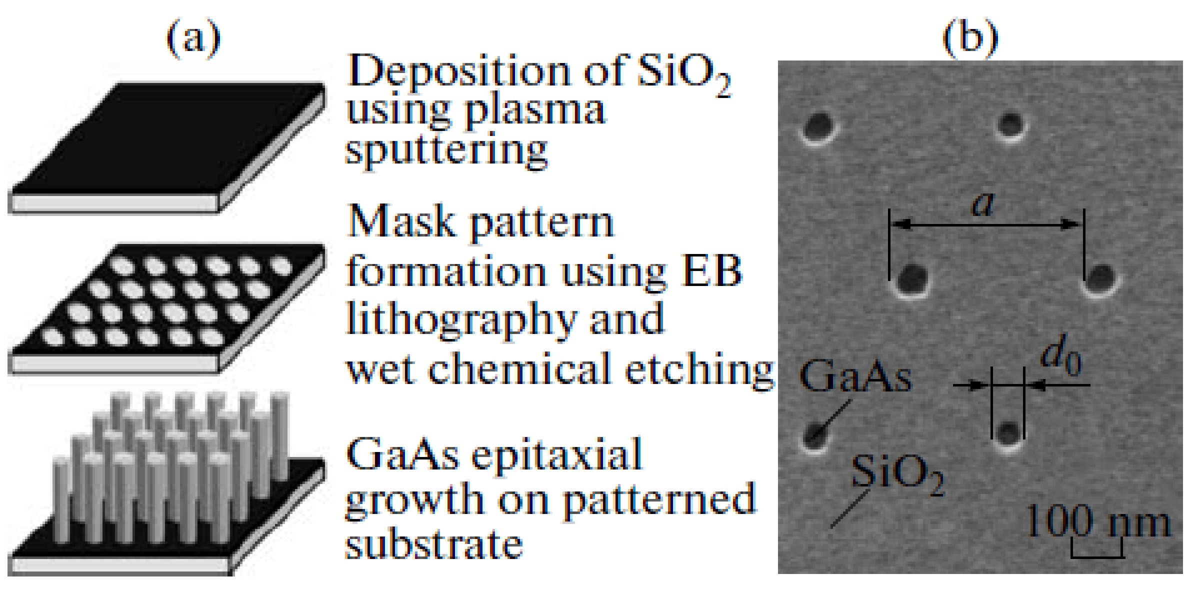
An ensemble of GaAs-NWs grown by MBE





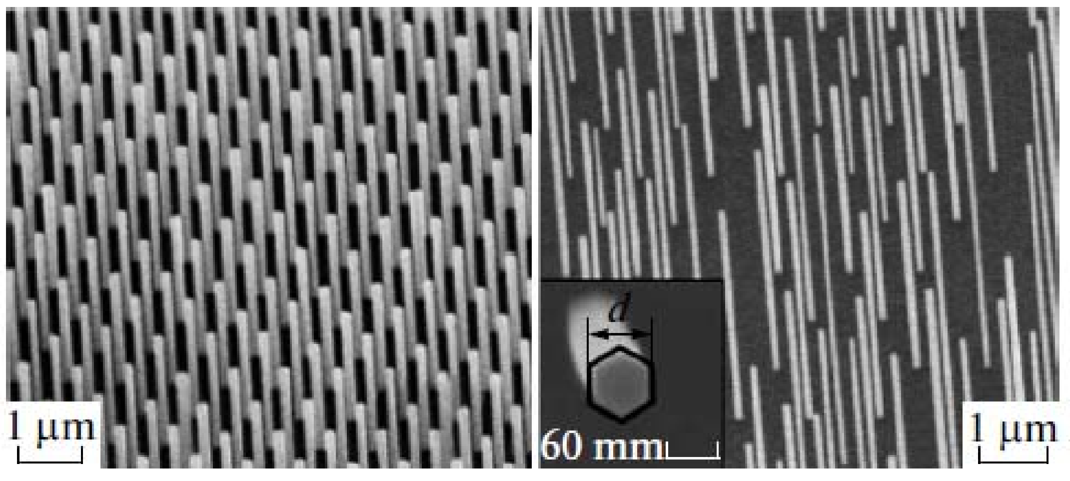
An individual GaAs-NW

- Formation of NWs by selective epitaxy on treated surfaces w/o a catalyst:



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

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



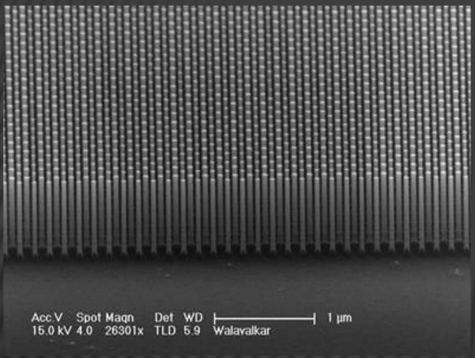
GaAs-NWs grown on the GaAs (111) surface for d_0 = 50 nm

- Other growth mechanisms such as self-assembly, etc.

2.3. Strained silicon nano-pillars (Axel Scherer's group)

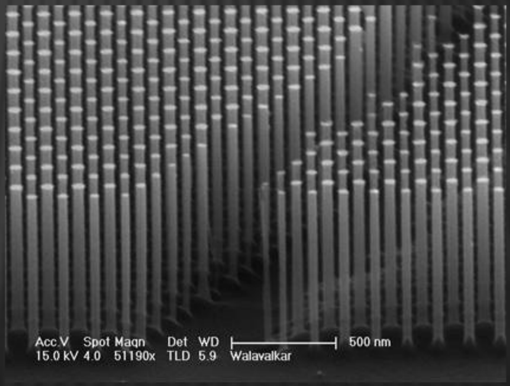
When small silicon pillars are oxidized, the silicon lattice expands by approximately 40%, which leaves the adjacent un-oxidized silicon under tremendous tensile strain. In nanowires, this strain can increase to the point where the silicon oxidation process is self-limited, leaving stable 2 ~ 10 nm wide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

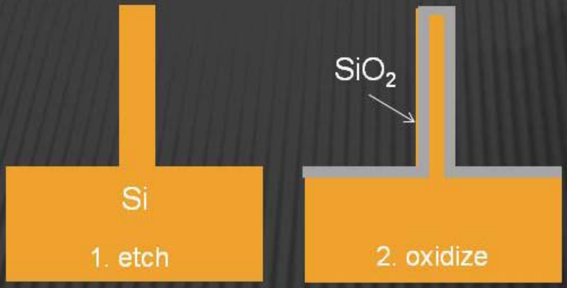
The nano-pillar diameter is controlled by the oxidization temperature.



A 5 minute etch provides excellent surface and sidewall quality

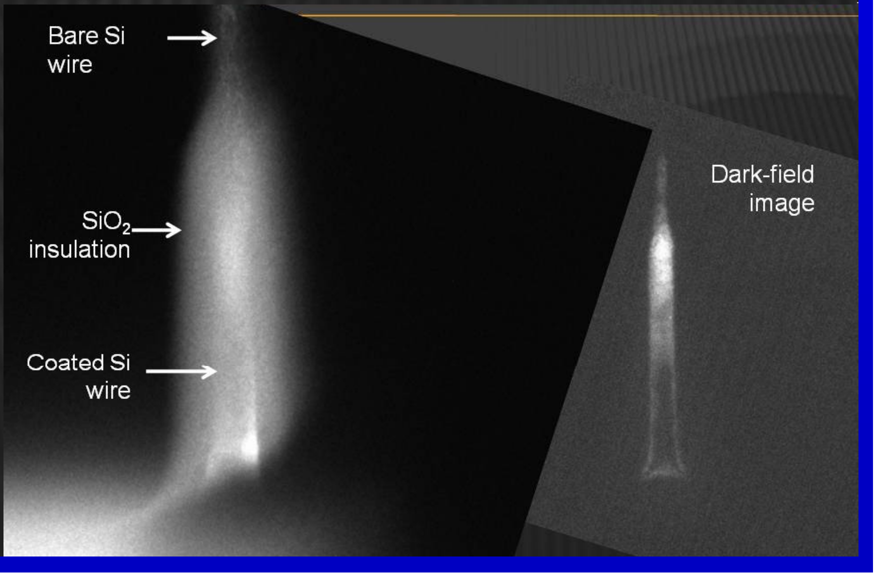
Etch mask of Al_2O_3 enables a 2000:1 selectivity towards the etch





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

Si → SiO_2 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 (ϕ), 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.

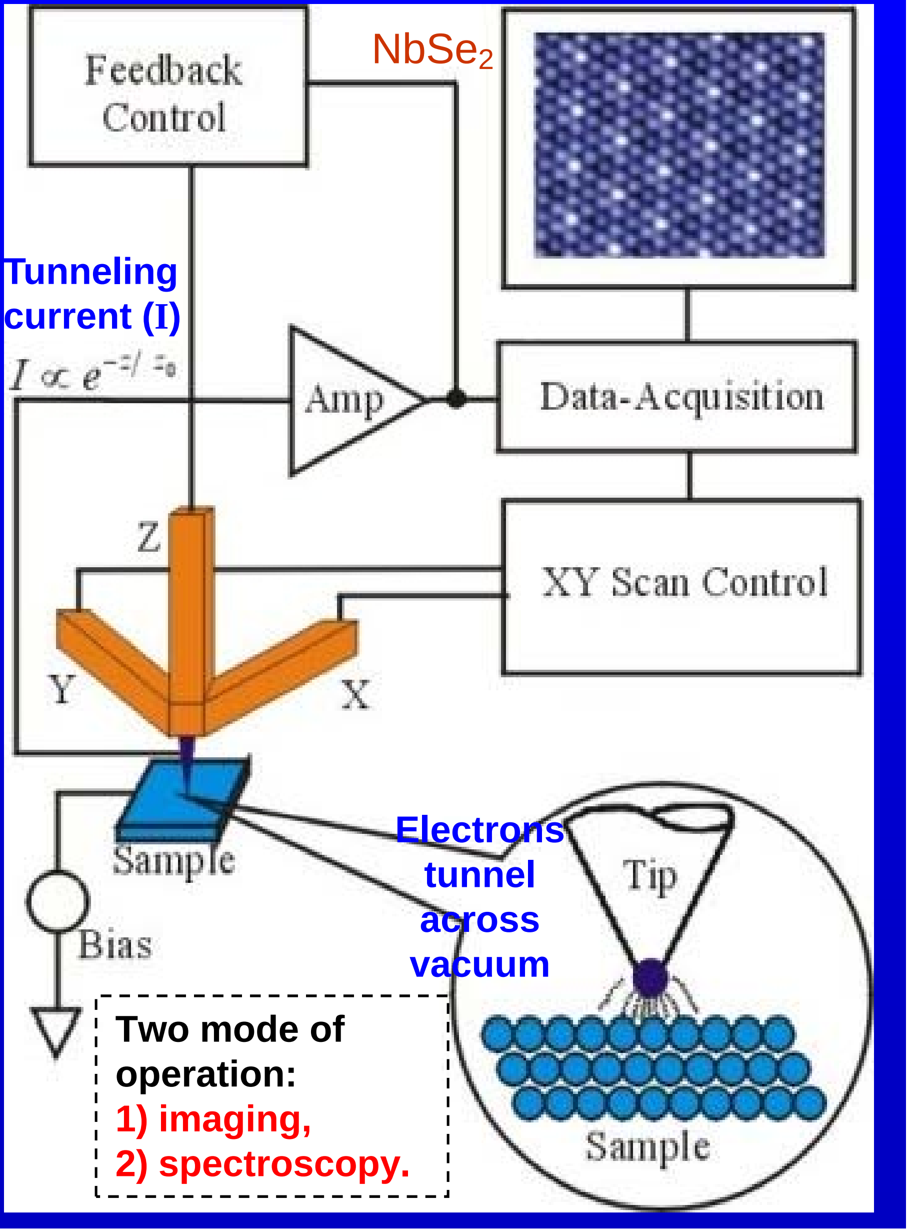
Two primary modes of operation:

1) Three-dimensional imaging

-- Under feedback control, the “constant current map”.

2) Spectroscopy

-- Fixed location differential conductance (dI/dV)-vs.-V map, under constant ϕ .

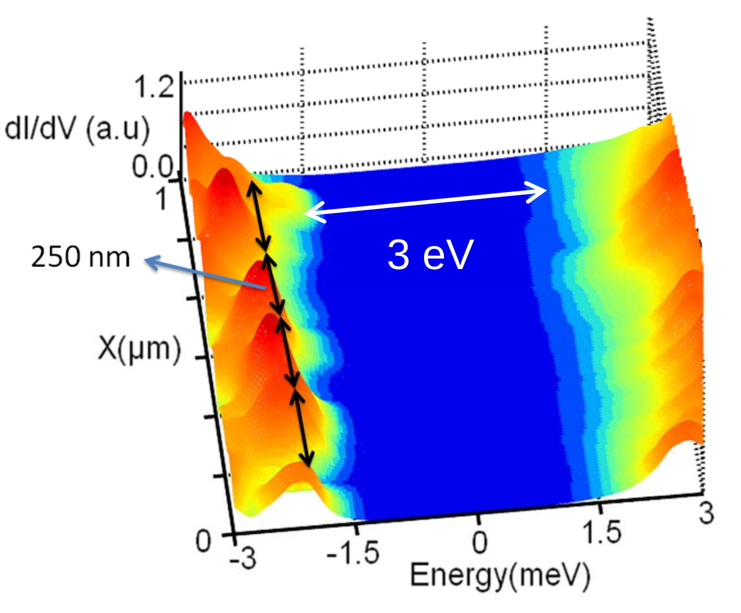


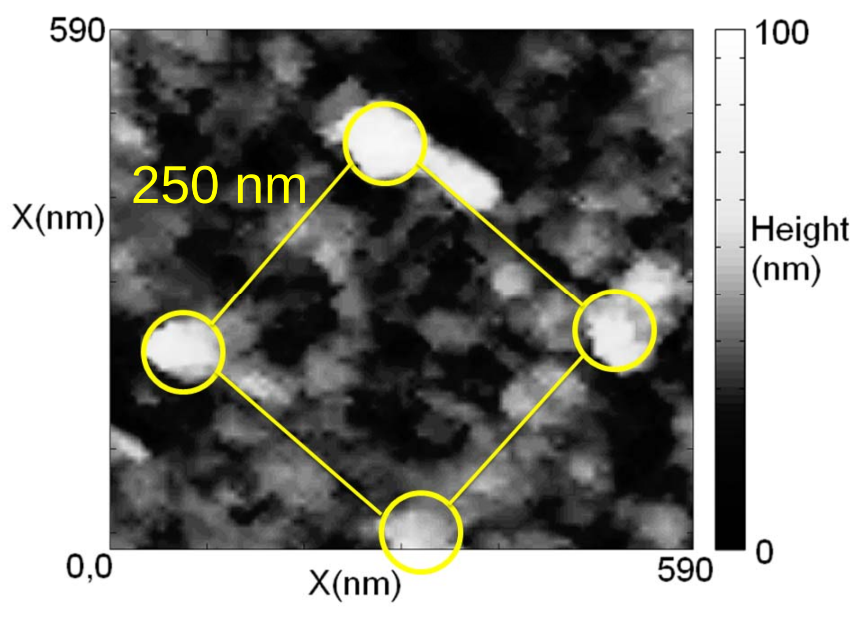
Two mode of operation:
1) imaging,
2) spectroscopy.

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



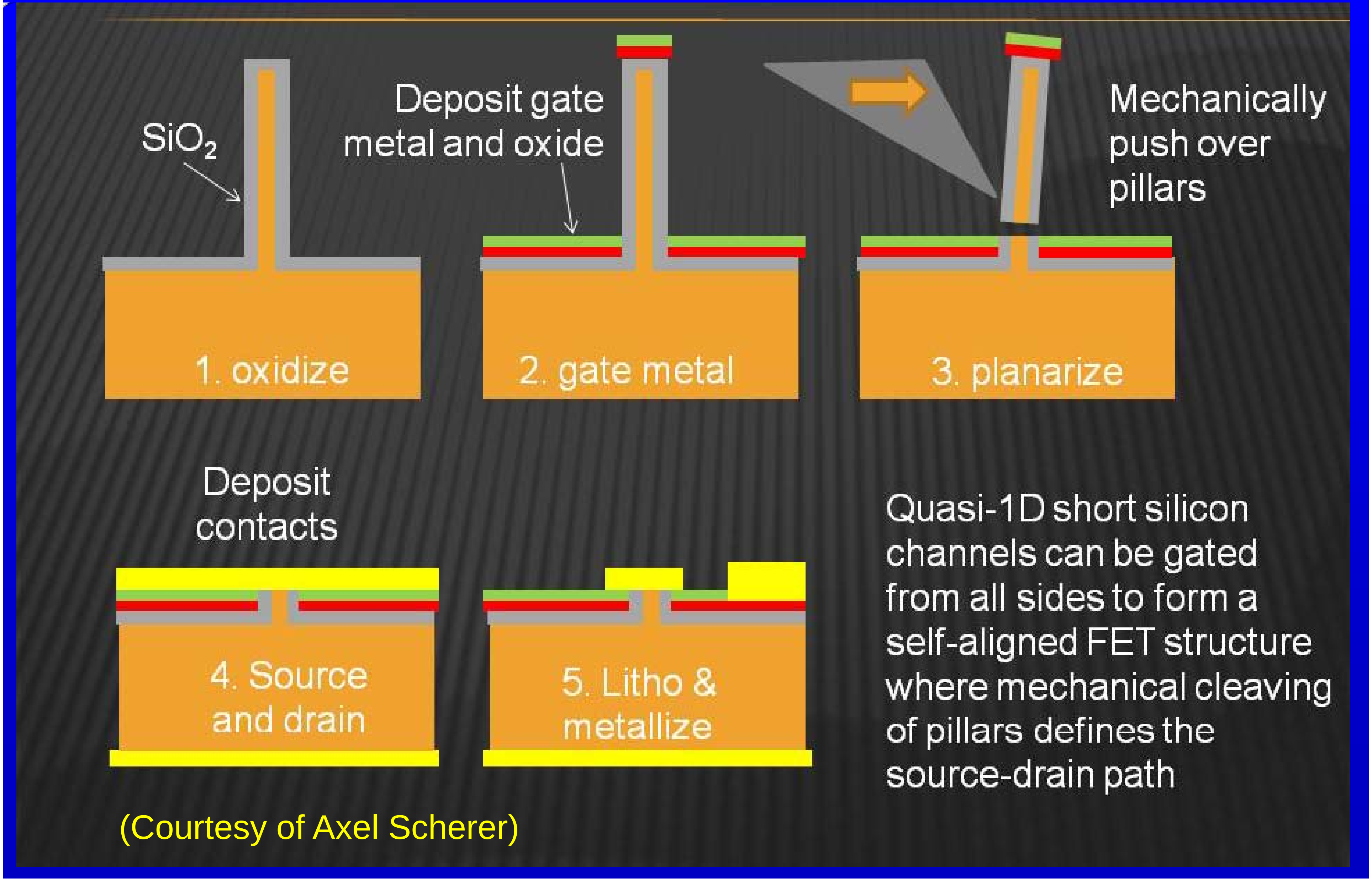


The energy gap increases from ~ 1.1 eV for crystalline silicon to ~ 3.o eV for the strained silicon nano-pillars.

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)

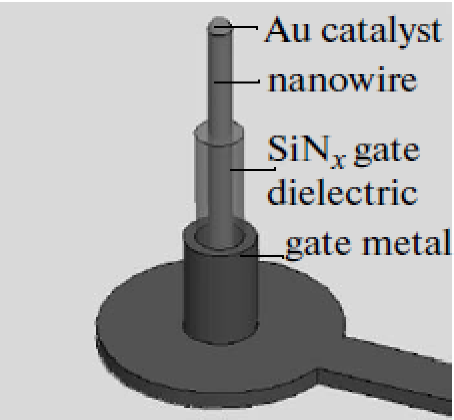
Making a transistor out of a strained silicon nano-pillar:

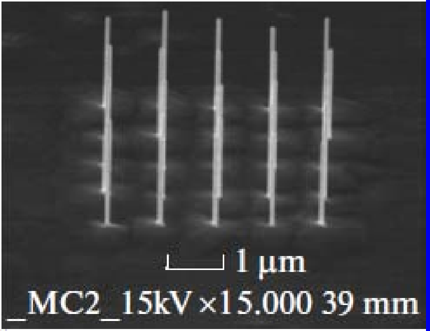


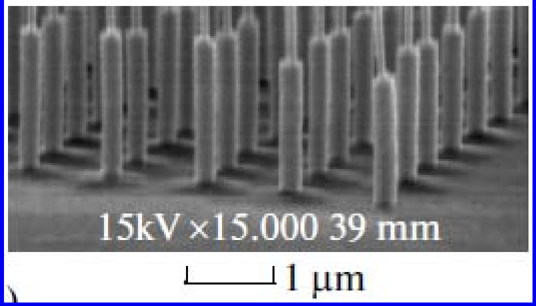
Quasi-1D short silicon channels can be gated from all sides to form a self-aligned FET structure where mechanical cleaving of pillars defines the source-drain path

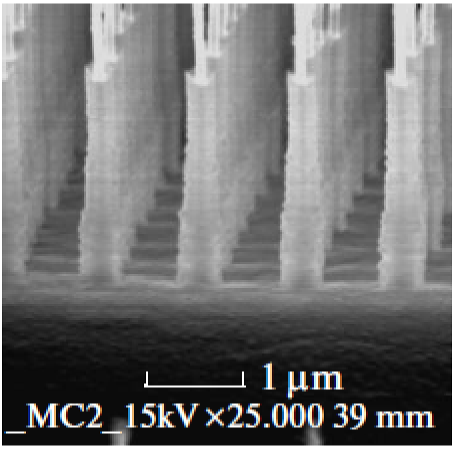
(Courtesy of Axel Scherer)

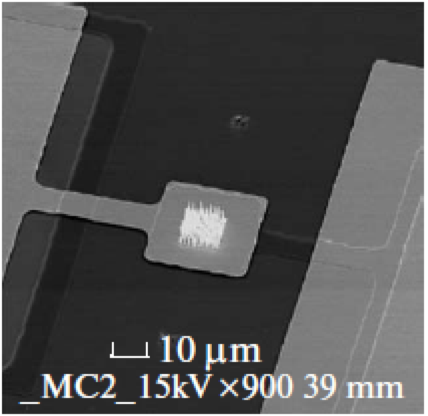
Similar transistor structures have been demonstrated in InAs nanowires with larger diameters and separations:

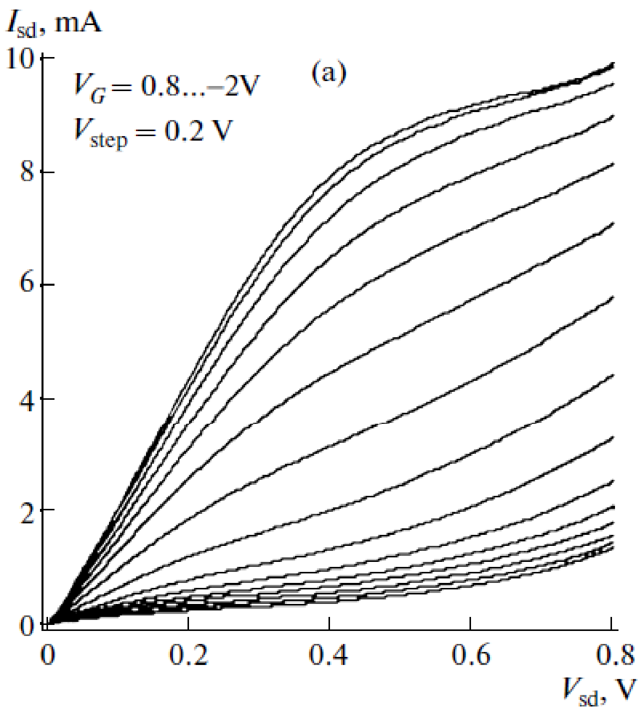












V. G. Dubrovskiia et al.,
Semiconductors 43, (2009)

1. **Nanotechnology & nanomaterials**

2. **Semiconducting nanowires**

3. **Graphene nanoribbons & related nanostructures**

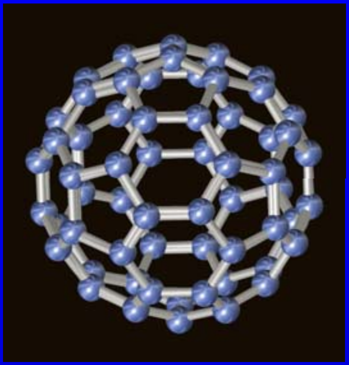
-- The rise of graphene.
-- Physics of graphene.
-- Novel phenomena of graphene and related structures.
-- Potential applications to light emission & photodetection.

3. Graphene Nanoribbons & Related Nanostructures

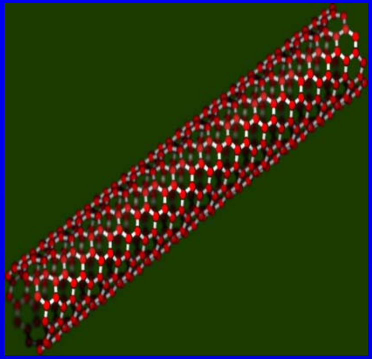
3.1. The Rise of Graphene

Carbon structures in different dimensions:

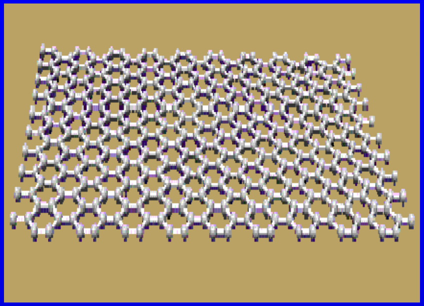
0D



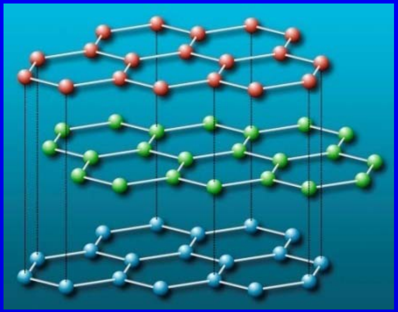
1D



2D



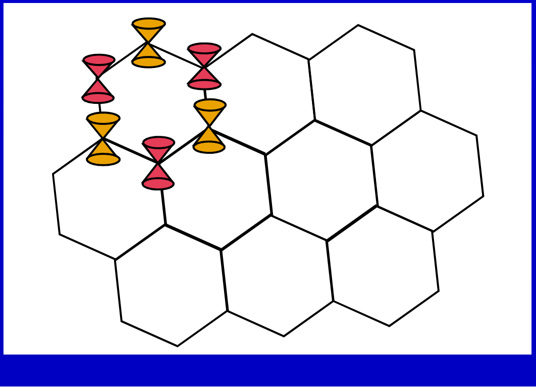
3D



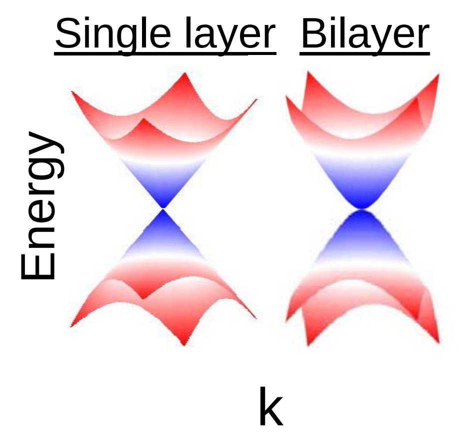
- Graphene consists of carbon atoms in honeycomb lattice.
- Unique Dispersion Relations: massless Dirac Fermions.
- First experimental isolation by Geim's group in 2004.

  [Novoselov et al, Science (2005).]

Two sublattices in the honeycomb lattice:



(Courtesy of M.W. Bockrath)



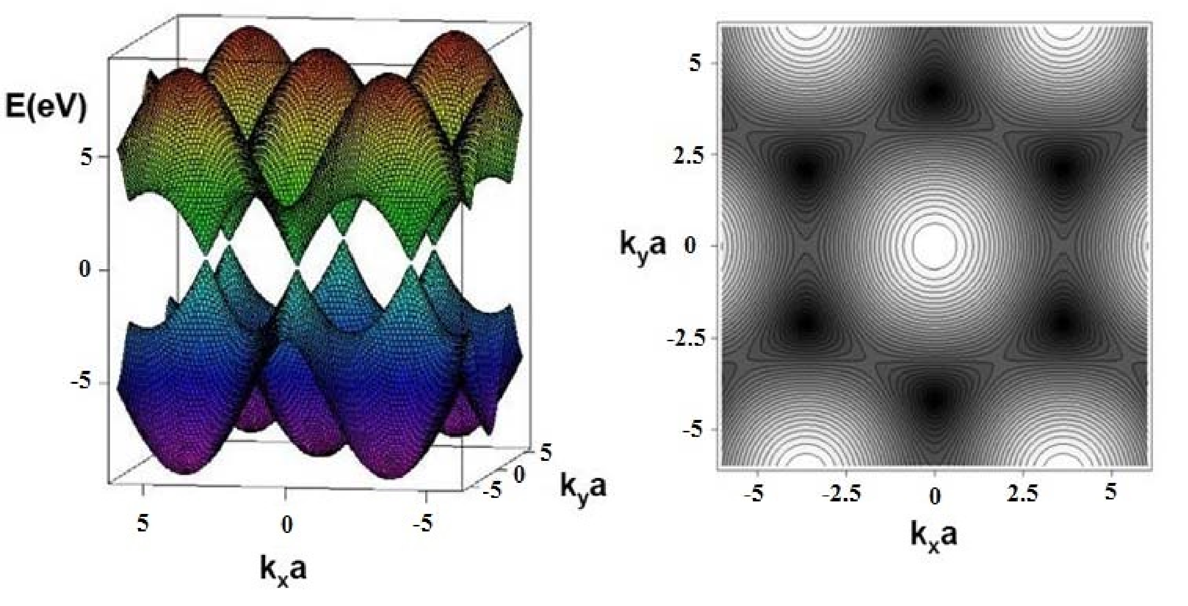
3.2. Physics of graphene

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

Near the “Dirac points” K & K'

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



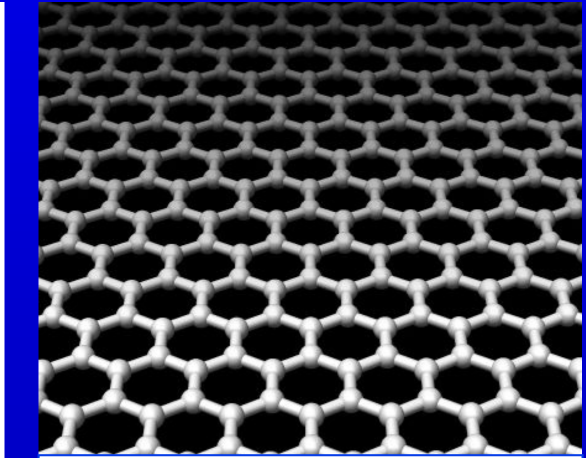
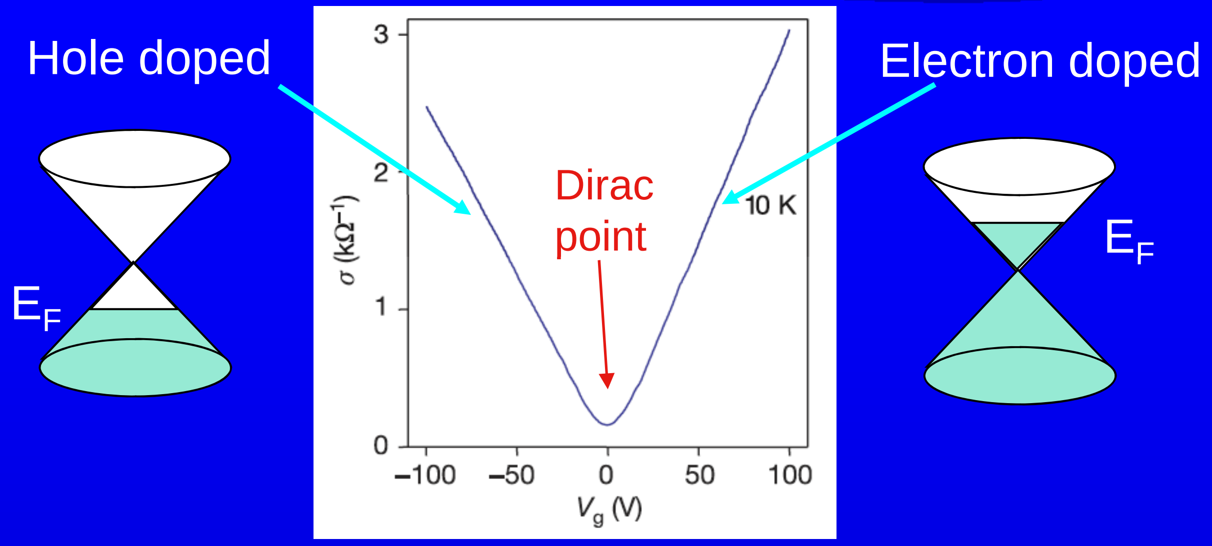
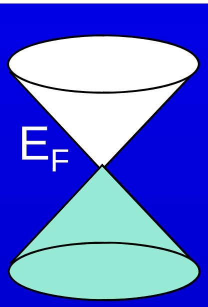


Image from: http://www.ece.mcgill.ca/~ts7kop/images/graphene_xyz.jpg

Images: Ph.D. thesis of Jinseong Heo, Caltech (2008).

Graphene bipolar field effect transistors (FETs)





The unique bandstructures of graphene suppress carrier backscattering, leading to extremely high mobility.

- Conductivity (σ) increases linearly with charge density (n): $\boldsymbol{\sigma \propto V_g \propto n}$
- Extremely high mobility: ~ 15,000 cm^2/Vs in as-prepared, non-optimized samples, compared to ~ 2,000 cm^2/Vs for silicon.
- Conductivity σ remains finite at Dirac point → σ_{min}

(Novoselov *et al*, *Nature*, 2005, Zhang et al, *Nature* 2005, Miao et al, *Science* 2007, Kim group, Fuhrer group.…)

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 cm^2/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

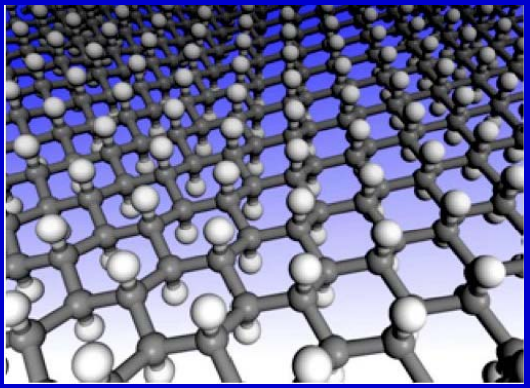
  → ballistic transistors

  → supercollimators & electronic lensing

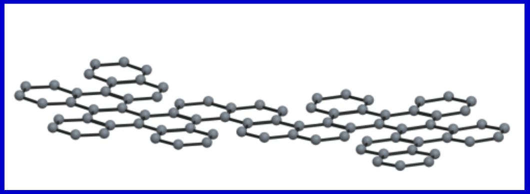
  → Schottky diodes & light emitting diodes

  → photodectors

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



Graphane
(0 ~ 3.5 eV)



Graphene nanoribbon
(0 ~ 200 meV)

3.3. Novel properties of graphene & related structures

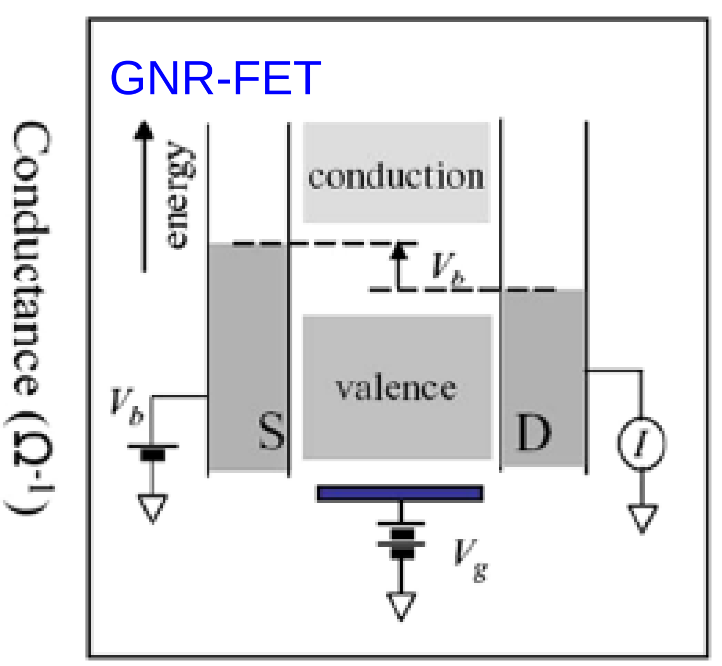
• Energy gap engineering of graphene nanoribbons (GNR):

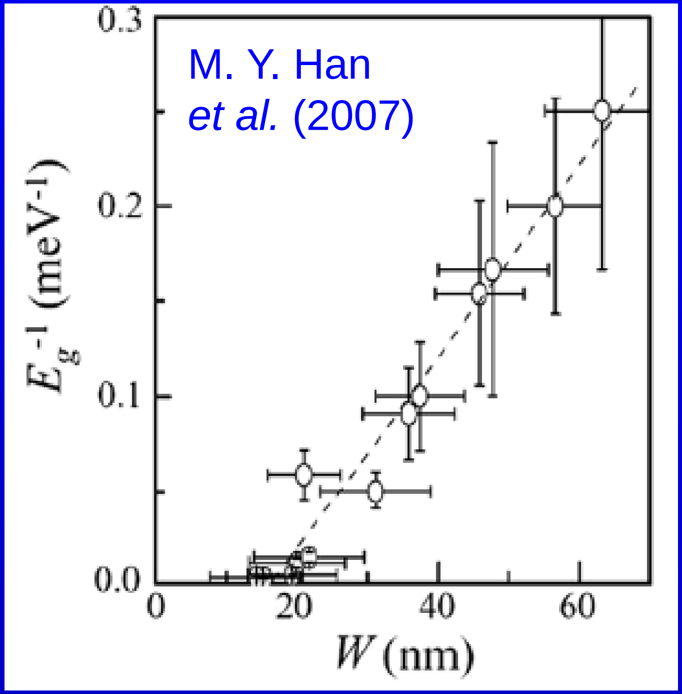
* Band gap induced by quantum confinement.

* GNR field effect transistors (FETs).

* Lithographically or chemically defined nanoribbons.

$$E_g = \frac{0.2}{\left(W - W^*\right)} \frac{\text{eV}}{\text{nm}}$$





* On/Off ratio ~ 10^6.

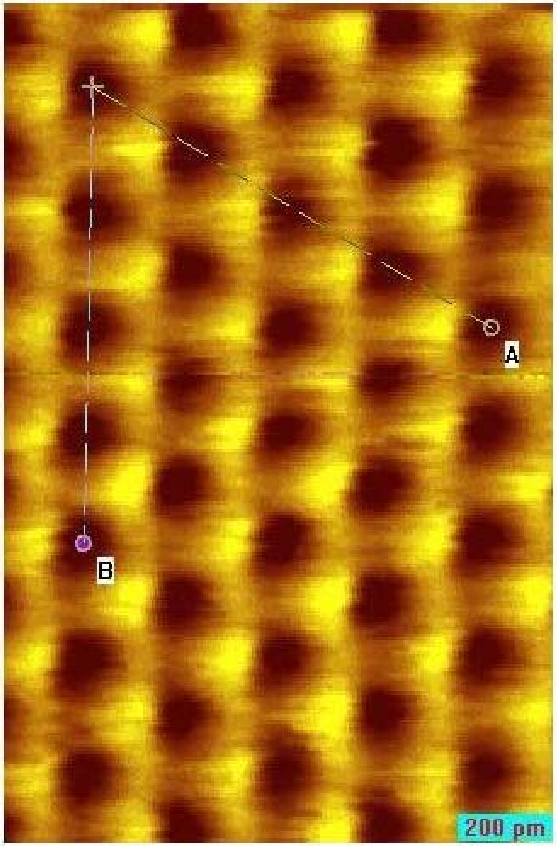
* Mobility ~ 200 cm^2/Vs.

- **Strain-induced modifications to the electronic properties of graphene:**

1. Mechanically exfoliated graphene on SiO_2.
2. CVD-grown graphene on Cu.

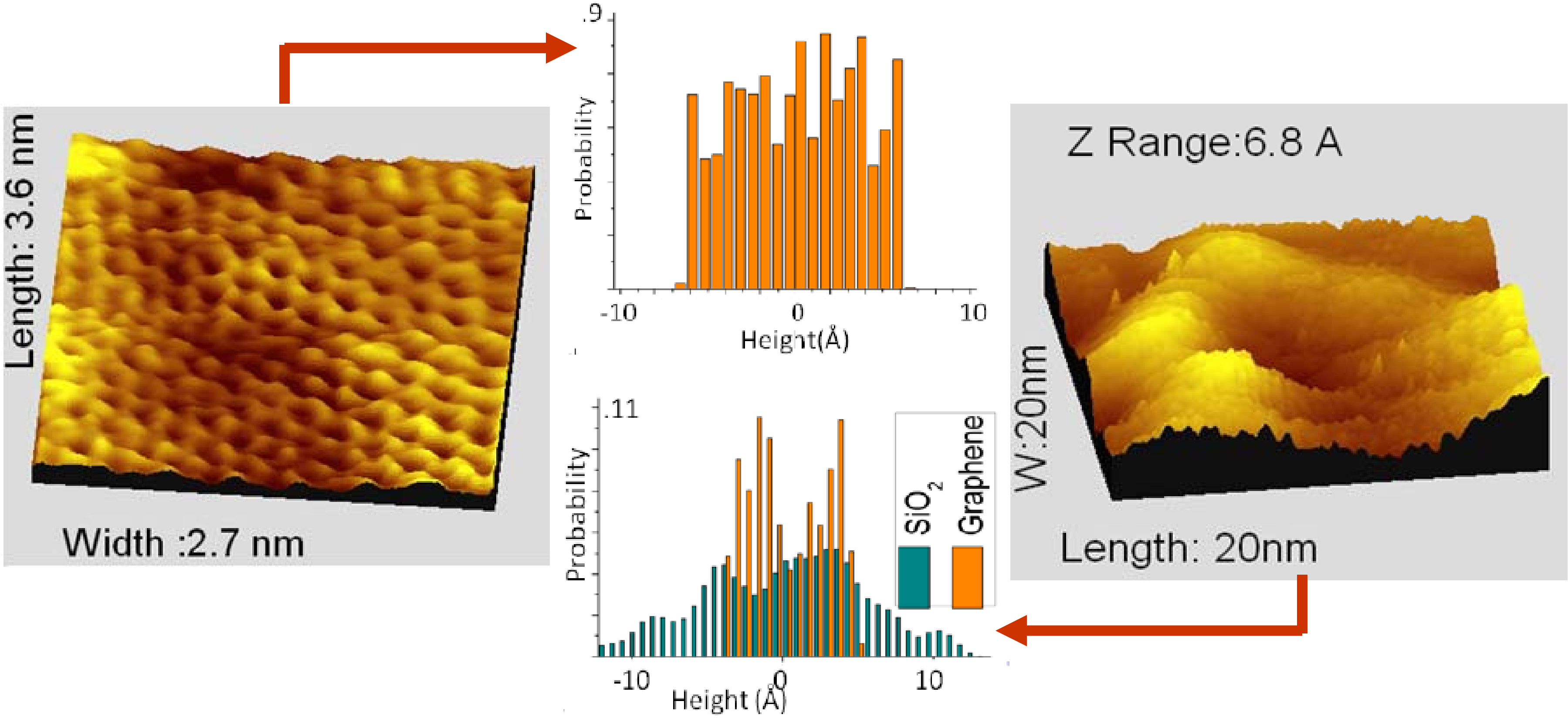
STM calibration on graphite

- 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 SiO_2

- 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 SiO_2 substrate.



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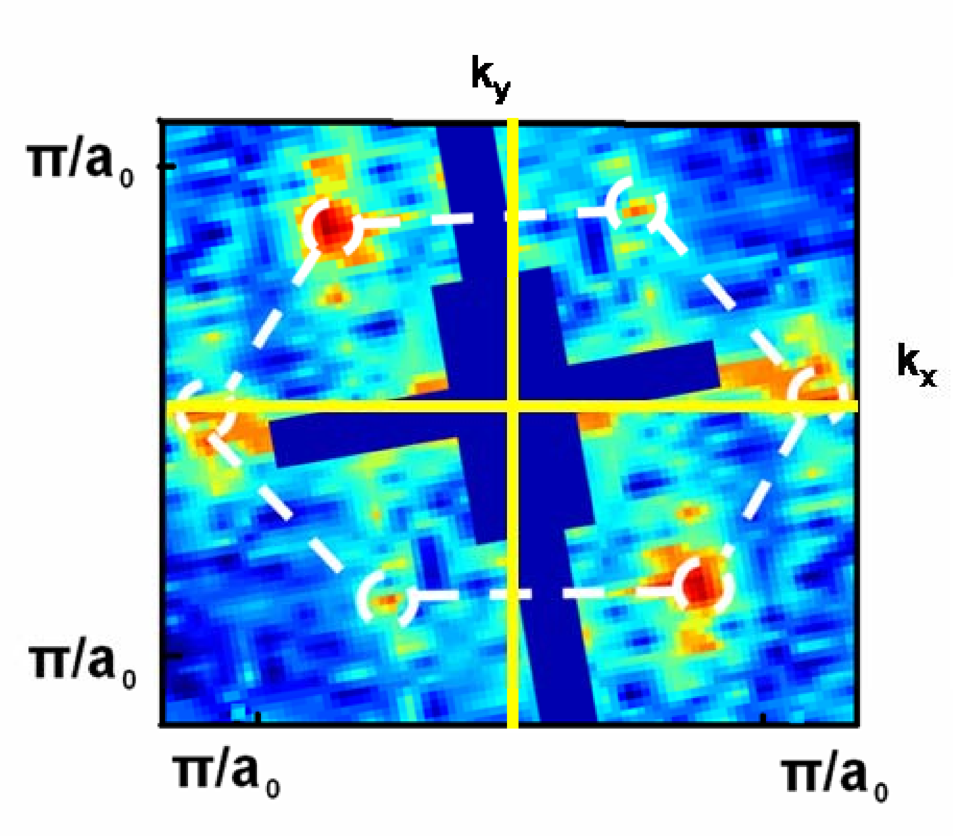


- Fourier transform of the topographic image of graphene reveals a strained-induced distorted reciprocal lattice.
- Local electronic properties are also modified by the strain fields.

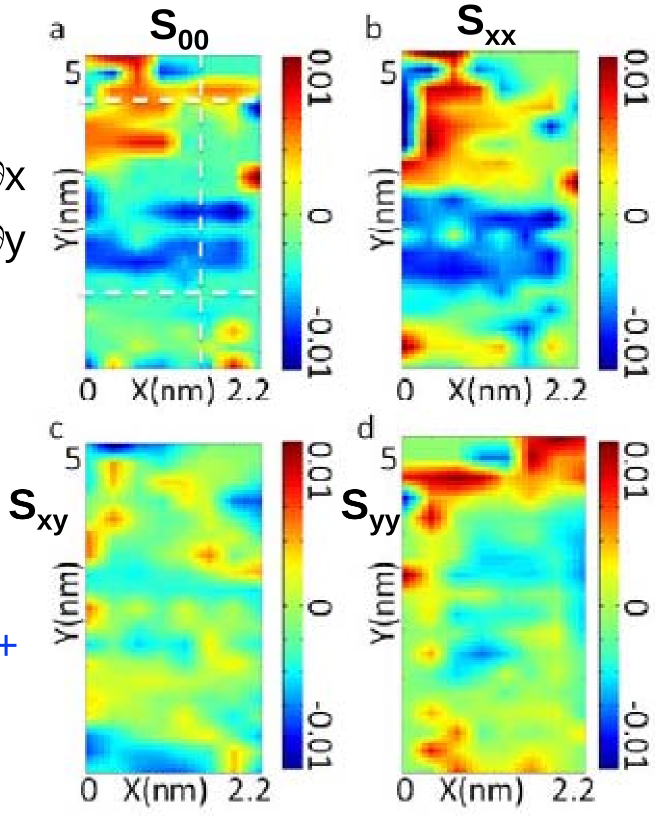
Strained-induced conductance modulations

- 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:

$S_{xx}(x,y) = \partial u_x(x,y)/\partial x$

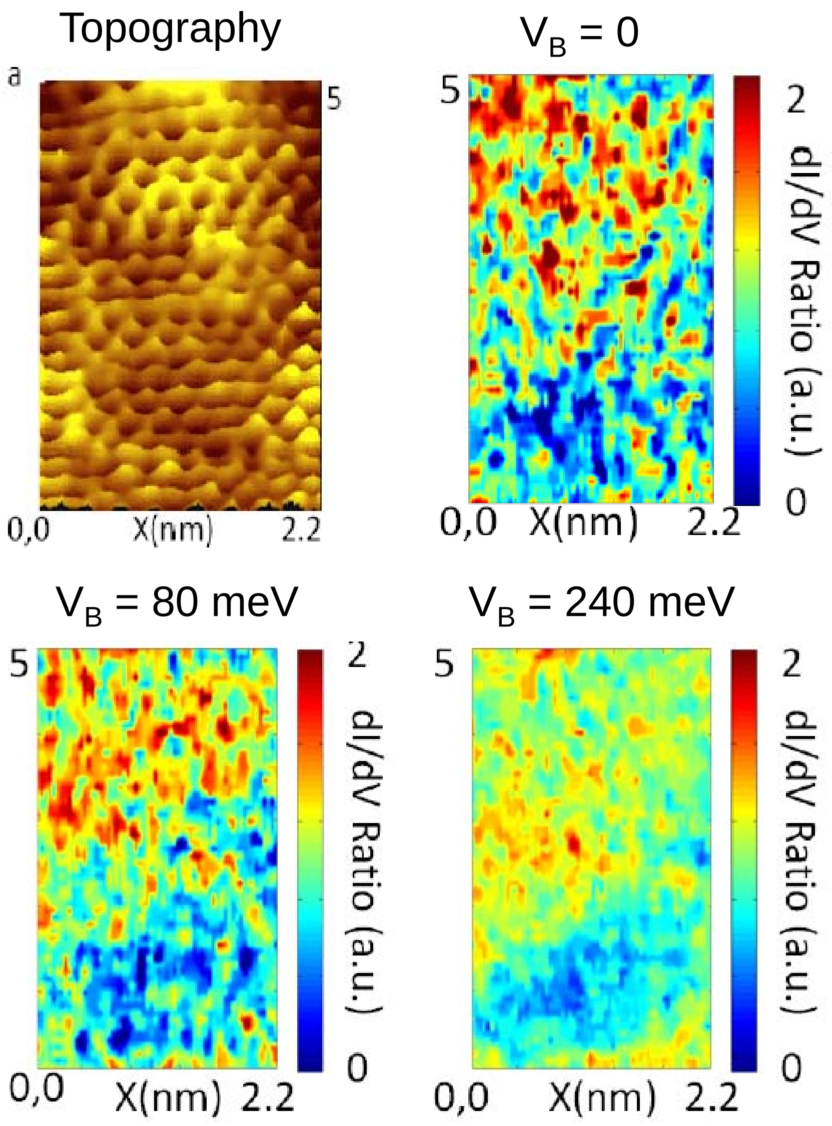
$S_{yy}(x,y) = \partial u_y(x,y)/\partial y$

$S_{xy}(x,y) = S_{xy}(x,y) = [\partial u_x(x,y)/\partial y + \partial u_y(x,y)/\partial x]/2$

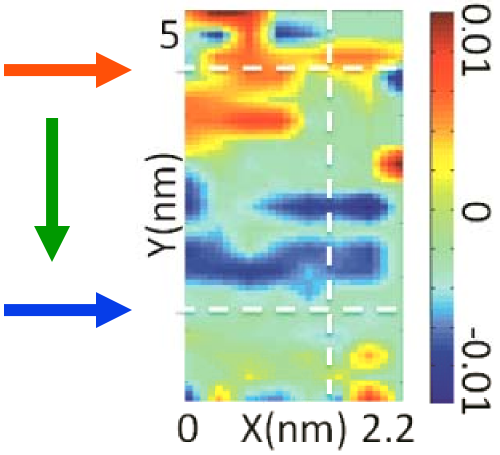


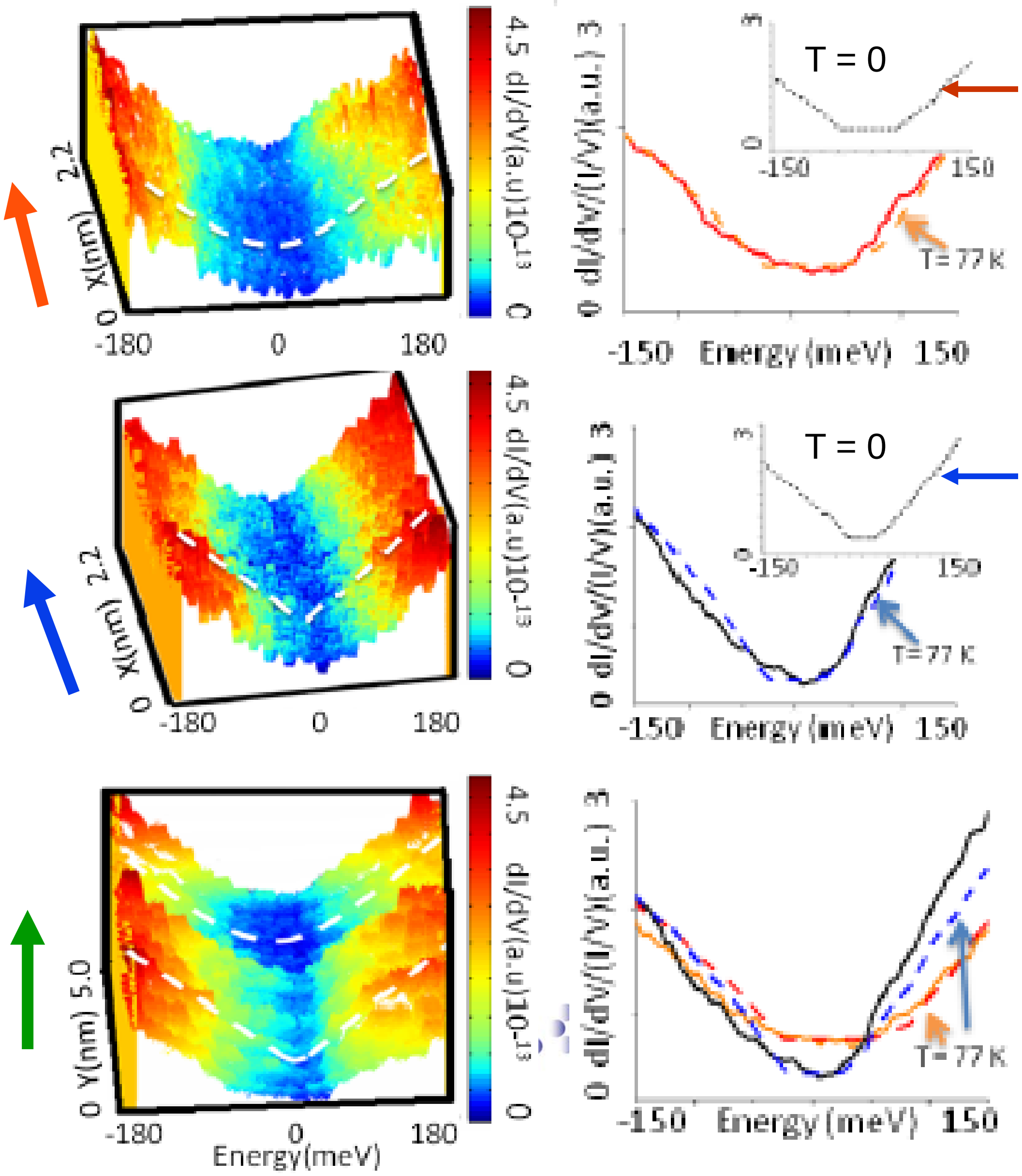
Displacement field:

$\mathbf{u}(x,y) = [u_x(x,y)\,\mathbf{e}_x + u_y(x,y)\,\mathbf{e}_y]$



Strain-induced modifications in the out-of-plane phonon-assisted tunneling gaps & conductance





Theoretical curve with ω_{ph} = 42 meV

Theoretical curve with ω_{ph} = 24 meV

ω_{ph} varies from 21 meV to 44 meV.

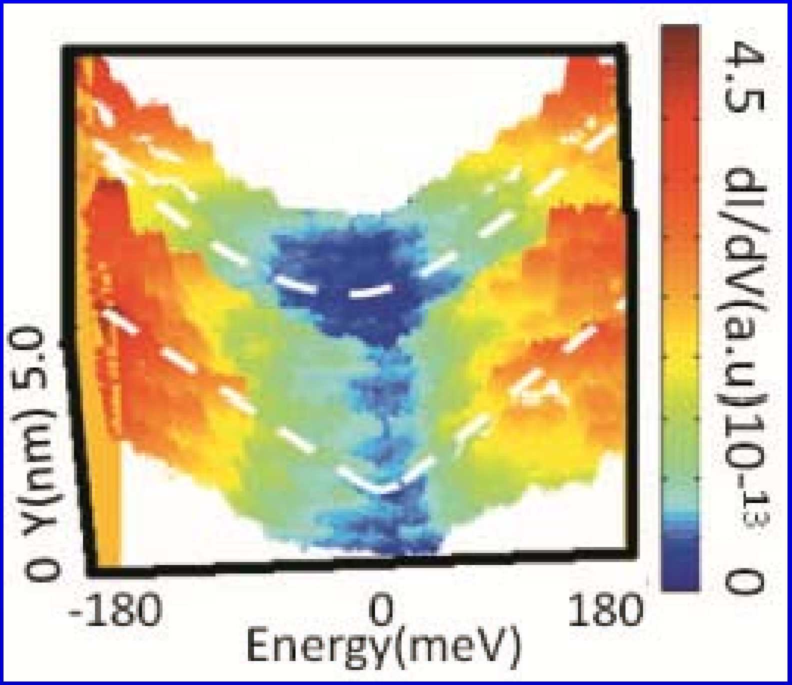
This work:

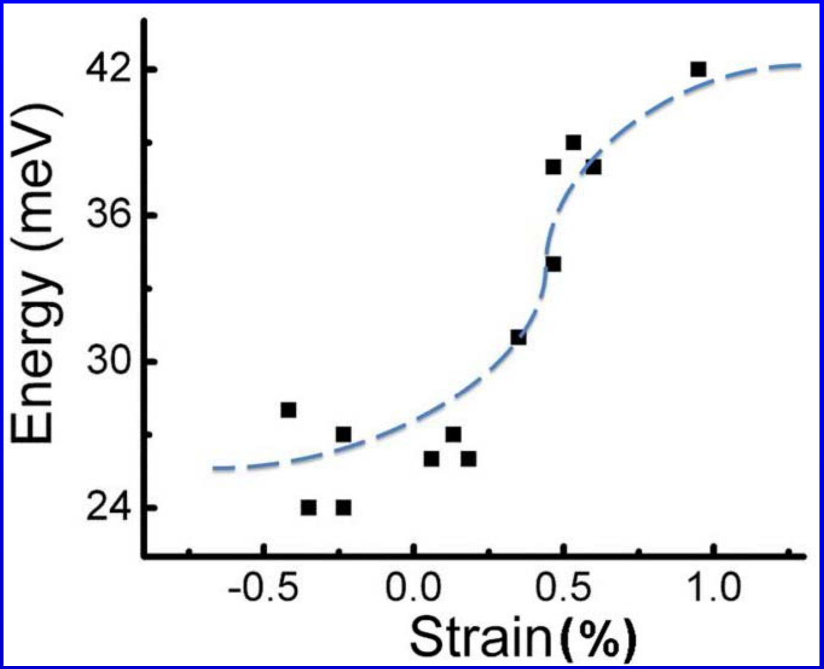
M.L. Teague *et al*, Nano Letters 9, 2542 (2009)

References:

- Y. Zhang et al, Nature Phys. **4** (2008).
- T.O. Wehling et al, PRL **101** (2008).

The out-of-plane phonon frequencies increase with increasing strain, suggesting coupling of π-electrons to the underlying phonons of the dielectric SiO_2.



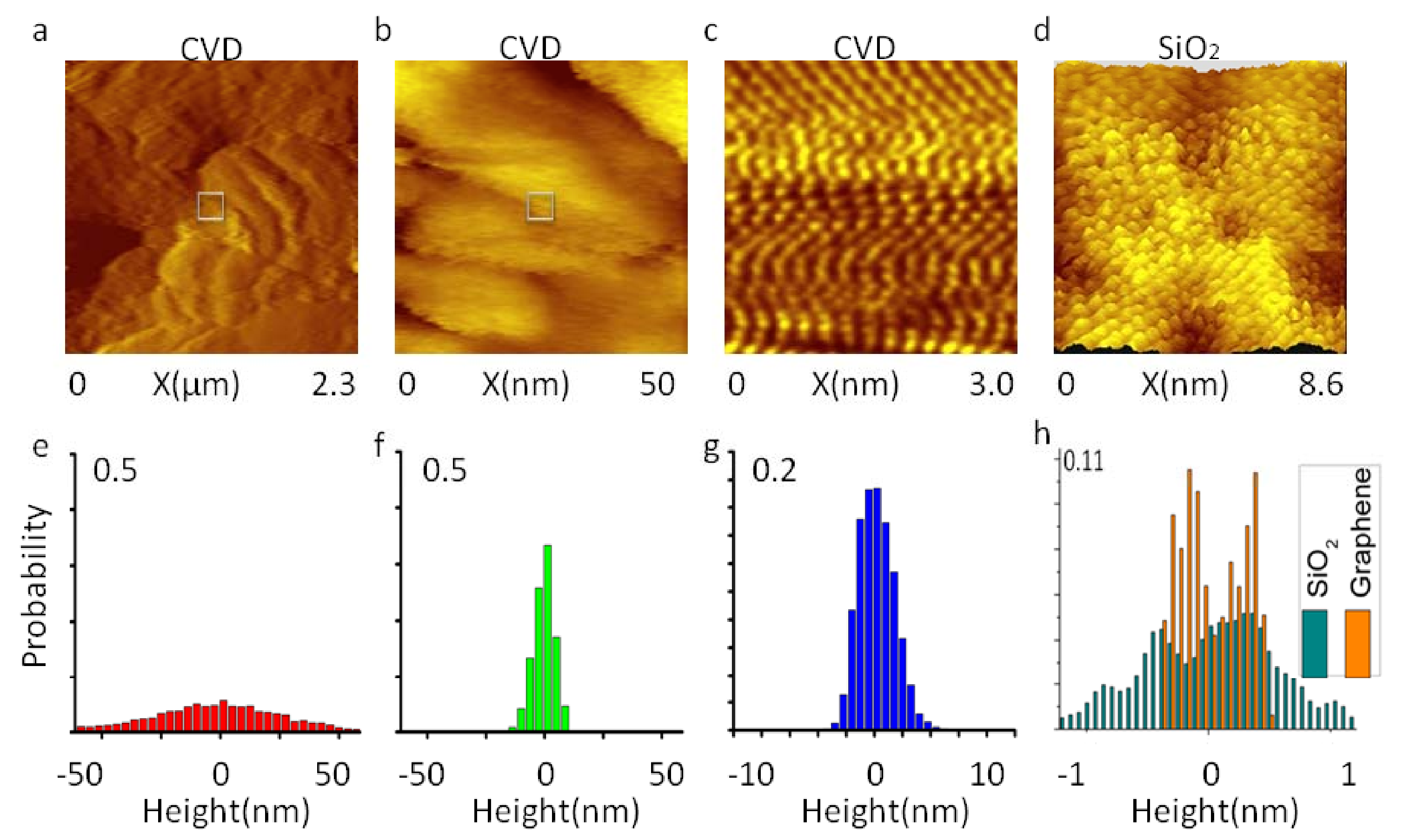


N.-C. Yeh *et al*, preprint, (2010).

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

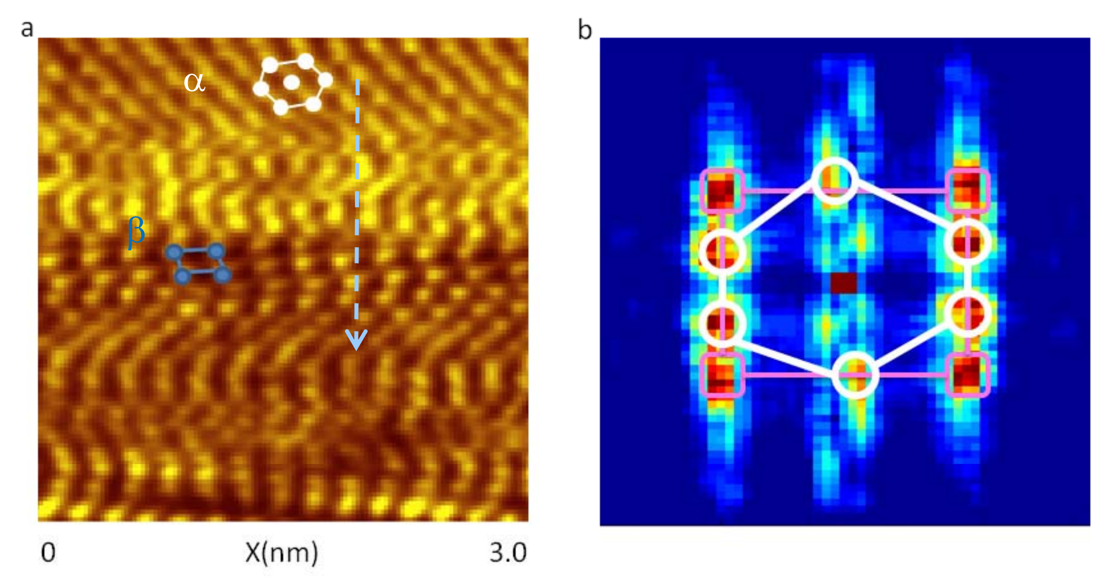
- CVD growth of graphene on copper foils at ~ 1000°C under hydrogen gas with CH_4 partial pressure.
- Large differences in the thermal contraction coefficients of graphene and copper lead to ripple structures.

[N.-C. Yeh *et al*, (2010)]



Modifications to electronic properties due to structural changes

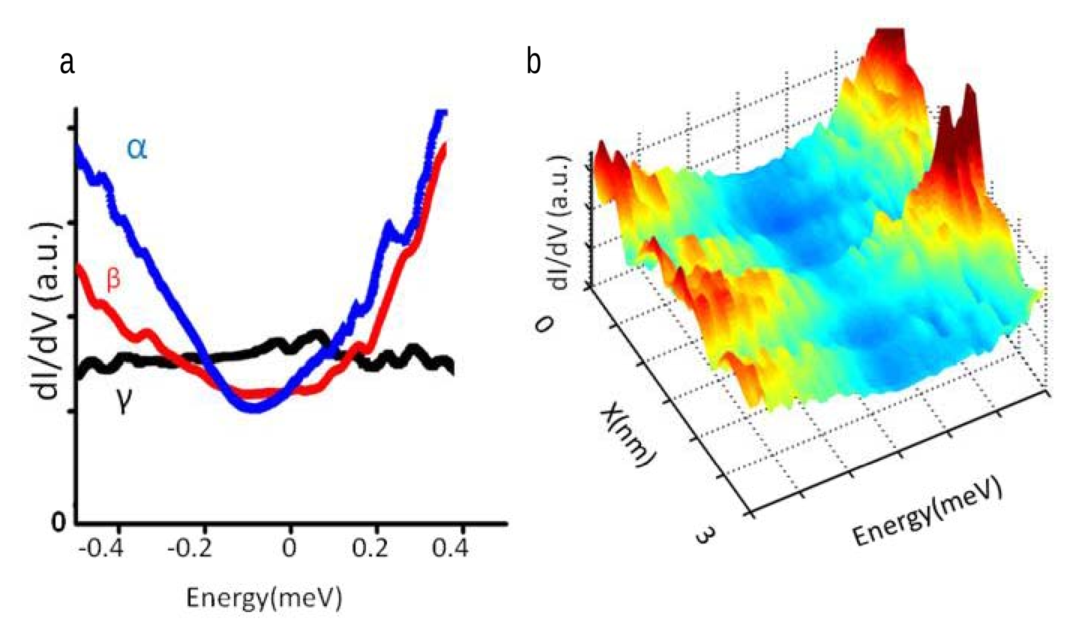
Topography (distorted structure)



Fourier-transformed structure

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

Conductance spectra of representative regions



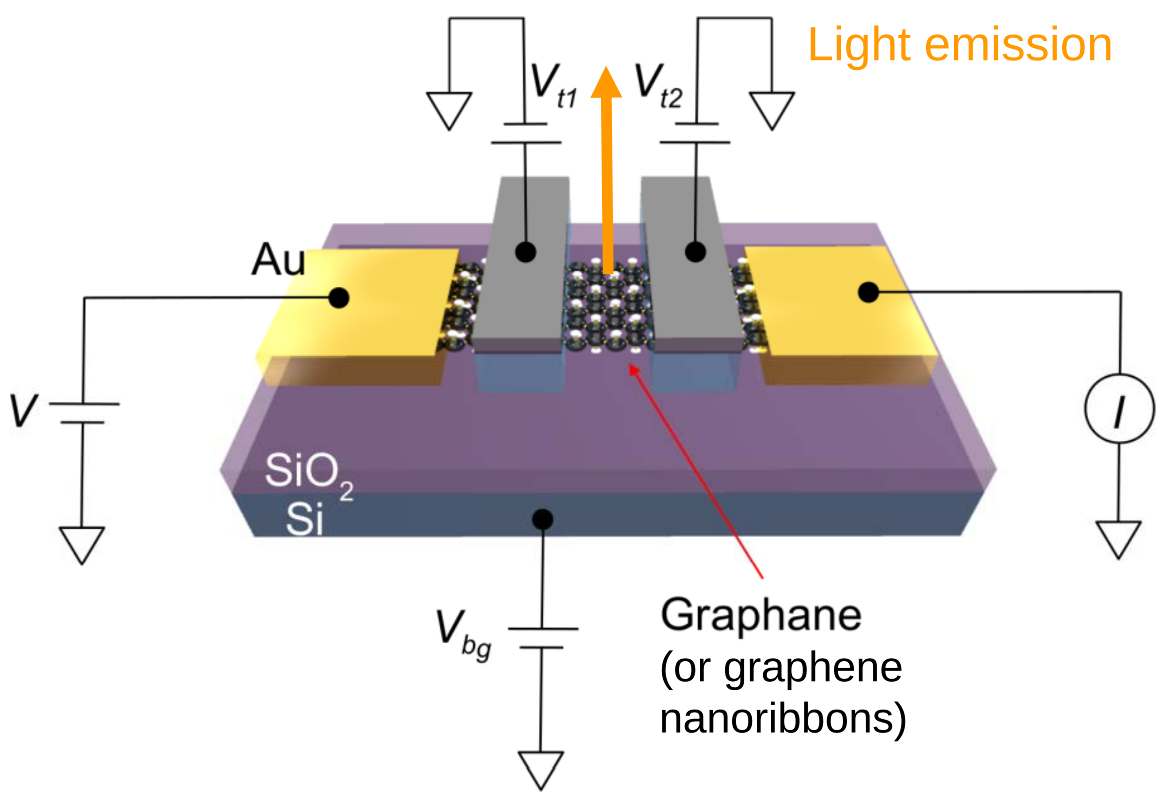
Conductance spectra along the dashed line in the upper left figure.

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.